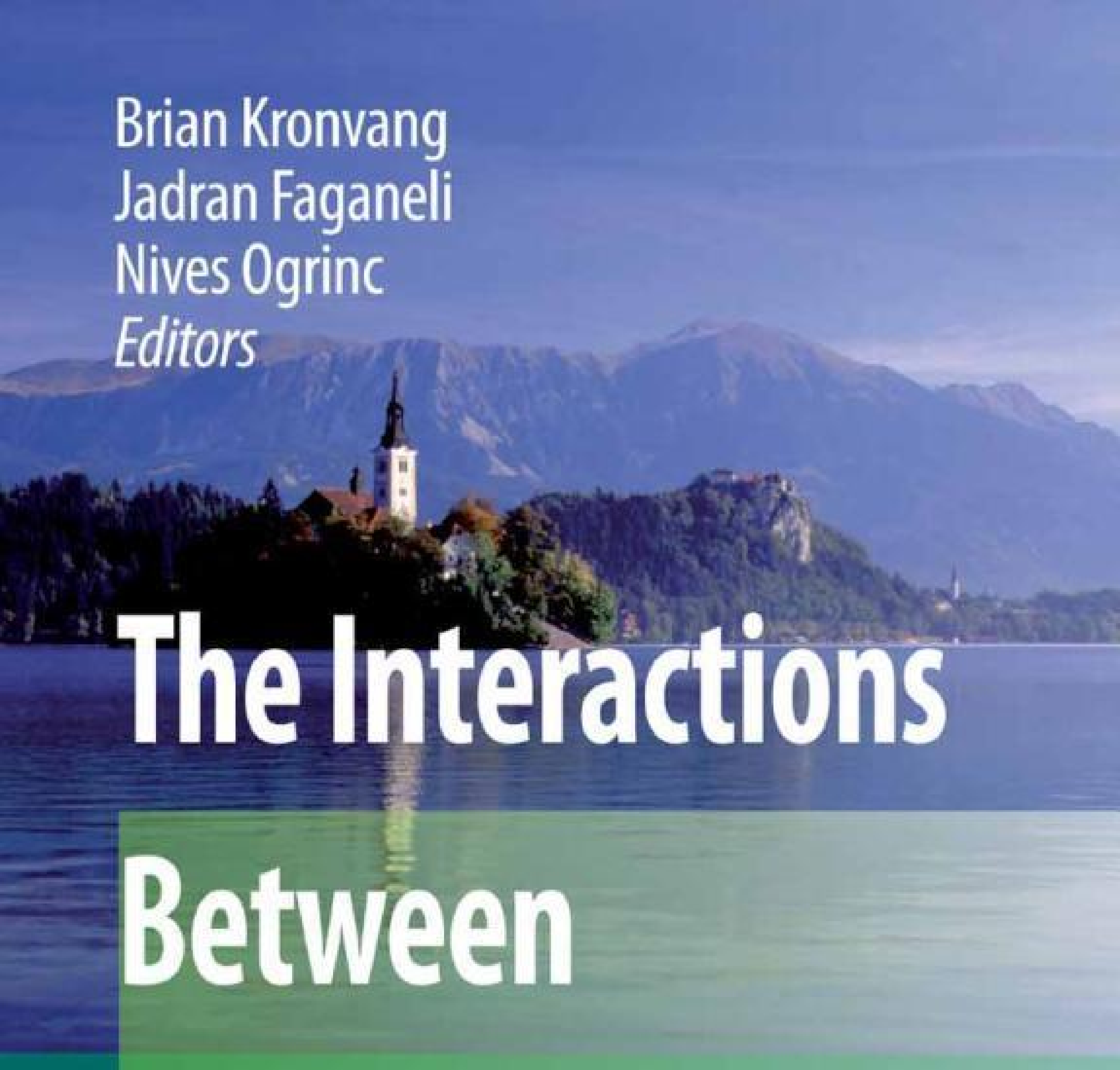
Brian Kronvang
Jadran Faganeli
Nives Ogrinc
Editors



The Interactions Between Sediments and Water

Springer

The Interactions Between Sediments and Water

The Interactions Between Sediments and Water

Edited by

BRIAN KRONVANG
National Environmental Research Institute,
Silkeborg, Denmark

JADRAN FAGANELI
National Institute of Biology,
Piran, Slovenia

and

NIVES OGRINC
Josef Stefan Institute,
Ljubljana, Slovenia

Reprinted from *Water, Air, & Soil Pollution: Focus*, Volume 6, Issues 5-6, 2006

Springer

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN-10 1-4020-5477-7 (HB)
ISBN-13 978-1-4020-5477-8 (HB)
ISBN-10 1-4020-5478-5 (e-book)
ISBN-13 978-1-4020-5478-5 (e-book)

Published by Springer,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

www.springer.com

Printed on acid-free paper

Cover image courtesy of Nives Ogrinc.

Table of Contents

Section 1: Sediment and Water Interactions in Streams

Section 2: Sediment and Water Interactions in Lakes

Section 3: Sediment and Water Interactions in Coastal Water

Section 4: Linking Catchments and Streams

Acknowledgements

Jozef Stefan Institute, Slovenia

National Institute of Biology, Slovenia

Environment Canada

National Water Research Institute, Canada

The University of Plymouth, United Kingdom

National Environmental Research Institute, Ministry of the Environment, Denmark

UNESCO

Slovenian Research Agency

International Association for Sediment & Water Science (IASWS)

The Organizing Committee and the Editors are grateful to the institutions that supported the 10th International IASWS 2005 Symposium held in Bled, Slovenia, and this special issue of *Water, Air, & Soil Pollution: Focus.*

Water, Air, and Soil Pollution: Focus (2006) **6:** 1–5
DOI: 10.1007/s11267-006-9060-3

INTERACTIONS BETWEEN SEDIMENT AND WATER: PERSPECTIVES ON THE 10TH INTERNATIONAL ASSOCIATION FOR SEDIMENT WATER SCIENCE SYMPOSIUM

ELLEN L. PETTICREW[1,*], IAN G. DROPPO[2], NIVES OGRINC[3], BRIAN KRONVANG[4] and JADRAN FAGANELI[5]
[1]School of Geography, University of Plymouth, Plymouth, UK
[2]National Water Research Institute, Burlington, Canada
[3]Department of Environmental Science, Jožef Stefan Institute, Ljubljana, Slovenia
[4]National Environmental Research Institute, Silkeborg, Denmark
[5]Marine Biological Station, National Institute of Biology, Piran, Slovenia
*(*author for correspondence, e-mail: ellen.petticrew@plymouth.ac.uk; phone: +44-1752-233060; fax: +44-1752-233054)*

Abstract. The 10th International Symposium on Interactions Between Sediment and Water was held in Lake Bled, Slovenia from August 28 to September 3, 2005. Approximately 155 delegates, attended the symposium where talks and posters addressed five themes incorporating the physical, chemical, biological, and/or management aspects of lacustrine, riverine, estuarine, and/or marine sediment were presented. A review of the symposium themes and plenary talks was provided. As well, this symposiums' focus is put into context with respect to historical changes noted over the 29 years that the International Association for Sediment Water Science (IASWS) has been meeting.

Keywords: sediment, water, aquatic science, IASWS

The International Association for Sediment Water Science (IASWS) developed from a meeting in Amsterdam in 1976, held to respond to a need for specific discussions on sediment–water interactions. At that time collaborations between academic disciplines and/or different aquatic environments was novel, and the value of meeting to discuss riverine, lacustrine and marine sediment–water issues was recognized, such that it has continued on a 3-year cycle. This 10th symposium held in Lake Bled, Slovenia brought together an interdisciplinary group of 155 scientists from 35 countries that included geochemists, aquatic ecologists, sedimentologists, geomorphologists, environmental engineers and ecosystem managers. This symposium was structured around five themes: (1) Source, fate and effect of sediments in marine and freshwater ecosystems, (2) Modeling the movement of aquatic sediments, (3) Sediment-associated nutrient and contaminant processes, (4) Assessing and/or restoring disturbed catchments and (5) Biogenic influences on sediment–water interactions from the micro- to macro-scale. These process-oriented themes facilitated interdisciplinary interactions and incorporated 132 oral presentations and 121 poster presentations. Of these, 31 papers are presented in this special issue but are grouped by their aquatic environment: streams, lakes, coastal waters and estuaries, and catchment linkages. A special issue of RMZ – Materials and Geoenvironment (Faganeli, Ogrinc, & Horvat, 2005) contains the abstracts of all of the talks and posters that are as well posted via links on the IASWS website (www.iasws.com) until 2008.

Six plenary speakers were invited with Bojan Ogorelec from the Geologic Survey of Slovenia opening with a sediment–water introduction to our symposium location, by providing a summary of Lake Bled sediment studies undertaken over the past 30 years. The other plenaries were invited to present extended talks on their research as it linked to the five symposium themes. Philip Meyers, addressing theme 1, summarized his work using stable isotopes of C, N and H in lake sediments to determine the source of organic sediments (terrestrial or lacustrine) which allows reconstruction of the paleoproductivity and paleohydrology of the systems (Meyers, 2006). Lynn Walter's plenary characterized theme 2 by modelling geochemical fluxes of weathering products from rocks and soils, on the landscape scale, in both America and Slovenia. The third theme was introduced by Han Golterman who hosted the initial 1976 IASWS meeting in Amsterdam. He provided an historical overview of sediment phosphate and nitrate chemistry as well as suggesting nine papers he felt were seminal to sediment–water science from the first IASWS meeting! Ulrich Förstner, another long-term member of the Association presented a plenary talk addressing theme 4, assessing and/or restoring disturbed catchments. The case studies of the River Rhine and Elbe (Heise and Förstner, 2006) reinforced the need for linked scientific, political and economic efforts to effectively determine and address problems of contaminated sediments in large, heavily populated river basins. The final theme of biogenic influences on sediment–water interactions was exemplified by the plenary of Mark Hines who worked over a range of temporal and biological scales to assess the impacts of organisms on sediment redox conditions (Hines, 2006).

Some of the themes in the past nine IASWS symposia have been similar or overlapping with those of the Lake Bled meeting, with sediment-associated nutrients and contaminants being the dominant recurring issue over the 30 years. Of interest is the number of research presentations on phosphorus, which was a dominant theme in the early meetings when eutrophication of lakes was a major scientific and political concern. Over the 29-year period of IASWS meetings, the emphasis on phosphorus was overtaken by contaminant (heavy metal and organic) studies, but due to recent European issues related to the Water Framework Directive a revitalized emphasis (viz. 27 presentations) on quantifying transfers (Mayer et al., 2006; Van Hullebusch, Auvray, Deluchat, Chazal, & Baudu, 2005), estimating stored loads (Ballentine et al., 2006; Hupfer & Lewandowski, 2005) and standardising techniques (Golterman, 2005; Lukkari, Leivuori, & Henning, 2005) for measuring and monitoring phosphorus has emerged. Several of the seminal papers Golterman selected from the 1976 symposium laid the foundations for the current work. It would be interesting to know which papers from this meeting will be considered influential in the future of aquatic science. Clearly the international concern regarding fluxes, impacts, and methods of remediating organic and heavy metal pollution associated with sediments is not likely to disappear quickly, as the growth of both the human population and industry continues to exacerbate these problems. A range of sediment-related contaminant issues were addressed in 45 presentations at the 10th symposium, indicating the continuing dominance of this theme.

Scales of study have always varied greatly in the presentations at IASWS although recently there has been more emphasis on landscape scale case studies (Auvray et al., 2005; Ulaga, 2005) and comparative studies incorporating a range of biogeoclimatic zones (Dedkov, Mozzherin, Gusarov, & Safina, 2005; Kronvang et al., 2005). Micro-scale techniques to evaluate process-response continued to play a dominant role in the presentations. For example, detailed characterization of both flows in marine sediments (Goharzadeh & Khalili, 2005) and the nature of the bed material (Packman & Marion, 2005) have been improved appreciably by precise micro-scale measurement techniques. There was considerable discussion following many presentations about the ability of up-scaling small-scale experimental results to the 'real-world' situation. These process-based small-scale studies should be designed with consideration of their ability to inform the needs of these larger scale research questions. A recognized benefit of combining the range of scales at one symposium is to encourage the interaction and information exchange between groups.

Another recurring theme which remained important at Lake Bled was sediment dynamics. Many different perspectives on physical processes within rivers, lakes and marine systems were presented. Monitoring of sediment erosion, transport and deposition garnered a lot of attention at the symposium, with new techniques and problems with accepted techniques being presented. Clays, labelled with rare earth elements, were shown to be an effective new technique for tracking sediment movement in freshwater and marine systems (Suzuki & Spencer, 2005), while the dating chronology of cesium-137, from radioactive fallout, was shown to be problematic in cores from coastal lagoons (Foster, Proffitt, Mighall, & Walling, 2005) where saltwater intrusions were believed to be displacing sediment-associated cesium. Problematic and/or negative results from experiments undertaken rigorously provide valuable information for revising our view of how environmental systems are operating, and therefore are welcomed at these symposia.

While assessment and restoration of aquatic systems or habitats is an expected end product and/or underlying rationale for much of the work that is undertaken by members of IASWS, the earlier meetings did not thematically address it. At this meeting three oral sessions and a poster session dealt with both natural and anthropogenically disturbed systems and approaches to remediating the environmental problems. With the current funding emphasis on multi-agency research networks tackling large-scale problems, we expect to see more of this type of work in the future. It is clear that there is great benefit of integrated and holistic approaches to evaluating aquatic ecosystems which include socio-economic considerations, as there is a profound need for delivering clear messages and advice to governmental agencies and ecosystem managers. Related to these issues is one of international standards of monitoring. Eckelhart, Schindl, Stdnicka, and Summer, (2005) emphasized the importance of international laws and regulations which must be in place, along with an accepted and accurate protocol, in order to effectively collect data which are useful and comparable for addressing cross- and multi-border contaminant issues. The role of environmental policy has been a small but important contribution of work presented at IASWS meetings. For example Skei (2005), over the years, has presented evolving plans for sediment remediation by the Norwegian government to address aquatic and biological contamination due to a long history of industrial pollution delivered to the local fjords. Difficult decisions, involving risk assessment and acceptable levels of scientific knowledge of the significant environmental processes, are required for the development of policy. Much of what is produced by IASWS researchers should be used to inform this process. While the Association considers itself broadly interdisciplinary we potentially may need to seek out more interaction with policy and implementation personnel in order to be forewarned of the type of questions and quality of data these individuals require for moving forward.

Acknowledgments

The authors would like to acknowledge the financial and in-kind support from the International Association for Sediment Water Science (IASWS), the National Water Research Institute (NWRI) of Environment Canada, the National Environmental Research Institute, Denmark (NERI), and the School of Geography, University of Plymouth. The editors of this special issue greatly acknowledge the work of Anne-Dorthe Villumsen, (NERI, Denmark) who managed the manuscript review process and assisted with the communication between authors, reviewers and the publishers. The symposium organizing committee of Nives Ogrinc, Jadran Faganeli and Milena Horvat would like to acknowledge the financial support provided for this 10th International Symposium on “The Interactions Between Sediments and Water” from the Slovenian Research Agency and the UNESCO-IHP programme. Many other institutions and companies also provided financial support and are identified in the symposium abstract publication (Faganeli et al., 2005) and on the Slovenian IASWS website (www.icjt.org/iasws2005).

References

Auvray, I., Berthelin, J., Faure, P., Mansuy, L., Jeanneau, L., Ramelli, M. (2005). Organic matter biodegradability and nutrient availability in aerobic and anerobic conditions along an upstream–

downstream sequence of river sediments (Moselle catchment area). *RMZ – Materials and Geoenvironment, 52*, 182.

Ballentine, D. J., Walling, D. E., Collins, A. L., & Leeks, G. J. (2006). Phosphorus storage in fine channel bed sediments. *Water, Air and Soil Pollution: Focus* (in press).

Dedkov, A. P., Mozzherin, V. I., Gusarov, A. V., & Safina, G. R. (2005). Global erosion, suspended sediment yields and its changeability. *RMZ – Materials and Geoenvironment, 52*, 204.

Eckelhart, A., Schindl, G., Stdnicka, M., & Summer, W. (2005). Comparing and standardizing suspended sediment information in international river basins. *RMZ – Materials and Geoenvironment, 52*, 207.

Faganeli, J., Ogrinc, N., & Horvat, M. (Eds.) (2005). *RMZ – Materials and Geoenvironment, 52*, 395.

Foster, I., Proffitt, H., Mighall, T., & Walling, D. (2005). Post-depositional ^{137}Cs mobility in the sediments of three shallow coastal freshwater lagoons, Southwest England. *RMZ – Materials and Geoenvironment, 52*, 214.

Goharzadeh, A., & Khalili, A. (2005). Flow measurement at the water–sediment interface. *RMZ – Materials and Geoenvironment, 52*, 225.

Golterman, H. (2005). Reviewing the chemistry of phosphate and nitrogen compounds in sediments. *RMZ – Materials and Geoenvironment, 52*, 227.

Heise, S., & Förstner, U. (2006). Risks from historical contaminated sediments in the Rhine basin. *Water, Air and Soil Pollution: Focus* (in press).

Hines, M. E. (2006). Microbially mediated redox cycling at the oxic-anoxic boundary in sediments: Comparison of animal and plant, habitants. *Water, Air and Soil Pollution: Focus* (in press).

Hupfer, M., & Lewandowski, J. (2005). Phosphorus retention and early diagenetic phosphorus transformation in Lake Arendsee (Germany). *RMZ – Materials and Geoenvironment, 52*, 242.

Kronvang, B., Hejzlar, J., Boers, P., Jensen, J. P., Andersen, T., Arheimer, B. (2005). Calculation of a nutrient retention in European catchments applying a standard tool: EUROHARP-NUTRET. *RMZ – Materials and Geoenvironment, 52*, 264.

Lukkari, K., Leivuori, M., & Henning, S. J. (2005). Phosphorus extraction methods tested on sediments from the Gulf of Finland. *RMZ – Materials and Geoenvironment, 52*, 274.

Mayer, T., Rosa, F., Mayer, R., & Charlton, M. (2006). Relationship between the sediment geochemistry and phosphorus fluxes in a Great Lakes coastal marsh, Cootes Paradise, ON, Canada. *Water, Air and Soil Pollution: Focus* (in press).

Meyers, P. A. (2006). An overview of sediment organic matter records of human eutrophication in the Laurentian Great Lakes region. *Water, Air and Soil Pollution: Focus* (in press).

Packman, A. I., & Marion, A. (2005). Effect of sediment structure on hyporheic exchange and pore water transport. *RMZ – Materials and Geoenvironment, 52*, 298.

Skei, J. (2005). Sediment remediation in Norway – National status and plans. *RMZ – Materials and Geoenvironment, 52*, 339.

Suzuki, K., & Spencer, K. L. (2005). Development and evaluation of rare earth elements (REE) labelled clays as fine sediment transport tracers in the marine environment. *RMZ – Materials and Geoenvironment, 52*, 351.

Ulaga, F. (2005). Concentrations and transport of suspended sediment in Slovene rivers. *RMZ – Materials and Geoenvironment, 52*, 131–135.

Van Hullebusch, E. D., Auvray, F., Deluchat, V., Chazal, P. M., & Baudu, M. (2005). Impact of alum treatment on phosphorus sediment fractionation and short term release in a polymictic shallow lake: Influence of pH conditions. *RMZ – Materials and Geoenvironment, 52*, 63–66.

Water, Air, and Soil Pollution: Focus (2006) **6:** 7–16
DOI: 10.1007/s11267-006-9029-2

PHOSPHORUS STORAGE IN FINE CHANNEL BED SEDIMENTS

DEBORAH J. BALLANTINE[1,3,*], DESMOND E. WALLING[1], ADRIAN L. COLLINS[1]
and GRAHAM J. L. LEEKS[2]
[1]Department of Geography, University of Exeter, Exeter EX4 4RJ, UK
[2]Centre for Ecology and Hydrology, Wallingford, Oxfordshire OX10 8BB, UK
[3]SEPA, Carseview House, Castle Business Park, Stirling FK9 5AD, Scotland
([*]author for correspondence, e-mail: deborah.ballantine@sepa.org.uk;
phone: +44-1786-452590)

(Received 07 September 2005; accepted 30 January 2006)

Abstract. Deposition and storage of fine sediment on channel beds represents an important component of a catchment's sediment budget and can have important implications for sediment-associated P fluxes, due to storage and remobilisation, and for P concentrations through water–sediment interactions. Spatial and temporal variations in P content and storage in fine bed sediment have been studied in two UK lowland catchments, the Rivers Frome and Piddle in Dorset. Fine bed sediment was sampled in representative reaches on a bi-monthly basis using a re-suspension cylinder, and the resulting samples were analysed for total P, a range of P fractions and particle size. The results demonstrate significant spatial and temporal variability in PP concentrations and storage, with maximum and minimum P concentrations and storage occurring in late summer and winter, respectively. Temporal variations in concentrations reflect residence times of the sediment and ambient P concentrations, while variations in storage are mainly due to hydrological regimes. Spatial variations reflect catchment characteristics, the location of inputs and local variations in hydrological and channel bed conditions.

Keywords: bed sediment, phosphorus, storage, study area, UK

1. Introduction

Phosphorus (P) plays a key role in the eutrophication of surface waters. Because a large proportion of the TP load of a river can be transported in association with sediment, sediment-associated P (PP) can represent a significant long-term source of potentially available P to the river system (Sharpley, Smith, Jones, Berg, & Coleman, 1992). The sediment delivery system therefore plays an important role in the P dynamics of river systems, since the deposition and storage of sediment on channel beds and its subsequent remobilisation can exert an important influence on the routing, transport and fate of PP (Owens & Walling, 2002). P enters rivers from diffuse catchment sources (mainly agriculture) and point (effluent) sources. P concentrations in sediment will therefore reflect the underlying geology and soil type of the source area, the enrichment of soils with

P from fertiliser and manure, as well as the existence and location of point sources, such as sewage treatment works (STWs) and urban areas. Diffuse inputs of P are commonly highest during winter storm events and a proportion of the PP that is flushed into the stream channel under high flows will be deposited and stored on the riverbed during downstream transport (Jarvie et al., 2005). Although channel bed storage of fine sediment and PP is generally temporary, with variations apparent on a monthly basis but with little or no net loss occurring on the annual time scale, such storage has important implications for the delivery and fate of PP (Walling et al., 2003). At times of maximum in-channel storage, the magnitude of upstream PP fluxes may be greatly underestimated if losses to bed storage are not considered, and potential environmental problems associated with elevated P levels, including the degradation of water quality and aquatic habitats, may be underestimated (Walling et al., 2003). Furthermore, whilst in storage, sediment can play an important role in buffering concentrations of soluble P, and will either absorb or release P depending on the concentrations of P in surface waters (House & Denison, 1998). Further information on the transport and storage of PP at the catchment scale is therefore required and the study reported in this paper aims to contribute to an improved understanding of the spatial and temporal variability of sediment-associated P concentrations and storage associated with fine channel bed sediments.

2. Study Areas

Two lowland groundwater-fed catchments (shown in Figure 1), the Frome (425 km^2) and the Piddle (183 km^2) in Dorset were selected for this investigation as part of the LOCAR (Lowland Catchment Research) thematic programme funded by the UK Natural Environment Research Council. Both catchments are primarily underlain by chalk (ca. 65% of their area), although outcrops of Jurassic limestone and Cretaceous Upper Greensand occur in the headwaters, and Tertiary sands and gravels are found in the lower reaches. The headwater areas of both catchments are dominated by chalk outcrops, with steep slopes and maximum elevations of 264 m and 273 m a.s.l. in the Frome and Piddle catchments, respectively. In contrast the lower reaches of both catchments are characterised by gentle relief and extensive well-developed floodplains. Agricultural land accounts for >80% of each of the catchments, and land use is dominated by grassland and cereal cultivation (Natural Environment Research Council, 2000). Average annual precipitation is ~932 mm in the Frome and ~888 mm in the Piddle for the period 1972–1997 (Collins, Walling, & Leeks, 2005). The average daily flows of the Frome and Piddle are 6.44 m^3 s^{-1} and 2.46 m^3 s^{-1}, respectively, (NRFA). The mainly rural catchments are noted as being of high amenity value, with the Frome reported to be the last natural chalk salmon stream in the UK.

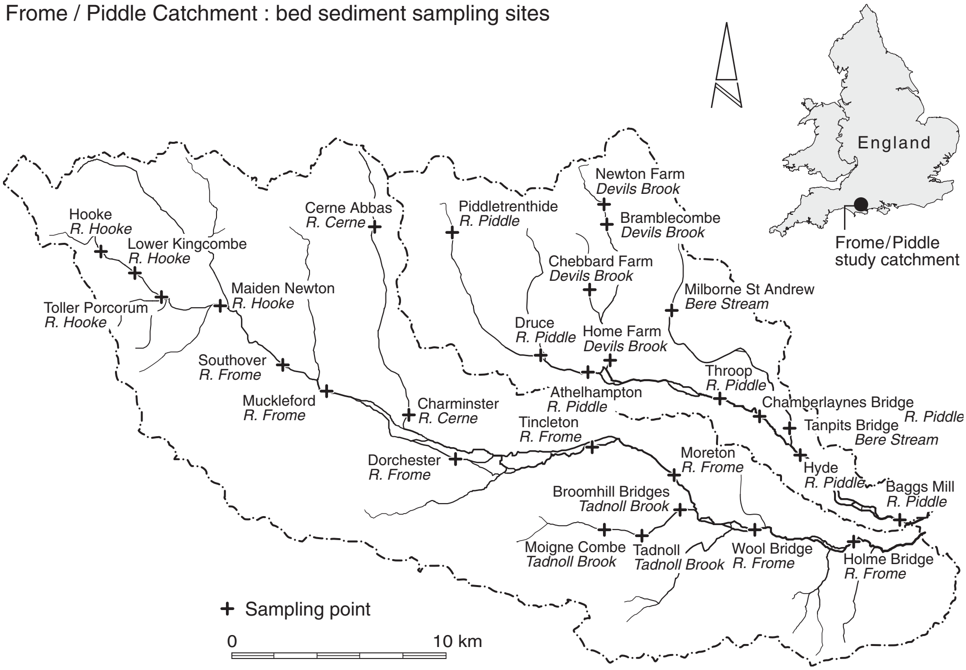


Figure 1. The location of the study catchments and the individual bed sediment sampling sites.

3. Materials and Methods

3.1. FIELD SAMPLING

Measurements of fine-grained bed sediment storage were made at approximately bimonthly intervals at 16 sites along the main channel of the Frome and 13 sites along the main channel of the River Piddle and their primary tributaries over the period January 2003–September 2004 (*n*=250) (Figure 1 and Table I). Each sampling site was selected to be representative of the channel bed in the adjacent reach. The approach employed follows that proposed by Lambert and Walling (1988). A metal cylinder (height 1.0 m; surface area 0.16 m^2) was carefully lowered onto, and pushed into, the channel bed, in order to create a seal. A metal rod was then used to stir the water inside the cylinder and to agitate the upper 5 cm of the channel bed, in order to mobilize the fine sediment stored both as a surface drape and within the surface layers of riverbed gravels. A representative aliquot of the turbid water was collected in a 0.5 l bottle and the sediment concentration associated with the sample was used to provide an estimate of sediment storage (g m^{-2}) on the channel bed. This procedure was repeated twice at each sampling site, in order to take account of local spatial variability in sediment storage resulting from variations in water depth and channel bed mor-

TABLE I

Average phosphorus content and specific surface area of the <63 μm fraction of bed sediment collected from the Rivers Frome and Piddle and estimates of mean channel bed storage of <63 μm sediment and total phosphorus

Catchment	Site	*n*	TP ($\mu g\ g^{-1}$)	CV %	IP ($\mu g\ g^{-1}$)	CV %	OP ($\mu g\ g^{-1}$)	CV %	AAP ($\mu g\ g^{-1}$)	CV %	SSA	CV %	% AAP	IP/OP	% IP	% OP	TP ($g\ m^{-2}$)	Sediment ($kg\ m^{-2}$)
Frome	Hooke	4	1,458	39	550	91	908	56	32	66	0.39	12	2.19	0.61	37.72	62.28	1.23	0.80
	Lower Kingcombe	10	1,111	73	401	73	775	79	138	46	0.43	11	12.42	0.52	36.09	63.91	1.99	2.63
	Toller Porcorum	4	981	51	436	77	436	49	95	54	0.48	7	9.68	1.00	44.44	55.56	0.64	0.55
	Tollerford	10	1,366	116	450	95	915	130	140	35	0.44	29	10.25	0.49	32.94	67.06	0.63	0.65
	Southover	10	910	92	297	94	612	99	114	39	0.42	9	12.53	0.49	32.64	67.36	0.84	1.05
	Muckleford	10	1,252	70	329	76	923	73	117	61	0.43	10	9.35	0.36	26.28	73.72	1.47	1.49
	Cerne Abbas	10	1,407	68	444	98	964	70	123	39	0.41	18	8.74	0.46	31.56	68.44	1.49	0.94
	Charminster	10	1,379	61	576	76	803	76	67	75	0.41	18	4.86	0.72	41.77	58.23	0.86	0.73
	Long Bridge	10	1,068	83	306	107	762	83	108	50	0.47	12	10.11	0.40	28.65	71.35	0.85	0.59
	Tincleton	10	1,206	75	362	92	843	72	89	54	0.48	9	7.38	0.43	30.02	69.98	0.56	0.53
	Moreton	10	1,315	109	456	118	858	110	199	96	0.40	16	15.13	0.53	34.68	65.32	1.16	0.76
	Tadnoll	8	1,342	44	751	67	591	8	353	48	0.58	2	26.30	1.27	55.96	44.04	1.33	0.74
	Moigne Combe	4	3,093	64	1,903	87	1,189	36	507	28	0.47	3	16.39	1.60	61.53	38.47	1.44	0.41
	Broomhill	10	950	89	331	123	619	78	185	74	0.44	15	19.47	0.53	34.84	65.16	0.52	0.69
	Wool Bridge	9	1,805	95	629	57	1,176	117	186	66	0.42	8	10.30	0.53	34.85	65.15	1.86	1.24
Piddle	Holm Bridge	10	1,471	69	595	70	876	76	261	49	0.44	8	17.74	0.68	40.45	59.55	1.13	0.89
	Piddletrenthide	10	1,033	49	354	54	673	54	61	76	0.48	20	5.91	0.53	34.27	65.73	1.76	1.30
	Druce Farm	10	1,038	72	358	67	680	79	49	62	0.52	7	4.72	0.53	34.49	65.51	5.33	4.34
	Newton Farm	4	773	55	416	106	356	45	111	35	0.45	17	14.36	1.17	53.82	46.18	1.16	1.45
	Cheselbourne	3	1,019	104	368	116	651	102	48	72	0.39	17	4.71	0.57	36.11	63.89	0.66	0.68
	Bramblecombe	10	939	36	298	27	641	57	93	8	0.59	9	9.90	0.46	31.74	68.26	0.26	0.26
	Home Farm	10	1,154	66	269	90	886	64	84	74	0.47	18	7.28	0.30	23.31	76.69	1.02	1.18
	Athelhampton	10	1,116	66	316	69	800	70	51	76	0.51	10	4.57	0.40	28.32	71.68	3.33	0.29
	Milburn St Andrews	10	936	91	340	96	596	97	47	43	0.42	11	5.02	0.57	36.32	63.68	1.71	1.67
	Throop	10	1,068	64	221	85	847	63	53	112	0.41	0	4.96	0.26	20.69	79.31	0.44	0.39
	Chamberlayne's Bridge	10	972	84	259	74	713	99	78	66	0.49	12	8.02	0.36	26.65	73.35	0.81	0.94
	Tanpits	10	2,228	61	1,077	53	1,151	73	88	59	0.46	14	3.95	0.94	48.34	51.66	4.19	2.08
	Hyde	10	2,065	76	843	68	1,222	86	178	80	0.43	12	8.62	0.69	40.82	59.18	4.53	1.91
	Baggs Mill	10	1,224	45	465	59	759	59	204	49	0.38	22	16.67	0.61	37.99	62.01	1.40	1.45

TP Total phosphorus, *IP* inorganic phosphorus, *OP* organic phosphorus, *AAP* algal available phosphorus, *SSA* specific surface area, *IP/OP* inorganic/organic phosphorus ratio, *CV* co-efficient of variation phology or texture. One sample was collected in the thalweg, where sediment storage was considered to be lowest and another adjacent to the river bank visibly exhibiting the greatest storage, with the average of the two being taken to provide an estimate of sediment storage at each location. In addition, a bulk sample of the water and remobilised sediment within the cylinder was collected from the location used to represent the area of maximum sediment storage at each sampling site, by pumping the turbid water into an acid washed 25 l polyethylene can. Low flow conditions on one sampling visit to Cheselbourne and high flows experienced twice at Tadnoll and once at Wool Bridge inevitably resulted in the coverage of the sampling sites being incomplete on three occasions.

3.2. LABORATORY ANALYSES

The sediment concentrations associated with the individual 0.5 l sample bottles ($C_s(t)$, g l^{-1}) were determined by filtration using glass microfibre filters and the amount of fine sediment released per unit surface area of channel bed ($Br(t)$, g m^{-2}), which was used as a measure of sediment storage, was estimated as:

$$Br(t) = \frac{C_s(t)V(t)}{A}$$

Where $V(t)$ is the volume of water enclosed in the sampling cylinder (l), calculated as the product of the depth of water in the cylinder and the cylinder surface area, and A (m^2) equates to the surface area of the sampled channel bed area.

The bulk water samples were allowed to settle before the clear supernatant was decanted and the sediment recovered by centrifugation. Following freeze-drying, the sediment samples were gently disaggregated and screened through a 63 μm sieve, in order to separate the clay and silt fraction (<63 μm). The total P (TP) and inorganic P (IP) content of the <63 μm fraction were determined by UV visible spectrophotometry following chemical extraction with hydrochloric acid and sodium hydroxide using the molybdenum blue method described by Mehta, Legg, Coring, and Black (1954) while the organic P (OP) fraction was calculated by subtraction. The algal available fraction (AAP) was extracted using 0.1 M sodium hydroxide, as described by Dorich, Nelson, and Sommers (1985). This chemical extraction method was chosen as the 0.1 M NaOH-extractable phosphorus fraction was found by Dorich et al. (1985) to be significantly correlated with two-day and 14-day available phosphorus for an alga, thereby implying that NaOH-extractable phosphorus could be used to estimate both short and long-term available phosphorus in sediments. The specific surface area of the sediment samples was also estimated using a Coulter LS130 laser diffraction granulometer, after pre-treatment with 30% hydrogen peroxide to remove the organic matter, followed by dispersion in an ultrasonic disintegrator. Data was analysed using Kruskal Wallis and Mann Whitney non-parametric statistical tests.

4. Results and Discussion

Table I presents information on the mean P content of bed sediment collected from the Rivers Frome and Piddle and their primary tributaries. Comparison of the values shows that the range of values for the River Frome (910–3,093 μg g^{-1}) is greater than for the River Piddle (773–2,228 μg g^{-1}), which reflects several contrasts in catchment characteristics, channel and hydrological conditions, which will influence the P content of sediment. Considering all the samples collected there is no significant difference in TP values between sites on the River Frome (Kruskal Wallis (KW) $P>0.05$) but a significant difference was found between sites for the River Piddle (KW $P=0.001$), with the high values of TP measured at Tanpits being significantly different from values measured at other sites (Mann Whitney (MW) $P>0.05$). Comparison with other studies (Owens & Walling, 2002) shows that the values for TP measured are relatively low, reflecting the rural nature of the two catchments. The low spatial variation in TP values reflects the dominance of diffuse sources in controlling P entry to the two rivers rather than point sources related to industry and STWs. Elevated TP concentrations measured in sediment collected at Wool Bridge on the River Frome and at Hyde on the River Piddle reflect inputs of sediment with high TP content from the Bere Stream and Tadnoll Brook tributaries, since the sampling sites on the main channel were located downstream from the confluences with these tributaries.

Mean values for IP in the River Frome and River Piddle follow the same pattern as TP concentrations, with higher concentrations recorded in the River Frome than in the River Piddle (Table I). IP values on the River Frome show no significant difference between sites, whilst on the River Piddle, IP values measured at Tanpits on the Bere Stream and Hyde were significantly higher than values at other sites (MW $P>0.05$). Values for OP range from 436 to 1,189 μg g^{-1} for the River Frome and from 356 to 1,222 μg g^{-1} for the River Piddle. No significant differences were found between sites on either of the rivers for OP.

Comparing the percentage contribution of IP to TP between catchments, a higher mean contribution from IP is noted in the River Frome than in the Piddle. The IP/OP ratio, which reflects the importance of the IP fraction, presented in Table I, is commonly less than 1. This demonstrates that the OP fraction is generally more important, and reflects the rural undisturbed nature of the catchments studied. The sites at Tadnoll and Moigne Combe on the River Frome have IP/OP values greater than 1, which must be seen as high for this study, and these reflect the increased importance of diffuse agricultural sources of P in the Tadnoll Brook tributary. Point sources and STWs commonly provide important sources of IP, and the relatively low importance of this fraction and the lack of increase around Dorchester, the largest town in the two catchments with an average population of 16,600, indicate that the effects of point source inputs could not be detected.

Algal available P (AAP) contributions to TP are higher for the River Frome (range 2%–26%) than for the River Piddle (range 4%–17%). These results reflect the higher IP concentrations in the Frome, the fraction from which AAP mainly derives, and with which AAP concentrations are significantly correlated (Pearson's $r=0.298$, $P>0.01$). AAP concentrations and contributions to TP are lower for the Piddle than the Frome, reflecting both the lower levels of IP and possibly the higher levels of uptake by the more abundant in-stream vegetation in the River Piddle noted by the authors in the summer growing season.

Specific surface area (SSA) values are also presented in Table I. These show a significant difference between sites in the River Piddle (KW $P=0.00$), but not between sites in the River Frome (KW $P>0.05$). The difference between sites on the Piddle does not, however, explain the variation in TP concentrations, as a Pearson's test showed only a very weak inverse relationship between SSA and TP content ($r=-0.121$).

To highlight their significance, the P concentrations reported above have been linked to the total amounts of fine sediment stored in the channel to provide estimates of TP storage per unit area at the sampling sites in the rivers, and mean values of both sediment and P storage for the study period are presented in Table I. The spatial variation of sediment and P storage between sites evident from these data reflects the presence of an available source of sediment to the channel system as well as the local hydraulic conditions. Comparing the two rivers, TP storage per unit area is generally higher at sites on the River Piddle, particularly at Druce Farm, Hyde and Tanpits, than on the River Frome. This may reflect the influence of the underlying geology and water abstraction, as the lower flows in the Piddle provide more favourable conditions for fine sediment and hence PP accumulation. The amount of TP in storage is controlled primarily by the amount of fine sediment in storage, rather than the TP concentrations, since a Pearson's test showed a stronger correlation between TP storage and sediment storage ($r=0.735$, $P>0.01$) than between TP storage and TP concentrations ($r=0.436$, $P>0.01$).

Table I also presents values for the coefficient of variation (CV) for the concentrations of TP and the P fractions, the associated values of storage and SSA. The wide ranges reflect the temporal variability of the concentrations and storage at individual sampling sites. CV values for TP and TP storage alone range from 36% to 116% and 30% to 165%, respectively, indicating that such temporal variability can be appreciable. In contrast, CV values presented for SSA are characterised by a small range, which indicates limited variability over the duration of the sampling period, and suggests that SSA exerts minimal influence on temporal variations in the TP content of channel bed sediment.

Figure 2 presents information on the temporal variation of the mean TP, IP, OP and AAP content of bed sediment, and both sediment and TP storage for all sites over the study period. A seasonal influence is apparent for all the variables, with maximum concentrations of TP, IP and OP occurring in September 2003, when maximum sediment and TP storage also occur. The timing of maximum TP concentrations may reflect enrichment associated with increased residence times

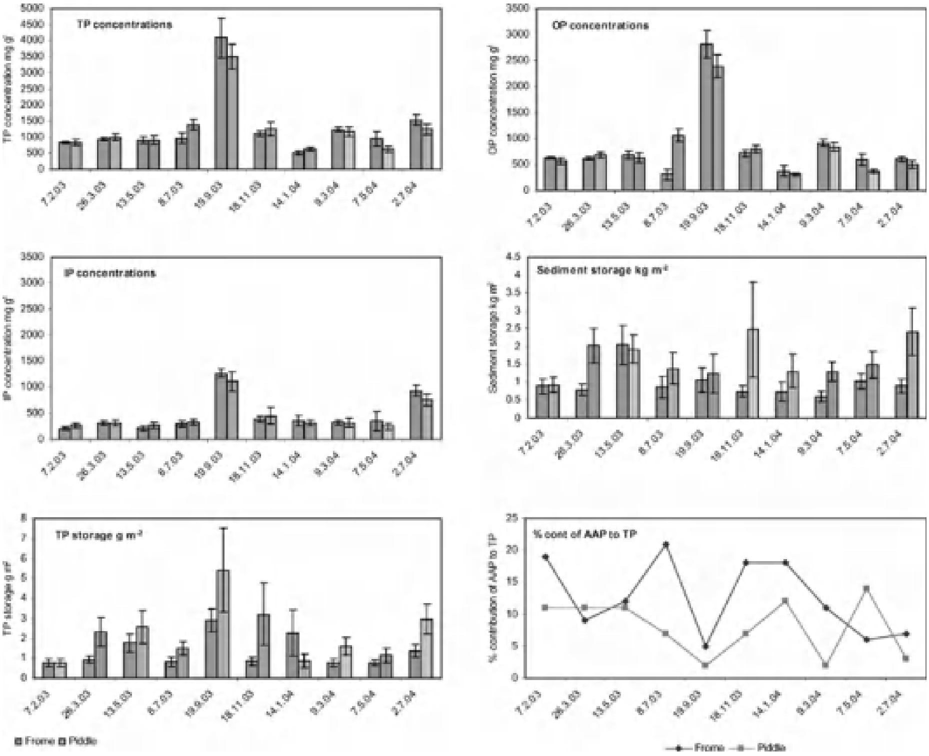


Figure 2. Temporal variations in the mean total phosphorus (*TP*), inorganic phosphorus (*IP*), organic phosphorus (*OP*) concentrations, percentage contribution of algal available phosphorus (*AAP*) to total phosphorus, total phosphorus storage and fine sediment storage for all sites in the catchments of the Frome and Piddle. *Error bars* show one standard error of the mean.

on the channel bed, sorption of soluble P from the water column to inorganic sediments and the build up of organic matter. For this study lower concentrations of TP, IP and OP tended to occur in the winter months. AAP followed a different trend, suggesting that concentrations reflect different controls to those influencing TP, IP and OP concentrations. This fraction tends to be at a maximum in the winter and a minimum in late spring and late summer, which implies that it is influenced by the biological activity and uptake in the summer growing season. At times when much P is being used for plant growth, concentrations are low, but when instream growth is minimal, concentrations are high. IP and OP concentrations also vary significantly throughout the year (KW P=0.00 IP; P= 0.00 OP), with concentrations in September 2003 and 2004 noted as being statistically different (MW P=0.00 in September 2003 and 2004 for both fractions). The low IP concentrations found in spring and early summer coincide with times of maximum instream vegetation growth, while maximum OP concentrations occur in the late summer period and may reflect the dieback of instream vegetation and the associated accumulation of organic matter.

Figure 2 also shows the seasonal trends in the mean values of TP and sediment storage for the sampling sites in the two rivers over the study period. Maximum storage of TP was observed in September 2003 of the first sampling year and the tendency towards a similar increase in the second sampling year suggests that this pattern of accumulation occurs on an annual cycle. The findings from this study indicate a seasonal cycle of winter export of sediment with a low P content. With the onset of lower flows in spring, sediment starts to accumulate on the channel bed and this continues through the summer, with occasional partial remobilisation by temporary high flows. Sediment with an initial low TP content has the capacity to adsorb P from the overlying water column or from biological debris, reflected in the increased P concentrations in sediment as the year progresses. Maximum storage and concentrations occur in late summer, after which, the onset of high flows remobilises the stored sediment to return to low storage values. At this time, recently eroded sediment with a lower P content again becomes dominant. This cycle is clearly heavily dependent on the hydrometeorological conditions and while the precise pattern can be expected to vary between years, there is an underlying annual trend of accumulation and export of fine sediment and P, which serves to renew the physical, chemical and biological capacity of the river to accumulate P during the subsequent year.

5. Conclusion

The findings outlined above provide an insight into the spatial and temporal variation of the content of TP and its various fractions in fine bed sediments within the study catchments. Spatial and temporal trends in the storage of P in channel bed sediment are also evident within these lowland permeable catchments. Mean TP concentrations in sediment measured in the study catchments are relatively low and tend to be controlled by landuse activities. Given the relatively unpolluted nature of the catchments, these results provide useful information on reference conditions for PP in bed sediments. Clear seasonal trends have also been identified. Highest P concentrations in sediment occur in the summer season, which is acknowledged to be the critical time for P impacts in rivers, when eutrophication risk is highest. Maximum TP storage also occurs in this critical season, however it may be preferable from an ecological and biological perspective that the phosphorus is stored in bed sediments at this time rather than in the water column. In an attempt to place the point estimates of P storage in the broader context of the study river's behaviour, reference can be made to the estimates of mean total P storage in fine channel bed sediments for the Frome and Piddle catchments reported by Collins et al. (2005). The values of 1,085 and 1,003 kg, for the Frome and Piddle catchments, respectively, are equivalent to between 12% and 36% and 41% and 80% of the total annual P flux for the two catchments. Catchment scale studies such as this are useful from a management perspective, since elevated concentrations of TP in sediment can provide information on P sources. In addition, since the amount of fine sediment in storage exerts a key control on P storage, an understanding of the zones within the catchment where storage values are high is an important requirement in the development of management plans and in reducing the mobilisation of sediment into the fresh water environment.

Acknowledgements

The financial support of the UK Natural Environment Research Council in providing the studentship for the author through Grant NER/T/S/2001/00936 within the LOCAR thematic research programme is gratefully acknowledged.

References

Collins, A. L., Walling, D. E., & Leeks, G. J. L. (2005). Storage of fine-grained sediment and associated contaminants within the channels of lowland permeable catchments in the UK. In D. E. Walling & A. Horowitz (Eds). *Proceedings of symposium Sediment Budgets 1 held during the Seventh IAHS Scientific Assembly* (pp. 259–268). Foz do Iguacu, Brazil, April 2005, IAHS publication 291.

Dorich, R. A., Nelson, D. W., & Sommers, L. E. (1985). Estimating algal available phosphorus in suspended sediments by chemical extraction. *Journal of* Environmental Quality, *14*, 400–405.

House, W. A., & Denison, F. H. (1998). Phosphorus dynamics in a lowland river. *Water Research, 32*, 1819–1830.

Jarvie, H. P., Jurgens, M. D., Williams, R. J., Neal, C., Davies, J. J. L., Barrett, C., et al. (2005). Role of river bed sediments as sources and sinks of phosphorus across two major eutrophic UK river basins: The Hampshire Avon and Herefordshire Wye. *Journal of Hydrology, 304*, 51–74.

Lambert, C. P., & Walling, D. E. (1988). Measurement of channel storage of suspended sediment in a gravel-bed river. *Catena, 15*, 65–80.

Mehta, N. C., Legg, J. O., Coring, C. A. I., & Black, C. A. (1954). Determination of organic phosphorus in soils: 1. Extraction methods. *Soil Science Society of America Journal, 18*, 443–449.

National River Flow Archive, National Water Archive, Natural Environment Research Council, CEH Wallingford. http://www.nwl.ac.uk/ih/nrfa/spatialinfo/index/indexCatchmentSpatialInfo.html (accessed 15/08/05)

Natural Environment Research Council (2000). Land Cover Map. CEH Monks Wood.

Owens, P. N., & Walling, D. E. (2002). The phosphorus content of fluvial sediment in rural and industrialized river basins. *Water Research, 36*, 685–701.

Sharpley, A. N., Smith, S. J., Jones, O. R., Berg, W. A., & Coleman, G. A. (1992). The transport of bioavailable phosphorus in agricultural runoff. *Journal of Environmental Quality, 21*, 30–35.

Walling, D. E., Owens, P. N., Carter, J., Leeks, G. J. L., Lewis, S., Meharg, A. A., et al. (2003). Storage of sediment-associated nutrients and contaminants in river channel and floodplain systems. *Applied Geochemistry, 18*, 195–220.

Water, Air, and Soil Pollution: Focus (2006) **6:** 17–27
DOI: 10.1007/s11267-006-9040-7

QUANTIFICATION OF THE EROSION RESISTANCE OF UNDISTURBED AND REMOULDED COHESIVE SEDIMENTS

ROBERT BANASIAK* and RONNY VERHOEVEN
Hydraulics Laboratory, Department of Civil Engineering, Ghent University,
St-Pietersnieuwstraat 41, 9000 Gent, Belgium
*(*author for correspondence, e-mail: robert.banasiak@ugent.be; phone: +32-9-2643284;*
fax: +32-9-2643595)

(Received 2 September 2005; accepted 6 June 2006)

Abstract. Cohesive sediments besides their typical heterogeneity are characterised by structural discontinuity. Particularly, organic consolidated muds are a good example of sediments that consist of vast aggregates, pore water and gaseous products. The texture of a cohesive sediment bed is a result of a number of mutually affecting factors, such as deposition history, mineral and organic composition, kind of biota and oxygen uptake. The presented work attempts to quantify the effect of sediment physical properties and sediments structure on the sediment erosion potential, considering incipient motion and erosion rate. This quantification is made on the basis of comparative testing of both unremoulded and remoulded samples of a river mud. Due attention is paid to sediment handling to preserve the delicate structure of the sediment for the laboratory experiments. Mud with two degrees of consolidation has been examined in a tilting flume under different flow situations. The test results show a typical increase of erosion strength with dry matter concentration of the mud. It has also been found that the structural properties increase the erosion strength for the less consolidated mud. An opposite effect has been recorded for a more consolidated deposit. As a consequence, due to the sediment structure, the original beds differ much less in erosion resistance in relation to the dry mass concentration than their disturbed analogues. Finally, the erosion resistance of the examined mud is compared with data from the literature.

Keywords: erosion, river mud, sediment structure, unremoulded and remoulded samples

1. Introduction

The cohesive sediments, whether they are transported or deposited in rivers, estuaries or reservoirs, usually contain a considerable amount of organic matter. The presence of the organic matter affects the fine sediment movement in all its phases; during the settling of suspended material, consolidation of settled sediments and erosion. The impact of organic matter and associated biological activities on the settling and consolidation process is quite well understood (Black, Tolhurst, Paterson, & Hagerthey, 2002; Heinzelmann & Wallisch, 1991; Montague, 1986; Prochnov, Schweim, & Köngeter, 2000).

Regarding the consolidation, it is a complex process governed by physical and biochemical transformations. In a physical meaning, the consolidation is the solid matter compaction and pore water release from the sediment, which continues until the buoyant weight of the overlying deposit is counteracted by the sediment strength to support part of its weight. This process results in the breakup and reorganization of a freshly deposited matrix of flocs and aggregates. Even after a long period of consolidation, however, the sediment usually still constitutes of compacted solids and voids filled with water and gaseous products. The presence of these voids can be attributed in a large extend to the micro- and macro-organism activity (bioturbation). The decomposition of organic matter within the deposit leads to production of gases, while different species (worms, larvae) drill the sediment bed. The voids formed weaken the sediment by the decrease of the bulk density and disruption of the interparticle bounds (Banasiak, Verhoeven, De Sutter, & Tait, 2005; Wijdeveld & Kesteren van, 1999). The complexity of the biochemical influence on sediment properties is made clear by the fact that settlement and ageing cannot only destabilize a bed by loosening of the bed structure, but also consolidate it basically by particle agglutination (secretion of exopolymers) and biofilm formation on the sediment surface. Further, the consolidation process, the physical characteristics of the sediment and the biogenic activity are stratified, i.e., they vary along the deposit depth. Apart from physical sedimentation history, this stratification results from the availability of dissolved oxygen, which determinates the presence of different type of biota and biochemical processes within a layer.

In view of the outlined complexity of the consolidation process, which determines the erosion potential of cohesive sediments, studies on the quantification of these effects are still ongoing and important as the knowledge of sediment erosion behaviour is very relevant to engineering practice and to the ecological evaluation of numerous aquatic environments.

The goal of this study is twofold. The first is the assessment of the erosion resistance of a natural cohesive sediment having a remarkable content of organic material and possessing a significant degree of consolidation along with marked structural properties developed in natural conditions. For this due effort is paid to the elaboration of the sediment handling procedure that preserves its natural delicate structure, both during the *in situ* sampling and the examination in the laboratory. The second goal is to quantify in some way the effect of the sediment structure on the erosion strength of the collected deposit. This is accomplished by testing in parallel undisturbed samples and samples handled so that their erosion resistance can be attributed to sediment cohesion only.

2. Experimental Method

2.1. SAMPLE COLLECTION AND PREPARATION

For the collection of undisturbed mud samples a set of boxes made of thin metal plates with a size of $20 \times 15 \times 5$ cm^3 were used. One side of the box can be detached

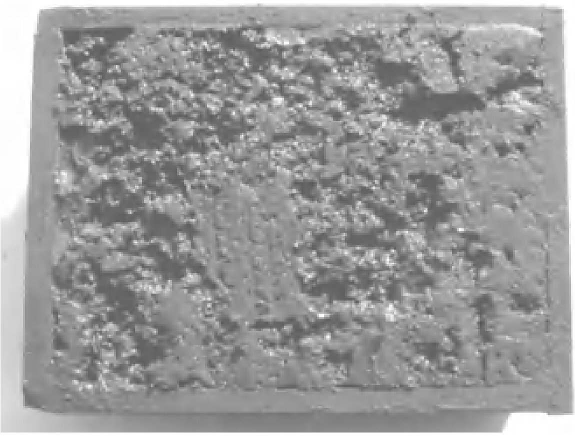


Figure 1. Sample of 'unremoulded' mud B.

allowing it to be pressed into the sediment, so that a fairly undisturbed core can be extracted from the river bed. This can be done with the use of a rod, to which the box is fixed forming a shovel, or manually, as in the present case because of an easy access to the deposit and a more accurate and efficient handling. Once a successful coring is made, the short side is put back to the box and the excess of the collected sediment is carefully removed by cutting the top-layer with a sharp knife (Figure 1). After cleaning, the box with sediment is weighted and ready to be placed in the flume in the laboratory.

After testing the undisturbed mud, we remoulded the sediment. The remoulded samples are meant here as a well mixed slurry obtained from the collected mud, poured and compacted in the coring/test boxes.

2.2. SEDIMENT PROPERTIES

The examined mud was collected from the tidal part of the Scheldt river in the city of Gent, Belgium. The sampling site is located downstream of a water level control weir. The sampling was performed close to the river bank during low water, when the sediment deposits raised over the water surface. The mud was sampled from two depths: between 5 and 10 cm (mud A) and between 20 and 30 cm beneath the sediment surface (mud B), where the sediment apparently was more consolidated. Eight samples were taken from each layer. The collected sediment was then analysed in the laboratory for its physical characteristics as given in Table I. The given average physical properties change with the collection depth. Mud A had a relatively high water content and a moderate ability to sustain the shape when extracted. The deeper more consolidated sediment possessed a developed structural strength appearing in a network of aggregates and numerous voids enclosed in the sediment body. For sediment B the effect of biodegradation

TABLE I

Mud average properties from the Scheldt river

	Sample A	Sample B
Collection depth (m)	0.05–0.1	0.2–0.3
Mean diameter d_{50} (μm)	26	25
Particles >0.063 mm (%)	13.5	12.5
Specific density (kg/m^3)	2,228	2,345
Bulk density (kg/m^3)	1,229	1,254
Dry matter concentration (g/l)	468	555
Water content (%)	163	126
Organic matter content (%)	10.11	8.94
Void content (%)	3.1	8.4

is pronounced by a smaller amount of organic mater and higher specific density. For the remoulded samples studied in parallel the physical properties should be considered as the same except a near-to-zero void ratio and an increased bulk density as well as dry matter concentration.

2.3. Description of the Test Flume and Procedure

Experiments were conducted in a tilting 11 m long recirculating flume with a semi-circular cross-section and diameter of 0.39 m, which originally was designed to study in-sewer sediment transport processes (De Sutter et al., 2000). For the purpose of the current study, in the invert of the flume a flat 0.25 m wide bottom is installed in order to represent geometrically the presence of a sediment deposit. The boxes with the sediment were put in a bottom opening located 6 m from the flume entry. The flume walls and bottom are covered with an abrasive paper to increase the hydraulic roughness. The flume has a maximum discharge capacity of 40 l/s, flows with water depths up to 0.15 m and velocities up to approximately 1 m/s can be realised.

During the erosion tests, the samples are subjected to constant flows varied from run to run. After each run the box with sediment is removed and weighted so that from the loss of material the erosion rates can be determined. Each sample was used in one to four runs, depending on the flow rate and eroded mass.

2.4. Bed Shear Stress

The action of the flow on the sediment surface was determined through flow velocity measurements performed using a 3D down looking acoustic Doppler velocitimeter (ADV). The ADV periodically emits a short acoustic signal, and three receivers measure the Doppler shift which is related to the local velocity component. It allows for the determination of the water velocity component along three perpendicular axes. The probe measures the velocity in a small volume (3–9 mm high) located 6 cm beneath the transmitter, which minimises the disturbances within the flow measurement volume. The three orthogonal flow velocity vectors were measured at a frequency of 25 Hz to monitor the velocity variation with time.

From the ADV measurements it is possible to estimate the shear stress. The ADV measures three orthogonal velocity vectors V_x, V_y and V_z in streamwise, lateral, and vertical directions, respectively. The bed shear stress τ_b is estimated using:

$$\tau_b = -\rho \overline{u'w'}; \tag{1}$$

where $u' = V_x - \overline{V_x}$ and $w' = V_z - \overline{V_z}$ are recorded near the flume bottom.

The local bed shear stress over the sediment bed was recorded by the ADV in six points situated in a rectangular matrix and spaced by a distance of 6 cm (x-coordinate) and 3 cm (y-coordinate) with a 60 s long recording in each point. The recording in each point is randomly influenced by the topography of the sediment or particular aggregates. A reliable erosion rate $E=f(\tau_b)$ relationship can be established if sufficient spatial and temporal averages of the shear stress values are used (Banasiak & Verhoeven, 2004).

3. Results and Discussion

3.1. EROSION

The cohesive sediment follows principally two modes of erosion: a surface erosion and bulk erosion (Krone, 1999; Mehta, Hayter, Parker, Krone, & Teeter, 1989). The surface erosion is carrying away the soil surface particles, particle by particle. The surface erosion rate increases linearly with shear stress until the pressure fluctuations and surface shear become sufficiently large to dislodge chunks of the bed surface. This change in the erosion process was also clearly demonstrated in the current study during the erosion of unremoulded mud by the appearance of pits in the sample surface once the shear stress exceeds the critical shear stress for bulk erosion. For the compacted remoulded mud B the erosion within the applied shear stress rates was restricted only to slow surface erosion.

The flow-induced shear deforms the aggregates at the bed surface. If due to this process, the interparticle bonds connecting an aggregate to its neighbours are ruptured, the aggregate will be entrained. A bond is broken when a certain threshold of internal stresses is exceeded. It must be noted that the shear stress and the bond strength are both stochastic variables, while the strength presents a spatial distribution at a given degree of consolidation. As a consequence, no distinct time averaged critical shear stress, for which the motion begins, can be found from the current results. For the same reason a significant scatter of erosion rates related to the near-bed Reynolds stress is observed (Figure 2). Difficulties in

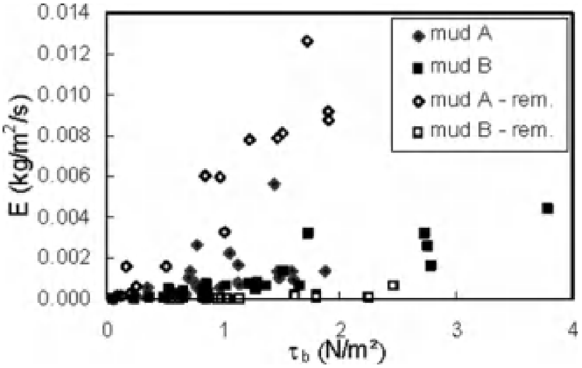


Figure 2. Erosion as a function of bottom Reynolds shear stresses.

establishing a simple deterministic approach relating flow and bed strength have also been encountered in earlier studies (Mitchener & Torfs, 1996; Parchure & Mehta, 1985; Tolhurst et al., 2000). Nevertheless, due to significant differences in sediment properties, a fairly clear quantification of the erosion capability of mud can be made. When considering the erosion of the unremoulded samples, one can see in Figure 2 that a larger scatter of erosion rates as a function of shear stress is recorded for mud A, which situates above those for mud B. The shear stress needed to erode mud B at a given rate are sometimes twice as big as in the case of mud A. Reasonably, more aged and consolidated sediment displays a stronger resistance to erosion. The erosion behaviour indicates also that a freshly deposited sediment displays a higher heterogeneity than the older one.

An interesting insight into the influence of the structure on the sediment erodibility is delivered by the comparison between the erosion for remoulded and unremoulded samples. The differences between the erosion of the remoulded mud A and B is evidently more striking than in the case of unremoulded samples. Mud A after mixing is weaker than in its original state. An opposite effect is recorded for mud B. These shifts in the erosion relationships may have the following reasons. The homogenisation of mud A destroyed the framework of organic elements (small debris) and interparticle bonds that are more resistible than their random and loose arrangement in the mixed mud with relatively high water content. On the other hand, in the case of unremoulded mud B, which contained more decomposed organic material, the erodibility is believed to be strongly affected by the voids forming erosion spots on the sediment surface, and, likely more important, by the decrease of cohesive strength of the sediment body. This decomposed organic material contributes to the formation of a mud skeleton that is much easier to be disintegrated than its compacted voidless analogue. The impact of the structural frameworks on the sediment erodibility is also illustrated by Figure 3, which presents the erosion rates *versus* dry matter concentration in the deposit at a shear stress of 2 N/m^2. The differences in erosion due to frameworks increase with flow action and can reach several hundred percent.

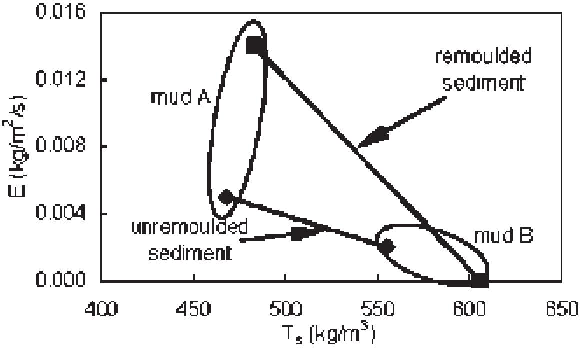


Figure 3. Effect of the sediment structure on the erosion related to the dry matter concentration T_s (τ_b=2.0 N/m^2).

3.2. EROSION FUNCTIONS

The erosion rate of a homogeneous material can be described by Equation (2) (Kuijper, Cornelisse, & Winterwerp, 1989):

$$E = M\left(\frac{\tau_b - \tau_{cr}}{\tau_{cr}}\right)^b \tag{2}$$

The erosion rate constants M and b in Equation (2) are characterising parameters for the erosion behaviour of a homogeneous sediment with a constant concentration gradient and constant critical shear stress τ_{cr}.

Another correlation may be sought using the dimensional excess shear stress as governing parameter; this type of formula was originally proposed for soft and mostly stratified beds:

$$E = A(\tau_b - \tau_{cr})^n \tag{3}$$

with A and n empirical values. Clearly, because of the stochastic nature of the erosion, the results do not correlate uniquely and a strict relationship following Equations (2) and (3) cannot be found. Therefore, the erosion coefficient are determined as such that the erosion curve follows the upper and lower limit of the erosion resistance (Figure 4). As Table II shows, the erosion coefficients can vary within nearly one order of magnitude for a specific mud (mud A). At this point it may be questioned whether the weaker trend is not more indicative for determination of the mobility of such sediment deposits. Local erosion spots of weaker material, on a larger scale, increase the roughness of the bed and induce extra turbulent eddies with as a consequence higher stresses that may cause a progressive erosion.

When using the above mentioned approach for erosion formulations one has to agree with a statement (Krone, 1999; Lavelle & Mofjeld, 1987) that time-averaged shear stress created by turbulent flow is a dull tool for the determination

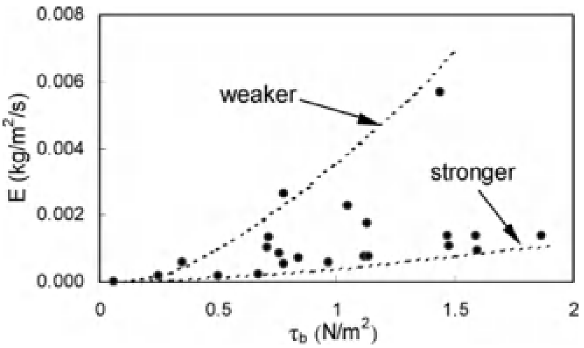


Figure 4. Fitting Equation (1) to the erosion rates for mud A as an upper and lower limit of the erodibility.

of the bed strength because of the aforementioned reasons, but it is the independent variable that we have to work with. Even the used ADV equipment does not allow to go beyond it due to limitation in the sampling frequency and the velocity data correlation. Therefore it is quite obvious that the erosion coefficients are sensitive to the adopted τ_{cr}, in particular in case of Equation (2) in which it is used for the normalisation.

3.3. COMPARISON WITH OTHER DATA

A comparison between the obtained results and other data is not straightforward. Parchure and Mehta (1985) listed following likely specific causes for the difficulty in data comparison: (1) influence of sediment type and bed preparation procedure; (2) temperature differences; (3) influence of apparatus on the stochastic nature of the bed shear stress; (4) effect of relatively high concentrations on τ_b; and (5) errors in estimating the magnitude of τ_b. Nevertheless, some selected studies are reported to allocate the obtained results among the existing data and to generate a wider view on the erodibility of cohesive sediment.

Schweim, Welzel, Spork, and Köngeter (1999) reported on the study on the mud from the Grangent reservoir on the Loire river, France. The sediment had similar properties as the mud in the current study, i.e., contained 15% of fine sand, 19% of organic matter, and 66% silt and clay. In natural bottom condition 9% of the void volume of the mud was filled with gas instead of water. The examination was performed in an annular flume. The erosion tests were preceded by a deposition phase, where the sediment bed could develop from a uniform 30 g/l suspension flow, during a period varying between 3 and 21 days. The resuspension tests were performed within a bottom shear stress range up to 0.74 N/m and erosion rates reached about 2.2E−04 kg/m^2/s. The critical shear stress was found to be 0.1–0.2 N/m^2, increasing with the consolidation period, and the erosion rate constant M (linear fit of Equation (1), i.e., b=1). The mass erosion was determined to be 4-5.1E−05 kg/m^2/s, which is

TABLE II

Erosion rate parameters

Mud	τ_{cr} (N/m^2)	M (kg/m^2/s)	*b* (−)	*A* (s/m)	*n* (−)
A	0.15	3.5-28. 5E−05	1.4	0.6–4	1.4
B	0.15	1.7E−05- 1.1E−04	1.6–1.2	4.5E−0.4- 1E−01	1.2
A – remoulded	0.1	3.4E−04	1.2	5.4	1.2
B – remoulded	2.2	3.0E−05	1.7	0.1	1.7

similar to the results obtained for the mud B. An explanation for that relatively high erosion resistance can be found in the fact that the flow affected deposition results in a stronger sediment bed formation since the settled particles are allocated by the flow in a more stable position (Lau & Droppo, 2000). Unfortunately, Schweim et al. did not provide any details about the physical properties of their artificially developed sediment bed.

Ravens and Gschwend (1999) performed *in situ* measurements of sediment erodibility using a portable flume. In the absence of algal mats their experiments on sites exhibiting a range of bed properties indicated quite uniform erodibility of surface sediment (2–3 mm deep) with a critical shear stress of 0.1±0.04 N/m^2 and erosion rates reaching approximately 10^{-3} kg/m^2/s for shear stresses up to 0.5 N/m^2. Although in those tests a relatively low range of shear stresses was applied a fairly good match with the mud A of the present study can be found.

Witt and Westrich (2003) examined sediment collected from the reservoir Marckolmsheim, located in the upper River Rhine, Germany. Manually homogenised samples with a bulk density of 1.69 g/cm^3 (the bulk density of undisturbed cores was determined to 1.55 g/cm^3) were subjected to varied flow with shear stress conditions ranging from 2 to 7 N/m^2. For a range 2–4 N/m^2 the erosion rate was estimated to be between 0.0002–0.0006 kg/m^2/s. Although in the present study the turbulent shear stress recorded over the remoulded mud B was up to 2.5 N/m^2, the erosion rates are in the same order of magnitude. Somewhat larger erosion resistance in case of the Rhine reservoir sediment can be attributed to its higher bulk density, indicating a higher degree of consolidation of the *in situ* deposit.

The remoulded sediment B displayed a relatively high capacity to resist the erosion. Until the shear stress reached approximately 2.2 N/m^2, no apparent erosion occurred. The erosion resistance of this material can be compared to an artificial mixture of clay and sand studied elsewhere (De Sutter, 2000; Torfs, 1995). The critical shear stresses for this mud are equivalent to the value of about 2 N/m^2 obtained for a mixture containing 80% and 20% of sand and clay respectively. However, despite of several attempts to be found in the literature, it must be stressed that a reverse transfer of data, i.e., from an inorganic artificial mixture to a real mud is likely to produce misleading estimates. The erosion potential of an undisturbed sediment, although possessing some similar physical properties, can be much different, alike in the present case.

Mitchener and Torfs (1996) reported on the *in situ* measurement of undisturbed deposits performed in several intertidal sites. They attempted to relate the obtained erosion stress to the bulk density and sand content. The estimates of the critical shear stress varied from 0.05 N/m for soft, sand free beds to 1.9 N/m^2 for sandy, consolidated beds. The overall trend was a slight increase with the sand content and the average value was around 0.2 N/m^2. Next to the significant scatter of the results, there was little indication about an increase in shear stress with density for individual sites. Mitchener and Torfs also noticed that for the undisturbed samples the erosion stress generally was lower than for an artificially created beds from natural mud tested in the laboratory. The reason for that was attributed to the time-related structural influences, such as biological growth and chemical reactions, which were not possible to develop in a time-limited preparation procedure in the tests of redeposited ‘young’ sediments.

4. Conclusions

The structure has a big potential to modify the erosion strength both for less and more consolidated cohesive sediments and appears to ‘level’ the erosion stresses. When the sediment is highly concentrated and compacted, i.e., it possesses little or no voids, it exhibits a high resistance against erosion due to the cohesion force. The presence of voids developed in a long-term consolidation process cause an evident reduction in this strength. However, in the earlier stage of consolidation the interparticle bonds tend to increase the sediment strength.

The erosion parameters in general depend on the type of sediment and flow and can be determined experimentally. In laboratory procedures, however, the beds are often prepared by pouring a thick slurry of sediment and fluid in the apparatus or by remoulding previously formed beds. In some cases beds are also artificially compacted. This paper emphasises that the sediment treatment may have a big impact on the outcome of an experimental study. For the specific sediment studied here, which is representative for mud, the preservation or destruction of natural structural strength leads to differences in erosion rates in a range of one order of magnitude.

References

Banasiak, R., & Verhoeven, R. (2004). ADV measurements of turbulence over an eroded sediment bed in a semicircular flume. *12th International Conference on Transport & Sedimentation of Solid Particles* (pp. 113–124). Prague, Czech Republic, September 2004.

Banasiak, R., Verhoeven, R., De Sutter, R., & Tait, S. (2005). The erosion behaviour of biologically active sewer sediment deposits: Observations from a laboratory study. *Water Research*, *39*, 5221–5231.

This page intentionally blank

Black, K. S., Tolhurst, T. J., Paterson, D. M., & Hagerthey, S. E. (2002). Working with natural cohesive sediments. *Journal of Hydraulic Engineering*, *128*(1), 3–8.

De Sutter, R. (2000). Erosion and transport of cohesive sediment mixtures in unsteady flow. *PhD Thesis*, Ghent University, p. 283.

De Sutter, R., Rushforth, P. J., Tait, S. J., Huygens, M., Verhoeven, R., & Saul, A. J. (2000). The erosion of cohesive mixed deposits: Implications for sewer flow quality modelling. *Urban Water*, *2*, 285–294.

Heinzelmann, C., & Wallisch, S. (1991). Benthic settlement and bed erosion. A review. *Journal of Hydraulic Research*, *29*(3), 335–371.

Krone, R. B. (1999). Effect of bed structure on erosion of cohesive sediments. *Journal of Hydraulic Engineering*, *125*(12), 1297–1301.

Kuijper, C., Cornelisse, J. M., & Winterwerp, J. C. (1989). Research on erosive properties of cohesive sediments. *Journal of Geophysical Research*, *94*, 341–350.

Lau, Y. L., & Droppo, I. G. (2000). Influence of antecedent conditions on critical shear stress of bed sediments. *Water Research*, *34*, 663–667.

Lavelle, J. W., & Mofjeld, H. O. (1987). Do critical stresses for incipient motion and erosion really exist? *Journal of Hydraulic Engineering*, *113*, 370–385.

Mehta, A. J., Hayter, E. J., Parker, W. R., Krone, R. B., & Teeter, A. M. (1989). Cohesive sediment transport. Part I: Process description. *Journal of Hydraulic Engineering*, *115*, 1076–1093.

Mitchener, H., & Torfs, H. (1996). Erosion of mud/sand mixtures. *Coastal* Engineering, *29*, 1–25.

Montague, C. L. (1986). Influence of biota on the erodibility of sediments. *Estuarine cohesive sediment dynamics. Lecture notes on coastal and estuarine studies*, *14* (pp. 219–250). Berlin Heidelberg New York: Springer.

Parchure, T. M., & Mehta, A. J. (1985). Erosion of soft cohesive deposits. *Journal of Hydraulic Engineering*, *111*, 1308–1326.

Prochnov, J. V., Schweim, C., & Köngeter, J. (2000). Biogenic influences on the formation and long-term dynamics of cohesive sediments. *Journal of Sediment Research*, *15*, 274–283.

Ravens, T. M., & Gschwend, P. M. (1999). Flume measurements of sediment erodibility in Boston Harbour. *Journal of Hydraulic Engineering*, *125*(10), 998–1005.

Schweim, C., Welzel, J., Spork, V., & Köngeter, J. (1999). Sediment management during reservoir depletion – Experimental investigations of mud siltation and resuspension. In Jayawardena, Lee, & Wang (Eds.), *River Sedimentation*. Rotterdam: Balkema, ISBN 9058090345.

Torfs, H. (1995). Erosion of mud/sand mixtures. *PhD Thesis*, Katholieke Universiteit Leuven, p. 185.

Tolhurst, T. J., Black, K. S., Paterson, D. M., Mitchener, H. J., Termaat, G. R., & Shayler, S. A. (2000). A comparison and measurement standardisation of four in situ devices for determining the erosion shear stress of intertidal sediments. Continental Shelf Research, *20*, 1317–1334.

Wijdeveld, A. J., & Kesteren van, W. G. M. (1999). Gas production in sediment layers. *Project description*. The Netherlands: WL Delft Hydraulics, Z2499.

Witt, O., & Westrich, B. (2003). Quantification of erosion rates for undisturbed contaminated cohesive sediment cores by image analysis. *Hydrobiologia*, *494*(1–3), 266–271.

Water, Air, and Soil Pollution: Focus (2006) **6:** 29–37
DOI: 10.1007/s11267-006-9051-4

SPATIAL AND TEMPORAL VARIATIONS IN THE SEDIMENT HABITAT OF *RANUNCULUS* SPP. IN LOWLAND CHALK STREAMS – IMPLICATIONS FOR ECOLOGICAL STATUS?

STEWART J. CLARKE[1,*], GERALDENE WHARTON[2] and JACQUELINE A. COTTON[3]
[1]*English Nature, Northminster House, Northminster Road, Peterborough PE1 1UA, UK*
[2]*Centre for Aquatic and Terrestrial Environments, Department of Geography, Queen Mary, University of London, London, UK*
[3]*Environment Agency, North East Region, Leeds, UK*
*(*author for correspondence, e-mail: stewart.clarke@english-nature.org.uk; phone: +44-01733-455564; fax: +44-01733-568834)*

Abstract. *Ranunculus* spp. are the dominant plants of lowland chalk stream habitats in England. The spatial variability of sediment characteristics (silt–clay, organic matter, total phosphorus and total nitrogen content) within stands of *Ranunculus* spp. was investigated in 12 rivers in lowland England. Variability was found to be high and there were no discernible differences between samples taken from within *Ranunculus* and a limited number of samples from bare substrate. For two of these rivers, comparisons were also made between reaches upstream and downstream of waste water treatment works outfalls in terms of the characteristics of the sediments within *Ranunculus* stands. In one river a clear increase in sediment nutrient, fine and organic material content was observed downstream but in the other there was no consistent difference. Temporal variability was considered for two rivers in the Frome catchment, Dorset, by analysing the monthly variability in sediment organic matter and silt–clay content beneath *Ranunculus* stands over an annual cycle of growth and die-back. Whilst a clear pattern of fine and organic material retention consistent with seasonal plant growth patterns was evident at one site, the three sites displayed different temporal patterns. This inconsistency is believed to reflect differences in sediment supply at the three sites.

Keywords: sediment, *Ranunculus* spp., river monitoring

1. Introduction

Lowland streams on chalk geology are vulnerable to siltation as they have stable groundwater-dominated flows and lack the high flows required to scour and remove accumulated fine sediments (Environment Agency, 2004). This is further exacerbated by low flows caused by abstraction and over-sized channels. The accumulated fine sediments cause problems for salmonid fish spawning and macroinvertebrates and are also a significant source of phosphorus which in excess, can cause algal problems and a loss of submerged plant diversity. Whilst point sources of phosphorus and nitrogen are generally the most significant contribution to English rivers, diffuse sources (often associated with fine sediments) have been shown to account for over 40% of annual inputs (cf. Mainstone & Parr, 2002).

The low gradients, shallow water depths and moderate fertility of chalk streams promote diverse and abundant growths of submerged and floating leaved aquatic plants. These macrophytes are able to grow throughout the channel width, reaching high levels of biomass (e.g., Dawson, 1976) and have been referred to as 'biological engineers' (Sand-Jensen, 1997) because they alter flow and sediment dynamics to provide and modify in-stream habitats for in-stream fauna (e.g., Hearne & Armitage, 1993). The dominant macrophyte species of English lowland chalk streams are the water crowfoots *Ranunculus* spp. and chalk stream management, predominantly for fisheries, has tended to favour these species and promote their dominance. As a result many chalk streams support dense stands of *Ranunculus* which can achieve over 80% cover of a given reach (Cotton, Wharton, Bass, Heppel, & Wotton, 2006) and play an important role in modifying flow velocities and sediment deposition patterns. *Ranunculus* stands can trap large quantities of fine sediments, up to 0.01 m^3/m^2 of *Ranunculus* (Wharton et al., 2006), and hence an understanding of their influence is a critical step in managing in-stream sediment and nutrient dynamics.

The aim of this study was to examine spatial and temporal variability in sediment characteristics within and around *Ranunculus* stands in lowland chalk streams in England. A study of the spatial variability of the sediment habitat of *Ranunculus* across 12 sites was conducted in 1997–1998 (Clarke, 2000). Temporal variability was studied using monthly samples of sediment deposited within *Ranunculus* stands for three sites in the River Frome catchment, Dorset (UK) during 2003 (Wharton et al., 2006; Wheater & Peach, 2004).

2. Materials and Methods

For the spatial study, sediments underlying *Ranunculus penicillatus* subsp. *pseudofluitans*, the most abundant *Ranunculus* species in British rivers (Preston & Croft, 1997), were sampled using a perspex corer (~100 mm diameter) from 100 m reaches in 12 streams. Samples were taken to a depth of 10–15 cm below the sediment surface to encompass the trapped deposits within the macrophyte stands and the substrate in the rooting zone of the submerged macrophytes. At each site an indication of sediment condition in bare, unvegetated areas was obtained from two control samples using the same Perspex corer. In two of the streams in Hampshire (Itchen and Test) the sampling was undertaken using paired sites up- and downstream of waste water treatment work outfalls (size 24,500 and 49,435 population equivalent, Itchen and Test, respectively) to investigate the effect of a point source on sediment nutrient concentrations. At these two sites, 10 sediment samples were taken from beneath *Ranunculus* at both the up- and downstream sites. All samples were randomly located within a stratified framework (within plant stands or within bare bed areas). Sediment samples were analysed for total phosphorus, total nitrogen, organic matter and silt–clay content. Full details of the analytical methods are given in Clarke and Wharton (2001).

For the temporal study at three sites in the River Frome catchment, six sediment samples were collected within a single *Ranunculus* stand on a monthly basis throughout 2003. Samples were taken using 37 mm diameter Perspex cores. The organic matter content (%) was determined by loss on ignition. The particle size distribution was measured using a Beckman Coulter Laser Particle Size Analyser (see Cotton et al., 2006).

3. Results

The results are presented according to the different spatial and temporal scales sampled: sediment characteristics across the 12 rivers; differences between upstream and downstream on the rivers Itchen and Test; and seasonal variability between sites through the length of the Frome catchment. Table I displays the mean values for sediment characteristics across the 12 rivers sampled. Based on this limited sample size there is little difference between the characteristics of sediments underneath *Ranunculus* and those sediments with no plants within vegetated reaches. However, all sediments exhibited a high degree of variability across the 12 sites with high standard deviations relative to the mean values. Regression analysis indicated significant but weak relationships between silt–clay content and total nitrogen (r^2=0.15, f<0.01) and also between silt–clay content and organic matter (r^2=0.15, f<0.01). There was no significant relationship between phosphorus and silt–clay (r^2=0.006, f=0.5) or between phosphorus and organic matter (r^2=0.07, f=0.02).

Figure 1 shows the sediment characteristics of *Ranunculus* sediments upstream and downstream of the waste water treatment outfalls on the rivers Itchen and

TABLE I

Characteristics of sediments from within *Ranunculus* stands (n=84) and from bare sediment (no plants, n=26) in 12 rivers

	Percent silt/ clay (%)	Percent organic matter (%)	Total P (μg/g)	Percent total N (%)
Sediment from within *Ranunculus*	23.6±13.9	3.9±2.4	742±463	0.112±0.109
Bare sediment	24±14.9	5.1±4.1	920±565	0.091±0.082

Figures given are mean values ± 1 S.D.

Test. Monthly water chemistry monitoring by the Environment Agency of England and Wales for the year of sediment sampling (1997–1998) indicated that the effluent from the works resulted in significant increases of phosphorus (four- and threefold on Itchen and Test, respectively) and ammonia (five- and threefold on Itchen and Test, respectively). However, sediment parameters did not show the same consistent increase in the downstream sites. Mean sediment phosphorus increased significantly downstream (65%) in the Itchen but decreased (11%) in the Test. Similarly, mean silt–clay and organic matter increased downstream in the Itchen (14% and 75%, respectively) but decreased at downstream sites on the

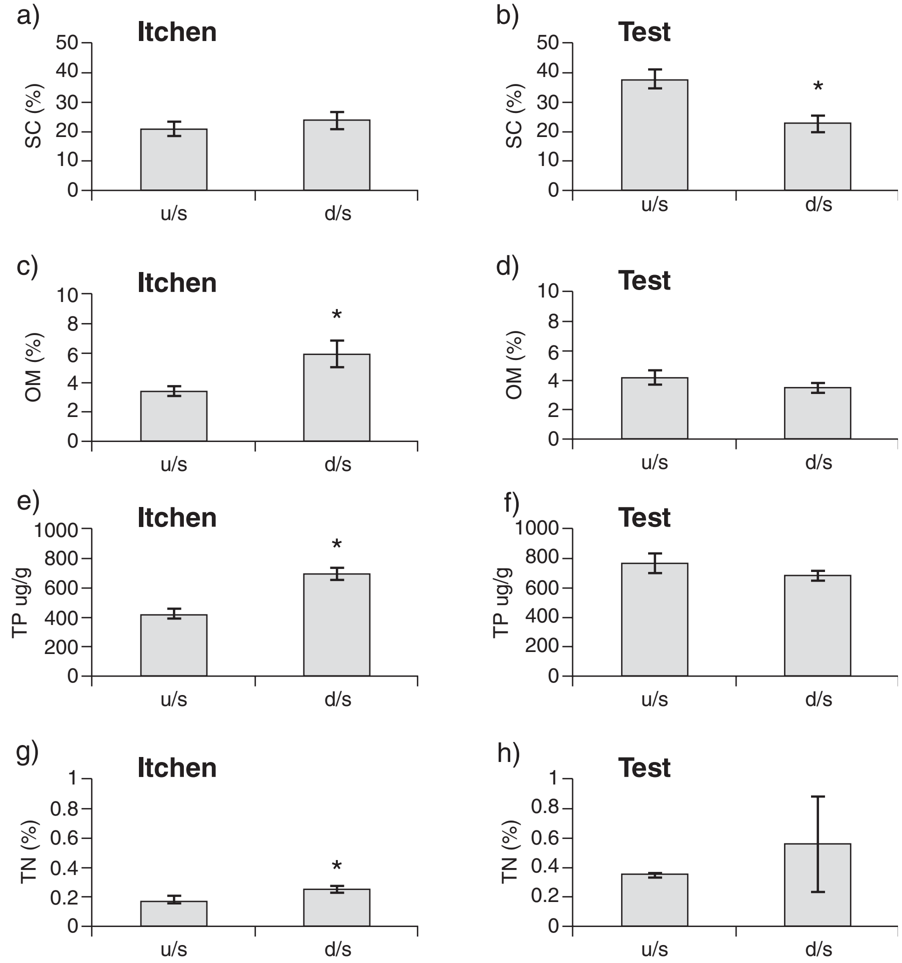


Figure 1. Mean values and standard error for sediment characteristics of samples from within *Ranunculus penicillatus* subsp. *pseudofluitans* stands in the Itchen and Test *upstream* and *downstream* sites ($n=10$). An * denotes a statistically significant difference between *upstream* and *downstream* sites ($P<0.05$) as determined through Mann–Whitney U tests.

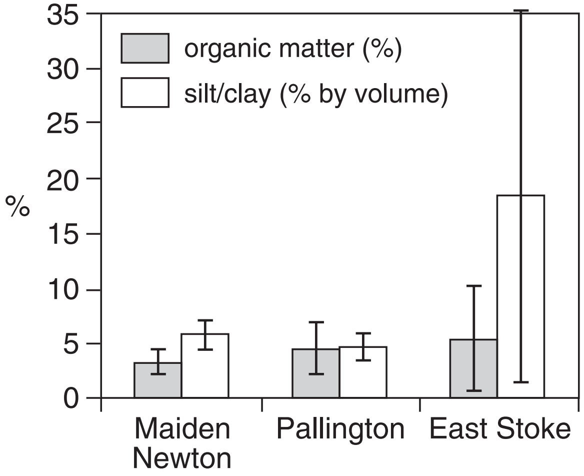


Figure 2. Mean silt–clay content and organic matter content of fine sediments deposited beneath *Ranunculus* stands in the Frome during 2003.

Test (41% and 18%, respectively). Only total nitrogen showed downstream increases in both rivers, with a 41% increase in mean concentration in the Itchen and a 60% increase in the Test.

Longitudinal differences in the silt–clay content of sediments deposited under *Ranunculus* stands in the River Frome catchment are presented in Figure 2. Silt–clay contents were relatively low at both Maiden Newton and Pallington when compared with the mean figures reported for the 12 rivers (Table I) and there was limited variability throughout the year at these two sites (Figure 3a). In contrast, silt–clay content was higher and more variable through the year (Figure 2) in the reach furthest downstream at East Stoke with a clear peak in retained silt and clay in late autumn (Figure 3a). The organic matter content of sediments deposited underneath *Ranunculus* stands at the three River Frome sites were generally higher (Figure 2) than across the 12 rivers (Table I). Once again, variability was highest at the downstream site, East Stoke (Figure 2) and there were clear peaks in organic matter content in both August and November 2003 (Figure 3b). A less pronounced August peak in organic matter content was observed at the upstream site, Maiden Newton (Figure 3b). At the middle reach site, Pallington, the highest organic matter levels were recorded for March and April and then declined throughout 2003 to December (Figure 3b).

4. Discussion

This analysis of 12 river reaches (Table I) suggests that sediments within vegetated reaches of lowland chalk streams are highly heterogeneous (see also

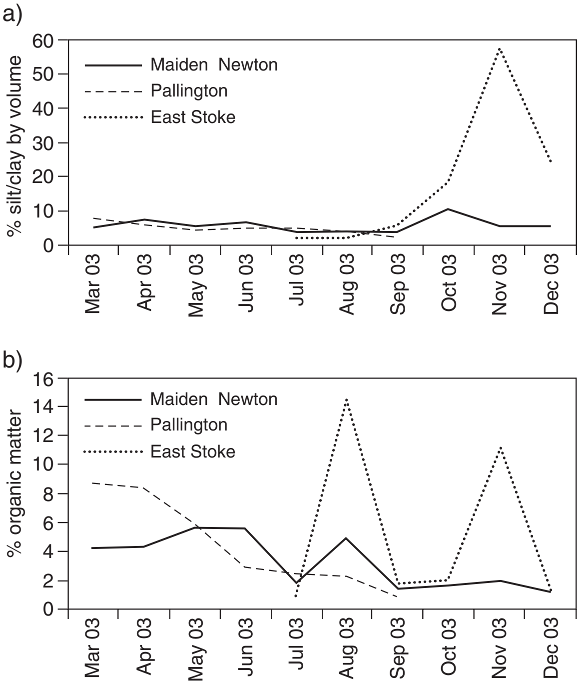


Figure 3. Fine sediment deposited beneath *Ranunculus* stands at sites within the River Frome. **a** Silt–clay content; **b** Organic matter content.

Clarke & Wharton, 2001) and based on this small sample there seems to be no clear evidence that *Ranunculus* stands are influencing sediment nutrient characteristics at a patch scale (*sensu* Sand–Jensen, 1997). This is in contrast to a reach scale study of nutrient retention in a Danish lowland stream where greater amounts of nitrogen and phosphorus were stored in reaches with submerged macrophytes than in reaches of sand and gravel (Svendsen & Kronvang, 1993). This difference may reflect the different spatial scales at which the two studies were focused. The concentrations of sediment total phosphorus within the *Ranunculus* stands are similar to those recorded elsewhere (Demars, 2002; Schneider & Melzer, 2004). Values for silt–clay, total nitrogen and organic matter are similar to those found beneath other macrophyte species in lowland England (Clarke, 2000). Thus, the results presented here suggest that *Ranunculus* is able to grow on the relatively wide range of sediment types found in these lowland streams.

The influence of a major point source on the nutrient levels of river bed sediments was investigated through comparisons of *Ranunculus* sediment habitat upstream and downstream of waste water treatment outfalls on the rivers Itchen and Test. Additional nutrient loading is anticipated to enhance *Ranunculus* growth, sediment trapping and retention of sediment-bound phosphorus. However, the two rivers varied in their response to the waster water effluent input. Sediment total phosphorus concentrations increased downstream in the Itchen as expected but on the Test sediment total phosphorus and nitrogen concentrations did not change significantly. The different responses do not reflect the relative sizes of the treatment works but may reflect differences in stream flow and hence nutrient loads (mean flows are 5.34 and 10.9 m^3/s for the Itchen and Test, respectively (Institute of Hydrology, 1999)) as well as physical characteristics of the sampled reaches. We suggest coarsening of river bed sediments downstream on the Test results in a reduced potential for the trapping of fine organic material and binding of phosphorus in the sediments at this site.

Monthly sampling in the River Frome has demonstrated temporal and within-site variability in the retention of fine sediments within *Ranunculus* stands. The temporal pattern not only relates to varying macrophyte cover but also fine sediment inputs and changing discharges (see also Cotton et al., 2006). For example, the increased sediment supply during a flood event resulted in increased retention of silt and clay and organic matter at East Stoke in November 2003. In addition to the temporal differences in the sediment habitat of *Ranunculus,* data on mean silt–clay and organic matter content from the River Frome catchment show little difference across all three sites. However, the silt–clay and organic matter contents of the sediments at East Stoke were much more variable perhaps due to increased sediment supply during higher discharges at this downstream site. The results from the River Frome thus further indicate the highly heterogeneous nature of the sediments beneath *Ranunculus* plants.

5. Conclusions

Sediment conditions (nutrients and fine materials in particular) are an important aspect of the ecological status in lowland streams and sediments may present a significant sink for nutrients. Consequently, some monitoring of sediments may appear desirable in assessing river quality status. This study, which suggests a high degree of spatial variability within sediments from a suite of similar rivers, indicates that obtaining representative samples of river sediments and characterising the inherent variability is likely to be very difficult. Evidence from two sites on the Test and Itchen shows that even where there is a major point source of nutrients and fine sediments it is difficult to discern a clear spatial (downstream) change in sediment conditions. Whilst the temporal sampling on the Frome has demonstrated patterns of change in sediment characteristics that appear to correspond with seasonal patterns of plant growth it is clear that wider catchment scale processes (sediment supply and discharge) are responsible for some of the observed temporal variability. From this analysis it would seem that the European Union Water Framework Directive (European Commission, 2000) approach to ecological status classification which utilises biological elements (e.g., macrophytes, phytobenthos, macroinvertebrates, fish) to integrate this variability and different scales of influence is well justified.

Acknowledgements

The authors gratefully acknowledge the Environment Agency and Queen Mary, University of London for provision of a studentship to SJC; the award of a NERC LOCAR Grant (NER/T/S/2001/00932); and the support of the Frome/Piddle Catchment Service Team and the NERC LOCAR Data Centre.

References

Clarke, S. J. (2000). Sediment–macrophyte relationships in lowland English rivers: Using macrophytes for biological assessment. *PhD Thesis*. Department of Geography, Queen Mary, University of London. 354 pp.

Clarke, S. J., & Wharton, G. (2001). Sediment nutrient characteristics and aquatic macrophytes in lowland English rivers. *Science of the Total Environment*, *266*, 103–112.

Cotton, J. A., Wharton, G., Bass, J. A. B., Heppell, C. M., & Wotton, R. S. (2006). The effects of seasonal changes to in-stream vegetation cover on patterns of flow and accumulation of sediment. *Geomorphology, 77*(3–4), 320–334.

Dawson, F. H. (1976). The annual production of the aquatic macrophyte *Ranunculus penicillatus* var. *calcareus* (R. W. Butcher) C. D. K. Cook. *Aquatic Botany*, *2*, 51–73.

Demars, B. O. L. (2002). Aquatic vascular plants in nitrate-rich calcareous lowland streams: Do they respond to phosphorus enrichment and control? *PhD Thesis*. Department of Biology, University of Leicester. 214 pp.

Environment Agency (2004). *The state of England's chalk rivers*. Bristol: Environment Agency. 78 pp.

European Commission (2000). Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *Official Journal of the European Communities*, *L327*, 1–72.

Hearne, J. W., & Armitage, P. D. (1993). Implications of the annual macrophyte growth cycle on habitat in rivers. *Regulated Rivers*, *8*, 313–322.

Institute of Hydrology (1999). *National River Flow Archive*. Wallingford, UK: Institute of Hydrology.

Mainstone, C. P., & Parr, W. (2002). Phosphorus in rivers – ecology and management. *Science of the Total Environment*, *282–283*, 25–47.

Preston, C. D., & Croft, J. M. (1997). *Aquatic Plants in Britain and Ireland*. Colchester: Harley Books. 365 pp.

Sand-Jensen, K. (1997). Macrophytes as biological engineers in the ecology of Danish streams. In K. Sand-Jensen & O. Pedersen (Eds.), *Freshwater Biology – Priorities and Development in Danish Research* (pp. 74–101). Copenhagen: G. E. C. Gad.

Schneider, S., & Melzer, A. (2004). Sediment and water nutrient characteristics in patches of submerged macrophytes in running waters. *Hydrobiologia*, *527*, 195–207.

This page intentionally blank

Svendsen, L. M., & Kronvang, B. (1993). Retention of nitrogen and phosphorus in a Danish lowland river system: Implications for the export from the watershed. *Hydrobiologia*, *251*, 123–135.

Wharton, G., Cotton, J. A., Wotton, R. S., Bass, J. A. B., Heppell, C. M., Trimmer, M., et al. (2006). Macrophytes and suspension-feeding invertebrates modify flow and fine sediments in the Frome and Piddle Catchments, Dorset (UK). *Journal of Hydrology, 330*(1–2), 171–184.

Wheater, H. S., & Peach, D. (2004). Developing interdisciplinary science for integrated catchment management: The UK Lowland Catchment Research (LOCAR) Programme. *International Journal of Water Resources Development*, *20*(3), 369–385.

Water, Air, and Soil Pollution: Focus (2006) **6:** 39–47
DOI: 10.1007/s11267-006-9054-1

CAN NUTRIENT SPIRALLING BE USED TO DETECT SEASONAL NUTRIENT UPTAKE IN A FORESTED STREAM?

SULFIKAR HANAFI, MICHAEL R. GRACE* and BARRY T. HART
Water Studies Centre, School of Chemistry, Monash University, Wellington Road PO Box 23, Clayton, Victoria 3800, Australia
*(*author for correspondence, e-mail: mike.grace@sci.monash.edu.au; phone: +61-3-99054078; fax: +61-3-99054196)*

(Received 23 September 2005; accepted 21 February 2006)

Abstract. Nutrient spiralling measurements were conducted in Lyrebird Creek, a forested stream in the Dandenong Ranges, Victoria, Australia. Spiralling indices from several nutrient (NH_4^+, PO_4^{3-}) enrichment experiments were correlated with seasonal variation in factors thought to control nutrient uptake, i.e., temperature, light and algal biomass. It was hypothesized that nutrient uptake would be higher in summer as increased temperatures would promote both biotic and abiotic processes and higher light levels in summer would stimulate photosynthesis. However, results did not support this hypothesis. Uptake length for NH_4^+–N and PO_4^{3-}–P and uptake velocity were not correlated with chlorophyll-*a*, light or temperature ($r^2<0.30$, $P>0.1$) despite the seasonality of these biophysical factors ($r^2>0.42$, $P<0.02$). Lyrebird Creek might had no seasonal trend in nutrient uptake and/or nutrient spiraling measurements only appears suitable for contrasting streams with large differences in biophysical factors that supports biotic and abiotic nutrient processing. In addition, small errors in measuring a nutrient concentration can result in a large range in the estimated S_w and increased difficulty in determining significant differences in nutrient spiralling indices.

Keywords: nutrient spiralling, forested stream, seasonal variation, biophysical factors, ecosystem processes

1. Introduction

Stream processes modify nutrient concentrations during downstream transport (Meyer & Likens, 1979). Thus, an understanding of in-stream processes is vital in managing nutrient movement from the catchment to the receiving waters (e.g., estuaries, wetlands, lakes). Webster and Patten (1979) introduced the concept of ‘nutrient spiralling’ to explain nutrient movement in lotic ecosystems. As a nutrient atom enters a stream, it is cycled through biotic and abiotic compartments while being transported downstream. The combination of these uptake and longitudinal transport processes, thus resemble a spiral. The distance a nutrient molecule travels while completing a cycle through the biotic and abiotic compartments is called the ‘spiralling length’ (S) (Newbold, Elwood, O’Neill, & Winkle, 1981) and is commonly measured as the uptake length (S_w) (Stream Solute Workshop, 1990). Streams with short spiralling lengths retain more nutrient with less transported downstream.

Spiralling length is measured by injecting a nutrient solution into the stream and observing concentration changes between upstream and downstream sampling stations. To correct for dilution, a conservative tracer is injected simultaneously. Uptake length is then calculated as:

$$S_\mathrm{w} = \frac{x}{\ln\left(\frac{C_{Nut-Up}}{C_{Nut-Do}}\right) - \ln\left(\frac{C_{Con-Up}}{C_{Con-Do}}\right)} \tag{1}$$

where x is stream reach length, $C_\mathrm{Nut\text{-}Up}$ and $C_\mathrm{Nut\text{-}Do}$ are nutrient concentrations at upstream and downstream stations, and $C_\mathrm{Con\text{-}Up}$ and $C_\mathrm{Con\text{-}Do}$ are conservative tracer concentrations at the same stations.

To correct for the effect of discharge, Davis and Minshall (1999) recommended uptake velocity (V_f) as a measure of benthic demand for nutrients relative to supply. V_f (m/s) is calculated as:

$$V_f\left(ms^{-1}\right) = \frac{Q}{w \cdot S_w} \tag{2}$$

where Q=discharge (m^3/s), w=width (m), and S_w=uptake length (m).

Spiralling has been used to measure the nutrient utilization capacity of a stream (e.g., Hart, Freeman, McKelvie, Pearse, & Ross, 1991; Kopacek & Blazka, 1994; Mulholland, Newbold, Elwood, & Ferren, 1985), and to compare nutrient uptake between contrasting stream conditions (Maltchik, Molla, Casado, & Montes, 1994; Merseburger, Marti, & Sabater, 2005). There are few studies measuring seasonal variation of nutrient uptake using the nutrient spiralling approach, particularly for the Mediterranean-type climate region in the Southern Hemisphere. We expected higher V_f in summer than in winter as higher temperatures and light intensity in summer should increase nutrient uptake (Butturini & Sabater, 1998; Gardner et al., 2000) through greater algal growth (Hill, Ryon, & Schilling, 1995). Higher temperatures should also increase the kinetics of abiotic reactions (Suplee & Cotner, 2002).

Our purpose was to examine the viability of nutrient spiralling as an indicator of stream function by conducting seasonal nutrient enrichment experiments and investigating correlations of S_w and V_f with stream biophysical factors (e.g., algal biomass, temperature, light).

2. Materials and Methods

2.1. Study Sites

Lyrebird Creek drains 724 ha of forested catchment area, 37 km to the east of Melbourne, Australia (37°49.82′S, 145°23.82′E), with only 0.1% of the catchment covered by hard surfaces such as buildings and roads (Walsh, 2000). The creek is highly shaded by Eucalypts (*Eucalyptus regnans*) with tree ferns (*Cyathea australis*) underneath. Baseflow discharge ranged between 1 and 10 l/s. During baseflow the average stream depth and width were 5 cm and 80 cm, respectively. The stream sediments overlying the bedrock were fine silt and gravel/pebbles covered by organic matter. Large woody debris had accumulated in some sections. Ambient stream water concentrations of NH_4^+–N, PO_4^{3-}–P, and NO_3^-–NO_2^- (NO_x) were (yearly median at baseflow±%RSD; Taylor, Roberts, Walsh, & Hatt, 2004) 18±8, 3±15 and 310±10, respectively suggesting possible P limitation. Benthic biomass, measured as chlorophyll-*a* concentration (APHA, 2005) varied between 4 and 121 mg/m^2.

2.2. SPIRALLING EXPERIMENTS

Ambient nutrient concentrations were determined from water samples (three to five replicates) collected at upstream and downstream stations prior to nutrient enrichment. Enrichment involved co-injecting NH_4^+ as NH_4Cl, PO_4^{3-} as KH_2PO_4, and Br^- as KBr into an 80 m reach, from mid-day until late afternoon, 13 times between December 2002 and March 2004. Nutrient enrichment was kept as low as possible to avoid saturation of benthic uptake (Hart, Freeman, & McKelvie, 1992; Mulholland et al., 2002). Stream water was confined near the injection point (8 m above the upstream sampling point) to ensure complete mixing of the added nutrient solution with stream water. Water samples were collected every 5 min for 90–120 min. Samples were immediately filtered through 0.2 μm GHP membrane filter paper (Gelman–Pall 47 mm dia.), into HDPE tubes, stored on dry ice and kept frozen for later analysis. Flow injection analysis (Lachat Quick Chem 8000) was performed with standard QA procedures (WSC, 2001) using the automated phenate colorimetric method for NH_4^+–N, molybdenum blue colorimetry for PO_4^{3-}–P, cadmium reduction method for nitrate–nitrite, and phenol red colorimetry for bromide (APHA, 2005).

2.3. BIOPHYSICAL MEASUREMENTS

Stream water temperature and surface light were recorded during each experiment using a calibrated Horiba U-10 meter and Odyssey™ light loggers (Dataflow Systems Pty Ltd, Queensland, Australia). Wetted stream width was measured at 5 m intervals after each experiment. Chlorophyll-*a* sampling was undertaken every season. Samples of sediment, rock or large woody debris were taken from 33 random locations along the stream reach, and their surface areas measured. Biomass attached to big rocks or wood was sampled using a 6.6-cm^2 corer. Samples were frozen and stored in the dark before laboratory analysis. The chlorophyll extraction and determination followed APHA (2005) using a Hitachi U-2000 spectrophotometer.

2.4. DATA ANALYSIS

Data was grouped into summer (December–April) and winter (May–July). A general linear model (GLM, Systat Ver. 11) was used to investigate differences in the ambient concentrations of NH_4–N and PO_4–P, average chlorophyll-*a* (Chl-*a*), average stream water temperature, and average surface light (light) and V_f and S_w. Light and Chl-*a* data were log_{10}-transformed, $V_{f[PO4\text{-}P]}$ was square root-transformed, and $S_{w[PO4\text{-}P]}$ and $S_{w[NH4\text{-}N]}$ was inverse-transformed to minimize the influence of outliers and to normalize the distribution. No transformation was required for NH_4^+–N, PO_4^{3-}–P, and $V_{f[NH4\text{-}N]}$. Multiple regression analysis was used to examine relationships between spiralling indices and the independent variables (temperature, Chl-*a*, and light).

3. Results

3.1. BIOPHYSICAL CHARACTERISTICS

Water temperature ranged from 8.5 to 16.9 °C and was significantly different between seasons ($r^2=0.84$, $P<0.001$). As expected, the light climate was significantly higher ($r^2=0.73$, $P<0.001$) in summer (58–579 $\mu mol\ m^{-2}s^{-1}$) than in winter (7–21 $\mu mol\ m^{-2}s^{-1}$). Biomass responded as expected to seasonal patterns in light and temperature, and was higher in summer (1.84 to 8.6 $mg\ m^{-2}$) than in winter (0.84 to 1.84 $mg\ m^{-2}$) ($r^2=0.42$, $P=0.014$, $n=14$) in accordance with Taylor et al. (2004), who previously noted no significant biomass differences within season, but large differences between summer and winter. Stream discharge varied by over an order of magnitude in summer from 1.1 to 44 l/s, and from 6.2 to 21 l/s in winter. The 'high' flows were both on receding limbs of flood hydrographs. Overall, median discharges were lower in summer than winter. Ambient NH_4^+–N and PO_4^{3-}–P concentrations did not vary seasonally ($r^2<0.10$, $P>0.20$; $n=14$). In summer, PO_4^{3-}–P and PO_4^{3-}–P concentrations ranged between (mean±SD, $n=5$) 11±3 to 24±5 μg/l and 1±1 to 7±4 μg/l, respectively. In winter, ambient NH_4^+–N and PO_4^{3-}–P concentrations ranged from 8±4 to 23± 2 μg/l and 4±4 to 7±2 μg/l, respectively. These results agree with the ambient nutrient measurements of Hatt, Fletcher, and Walsh (2004) over the same period.

3.2. SPIRALLING EXPERIMENT

The levels of nutrient enriched above the ambient concentration (i.e., nutrient enrichment factors) were 1.6 to 10 times the ambient nutrient concentration.

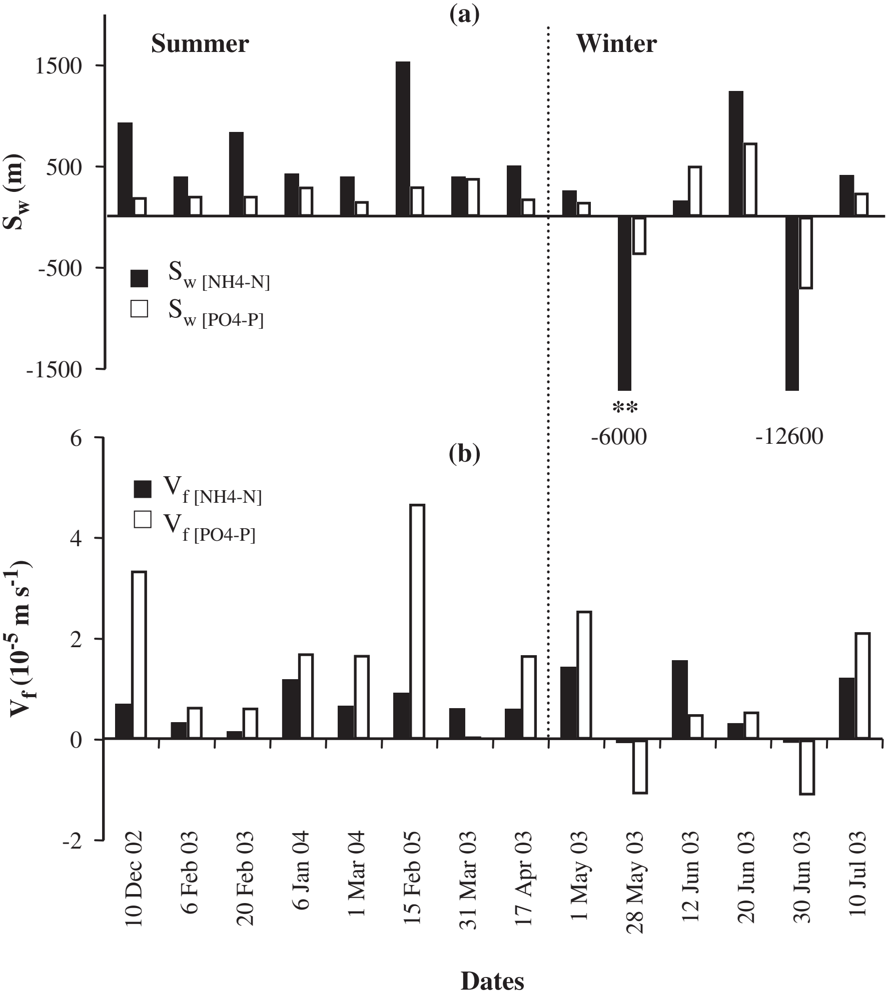


Figure 1. **a** Uptake length (S_w, in m) and **b** uptake velocity (V_f, in m/s) in summer and winter. Two negative values for $S_{w[NH4\text{-}N]}$ (*marked with asterisk*) were from experiments conducted seven days after flood events.

Uptake length and V_f for NH_4^+–N and PO_4^{3-}–P did not correlate with the enrichment factors ($r^2<0.09$, $P>0.2$). Figure 1a shows two negative outliers for S_w derived from experiments conducted seven days after winter flood events (28 May 2003 and 30 June 2003).

The $S_{w[NH4-N]}$ for 30 June 2003 was highly negative, resulting in a very skewed distribution even after transformation. However, another experiment conducted 14 days after a large flood in summer (15 Feb 2005) resulted in the highest $V_{f[PO4-P]}$ recorded (Figure 1b). For this event, $S_{w[NH4-N]}$ and $S_{w[PO4-P]}$ were 1,500 m and 300 m, respectively.

3.3. SEASONAL VARIATION AND CORRELATION WITH BIOPHYSICAL FACTORS

The V_f and S_w measurements for NH_4^+–N and PO_4^{3-}–P were not correlated with discharge ($r^2<0.30$, $P>0.05$) and showed no seasonal trends ($r^2<0.30$, $P>0.05$), irrespective of the two outliers, and despite the seasonal differences in the stream's biophysical characteristics. There were no strong associations between these spiralling indices and chl-*a*, light, and temperature ($r^2<0.30$, $P>0.1$). However $V_{f[PO4\text{-}P]}$ showed moderate correlation with light ($V_{f[PO4\text{-}P]}$ $r^2=0.34$, $P=0.03$).

4. Discussion

No seasonal pattern was observed in the spiralling indices for NH_4^+–N and PO_4^{3-}–P in Lyrebird Creek. This finding may be interpreted in two ways. First, there actually was no seasonal pattern in nutrient uptake. It appears that differences in algal biomass, indicated by Chl-*a* concentrations, between seasons are insufficient to cause detectable differences in the spiralling indices. This suggests that benthic algae are not the dominant factor in nutrient uptake in this stream. Webster and Meyer (1997) argued that organic matter related processes control most of the nutrient uptake in forested streams, and heterotrophs like bacteria and fungi play the dominant role in these processes (Meyer, 1994). The fact that bacterial and fungal biomass are related to the amount and type of organic matter (Findlay et al., 2002) supports the findings that nutrient S_w may correlate with the benthic organic matter (e.g., Mulholland et al., 1985; Webster et al. 2000). In Lyrebird Creek, there was no distinct seasonality in the amounts of coarse particulate organic matter present (subjective observation).

Second, spiralling measurements may not be capable of differentiating seasonal differences due to lack of sensitivity of this technique and/or the inherent variability in stream conditions. Spiralling measures the use of stream nutrients by both the biotic and abiotic components in the stream. Both components are influenced directly and indirectly by nutrients, light and temperature in processing nutrients. The key question is then 'how much change in biophysical factors is required for observable changes in biotic and abiotic nutrient processing?'

Using a single addition technique, Marti and Sabater (1996) found no significant seasonal trend for $S_{w[NH4\text{-}N]}$ and $S_{w[PO4\text{-}P]}$ in a heavily shaded Mediterranean stream. However, after logging of riparian trees, temperature differences between summer and winter were increased resulting in observable seasonal differences for $S_{w[NH4\text{-}N]}$ (but not $S_{w[PO4\text{-}P]}$). They found no differences within a season in S_w at low discharge (<100 l/s) for both nutrients before and after logging, even though the stream detritus input was decreased from 10% surface coverage to 2% (Butturini & Sabater 1998). Simon, Townsend, Biggs, and

Bowden (2005) reported that seasonal patterns in S_w for NH_4^+, NO_3^-, and PO_4^{3-} in two riparian grass streams in the southern part of New Zealand were largely influenced by discharge and that there was no seasonal pattern in nutrient V_f.

Using ^{32}P addition Mulholland et al. (1985) found relatively large differences in $S_{w[PO4\text{-}P]}$ between autumn (shortly after leaf fall), and summer in a forested stream in Tennessee, USA, although no replicate measurements for each season were made. Webster et al. (2000) found differences in S_w for nitrogen (ammonium and nitrate) and phosphorus after removing all leaf litter and woody debris in one of two similar forested streams (in terms of size and primary production).

These observations suggest that spiralling indices are only sensitive to relatively large differences in biophysical factors such as the observed seasonality in these factors in the northern hemisphere, where most trees lose all of their leaves in autumn adding substantially to the standing stock of organic matter. The riparian Eucalypts have no seasonal leaf abscission, and thus, there are no large seasonal differences in organic matter accumulation. This lack of seasonality of organic matter accumulation is probably the reason we find no detectable seasonal changes in spiralling indices.

A further reason why there is a difficulty in determining significant differences in nutrient spiraling indices is that small errors in measuring nutrient concentrations can result in a large range in the estimated S_w. This is particularly evident in situations where there is low nutrient uptake. This is illustrated using the data for the relatively high and low NH_4^+–N retention cases of 12 June 2003 and 30 June 2003, respectively (Figure 1b). Assuming a very small error of 2 μg/l in the measurement of the downstream concentrations would result in the S_w value ranging between 130 and 188 m for the high NH_4^+–N retention case and between −2,190 and 3,550 m for the low NH_4^+–N retention case. Larger range in spiraling indices would be expected for low concentration of nutrient (i.e., <20 μg/l) because error in measuring low concentrations is generally higher than the high concentrations (Horwitz, Kamps, & Boyer, 1980).

5. Conclusions

The spiraling technique can only be used for comparison studies when the differences in nutrient uptake between systems are large. Small errors in measuring nutrient concentrations can result in a large range in the estimated spiraling indices, which add further difficulty in determining significant differences in nutrient uptake. These results highlight the need for an investigation into the sensitivity of uptake indices to the magnitude of variation in measuring nutrient concentrations in stream water samples, within the concentration ranges typically used in spiraling experiments. In addition, there is a need to conduct several spiraling experiments in a system that has much larger differences in biophysical factors between seasons.

Acknowledgements

We thank Shane Perryman and two referees for suggested improvements to the manuscript, Simon Roberts for technical advice, and S. Perryman, A. Saefumillah, Z. Fikar, N. Tantreantjitmun, K. Lansdown, S. Imberger, K O'Dea, Munir, E. Ammade, Quyen, W. Diah, O. Teu-Ngeun and E. King for assistance with fieldwork. This study was partially funded by an Australian Development Scholarship (Sulfikar).

References

APHA (2005). *Standard methods for the examination of water and wastewater*. Washington, District of Columbia: American Public Health Association, Centennial Edition.

Butturini, A., & Sabater, F. (1998). Ammonium and phosphate retention in a Mediterranean stream: Hydrological *versus* temperature control. *Canadian Journal of Fisheries and Aquatic Sciences*, *55*, 1938–1945.

Davis, J. C., & Minshall, G. W. (1999). Nitrogen and phosphorus uptake in two Idaho (USA) headwater wilderness streams. *Oecologia*, *119*, 247–255.

Findlay, S., Tank, J., Valett, H. M., Mulholland, P. J., McDowell, W. H., Johnson, S. L., et al. (2002). A cross-system comparison of bacterial and fungal biomass in detritus pools of headwater streams. *Microbial Ecology*, *43*, 55–66.

Gardner, W. S., Lavrentyev, P. J., Boortsma, H. A., Cavaletto, J. F., Troncone, F., & Cortner, J. B. (2000). Effects of natural light on nitrogen dynamics in diverse aquatic environments. *Verhandlungen Internationale Vereinigung für Theoretische und Angewandte Limnologie*, *27*, 64–73.

Hart, B. T., Freeman, P., & McKelvie, I. D. (1992). Whole-stream phosphorus release studies: Variation in uptake length with initial phosphorus concentration. *Hydrobiologia*, *235/236*, 573–584.

Hart, B. T., Freeman, P., McKelvie, I. D., Pearse, S., & Ross, D. G. (1991). Phosphorus spiralling in Myrtle Creek, Victoria, Australia. *Verhandlungen Internationale Vereinigung für Theoretische und Angewandte Limnologie*, *24*, 2065–2070.

Hatt, B. E., Fletcher, T. D., & Walsh, C. J. (2004). The influence of urban density and drainage infrastructure on the concentration and loads of pollutants in small streams. *Environmental Management*, *34*, 112–124.

Hill, W. R., Ryon, M. G., & Schilling, E. M. (1995). Light limitation in a stream ecosystem: Responses by primary producers and consumers. *Ecology*, *76*, 1297–1309.

Horwitz, W., Kamps, L. R., & Boyer, K. W. (1980). Quality assurance in the analysis of foods for trace constituents. *Journal - Association of Official Analytical Chemists*, *63*, 1344–1453.

Kopacek, J., & Blazka, P. (1994). Ammonium uptake in alpine streams in the high Tatra mountains (Slovakia). *Hydrobiologia*, *294*, 157–165.

Maltchik, L., Molla, S., Casado, C., & Montes, C. (1994). Measurement of nutrient spiralling in a Mediterranean stream: Comparison of two extreme hydrological periods. *Archiv fur Hydrobiologie*, *130*, 215–227.

Marti, E., & Sabater, F. (1996). High variability in temporal and spatial nutrient retention in Mediterranean streams. *Ecology*, *77*, 854–869.

Merseburger, G. C., Marti, E., & Sabater, F. (2005). Net changes in nutrient concentrations below a point source input in two streams draining catchments with contrasting land uses. *Science of the Total Environment*, *347*, 217–229.

This page intentionally blank

Meyer, J. L. (1994). The microbial loop in flowing waters. *Microbial Ecology*, *28*, 195–199.

Meyer, J. L., & Likens, G. E. (1979). Transport and transformation of phosphorus in a forest stream ecosystem. *Ecology*, *60*, 1255–1269.

Mulholland, P. J., Newbold, D. J., Elwood J. W., & Ferren, L. A. (1985). Phosphorus spiralling in a woodland stream: Seasonal variations. *Ecology*, *66*, 1012–1023.

Mulholland, P. J., Tank, J. L., Webster, J. R., Bowden, W. B., Dodds, W. K., Gregory, S. V., et al. (2002). Can uptake length in streams be determined by nutrient addition experiments? Results from an interbiome comparison study. *Journal of the North American Benthological Society*, *21*, 544–560.

Newbold, J. D., Elwood, J. W., O'Neill, R. V., & Winkle, W. V. (1981). Measuring nutrient spiralling in streams. *Canadian Journal of Fisheries and Aquatic Sciences*, *38*, 860–863.

Simon, K. S., Townsend, C. R., Biggs, B. J. F., & Bowden, W. B. (2005). Temporal variation of N and P uptake in 2 New Zealand streams. *Journal of the North American Benthological Society*, *24*, 1–18.

Stream Solute Workshop (1990). Concepts and methods for assessing solute dynamics in stream ecosystems. *Journal of the North American Benthological Society*, *9*, 95–119.

Suplee, M. W., & Cotner, J. B. (2002). An evaluation of the importance of sulfate reduction and temperature to P fluxes from aerobic-surfaced, lacustrine sediments. *Biogeochemistry*, *61*, 199–228.

Taylor, S. L., Roberts, S. C., Walsh, C. J., & Hatt, B. E. (2004). Catchment urbanisation and increased benthic algal biomass in streams: Linking mechanisms to management. *Freshwater Biology*, *49*, 835–851.

Walsh, C. J. (2000). Urban impacts on the ecology of receiving waters: A framework for assessment, conservation and restoration. *Hydrobiologia*, *431*, 107–114.

WSC (2001). *Analytical procedures manual*. Water Studies Centre, Monash University.

Webster, J. R., & Meyer, J. L. (1997). Organic matter budgets for streams: A synthesis. *Journal of the North American Benthological Society*, *16*, 141–161.

Webster, J. R., & Patten, B. C. (1979). Effects of watershed perturbation on stream potassium and calcium dynamics. *Ecological Monographs*, 51–72.

Webster, J. R., Tank, J. L., Wallace, J. B., Meyer, J. L., Eggert, S. L., Ehrman, T. P., et al. (2000). Effects of litter exclusion and wood removal on phosphorus and nitrogen retention in a forest stream. *Verhandlungen Internationale Vereinigung für Theoretische und Angewandte Limnologie*, *27*, 1337–1340.

Water, Air, and Soil Pollution: Focus (2006) **6:** 49–58
DOI: 10.1007/s11267-006-9055-0

DISSOLVED OXYGEN AND NUTRIENT FLUXES ACROSS THE SEDIMENT–WATER INTERFACE OF THE NECKAR RIVER, GERMANY: *IN SITU* MEASUREMENTS AND SIMULATIONS

INGO HAAG[1,*], GERHARD SCHMID[2] and BERNHARD WESTRICH[2]
[1]Consulting Engineers Dr.-Ing. Karl Ludwig, Herrenstr. 14 76133 Karlsruhe, Germany
[2]Institut für Wasserbau, University of Stuttgart 70550 Stuttgart, Germany
([*]author for correspondence, e-mail: ingo.haag@ludwig-wawi.de; phone: +49-721-9125122; fax: +49-721-9125119)

Abstract. A benthic *in situ* flume and a 1D biogeochemical sediment model to evaluate solute fluxes across the sediment–water interface have been developed. The flume was successfully used to determine oxygen and nutrient fluxes at various locations of the Neckar River in Germany. The experimental results were linked with vertical pore water concentration profiles and independently verified with the model. By combining experimental and model results we assessed the influence of dissolved oxygen concentrations in the water column and the availability of degradable organic matter on sediment oxygen demand. The results and the derived relations can be used to parameterize the sediment module of large scale water quality models, allowing one to assess the influence of sediment–water interactions on various aspects of river water quality. Moreover, the biogeochemical sediment model can help to improve the general understanding of the processes governing solute concentrations and fluxes in sediments and across their interfaces.

Keywords: ammonium, benthic flume, biogeochemical sediment model, methane, nitrate, phosphate, redox reactions, sediment oxygen demand (SOD)

1. Introduction

The solute flux across the sediment–water interface influences various aspects of the water quality of inland and coastal waters. One of the most prominent interactions is the flux of dissolved oxygen (DO) from the water body into the sediment, which is usually termed sediment oxygen demand (SOD) (DiToro, 2001). SOD may be a major contribution to the overall oxygen budget of inland waters, even in the case of large and deep rivers (e.g., Bachmann & Usseglio-Polatera, 1999). Moreover, fluxes across the sediment–water interface of rivers may play a decisive role with respect to nutrient and contaminant concentrations within these rivers and their export into the sea. Hence, it is important to quantify these sediment–water fluxes and enhance our understanding of the governing processes (DiToro, 2001).

To gain representative values of DO and nutrient fluxes across the sediment–water interface, we developed an *in situ* benthic flume and applied it at various

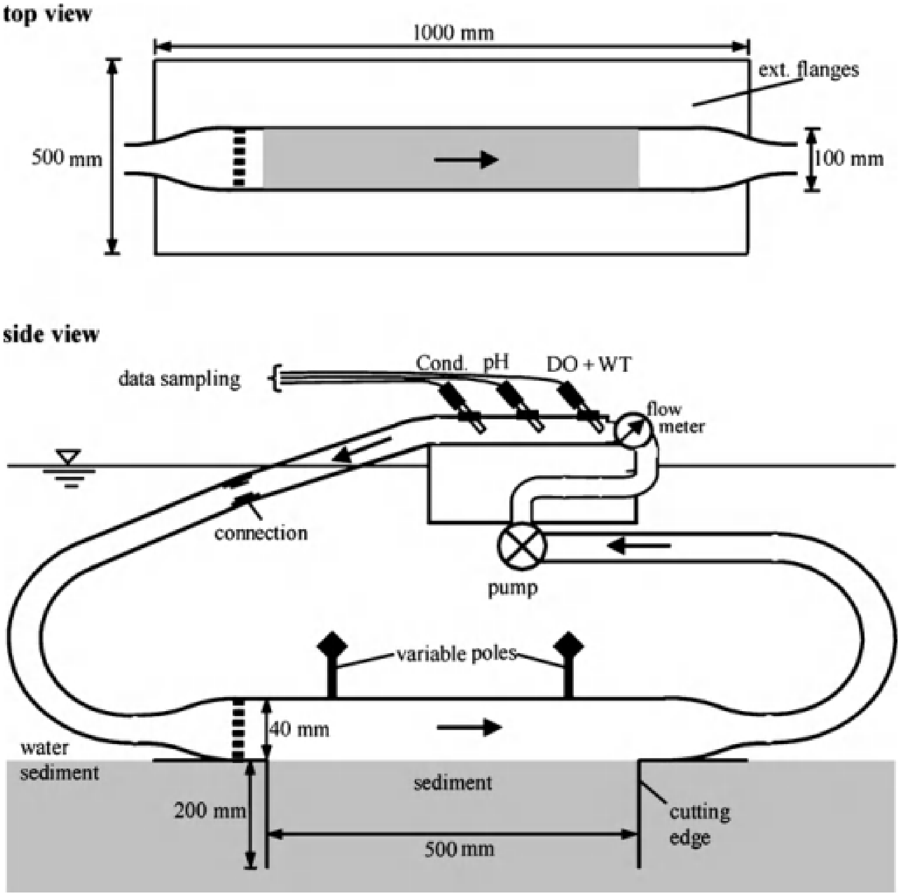


Figure 1. Schematic sketch of the benthic *in situ* system.

locations along the Neckar River in Germany. We also developed and applied a 1D vertical model of the relevant biogeochemical processes within the sediment and at its surface, in order to (1) independently verify the experimental results, (2) link the observed fluxes with pore water profiles, (3) extrapolate our findings to different boundary conditions and (4) establish a tool that can help to improve our under-standing of the governing processes.

2. Experimental and Numerical Methods

2.1. BENTHIC FLUME EXPERIMENTS IN THE NECKAR RIVER

The Neckar is a lock-regulated river, draining a densely populated 14,000 km^2 watershed in south-west Germany. Bottom sediments within the river reservoirs are mostly fine grained (silty loam) and usually contain high proportions of organic matter. Consequently, these sediments are a major sink for DO and play an important role in the transport and fate of nutrients and contaminants (Haag, 2003).

To further investigate DO and nutrient fluxes across the sediment–water interface, we developed an *in situ* benthic flume system which is schematically depicted in Figure 1. It is made up of the flume, a variable set of tubes to connect its inflow and outflow end, a controllable pump, a flow meter and a set of probes for DO, water temperature (WT), pH and conductivity. The flume has an opening at the bottom (0.05 m^2), a vertical cutting edge, and exterior flanges. The total volume of the system is 6.90 or 8.75 l with the short tubing and the long tubing, respectively.

To perform *in situ* measurements, the flume was carefully pushed into the sediment until the flanges rested on the sediment surface, preventing further penetration. Afterwards the ambient water was pumped through the system with a constant flow rate of 5 l/min which corresponds to a flow velocity of 2.1 cm/s within the flume. The system was kept open until all probes showed constant values for several minutes. Before closing the connection, four water samples were taken at the outflow end of the system. Two replicate samples were used to measure water borne biochemical oxygen demand (BOD) during the experiment, which was generally found to be negligible. The other two samples were later analysed in the laboratory for nutrient concentrations. After closing the connection, the ambient water was circled through the system with the changes of DO, pH, WT and conductivity recorded at a temporal resolution of 15 min. During the experiment, photosynthesis was prevented by darkening the system. Immediately after opening the connection at the end of each experiment, samples of the water discharging out of the system were collected in two 1-l bottles.

The water samples taken at the beginning and the end of each experiment were kept cool and dark until chemical analysis. Analyses of the following solutes were performed within 24 h of sampling according to European standards (with the methods given in parentheses, Wasserchemische Gesellschaft, 2001): Phosphate ($P–PO4^{3-}$, EN 1189-3), nitrate ($N–NO3^{-}$, EN ISO 10304-1), ammonium ($N–NH4^{+}$, EN ISO 10304-2). At each experimental site two grab samples of surficial sediment were taken, to determine the grain size distributions and the biochemical oxygen demand of 1 ml of the sediment (BODSED) according to DIN 38409 H52 (Wasserchemische Gesellschaft, 2001).

Eight experiments at seven different sites along the Neckar River were performed in July 2001. Experiments usually lasted for 3–6 h, with system internal DO levels not dropping below 3 mg/l. Reproducibility was ensured by repeating one experiment at the same location. This repetition was run for more than 15 h with internal DO levels dropping below 0.5 mg/l, enabling us to also investigate the effect of very low DO concentrations in the water column on SOD. Generally, care was taken not to erode any sediment before or during the

TABLE I

Reactions considered in the biogeochemical sediment model and their stoichiometries

Process	Stoichiometric relationship
Aerobic respiration	$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 106O_2 + 14H^+ \rightarrow 106CO_2 + 16NH_4^+ + HPO_4^{2-} + 106H_2O$
Denitrification (OM as reductant)	$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 84.8NO_3^- + 98.8H^+ \rightarrow 106CO_2 + 16NH_4^+ + HPO_4^{2-} + 42.4N_2 + 148.4H_2O$
Denitrification (CH4 as reductant)	$CH_{4(aq)} + 1.6NO_3^- + 1.6H^+ \rightarrow CO_2 + 0.8N_2 + 2.8H_2O$
Methane fermentation	$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 14H^+ \rightarrow 53CO_2 + 16NH_4^+ + HPO_4^{2-} + 53CH_{4(aq)}$
Nitrification	$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$
Methane oxidation	$CH_{4(aq)} + 2O_2 \rightarrow CO_2 + 2H_2O$
Methane gas phase equilibrium	$CH_{4(aq)} \leftrightarrow CH_{4(g)}$

experiments. However, to investigate the role of erosion events, the sediment surface was intentionally eroded prior to one experiment, by applying a high bottom shear stress (i.e., high pump rate). After eroding the sediment surface, the flow rate was reduced to 5 l/min again, and the experiment was not started until no more turbidity was visible and the probe readings had returned to normal.

2.2. The Mechanistic Biogeochemical Sediment Model

We also developed a mechanistic 1D vertical model of the relevant biogeochemical processes affecting DO and nitrogen fluxes within the sediment and across its surface. It accounts for (1) the respiration of macroorganisms, (2) the aerobic degradation of degradable organic matter (OM), (3) nitrification, (4) methane oxidation, (5) denitrification using OM as reductant, (6) denitrification using methane as reductant, (7) methane fermentation and (8) the equilibrium of dissolved methane (CH4(aq)) with methane gas bubbles (CH4(g)). These processes are modelled according to the reaction stoichiometries given in Table I. All redox processes are simulated as first order reactions, with a Monod-type influence of the oxidant concentration on reaction rates. DO inhibits denitrification and CH4(aq) fermentation, whereas $N–NO3^-$ only inhibits CH4 (aq) fermentation. Processes (1) through (7) are temperature corrected by Arrhenius-type coefficients. Equilibrium between CH4(aq) and CH4(g) is expressed as a function of pressure and temperature (DiToro, 2001). Redox processes involving manganese, iron and sulphur species are neglected, because their mobility is largely prevented by precipitation and adsorption, and because their contribution to SOD is negligible for the sediments under investigation (Park & Jaffe, 1999).

Solute transport within the sediment and across its interface is simulated by a 1D diffusive approach, using an effective diffusion coefficient (*D*eff) which takes into account mixture due to bioturbation and molecular diffusion. The effect of bioturbation is assumed to decreases exponentially with sediment depth (*z*) as proposed by Cai, Reimers, and Shaw (1995). Porosity and turtuosity are taken into account as factors reducing molecular diffusion within the sediment according to the findings of Boudreau (1997). Thus, the overall effective diffusion coefficient of a solute is expressed as follows:

$$D_{\mathrm{eff}}(z) = D_{\mathrm{bio},0} \cdot \exp\left(-3 \cdot \left(\frac{z}{z_{\mathrm{bio}}}\right)^4\right) + \Phi \cdot \frac{D_w}{1 - \ln(\Phi^2)} \tag{1}$$

where *D*bio,0 is the bioturbation coefficient at the sediment surface, *z*bio is the maximum depth of bioturbation, *D*w is the molecular diffusion coefficient of the solute in free water and Φ is the sediment porosity. Laboratory experiments with Neckar sediment showed that the resistance of the diffusive boundary layer is insignificant for the DO transport across the interface under the conditions of the benthic flume and within the range of shear stresses occurring in the river (Haag, 2003). Consequently, the model does not account for a diffusive boundary layer. The mass flux (*J*) of a solute across the interface is given by:

$$J = D_{\mathrm{eff}} \cdot \left.\frac{\mathrm{dC}}{\mathrm{dz}}\right|_{z\,=\,0} \tag{2}$$

where *C* is the solute’s concentration.

Model parameters were adjusted within meaningful ranges to approximately fit both the fluxes measured with the benthic flume and vertical concentration profiles of Neckar sediment recorded by Song and Müller (1999). A detailed description of the model, its theoretical basis, governing equations and parameters is given by Haag (2003).

3. Results and Discussion

3.1. SEDIMENT OXYGEN DEMAND (SOD)

The investigated sediments can be classified into two groups (Table II): At five sites (experiments 1a/b through 5) it consisted of silty loam with a BODSED of 0.15 to 0.25 mg ml^{-1} day^{-1}. The upper 2–3 cm were brown, indicating ferric oxides/hydroxides and thus oxic conditions. Below, this sediment type had the

TABLE II

Solute fluxes across the sediment–water interface

No. of experiment	BODSED (mg ml^{-1} day^{-1})	Duration (hh:mm)	WTmean (°C)	[a]SODsim (g m^{2} day^{-1})	[b]JDO (g m^{2} day $^{-1}$)	[b]JP–PO4 (g m^{2} day $^{-1}$)	[b]JN–NH4 (g m^{2} day $^{-1}$)	[b]JN–NO3 (g m^{2} day $^{-1}$)
1a	0.20	04:30	21.4	1.6	1.4	0.05	−0.42	0.36
1b	0.20	15:15	21.1	1.6	1.5	0.03	−0.22	0.35
2	0.25	06:21	18.9	1.6	1.4	0.06	−0.82	0.37
3	0.20	04:32	22.7	1.6	1.6	0.01	−0.17	0.27
4	0.23	03:20	22.1	1.6	1.7	−0.01	−0.13	0.47
5	0.15	04:08	26.0	1.6	1.5	0.04	−0.34	0.49
6	0.09	03:23	21.5	0.8	0.9	0.00	−0.01	0.21
7	0.08	05:57	22.6	0.8	0.7	0.02	No data	0.16

[a] Simulation results for 20 °C and 6 mg/l DO in the water column

[b] *In situ* measurements corrected to 20 °C by 1.065$^{(20\text{-}WT)}$

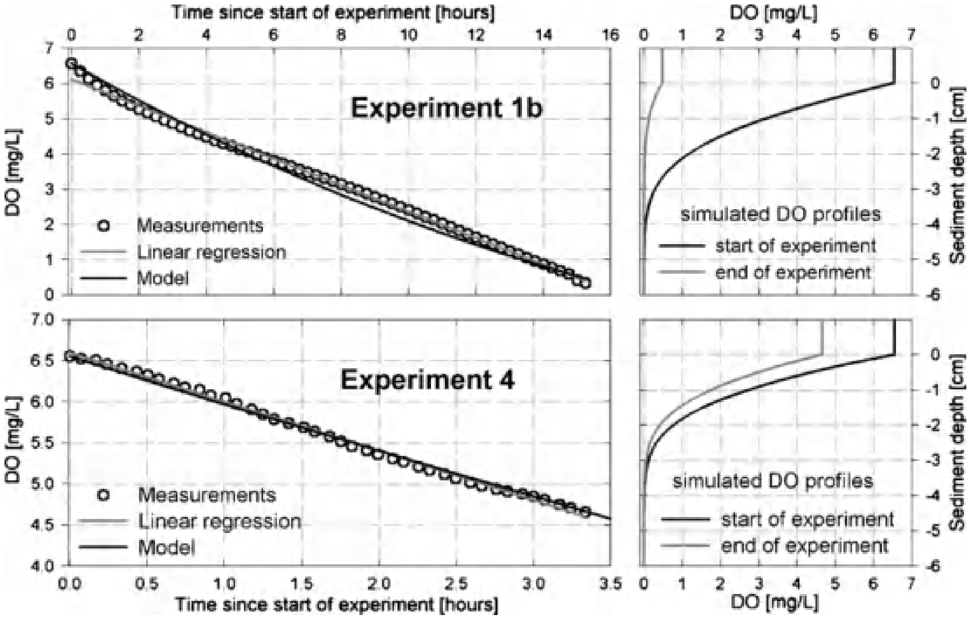


Figure 2. Measurements and simulation results of experiments 1b and 4.

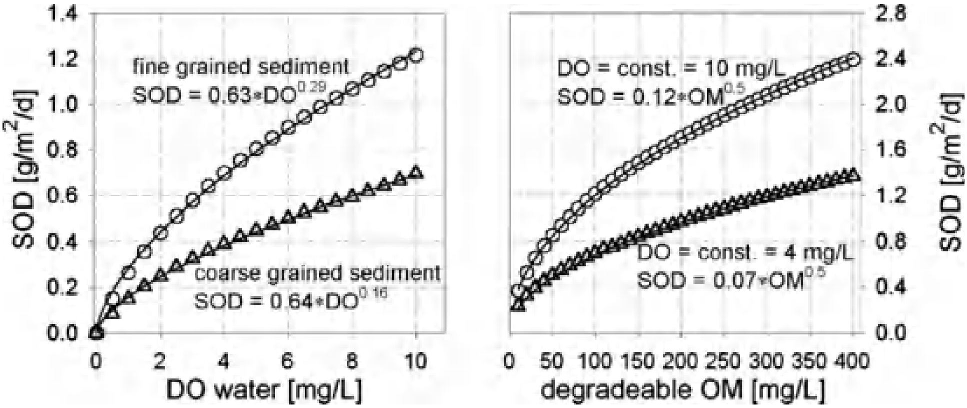


Figure 3. Dependence of SOD on concentrations of DO in the overlying water and degradable OM in the sediment as derived from simulation results.

typical colour and odour of sulphides, indicating anoxic conditions. At two sites (experiments 6 and 7), the sediment was much coarser (sandy loam) with a BODSED of approximately 0.10 mg ml^{-1} day^{-1}.

Results of DO depletion within the benthic system are exemplified in Figure 2. On the left hand side, measured DO concentrations are shown along with the results of a linear regression and simulated DO concentrations. The right hand side shows the simulated vertical concentration profiles of DO at the start and the end of the experiments. Note that experiment 1b was the exceptional long term experiment, whereas the duration of experiment 4 is within the typical range of 3–6 h.

In situ SOD experiments are commonly evaluated by assuming a zero order reaction (i.e., linear decay of DO). As can be seen from the right hand side of Figure 2, this is theoretically not correct. Due to the DO depletion in the overlying water, vertical DO gradients within the sediments and the resulting fluxes change over time (i.e., SOD decreasing over time). For the long term experiment 1b it can thus be seen that the simulated DO depletion is slightly non-linear. However, for the typical short term experiment 4 the change of gradient is quite small. Consequently, measured and simulated DO depletion are close to linear and simulation results are almost identical with the linear regression. An assessment of all experiments showed that calculating the SOD from the measurements of short term experiments (3–6 h) with a linear regression gives a good approximation of the theoretical SOD (Table II). However, to ensure the validity of the linear approximation, *in situ* experiments should not last too long.

We used the model to further assess the influence of DO in the overlying water and the availability of degradable OM on SOD. To simplify these analyses the respiration of benthic organisms was neglected. The graphs on the left hand side of Figure 3 show the dependence of SOD on DO in the overlying water for fine grained and coarse grained sediment of the Neckar River. The simulation results can be approximated with the power functions given in the plot. SOD of typical Neckar River sediments is significantly influenced by the DO concentration in the overlying water. In the case of the silty loam sediment, the SOD at 10 mg/l DO is approximately 0.5 g m^2 day^{-1} higher than at a DO concentration of 4 mg/l. These significant differences should be taken into account in large scale water quality models, e.g., by using the power functions given in Figure 3.

As is shown on the right hand side of Figure 3, SOD increases with the square root of the amount of degradable OM in the sediment. This is consistent with other theoretical analyses of SOD and numerous experimental results (e.g., DiToro, 2001). Our results also show a square root relation between BODSED and SOD (Haag, 2003), indicating that BODSED can be used as an easily measurable surrogate for the amount of degradable OM in the sediment.

Overall, the findings show that combining experimental results of BODSED with the theoretical dependence of SOD on the amount of degradable OM and the DO concentration in the overlying water could lead to a simplified approach to express spatial and temporal variability of SOD in large scale water quality models. Our results also indicate that the species assemblage and abundance of benthic organisms may exert a significant influence on SOD via respiration and bioturbation. However, we do not yet have sufficient biological data to assess these influences in a strictly quantitative way and include them in a comprehensive formula (Bachmann & Usseglio-Polatera, 1999; Haag, 2003).

3.2. NUTRIENT FLUXES

Since chemical analyses of nutrients were only performed at the start and the end of each experiment, fluxes of $N–NH4^+$, $N–NO3^-$ and $P–PO4^{3-}$ were determined using the resulting concentration differences. Model results showed that $N–NO3^-$ and $N–NH4^+$ fluxes are only moderately non-linear, in a similar way as has been demonstrated for DO. Consequently, the simple concentration difference approach can be used for an approximate estimate of $N–NO3^-$ and $N–NH4^+$ fluxes during short term experiments. Phosphate was not included in the model, because of its strong interactions with the solid phase (mineral precipitation, specific adsorption). Nonetheless, it was concluded from the relevant redox processes (Table I), that $P–PO4^{3-}$ fluxes can also be estimated from the simple concentration difference approach (Haag, 2003). The resulting nutrient fluxes are summarized in Table II. Note that positive values indicate fluxes from the water column into the sediment and *vice versa*.

In all experiments, $N–NO3^-$ was taken up by the sediment, whereas $N–NH4^+$ was released into the water. Ammonium is the result of (aerobic and anaerobic) mineralization of OM including denitrification. On the other hand it is used up by nitrification in the presence of DO (Table I). The negative $N–NH4^+$ fluxes show that nitrification consumes less $NH4^+$ than is produced by mineralization of OM. Moreover, the positive fluxes of $N–NO3^-$ show that denitrification in the suboxic layer alone dominates nitrification in the oxic layer. This is consistent with our model results and the concentration profiles presented by Song and Müller (1999). The results also show that denitrification and the subsequent volatilisation of N2 may be an important sink with respect to the large scale nitrogen budget. For example, upscaling of our experimental results showed that sediment bound denitrification in a 65 km reach of the Neckar River consumed approximately 300 tons of nitrogen during the months of April through October 1998 (Haag, 2003).

Surprisingly, the $P–PO4^{3-}$ fluxes were also directed towards the sediment (Table II). The pore water profiles of Song and Müller (1999) show high $P–PO4^{3-}$ concentrations in sediments below approximately 3 cm, with a sharp concentration decrease in the uppermost (oxic) layer. Phosphate is produced throughout the whole sediment profile from the mineralization of organic matter. However, the presence of oxides/hydroxides in the oxic layer provides specific adsorption sites for $P–PO4^{3-}$ (Dzombak & Morel, 1990), effectively reducing its concentration in the pore water solution. Obviously the concentration of $P–PO4^{3-}$ in the uppermost sediment layer was even lower than in the overlying water column, inducing a flux into the sediment. To test this hypothesis, we eroded the uppermost sediment layer with its assumed oxide/hydroxide barrier prior to experiment 4. In accordance with the hypothesis this resulted in the only experiment with a $P–PO4^{3-}$ release from the sediment (Table II). It is thus concluded that Neckar River sediments may temporarily trap $P–PO4^{3-}$. However, the trapped phosphorous may be released into the water column during erosion events and some time afterwards, until a new barrier is built.

4. Conclusions

It was shown that benthic *in situ* chambers or flumes, like the one described in this paper, can be successfully used to determine SOD and nutrient fluxes across the sediment–water interface. However, to cross-validate the *in situ* measurements with independent data (e.g., pore water profiles), to correctly interpret them and to extrapolate them to other boundary conditions, it is necessary to combine the experimental results with an adequate model. In the present case, we were able to verify and extrapolate our *in situ* measurements with a newly developed 1D biogeochemical sediment model. The model allowed us to establish relations between SOD and DO concentrations in the overlying water as well as between SOD and the amount of degradable organic matter in the sediment. On this basis, the results presented here, have been successfully used to independently parameterize the sediment module of a large scale water quality model for the Neckar River (Haag, 2003). Moreover, the newly developed biogeochemical sediment model can serve as a tool to further investigate solute concentrations and fluxes within sediments and the associated sediment–water interactions.

References

Bachmann, V., & Usseglio-Polatera, P. (1999). Contribution of the macrobenthic compartment to the oxygen budget of a large regulated river: The Mosel. *Hydrobiologia, 410*, 39–46.

Boudreau, B. P. (1997). *Diagenetic models and their implementation – Modelling transport and reactions in aquatic sediments*. Berlin Heidelberg New York: Springer, 414 pp.

Cai, W. J., Reimers, C. C., & Shaw, T. (1995). Microelectrode studies of organic carbon degradation and calcite dissolution at California continental rise site. *Geochimica et Cosmochimica Acta, 59*, 497–511.

DiToro, M. (2001). *Sediment flux modeling*. New York: Wiley, 624 pp.

Dzombak, D. A., & Morel, F. M. M. (1990). *Surface complex-ation modeling*. New York: Wiley, 416 pp.

Haag, I. (2003). Der Sauerstoffhaushalt staugeregelter Flüsse am Beispiel des Neckars – Analysen, Experimente, Simulationen. *Mitteilungen des Instituts für Wasserbau, Universität Stuttgart, 122*, 251 pp.

Park, S. S., & Jaffe, P. R. (1999). A numerical model to estimate sediment oxygen levels and demand. *Journal of Environmental Quality, 28*, 1219–1226.

Song, Y., & Müller, G. (1999). *Sediment–water interactions in anoxic freshwater sediments: Mobility of heavy metals and nutrients*. Berlin Heidelberg New York: Springer, 111 pp.

Wasserchemische Gesellschaft. (2001). *Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung*. Weinheim: Wiley-VCH.

Water, Air, and Soil Pollution: Focus (2006) **6:** 59–68
DOI: 10.1007/s11267-006-9056-z

OCCURRENCE OF SEDIMENT-BOUND PYRETHROIDS IN DANISH STREAMS AND THEIR IMPACT ON ECOSYSTEM FUNCTION

RASMUS B. LAURIDSEN[1,2,*], BRIAN KRONVANG[1] and NIKOLAI FRIBERG[1]
[1]Department of Freshwater Ecology, National Environmental Research Institute, Silkeborg, Denmark
[2]CEH Dorset, Winfrith Technology Centre, Winfrith Newburgh, Dorchester, Dorset DT2 8ZD, UK
*(*author for correspondence, e-mail: rasl@ceh.ac.uk; phone: +44-1305-213558; fax: +44-1305-213600)*

Abstract. In a total of 189 water samples collected from Danish streams no traces of the pyrethroid esfenvalerate were detected. However, pyrethroids have previously been found in sediments in 9 out of 30 streams investigated. We found that the shredding activity of the Trichopteran *Sericostoma personatum* and the amphipod *Gammarus pulex* was significantly reduced with increased concentration of the pyrethroid lambda-cyhalohtrin adsorbed to the leaves on which they fed. Predation rate on the Plecopteran *Leuctra nigra* by the leech *Erpobdella octoculata* increased significantly with increasing concentration of lambda-cyhalothrin on the leaves on which *L. nigra* was fed. Our results clearly indicate that the ongoing monitoring of pesticides is likely to underestimate pyrethroid occurrence and that sediment-bound pyrethroids have a potential negative impact on ecosystem function and biotic interactions in streams.

Keywords: ecosystem impact, pesticides, pyrethroid, stream bed sediment, water

1. Introduction

Pesticides are an integral part of modern agriculture that can potentially harm natural ecosystems. One example is the loss of pesticides to stream ecosystems and numerous studies report findings of pesticides in stream water (e.g., Kreuger, 1998; Mogensen & Spliid, 1995) and impacts on the biota (e.g., Hatakeyama, Fukushima, Kasai, & Shiraishi, 1994; Schultz & Liess, 1999). Pyrethroids are currently widely used insecticides and in 2003 they accounted for 83% of the area sprayed with insecticides in Denmark (Danish EPA, 2004). Dissolved pyrethroids are known to induce increased macroinvertebrate drift (e.g., Hechmann & Friberg, 2005), increased mortality and life cycle changes (Schulz & Liess, 2000). Pyrethroids are hydrophobic and have extremely high binding capacities to sediments (Wauchope, Buttler, Hornsby, Augutijnbeckers, & Burt, 1992). It is therefore likely that the primary route of pyrethroids into stream ecosystems will be through the sediments, but this has received little attention (Schulz & Liess, 1999).

Until now, national pesticide monitoring in Danish streams has focused entirely on water samples (Kronvang et al., 1999), ignoring sediment-bound pesticides. From the hundreds of streams surveyed in Denmark only few records of detection of pyrethroids in the water phase exist (Wiggers, 1999), whereas pyrethroids were detected in 9 out of 30 streams when the sediments were analysed (Kronvang, Laubel Larsen, & Friberg, 2003b). A contemporary study in the same 30 streams indicated that the invertebrate community was impacted by the sediment-bound pesticides (Friberg, Lindstrom, Kronvang, & Larsen, 2003). This suggests that the sampling strategy employed today seriously underestimates both occurrence and impact of pyrethroids on Danish streams.

The first aim of this study was to monitor the occurrence of pesticides in Danish streams and to model the likelihood of finding pyrethroids in water samples. By undertaking this analysis we can elucidate whether the sampling strategy currently used is inadequate to detect possible occurrence of pyrethroids in streams and hence underestimating their potentially impact on Danish ecosystems.

The second aim of this study was to investigate if pyrethroids, when sediment-bound, will impact the in-stream biota. To address this question we used an experimental set-up in the laboratory with the synthetic pyrethroid lambda-cyhalothrin bound to leaves. We used transformation of leaves into fine organic matter, predation (i.e., loss of organisms) and mortality as end-points for the impact of the lambda-cyhalothrin on invertebrates. By using degradation of organic matter and predation as end-points, this study allows us to predict the functional impact of pyrethroids on stream ecosystems.

2. Materials and Methods

2.1. MONITORING OF PESTICIDES IN STREAMS

Concentrations of 12 modern and currently applied pesticides were analysed in water samples collected from 25 first to second order streams (mean width (±SE): 2.02 ± 0.30 m) draining predominantly agricultural catchments and representing the different climatic and hydrogeological regions in Denmark. The 12 pesticides analysed covered a wide range of partition coefficients (*K*ow) and the amount of applied active ingredients in year 2000 in Danish agriculture varied considerably (Table I). Water sampling was conducted 8–16 times per year with more frequent sampling in the spraying season (late spring and early autumn) than in the remaining part of the year. Thus, one to two water samples were taken during the spring spaying season (May and June) and the autumn spraying season (September and October). A total of 189 water samples were collected in the 25 streams during the year 2000. All samples were analysed for pesticides with a

TABLE I

Chemical properties, detection frequency and concentration of 12 pesticides monitored. Chemical properties are also given for lambda-cyhalothrin (see text)

			25 smaller streams draining dominantly agricultural catchments			
			Number of water samples analysed = 189[b]			
Compound	*K*OW[a] (log *P*)	Applied amounts of active ingredients in Denmark in year 2000 (kg)	Detection frequency (%)	Average concentration[c] (ng l^{-1})	Median concentration[c] (ng l^{-1})	Maximum concentration (ng l^{-1})
Glyphosate (H)	<-3.4	878,000	73.9	132	77	1,400
Dimethoate (I)	0.70	26,600	2.1	46	27	120
Bentazone (H)	0.77	47,800	37.0	61	20	1,200
Ioxynil (H)	0.89	39,500	5.9	75	20	440
Pirimicarb (I)	1.7	999	3.8	23	26	42
Fenpropimorph (F)	2.6	118,600	1.6	49	27	110
Ethofumesate (H)	2.7	15,300	5.4	187	65	920
Diuron (H)	2.85	30,500	23.8	57	25	360
Terbuthylazine (H)	3.21	32,500	32.3	72	29	1,260
Propiconazole (F)	3.72	21,200	6.4	138	20	1,400
Pendimethalin (H)	5.18	243,300	11.1	75	38	580
Esfenvalerate (I)	6.22	760	0	–	–	–
Lambda -cyhalothrin (I)	7.0	645	Not monitored			

H Herbicide, *F* fungicide, *I* insecticide.

[a] *K*OW values from Tomlin (1997).

[b] Only 62 water samples analysed for in the case of esfenvalerate.

[c] Median and average pesticide concentration was calculated for pesticides revealing positive (above detection limit) analytical values.

general detection limit of 10 ng l^{-1}. Further information on the laboratory analysis conducted can be found in Kronvang et al. (1999) and Kronvang et al. (2003a).

2.2. LABORATORY EXPERIMENTS

Lambda-cyhalohtrin was chosen as model compound as it is a commonly used modern synthetic pyrethroid with low application rate and very high binding capacity to sediments (Hamer & Hill, 1994). With respect to the biota, we used macroinvertebrates as experimental organisms as they are frequently used in the bio-assessment of streams and rivers. As sediment we used leaves from riparian trees as these constitute the primary energy input into small streams, and because they are easy to handle in an experimental set-up. Leaves are consumed by invertebrates belonging to the functional feeding group shredders and they play a key role in the turnover of organic matter in streams.

2.3. MACROINVERTEBRATES

The caddis fly *Sericostoma personatum* Spence and the amphipod *Gammarus pulex* (L.), were used in the shredder experiment. The conversion of coarse particulate organic matter (CPOM), in the form of conditioned alder (*Alnus glutinósa* (L.)) leaves, to fine particulate organic matter (FPOM) was used as a measure of shredding activity.

In the predation experiment, predation rate of the predatory leach *Erpobdella octoculata* (L.) on the stonefly *Leuctra nigra* Olivier was measured with increasing lambda-cyhalothrin content of alder leaves fed on by *L. nigra*.

Macroinvertebrates used were similar in size within each species: *S. personatum* (12±4 mg DW); *G. pulex* (5.2±1.1 mg DW); *E. octoculata* (18.2± 0.9 mg DW) and *L. nigra* (0.39±0.02 mg DW). All macroinvertebrates used were collected in small first order pristine forest streams and acclimatised in CT-rooms at 10°C for one to two weeks before the experiments.

2.4. PREPARATION OF LEAVES

Alder leaves were conditioned in water from a pristine forest stream for seven days at 10°C and placed in 1 litre pesticide solution or tap water (controls) 24 h before usage. The pesticide solutions were made from the Karate® (Zeneca Agro Scandinavia) containing 2.5% lambda-cyhalothrin. Leaves (50 for each treatment) were placed in the following lambda-cyhalothrin concentrations: 0, 100, 300, 500, 1,000 and 1,500 ng l^{-1} (shredding experiments) and 0, 100 and 500 ng l^{-1} (predation experiments). To remove excess pesticide solution from the leaves they were dried between two pieces of filter paper for 5 s, while applying standardized pressure, before being transferred to the experimental set-up.

Acetone was used to extract lambda-cyhalothrin from a sub-set of leaves and the extract was analysed subsequently by gas chromatography and mass spectrometry (GC-MS/NCI (negative chemical ionisation)). Extraction efficiency of lambda-cyhalothrin from leaves was high and always above 70% (Lauridsen, 2002). Leaves used in all experiments were treated identically and it is therefore assumed that the relationship between lambda-cyhalothrin concentration in solution and contents in the leaves applies to all experiments.

2.5. Experimental Set-Up

All experiments were run for seven days in small, aerated aquariums (0.4 l) at 10°C in 12-h light-/dark-cycles. Ten individuals of *S. personatum* or seven individuals of *G. pulex* were kept on netting with 1 mm mesh size in each shredder experiment (six replicates for each concentration). After seven days the netting with invertebrates and remaining CPOM was lifted out and aquarium water was filtered through pre weighed Whatman® GF/C-filters (1.2 μm). FPOM produced (1.2 μm–1 mm) was determined by drying filters at 60°C until constant weight. In the predation experiment, 10 *L. nigra* and 2 *E. octoculata* were introduced to each aquarium (eight replicates for each concentration). The set-up was monitored daily and after seven days, the remaining *L. nigra* and *E. octoculata* were counted.

3. Results

3.1. Pesticides in Streams

Detection frequency of the 12 pesticides showed large variations, the highest being 74% for glyphosate and lowest 0% for the pyrethroid esfenvalerate (Table I). Highest average concentrations were detected for the herbicide ethofumesate (187 ng l^{-1}) and the highest concentration of pesticides measured was for glyphosate and propiconazole (1,400 ng l^{-1}) (Table I).We found a significant relationship ($N = 189$; corrected $R^2 = 0.60$; F-test, $P = 0.006$) between the detection frequency of pesticides (%) and the two explanatory variables: Partition coefficient and applied amounts of active ingredients (Aai in tonnes):

$$\text{Pesticide detection frequency} = 16.2 - (2.47 \times K_{\text{ow}}) + (0.0542 \times A_{\text{ai}}) \qquad (1)$$

3.2. Lambda-Cyhalothrin Content in Leaves

Analysis of the lambda-cyhalothrin content in seven leaf batches revealed a highly significant linear correlation between solution concentrations and leaf content ($R^2 = 0.84$; F-test, $P < 0.01$) and from the simple linear model, nanograms per liter can be converted to nanograms per gram by multiplying by 0.011 (the slope of the line).

3.3. SHREDDING ACTIVITY

Both species showed a significant reduction in shredding activity, measured as FPOM production, with increasing pyrethroid content of the leaves (Figure 1). Shredding activity by *S. personatum*was gradually reduced with increasing pyrethroid content and FPOM production reached the lowest level of 0.06 mg DW per gram of shredder per day when exposed to leaves containing 16.5 ng g^{-1} of lambda-cyhalothrin. The reduction was significant at 3.3 ng g^{-1} where FPOM production of *S. personatum* was reduced by approximately 50% (One Way ANOVA, $P < 0.05$). *G. pulex* exhibited a significant reduction in shredding activity with lambda-cyhalothrin content very similar to that for *S. personatum* (Figure 1). However, the reduction in shredding activity was not significant at 3.3 ng g^{-1} (One Way ANOVA, $P > 0.05$), but only at 5.5 ng g^{-1} lambda-cyhalothrin (One Way ANOVA, $P < 0.05$).

Mortality of *S. personatum* was low and between 0% and 3.3% during the different treatments in shredding trials (Table II). *G. pulex* mortality during shredding experiments was considerably higher (Table II) but neither *S. personatum* nor *G. pulex* mortality was linked to the content of lambda-cyhalothrin on leaves.

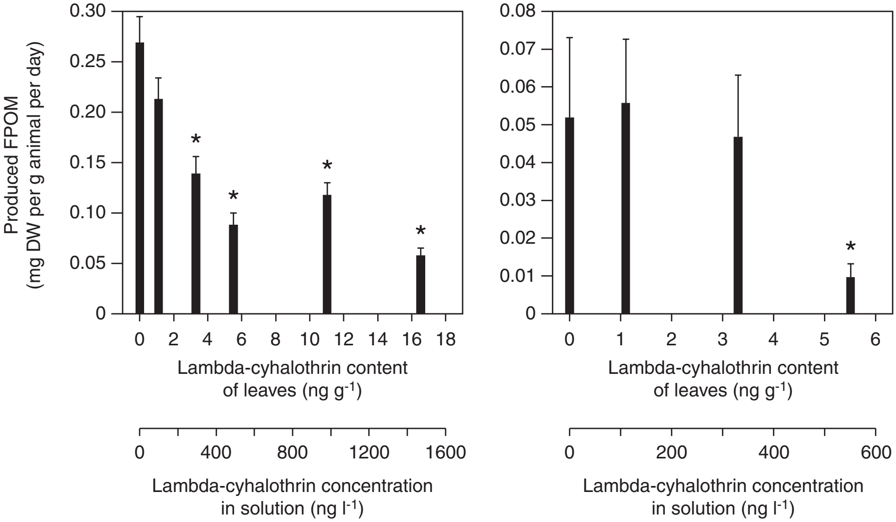


Figure 1. Mean FPOM production by macroinvertebrate shredders *S. personatum* and *G. pulex* with standard error. FPOM production is displayed as milligrams of dry weight produced per gram animal per day against lambda-cyhalothrin content in leaves. The two *x*-axes represent lambda-cyhalothrin content in leaves and concentration during contamination, respectively. *Denotes significant difference from control (One Way ANOVA, $P<0.05$).

TABLE II

Average mortality of the macroinvertebrates during experiments with different degree of leaf contamination

Lambda-cyhalothrin content in alder leafs (ng g^{-1})	Mortality avg.%±S.E.	
	Sericostoma	*Gammarus*
0.0	1.7±1.7	31.7±6.1
1.1	1.7±1.7	15.5±3.7
3.3	0.0±0.0	7.1±7.1
5.5	1.7±1.7	38.5±9.1
11.0	3.3±2.1	–
16.0	1.7±1.7	–

3.4. PREDATION RATE

The predation rate of *E. octoculata* on *L. nigra* increased after exposure of alder leaves in lambda-cyhalothrin. In controls with leaves not exposed for lambda-cyhalothrin the average number of disappeared (i.e., predated as no other sources of loss was evident) *L. nigra* was 0.43 ± 0.20 (4.3%), whereas 1.14 ± 0.46 (11.4%) and 2.63 ± 0.91 (26.3%) disappeared after exposure to leaves containing 1.1 and 5.5 ng g^{-1}, respectively (Figure 2). Predation rate on *L. nigra* was significantly higher at 5.5 ng g^{-1} compared with controls (Mann Whitney U test, $P < 0.05$). Number of *L. nigra* found dead also increased with the lambda-cyhalothrin content of the leaves (Figure 2) though this increase was not significant (Mann Whitney U test, $P > 0.05$).

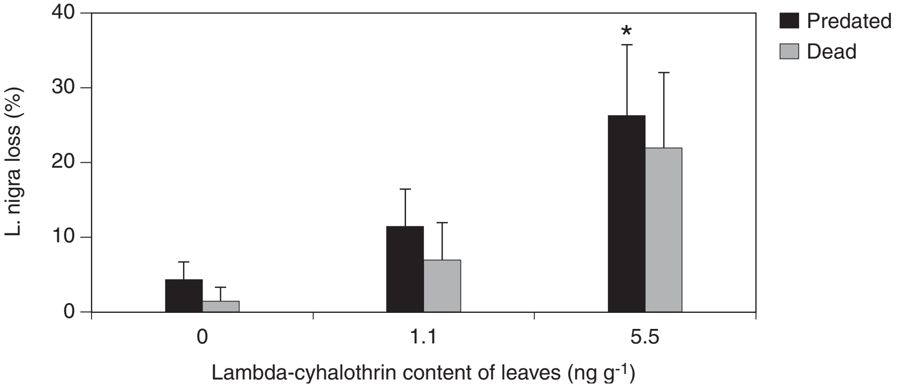


Figure 2. Fraction of missing *L. nigra* at the end of the experiment and the fraction of dead among the remaining *L. nigra* is displayed against lamba-cyhalothrin content of the leaves. *Denotes significant difference from control (Mann Whitney U test, $P < 0.05$).

4. Discussion

4.1. PESTICIDES IN STREAMS

Results from the water samples show that the detection frequency for pesticides heavily depends on both the physical chemistry of the substance and the amount of active ingredient applied. Lambda-cyhalothrin, which was not included in the monitoring programme, is among the substances applied in Danish agriculture (year 2000) with the highest partition coefficient and the lowest amount of active ingredients. We calculated an expected detection frequency for lambda-cyhalothrin of 0% in year 2000 based on Equation (1) and Table I, which is similar to another pyrethroid, esfenvalerate (Table I). Earlier monitoring has, however, detected both esfenvalerate and lambda-cyhalothrin in the sediment of Danish streams in concentrations up to 50 ng g^{-1} (Kronvang et al., 2003b). Due to their high partitioning coefficients the most likely entry route for pyrethroids from the terrestrial to aquatic environment besides wind drift and accidental spillage during equipment filling and cleaning is through surface runoff and subsurface runoff though drainage tills. The majority of pyrethroids entering streams from both the hydrological pathways will be particle bound. Runoff transport of highly pyrethroid-loaded organic matter to the stream from agricultural fields has previously been reported (e.g., Schulz and Liess, 1999). Transportation of particle bound pyrethroids will be transient and cause pulses of pyrethroids in the stream water, which is difficult to catch in water sampling. However, pyrethroid loaded particles will accumulate on the stream bed, which thereby acts as a sink for pyrethroids. Therefore, pyrethroid contamination of stream bed sediments does not necessarily originate from contaminated stream water. This contention is further supported by a study by Kreuger, Peterson, and Lundgren (1999), where high pyrethroid concentrations (10–80 ng g^{-1}) where found in the sediment after frequent pesticide analyses of the stream water had not revealed any pyrethroids.

4.2. SHREDDING ACTIVITY

The shredding experiments clearly show that macroinvertebrate shredding activity is reduced when the substrate is contaminated with lambda-cyhalothrin. Neither *S. personatum* nor *G. pulex* preferred non-contaminated leaves (Lauridsen, 2002) so the differences in shredding activity cannot be explained by lambda-cyhalohtrin having a repellent effect as shown in the terrestrial environment (Fisk & Wright, 1992). Therefore, our experiments clearly showed that lambda-cyhalothrin bound to leaves impaired shredding activity. Reduction in shredding activity followed the same trend for both species and appears to be a more sensitive end-point than mortality. The fact that approximately the same pesticide content affected both *S. personatum* and *G. pulex* renders it likely that this finding is applicable to all shredding insects and crustaceans and maybe detritivores in general. This implies that also pyrethroids bound to FPOM could potentially impact feeding rates of macroinvertebrates utilising this food resource (collectors).

4.3. PREDATION RATE

Results from the predation experiments show that contamination of the leaves with lambda-cyhalothrin significantly increases the predation rate of *E. octaculata* on *L. nigra*. This result give support to the theory that predator-/prey-interactions can be altered by the presence of pyrethroids which will cause changes in fitness and density of both the predator and the prey, maybe displacing the ecological equilibrium. These changes could affect other macroinvertebrate species from the same functional groups as well as organisms on other trophic levels of the food web.

5. Conclusion

Our monitoring of pesticides in Danish streams clearly shows that occurrence of pesticides in the water is dependent on chemical properties and applied amounts of the pesticide in question. Due to the highly hydrophobic nature and low application rates of pyrethroids they are unlikely to be found in stream water. However, the highly hydrophobic pyrethroids may be transported particle bound to the streams via the hydrological pathways, and the stream sediment therefore acts as a potential sink for pyrethroids.

Our results also clearly indicate that not only does the particle-bound pyrethroids affect the individual but they also influence the interactions between members of different levels of the food web. It is even possible that the pesticides will have a cascading effect through the ecosystem as described for herbicides in lakes by Lampert, Fleckner, Pott, Schober, and Storkel (1989). In this way the effects of pesticides at the individual level might have even stronger impact on the functioning of the entire stream ecosystem.

References

Danish EPA (2004). Bekæmpelsesmiddelstatistik 2003 (in Danish).

Fisk, T., & Wright, D. J. (1992). Comparative-studies on acylurea insect growth-regulators and neuroactive insecticides for the control of the armyworm *Spodoptera exempta* Walk. *Journal of Pesticide Science, 35*(2), 175–182.

Friberg, N., Lindstrom, M., Kronvang, B., & Larsen, S. E. (2003). Macroinvertebrate/sediment relationships along a pesticide gradient in Danish streams. *Hydrobiologia, 494*(1–3), 103–110.

Hamer, H. J., & Hill, I. R. (1994). The effects of lambda-cyhalothrin in aquatic field studies. In I. R.

Hill, F. Heimbach, P. Leeuwangh, & P. Matthiessen (Eds.), *Freshwater field tests for hazard assessment of chemicals* (331–338). London, UK: Lewis.

Hatakeyama, S., Fukushima, S., Kasai, F., & Shiraishi, H. (1994). Assessment of herbicide effects on algal production in Kokai River (Japan) using a model stream and *Selenastrum* bioassay. *Ecotoxicology, 3*(2), 143–156.

Hechmann, L. H., & Friberg, N. (2005). Macroinvertebrate community response to pulse exposure with the insecticide lambda-cyhalothrin using in-stream mesocosms. *Environmental Toxicology and Chemistry, 24*(3), 582–590.

Kreuger, J. (1998). Pesticides in stream water within an agricultural catchment in southern Sweden, 1990–1996. *Science of the Total Environment, 216*(3), 227–251.

Kreuger, J., Peterson, M., & Lundgren, E. (1999). Agricultural inputs of pesticide residues to stream and pond sediments in a small catchment in southern Sweden. *Bulletin of Environmental Contamination and Toxicology, 62*, 55–62.

Kronvang, B., Iversen, H. L., Vejrup, K., Mogensen, B. B., Hansen, A.-M., & Hansen, L. B. (2003a). Pesticides in streams and subsurface drainage water within two arable catchments in Denmark. Pesticide application, concentration, transport and fate facilitated transport and pesticides. Danish EPA. – *Pesticide Research, 69*, 141.

Kronvang, B., Laubel, A., Larsen, S. E., & Friberg, N. (2003b). Pesticides and heavy metals in Danish streambed sediment. *Hydrobiologia, 494*, 93–101.

Kronvang, B., Søndergaard, M., Mogensen, B., Nyeland, B., Andersen, K. J., Schwærter, R. C., & Nielsen, P. V. (1999). Monitoring of hazardous substances in Freshwater. NOVA 2003. *National Environmental Research Institute, Technical Quidance*, 27, (in Danish).

Lampert, W., Fleckner, W., Pott, E., Schober, U., & Storkel, K. U. (1989). Herbicide effects on plantonic systems of different complexity. *Hydrobiologia, 188/189*, 415–424.

Lauridsen, R. B. (2002). Effects of pesticides on stream macroinvertebrates – With special focus on the pyrthroid lambda-cyhalothrin. Ms.C. thesis, University of Copenhagen, Denmark, 96 pp.

Mogensen, B. B., & Spliid N. H. (1995). Pesticides in Danish watercourses – Occurrence and effects. *Chemosphere, 31*(8), 3977–3990.

Schulz, R., & Liess, M. (1999). A field study of the effects of agriculturally derived insecticide input on stream macroinvertebrate dynamics. *Aquatic Toxicology, 46*, 155–176.

Schulz, R., & Liess, M. (2000). Toxicity of fenvalerate to caddisfly larvae: Chronic effects of 1- vs 10-h pulse-exposure with constant doses. *Chemosphere, 41*(10), 1511–1517.

Tomlin, C. D. S. (1997). *The pesticide manual,* 11th ed. (p. 1599). Farnham, Surrey, UK: British Crop Protection Council.

Wauchope, R. D., Buttler, T. M., Hornsby, A. G., Augustijnbeckers, P. W. M., & Burt, J. P. (1992). The SCS ARS CES pesticide properties database for environmental decision making. *Review of Environmental Contamination Toxicology*, *123*, 1–155.

Wiggers (1999). Pesticider i vandløb, kilder og søer i Århus Amt (p. 46), Aarhus, Denmark: Aarhus Amt (in Danish).

Water, Air, and Soil Pollution: Focus (2006) **6:** 69–78
DOI: 10.1007/s11267-006-9057-y

DEVELOPMENT OF LAYERED SEDIMENT STRUCTURE AND ITS EFFECTS ON PORE WATER TRANSPORT AND HYPORHEIC EXCHANGE

AARON I. PACKMAN[1,*], ANDREA MARION[2], MATTIA ZARAMELLA[2], CHENG CHEN[1], JEAN-FRANÇOIS GAILLARD[1] and DENIS T. KEANE[3]
[1]*Department of Civil and Environmental Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA*
[2]*Department of Hydraulic, Maritime, Environmental, and Geotechnical Engineering, University of Padua, Padua, Italy*
[3]*DND-CAT Synchrotron Research Center, Northwestern University/Advanced Photon Source, Argonne, IL 60439, USA*
*(*author for correspondence, e-mail: a-packman@northwestern.edu; phone: +1-847-4919902; fax: +1-847-4914011)*

Abstract. Hyporheic exchange is known to provide an important control on nutrient and contaminant fluxes across the stream-subsurface interface. Similar processes also mediate interfacial transport in other permeable sediments. Recent research has focused on understanding the mechanics of these exchange processes and improving estimation of exchange rates in natural systems. While the structure of sediment beds obviously influences pore water flow rates and patterns, little is known about the interplay of typical sedimentary structures, hyporheic exchange, and other transport processes in fluvial/alluvial sediments. Here we discuss several processes that contribute to local-scale sediment heterogeneity and present results that illustrate the interaction of overlying flow conditions, the development of sediment structure, pore water transport, and stream-subsurface exchange. Layered structures are shown to develop at several scales within sediment beds. Surface sampling is used to analyze the development of an armor layer in a sand-and-gravel bed, while innovative synchrotron-based X-ray microtomography is used to observe patterns of grain sorting within sand bedforms. We show that layered bed structures involving coarsening of the bed surface increase interfacial solute flux but produce an effective anisotropy that favors horizontal pore water transport while limiting vertical penetration.

Keywords: fluvial processes, hyporheic exchange, sediment structure, sediment transport, solute transport, streams and rivers, streambeds, surface–groundwater interactions

1. Introduction

There has been considerable interest in the role of surface–subsurface interactions in a variety of geochemical and ecological processes, such as sediment diagenesis, benthic microbial growth, and contaminant transport (Boudreau & Jorgensen, 2001; Winter, Harvey, Franke, & Alley, 1998). In streams and rivers, exchange with the underlying hyporheic zone is now known to play an extremely important role in nutrient and carbon dynamics, as well as being a defining feature of benthic habitat (Brunke & Gonser, 1997; Jones & Mulholland, 2000). A variety of models have been applied to develop quantitative estimates of hyporheic exchange. These can generally be subdivided into two classes: models using an effective parameterization of solute transport observed in the main stream, and models that explicitly calculate interfacial pore water flows and solute mixing (Packman & Bencala, 2000). In both cases, variability within river channels makes it a major challenge to relate local interfacial fluxes to reach-average hyporheic exchange, and there is little general understanding of how exchange fluxes can be integrated to assess net transport at larger scales. Here, we outline the local-scale processes that are responsible for development of fine-scale structure in sediment beds, present new results that illuminate fine-scale pore structure, and show the effects of layered and armored structures on net hyporheic exchange.

2. Development of Fine-Scale Layered Structures in Streambeds

2.1. Processes

Fluvial systems are inherently dynamic and heterogeneous. Not only does episodic cut-and-fill result from variability in river flows and sediment inputs (Leopold, Wolman, & Miller, 1964), but substantial local heterogeneity occurs because of differential sediment transport and grain sorting (Powell, 1998). Basic sorting of river beds results from differential transport of sediment grains of different size, shape, or density. Many processes give rise to fine-scale layering within the sediment bed. The best known of these is the armoring process, whereby preferential removal of finer sediments gives rise to a coarser surface layer (Church, McLean, & Wolcott, 1987; Marion & Fraccarollo, 1997a). The structure resulting from this process is illustrated in Figure 1a. In addition, preferential transport of finer sediments in bedforms gives rise to buried layers of coarse sediments, as shown in Figure 1b (Blom, Ribberink, & de Vriend, 2003). The results of these processes are readily seen in natural river beds, as illustrated in Figure 1c (Huggenberger, Hoehn, Beschta, & Woessner, 1998). While larger-scale layered features are readily apparent in the field, difficulties in sampling sediments and characterizing *in situ* structure mean that relatively little is known regarding the development of local-scale structural heterogeneity, particularly in sandy streambeds.

2.2. Methods

The formation of sediment structure was observed in a recirculating laboratory flume. The flume used for all experiments has a working channel 7.5 m long, 20 cm wide and 40 cm deep. The main channel is constructed of an abrasion-

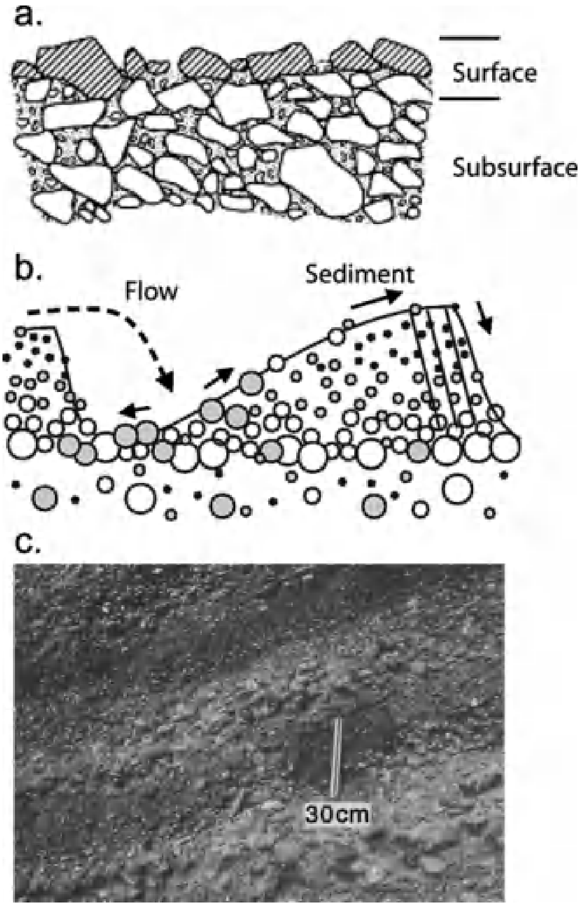


Figure 1. Modes of sediment sorting. **a** Surface armor layer (Powell, 1998 after Church et al., 1987), **b** buried coarse sediment layer (Blom et al., 2003), **c** complex layered structures observed in a vertical cut of a natural gravel-bed river (Huggenberger et al., 1998).

resistant transparent plastic, which allows direct observation of sediment transport and surface topography through the side-walls.

Two types of experiments were conducted to observe the formation of layered sediment structures. In the first set of experiments, the bed was composed of a mixture of sand and pea gravel. The gravel had a median diameter of 6 mm, porosity of 0.38, and hydraulic conductivity of 15 cm/s. This is the same material that we have previously used to study turbulent and bedform-induced flow coupling with gravel beds (Packman, Salehin, & Zaramella, 2004). The sand had a median diameter of 0.8 mm, porosity of 0.38, and hydraulic conductivity of 0.085 cm/s. To observe the armoring process, a bed composed of a mixture of 50% gravel and 50% sand (by weight) was subjected to a uniform flow with a mean velocity of 83 cm/s and depth of 12 cm. Exported sediments were retained in a sediment trap located at the downstream end of the channel, leaving a coarse static armor layer on the bed surface.

The composition of the armor layer was determined after each experiment. Surface sediment samples and conversion to volumetric composition were obtained using the methods described in Marion and Fraccarollo (1997b). Paraffin wax was poured into a steel frame of 8.5 × 12.5 cm to a depth of approximately 1 cm. Once the wax solidified, the sediment sample was removed *in toto* and transferred to a container, where the wax was removed using hot water. The size distribution of the collected sediments was then determined by sieving. The procedure was then repeated in order to obtain the size distribution of the underlying sediments in the bed. These measurements were repeated at two locations on the bed surface in each experiment.

The second set of experiments was conducted with Ottawa F-110 fine sand (US Silica, Ottawa, IL, USA) with a median diameter of 0.12 mm and a porosity of 0.4. These experiments were used to observe the formation of layered structures within bedforms. A bed of this fine sand was subjected to a uniform flow of 28 cm/s at 15 cm depth for 24 h. No sediment trap was used in this experiment, so that sediment transported past the downstream end of the channel was carried through the pump and return piping to the upstream end of the channel. This allowed the bedform field to come to a dynamic equilibrium condition with constant mean bedform shape. The resulting bedforms had a mean height of 1.9 cm and wavelength of 11.9 cm. Following generation of bedform topography, the flow was stopped and small cores, 3.2 mm in diameter and 3–4 cm long, were obtained from the bed for analysis.

The internal structure of the cores from the sand-bed experiments was determined by X-ray Micro-Tomography (XMT) performed at the Advanced Photon Source (APS). Originally developed for medical applications, 3D X-ray Computed Tomography (CT) has recently been used for a variety of geosciences research. An overview of these methods can be found in Clausnitzer and Hopmans (2000) and Cislerova and Votrubova (2002). The major advantage of the use of a synchrotron radiation source such as the APS is that the tomography is performed using a monochromatic beam, which eliminates beam-hardening artifacts that result from the interaction of X-rays of different energy with different materials in the sample. This method allows *in situ* structure to be determined in three dimensions with near-micron-scale resolution. Here we present three-dimensional tomographic reconstructions of sediment cores that reveal patterns of grain sorting within bedforms. The CT images were displayed in 3D using the IDL software package (ITT Visual Information Solutions, Boulder) and filtered using the Blob3D routine (Ketcham, 2005).

2.3. RESULTS

The structure of a core obtained from a sand dune and resolved at the grain scale is presented in Figure 2. Analysis of the core by XMT reveals two important structural features within the dune. First, the sediments in the upper portion of the bed, just under the bed surface, are distinctly finer than those deeper in the dune. In particular, there is a notable absence of large particles in the upper part of the core, while the lower part of the core contains a mixture of larger and smaller sand grains. This behavior is expected because of sorting by size that occurs during the migration of the sand dunes, as was illustrated previously in Figure 1. Further, the larger grains that occur deep in the dune can be seen to be organized into layered structures, as shown in Figure 2. Such structures are expected to form as larger particles deposit at the bottom of the active sediment transport layer. Multiple layered structures are apparent at depth in the bedform, reflecting sorting during a series of sediment transport events. While this type of sorting was previously hypothesized to occur in dunes, as illustrated in Figure 1, to the best of our knowledge this is the first direct observation of the formation of these features within a sand bed.

The size distributions observed in experiments with gravel–sand mixtures are reported in Figure 3a. The d_{50} of the gravel and sand differed by almost an order of magnitude (6.0 and 0.8 mm, respectively). The mixture had a d_{50} of 2.3 mm and a wide size distribution as shown in Figure 3a. Because of the in-filling of pores in the gravel by the sand, the hydraulic conductivity of the mixture was essentially the same as that of the sand (0.085 cm/s). This is consistent with the similarity of the d_{10} of these two sediments, which can be seen in the size distribution curves. The size distribution of the armor layer, measured at the end of the experiment, was quite similar to that of the pure gravel. It was not possible to measure the *in situ* permeability of this layer, but it can be assumed to also approach that of the gravel, 15 cm/s, nearly 20 times greater than that of the mixture.

3. Effect of Heterogeneity on Hyporheic Exchange

3.1. PROCESSES

The structural heterogeneity that occurs on many different scales in river systems is obviously important for all surface–subsurface interactions, but little is known about the way in which sediment structure influences hyporheic exchange. At larger scales, it has been observed that solute exchange is often characterized by multiple exchange timescales (Choi, Harvey, & Conklin, 2000). More detailed information is available for a few study sites. Wondzell and Swanson (1996) found that exchange in a mountain stream was dominated by preferential transport through relict stream channels. Cardenas, Wilson, and Zlotnik (2004) showed that sediment heterogeneity played a substantial role in mediating hyporheic exchange in a low-gradient sand-and-gravel stream. Wörman, Packman, Johansson, and Jonsson (2002) found that variability in local streambed hydraulic conductivity

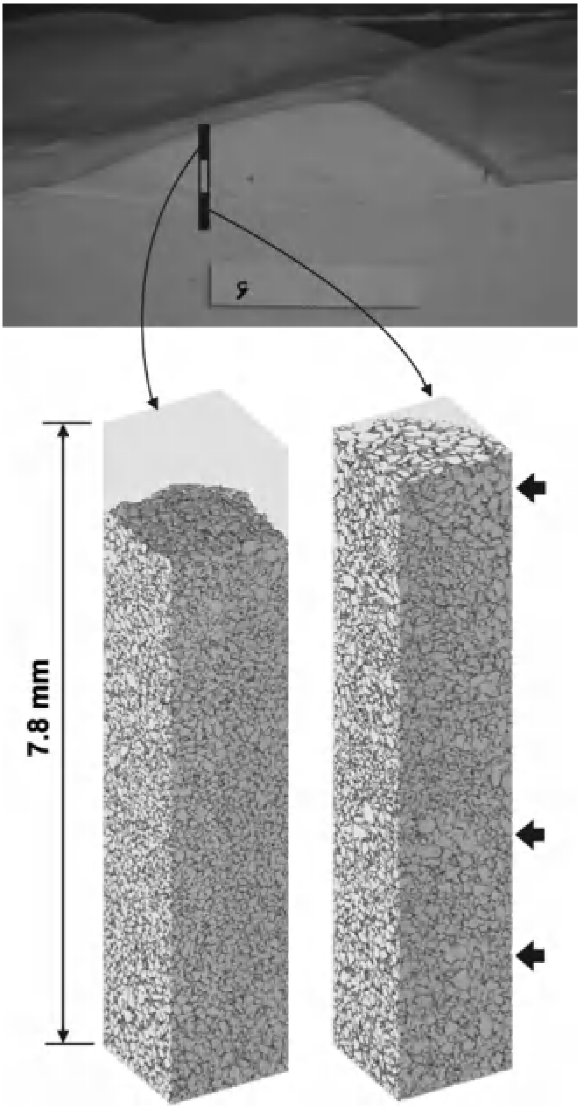


Figure 2. Pore-scale structure resulting from sediment sorting. A core was obtained from a naturally formed bedform and imaged by XMT. Imaging of the pore structure reveals that the near-surface sediments (*left*) are distinctly finer than those found deeper in the bedform (*right*). The coarser grains are also organized into layered structures, as indicated by *arrows*. Both images have been produced with 7.8 μm cubic voxels.

contributed substantial uncertainty to estimates of hyporheic exchange in a small agricultural stream.

While these site-based studies are extremely useful to demonstrate the effects that heterogeneity can have on hyporheic exchange, very little is known about the processes that mediate the relationship between the development of sediment structure, development of pore water flows, and overall hyporheic exchange. Investigating a similar phenomenon, Colbeck (1997) observed that high-permeability horizontal layers captured airflow in snowpacks. Salehin, Packman, and Paradis (2004) conducted a series of stream-subsurface exchange experiments with artificially constructed two-dimensional bed structures and found that preferential flow through high-permeability lenses increased interfacial flux, but the bed structure produced an effective anisotropy that limited vertical solute penetration. To the best of our knowledge, no controlled experiments have previously been performed to observe stream-subsurface exchange with naturally formed sediment heterogeneity.

3.2. METHODS

A series of solute injection experiments were performed to assess stream-subsurface exchange with sediment beds of various structure. All experiments were performed in the 7.5 m flume using the gravel and sand sediments described previously. Solute injection experiments were conducted with gravel alone, with a homogeneous mixture of 50% gravel and 50% sand, with a layered bed composed of 3 cm of gravel underlain by 12 cm of the gravel–sand mixture, and with the armored bed detailed in Figure 3a. All sediment beds were flat (lacking bedforms) and had a total depth of 15 cm. Solute injections were performed following the procedures described in Packman et al. 2004 with mean stream velocities between 18 and 21 cm/s, stream flow depths of 12 to 15 cm, and uniform flow conditions. Sodium chloride was used as a conservative tracer, and salt concentrations were measured using an Oakton Con-200 conductivity meter. Because a recirculating flume was used, in-stream concentrations are directly linked to stream-subsurface exchange. Results will be presented as the decrease in the normalized in-stream salt concentration, $C(t)/C_0$, where $C(t)$ is the concentration at time t and is C_0 is the initial well-mixed concentration in the stream.

3.3. RESULTS

The structural and hydrogeologic characteristics of the streambed sediments strongly influenced hyporheic exchange, as shown in Figure 3b. Exchange with the high-permeability gravel was very rapid, causing the bed to become essentially completely mixed after a few hours (to the complete depth of the bed, 15 cm). This resulted in a final normalized tracer concentration of 0.825, corresponding to complete dilution of the added salt throughout both the surface water and pore water. Exchange with the gravel–sand mixture bed was much slower, as expected. In fact the interfacial flux, corresponding to the initial slopes of the curves shown in Figure 3b (i.e., $d(C/C_0)/dt$ for $t \rightarrow 0$), should be proportional to the permeability of the sediments. Exchanges with the layered and armored beds were both intermediate, but showed different dynamics. Exchange

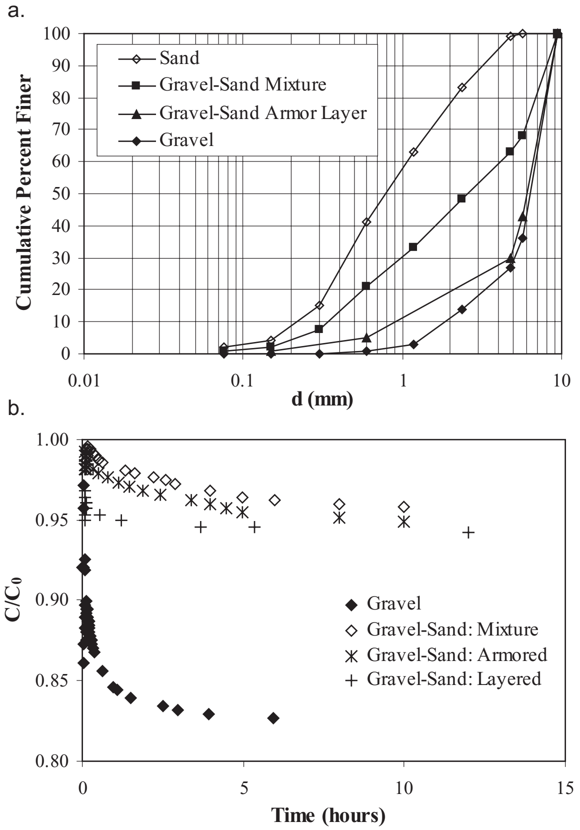


Figure 3. **a** Size distribution of gravel, sand, gravel–sand mixture, and armor layer of mixed bed. **b** Comparison of solute exchange with sand and gravel beds of different structure.

with the layered bed was initially very rapid as the solute penetrated the upper 3 cm gravel layer, and then the exchange rate decreased dramatically. Exchange with the armored bed was greater than with the mixed bed, but less than with the layered gravel bed. What is especially notable here is that the exchange rate $(d(C/C_0)/dt)$ with the layered bed was clearly less than that of either the armored or mixture bed after around t=4 h. This indicates that the strong vertical gradient in permeability at the base of the gravel layer produced localized anisotropy that suppressed further vertical solute transport.

4. Conclusions

A lack of information on the fine-scale structure of streambeds hinders estimation of hyporheic exchange rates in streams and rivers. Here we presented new observations that illustrate both the formation of layered structures in sand beds at the grain scale, and the effects of layered heterogeneity on net stream-subsurface exchange. Both natural armoring and the emplacement of a coarse sediment layer at the bed surface increased interfacial flux. However, layered heterogeneity also decreased vertical transport to depth in the bed. These results are congruent with the earlier results of Colbeck (1997) and Salehin et al. (2004) Much more information on the fine-scale heterogeneity of streambeds will be necessary before truly general conclusions can be drawn regarding the effects of sediment structure on pore water transport and hyporheic exchange, but the results presented here are expected to be found in natural streams that are armored or have other forms of layered heterogeneity.

Acknowledgements

This work was supported by the US National Science Foundation (NSF) grants BES-0196368 and HS-0310657. The XMT experiments were performed at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) Synchrotron Research Center located at Sector 5 of the Advanced Photon Source. DND-CAT is supported by the E.I. DuPont de Nemours & Co., The Dow Chemical Company, the US National Science Foundation through Grant DMR-9304725 and the State of Illinois through the Department of Commerce and the Board of Higher Education Grant IBHE HECA NWU 96. Use of the Advanced Photon Source was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38. We thank Susa Stone and Danilo Giuliani for their help with the laboratory experiments and analysis.

References

Blom, A., Ribberink, J. S., & de Vriend, H. J. (2003). Vertical sorting in bed forms: Flume experiments with a natural and a trimodal sediment mixture. *Water Resources Research*, *39*, 1025. DOI: http://dx.doi.org/10.1029/2001WR001088.

Boudreau, B. P., & Jorgensen, B. B. (Eds.) (2001). *The benthic boundary layer* (p. 440). Oxford University Press.

Brunke, M., & Gonser, T. (1997). The ecological significance of exchange processes between rivers and groundwater. *Freshwater Biology*, *37*, 1–33.

Cardenas, M. B., Wilson, J. L., & Zlotnik, V. A. (2004). Impact of heterogeneity, bed forms, and stream curvature on subchannel hyporheic exchange. *Water Resources Research*, *40*, W08307. DOI http://dx.doi.org/10.129/2004WR003008.

Choi, J., Harvey, J. W., & Conklin, M. H. (2000). Characterizing multiple timescales of stream and storage zone interaction that affect solute fate and transport in streams. *Water Resources Research*, *36*, 1511–1518.

Church, M. A., McLean, D. G., & Wolcott, J. F. (1987). River bed gravels: Sampling and analysis. In C. R. Thorne, J. C. Bathurst, & R. D. Hey (Eds.), *Sediment transport in gravel-bed rivers* (pp. 43–79). Chichester: Wiley.

Cislerova, M., & Votrubova, J. (2002). CT derived porosity distribution and flow domains. *Journal of Hydrology*, *267*, 186–200.

Clausnitzer, V., & Hopmans, J. W. (2000). Pore-scale measurements of solute breakthrough using microfocus X-ray computed tomography. *Water Resources Research*, *36*, 2067–2079.

Colbeck, S. C. (1997). Model of wind pumping for layered snow. *Journal of Glaciology*, *43*, 60–65.

Huggenberger, P., Hoehn, E., Beschta, R., & Woessner, W. (1998). Abiotic aspects of channels and floodplains in riparian ecology. *Freshwater Biology*, *40*, 407–425.

Jones, J. B., & Mulholland, P. J. (Eds.) (2000). *Streams and ground waters* (p. 425). San Diego: Academic.

Ketcham, R. A. (2005). Computational methods for quantitative analysis of three-dimensional features in geological specimens. *Geosphere*, *1*, 32–41.

Leopold, L. B., Wolman, M. G., & Miller, J. P. (1964). *Fluvial processes in geomorphology* (p. 535). San Francisco: Freeman.

Marion, A., & Fraccarollo, L. (1997a). Experimental investigation of mobile armouring development. *Water Resources Research*, *33*, 1447–1453.

Marion, A., & Fraccarollo, L. (1997b). A new conversion model for areal sampling of fluvial sediments. *Journal of Hydraulic Engineering*, *123*, 1148–1151.

Packman, A. I., & Bencala, K. E. (2000). Modeling methods in the study of surface–subsurface hydrologic interactions. In J. B. Jones & P. J. Mulholland (Eds.), *Streams and ground waters* (pp. 45–80). San Diego: Academic.

Packman, A. I., Salehin, M., & Zaramella, M. (2004). Hyporheic exchange with gravel beds: Basic hydrodynamic interactions and bedform-induced advective flows. *Journal of Hydraulic Engineering*, *130*, 647–656.

Powell, D. M. (1998). Patterns and processes of sediment sorting in gravel-bed rivers. *Progress in Physical Geography*, *22*, 1–32.

Salehin, M., Packman, A. I., & Paradis, M. (2004). Hyporheic exchange with heterogeneous streambeds: Modeling and laboratory experiments. *Water Resources Research*, *40*, W11504. DOI: http://dx.doi.org/10.1029/2003WR002567.

Winter, T. C., Harvey, J. W., Franke, O. H., & Alley, W. M. (1998). Ground water and surface water: A single resource. *USGS Circular*, *1139*, 79 pp.

Wondzell, S. M., & Swanson, F. J. (1996). Seasonal and storm dynamics of the hyporheic zone of a 4th order mountain stream. 1: Hydrologic processes. *Journal of the North American Benthological Society*, *15*, 3–19.

Wörman, A., Packman, A. I., Johansson, H., & Jonsson, K. (2002). Effect of flow-induced exchange in hyporheic zones on longitudinal transport of solutes in streams and rivers. *Water Resources Research*, *38*, 1001. DOI: http://dx.doi.org/10.129/2001WR000769.

Water, Air, and Soil Pollution: Focus (2006) **6:** 79–87
DOI: 10.1007/s11267-006-9058-x

STREAMBED SEDIMENT GEOCHEMICAL CONTROLS ON IN-STREAM PHOSPHORUS CONCENTRATIONS DURING BASEFLOW

MARCEL VAN DER PERK[1,*], PHILIP N. OWENS[2], LYNDA K. DEEKS[2]
and BARRY G. RAWLINS[3]
[1]Department of Physical Geography, Utrecht University P.O. Box 80 115 3508 TC Utrecht, The Netherlands
[2]National Soil Resources Institute, Cranfield University, North Wyke Research Station, Okehampton, Devon EX20 2SB, UK
[3]British Geological Survey , Keyworth, Nottingham NG12 5GG, UK
*(*author for correspondence, e-mail: m.vanderperk@geo.uu.nl; phone: +31-30-2535565; fax: +31-30-2531145)*

Abstract. A spatially extensive geochemical data set of stream water and bed sediment composition across the Tamar catchment in south-west England was analysed to identify the key bed sediment properties that control the in-stream dissolved reactive phosphorus (DRP) concentrations during baseflow conditions. Linear regression analysis of the streamwater DRP concentrations and the distribution coefficient K_d for DRP revealed that the former is positively correlated with total SiO_2 and Al_2O_3, and negatively correlated with K_2O. The primary control on these major element distributions is the dominant bedrock geology. The data suggest that streamwater DRP concentrations are mainly controlled by adsorption to clay minerals. Where P concentrations in streamwater were considerably elevated by inputs from point sources, DRP concentrations are also controlled by precipitation of hydroxyapatite.

Keywords: bed sediments, distribution coefficient, England, geochemistry, major element chemistry, phosphorus, Tamar catchment

1. Introduction

In recent decades, the transfer of phosphorus (P) in river basins has increasingly attracted the interest of earth and environmental scientists because of its potential for eutrophication of rivers, lakes, wetlands, estuaries, and coastal seas. Phosphorus enters the river network via diffuse sources (particularly agriculture) and point sources (particularly effluents from sewage treatment works (STWs)). Diffuse P inputs occur primarily via surface pathways as a result of winter storm events. In the UK it is generally assumed that P inputs via groundwater are small due to the retention of mobile P by P–poor subsoil with a high phosphate adsorption capacity (Heathwaite & Dils, 2000).

The interaction between the water column and bed sediments is a key process governing concentrations of both particulate and dissolved P in surface water systems due to deposition and resuspension of sediment and sorption processes (Owens & Walling, 2002; Jarvie et al., 2005). In catchments where dissolved P concentrations are elevated due to anthropogenic emissions from point or diffuse sources, sediments often act as a sink for streamwater P, although bed sediments may also act as a source of dissolved P to overlying waters during low-flow conditions (Jarvie et al., 2005).

This study aims to identify and quantify the role of bed sediment geochemical properties on streamwater P concentrations at the catchment scale during baseflow conditions. For this purpose, an extensive geochemical data set of stream water and bed sediment composition throughout the Tamar catchment in south-west England was examined.

2. Materials and Methods

2.1. Study Area

The Tamar catchment situated in south-west England covers an area of 1,274 km^2 with the River Tamar forming a natural county boundary between Devon and Cornwall (Figure 1). The north of the catchment has an elevation of around 200 m above mean sea level (amsl), rising to the east (>500 m amsl on Dartmoor) and to the west (>300 m amsl on Bodmin Moor). Bedrock geology in the north of the catchment is predominantly sandstones and argillaceous sedimentary rocks from the Carboniferous period. Further south, the Lower Carboniferous rocks are dominated by fine-grained sedimentary sequences. Outcrops of granite occur on the eastern (Dartmoor) and western (Bodmin Moor) sides of the catchment (see Rawlins, O'Donnell, & Ingham, 2003).

Land use within the catchment is predominantly grassland (72%) with small patches of arable land (6%). Forest covers approximately 17% of the catchment (Fuller, Groom, & Jones, 1994). The human population in this agriculturally dominated catchment is sparsely scattered in small towns, villages, and isolated farmsteads. There are 50 registered STWs in the catchment (South West Water, personal communication). The largest STW serves a population of about 13,100 people in Launceston and discharges its effluent into the River Tamar. The other STWs each serve on average approximately 390 inhabitants.

2.2. Field Sampling and Laboratory Analysis

In September 2002, the British Geological Survey (BGS) undertook a geochemical survey in the Tamar catchment (Rawlins et al., 2003), which included the collection and analysis of 483 samples of streamwater and streambed sediment. The hydrological conditions in the Tamar catchment were relatively consistent throughout the sampling period, with flows ranging from 2.7 to 3.8 $m^3\ s^{-1}$ at the

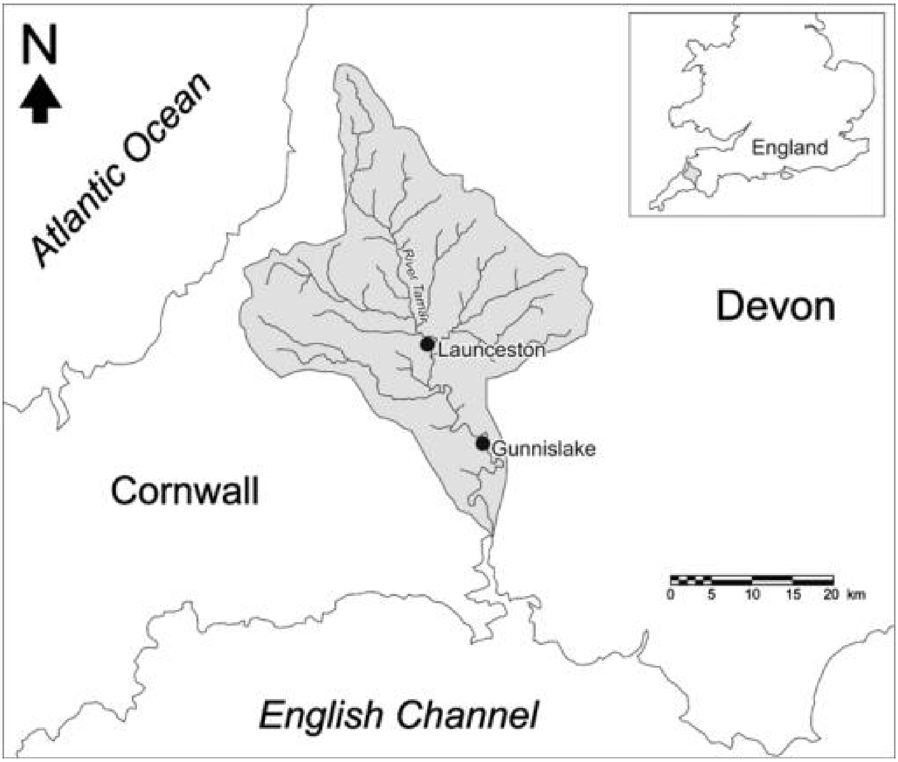


Figure 1. Location of the Tamar catchment in England.

Gunnislake gauging station (mean flow 22.6 $m^3\ s^{-1}$). The samples from bed sediment and streamwater are therefore considered to be representative of baseflow conditions. The field and laboratory methods are summarised below; for a more detailed description of the analytical procedures and quality assurance and control, see Rawlins et al. (2003).

At each of 483 sites, which were distributed evenly across the catchment, a single bed sediment sample was collected from the centre of the channel. After removal of the oxidised surface layer at each site, active sediment up to a maximum depth of 10–15 cm was wet-sieved using local stream water through a 150 μm mesh to yield a sample mass of approximately 100 g. The range of bedrock types across the catchment result in differing bed sediment grain-size distributions, therefore different quantities of bed material needed to be sieved at each site to ensure collection of a representative quantity of the fine sediment. On return to the laboratory, all sediment samples were initially air-dried and then freeze-dried, coned and quartered, and ground until 95% was <53 μm. The pulverised material was further sub-sampled to obtain portions for analysis.

A 12 g aliquot was analysed for a range of major (Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, MnO, and Fe_2O_3) and around 40 other minor elements by wavelength-dispersive X-Ray fluorescence spectrometry (XRFS). All major element concentrations are expressed in percent dry weight of oxide.

Water samples were collected at the same locations as streambed sediment samples, but prior to and slightly upstream of the latter to avoid contamination by disturbed sediment or pore water. At each location, four samples were collected: two for multi-element analysis of Na^+, K^+, Ca^{2+}, Mg^{2+} and total dissolved P (TDP) by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), the third for determination of Cl^-, SO_4^{2-}, and NO_3^- by Ion Chromatography (IC), and the fourth for the analysis of dissolved (molybdate) reactive phosphorus (DRP). All samples were filtered through 0.45-μm cellulose filters and collected in new, 30-ml polystyrene bottles, which had been rinsed with filtered water from the site before collection of the actual sample. Previous studies have demonstrated that it is not possible to devise reliable sample treatment and storage protocols for RP in natural waters because each sample has varying physico-chemical parameters (Gardolinski et al., 2001). However, in controlled experiments conducted in their study, Gardolinski et al. (2001) showed that storage of natural water samples at 4°C was effective in maintaining DRP concentrations for up to eight days. In our survey, the bottle containing the water sample for DRP was kept at 4°C until analysis within 72 h of collection. The streamwater samples were analysed for electrical conductivity and pH within 10 h after sampling and alkalinity within 24 h. Furthermore, dissolved organic carbon (DOC) was determined using a Shimadzu TOC 5000 analyser in samples pre-treated by the addition of a small volume of 10% HCl and sparged with inert gas to remove any inorganic carbon.

2.3. STATISTICAL ANALYSIS AND GEOCHEMICAL MODELLING

The relationships between P concentrations in streamwater and bedrock geology, STW effluent discharge, and streambed sediment chemistry were investigated using analysis of variance (Kruskal–Wallis rank sum test) and multiple linear regression. The study area was subdivided into three geological regions: (1) Carboniferous shale and sandstone; (2) Upper Devonian and Lower Carboniferous slate and mudstone; and (3) igneous rocks. The quantity of STW effluent discharge as a proportion of the total water discharge at each sampling location was estimated from the mean monthly discharge at Gunnislake ($3.0\ m^3\ s^{-1}$) during September 2002, the number of people connected to the STWs, and the upstream area of each sampling point, assuming a spatially constant specific runoff and a STW effluent discharge of $0.150\ m^3\ s^{-1}$ per inhabitant connected. Data on the locations of the STWs and the number of inhabitants connected were provided by South West Water – the company that supplies sewerage services for the Tamar catchment area. To further investigate the streambed sediment geochemical control on streamwater P concentrations, the relationship between the apparent distribution coefficient K_d for DRP and major element chemistry of the streambed sediment was explored for various levels of streamwater DRP. The apparent K_d (l kg^{-1}) was calculated by dividing the streambed P concentration (recalculated to mg P kg^{-1}) by the streamwater DRP concentration (mg l^{-1}). For the regression analyses, the P concentrations and explanatory variables were logtransformed by taking their natural logarithm if the regression residuals were not normally distributed or depended on the response variable. Variables were only included in the regression equation if their regression coefficients were significant at the $\alpha=0.05$ level and the sign of the regression coefficient could be physically justified. For example, this meant that in the case of the regression between streamwater P and major element chemistry of bed sediments, the regression coefficient for SiO_2 must be positive and the regression coefficient for K_2O must be negative.

The aqueous speciation and saturation indices of phosphate (PO_4^{3-}) species were evaluated using the PHREEQC geochemical model (Parkhurst & Appelo 1999). The model input comprised the major dissolved constituent concentrations, alkalinity, pH, and the DRP concentrations. The model output was specifically evaluated for the saturation index of hydroxyapatite ($Ca_5(PO_4)_3OH$).

3. Results and Discussion

The DRP and TDP concentrations were strongly correlated ($r=0.973$) and the mean ratio DRP/TDP was 0.48±0.34 (mean±standard deviation) for samples with DRP and TDP concentrations above the determination limit ($N=368$). Non-reactive P (TDP–DRP) was slightly but significantly ($\alpha=0.05$, $P<0.001$) positively correlated with DOC ($r=0.272$).

Table I shows the distribution statistics for major element chemistry of streambed sediments and streamwater P concentrations for sampling locations without upstream registered STW effluent discharges in the three major geological regions in the Tamar catchment. In addition, streamwater P concentrations in streams influenced by upstream STW discharges are listed. The results from the Kruskal-Wallis test indicated that sediment P_2O_5 concentrations were significantly different between the geological regions ($\alpha=0.05$, $P<0.001$). The P_2O_5 concentrations were highest in the stream sediments on igneous bedrock and lowest on Carboniferous shale and sandstone. In contrast to the DRP concentrations, TDP concentrations differed significantly between the streams in the different geological regions ($\alpha=0.05$, $P=0.009$). Both the mean DRP concentration and the mean TDP concentration in streams with upstream STW discharges were found to be significantly higher ($\alpha=0.05$, $P<0.001$) than in streams without upstream STW discharges.

The PHREEQC model output shows that the streamwater was generally undersaturated with respect to hydroxyapatite. The saturation index for hydroxyapatite was -6.10 ± 3.84 ($N=262$) for samples without upstream STW

TABLE I

Major element chemistry of streambed sediments (without upstream STW discharges) and DRP and TDP concentrations in streamwater (without and with upstream STW discharges) for different geological regions in the Tamar catchments

Parameter	Geology[a]	*N*	Mean	St. dev.	1st quartile	Median	3rd quartile
SiO_2 (%)	1	241	59.2	3.5	57.1	58.4	61.1
	2	200	55.0	5.3	52.3	55.2	58.3
	3	21	48.1	3.9	45.4	47.2	50.7
Al_2O_3 (%)	1	241	18.5	2.5	17.2	19.0	20.2
	2	200	18.7	2.8	17.0	18.9	20.7
	3	21	16.7	2.6	14.9	16.9	18.2
Fe_2O_3 (%)	1	241	7.47	1.71	6.37	7.42	8.35
	2	200	8.61	2.09	7.30	8.35	9.65
	3	21	10.20	2.59	9.17	11.0	11.7
MnO (%)	1	241	0.21	0.13	0.11	0.17	0.27
	2	200	0.49	0.76	0.17	0.27	0.49
	3	21	0.47	0.31	0.19	0.38	0.74
K_2O (%)	1	241	2.83	0.55	2.56	2.91	3.23
	2	200	3.21	0.64	2.79	3.17	3.65
	3	21	2.87	0.76	2.33	2.78	3.30
CaO (%)	1	241	0.28	0.10	0.21	0.26	0.33
	2	200	0.51	0.50	0.29	0.38	0.54
	3	21	1.22	1.01	0.55	1.14	1.45
P_2O_5 (%)	1	241	0.18	0.09	0.13	0.16	0.21
	2	200	0.24	0.10	0.17	0.22	0.28
	3	21	0.36	0.12	0.26	0.36	0.44
DRP (mgl^{-1})	1	235	0.021	0.039	0.005	0.011	0.021
	2	185	0.020	0.026	0.005	0.012	0.025
	3	18	0.218	0.465	0.002	0.019	0.042
	STW	21	0.255	0.443	0.038	0.054	0.166
TDP (mgl^{-1})	1	241	0.053	0.070	0.020	0.035	0.057
	2	200	0.038	0.036	0.015	0.030	0.051
	3	21	0.199	0.374	0.026	0.030	0.092
	STW	21	0.282	0.458	0.049	0.083	0.230

[a] Geology: 1=Shale and sandstone (Carboniferous); 2=Slate and mudstone (Upper Devonian and Lower Carboniferous); 3=igneous rocks; STW = STW effluent discharge upstream from sampling point.

influence and −2.24±2.12 (*N*=21) for samples influenced by upstream STW. Only for seven sampling locations was the streamwater supersaturated with respect to hydroxyapatite. The mean DRP concentration for these samples was 0.784 mg l^{-1}.

The regression equation relating the DRP concentrations (mg l^{-1}) with the logtransformed stream sediment P_2O_5, the logtransformed major element concentrations (percent weight), and the proportion of STW discharge (*STWprop*) (−) to the total discharge, is:

$$\begin{aligned}\ln(\mathrm{DRP}) = -26.922 + 0.756\ln(\mathrm{P_2O_5}) + 5.470\ln(\mathrm{Al_2O_3}) + 3.029\ln(\mathrm{SiO_2})\\ -3.323\ln(\mathrm{K_2O}) + 0.665\ln(\mathrm{CaO}) + 31.358\,\mathit{STWprop}\\ \left(R^2 = 0.241;\ N = 413;\ \text{samples for which DRP} > 0\right)\end{aligned}$$

This equation shows that DRP in stream water is positively related to the proportion of STW discharge and the P_2O_5, SiO_2, and Al_2O_3 concentrations in bed sediment, but negatively related to K_2O. SiO_2 is commonly considered to represent the coarser grain size fractions with limited adsorption capacity for P. Although Al_2O_3 is usually related to the clay mineral fraction and thus the fine grain size fractions (e.g., Tebbens, Veldkamp, & Kroonenberg, 2000), in the Tamar catchment the Al_2O_3 is apparently also abundant in the coarse fractions of weathered slates and shales. K_2O is a component of both feldspar minerals and illite (clay). The negative relationship between streamwater P and the K_2O concentration in bed sediment suggests that adsorption to clay minerals controls the streamwater P concentrations in the Tamar catchment. The DRP concentrations are also positively related to the CaO concentration in bed sediment. This may be attributed to their common agricultural source (fertiliser and lime application).

Table II presents the relationships between the logtransformed K_d values for DRP and the logtransformed major element concentrations in the bed sediment for different DRP concentration levels in streamwater. At DRP concentrations less than 0.025 mg l^{-}, the K_d value shows generally the same, but inverse, relationships with SiO_2, Al_2O_3, and K_2O as for DRP. For DRP concentrations between 0.025 mg l^{-1} and 0.050 mg l^{-1}, MnO is included as explanatory variable in the regression model instead of K_2O, which may suggest that P is also controlled by adsorption to MnO. For this concentration range, MnO, SiO_2, and Al_2O_3 together explain 50% of the total variation in the K_d values. For DRP concentrations greater than 0.050 mg l^{-1}, there is no significant relationship between the logtransformed K_d values and any of the major element concentrations in the streambed sediment. At these concentrations, the variation in DRP is likely to be mainly controlled by point source emissions and DRP is not at, or near, equilibrium with the streambed sediment.

The dissolved P measured in the stream under baseflow conditions without influence from STW discharges may be derived from inputs from groundwater equilibrated with P in the bedrock or release of dissolved P from streambed sediments. Regardless of the precise source of the dissolved P, the relationships found in this study emphasise the importance of bed sediment composition for controlling streamwater P concentrations during baseflow. Biological uptake by aquatic macrophytes and benthic algae has an important influence on the seasonal variation of stream water P concentrations (e.g., Neal et al., 2005). Nevertheless,

TABLE II

Results from the regression analysis of the logtransformed apparent distribution coefficient K_d ($l\ kg^{-1}$) for DRP with major element concentrations in the streambed sediment

DRP (mgl^{-1})	N	Regression equation $\ln(K_d)$	R^2
All	412	$20.805+3.441\ \ln(K_2O)-4.640\ \ln(Al_2O_3)$	0.100^*
$0.0025<DRP\leq 0.025$	265	$24.684+1.352\ \ln(K_2O)-1.938\ \ln(SiO_2)-2.390\ \ln(Al_2O_3)$	0.145^*
$0.025<DRP\leq 0.050$	59	$24.020-2.715\ \ln(SiO_2)-0.930\ \ln(Al_2O_3)+0.159\ \ln(MnO)$	0.507^*
$DRP>0.050$	57	Not significant	0.000

$^*P<0.001$

the effect of this on the spatial distribution of stream water P concentrations across the Tamar catchment is likely to be minor, particularly in the streams not affected by point source discharges.

4. Conclusions

In this study we found significant relationships between concentrations of streamwater P and streambed sediment concentrations of P_2O_5 and five major elements (SiO_2, Al_2O_3, K_2O, MnO, and CaO) which are related to the dominant bedrock geology. The negative relationship between the distribution coefficient K_d for DRP and sediment SiO_2 and the positive relationship with sediment K_2O suggests that adsorption to the surface of clay minerals is a dominant control on streamwater P concentrations. The K_d values are also negatively related to Al_2O_3 which indicates that Al_2O_3 is primarily present in the coarse particle size fraction with limited sorption capacity for P. This is despite Al_2O_3 generally having a strong correlation with clay content. Where DRP concentrations in streamwater are considerably elevated by inputs from point sources, DRP concentrations are also controlled by precipitation of hydroxyapatite.

The results of this study provide evidence demonstrating that for low streamwater P concentrations ($DRP<0.050$ mg l^{-1}), sediment geochemical properties have an important influence on streamwater P concentrations in the overlying water column and the distribution coefficient for P during baseflow conditions. Since the distribution coefficient indicates the likely trend in streamwater P concentrations, these findings may also be relevant for periods of higher discharges when streamwater P is likely to be more frequently out of equilibrium with streambed sediment P. Therefore, information on the geochemical and particle size composition of streambed sediment could help to improve model predictions of P concentrations in surface waters and P export from catchments.

This page intentionally blank

Acknowledgements

This work was undertaken as a subproject of the BBSRC grant 89/MAF 12247 – "Scale and uncertainty in modelling phosphorus transfer from agricultural grasslands to watercourses: development of a catchment scale management tool" and we would like to acknowledge the contribution of the other project partners, especially Keith Beven and Phil Haygarth. The first author would like to acknowledge the NWO/British Council grant PPS785 for a sabbatical at NSRI, North Wyke. The BGS wishes to acknowledge the Environment Agency (SW region) which contributed funding to the geochemical survey of the Tamar catchment. This paper is published with the permission of the Director of the BGS (NERC).

References

Fuller, R. M., Groom, G. B., & Jones, A. R. (1994). The land cover map of Great Britain: An automated classification of Landsat Thematic Mapper data. *Photogrammetric Engineering and Remote Sensing, 60*, 553–562.

Gardolinski, P., Hanrahan, G., Achterberg, E. P., Gledhill, M., Tappin, A. D., House, W. A., et al. (2001). Comparison of sample storage protocols for the determination of nutrients in natural waters. *Water Research, 35*, 3670–3678.

Heathwaite, A. L., & Dils, R. M. (2000). Characterising phosphorus loss in surface and subsurface hydrological pathways. *Science of the Total Environment, 251–252*, 523–538.

Jarvie, H. P., Jürgens, M. D., Williams, R. J., Neal, C., Davies, J. J. L., Barrett, C., et al. (2005). Role of river bed sediments as sources and sinks of phosphorus across two major eutrophic UK river basins: the Hampshire Avon and the Herefordshire Wye. *Journal of Hydrology, 304*, 51–74.

Neal, C., House, W. A., Jarvie, H. P., Neal, M., Hill, L., & Wickham, H. (2005). Phosphorus concentrations in the River Dun, the Kennet and Avon Canal and the River Kennet, southern England. *Science of the Total Environment, 344*, 107–128.

Owens, P. N., & Walling, D. E. (2002). The phosphorus content of fluvial sediment in rural and industrialized river basins. *Water Research, 36*, 685–701.

Parkhurst, D. L., & Appelo, C. A. J. (1999). *User's guide to PHREEQC (Version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*. USGS Water Resources Investigations Report 99-4259, 310 pp.

Rawlins, B. G., O'Donnell, K., & Ingham, M. (2003). *Geochemical survey of the Tamar catchment (south-west England)*. British Geological Survey Report CR/03/027, 232 pp.

Tebbens, L. A., Veldkamp, A., & Kroonenberg, S. B. (2000). Natural compositional variation of the river Meuse (Maas) suspended load: A 13 ka bulk geochemical record from the upper Kreftenheye and Betuwe Formations in northern Limburg. *Netherlands Journal of Geosciences, 79*, 391–409.

Water, Air, and Soil Pollution: Focus (2006) **6:** 89–99
DOI: 10.1007/s11267-006-9059-9

AN OVERVIEW OF SEDIMENT ORGANIC MATTER RECORDS OF HUMAN EUTROPHICATION IN THE LAURENTIAN GREAT LAKES REGION

PHILIP A. MEYERS
Department of Geological Sciences, The University of Michigan, 1100 North University Avenue, Ann Arbor, MI 48109-1005, USA
(author for correspondence, e-mail: pameyers@umich.ed; phone: +1-734-7640597; fax: +1-734-7634690)

Abstract. The isotopic and molecular compositions of organic matter buried in lake sediments provide information that helps to reconstruct past environmental conditions and to assess impacts of humans on local ecosystems. This overview of sedimentary records from the North American Great Lakes region describes examples of applications of organic geochemistry to paleolimnological reconstructions. These lakes experienced a succession of human-induced environmental changes that started after completion of the Erie Canal in 1825. Agricultural deforestation in the mid-nineteenth century released soil nutrients that increased algal productivity and caused an associated increase in algal biomarkers in sediment records. Eutrophication that accompanied magnified delivery of municipal nutrients to the lakes in the 1960s and 1970s created excursions to less negative $\delta^{13}C$ values in sediment organic matter. Increased organic carbon mass accumulation rates mirror the isotopic evidence of eutrophication in the Great Lakes.

Keywords: Laurentian Great Lakes, biomarker molecules, organic carbon isotopes, organic carbon mass accumulation rates

Abbreviations

TOC	total organic carbon
MAR	mass accumulation rate

1. Introduction

Eutrophication is defined by the Glossary of Geology as “the artificial or natural enrichment of a lake by influx of nutrients required for the growth of aquatic plants.” A lake becomes eutrophic when it is enriched in bioavailable nitrogen and phosphorus and achieves high rates of primary production of organic matter. The associated magnified export of organic matter can draw down dissolved oxygen in the hypolimnion when the oxidation rates of organic matter exceed the ventilation rates of the lake basin. In current usage, the term ‘eutrophication’ has come to imply a human modification of a previously natural state, largely because examples of lake eutrophication resulting from urban sewage, synthetic fertilizers, and phosphate detergents have become widespread since the middle of the twentieth century.

The amount and isotopic composition of organic matter in lake sediments are important to reconstructing past productivity rates. Increases in the MARs of TOC and in the organic $^{13}C/^{12}C$ ratio have been widely used as an indicator of enhanced aquatic productivity in lakes (e.g., Bernasconi, Barbieri, Simona 1997; Hodell & Schelske, 1998; Hollander & MacKenzie, 1991; Hollander, MacKenzie, & ten Haven, 1992; Schelske & Hodell, 1991; Teranes & Bernasconi, 2005). Phytoplankton (C_3 algae) preferentially remove dissolved $^{12}CO_2$ from water and leave the remaining dissolved inorganic carbon depleted in ^{12}C (e.g., Hollander & MacKenzie, 1991; Hodell & Schelske, 1998; Meyers & Teranes, 2001). When productivity is high, the availability of $^{12}CO_2$ gradually diminishes, and a progressively greater fraction of the $^{13}CO_2$ is incorporated into organic matter. The amount of organic matter that becomes buried in lake sediments is commonly diminished by metabolism and remineralization during and after sedimentation, but the carbon isotopic composition is relatively unaffected by these post-photosynthetic processes (Meyers & Eadie, 1993; Schelske & Hodell, 1995). However, $\delta^{13}C$ values often need to be corrected for the Suess Effect – the shift to more negative $\delta^{13}C$ values of atmospheric CO_2 caused by fossil fuel combustion – especially in lakes with large surface to volume ratios, such as the Laurentian Great Lakes (Schelske & Hodell, 1995), and sometimes even in smaller lakes (e.g., Routh et al., 2004). The shift from pre-industrial atmospheric isotopic values approached −1.7‰ by 2004 (McCarroll & Loader, 2004), with two-thirds of the shift occurring since 1940 (Keeling et al., 1989; Francey et al., 1999). The shift to more negative $\delta^{13}C$ values is sufficient to mask the impact of eutrophication in lakes where dissolved inorganic carbon equilibrates isotopically with atmospheric CO_2.

Eutrophication can also leave an imprint on the molecular composition of the organic matter that accumulates in lake sediments. The organic matter is typically derived from a variety of plant-types, many of which have distinctive lipid biomarker–molecule distributions. Increases in organic matter contributions from aquatic algae and photosynthetic bacteria that accompany eutrophication can be identified by proportional increases of the C_{17} *n*-alkane, the C_{16} and C_{18} *n*-alkanoic acids, the C_{16} to C_{22} *n*-alkanols, and the C_{27} and C_{28} sterols (e.g., Cranwell, Eglinton, & Robinson, 1987; Neunlist, Rodier, & Llopiz, 2002). In contrast, vascular land plants and emergent macrophytes produce large proportions of C_{27}, C_{29}, and C_{31} *n*-alkanes, C_{24}–C_{30} *n*-alkanoic acids, C_{22} to C_{30} *n*-alkanols, and C_{29} sterols (e.g., Cranwell et al., 1987; Eglinton & Hamilton, 1967; Neunlist et al., 2002; Rieley, Collier, Jones, & Eglinton, 1991). Some caution is necessary in using the *n*-alkanoic acid biomarkers because the *n*-C_{16} and *n*-C_{18} acids are ubiquitous components of biota and because they are more susceptible to degradation and alteration than other types of lipid biomarkers (e.g., Meyers & Eadie, 1993).

2. Human Impacts on the Laurentian Great Lakes

Lakes Superior, Huron, Michigan, Saint Clair, Erie, and Ontario comprise the Laurentian Great Lakes (Figure 1). After the first permanent European colonies were established in the Great Lakes region around 1700, a succession of environmental changes was started that accelerated after completion of the Erie Canal in 1825. Forests were clear-cut and replaced by farmland, towns and cities grew, heavy industry became established, and some parts of the lakes evolved from oligotrophy to eutrophy as nutrient loadings increased. Evidence of many of these changes is recorded in the amount and composition of the organic matter in sediments that were deposited at various stages in the paleoenvironmental histories of the lakes.

Except in Lakes Erie and Saint Clair, water depths of 100 m to more than 200 m are common in the Great Lakes. The minor water turbulence at these

Figure 1. The Laurentian Great Lakes of North America and their drainage basins. Overall flow of water is from Lake Superior to Lake Ontario and then to the North Atlantic Ocean via the St. Laurence River between the province of Ontario in Canada and the State of New York in the United States.

depths and the absence of large bottom-dwelling fauna combine to minimize sediment disturbance in the lake floors. Age resolutions of sediment-core samples are ~two years in high-deposition areas such as the Eastern Basin of Lake Erie and better than a decade in most parts of the Great Lakes (Robbins & Edgington, 1975).

3. Case Studies of Eutrophication in the Great Lakes Region

Conversion of formerly forested areas to farm fields increased erosion of soil, release of soil nutrients, and production of algal organic matter in the Great Lakes starting in the early 19th century (Schelske, Stoermer, Conley, Robbins, & Glover, 1983). The increase in primary productivity was gradual until 1950, when introduction of phosphate-based detergents magnified delivery of bioavailable phosphorus to the lakes and greatly amplified algal production of organic matter.

3.1. Biomarker Record of Increased Productivity in Saginaw Bay, Lake Huron

A sediment core collected in 1975 from the Saginaw Bay of Lake Huron records the progressive increase in algal production of organic matter since opening of the Erie Canal that is common in the Great Lakes (Figure 2). TOC concentrations increase gradually starting approximately with the clearing of land for farming in the Saginaw Bay catchment that followed American settlement of the area after 1825. The concentrations rise abruptly to 2%–2.5% at about 1950, which corresponds to the large growth of human population in the Great Lakes region that followed World War II. Concentrations of aquatic geolipid biomarkers also start to increase in sediments deposited after ~1840 (Meyers & Takeuchi, 1981), and relative proportions of land-plant *n*-alkanols, sterols, and *n*-alkanes consequently become smaller (Figure 2). Although part of the increase in the ratios of C_{26}/C_{16} *n*-alkanols, C_{29}/C_{27} sterols, and C_{29}/C_{17} *n*-alkanes in older sediment could reflect selective diagenetic loss of the algal components, the consistent change among these three biomarker ratios more likely indicates a progressively larger contribution of algal organic matter towards 1975. Interestingly, the lowering of the C_{29}/C_{27} sterol ratio suggests that algal productivity started to increase soon after the start of European-style agriculture in the Saginaw Bay catchment.

3.2. Two-Core Record of Lake Ontario Eutrophication

Sediments deposited in Lake Ontario over the last 150 years provide a high-resolution record of the impacts of nutrient enrichment and the effects of nutrient-abatement efforts in this lake. Algal growth began to be stimulated by watershed

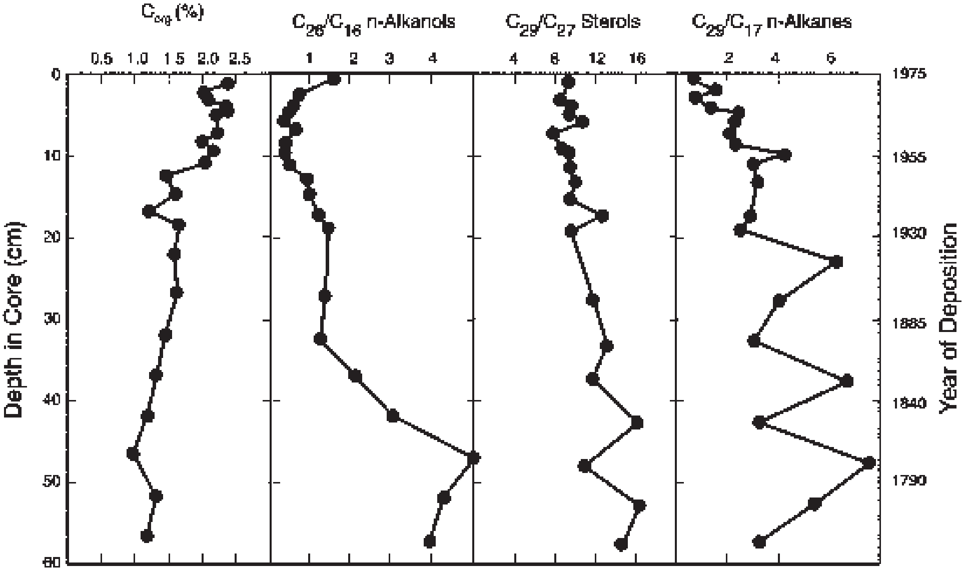


Figure 2. Concentrations of organic carbon and ratios of land-plant and algal *n*-alkanols, sterols, and *n*-alkanes in a sediment core from Saginaw Bay (water depth, 9 m) of Lake Huron. Progressive eutrophication of the bay is evident in increased organic carbon and decreases in the three biomarker ratios since the advent of agriculture in the mid-1800s. Data from Meyers and Takeuchi (1981).

deforestation, which occurred between 1820 and 1850 (Schelske et al., 1983) and resulted in increased delivery of soil-derived phosphorus to the lake. Schelske, Robbins, Gardner, Conley and Bourbonniere (1988) note that organic carbon concentrations in Lake Ontario cores follow the increases in phytoplankton abundance expected from the phosphorus enrichments. TOC MARs increase gradually in response to the higher productivity until 1975–1980, when they start to drop in more recent sediment (Hodell & Schelske, 1998). The Suess-corrected ^{13}C values of buried organic carbon reflect the productivity increase by becoming over 2‰ less negative, maximizing at −24.5‰ in sediments deposited in 1975–1980 (Figure 3). The subsequent negative shift in more recent sediments mirrors a mandated decrease in dissolved phosphate delivery to the Great Lakes. These changes in organic carbon mass accumulation rates and carbon isotope values are evidence that improved wastewater treatment can successfully reverse eutrophication. However, Schelske et al. (1983) hypothesize that algal communities in Lakes Erie and Ontario have been silica-limited since the onset of eutrophy associated with deforestation in the nineteenth century, which suggests that lake ecosystems do not easily return to their pre-eutrophic states.

A noteworthy feature of the Lake Ontario sedimentary record of Hodell and Schelske (1998) is that it compares the paleoproductivity records in two cores collected six years apart at the same location. The 1987 horizon of the 1993 core

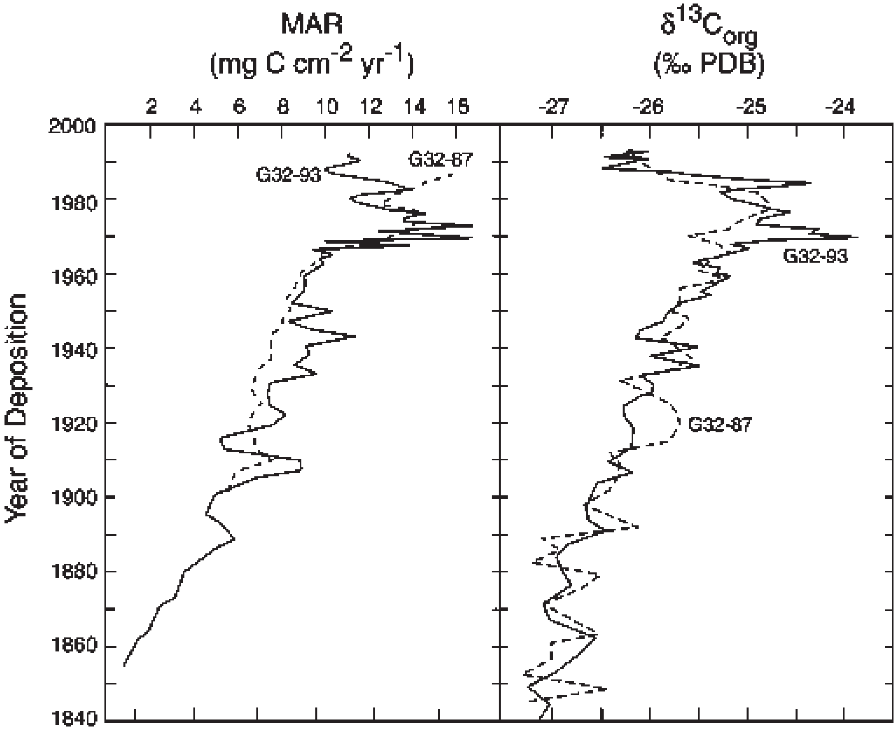


Figure 3. Comparison of organic carbon mass accumulation rates and δ^{13}C values in sediment cores collected in 1987 and 1993 from site G32 (water depth, 158 m) in the Rochester Basin of Lake Ontario. The two parameters track human-induced increased algal productivity in this lake and subsequent decreased productivity after phosphate controls were imposed. Data from Hodell and Schelske (1998).

contains ~20% less organic carbon than the sediment that had been freshly deposited in 1987. This loss indicates the extent of post-depositional remineralization of organic matter that occurs in this lacustrine setting. The remineralization appears to be confined to the upper part of the sediment, inasmuch as TOC MARs of the deeper parts of the 1987 and 1993 cores agree well (Figure 3). Furthermore, the organic matter remineralization has no measurable impact on the organic ^{13}C values preserved in these cores (Figure 3), confirming the durability of this paleoproductivity proxy.

3.3. PRE-HISTORIC AND RECENT EUTROPHICATION OF CRAWFORD LAKE, ONTARIO

Two periods of human-induced eutrophication are evident in a core that records a thousand years of sediment accumulation in Crawford Lake, Ontario, which is within the Lake Ontario drainage basin. As described by Ekdahl et al. (2004), the first period spans 1270–1485 CE, which is several centuries before European colonization of this part of North America. Eutrophication is evident in a two-century-long period of increased MARs of authigenic calcite and organic carbon, larger calcite $\delta^{13}C$ values, and decreased organic matter C/N values (Figure 4). The decrease in C/N values indicates an increased contribution of algal-derived organic matter to the sediments (e.g., Meyers, 1994, 2003). In addition, important productivity-related changes appeared in the algal assemblages (Ekdahl et al., 2004). Archeological remains show that native Americans (Iroquian Indians) occupied large settlements on the shore of Crawford Lake twice during this period. They evidently released soil nutrients through their farming and contributed human wastes to the lake that caused the two-century-long period of eutrophication.

The second period of eutrophication in the Crawford Lake record starts soon after the expansion of European settlement of the Great Lakes region in the first half of the nineteenth century. Calcite and organic carbon MARs again increase, and C/N values further decrease (Figure 4). However, unless Suess corrections are applied to the calcite $\delta^{13}C$ values, these isotopic paleoproductivity proxies

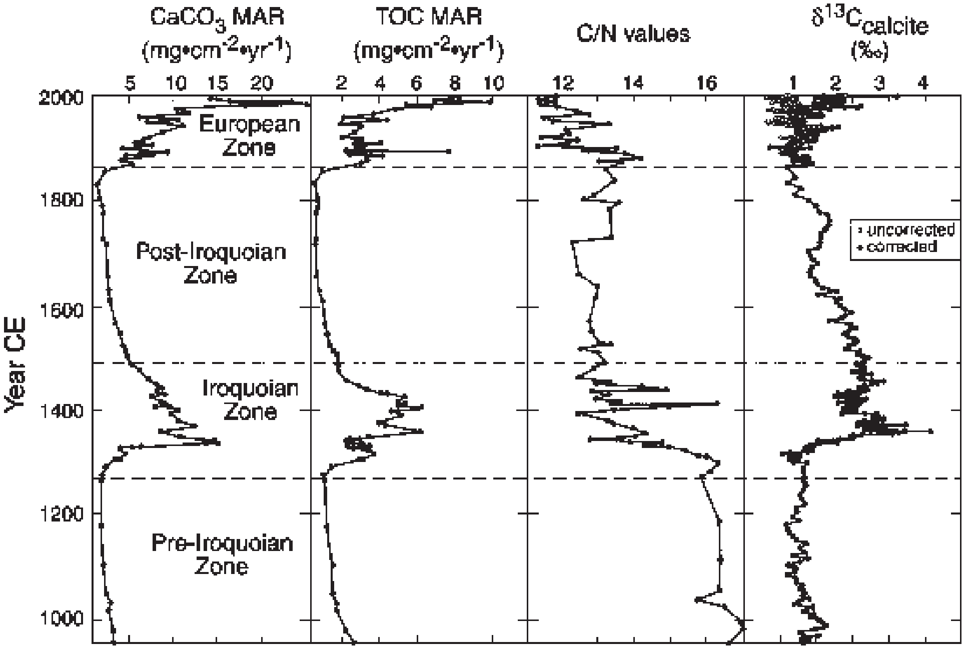


Figure 4. Geochemical evidence of intervals of pre-European and European eutrophication in Crawford Lake, Ontario. Increases in mass accumulation rates of calcium carbonate and organic carbon, decreases in organic matter C/N values, and increases in carbonate $\delta^{13}C$ values record periods of greater algal productivity around 1,400 and after the mid-1800s. Corrections for the Suess Effect reveal the otherwise hidden effect of modern eutrophication on the isotopic record. Data from Ekdahl et al. (2004).

become smaller, which implies that productivity decreases. Only when the values are corrected for the Suess effect do they agree with the other three paleoproductivity proxies in recording an increase in primary productivity (Figure 4).

Two features of the Crawford Lake eutrophication record are especially significant. The first is that human-induced eutrophication is not just a recent phenomenon; pre-industrial humans were also capable of perturbing the natural nutrient cycle of lakes. The second feature is the sobering evidence that once the nutrient cycle of a lake ecosystem is perturbed, the lake may not return to its pre-disturbed state. Two lines of evidence record a permanent change in the Crawford Lake ecosystem: (1) the lowered C/N values (Figure 4) that indicate a larger contribution of algal organic matter after ~1,500, and (2) the irreversibly altered diatom assemblage in the post-1500 lake (Ekdahl et al., 2004).

3.4. EUTROPHICATION-INDUCED CALCITE DISSOLUTION

High sedimentation rates in the Eastern Basin of Lake Erie allow reconstruction of a near-annual record of the history of eutrophication of this lake. As shown in Figure 5, concentrations of TOC progressively increase to peak between 1970–1980 before starting to decrease after nutrient limitation measures were enacted in the mid-1970s. Suess-corrected ^{13}C values simultaneously decrease as TOC concentrations increase, and they return to lower values at the core top. During times of eutrophication, increased biogenic removal of dissolved CO_2 from the epilimnion can raise the pH of seasonally warmed surface waters of a lake and accelerate precipitation of authigenic calcite (e.g., Dean, 1999; Hollander et al., 1992; Schelske et al., 1988). However, the concentration of $CaCO_3$ decreases in Lake Erie sediments deposited between 1960–1990 (Figure 5), which is the reverse of what would be expected during this period of heightened lake productivity. Dean (1999) observes similar decreases in calcium carbonate concentrations in sediments of lakes in which organic carbon delivery has been increased by eutrophication. He concludes that oxidative decomposition of the increased amount of organic carbon in bottom sediments has lowered the pH of interstitial waters and has caused *in situ* dissolution of the $CaCO_3$. This observation raises the possibility that eutrophication can have unexpected effects on the biogeochemical cycles of carbonate-hosted elements and other pH-sensitive materials in the sediments of lakes.

4. Summary and Overview

Organic matter constitutes a minor fraction of lake sediments, yet it provides important information for paleoenvironmental reconstructions. Sediment organic matter is made up of the residue of former biota. The amounts and types of organic matter present in sediments consequently reflect environmental conditions

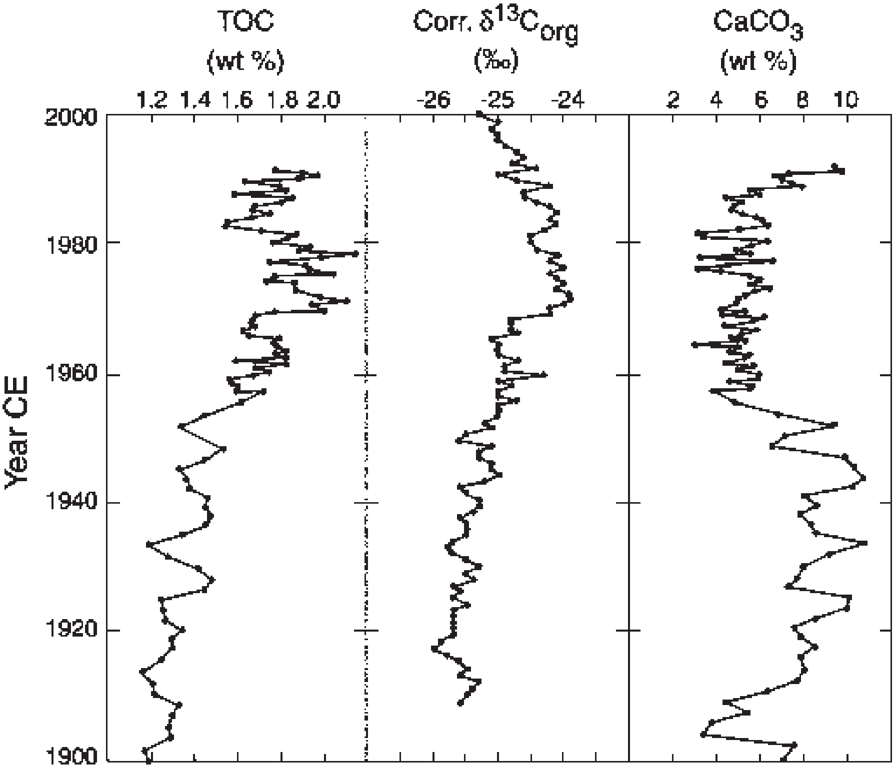


Figure 5. Record of human eutrophication evident in increasing organic carbon concentrations in a sediment core collected in 1991 from the Eastern Basin of Lake Erie (water depth, 60 m) and in increasing organic δ^{13}C values from a core collected at the same location in 2003. Sedimentation rates of both cores were determined by ^{137}Cs radiometric dating. Increased organic matter delivery to bottom sediments has increased post-depositional dissolution of calcium carbonate, as evident in the 1991 core (Meyers, unpublished).

that impacted ecosystems in and around a lake at different times in the past. Progressive eutrophication of lacustrine systems, changes in watershed vegetation, and the advent of agriculture are some of the paleoenvironmental aspects that can be inferred from the organic geochemical compositions of lake sediments.

Human impacts on the Laurentian Great Lakes date largely from the early nineteenth century when expansive European-type settlement of the region started. Forests were clear-cut to open land for agriculture, which released nutrients formerly stabilized in soils to the lakes and amplified algal productivity. Increases in the contribution of algal-derived components to the *n*-alkane, *n*-alkanol, and sterol compositions of sediments record the onset of greater in-lake production of organic matter dating from this time. However, true eutrophication did not become widespread in the Great Lakes until the mid-twentieth century, when urban centers expanded and phosphorus delivery to the lakes was magnified. Dramatic increases in the mass accumulation rates of organic carbon and in organic $\delta^{13}C$ values peaked between 1970 and 1980. Controls on phosphorus delivery that were mandated in 1975 resulted in a partial reversal of the eutrophication, a trend that continues to today.

Evidence of pre-historic episodes of human eutrophication also exists in the Great Lakes region. Sediments of Crawford Lake, Ontario, record the impact of Iroquian settlements between 1270 and 1485 CE that elevated algal productivity and irreversibly altered the lake ecosystem. This example suggests that lake ecosystems do not easily return to their original states once they have been perturbed by eutrophication and possibly other human impacts.

Acknowledgments

I am grateful to Jadran Faganeli and an anonymous reviewer for their helpful comments. This overview is based on material presented at the Tenth International Symposium on the Interactions Between Sediments and Water Held at Lake Bled, Slovenia, in 2005. I thank the organizers and sponsors of this conference for making my participation possible. Some of the research described in this contribution was supported by grants from the Cooperative Institute for Limnology and Ecosystems Research using funds supplied by the US National Oceanic and Atmospheric Administration.

References

Bernasconi, S. M, Barbieri, A., & Simona, M. (1997). Carbon and nitrogen isotope variations in sedimenting organic matter in Lake Lugano. *Limnology and Oceanography*, *42*, 1755–1765.

Cranwell, P. A., Eglinton, G., & Robinson, N. (1987). Lipids of aquatic organisms as potential contributors to lacustrine sediments. *Organic Geochemistry*, *11*, 513–527.

Dean, W. E. (1999). The carbon cycle and biogeochemical dynamics in lake sediments. *Journal of Paleolimnology*, *21*, 375–393.

Eglinton, G., & Hamilton, R. J. (1967). Leaf epicuticular waxes. *Science*, *156*, 1322–1334.

Ekdahl, E. J., Teranes, J. L., Guilderson, T. P., Turton, C. L, McAndrews, J. H., Wittkop, C. A., et al. (2004). Prehistorical record of cultural eutrophication from Crawford Lake, Ontario. *Geology*, *32*, 745–748.

Francey, R. J., Allison, C. E., Etheridge, D. M., Trudinger, C. M., Enting, I. G., Leuenberger, M., et al. (1999). A 1000-year high precision record of $\delta^{13}C$ in atmospheric CO_2. *Tellus*, *51B*, 170–193.

Hodell, D. A., & Schelske, C. L. (1998). Production, sedimentation, and isotopic composition of organic matter in Lake Ontario. *Limnology and Oc*eanography, *43*, 200–214.

Hollander, D. J., & MacKenzie, J. A. (1991). CO_2 control on carbon-isotope fractionation during aqueous photosynthesis: A paleo-pCO_2 barometer. *Geology*, *19*, 929–932.

Hollander, D. J., MacKenzie, J. A., & ten Haven, H. L. (1992). A 200 year sedimentary record of progressive eutrophication in Lake Greifen (Switzerland): Implications for the origin of organic-carbon rich sediments. *Geology*, *20*, 825–828.

This page intentionally blank

Keeling, C. D., Bacastow, R. B., Carter, A. F., Piper, S. C., Whorf, T. P., Heimann, M., et al. (1989). A three-dimensional model of atmospheric CO_2 transport based on observed winds: 1. Analysis of observational data. In D. H. Peterson (Ed.), *Aspects of climate variability in the Pacific and Western Americas. Geophysical monograph 55* (pp. 165–236). Washington, District of Columbia, USA: AGU.

McCarroll, D., & Loader, N. J. (2004). Stable isotopes in tree rings. *Quaternary Science Reviews*, *23*, 771–801.

Meyers, P. A. (1994). Preservation of source identification of sedimentary organic matter during and after deposition. *Chemical Geology, 144*, 289–302.

Meyers, P. A. (2003). Applications of organic geochemistry to paleolimnological reconstructions: A summary of examples from the Laurentian Great Lakes. *Organic Geochemistry*, *34*, 261–289.

Meyers, P. A., & Eadie, B. J. (1993). Sources, degradation, and recycling of organic matter associated with sinking particles in Lake Michigan. *Organic Geochemistry*, *20*, 47–56.

Meyers, P. A., & Takeuchi, N. (1981). Environmental changes in Saginaw Bay, Lake Huron, recorded by geolipid contents of sediments deposited since 1800. *Environmental Geology*, *3*, 257–266.

Meyers, P. A., & Teranes, J. L. (2001). Sediment organic matter. In W. M. Last & J. P. Smol (Eds.), *Tracking environmental changes using lake sediments – Volume II: Physical and chemical techniques* (pp. 239–269). Dordrecht: Kluwer.

Neunlist, S., Rodier, C., & Llopiz, P. (2002). Isotopic biogeochemistry of the lipids in recent sediments of Lake Bled (Slovenia) and Baldeggersee (Switzerland). *Organic Geoche*mistry, *33*, 1183–1195.

Rieley, G., Collier, R. J., Jones, D. M., & Eglinton, G. (1991). The biogeochemistry of Ellesmere Lake, UK – I: Source correlation of leaf wax inputs to the sedimentary record. *Organic Geochemistry*, *17*, 901–912.

Robbins, J. A., & Edgington, D. N. (1975). Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137. *Geochimica et Cosmochimica Acta*, *39*, 285–304.

Routh, J., Meyers, P. A., Gustafsson, Ö., Baskaran, M., Hallberg, R., & Scholdström, A. (2004). Sedimentary geochemical characteristics of Lake Brunnsviken, Sweden: A record of human-induced environmental changes in the watershed. *Limnology and Oceanography*, *49*, 1560–1569.

Schelske, C. L., & Hodell, D. A. (1991). Recent changes in productivity and climate of Lake Ontario detected by isotopic analysis of sediments. *Limnology and Oceanography*, *36*, 961–975.

Schelske, C. L., & Hodell, D. A. (1995). Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. *Limnology and Oceanography*, *40*, 918–929.

Schelske, C. L., Robbins, J. A., Gardner, W. S., Conley, D. J., & Bourbonniere, R. A. (1988). Sediment record of biogeochemical responses to anthropogenic perturbations of nutrient cycles in Lake Ontario. *Canadian Journal of Fisheries and Aquatic Science*, *45*, 1291–1303.

Schelske, C. L., Stoermer, E. F., Conley, D. J., Robbins, J. A., & Glover, R. M. (1983). Early eutrophication in the Lower Great Lakes: New evidence from biogenic silica in sediments. *Science*, *222*, 320–322.

Teranes, J. L., & Bernasconi, S. M. (2005). Factors controlling $\delta^{13}C$ values of sedimentary carbon in hypertrophic Baldeggersee, Switzerland, and implications for interpreting isotope excursions in lake sedimentary records. *Limnology and Oceano*graphy, *50*, 914–922.

Water, Air, and Soil Pollution: Focus (2006) **6:** 101–110
DOI: 10.1007/s11267-006-9030-9

THE INFLUENCE OF *CHIRONOMUS PLUMOSUS* LARVAE ON NUTRIENT FLUXES AND PHOSPHORUS FRACTIONS IN ALUMINUM TREATED LAKE SEDIMENT

FREDE Ø. ANDERSEN*, MICHAEL JØRGENSEN and HENNING S. JENSEN
Institute of Biology, University of Southern Denmark, Campusvej 55 5230 Odense M, Denmark
*(*author for correspondence, e-mail: foa@biology.sdu.dk; phone: +45-65502607;*
fax: +45-65930457)

Abstract. One of the methods to diminish the internal phosphorus (P) loading is inactivation of P by aluminum (Al). After addition of Al to lake water an $Al(OH)_3$ floc is formed, which settles to the bottom and initially form a lid on the sediment surface. The effects of *Chironomus plumosus* larvae on sediment nutrient fluxes and P binding-sites in the sediment after addition of Al were tested. *C. plumosus* larvae were added to sediment cores in which sediment–water fluxes of nutrients were measured four times. After one month, the sediment was sectioned with depth and P fractions were measured by sequential chemical extraction. The chironomids created burrows through the Al layer which caused a significantly increased efflux of P from the Al treated sediment, because the P had only limited contact to the added Al. The chironomids also affected the P fractions in the sediment by their bioturbating activity. Thus, they caused increased Al concentrations in the upper part of the Al treated sediment. This created an enhanced contact between Al and P in the upper 7 cm of the sediment and, as a result, an increased binding of P to Al and a lowered porewater P. The DIP efflux is therefore expected to be lowered after the initial phase. Al had no effects on the nitrogen fluxes, but the chironomids enhanced the NH_4^+ release, and decreased the NO_3^- release or increased the NO_3^- uptake by the sediments.

Keywords: bioirrigation, bioturbation, chironomids, lake restoration, nitrogen, phosphorus, sediment

1. Introduction

Although the external phosphorus (P) loading of many eutrophic lakes has been lowered during recent decades, the internal P loading may still persist. To reduce the internal loading, several methods have been applied (Cooke et al., 1993). One of these methods is the addition of aluminum (Al) to the lake. Al has a high affinity for dissolved inorganic phosphate (DIP) and will bind this without being redox sensitive. The Al is often applied as $Al_2(SO_4)_3$ or as $AlCl_3$ which hydrolyze at pH between 5.5 and 9 and precipitate as amorphous $Al(OH)_3$ flocs (Cooke et al., 1993). The Al may be mixed into the surface water of the lake (e.g., Reitzel, J. Hansen, Andersen, K. S. Hansen, & Jensen, 2005). The $Al(OH)_3$ flocs will both bind DIP and trap suspended particulate matter on the way to the bottom.

To act as an efficient barrier for DIP diffusing upward through the surface sediment in the early phase of the treatment, it is important that the Al layer is unbroken. The Al layer may be broken by resuspension if the lake is shallow, but another possibility is bioirrigation by benthic fauna. Many shallow eutrophic lakes have a dense population of *Chironomus plumosus* L. larvae of up to 2–3,000 fourth instar larvae m^{-2} (Gallepp, 1979; Hilsenhoff, 1966). However, the density is very variable and the bioturbation may also depend on the developmental stage of the larvae. In the sediment, *C. plumosus* create U-shaped burrows with walls made of detritus, diatoms, filamentous algae and sand glued together by mucus (Pelegrí & Blackburn, 1996).

Several studies have dealt with bioturbation by chironomids (e.g., Andersen & Jensen, 1991; Hansen, Mouridsen, & Kristensen, 1998; Lewandowski & Hupfer, 2005; Pelegrí & Blackburn, 1996; Svensson, 1998). The chironomids ventilate their burrows and thereby supply the sediment with electron acceptors like O_2 and NO_3^- which stimulate the bacterial degradation of organic matter. The pumping of water between the sediment and the overlying water also enhances the fluxes of nutrients. Thus, increased release of DIP to the water has been observed as a combined effect of ventilation, enhanced decomposition of organic matter, and release from the chironomids (e.g., Andersen & Jensen, 1991; Fukuhara & Sakamoto, 1987; Hansen et al., 1998). However, Andersen and Jensen (1991) also observed a flux of DIP to the sediment during winter conditions likely due to binding of DIP to oxidized iron (Fe). The transport of O_2 to the sediment also has important effects on processes in the nitrogen cycle and on the fluxes of inorganic nitrogen ions (e.g., Andersen & Jensen, 1991; Fukuhara & Sakamoto, 1987; Pelegri & Blackburn, 1996). Several studies indicate that larvae of *C. plumosus* are rather robust to both high Al concentrations and low pH (Havas & Likens, 1985; Narf, 1990; Warner, 1971), and their bioturbation may therefore continue after an Al treatment of lake sediments.

Narf (1990) observed that *Chironomus tentans* Fabricius larvae made burrows in the Al layer and that DIP rich water was pumped to the overlying water through the burrows. Al was also mixed into the sediment by the bioturbation activity of *C. tentans*. Since *C. plumosus* is the most common species of chironomids in shallow eutrophic lakes in Denmark, the ability of *C. plumosus* to transport DIP through the Al layer was studied in the present investigation. The effects of *C. plumosus* and Al treatments on the composition of P forms in different depths of the sediment by sequential fractionations were also studied.

2. Materials and Methods

The experiment was conducted in sediment cores (diameter 5.2 cm, length 40 cm) placed in four water filled tanks (five cores in each) in darkness in a temperature controlled room (15°C). The cores were sampled at 4 m depth in eutrophic Lake Store Søgård, Denmark, 27 May 2003. The length of the water column in each core was adjusted to 12.5 cm. Between flux measurements, the cores were immersed in the tanks and the water in the cores were mixed with the tank water by a pump. After 14 days, fluxes of DIP and inorganic N ions were measured. After this, eight fourth instar larvae of *C. plumosus*, collected in a pond, were added to each core in two of the tanks (abundance ~ 3,700 m^{-2}) and fluxes were again measured in all cores. A net over the upper opening of the cores prevented chironomid larvae to escape. Six days after the addition of chironomids, $AlCl_3$ (PAX-XL-60, Kemira) adjusted to pH 7.5 with 2 M NaOH was added to the cores in one of the tanks to which chironomids previously were added (Al+Chir) and similarly to the cores in one of the tanks without chironomid addition (Al). The Al treated cores received 0.8 ml Al-solution corresponding to 32 g Al m^{-2}, which was the dose applied in a successful treatment of Danish Lake Sønderby (Reitzel et al., 2005). The other two groups of cores not treated with Al, were only treated with chironomids (Chir) or left untreated (Control). Sediment–water fluxes were measured as changes in concentrations over one day immediately after the Al addition and again after eight days. During flux measurements, the cores were emerged above the water level in the tank and the water was mixed by a rotating magnet in each core. The overlying water was sampled in each core at the beginning and at the end of the flux measurements. The samples for DIP analysis were preserved with 50 μL 2 M H_2SO_4 for, and the samples for analysis of NO_2^-, NO_3^- and NH_4^+ were stored frozen. DIP was measured spectrophotometrically as molybdate reactive P (Murphy & Riley, 1962). NO_3^- and NO_2^- were analyzed by flow injection analysis (Tecator FIAstar 5010, Application Note 62/83). NH_4^+ was analyzed by spectrophotometry according to Bower and Holm-Hansen (1980). Results for sediment–water fluxes of nutrients were analyzed statistically by use of ANOVA followed by pairwise *t*-test. Differences were considered significant at $P<0.05$.

After the experiment, the upper 5 cm of the sediment was cut into 1 cm slices and the next 10 cm was cut into 2 cm slices. The sectioning of the sediment was conducted in a glove bag with N_2 to avoid oxidation of reduced Fe. Slices from the same depth of the five cores from each tank were pooled. The fresh sediment was then subjected to a five-step sequential extraction scheme slightly modified after Psenner and Pucsko (1988) to discriminate between various P compounds in the sediment. In step 1, P was extracted with anoxic deionized H_2O (P_{water}). In step 2, redox sensitive P, which primarily is composed by Fe bound P (P_{BD}), was extracted by bicarbonate–dithionite solution (BD: 0.11 M $Na_2S_2O_4$, 0.11 M $NaHCO_3$). In step 3, 0.1 M NaOH-solution was used for extracting P adsorbed to clay minerals, Al oxides and humic acids (P_{NaOH}). In step 4, 0.5 M HCl was used to extract P bound to calcium (P_{HCl}). Finally in step 5, the sediment was combusted (520°C, 2 h) and DIP extracted by boiling in 1 M HCl (120°C, 30 min) to give the residual P pool (P_{Res}). To determine the amount of non-reactive phosphate extracted in step 1–3, samples of the extracts were wet oxidized, total-P (TP) was measured as DIP and non-reactive phosphate calculated as the difference between TP and DIP. This fraction is supposed mainly to consist of degradable organic P compounds (org-P_{Labile}). TP in the sediment was also determined on parallel non-extracted samples (same method as step 5), and the P fractions were normalized to these determinations, as TP determination is assumed to be less subject to errors than summing of the different P pools. The largest deviation of the sum of fractions from TP was 19% (in 26 cases the deviation was in the range 0%–10%, and in 14 cases it was 10%–19%). Al was measured in the NaOH extracts (Al_{NaOH}) by flame atomic absorbance spectrometry at 309 nm with a N_2O flame. Reitzel et al. (2005) has shown that reactive Al added in a lake treatment is recovered in the NaOH step.

3. Results

After the addition of the $AlCl_3$, a ~10 mm layer of Al floc was formed on the sediment surface. The added *C. plumosus* created visible burrows through the Al layer. During the experimental period, the chironomids reworked the Al layer into the sediment, where it was visible as a white layer. Depth integrated concentrations of Al_{NaOH} in the 0–15 cm layer of the sediment at the four different treatments were: Al+Chir 272, Al 272, Chir 249, and Control 230 g Al m^{-2}. The increase in Al concentration in the Al-enriched cores relative to the non-Al treated cores (23–42 g Al m^{-2}) thus were in the same range as the amount of Al added (32 g Al m^{-2}). After the experiment, the Al enrichments especially appeared in the 0–3 cm depth (Figure 1).

Apart from the Al+Chir treatment which showed slightly increasing concentrations of TP from the surface to 4 cm depth, the concentration was relatively uniform in the upper 5 cm of the sediment (Figure 2). At all treatments decreasing concentrations of TP were observed below 5 cm depth.

The upper 15 cm of the sediment in the Control treatment had the following mean composition: P_{Water} 4%, P_{BD} 37%, P_{NaOH} 15%, org-P_{Labile} 18%, P_{HCl} 13%, and P_{Res} 13%. The effects of the treatments on the compositions of the P fractions were primarily observed in the upper part of the sediment (Figure 2). The concentration of the P_{Water} decreased in the 0–2 cm depth as an effect of Al, and presence of chironomids further enhanced this effect. The chironomids had a similar effect on P_{BD} at the Al treatment. In contrast, the P_{NaOH} fraction was significantly increased in the upper sediment as an effect of Al, and chironomids further increased the concentration of P_{NaOH}. The P_{HCl} fraction was affected by neither Al nor chironomids. The org-P_{Labile} fraction was unaffected by the Al treatment, whereas chironomids increased the concentration in the upper 2–3 cm. The P_{Res} was not affected by Al, but chironomids increased the concentration of this fraction at the sediment surface in the Al treatment.

Flux measurement no. 1 showed that the cores in the four tanks initially had similar DIP fluxes (Figure 3). Addition of chironomids significantly increased the DIP release from the sediment as compared to cores without chironomids. After addition of Al, the DIP release was immediately reduced at all treatments, but the

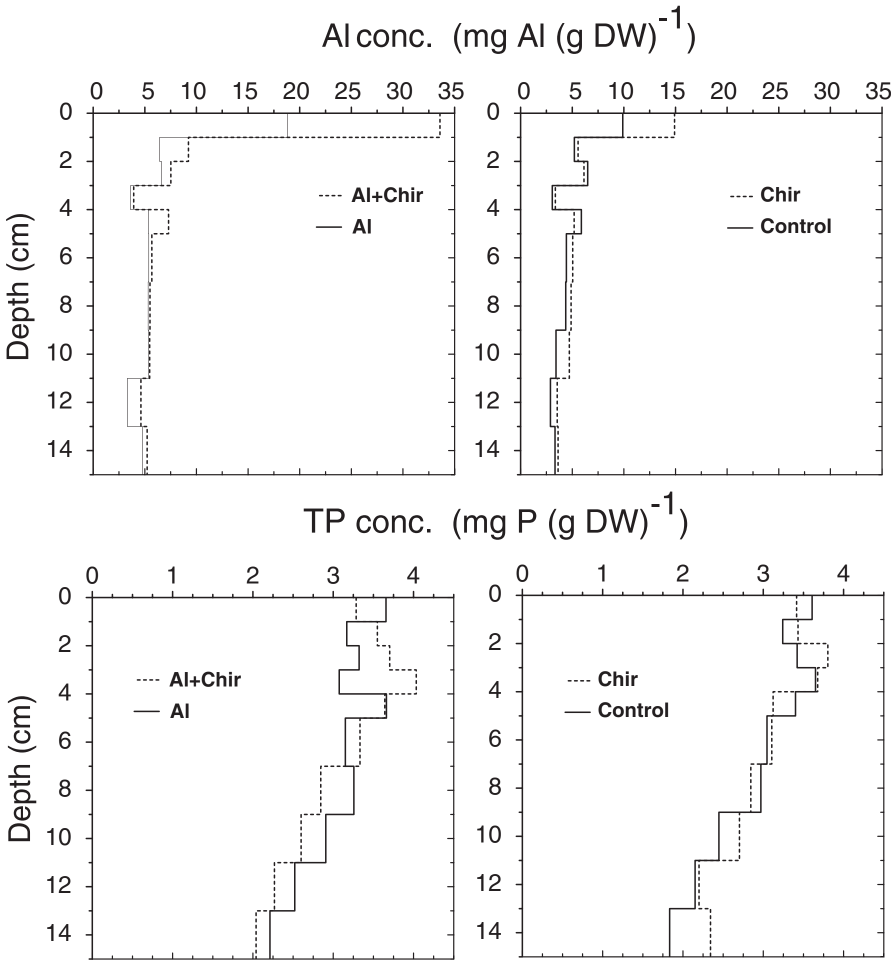
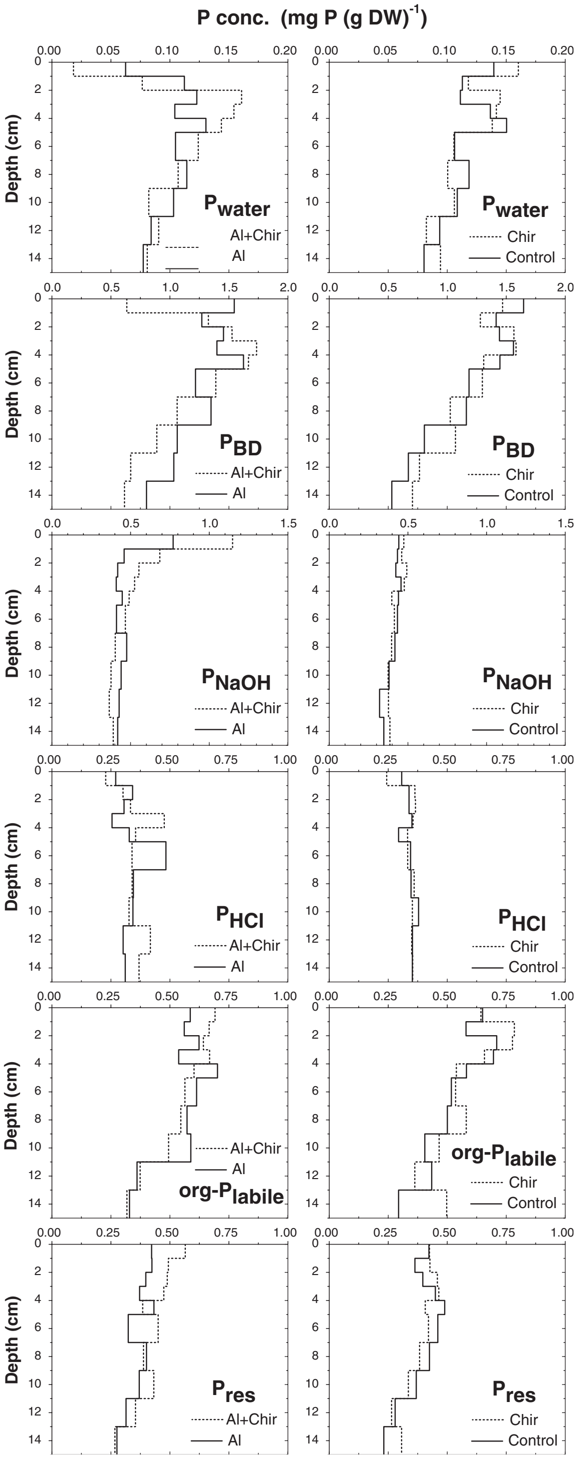


Figure 1. Aluminum and total-P (*TP*) concentrations at different depths in untreated sediment (*Control*) and in sediment to which aluminium and chironomids (*Al+ Chir*), aluminium (*Al*), or chironomids (*Chir*) were added. Subsamples from the same depths of five cores were pooled before measurements.

DIP release was less reduced in cores with than without chironomids. A similar pattern was observed at the second flux measurement after the Al addition although the flux rates in general tended to be higher.

No significant differences in the NO_2^- fluxes between the treatments were observed (results not shown), and NO_2^- fluxes were quantitatively insignificant (max. 0.4 mmol d^{-1} m^{-2}) compared to fluxes of NO_3^- (max. 25.5 mmol d^{-1} m^{-2}) and NH_4^+ (max. 8.6 mmol d^{-1} m^{-2}). The NO_3^- fluxes were initially only slightly affected by addition of chironomids, but later at flux no. 3 and 4, the chironomids either lowered the release or increased the uptake significantly (Figure 3). The


P conc. (mg P (g DW)$^{-1}$)
0.00 0.05 0.10 0.15 0.20
0.0 0.5 1.0 1.5 2.0
0.0 0.5 1.0 1.5
0.00 0.25 0.50 0.75 1.00
Depth (cm)
0 2 4 6 8 10 12 14
P$_{water}$
P$_{BD}$
P$_{NaOH}$
P$_{HCl}$
org-P$_{labile}$
P$_{res}$
Al+Chir
Al
Chir
Control

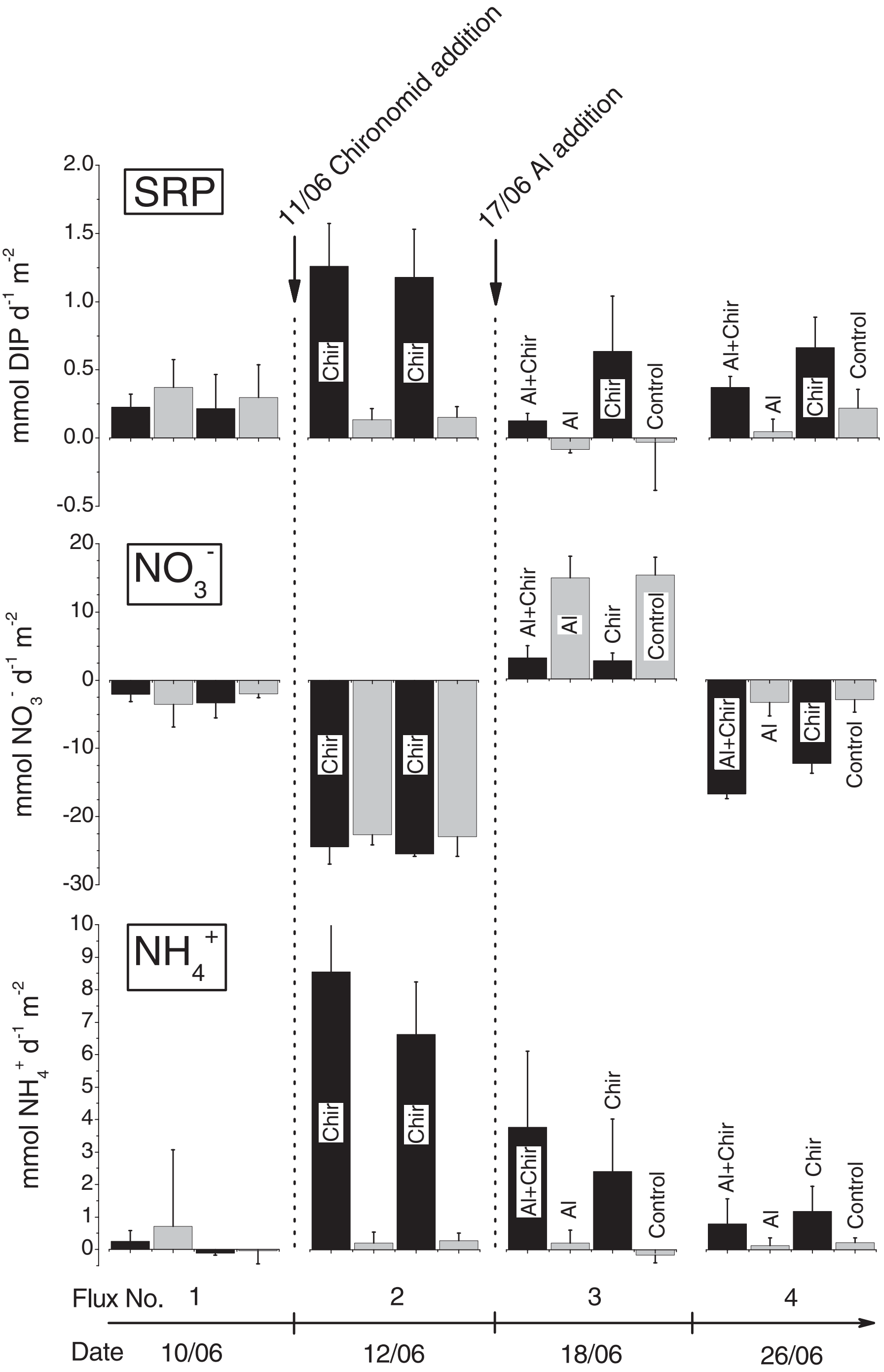
NO_3^- fluxes varied over time, but apart from flux no. 3 an uptake of NO_3^- by the sediment was always observed. Chironomids significantly increased the NH_4^+ release from the sediment as compared to treatments without added chironomids, where the NH_4^+ fluxes in general were low (max. 0.7 mmol d^{-1} m^{-2}). The elevated release in the chironomid treatments decreased over time. The Al treatment had no significant effects on either NH_4^+ or NO_3^- fluxes in treatments with and without chironomids.

4. Discussion

The immediate increase in the DIP release from the sediment after addition of *C. plumosus* was similar to previous observations (e.g., Andersen & Jensen, 1991; Fukuhara & Sakamoto, 1987; Hansen et al., 1998). The high initial DIP release may be explained by the increased irrigation by the chironomids combined with the high DIP concentrations in the porewater compared to the overlying water. However, decreased release or an uptake of DIP by the sediment after addition of chironomids have also been observed, indicating redox control of DIP fluxes from Fe-rich sediments (Andersen & Jensen, 1991; Lewandowski & Hupfer, 2005). The stimulating effect of chironomids on DIP release continued after the addition of Al to the sediment cores, however, with a lower rate. The explanation for the effect of chironomids on the efflux is the creation of burrows through the layer of Al floc on the sediment surface through which P from deeper layers may be transported with only limited contact to the added Al, and thus with lower possibility of P sorption by Al. Narf (1990) also found a release of DIP after Al was added to sediments with chironomids, but with slightly lower rates from d 20 to 40 at the end of the experiment. Narf suggested that the continued DIP release could be due to reworking of Al into the sediment, thus making the Al less efficient in binding P. In an analysis of the sediment of five lakes one year after a treatment with Al, Narf in general found elevated Al concentrations between 0 and 7.5 cm sediment depth as a result of sediment mixing by *C. tentans*. Reitzel et al. (2005) also noticed a burial of Al in the sediment of an Al treated lake.

In the present experiment, a faster burial of the Al floc was visible in the cores with chironomids, but the measurements of Al in the Al treated sediment revealed a higher concentration in the upper 3 cm of the sediment when chironomids were added. The Al concentration in the upper cm of the Al+Chir sediment increased the Al concentration by 78% compared to the Al treatment. Chironomids also increased the Al concentration by 51% in the upper cm of the non-Al treated

◀*Figure 2*. Concentrations of various P fractions extracted from different depths of untreated sediment (*Control*) and in sediment to which aluminium and chironomids (*Al+Chir*), aluminium (*Al*), or chironomids (*Chir*) were added. Subsamples from the same depths of five cores were pooled before measurements.


11/06 Chironomid addition
17/06 Al addition
SRP
mmol DIP d^{-1} m^{-2}
2.0
1.5
1.0
0.5
0.0
-0.5
Chir
Chir
Al+Chir
Al
Chir
Control
Al+Chir
Al
Chir
Control
NO$_3^-$
mmol NO$_3^-$ d^{-1} m^{-2}
20
10
0
-10
-20
-30
Chir
Chir
Al+Chir
Al
Chir
Control
Al+Chir
Al
Chir
Control
NH$_4^+$
mmol NH$_4^+$ d^{-1} m^{-2}
10
9
8
7
6
5
4
3
2
1
0
Chir
Chir
Al+Chir
Al
Chir
Control
Al+Chir
Al
Chir
Control
Flux No.
1
2
3
4
Date
10/06
12/06
18/06
26/06

sediment. The increase in Al concentration at both chironomid treatments may be related to increases in organic matter content in the surface sediment. Thus, at the end of the experiment the Al+Chir treatment had 29.0% organic matter in the upper 1 cm of the sediment vs. 25.4% in Al, and similarly, Chir had 28.2% vs. 24.8% in Control. Both bioturbating activity and excretion from the chironomids may have contributed to the increase in organic matter. Recent results indicate that DIP–Al–humic matter complexes may be formed in lake water (Ada de Vicente, personal communication). However, it is not possible on basis of our data to establish the relationship between organic matter and the Al content.

The increased Al concentration in the upper part of the Al treated sediment resulted in a significantly higher concentration of Al bound P (measured as P_{NaOH}). In the Al treatment, the elevated P_{NaOH} concentration was only apparent in the upper cm, whereas in the Al+Chir treatment, the P_{NaOH} concentration was further increased down to 7 cm depth. This indicates that the chironomids enhance the binding of DIP to Al by their reworking. This binding is also reflected in the lower P_{water} concentration (partly porewater DIP) in the Al+Chir treatment. Although an increase in Al concentration also was observed in the upper cm of the sediment at the Chir treatment to which no Al was added, it did not result in an increased binding of P to Al (P_{NaOH}) as well as a lower P_{water} concentration. This indicate that the 'old' Al in these cores were non-reactive with respect to binding of DIP. The lower concentration of P_{BD} in the upper cm of the Al+Chir indicate that some P may be mobilized when Fe^{3+} is reduced and then immobilized by binding to Al (Hansen, Reitzel, Jensen, & Andersen, 2003).

As indicated by the enhanced DIP release rates, the presence of *C. plumosus* initially diminished the barrier effect of the Al layer. Based on similar observations and on the burial of Al, Narf (1990) concluded that the presence of chironomids may shorten the period of effectiveness of an Al treatment. However, the high initial efflux of DIP may be due to high DIP concentrations present in the porewater before the Al treatment. The higher concentration of P_{NaOH} in the upper 7 cm sediment at the Al + Chir treatment at the end of the present study indicate that chironomids stimulate a permanent non-redox sensitive binding of P to Al and thereby lower the DIP concentration in the porewater. Therefore, if sufficient Al is added to the sediment, the release of DIP from the sediment should decrease after the initial phase. Since the present study only lasted nine days, and the flux experiments by Narf 44 days after the Al addition, there is a need for long term studies on the effect of bioturbating and bioirrigating zoobenthos on Al treatments of lake sediments.

◀ *Figure 3.* Nutrient fluxes between sediment and water during the experimental period. Flux no. 1 was on untreated cores. Before flux no. 2, two groups of cores were added chironomid larvae (*Chir*). Before flux no. 3, one group of chironomid treated cores and one untreated group were added Al. Means ± SD are shown. Positive values indicate release from the sediment.

Acknowledgement

This study was supported by a grant (no. 21020463) from The Danish Natural Science Research Council and by Centre for Lake Restoration (CLEAR).

References

Andersen, F. Ø., & Jensen, H. S. (1991). The influence of chironomids on decomposition of organic matter and nutrient exchange in a lake sediment. *Verhandlungen Internationale Vereinigung für Theoretische und Angewandte Limnologie*, *24*, 3051–3055.

Bower, C. E., & Holm-Hansen, T. (1980). A salicylate–hypochlorite method for determining ammonia in seawater. *Canadian Journal of Fisheries and Aquatic Sciences*, *37*, 794–798.

Cooke, G. D., Welch, E. B., Martin, A. B., Fulmer, D. G., Hyde, J. B., & Schrieve, G. D. (1993). Effectiveness of Al, Ca, and Fe salts for control of internal phosphorus loading in shallow and deep lakes. *Hydrobiologia*, *253*, 323–335.

Fukuhara, H., & Sakamoto, M. (1987). Enhancement of inorganic nitrogen and phosphate release from lake sediment by tubificid worms and chironomid larvae. *Oikos*, *48*, 312–320.

Gallepp, G. W. (1979). Chironomid influence on phosphorus release in sediment–water microcosms. *Ecology*, *60*, 547–556.

Hansen, K., Mouridsen, S., & Kristensen, E. (1998). The impact of *Chironomus plumosus* larvae on organic matter decay and nutrient (N, P) exchange in a shallow eutrophic lake sediment following a phytoplankton sedimentation. *Hydrobiologia*, *364*, 65–74.

Hansen, J., Reitzel, K., Jensen, H. S., & Andersen, F. Ø. (2003). Effects of aluminium, iron, oxygen, and nitrate additions on phosphorus release from the sediment of a Danish softwater lake. *Hydrobiologia*, *492*, 139–149.

Havas, M., & Likens, G. E. (1985). Toxicity of aluminum and hydrogen ions to *Daphnia catawba*, *Holopedium gibberum*, *Chaoborus punctipennis*, and *Chironomus anthracinus* from Mirror Lake, New Hampshire. *Canadian Journal of* Zoology, *63*, 1114–1119.

Hilsenhoff, W. L. (1966). The biology of *Chironomus plumosus* (Diptera: Chironomidae) in Lake Winnebago, Wisconsin. *Annals of the Entomological Society of America*, *59*, 465–473.

Lewandowski, J., & Hupfer, M. (2005). Effect of macrozoobenthos on two-dimensional small-scale heterogeneity of pore water phosphorous concentrations in lake sediments: A laboratory study. *Limnology and Oceanography, 50*, 1106–1118.

Murphy, J., & Riley, J. P. (1962). A modified single solution method for determination of phosphate in natural waters. *Analytica Chimica Acta*, *27*, 31–36.

Narf, R. P. (1990). Interaction of Chironomidae and Chaoboridae (Diptera) with aluminum sulfate treated lake sediments. *Lake and Reservoir Management*, *6*, 33–42.

Pelegrí, S. P., & Blackburn, T. H. (1996). Nitrogen cycling in lake sediments bioturbated by *Chironomus plumosus* larvae, under different degrees of oxygenation. *Hydrobiologia*, *325*, 231–238.

Psenner, R., & Pucsko, R. (1988). Phosphorus fractionation: Advantages and limits of the method for the study of sediment P origins and interactions. *Archiv für Hydrobiologie–Beiheft Ergebnisse der Limnologie*, *30*, 43–59.

Reitzel, K., Hansen, J., Andersen, F. Ø., Hansen, K. S., & Jensen, H. S. (2005). Dosing of aluminum relative to the potentially mobile phosphorus pool in the sediment to inhibit internal phosphorus loading in a shallow, hypertrophic Danish lake. *Environmental Science & Technology*, *39*, 4134–4140.

Svensson, J. M. (1998). Emission of N_2O, nitrification and denitrification in a eutrophic lake sediment bioturbated by *Chironomus plumosus*. *Aquatic Microbial Ecology*, *14*, 289–299.

Warner, R. W. (1971). Distribution of biota in a stream polluted by acid mine-drainage. *The Ohio Journal of Science*, *71*, 202–215.

Water, Air, and Soil Pollution: Focus (2006) **6:** 111–121
DOI: 10.1007/s11267-006-9031-8

STUDY OF POLLUTION OF THE PLITVICE LAKES BY WATER AND SEDIMENT ANALYSES

NADA HORVATINČIĆ[1,*], JOSÉ LUIS BRIANSÓ[2], BOGOMIL OBELIĆ[1],
JADRANKA BAREŠIĆ[1] and INES KRAJCAR BRONIĆ[1]
[1]Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia
[2]Universitat Autònoma de Barcelona, 008193 Bellaterra, Spain
*(*author for correspondence, e-mail: nada.horvatincic@irb.hr; phone: +385-1-4560943; fax: +385-1-4680239)*

Abstract. The process of eutrophication in form of intense plant growth has been observed in some lakes and water streams at the Plitvice Lakes National Park in central Croatia. Here we investigate whether this phenomenon is a consequence of anthropogenic pollution or due to naturally produced organic matter in the lakes. We applied chemical analysis of water at two springs and four lakes (nutrients, dissolved organic carbon (DOC), trace elements) and measurements of surface lake sediments (mineral and organic fraction analyses, trace elements) in four different lakes/five sites. The chemical composition of water does not indicate recent anthropogenic pollution of water because the concentrations of most trace elements are below detection limits. The concentrations of DOC and nutrients are slightly higher in the area of increased eutrophication-plant growth. Also the content of organic matter in the sediment is at the highest level in areas with highest C/N ratio indicating that the organic fraction of this sediment is mainly of terrestrial origin. There is no significant difference among the trace element concentration in the upper segment of all cores, deposited approximately during last 50 years when higher anthropogenic influence is expected due to development and touristic activity, and the lower part of the cores, corresponding to the period approximately 100–200 years before present. The content of trace elements and organic matter in sediments decreases from the uppermost lake downstream. According to our results there is no indication of recent anthropogenic pollution in water and sediment. Higher concentrations of DOC in water as well as phosphorus and some other elements in the lake sediment can be a consequence of input of natural organic matter to the lake water.

Keywords: Plitvice Lakes, lake sediment, trace elements, water pollution, eutrophication

1. Introduction

The Plitvice Lakes are a series of lakes, tufa barriers and waterfalls located in the Dinaric Karst of Central Croatia (Figure 1). In this area tufa, a freshwater calcium carbonate, precipitates very intensively in presence of macrophites and microphites forming numerous barriers. At the same time calcium carbonate precipitates as lake sediment at the bottom of the lakes. Previous investigations of physical–chemical conditions of tufa precipitation from the freshwater at the Plitvice Lakes area (Srdoč, Horvatinčić, Obelić, Krajcar, & Sliepčević, 1985a; Horvatinčić, Srdoč, Šilar, & Tvrdiková, 1989) showed that process of calcium carbonate precipitation is

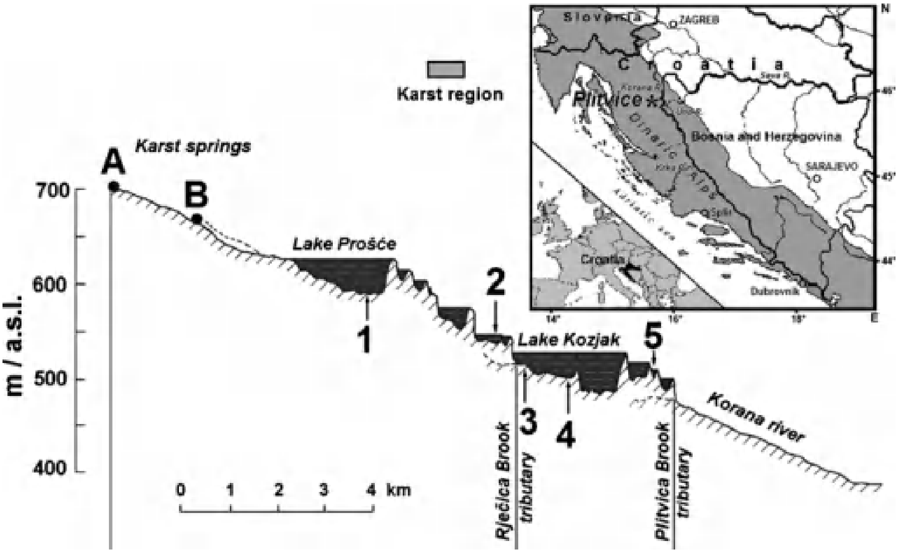


Figure 1. Sampling sites for sediment samples at Plitvice Lakes area: *1* – Lake Prošće, *2* – Lake Gradinsko, *3* – Lake Kozjak K2 (Rječica Brook tributary), *4* – Lake Kozjak K1, *5* – Lake Kaluđerovac. Surface water samples were collected at the same location or close to it, and at two main springs: *A* – Crna Rijeka and *B* – Bijela Rijeka.

accelerated in streams and lakes where saturation index of $CaCO_3$ exceeds 3, and in most cases it is between 4 and 6. Also the influence of the biological component (Chafetz, Srdoč, & Horvatinčić, 1994; Plenković-Moraj, Horvatinčić, & Primc-Habdija, 2002) is significant for tufa precipitation in this area. The whole karstic environment of Plitvice Lakes, including water, soil and air, is very sensitive to any kind of pollution. Although the Plitvice Lakes area is protected as the national park and is scarcely populated, some contamination by local settlements, tourism activities and traffic is possible. Moreover, the lakes are located in mostly deciduous forest, and huge amount of leaves are transported into the lakes every year. Anthropogenic influence on ^{14}C activity and some aliphatic and polycyclic aromatic hydrocarbons of recent lake sediment in lakes Kozjak and Prošće were published in Srdoč et al. (1992). Additionally, some preliminary measurements of dissolved organic carbon (DOC) in water in this area showed that increase of DOC can disturb or even stop the process of tufa precipitation (Srdoč et al., 1985a). In last decades the process of eutrophication in the Plitvice Lakes has been observed in the form of intense plant growth in some lakes, tufa barriers and water streams. This process is attributed to influx of nutrients into lakes and streams from natural and anthropogenic sources resulting in deterioration of water quality (Dodds, Jones, & Welch, 1998; Walpersdorf, Neuman, & Stuben, 2004). The mineralogical and chemical compositions of lake sediments reflect natural environmental changes or human impact during the sedimentation process (Bilali, Rasmussen, Hall, & Fortin, 2002; Belzile, Chen, Gunn, & Dixit, 2004; Yang & Rose, 2005).

In this paper we investigate the observed eutrophication process in some lakes to determine whether it is a consequence of anthropogenic pollution or due to the input of natural organic matter to the lake water. For this purpose we analysed lake water for nutrients, DOC and trace elements and surface lake sediments for mineral and organic fraction and trace elements.

2. Sampling and Methods

Surface water samples were collected seasonally during 2003 and 2004 at 15 sampling points including springs, lakes, streams between lakes and tributaries. Temperature, pH, conductivity and dissolved oxygen were measured *in situ*. Trace elements (B, Al, Cr, Sr, Mn, Fe, Ni, Cu, Zn, Cd, Ba, Pb, P) were measured by ICP MS (water samples filtrated by 0.22 μm filter), most anions (SO_4^{2-}, Cl^-, F^-, NO_3^-, NO_2^-, HPO_4^{2-}) were measured by ionic chromatography with conductivity detector, ammonium by spectrophotometer (the Nessler method), while DOC was determined by catalytic combustion and measured by an IR detector.

Samples of top 45 cm of surface lake sediments were collected at five points in four lakes (Figure 1): Lake Prošće, Lake Gradinsko, Lake Kozjak and Lake Kaluđerovac. In Lake Kozjak two locations were selected: site K1, in the middle of the lake, where no eutrophication process was observed, and site K2 near the mouth of the Rječica brook, with intensive plant growth from the lakes. Same phenomenon was also observed in lakes Prošće, Gradinsko and Kaluđerovac, although less intensive.

In the lake sediments the mineralogical analyses, organic fraction elemental analyses as well as trace element analyses (Al, B, Ba, Cd, Cr, Cu, Mn, Ni, Sr, P, Pb, Zn) were performed. The qualitative mineralogical analyses were performed by X-ray diffraction method and scanning electron microscopy. For organic fraction analyses sediment sample was treated by 1N HCl and the rest was analysed by the Perkin Elmer 2400 Series II CHNS Analyser.

3. Results and Discussion

3.1. WATER ANALYSES

We selected five sampling points of surface water that are close to the sites of the sediment sampling, and also two main springs (Crna Rijeka and Bijela Rijeka) which serve as the reference points for natural water composition (Figure 1). In Table I we present data about the investigated lakes, and the results of some measured parameters in water that are important for studying pollution of the lakes. Surface water sampling and measurements were performed in different

TABLE I

Data about lake areas, water depth of sediment sampling and sedimentation rates calculated according to ^{137}Cs and ^{210}Pb measurements. Results of physical and chemical measurements of two spring waters and surface waters at four lakes/five sites are presented as the mean values and the range of minimum and maximum values including all seasonal measurements

		Bijela Rijeka spring	Crna Rijeka spring	Lake Prošće	Lake Gradinsko	Lake Kozjak K1	Lake Kozjak K2	Lake Kaluđerovac
Lake area (km^2)				0.68	0.08	0.82	0.82	0.02
Water depth (m) of sediment sampling				19	5	21	2	3
Sedimentation rate[a] [kg/(m^2 year)]	^{137}Cs			0.54–0.92	1.4	0.76	–	1.8
	^{210}Pb			1.2–1.3	3.4–4.4	0.8–0.95	–	2.6–2.72
Surface water								
Temperature (°C)		7.6 (7.1–8.1)	7.8 (7.6–8.0)	11.0 (3.7–19.8)	12.4 (0.6–22.7)	12.6 (3.6–21.8)	8.8 (4.2–10.4)	12.8 (3.3–21.8)
pH		7.51 (7.37–7.68)	7.46 (7.29–7.57)	8.23 (8.14–8.40)	8.22 (7.88–8.40)	8.31 (8.15–8.44)	8.17 (7.96–8.30)	8.45 (8.29–8.53)
Conductivity (µS/cm)		478 (474–480)	423 (409–433)	410 (400–416)	373 (303–404)	390 (377–404)	503 (494–512)	380 (353–400)
O_2 (mg/l)		11.5 (9.5–16.0)	10.5 (8.6–14.4)	10.9 (10.1–12.1)	8.8 (5.8–10.4)	10.1 (8.1–12.5)	10.2 (8.1–11.3)	9.7 (7.3–11.2)
DOC (mgC/l)		0.63 (0.36–1.03)	0.44 (0.23–0.66)	1.27 (0.76–2.01)	1.12 (0.64–1.74)	1.14 (0.68–1.99)	1.26 (0.99–2.09)	0.96 (0.74–1.27)
NO_3^-/N (mg/l)		1.2 (1.0–1.5)	1.0 (0.7–1.8)	0.7 (0.5–0.9)	0.6 (0.4–0.9)	0.6 (0.4–0.9)	0.9 (0.7–1.0)	0.6 (0.4–0.9)
NH_4^+/N (mg/l)		0.01 (0–0.03)	0.03 (0–0.13)	0.07 (0.02–0.12)	0.04 (0.02–0.07)	0.03 (0.01–0.05)	0.04 (0.01–0.18)	0.02 (0.01–0.03)

[a] ^{137}Cs and ^{210}Pb analyses of sediment samples were performed by gamma spectrometry using a low-background, well-type, high-purity germanium (HPGe) detector of 240 cm^3 active volume and 40 mm active well depth (Gäbler & Suckow, 2003).

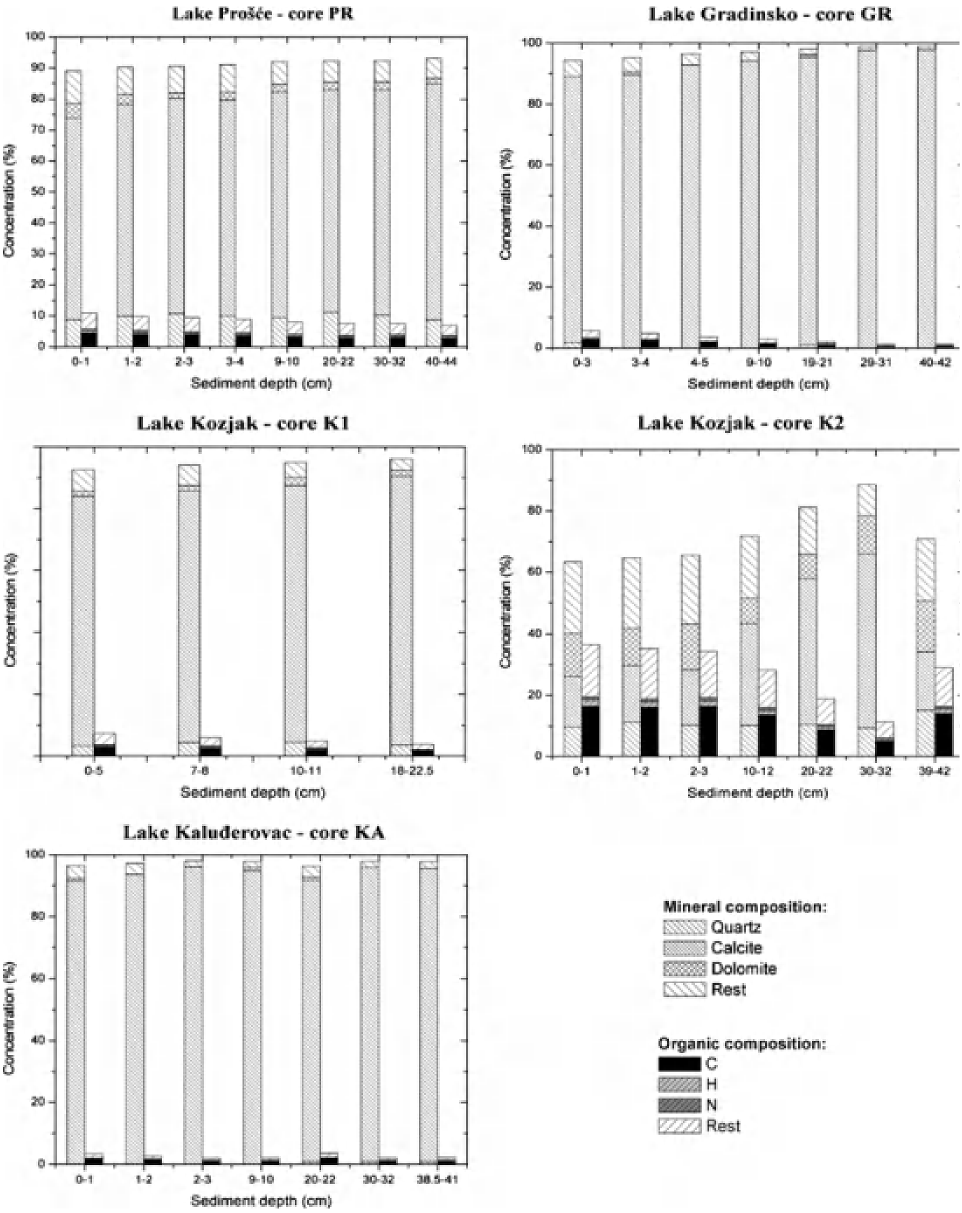


Figure 2. Lake sediment composition at different sediment depth of five sediment cores: mineral (*left column*) and organic fraction (*right column*).

seasons and the mean values as well as the range between the lowest and the highest measured values are shown in Table I. The seven sampling sites in Table I are arranged in the downstream direction, i.e., from the springs to Lake Prošće to Lake Kaluđerovac (Figure 1).

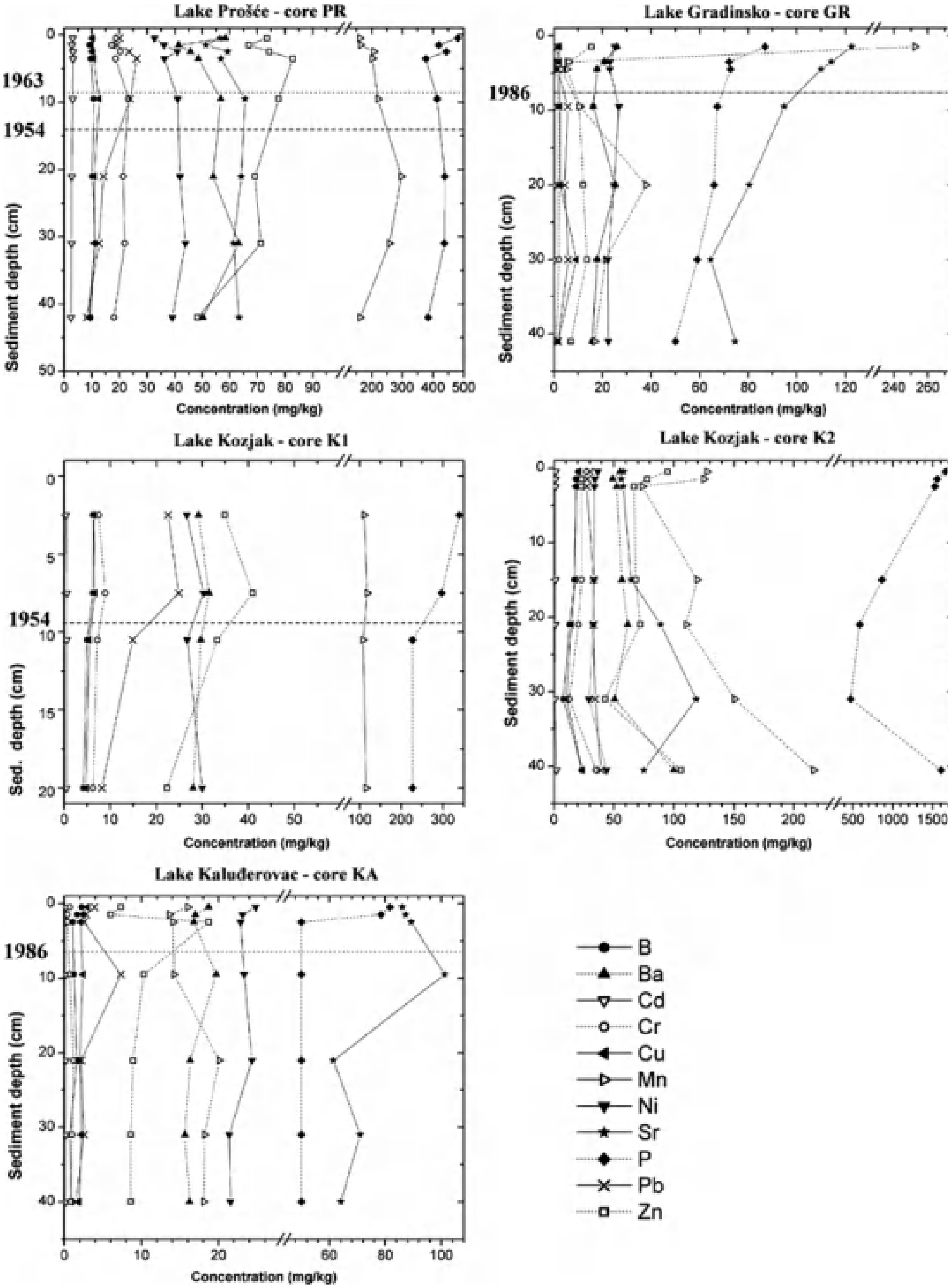


Figure 3. Trace element distributions in five sediment cores. Results are expressed in mg/kg of dry sediment. Years corresponding to ^{137}Cs fallout peaks are given at the *left side* of each core, except for core K2.

In spring water, temperature is constant throughout the year showing very small fluctuations. Temperature fluctuations increase downstream being higher in smaller lakes. The exception is Lake Kozjak site K2 because of the Rječica brook confluence. pH values show steady increase in the downstream direction, as the consequence of CO_2 outgassing and simultaneous precipitation of calcium carbonate in form of tufa and lake sediments. The consequence of strong calcite precipitation is also a decrease of the conductivity in the downstream direction. The concentration of dissolved oxygen in surface water is higher because of mixing of water and air in the numerous waterfalls and streams.

Concentrations of nutrients (nitrates, ammonium) are on the average higher in Prošće and Kozjak site K2, and for the other sites the ranges of measured concentrations are lower. It is interesting that the highest nitrate concentration is observed in the spring waters (Table I). This can be explained by percolating of groundwater through the humus layer and transporting by surface water from the wooded environment. Concentrations of nitrites and phosphates at all sites are below the detection limits. Concentrations of trace elements that are important as indicators of anthropogenic pollution are below detection limits for all seven sites, e.g., for Cd, Pb<0.5 μg/l, for Cr, Cu, Mn<1 μg/l, for Ni<2 μg/l and for P$<$ 20 μg/l. Concentrations of other trace elements (B, Ba, Sr) are much lower than the maximal allowable concentrations (MAC) for natural waters.

The concentration of DOC is the lowest in the spring water, while the highest mean values are at the Lake Kozjak site K2 and Prošće (Table I). For other sites, a slight downstream decrease of DOC is observed. The observed increase of DOC in the uppermost Lake Prošće compared to DOC in the springs can be explained in the following way: the two main springs (Figure 1) form the Matica River that feeds the Lake Prošće passing through the peat bogs that were formed there in the past (Srdoč et al., 1985b) and bringing about higher DOC concentration in the lake.

3.2. Sediment Analyses

Sedimentation rates determined by ^{137}Cs and ^{210}Pb (Table I) (Obelić et al., 2005) show remarkable differences. They are approximately twice as high for the smaller lakes Gradinsko and Kaluđerovac compared to the bigger lakes Prošće and Kozjak. Sedimentation rate determined by ^{14}C method using several 12-m long sediment cores (Srdoč et al., 1986) was 1.4–1.5 mm per year for the Lake Prošće, and 0.8–1.0 mm per year for the Lake Kozjak. All three methods (^{14}C, ^{137}Cs and ^{210}Pb) gave higher sedimentation rate in the Lake Prošće by a factor of about 1.5. Hence, approximately 40 cm long sediment cores used in this study are 100–200 years old.

Qualitative mineralogical analyses have shown that dominant components of inorganic fraction of the sediment are calcite, dolomite and quartz, and the minor components, detected in some samples are aragonite, quartz, feldspars and minerals of the filosilicates group. The semi-quantitative analyses have been focused only on the three main components (Figure 2). Calcite is the major component of most sediments as the result of calcite precipitation from the DIC in water. At all these sites water is supersaturated with the respect to $CaCO_3$ (Srdoč et al., 1985a; Horvatinčić, Krajcar Bronić, & Obelić, 2003) and precipitation of lake sediment is very intensive, as shown by a relatively high sedimentation rate. The mineralogical composition of the core K2 is an exception. It is taken at the confluence of Rječica brook and Kozjak Lake (Figure 1, site 3), where transport of organic material (leaves and humus) to the lake is significant and the plant growth on the bottom of the lake is very intensive.

Analyses of organic fraction show a significant difference in content of organic matter for different sediment cores (Figure 2). Generally, the content of organic matter in lake sediments decreases downstream. The exception is again core K2 with highest content of organic matter. This is also visible in the sediment colour: core K2 is black, while the other sediment cores are dark grey (Prošće) to light grey coloured (Kaluđerovac).

The *C*/*N* ratio in the sediments, which is a good indicator of organic carbon sources (Ruban, Brigault, Demare, & Philippe, 1999; Talbot & Laerdal, 2000; Vreča & Muri, 2006) has the following ranges: Lake Prošće, 9.4–12.2 (mean 10.8); Lake Gradinsko, 8.3–9.7 (mean 8.8); Lake Kozjak K1, 8.8–10.9 (mean 9.9); Lake Kaluđerovac, 9.0–14.0 (mean 11.2). The highest *C*/*N* ratio was found in sediment of Lake Kozjak site K2, from 13.0 to 16.8 (mean 15.1), showing that organic fraction of this sediment is mainly of terrestrial origin. The *C*/*N* ratios of other sediments indicate the phytoplankton as the major source of autochthonous organic matter in the lake sediment. There is no systematic change of *C*/*N* ratio with the sediment depth.

Trace element distribution expressed in milligrams per kilogram (mg/kg) of dry sediment for all five sediment cores is presented in Figure 3. The distribution of most of trace elements (e.g., for B, Ba, Cr, Cu, Ni, Cd) along the sediment depth is quite uniform for all sediment cores. The concentration of certain elements slightly increases at the top 10 cm of the cores, corresponding to the last 40–50 years according to ^{137}Cs and ^{210}Pb dating. This is the case for phosphorus in all sediment cores, lead in cores PR and K1, zinc in cores PR, GR, K1 and K2, strontium in cores GR and KA, and cadmium in core PR.

If we compare all sediment cores, then we can conclude that the highest concentrations of most elements are in cores K2 and PR, then follows K1 and the lowest concentrations are in cores GR and KA. Particularly high concentration of phosphorus is determined in core K2 (400 to 1,600 mg/kg), and quite high in PR core (approximately 400 mg/kg). This correlates to the highest content of organic matter found in these two sediment cores. The core PR has been retrieved from the Lake Prošće where most of trace elements are transported from the springs and the Matica River flowing over peat bog area. The Matica River feeds the lake system and therefore concentration of trace elements as well as that of organic fraction in this core is higher than in the downstream lakes. The highest concentration of all elements in core K2, particularly phosphorus, can be explained by the transport of terrestrial material from the Rječica brook to the Lake Kozjak.

Bilali et al. (2002) showed that some trace elements have different relative affinities to organic and mineral fraction. We also noticed the positive correlation between concentration of organic carbon and Pb (r^2=0.78, n=5), Cd (r^2=0.89, n=4) and Zn (r^2=0.93, n=4) in the sediment. The highest concentrations of Pb (30–40 mg/kg), Cd (0.6–2.1 mg/kg) and Zn (42–105 mg/kg) were found in Lake Kozjak, core K2, having high organic fraction, while the lowest concentration of the same trace elements were found in core KA, that has the lowest organic carbon fraction (Pb 5–10 mg/kg, Cd<0.2 mg/kg, Zn 6–20 mg/kg).

The concentrations of trace elements in the sediment that can be mainly of anthropogenic origin, e.g., Cd, Cr, Cu, Ni, Pb and Zn, and therefore can indicate some anthropogenic contamination, are much lower than the MAC for metals in soil in the European Union (Adriano, 2001). The natural origin of trace elements at such concentrations is also possible. The exception is the maximal measured value of Cd in sediment core PR (3.2 mg/kg), indicating a possibility of anthropogenic contamination, probably from fertilizers, but the natural origin cannot be excluded.

4. Conclusion

To investigate the eutrophication process that was observed at several locations in the Plitvice Lakes area we performed chemical analyses of water at two springs and four lakes (nutrients, DOC, trace elements) to determine the present status of water quality. Also, measurements of mineral and organic fraction and trace elements in lake sediments deposited over the last 100–200 years in four lakes at five sites were performed to determine the impact of human activities and/or natural processes resulting in changes of water and sediment composition.

The chemical composition of water, particularly concentration of trace elements which are bellow detection limit, does not indicate a significant recent anthropogenic pollution of water. Slightly higher concentrations of nitrates and ammonia in spring water as well as in Lake Kozjak site K2, where a more intensive plant growth was observed, indicate the influence of natural environment, e.g., percolating of groundwater through humus and transport by surface water from the wooded environment. Concentration of DOC is at the highest level in the area where significant eutrophication was observed (site K2). The steady decrease of DOC in the downstream direction is also observed.

The composition of minerals for each sediment core shows prevalent presence of calcite, except for the core K2 from Lake Kozjak, where a significant fraction of dolomite and quartz was measured. Also, the content of organic matter is at the highest level in this core (11.4% to 36.6%) with the highest *C*/*N* ratio (15.1), showing that this sediment is mainly of terrestrial origin, e.g., formed by a transport of terrestrial material by the Rječica Brook. The *C*/*N* ratios of other sediments range from 8.8 to 11.2 indicating the phytoplankton as the major source of autochthonous organic matter in the lake sediment.

The concentration of most trace elements including phosphorus is the highest at the location K2 and the consequence is an intensive plant growth in this area. Also, the content of trace elements, as well as organic matter, decreases from the uppermost Lake Prošće downstream to the Lake Kaluđerovac (the exception is core K2). This fact indicates that the most of trace elements in sediments are probably of natural origin due to transport from the main springs as well as from the Matica River (peat bog area) into the Lake Prošće and their steady deposition along downstream lakes.

Concentration of trace elements in the 40 cm long sediment cores from five different locations is much lower than MAC for metals in soils in European Union. There is no significant difference among the trace element concentration in the top segment of all cores, corresponding to last 50 years when higher anthropogenic influence can be expected, and the lower part of the cores, corresponding to the period 100–200 years before present. Analyses of lake sediment show no significant contamination caused by anthropogenic influence. Higher concentrations of DOC in water as well as phosphorus and some other elements in lake sediment can be a consequence of input of natural organic matter (humus) to the lake water by natural process.

Acknowledgement

Work funded by EU project ICA2-CT-2002-10009 and by the Project 0098014 by the Ministry of Science, Education and Sport of the Republic of Croatia.

References

Adriano, D. C. (2001). *Trace element in the terrestrial environment* (p. 680). Berlin Heidelberg New York: Springer.

Belzile, N., Chen, Y.-W., Gunn, J. M., & Dixit, S. S. (2004). Sediment trace metal profiles in lakes of Killarney Park, Canada: From regional to continental influence. *Environmental Pollution*, *130*, 239–248.

Bilali, L. E., Rasmussen, P. E., Hall, G. E. M., & Fortin, D. (2002). Role of sediment composition in trace metal distribution in lake sediments. *Applied Geochemistry*, *17*, 1171–1181.

Chafetz, H., Srdoč, D., & Horvatinčić, N. (1994). Early diagenesis of Plitvice Lakes waterfall and barrier travertine deposits. *Geographie Physique et Quaternaire*, *48*, 245–255.

Dodds, W. K., Jones, J. R., & Welch, E. B. (1998). Suggested classification of stream trophic state: Distributions of temperate stream types by chlorophyll, total nitrogen and phosphorus. *Water Research*, *32*(5), 1455–1462.

This page intentionally blank

Gäbler, H. E., & Suckow, A. (2003). Chronology of anthropogenic heavy-metal fluxes and Pb isotope ratios derived from radiometrically dated lake sediments in northern Germany. *Water, Air, and Soil Pollution*, *144*, 243–262.

Horvatinčić, N., Krajcar Bronić, I., & Obelić, B. (2003). Differences in the ^{14}C age, δ^{13}C and δ^{13}O of Holocene tufa and speleothem in the Dinaric karst. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *193*, 139–157.

Horvatinčić, N., Srdoč, D., Šilar, J., & Tvrdiková, H. (1989) Comparison of the ^{14}C activity of groundwater and recent tufa from karst areas in Yugoslavia and Czechoslovakia. *Radiocarbon*, *31*, 884–892.

Obelić, B., Horvatinčić, N., Barešić, J., Briansó, J. L., Babinka S., & Suckow, A. (2005). Anthropogenic pollution in karst lake sediments (Croatia). In M. Özkul, S. Yagiz & B. Jones (Eds.), *Proceedings of the 1st International Symposium on Travertine* (pp. 188–196). Turkey: Denizli, September 2005.

Plenković-Moraj, A., Horvatinčić, N., & Primc-Habdija, B. (2002). Periphyton and its role in tufa deposition in karstic waters (Plitvice Lakes, Croatia). *Biologia (Bratislava)*, *57*, 423–432.

Ruban, V., Brigault, S., Demare, D., & Philippe, A.-M. (1999). An investigation of the origin and mobility of phosphorus in freshwater sediments from Bort-Las-Orgues Reservoir, France. *Journal of Environmental Monitoring*, *1*, 403–407.

Srdoč, D., Horvatinčić, N., Ahel, M., Giger, W., Schaffner, C., Krajcar Bronić, I., Petriciolo, D., Pezdič, J., Marčenko, E., & Plenković, A. (1992). Anthropogenic influence on the ^{14}C activity of recent lake sediment: A case study. *Radiocarbon*, *34*, 585–592.

Srdoč, D., Horvatinčić, N., Obelić, B., Krajcar, I., & Sliepčević, A. (1985a). Procesi taloženja kalcita u krškim vodama s posebnim osvrtom na Plitvička jezera (Calcite deposition processes in karstwaters with special emphasis on the Plitvice Lakes, Yugoslavia). *Carsus Iugoslaviae (Krš Jugoslavije)*, *11*(4–6), 101–204 (in Croatian with English Abstract).

Srdoč, D., Obelić, B., Horvatinčić, N., Culiberg, M., Šercelj, A., & Sliepčević, A. (1985b). Radiocarbon dating and pollen analyses of two peat bogs in the Plitvice National Park area. *Acta Botanica Croatica*, *44*, 41–46.

Srdoč, D., Obelić, B., Horvatinčić, N., Krajcar Bronić, I., Marčenko, E., Merkt, S., Wong, H. & Sliepčević, A. (1986). Radiocarbon dating of lake sediments from two karstic lakes in Yugoslavia. *Radiocarbon*, *28*, 495–502.

Talbot, M. R., & Laerdal, T. (2000). The late Pleistocene–Holocene paleolimnology of Lake Victoria, East Africa, based upon elemental and isotopic analyses of sedimentary organic matter. *Journal of Paleolimnology*, *23*, 141–164.

Vreča, P., & Muri, G. (2006). Changes in accumulation of organic matter and stable carbon and nitrogen isotopes in sediments of two Slovenian mountain lakes (Lake Ledvica and Lake Planina). *Limnology and Oceanography*, *51*(2), 781–790.

Walpersdorf, E., Neuman, T., & Stuben, D. (2004). Efficiency of natural calcite precipitation compared to Lake Marl application used for water quality improvement in an eutrophic lake. *Applied Geochemistry*, *19*, 1687–1698.

Yang, H., & Rose, N. (2005). Trace element pollution in some UK lake sediments, their history, influence factors and regional differences. *Environment International*, *31*, 63–75.

Water, Air, and Soil Pollution: Focus (2006) **6:** 123–130
DOI: 10.1007/s11267-006-9032-7

MODELLING PHOSPHORUS RETENTION IN LAKES AND RESERVOIRS

J. HEJZLAR[1,2,*], K. ŠÁMALOVÁ[1,2], P. BOERS[3] and B. KRONVANG[4]
[1]Hydrobiological Institute, AS CR, Na Sádkách 7 370 05 České Budějovice, Czech Republic
[2]Faculty of Biological Sciences, USB, České Budějovice, Czech Republic
[3]RIZA, P.O. Box 17 8200AA Lelystad, The Netherlands
[4]National Environmental Research Institute, P.O. Box 314, Vejlsøvej 25 8600 Silkeborg, Denmark
*(*author for correspondence, e-mail: hejzlar@hbu.cas.cz; phone: +420-389025876*
fax: +420-385310248)

(Received 20 October 2005; accepted 5 June 2006)

Abstract. Steady-state models for the prediction of P retention coefficient (R) in lakes were evaluated using data from 93 natural lakes and 119 reservoirs situated in the temperate zone. Most of the already existing models predicted R relatively successfully in lakes while it was seriously under-estimated in reservoirs. A statistical analysis indicated the main causes of differences in R between lakes and reservoirs: (a) distinct relationships between P sedimentation coefficient, depth, and water residence time; (b) existence of significant inflow–outflow P concentration gradients in reservoirs. Two new models of different complexity were developed for estimating R in reservoirs: $R = 1.84\tau^{0.5}/(1 + 1.84\tau^{0.5})$, where τ is water residence time (year), was derived from the Vollenweider/Larsen and Mercier model by adding a calibrated parameter accounting for spatial P non-homogeneity in the water body, and is applicable for reservoirs but not lakes, and $R = 1 - 1.43/[\mathrm{P_{in}}]([\mathrm{P_{in}}]/(1 + \tau^{0.5}))^{0.88}$, where $[\mathrm{P_{in}}]$ is volume-weighted P concentration in all inputs to the water body ($\mu\mathrm{g\ l^{-1}}$), was obtained by re-calibrating the OECD general equation, and is generally applicable for both lakes and reservoirs. These optimised models yield unbiased estimates over a large range of reservoir types.

Keywords: phosphorus, retention, mass-balance model, lakes, reservoirs, statistical optimization

1. Introduction

Phosphorus retention in lakes and reservoirs is usually described according to Dillon and Rigler (1974) by the retention coefficient (R) which is defined as the fraction of the external P loading retained within the water body. This retention concept is a key element of the steady steady-state, mass-balance models that have been elaborated and widely used since the 1960s for predicting nutrient concentrations and trophic state in water bodies (e.g., Chapra, 1975; Larsen & Mercier, 1976; Nürnberg, 1984; Nürnberg & LaZerte, 2004; OECD, 1982; Prairie, 1989; Vollenweider, 1969; Vollenweider, 1976).

The need to provide catchment-scale nutrient retention estimates as part of the catchment modelling efforts of the EUROHARP project http://www.euroharp.org) gave us the idea to evaluate this type of models with a data set consisting not only predominantly of lakes as in most previous studies, but also including a representative subset of reservoirs. Our preliminary studies showed that the majority of the classic models predict P retention in lakes relatively well, while P retention in reservoirs was significantly under-predicted. Hence we investigated the cause of the different behaviour of reservoirs and re-analysed relationships between the nutrient retention coefficient and the basic hydrological and morphological variables used in the models. The aim of this paper is to discuss differences between P retention in lakes and in reservoirs and to suggest how to optimise phosphorus retention models for reservoirs.

2. Materials and Methods

The database of phosphorus retention coefficients (available on request) consisted of 119 records for reservoirs and 93 records for lakes. The majority of the data originated from Europe and North America. Only water bodies with positive P retention were included in the database. Negative P retention (i.e., net release) was considered as a contradicting signal for the steady-state conditions assumed in this modelling approach and such data were therefore not considered.

P retention data were evaluated according to two basic approaches used in the classic steady-state P models of the 1960s and 1970s. In the first approach the P balance is solved assuming concentration-related P losses (Vollenweider, 1969), and retention coefficient R is calculated as:

$$R = \frac{\sigma\tau}{\sigma\tau + 1} \tag{1}$$

where σ is P sedimentation coefficient (year^{-1}) and τ is water residence time (year). In the second approach, the P balance is based on the areal P loading (Chapra, 1975; Vollenweider, 1975) and R is given as:

$$R = \frac{v}{v + q_{\mathrm{w}}} \tag{2}$$

where v is P apparent settling velocity (m year^{-1}) and q_{w} is areal water load (m year^{-1}).

R, σ, and v were calculated from the measured data on volume-weighted inflow ([$\mathrm{P_{in}}$]) and outflow ([$\mathrm{P_o}$]) concentrations, τ, and mean depth (z) according to Chapra (1975) and Vollenweider (1975).

The evaluation of retention data from lakes and reservoirs included (a) correlation analysis among logarithmically transformed data on latitude, hydrological variables, depth, P concentrations, and R for the whole data set and for the subsets of lakes and reservoirs; (b) testing of the significance of selected relationships by regression analysis; and (c) parameter optimisation of selected functions with the Solver (MS Excel).

3. Results and Discussions

3.1. Characteristics of Lake and Reservoir Subsets

Our data set for P retention covered wide ranges of geographical, morphological, hydrological, and P loading conditions. Significant differences existed between the lake and reservoir subsets (Table I). Geographically, reservoirs were generally located on lower latitudes than lakes. Mean depth distribution was similar for both types of water bodies, except for the deepest category (>50 m) in which there were hardly any reservoirs. Water residence time was markedly shorter and water load higher in reservoirs than in lakes, which is in concordance with general trend (Straškraba, Tundisi, & Duncan, 1993). The P concentrations in the input were higher in reservoirs, apparently because reservoirs have often been built in densely populated and intensively used catchments. The P sedimentation coefficients σ and v were higher in reservoirs.

The results of a correlation analysis of the P retention characteristics and their potential explanatory variables can be summarised like this:

(a) Geographical location was non-significant for P retention both in lakes and reservoirs.

(b) $[P_{in}]$ was positively correlated with the P retention characteristics (R: $P<0.001$; σ: $P<0.001$; v:$P<0.05$), but only for reservoirs. The non-existence of this type of correlations for lakes was caused by a group of lakes in our data set with high $[P_{in}]$ but very small P retention (Figure 1a). Most lakes from this group belonged to a type of lakes with high internal P loading like the lakes Norrviken, Geneva, and Hylke (Sas, 1989). The dependence of P retention on $[P_{in}]$ has been recognised and used in P retention modelling in lakes and reservoirs since the beginning of 1980s (Frisk, Niemi, & Kinnunen, 1980; Kennedy, 1999; OECD, 1982).

(c) Strong inter-relationship existed among z, τ, and σ, which can be seen by comparing Figures 1b-d. This fact opens the opportunity for modelling P retention in alternative ways provided that these inter-correlations are correctly described. For example, we can mention two different functional dependences in the classic models. First, the models derived from Equation (2) (Chapra, 1975; Vollenweider, 1975) include the hyperbolic relationship of σ on $\frac{1}{z}$ that can be seen also in the scatter plot in Figure 1c. Second, the model of Larsen and Mercier (1976) and Vollenweider (1976) is derived from

TABLE I

Medians, minimum–maximum ranges (in parenthesis), and significance of difference between means for lakes and reservoirs

	Latitude (°)	*z* (m)	τ (year)	q_{w} (m year^{-1})	[P$_{\mathrm{in}}$] (μg l^{-1})	[P$_{\mathrm{o}}$] (μg l^{-1})	*R*	*σ* (year^{-1})	*v* (m year^{-1})
Lakes	49	12	1.3	13	38	17	0.46	0.9	12
(N=93)	(43–61)	(0.7–190)	(0.012–56)	(0.7–374)	(4–2153)	(3–1421)	(0.02–0.96)	(0.06–34)	(0.1–244)
Reservoirs	39	8	0.2	48	91	48	0.43	4.4	36
(N=119)	(26–52)	(1.1–58	(0.004–6)	(1.7–1181)	(13–2509)	(8–2077)	(0.01–0.99)	(0.05–403)	(2–1008)
Dif.$^{+}$	***	**	***	***	***	***	ns	***	***

$^{+}$, Dif. – results of the two-sample *t*-test assuming unequal variances: **$P<0.01$; ***$P<0.001$; *ns* non-significant

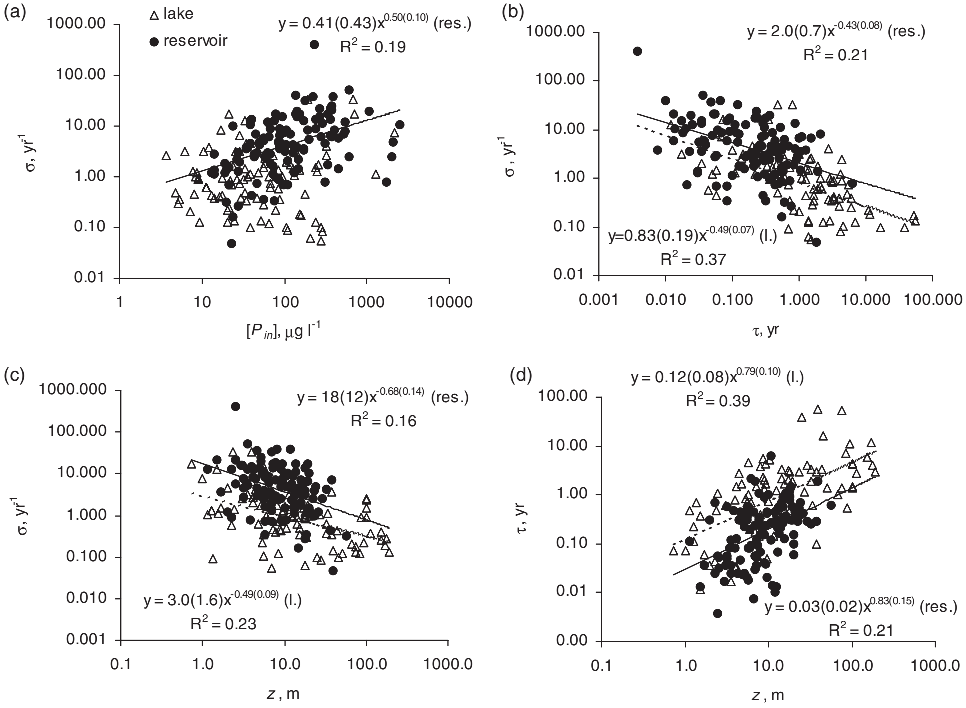


Figure 1. Selected relationships between P sedimentation coefficient (σ), input P concentration [P_{in}], water residence time τ, and mean depth (z) for lake (*open triangles* and *dashed line*) and reservoir (*full circles* and *full line*) subsets. Regression equations contain standard error of parameter estimates in parenthesis.

Equation (1) by substitution of σ by its dependence on τ, i.e., $\sigma = \frac{1}{\sqrt{\tau}}$, to give the formulation of retention coefficient:

$$R = \frac{\sqrt{\tau}}{1 + \sqrt{\tau}}. \tag{3}$$

Interestingly, our lake subset of P retention data gave almost exactly the same parameters for the relationship between τ and σ (i.e., $\sigma=0.83\tau^{-0.49}$; Figure 1b) as in the original paper of Mercier and Larsen (1976) (cf. relationship (7): $\sigma=0.761\tau^{-0.472}$).

(d) The relationships between z, τ, and σ ($P<0.05$) differed significantly in parameters between the lake and reservoir subsets (Figure 1b-d), and we consider these differences as the key point for explaining the difference in P retention between lakes and reservoirs. The differences in P retention seem to derive from the different relationships between τ and z in lakes and reservoirs (Figure 1d). Water residence time is on average 3.3–4 times longer in lakes than in reservoirs with similar depth (as calculated for the range of depth between 1 and 100 m with the regression equations in Figure 1d). This difference can have limnological consequences with implications also for P-retention. Higher flow at a similar depth in reservoirs implies that reservoirs have less stable as well as shorter periods of thermal stratification, which can be further augmented by the fact that outlets of reservoirs are often located near the bottom. Higher inflow and less stable stratification means that more dissolved oxygen is available at the water-sediment interface in the hypolimnion of reservoirs than in lakes, and thus sediments in reservoirs are on average more oxygenated and consequently have larger capacity for P-binding and are less prone to P release than sediments in lakes.

3.2. EVALUATION OF MODELS

A comparison of R measured and predicted by representatives of various types of models from the literature is presented in Table II. A relatively high error of prediction can be seen with all models, which conforms to the scatter within the data set. The classic models I to V slightly over-predicted P-retention in lakes (on average by 8%–18%) except for the model of Prairie (1989) that gave a lower mean value (−9%). P-retention in reservoirs was significantly underestimated (by 9%–36%), except for the model OECD (1982) that gave higher results (+11%). The models based on the dependence of σ as a function of $\tau^{-0.5}$ (i.e., models I and III) showed lower absolute mean error (AME) for both lakes and reservoirs if compared with the models that use the negative hyperbolic dependence of σ on depth (i.e., $\sigma = \frac{v}{z}$; models II, IV, and V). A relatively small difference in results for lakes and reservoirs and a low prediction error had model III (i.e., the general equation of OECD, 1982). This model includes also the dependence of P-retention on $[P_{in}]$, which apparently compensated the differences between lakes and reservoirs in the relationships among σ, τ, and z. This small comparison of

TABLE II

Average measured R (R_{meas}) and differences between averages of predicted R (R_{model}) and R_{meas} with absolute mean error of individual predictions in parenthesis for all data and for subsets of lakes and reservoirs using models I to V^{+}

Data set	$R_{meas} \times$ 100	$(R_{model} - R_{meas}) \times 100$						
		I	II	III	IV	V	VI	VII
all data	45	−6(18)	−5(21)	7(17)	1(21)	−10(20)	7(19)	0(16)
lakes	46	3(15)	7(20)	8(17)	6(19)	−4(17)	16(21)	4(16)
reservoirs	45	−14(21)	−15(22)	5(18)	−4(23)	−16(23)	0(18)	−4(17)

$^{+}$, I: $R = \tau^{0.5}/(1 + \tau^{0.5})$ (Larsen & Mercier, 1976; Vollenweiver, 1976); II: $R = 16/(16 + q_w)$ (Chapra, 1975); III: $R = 1 - 1.55/[P_{in}]([P_{in}]/(1+\tau^{0.5}))^{0.82}$ (OECD, 1982); IV: $R = 15/(18 + q_w)$ (Nürnberg, 1984); V: $R = (0.25 + 0.18\tau)/(1 + 0.18\tau)$ (Prairie, 1989); VI: $R = 1.84\tau^{0.5}/(1 + 1.84\tau^{0.5}).(1 + 1.84\tau^{0.5})$ (this study); VII: $R = 1 - 1.43/[P_{in}]([P_{in}]/(1+\tau^{0.5}))^{0.88}$ (this study).

diverse types of models indicated that (a) P-retention in reservoirs has to be predicted by differently parametrised models in comparison with models for lakes if these models are based only on hydrological and morphological variables (i.e., τ and z) and (b) a general model for both lakes and reservoirs must include other variables like inflow P concentration.

These results described above encouraged us to proceed in selecting and calibrating the best suitable P-retention models for our dataset in two ways.

Firstly, we developed a simple model for reservoirs only. For this purpose we adjusted the Vollenweider/Larsen–Mercier model, i.e., Equation (3), to fit the dependence of σ on τ according to Figure 1b in the form of

$$R = \frac{a\sqrt{\tau}}{1 + a\sqrt{\tau}}. \tag{4}$$

The optimised value of coefficient a for the reservoir subset was 1.84, and lied within the confidence interval of the regression equation in Figure 1b. Compared with the classic models, this model gave the lowest prediction error (Table II). However, it is clear that it cannot be used in lakes because of highly over-estimated retention results.

Secondly, in order to set up a general model for both lakes and reservoirs in our entire dataset we optimised parameters of the OECD model (OECD, 1982):

$$R = 1 - \frac{a}{[\mathrm{P}_{\mathrm{in}}]}\left(\frac{[\mathrm{P}_{\mathrm{in}}]}{1 + \sqrt{\tau}}\right)^{b}. \tag{5}$$

The optimised values for parameters a and b were 1.43 and 0.88, respectively. This model only slightly over-predicted or under-predicted the average values of R in lakes or reservoirs, respectively (model VII in Table II). The prediction error was for reservoirs the best of all the tested models and for lakes differed only by 0.01 from that obtained with the Vollenweider/Larsen–Mercier model.

4. Conclusions

We can conclude with a general statement as in similar studies before that simple empirical P retention models can be useful management and research tools if the limitations of the models are recognised. The P retention models for reservoirs were developed in this study from data covering a broad geographic area and a wide range of limnological conditions. The developed models should be applied with caution, however, to water bodies not being in steady-state conditions. The models probably will work equally well throughout the whole temperate region, but they should be tested before being used in other areas of the world.

Acknowledgements

This study was supported by the EU project EUROHARP, no. EVK1-CT-2001-00096, the Grant Agency of the AS CR, project no. A3017301, and partly by the projects AS CR no. 1QS600170504 and MSM 6007665801. We are grateful Dr Gertrud K. Nürnberg for the help with collecting the P retention data from lakes.

References

Chapra, S. C. (1975). Comment on 'An empirical method of estimating the retention of phosphorus in lakes', by W. B. Kirchner and P. J. Dillon. *Water Resources Research, 2*, 1033–1034.

Dillon, P. J., & Rigler, F. H. (1974). A test of a simple nutrient budget model predicting the phosphorus concentration in lake water. *Journal of the Fisheries Research Board of Canada, 31*, 1771–1778.

Frisk, T., Niemi, J. S., & Kinnunen, K. A. I. (1980). Comparison of statistical phosphorus-retention models. *Ecological Modelling, 12*, 11–27.

Kennedy, R. H. (1999). Basin-wide considerations for water quality management: Importance of phosphorus retention by reservoirs. *International Review of Hydrobiology, 84*, 557–566.

Larsen, D. P., & Mercier, H. T. (1976). Phosphorus retention capacity in lakes. *Journal of the Fisheries Research Board of Canada, 33*, 1742–1750.

Nürnberg, G. K. (1984). The prediction of internal phosphorus load in lakes with anoxic hypolimia. *Limnology and Oceanography, 29*, 111–124.

Nürnberg, G. K., & LaZerte, B. D. (2004). Modeling the effect of development on internal phosphorus load in nutrient-poor lakes. *Water Resources Research, 40*, art. no. w01105 (Jan 27).

OECD (1982). *Eutrophication of Waters: Monitoring, Assessment and Control*. Paris: OECD.

Prairie, Y. T. (1989). Statistical models for the estimation of net phosphorus sedimentation in lakes. *Aquatic Sciences, 51*, 192–210.

Sas, H. (1989). *Lake Restoration by Reduction of Nutrient Loading: Expectations, Experiences, Extrapolations*. Richarz: Academia Verlag.

Straškraba, M., Tundisi, J. G., & Duncan, A. (1993). State-of-the-art of reservoir limnology and water quality management. In M. Straškraba, J. G. Tundisi & A. Duncan (Eds.), *Comparative Reservoir Limnology and Water Quality Management* (pp. 113–188). Dordrecht: Kluwer.

Vollenweider, R. A. (1969). Möglichkeiten und Grenzen elementarer Modelle der Stoffbilanz von Seen. *Archiv fuÉr Hydrologie, 66*, 1–36.

Vollenweider, R. A. (1975). Input–output models with special reference to the phosphorus loading concept in limnology. *Schweizerische Zeitschrift Hydrobiologie, 37*, 53–84.

Vollenweider, R. A. (1976). Advances in defining critical loading levels for phosphorus in lake eutrophication. *Memorie dell'Istituto Italiano di Idrobiologia, 33*, 53–83.

Water, Air, and Soil Pollution: Focus (2006) **6:** 131–139
DOI: 10.1007/s11267-006-9033-6

RELATIONSHIP BETWEEN THE SEDIMENT GEOCHEMISTRY AND PHOSPHORUS FLUXES IN A GREAT LAKES COASTAL MARSH, COOTES PARADISE, ON, CANADA

T. MAYER[1,*], F. ROSA[1], R. MAYER[2] and M. CHARLTON[1]
[1]Environment Canada, 867 Lakeshore Rd., Burlington, ON L7R 4A6, Canada
[2]74 Resurrection Rd., Toronto M9A 5H1, Canada
([*]author for correspondence, e-mail: tanya.mayer@ec.gc.ca; phone: +1-905-3364506; fax: +1-905-3366430)

(Received 1 March 2006; accepted 7 June 2006)

Abstract. Cootes Paradise is a coastal wetland, adjacent to Hamilton Harbour at the western tip of Lake Ontario. The marsh has been considerably degraded due to the excessive sediment and nutrient input from sewage treatment plants (STPs), marsh tributaries and Combined Sewer Overflows (CSOs). Although there has been reduction in nutrient loadings from external sources, high nutrient levels, and a prolific algal growth remain a problem in Cootes Paradise. To assess the importance of external *versus* internal nutrient loadings to the marsh, nutrient fluxes from sediments were estimated using porewater profiles at three locations from 2001 and five additional sites from 2002. The fluxes varied between 0.27 and 5.25 mg P m^{-2} day^{-1}, with sites receiving outfalls of STP and CSO having highest fluxes (~5 mg P m^{-2} day^{-1}). Mean phosphorus release rate of 2.02 mg P m^{-2} day^{-1} was calculated from the spatial distribution of the non-apatite inorganic phosphorus (NAI-P) in sediments, employing a relationship between the NAI-P and P fluxes. The results confirm that sediment P geochemistry is important in regulating the P pool in porewater which, consequently, governs the P fluxes from sediments.

Keywords: phosphorus, fluxes, sediments, porewater, wetlands

1. Introduction

Cootes Paradise, a 250-ha coastal wetland at the western tip of Lake Ontario, has been considerably degraded due to excessive sediment and nutrient inputs from Sewage Treatment Plant (STP) and Combined Sewer Overflows (CSOs). Reduction of nutrient loadings from point sources through upgrades in Sewage Treatment Plant (STP) discharging into the marsh and reduction in Combined Sewer Overflow (CSO) events were major initiatives in the restoration efforts. Although some improvement in water quality has been achieved, the marsh has not fully recovered and restoration efforts remain a challenge.

Phosphorus is a major factor in the excessive and deleterious fertilization of lakes and remains a principal subject of the water quality control in many freshwater environments. Extensive research has revealed that sediments play a major role in sequestering phosphorus from the water column (Gunnars &

Blomqvist, 1997; Val Klump, Edgington, Sager, & Robertson, 1997). However, whether sediments act as a P source or sink is determined by sediment composition and limnological conditions (Caraco, Cole, & Likens, 1991; Hupfer & Uhlmann, 1991; Ostrofsky, Osborne, & Zebulske, 1989). The extent to which sediments recycle P to overlying water is critical for controlling eutrophication of the lakes. To assess the importance of P loadings from sediments in Cootes Paradise, an investigation into a sediment P release was initiated in 2001. Three sites, representative of different sedimentary environments were studied. The results revealed substantial differences in nutrient fluxes between the investigated sites (Mayer, Rosa, & Charlton, 2005) and suggested a relationship between nutrient fluxes and sediment geochemistry. However, because the earlier results were based on a limited number of sites, a larger data base was essential to confirm the relationship. A large spatial grid of surficial sediments had to be surveyed to provide meaningful estimates of nutrient regeneration from sediments. The objective of this study was to determine the relationship between the porewater composition and sediment geochemistry and using this relationship calculate the P release rates from the total contributing area of the marsh.

2. Materials and Methods

2.1. FIELD PROCEDURES AND LABORATORY ANALYSIS

A detailed survey of nutrient fluxes from Cootes Paradise sediments was conducted in 2001 at three sites (Mayer et al., 2005), namely, West Pond (WP), Boat House (BH), and at the mouth of the Chedoke Creek (CC). Recognizing the limitations of three sites covering a large area of the marsh, five additional sites (Figure 1a) covering the marsh diverse zones, were sampled in 2002. Westdale Cut, where sites C and D are located, has been a receptor of the CSO until 2000. At each site, sediment porewater profiles were obtained by deployment of porewater samplers and sediment cores were collected. Porewater was sampled using the acrylic porewater samplers (peepers) fitted with the inert 0.45-μm polysulfone membrane (Gelman Scientific, Inc.). The peepers were filled with oxygen-free double distilled water. Prior to deployment, the samplers were kept for several days in oxygen-free water. Details concerning their preparation are given in Azcue and Rosa (1996). On July 25, 2002, several assembled samplers were placed in the sediments and allowed to equilibrate for two weeks at each sampling location. After retrieval, samples were withdrawn from each cell immediately and transferred to plastic vials. The samples were preserved with 10 μl of 7% H_2SO_4 and stored at 4 °C until analyses. An ascorbic acid technique (Environment Canada Protocol, 1979) was used to determine soluble reactive phosphorus (SRP), which includes mostly $H_2PO_4^-$ and HPO_4^{2-} species, denoted further as PO_4–P. The cores were sliced into 1-cm sections to a depth of 20 cm

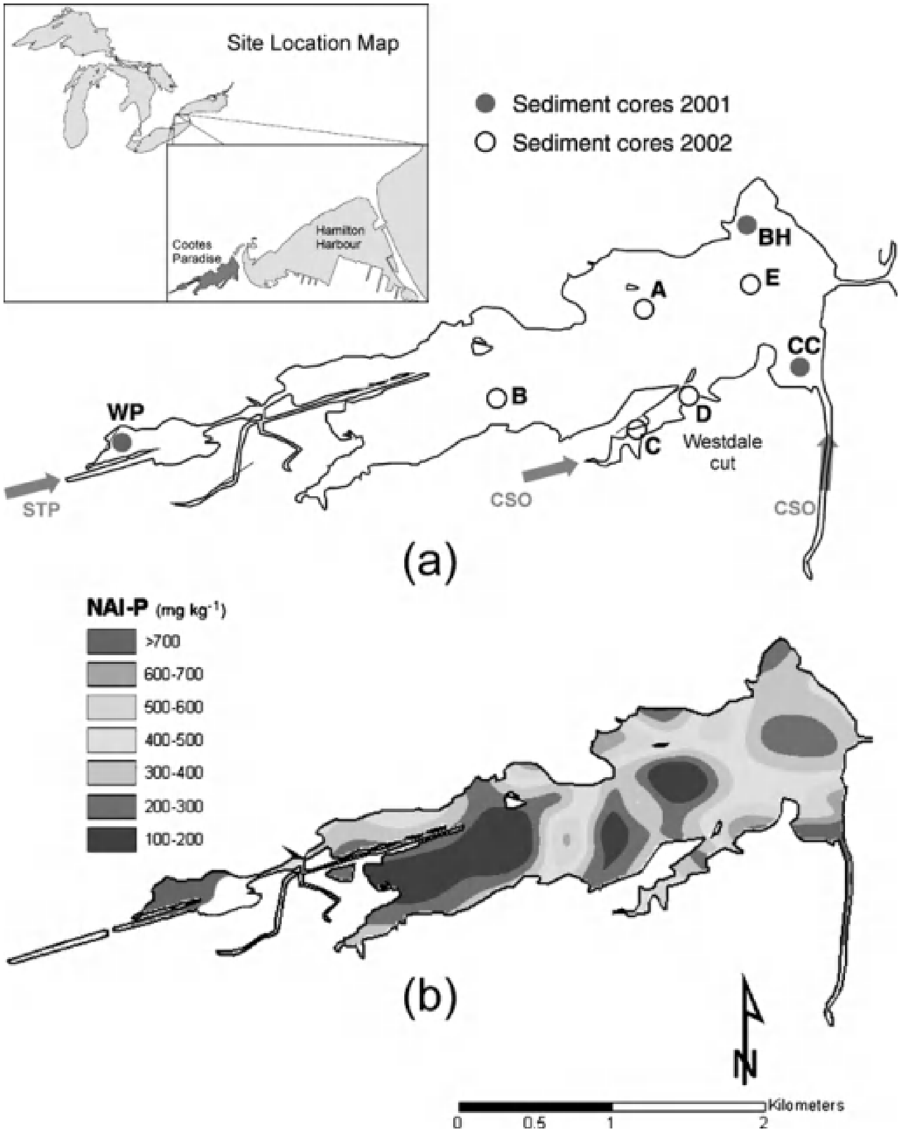


Figure 1. (a) Locations of porewater and sediment core sampling sites from years 2001 and 2002, showing input from STP and CSOs. Inset shows the location of Cootes Paradise relative to Hamilton Harbour and the Great Lakes. (b) Spatial distribution of the NAI-P concentrations in surficial sediments of Cootes Paradise.

and into 2-cm sections further down. The sectioned sediments were frozen and subsequently freeze-dried. In addition to core samples, a large grid (more than 50) of surficial sediments was sampled using a Mini Shipek grab sampler. The top 3 cm of sediment was collected into a polystyrene vial for analysis from each site. The collected sediment was treated in the same way as core sediment samples.

Homogenized sediments were used for all analyses. Water content and porosity of sediment was determined gravimetrically. Loss on ignition (LOI) was determined gravimetrically after igniting the dry sediment at 550 °C in a muffle furnace for 2 h. Total phosphorus (TP) concentrations were determined on ignited sediments using a 16-h 1 N HCl extraction. Forms of P, non-apatite inorganic phosphorus (NAI-P) and apatite-P (A-P) were determined by sequential extraction of Williams, Jaquet, and Thomas (1976). Organic P (O-P) was calculated by difference between the TP and the sum of the NAI-P and A-P concentrations. Coefficients of variation determined from six replicate analyses of standard Lake Ontario sediments for all P forms were typically less than 10%.

2.2. Spatial Analysis

The analysis of spatial distribution of phosphorus in sediments was done utilizing ESRI ArcView 8.3™ geographic information system (GIS) software. The data were generated from the NAI-P concentrations of surficial sediments collected from sites whose locations in Cootes Paradise were determined using a Global Positioning System (GPS). Replicate samples were used for the NAI-P analyses and their means were used for the spatial analyses. The NAI-P concentrations were put into the GIS as attributes of each of the sampling points. The concentration values were used to create interpolated concentration–isolines (contours) for Cootes Paradise. The spline interpolation function was chosen because of the sampling pattern (irregular) and the resulting smooth surface which passes through all the data points. Coloured regions between isolines (Figure 1b) illustrate areas of concentration within a specified range. The surface area of each concentration range was calculated in the GIS (Table I).

TABLE I

Mean fluxes corresponding to discrete NAI-P concentration ranges

NAI-P range (mg kg^{-1})	Average [NAI-P] (mg kg^{-1})	F (mg P m^{-2} day^{-1})	Percentage of total area (%)	Area (m^2)
100–200	143	0.28	15.49	371,827
200–300	260	1.15	21.63	519,004
300–400	349	1.80	27.01	648,135
400–500	449	2.55	17.03	408,717
500–600	535	3.18	8.07	193,658
600–700	626	3.86	3.87	92,807
700–800	754	4.80	2.31	55,452
900–1,000	965	6.37	4.00	110,400

3. Results and Discussion

3.1. POREWATER AND SEDIMENT GEOCHEMISTRY

The highest porewater PO_4–P concentrations (maximum ~3 mg l^{-1}) were measured at the edge of Westdale Cut, site C, followed by the Westdale Cut site D (maximum 2 mg l^{-1}, Figure 2). These concentrations are lower than 7.5 and 5 mg P l^{-1} from the West Pond and Chedoke Creek sites, respectively (Mayer et al., 2005), but higher than porewater PO_4–P concentrations at the open water sites (sites A, B, E).

Three operationally defined forms of phosphorus (Mayer et al., 2005), namely NAI-P, A-P and O-P were determined in surficial and core sediments. The NAI-P is generally considered to be a measure of the maximum particulate P that can be rendered soluble during diagenesis (Logan, Oloya, & Yaksich, 1979) and includes P present in the porewater. Sediments from the Westdale Cut (sites C and D) had the highest TP concentrations (977–1,160 and 911–981 mg kg^{-1}, respectively). These sediments had also the highest content of organic matter (LOI) and porosity. The NAI-P concentrations in the top 4 cm varied between 140 and 676 mg kg^{-1}, with site C having the largest portion (54%) of the sedimentary TP in this fraction. The percentage of the sedimentary P in the NAI-P fraction at this site was twice to three times higher than that in open water sediments (18%–28%). Concurrently, the A-P fraction of sedimentary TP (30%) from site C was only about half of that present in sediments from open water sites (64%), indicating minor input of detrital terrigenous P to Westdale Cut. The LOI content of sediments and apportionment of sedimentary P indicate that much of the P deposited in this inlet is rapidly mineralized within the sediment column and may be readily recycled back into the water column. Sediments with highest TP concentrations had also the greatest proportion of the NAI-P and the largest dissolved P pool.

3.2. NUTRIENT FLUXES

Chemical exchange between sediment porewater and the overlying water is an important pathway for transport of nutrients. Whether sediments act as nutrient

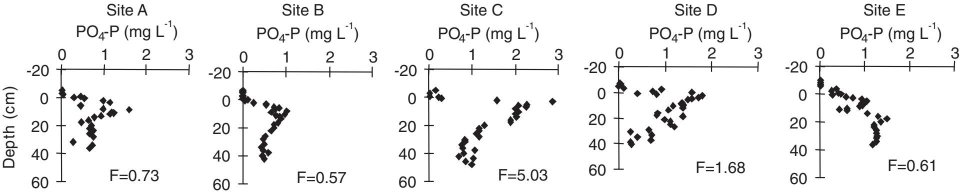


Figure 2. PO_4–P porewater profiles and calculated phosphorus fluxes (*F*) from five sites investigated in 2002. The units of fluxes are mg P m^{-2} day^{-1}.

source or sink depends on the sediment composition and limnological conditions. Studies of shallow lakes (Auer, Penn, Effler, & Van Orman, 1994; Phillips, Jackson, Bennett, & Chilvers, 1994; Sondergaard, Kristensen, & Jeppesen, 1993) have shown that sediments may be an important source of phosphorus to the overlying water, with the P release as high as 278 mg P m^{-2} day^{-1}.

A 1-D diffusion model, $F=-\varphi D_S(dC/dZ)_{Z=0}$, was used to estimate the P fluxes across the sediment–water interface; where, F is the diffusive flux of the porewater solute, φ is the porosity of sediments, C is the solute concentration and Z is the space coordinate. D_S is a diffusion coefficient estimated from free ion diffusion coefficient using an empirical relationship, $D_S=\varphi^n D$, where n is a constant ($n=2$, Lerman, 1979), and D is a diffusion coefficient of ion at infinite dilution (Li & Gregory, 1974). The solute concentration gradients $(dC/dZ)_{Z=0}$ were found by fitting the porewater data to a linear regression equation (Mayer et al., 2005) considering the solute concentrations between the depths 0 and 5 cm ($n=5$) below the sediment surface ($Z=0$ at the sediment–water interface). The goodness of fit (R^2) varied between 0.6862 and 0.9075 for the five sites investigated. The rationale for the method selection and the assumptions made for the calculation are presented in Mayer et al. (2005).

The calculated upward diffusive fluxes, F (0.57–5.03 mg P m^{-2} day^{-1}, Figure 2) from the locations sampled in 2002 are highest at the edge of the Westdale Cut (site C), followed by the site D located at the mouth of this inlet, where limnology is influenced by open water processes. The phosphorus release rates, calculated as diffusional flux F, are consistent with the rates estimated in our earlier study (0.27 and 5.25 mg P m^{-2} day^{-1}), but are noticeably lower than the laboratory estimates 1.67 to 28.8 mg P m^{-2} day^{-1} of Kelton, Chow-Fraser, and Jordan (2004) from the same area. Our results compare favorably with estimated release rates (0.10–7.01 mg P m^{-2} day^{-1}) for sediments with similar reductant-soluble P concentrations (Nurnberg, 1988) and compare exceptionally well with release rates 0.34–4.93 mg P m^{-2} day^{-1} of Val Klump et al. (1997) for Green Bay sediments, estimated by similar method.

Our initial study (Mayer et al., 2005) suggested that the magnitude of P fluxes from sediments is related to sedimentary phosphorus, particularly to the NAI-P. As only three sites were sampled in our previous study, we had insufficient data to prove the validity of the relationship between these two parameters. However, additional data confirmed highly significant relationship ($R^2=0.867$, $P<0.001$) between the sediment NAI-P and phosphorus fluxes, F (Figure 3), indicating that the NAI-P is a suitable surrogate for the P fluxes from sediments. The regression of all data (2001 and 2002) resulted in linear relationship (Figure 3), described by the equation: $F = 0.0074\ [\text{NAI-P}] - 0.7765$.

This relationship was employed to calculate the overall P flux from sediments in the main body of Cootes Paradise. Average NAI-P concentrations, obtained from field data for each concentration range (Table I) were used to calculate the fluxes corresponding to respective NAI-P concentration ranges (Table I). The

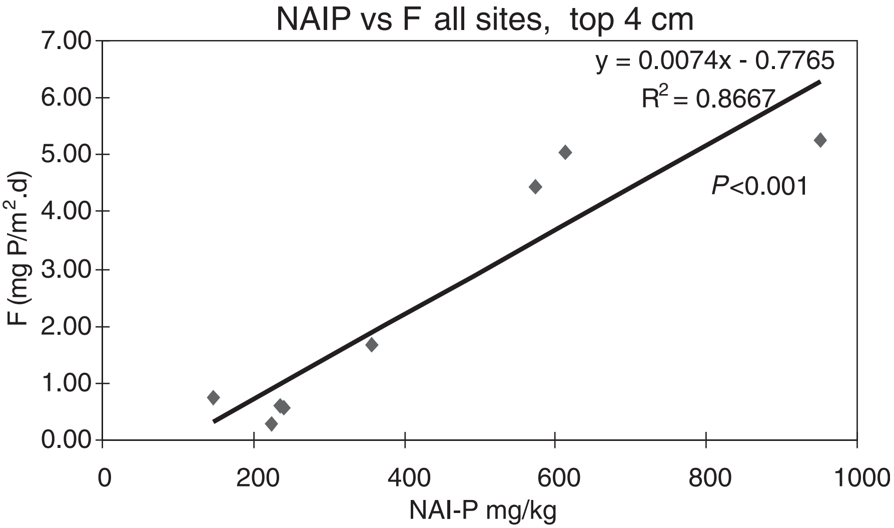


Figure 3. Relationship between the sedimentary NAI-P and phosphorus fluxes (*F*).

average P release rate 2.02 mg P m^{-2} day^{-1} was calculated as an areally-weighted mean of fluxes corresponding to tabulated NAI-P ranges (Table I). This value is comparable with an average sediment P release rate of 1.33 mg P m^{-2} day^{-1}, estimated by Nicholls (1999) from a mass balance calculation at the Bay of Quinte, a shallow eutrophic system, but is slightly lower than the time-weighted annual average P release rate of 9.7 mg P m^{-2} day^{-1} estimated by Penn et al. (2000) using intact sediment cores from the hypereutrophic Onondaga Lake.

Using the calculated P release rates and an average water depth of 1 m, a cumulative P release to 1-m-deep water column over 100 days of summer varies between 57 and 503 μg l^{-1}, with the greatest release in the inlets such as Westdale Cut and West Pond (Mayer et al., 2005). This corresponds to 0.57–5.03 μg l^{-1} P daily increase in 1-m water column during the highly productive summer time, when much of it is rapidly utilized by algae and bacteria, as seen from the high TP concentrations in water (55–275 μg l^{-1}, average 130 μg l^{-1}). On an annual basis, the release rates would likely be somewhat lower, as our calculations are based on summer conditions, when the water temperature was high and the P release is enhanced due to increased rates of respiration, microbially mediated mineralization of OP and greater sediment oxygen depletion.

The aerial loadings from sediments were estimated as a product of flux and corresponding area, determined from the GIS (Table I). The sum of these loadings 4.85 kg day^{-1} represents the total diffusive P loadings from sediments in the main body of the marsh.

The net internal loadings of P to the water column would be somewhat lower due to the particulate phosphorus flux to sediments. The calculated loadings from sediments of the main body of Cootes Paradise are only slightly lower than the Dundas STP loading of 5.74 kg P day^{-1}, calculated from the mean May–September loadings. The magnitude of internal loading is of concern as sediments may act as a nutrient source even after reduction of nutrient loadings from external sources and hinder the recovery of Cootes Paradise that would further delay the restoration efforts.

4. Summary and Conclusions

Although Cootes Paradise shows clear signs of degradation, it remains an important fish habitat at the western end of Lake Ontario. Phosphorus and sediment loadings are the overwhelming causes for degraded water quality in the marsh. The estimate of the sedimentary P input is essential to better target the remedial measures. The present study provides an estimate of the mean sedimentary P release rate based upon the survey of marsh sediments and relation established between the sediment NAI-P concentrations and P fluxes, obtained from 2001 and 2002 data. The phosphorus fluxes from five sites investigated in 2002 vary between 0.57 and 5.03 mg P m^{-2} day^{-1}, and the calculated mean sedimentary P release rate, estimated on the aerial basis using the GIS generated map, is 2.02 mg P m^{-2} day^{-1}. The results show that sediments are large reservoirs of phosphorus that may be an important source of nutrients to overlying water even after the reduction of the external loadings, making the marsh more resilient to restoration.

Acknowledgements

The authors acknowledge the assistance of C. Donnelly, S. Jabaji, A. Lawrence, D. Walsh and J. Ottmann. The input of D. Morin, C. Bakelaar and M. Walton to the GIS spatial analyses and the logistical support of T. Theÿsmeÿer are much appreciated. This work was supported by the Environment Canada, Ministry of Environment and the Regional Municipality of Hamilton Wentworth.

References

Auer, M. T., Penn, M. R., Effler, S. W., & Van Orman, E. L. (1994). Predicting the sediment response to lake restoration efforts. *Lake and Reservoir Management*, *9*, 52.

Azcue, J. M., & Rosa, F. (1996). Effects of sampling technique on the determination of major ions in sediment porewater. *Water Quality Research Journal of Canada*, *31*, 709–724.

Caraco, N. F., Cole, J. J., & Likens, G. E. (1991). Phosphorus release from anoxic sediments: Lakes that break the rules. *Verhandlungen Internationale Vereinigung für Theoretische und Angewandte Limnologie*, *24*, 2985–2988.

This page intentionally blank

Environment Canada Protocol (1979). *Analytical methods manual*, Inland Waters Directorate, Water Quality Branch, Ottawa, Canada, 340 pp.

Gunnars, A., & Blomqvist, S. (1997). Phosphate exchange across the sediment–water interface when shifting from anoxic conditions an – experimental comparison of freshwater and brackish-marine systems. *Biogeochemistry*, *37*, 203–206.

Hupfer, M., & Uhlmann, D. (1991). Microbially mediated phosphorus exchange across the mud–water interface. *Verhandlungen Internationale Vereinigung für Theoretische und Angewandte Limnologie*, *24*, 2999–3003.

Kelton, N., Chow-Fraser, P., & Jordan, I. (2004). Relationship between sediment phosphorus release rates and characteristics of the benthic microbial community in a hypereutrophic marsh. *Aquatic Ecosystem Health and Management*, *7*, 31–41.

Lerman, A. (1979). Chemical exchange across sediment–water interface. *Annual Review of Earth and Planetary Sciences*, *6*, 281–303.

Li, Y., & Gregory, S. (1974). Diffusion of ions in sea water and in deep-sea sediments. *Geochimica et Cosmochimica Acta*, *38*, 703–714.

Logan, T. J., Oloya, T. O., & Yaksich, S. (1979). Phosphate characteristics and bioavailability of suspended sediments from streams draining into Lake Erie. *Journal of Great Lakes Research*, *5*, 112–123.

Mayer, T., Rosa, F., & Charlton, M. (2005). Effect of sediment geochemistry on the nutrient release rates in Cootes Paradise Marsh, Ontario, Canada. *Aquatic Ecosystem Health and Management*, *8*, 133–145.

Nicholls, K. H. (1999). Effects of temperature and other factors on summer phosphorus in the Inner Bay of Quinte, Lake Ontario: Implication for climate warming. *Journal of Great Lakes Research*, *25*, 250–262.

Nurnberg, G. K. (1988). Prediction of phosphorus release rates from total and reductant soluble phosphorus in anoxic lake sediments. *Canadian Journal of Fisheries and Aquatic Sciences*, *45*, 574–580.

Ostrofsky, M. L., Osborne, D. A., & Zebulske, T. J. (1989). Relationship between anaerobic sediment phosphorus release rates and sedimentary phosphorus species. *Canadian Journal of Fisheries and Aquatic Sciences*, *46*, 416–419.

Penn, M. R., Auer, M. T., Doerr, S. M. Driscoll, C. T., Brooks, C. M., & Effler, S. W. (2000). Seasonality in phosphorus release rates from the sediments of hypereutrophic lake under a matrix of pH and redox conditions. *Canadian Journal of Fisheries and Aquatic Sciences*, *57*, 1033–1041.

Phillips, G. Jackson, R., Bennett, C., & Chilvers, A. (1994). The importance of sediment phosphorus release in the restoration of very shallow lakes (The Norfolk Broads, England) and implications for biomagnification. *Hydrobiologia*, *275/276*, 445–456.

Sondergaard, M., Kristensen, P., & Jeppesen, E. (1993). Eight years of internal phosphorus loading and changes in the sediment phosphorus profile of Lake Sobygaard, Denmark. *Hydrobiology*, *253*, 345–356.

Val Klump, J., Edgington, D. N., Sager, P. E., & Robertson, D. M. (1997). Sedimentary phosphorus cycling and a phosphorus mass balance for the Green Bay (Lake Michigan) ecosystem. *Canadian Journal of Fisheries and Aquatic Sciences*, *54*, 10–26.

Williams, J. D. H., Jaquet, J. M., & Thomas, R. L. (1976). Forms of phosphorus in the surficial sediments of Lake Erie. *Journal of the Fisheries Research Board of Canada*, *33*, 413–429.

Water, Air, and Soil Pollution: Focus (2006) **6:** 141–149
DOI: 10.1007/s11267-006-9034-5

RECENT SEDIMENT OF LAKE BLED (NW SLOVENIA): SEDIMENTOLOGICAL AND GEOCHEMICAL PROPERTIES

B. OGORELEC[1,*], B. BOLE[1], J. LEONIDAKIS[2], B. CERMELJ[3], M. MIŠIČ[1] and J. FAGANELI[3]
[1] *Geological Survey of Slovenia, Dimičeva 14 1000 Ljubljana, Slovenia*
[2] *PETROLTECNICA SRL, Rimini, Italy*
[3] *Marine Biological Station, National Institute of Biology, Piran, Slovenia*
*(*author for correspondence, e-mail: bojan.ogorelec@geo-zs.si; phone: +386-1-2809700; fax: +386-1-2809753)*

Abstract. Sediment cores collected in eutrophic subalpine Lake Bled (NW Slovenia) were analyzed sedimentologically in terms of grain size, mineralogy and sedimentation rates, and geochemically in terms of metals and nutrients. Surficial sediment is composed of dark gyttya type clayey silt with 5%–10% of organic matter. The sediment below is fine laminated and composed of homogenous silt and clayey silt: Mineralogically, low-Mg calcite prevails, followed by dolomite, quartz, partially of diatomaceous origin, and feldspar. Clay minerals are composed of muscovite/illite and chlorite. Authigenic minerals are pyrite and 'lake chalk' (low-Mg calcite). Lake sediment is especially polluted by Pb, Zn and P. Higher contents were found in the northwestern and eastern parts due to the particle input by local inflows. Increasing eutrophication and pollution, indicated by Cd, Cu, V, Cr, Co and total N and P enrichment in the top layers of the cores, started almost 100 years B.P., and especially 50 years ago.

Keywords: Julian Alps, lacustrine sediment, Lake Bled, metals, pollution, Slovenia

1. Introduction

Lake Bled (Figure 1) is a typical subalpine lake situated in Julian Alps in the NW part of Slovenia mostly subjected to local pollution sources including traffic, sewage and agriculture. The first systematic research of Bled sediment dates back to the 1970s of the last century (Molnar et al., 1978). Analyzing 15 surficial sediment samples and two short cores they presented basic petrographic and geochemical characteristics of the lake sediment. The age of the studied sediments was determined by palynological methods. The principal objective of their research was to decode the anthropogenic impact, especially the distribution of heavy metals, on Lake Bled due to the closeness of Jesenice steel factory. In this context the contaminated sediments of Moste impoundment on Sava river (Štern & Förstner, 1976) and the nearby uncontaminated oligotrophic Lake Bohinj (Molnar et al., 1978) were also studied. Afterwards, the research was mainly oriented towards formation of authigenic lacustrine limestone sediment in the western part of lake Bled using stable isotopes (Dolenec, Pezdic, Ogorelec, & Misic, 1984) and palynological reconstruction of the lake environment

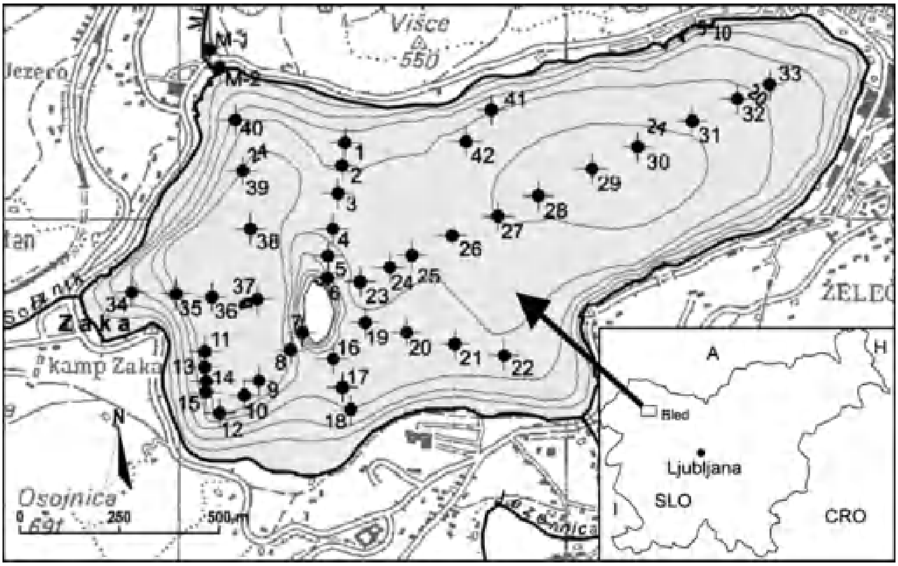


Figure 1. Location of sampling points in Lake Bled (NW Slovenia).

using a 6.7 m deep borehole (Schultze, 1984). The systematic research was continued in the 1980s and 1990s of the last century and focused on organic matter distribution and reactivity (Cermelj et al., 1996; Cermelj & Faganeli, 2003; Lojen, Ogrinc, & Dolenec, 1997, 1999; Muri, 2003; Muri, Cermelj, Faganeli, & Brancelj, 2002), pore water composition (Cermelj et al., 1996; Ogrinc, Lojen & Faganeli, 1997) and methanogenesis (Lojen et al., 1999; Ogrinc, Lojen, & Faganeli, 2002). The aim of the present study was to investigate the sedimentology, and metal geochemistry and pollution of lake sediments.

2. Study Area

Lake Bled occupies an area of 1.4 km^2 and volume of 26.10^6 m^3. The maximal depths of the western and eastern basins, divided by a small island, are 30.2 and 24.5 m, respectively. Lake Bled is, according to the thermal classification of lakes, a warm dimictic subalpine lake with an anoxic hypolimnion which is developed most of the year below a depth of 15 m (Molnar et al., 1978). The hypolimnion temperature varies between 4 and 8 °C. The input of nutrients causes the eutrophication of the lake as evidenced by the sporadic appearance of blooming algae *Oscillatoria rubescens* (Vrhovsek, Kosi, & Zupan, 1984). The inflows are two small streams, Mišca and Solznik, in the west while the water outflow proceeds through the Jezernica stream to the river Sava. Two amelioration projects were undertaken in the past: a fresh water inflow was diverted from the river Radovna introducing 4.10^6 m^3 of water yearly to the depth of 20 m, and a syphonic pumping of anoxic bottom water from the eastern basin. Hence, the mean water residence time dropped to about 1.1 year. The mean ^{210}Pb and ^{137}Cs recent sedimentation rates are higher in the western basin (2.4 mm year^{-1}) with respect to eastern (1.2 mm year^{-1}) due to the particulate matter inflow by local streams (Cermelj et al., 1996). Comparison with sedimentation rates deduced from palynological analyses, i.e., 1 mm year^{-1} in the western (Molnar et al., 1978) and 0.5 mm year^{-1} (Schultze, 1984) in the eastern basin, revealed about two-fold higher rates which were probably due to higher recent sedimentation and sediment compaction during Holocene. The core basement is from late last glacial period, dated to about 13800 B.P. Sediment is locally inhabited by clams *Anodonta cygnaea* and pelecypod *Planorbis planorbis.*

The oldest rocks in the lake hinterland are limestones, observable on Straža hill, of Permian age (Flügel, Ramovs, & Kochanski-Devidé, 1984). Most of the lake hinterlands and lake island are composed of Anizian dolomite (Buser & Cajhen, 1978). The castle rock is composed of Anizian algal limestone (Flügel, Ramovs, & Bucur, 1994). In the surroundings of Zaka bay, the marl and sandstone of Ladinian age are present while near Rečica a platy limestone with chert nodules of Cretaceous age is observed. The eastern part of Bled town lays on morena, from the Wurm glacial period, closing the lake (Kuscer, 1955). The lacustrine chalk from Zaka bay is also of the last glacial origin (Molnar et al., 1978).

3. Materials and Methods

Forty-two sediment cores, using a Meischner and Rumohr (1974) gravity core sampler, were collected in to study the sedimentological and geochemical properties, and pollution of the lake (Figure 1). The cores were sectioned on 1, 2 and 5 cm intervals. Grain size of sediment was determined by a wet sieving through a 63 μm sieve, while the finer fraction analyzed using Fritsch Analysette 2000 particle size analyzer. The fractions >63 μm were wet sieved through a 100, 200 and 500 μm sieves. Mineralogical analyses of bulk samples and clay fraction were performed using a Philips X-ray diffractometer. For geochemical analyses, the sediment samples were dried, homogenized and sieved through 0.1 mm mesh. The concentrations of Al, Ba, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Na, Ni, Pb, Sr, Va, Zn, Be, La and Mo were, after digestion with HF/HNO3/HCl, determined by ICP-ES. The concentrations of K were determined using AAS. Total C and N were determined using a Carlo Erba CHNS analyzer at 1,020 °C and organic C similarly after acidification with 1 M HCl (Hedges & Stern, 1984). The total P contents were analyzed by extraction with 1 M HCl after ignition at 550 °C (Aspila, Agemian, & Chau, 1976), while organic P by the difference in P contents of HCl extracts before and after ignition of the samples at 550 °C. Statistical

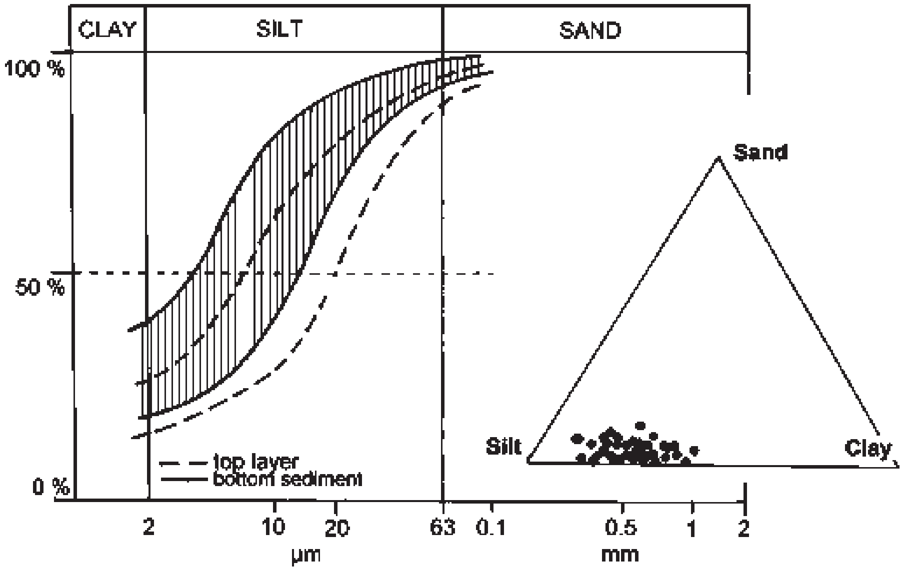


Figure 2. Cumulative curves of grain-size distribution and ternary diagram of Lake Bled sediment samples.

evaluation of data were performed using the Statgraphics Plus 5.0 (Stsc. Inc., USA) statistical programme.

4. Results and Discussion

4.1. SEDIMENTOLOGY

The surficial (2–3 cm deep) sediment is composed of a dark gyttja type clayey silt with 5%–10% organic matter and with a mean grain size of 10–15 µm (Figure 2). The sediment below is more compact with fine laminations (<1 mm). Below a depth of 10 cm is homogenous silt and clayey silt with a mean grain size of 5–10 µm. The content of the clayey fraction varies between 30% and 40% and the fraction >63 µm comprises only 0.5%–1%. In the mineral composition, the carbonate detrital grains prevail (55%–90%) mostly composed of low-Mg calcite (up to 5 mol% of $MgCO_3$) while the dolomite content varies between 6% and 12%. Other minerals are quartz (up to 15%), and feldspars (up to 8%). Among clay minerals (up to 15%), muscovite/illite and chlorite prevail. The quartz is mostly of detrital origin though, in part, is also of diatomaceous provenance. Authigenic pyrite (<3%) is formed in the deepest anoxic parts of the lake. Authigenic ‘lake chalk’ is formed (Dolenec et al., 1984) in the shallow coastal area south of Zaka bay (Figure 1), containing >98% of carbonate (low Mg-calcite) with a mean grain size of about 10 µm. The precipitation of calcite is mediated by the production of benthic macrophytes and phytoplankton.

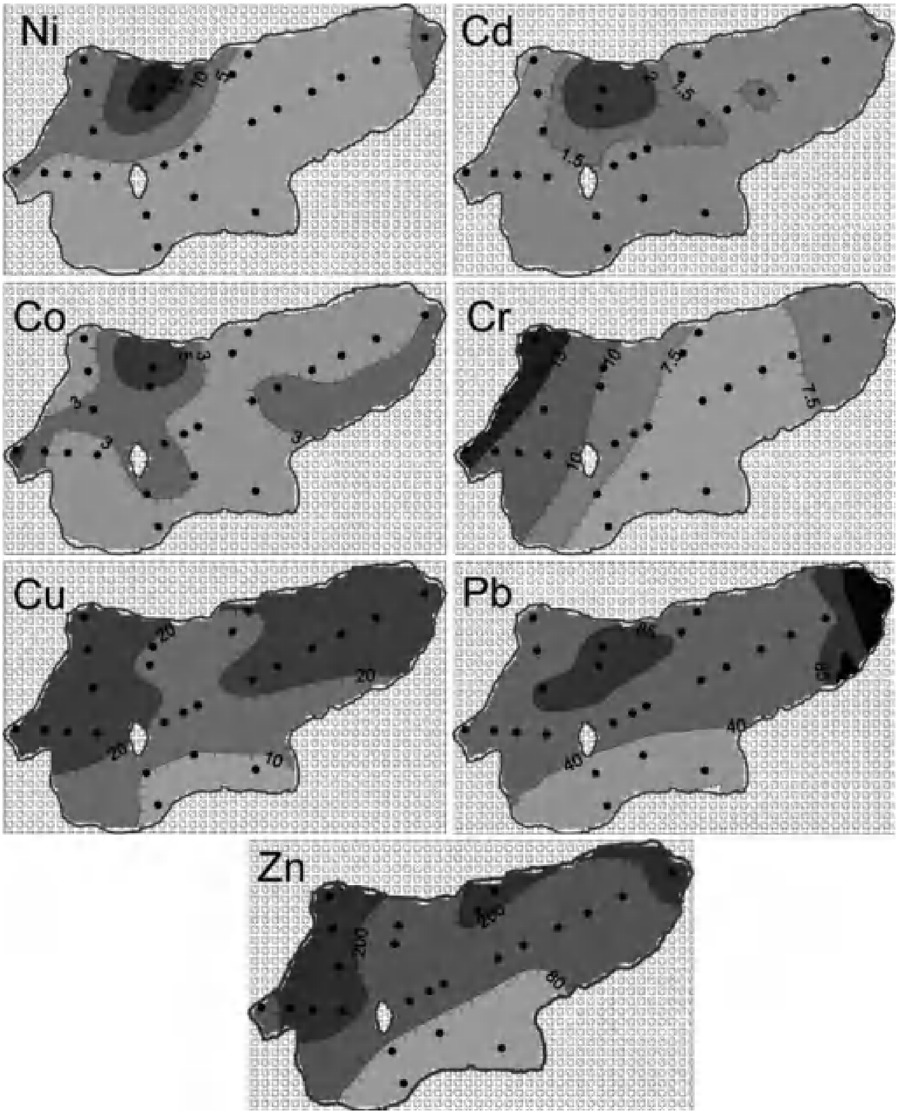


Figure 3. Areal distribution of Ni, Cd, Co, Cr, Pb and Zn (in ppm) in surficial sediment of Lake Bled.

4.2. GEOCHEMISTRY AND POLLUTION

The geochemical properties and contamination (pollution) of recent lake sediment were studied in terms of the occurrence and origin of Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Na, K, Li, Mg, Mn, Ni, Pb, Sr, V, Zn, Be, La, organic C, and total P (Table I). The areal distribution (Figure 3) of studied elements shows higher concentrations in the northwestern and eastern lake sediment samples due to the input of detrital

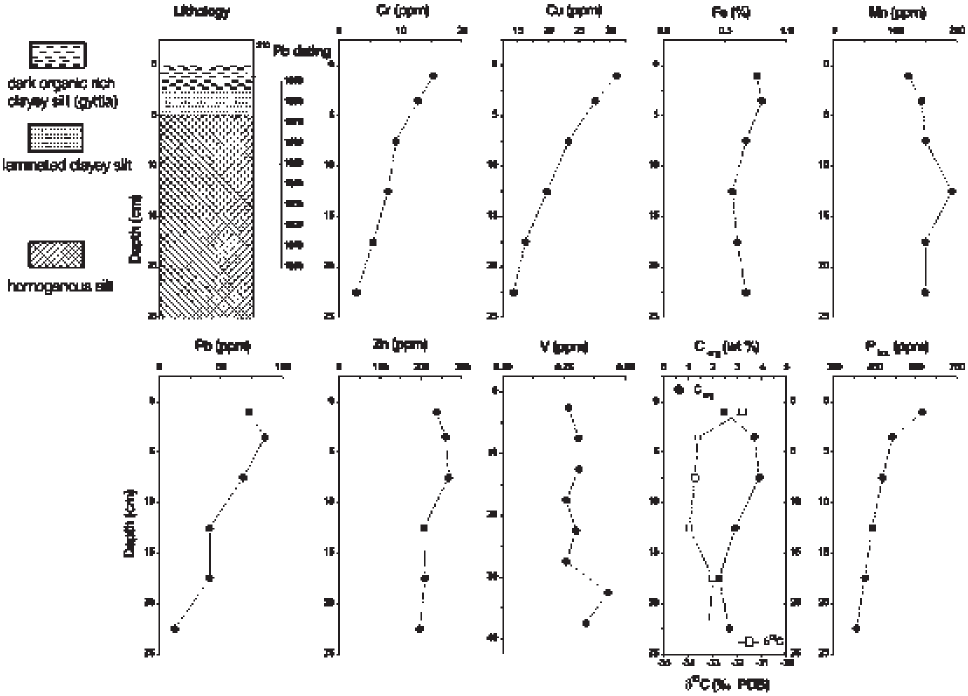


Figure 4. Vertical distribution of lithology, ^{210}Pb dating (Cermelj et al., 1996), Cr, Cu, Fe, Mn, Pb, Zn, V, $C_{org.}$, $\delta^{13}C_{org.}$ values (Cermelj et al., 1996) and $P_{tot.}$ in the western basin of Lake Bled.

material by inflows (streams and discharges). The enrichment factors (EF) and consequently the degree of pollution of lake sediment were determined on the basis of calculated differences between the normalized element concentrations versus Al (C/Al), it being one of the most abundant elements in the lake sediment, which were measured at the surface (s) and in the deepest (b) layers in some longer cores (Kemp, Dell, & Jaquet, 1976):

$$\mathrm{EF} = (\mathrm{C}/\mathrm{Al})\mathrm{s}/(\mathrm{C}/\mathrm{Al})\mathrm{b}.$$

Pb and Zn are enriched in most cores while Pb and Cd show the highest surficial enrichment factors (Table I). From metal accumulation rates (F), calculated from ^{210}Pb and ^{137}Cs sedimentation rates (v =1.2, 2.4 mm year^{-1}; Cermelj et al., 1996), porosity (ϕ =0.90; Cermelj et al., 1996), density ($\gamma = 2.5\mathrm{g}/\mathrm{cm}^3$; Cermelj et al., 1996) and surficial element contents (C):

$$\mathrm{F} = (1 -)\mathrm{v}\ \rho \mathrm{C}$$

(Suess & Djafari, 1977), it appears that Pb, Zn and P exhibit the highest positve deviations from the mean accumulation rate of each specific element suggesting an anthropogenic origin. Vertical sediment profiles (Figure 4) show increasing contents of Pb, Zn, Cr, V, and total N and P in the upper 10 cm of the core, i.e., in the last

TABLE I

Concentrations of elements in surficial sediment (0–5 cm) and enrichment factors (EF) in Lake Bled

	Concentrations		EF	
Element	Range	x±SD	Range	Number
Al (%)	0.19–0.72	0.41±0.16	1.0	26
Ba (ppm)	44.7–94.8	65.5±20.4		26
Ca (%)	16.4–31.7	24.3±5.4		22
Cd (ppm)	0.5–3.5	1.36±0.72	0.1–19.1	26
Co (ppm)	0.4–5.5	3.08±1.79	0.3–2.4	26
Cr (ppm)	5.32–18.3	9.29±4.18	0.5–1.6	26
Cu (ppm)	8.44–35.7	19.6±7.95	0.4–2.7	26
Fe (%)	0.23–1.08	0.55±0.24	0.7–1.2	26
K (%)	0.04–0.13	0.07±0.03		22
Li (ppm)	1.82–16.9	6.7±5.76		26
Mg (%)	0.56–3.6	1.14±0.73		22
Mn (ppm)	85.5–175.3	125.3±21.6	0.3–1.1	26
Na (%)	66–289	126.4±56.7		22
Ni (ppb)	1.4–20.58	5.56±5.26	0.2–2.9	26
Pb (ppm)	13.2–125.2	2.3±28.36	0.2–16.7	26
Sr (ppm)	107.8–215.5	152.1±33.25		26
V (ppm)	2.31–29.32	5.22±6.34	0.1–2.2	26
Zn (ppm)	40.9–272.1	45.7±78.2	0.4–4.1	26
Be (ppm)	0.11–0.37	0.21±0.08	0.8–1.8	17
La (ppm)	0.30–0.72	1.09±1.76	0.1–2.8	15
$C_{\mathrm{org.}}$ (%)	1.98–5.93	3.44±1.02		23
$N_{\mathrm{tot.}}$ (%)	0.57–0.99	0.81±0.11		21
$P_{\mathrm{tot.}}$ (ppm)	228–984	523±168		22

approx. 100 years, as well as Cd and Cu in the upper 5 cm of the core, i.e., in the last approx. 50 years. These results reflect increasing pollution and eutrophication over the last 100 years and especially over the last 50 years. It is interesting to note that the black carbon contents also began to increase about 50 years B.P. (Muri et al., 2002) while the highest PAH contents, mainly of pyrolitic origin, appeared about 50 years B.P., but afterwards gradually decreased towards recent values (Muri, 2003).

The studied elements can in general be divided according to their properties and quantities into carbonate bonded (Ca, Mg), nutrient (organic C, total N and P), mobile (Fe, Mn), lithogenic (Al, Ba, Cr, Li, K, Na, La), enriched (Pb, Zn, Cd, Co, Cu, Ni,) and miscellaneous (Sr, V, Be) elements. The investigated elements are mostly of lithogenic origin with the exception of enriched elements (not Ni) which are partly of anthropogenic origin, and nutrient elements which are mostly of biogenic and anthropogenic origins. The statistical analysis of Co, Cd, Cr, Cu, Ni, Pb, Zn contents versus grain size (clay, fine silt, medium silt, coarse silt and sand; Φ units from 1 to 9) shows that almost 88% of the total variance of their contents can be explained by the difference of grain size at different sampling locations. Cr, Cu, Ni, Pb, Zn show strong positive correlations with the clay fraction and negative with the medium silt fraction. Co strongly correlates with the coarse silt fraction content, while Cd shows no particular affinity to any of the sediment fractions. Similar results were obtained when applying canonical correlation using all geochemical and sedimentological variables. When standardized, from five sets of linear combinations, the most statistically significant can be written as follows:

$$\begin{aligned}\text{Set 1} = {} & -23.4833 \times \text{clay} + 7.4607 \times \text{fine silt} + 22.6866 \times \text{medium silt} \\ & + 14.9381 \times \text{coarsesilt} + 14.491 \times \text{sand}\end{aligned}$$

and

$$\begin{aligned}\text{Set 2} = {} & 0.243532 \times \text{Ni} + 1.92289 \times \text{Zn} + 2.1605 \times \text{Cr} + 0.732862 \times \text{Cu} \\ & + 1.95239 \times \text{Pb}\end{aligned}$$

The estimated correlation between both sets is 0.91 with a P value of 0.015, which is statistically significant at the 95% confidence level.

The presence of lithogenic elements is connected to the erosion of the shore rocks and to the input of detrital material into the lake by fresh water discharges and wind. Those of biogenic origin are connected with the primary production and subsequent degradation of sedimented organic matter (Cermelj & Faganeli, 2003). The origin of sedimentary $C_{org.}$ is, according to $\delta\,^{13}C_{org.}$ values averaging −33‰, mostly from deposited phytoplankton debris while the bacterial component seems also quantitatively important (Cermelj et al., 1996; Cermelj & Faganeli, 2003; Lojen et al., 1999; Ogrinc et al., 2002). The anthropogenic elements are a consequence of the use of natural (organic C, total N and P) and artificial (total N and P, K and Co) fertilizers, detergents (total P) and fossil fuels (mainly Cd, Pb and Zn) carried into the lake mostly in detrital form.

5. Conclusions

Surficial sediment of Lake Bled is composed of dark gyttya type clayey silt with 5%–10% of organic matter. The sediment below is fine laminated and composed of homogenous silt and clayey silt: Mineralogically, low-Mg calcite prevails, followed by dolomite, quartz, partially of diatomaceous origin, and feldspar. Clay minerals are composed of muscovite/illite and chlorite. Authigenic minerals are pyrite and low-Mg calcite deposited as ‘lake chalk’ in restricted area south of Zaka bay. The geochemical analyses revealed that the lake sediment is especially polluted by Pb, Zn and P. Higher contents were found in the northwestern and eastern parts due to the particle input by local inputs. Cd, Cu, V, Cr, Co and total N also show enrichment in the top layer of the cores, which started approximately 100 and especially 50 years ago. This information can be used to establish the relative contemporary levels of nutrients and pollutants in sediment and to identify long-term trends of pollution and eutrophication.

This page intentionally blank

References

Aspila, K. I., Agemian, H., & Chau, A. S. Y. (1976). A semi-automated method for determination of inorganic, organic and total phosphate in sediments. *Analyst, 101*, 187–197.

Buser, S., & Cajhen, J. (1978) Osnovna geološka karta SFRJ 1:100000, list Celovec (Klagenfurt). Beograd: Zvezni geološki zavod, Beograd.

Cermelj, B., & Faganeli, J. (2003). Anoxic degradation of biogenic debris in sediments of eutrophic subalpine Lake Bled (Slovenia). *Hydrobiologia, 494*, 193–199.

Cermelj, B., Faganeli, J., Ogorelec, B., Dolenec, T., Pezdic, J., & Smodis, B. (1996). The origin and recycling of sedimented biogenic debris in a subalpine eutrophic lake (Lake Bled, Slovenia). *Biogeochemistry, 32*, 69–91.

Dolenec, T., Pezdic, J., Ogorelec, B., & Misic, M. (1984). The isotopic composition of oxygen and carbon of the recent sediment from the Bled Lake and the Pleistocene lacustrine chalk from the Julian Alps. *Geologija, 27*, 161–170.

Flügel, E., Ramovs, A., & Bucur, J. J. (1994). Middle Triassic (Anisian) limestone from Bled – Northwestern microfacies and microfossils. *Geologija, 36*(1994), 157–181.

Flügel, E., Ramovs, A., & Kochanski-Devidé, V. (1984). A Middle Permian calcisponge/algal/cement reef: Straža near Bled, Slovenia. *Facies, 10*, 179–256.

Hedges, J. I., & Stern, J. (1984). Carbon and nitrogen determinations of carbonate containing solids. *Limnology and Oceanography, 29*, 657–663.

Kemp, A. L. W., Dell, T. C. I., & Jaquet, J. M. (1976). Cultural impact on the Geochemistry of sediments in Lake Erie. *Journal of the Fisheries Research Board of Canada, 33*, 440–446.

Kuscer, D. (1955). Prispevek h glacialni geologiji Radovljiske kotline. *Geologija, 3*, 136–150.

Lojen, S., Ogrinc, N., & Dolenec, T. (1997). Carbon and nitrogen stable isotope fractionation in the sediment of Lake Bled (Slovenia). *Water, Air, & Soil Pollution, 99*(1–4), 315–323.

Lojen, S., Ogrinc, N., & Dolenec, T. (1999). Decomposition of sedimentary organic matter and methane formation in the recent sediment of Lake Bled (Slovenia). *Chemical Geology, 159*, 223–240.

Meischner, D., & Rumohr, J. (1974). A light-weight-momentum gravity corer for subaqueous sediments. *Senckenbergiana Marittima, 6*, 105–117.

Molnar, F. M., Rothe, P., Foerstner, U., Stern, J., Ogorelec, B., Sercelj, A., et al. (1978). Lakes Bled and Bohinj: Origin, composition, and pollution of recent sediments. *Geologija, 21*(1.del), 93–164.

Muri, G. (2003). Composition and origin of organic matter in oxic and anoxic alpine lakes. Dissertation, Fakulteta za kemijo in kemijsko tehnologijo, Univerza v Ljubljani.

Muri, G., Cermelj, B., Faganeli, J., & Brancelj, A. (2002). Black carbon in Slovenian alpine lacustrine sediments. *Chemosphere, 46*(8).

Ogrinc, N., Lojen, S., & Faganeli, J. (1997). The sources of dissolved inorganic carbon in pore waters of lacustrine sediment. *Water Air and Soil Pollution, 99*, 333–341.

Ogrinc, N., Lojen, S., & Faganeli, J. (2002). A mass balance of carbon stable isotopes in an organic-rich methane-producing lacustrine sediment (Lake Bled, Slovenia). *Global and Planetary Change, 33*(1–2), 57–72.

Schultze, E. (1984). Contribution to paleolimnology of the Bled Lake, Slovenia and to evolution of adjoining vegetation and climate. *Geologija, 27*, 97–106.

Suess, E., & Djafari, D. (1977). Trace metal distribution in Baltic Sea ferromanganese concretions: Inferences on accretion rates. *Earth and Planetary Science Letters, 35*(1), 49–54.

Štern, J., & Förstner, U. (1976). Heavy metals distribution in the sediment of the Sava Basin in Slovenia. *Geologija, 19*, 259–274.

Vrhovsek, D., Kosi, G., & Zupan, M. (1984). The occurrence of *Oscillatoria rubecens* in Lake Bled. *Bioloski Vestnik, 32*(2), 45–56.

Water, Air, and Soil Pollution: Focus (2006) **6:** 151–157
DOI: 10.1007/s11267-006-9035-4

THE IMPACT OF LAKE-LEVEL FLUCTUATIONS ON THE SEDIMENT COMPOSITION

JAAN-MATI PUNNING*, JAANUS TERASMAA and TIIT VAASMA
Institute of Ecology, Tallinn University, Uus-Sadama 5, Tallinn 10120, Estonia
*(*author for correspondence, e-mail: mati@eco.tlu.ee; phone: +372-61-99833;*
fax: +372-61-99801)

Abstract. Lithological and granulometric investigations of the surface and short core sediments in L. Martiska (northeastern Estonia) showed that variations in the grain-size parameters and LOI content were influenced by the changes in deposition conditions during the regression and transgression phases monitored in the lake since the 1960s. During the regression and transgression phases displacement of the erosion-transport-accumulation zones in the lake took place depending on the bottom topography. The water level fluctuations are especially clearly reflected in grain-size variations in cores from peripherial area.

Keywords: lake-level fluctuations, palaeolimnology, resedimentation, sediment grain size

1. Introduction

Numerous sediment studies are focused on describing direct responses of various bioindicators, geochemical records and hydrological changes to the trophic state of a lake (Dearing, 1983; Engstrom, Swain, & Kingston, 1985). Less attention has been paid to sedimentary processes, especially to the grain size of lake sediments; however, these studies have been promising in investigating lake-level variations in small temperate lakes (Digerfeldt, 1986; Punning, Alliksaar, Terasmaa, & Jevrejeva, 2004).

The fluctuations of water level alter the lake morphometry and transform the characteristics of the sedimentation zones (erosion, transportation, accumulation; Håkanson, 1977) of the lake bed, thereby directly influencing sedimentation, resuspension as well as biogeochemical dynamics in the lake. Several studies have been successful in investigating water level variations in small temperate lakes (Dearing, 1997; Digerfeldt, 1986). Recent studies in palaeolimnology (Beierle, Lamoreux, Cockburn, & Spooner, 2002) have shown that the quantitative and qualitative analyses enable to describe sedimentological processes and distinguish the changes of the past environment. The main aim of this research was to study the lithological composition and grain-size parameters of sediments accumulated in a small lake and to compare the data with the historical evidences about its water level fluctuations.

2. Materials and Methods

The lithological composition and grain-size parameters of surface samples and short cores were studied in Lake Martiska (area 3.5 ha, maximum depth of 8.5 m) situated in northeastern Estonia (57°38′07″ N, 27°05′06″ E) in the area of the Kurtna Kame Field (Figure 1a, Table I). The lake lies in a deep glaciokarstic hollow, and its dynamic ratio (Håkanson & Jansson, 1983) is 0.08, which mean that sedimentation is very weakly influenced by wind/wave activities. Kurtna area lies in a transitional zone between densely populated and heavily industrialised oil shale mining and processing region and a sparsely inhabited territory with large

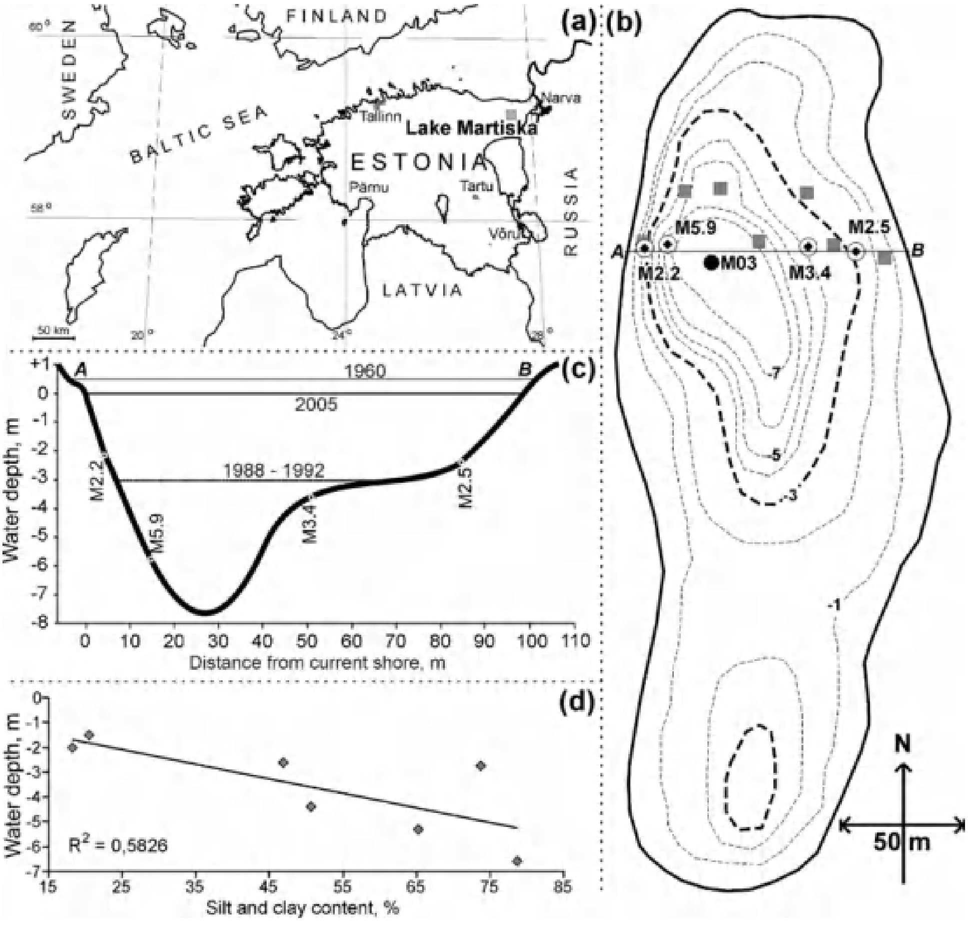


Figure 1. Location of L. Martiska in northeastern Estonia (**a**). The bathymetry of the lake and study sites: squares-surface samples from the northern part of the lake; M2.2., M2.5, M3.4 and M5.9 short cores, the number denotes water depth; M03 core dated by ^{210}Pb (**b**). Lake levels in 1960, 1988–1992 and 2005 and the studied sites along profile AB (**c**). Water depth and silt and clay content in the surface samples along profile AB (**d**).

TABLE I
Characteristics of the Lake Martiska

Characteristic	Value
Volume (V), m^3	80,000
Area (S), ha	3.5
Maximum depth, m	8.5
Average depth, m	2.3
Maximum length, m	370
Maximum width, m	140
Perimeter, m	870
Average slope inclination, %	8.0
Dynamic ratio	0.08
Shape factor	1.24
Water retention time, yr	1.6
Catchment area, ha	30

forests and mires. Pine forests with some other species are dominant on the poor sandy soils on the well sorted mostly fine-grain sands. Lake is closed and fed by groundwater and atmospheric precipitation, its yearly water level displacement is 20–30 cm. The lake is clearly stratified in summertime and the thermocline lies at a depth of 3–4 m. Strong oxygen deficiency occurs in the water deeper than 3–4 m practically all over the year, except during the spring and autumn overturn periods. The area is severely affected by oil shale mining and processing (Punning, 1994). The pumping out of groundwater in the area began in the 1960s resulting in a 3.0–3.5 m drop of the lake water level (Figure 1c). Since 1991 the production of oil shale has continuously declined, and the use of environmentally friendlier technologies has led to the restoration of the natural state of the lake environments.

Detailed mapping of the contemporary lake and mineral bottom topography was done in the wintertime of 1987 and 2003 from ice using a measuring disc of 10 cm diameter and a Belarus type corer (2003 data see on Figure 1b). Ten surface sediment samples (0–10 cm) and five short cores (0–30 cm) were collected in 2003 using a modified Livingstone–Vallentyne piston corer. The cores were taken from different depths and are nominated in Figure 1b and c according the water depth at the coring site in metres.

The concentration of dry matter in sediment was determined by drying the samples at 105°C to constant weight. Organic matter was measured as loss-on-ignition (LOI) after the heating samples at 550°C for 120 min. One core (Figure 1b, core M03) was radiometrically dated. Direct gamma assay was used to measure ^{210}Pb activity in samples and CRS ^{210}Pb model was used to determine dates (Appleby et al., 1986). The surface samples were analysed using wet sieving through four metallic woven mesh sieves (36, 63, 100 and 315 μm), which were stacked vertically and placed in a Fritsch Vibratory Sieve Shaker ‘Analysette 3’

PRO. Mineral particle size partitioning was determined from the amount of sediment remaining in each specific sieve (Last, 2001). In the current study the grain-size fractions were amalgamated into two main groups: sand (>63 µm) and silt and clay (<63 µm) (Terasmaa, 2005). The short-core samples were treated by the hydrogen peroxide and then the grain size was analysed using a Fritsch Laser Particle Size 'Analysette 22'. Results are given following the terminology of Folk (1980) in terms of median grain size (Φ_{50}=–log$_2$D (mm)). In this scale coarser fractions have smaller Φ_{50} values and Φ_{50} for silt and clay fractions is >5.

3. Results

The lithological composition of the seven samples taken from surface layers on profile AB (Figure 1 b,d) of L. Martiska varied largely due to the different depths and slope inclinations. The analysed sediments consisted mainly of unconsolidated dark brownish gyttja (mud like lake sediment) of the water content from 86.6 to 95.6% and LOI values from 24 to 74.2%. In the deeper northernmost area the correlation between the proportion of silt and clay and water depth is 0.5826 (Figure 1d). In the cores taken from deeper areas (M3.4 and M5.9) the dominating fraction is medium-size silt in all the studied samples (median diameter 6–10 µm) (Figure 2). In the cores from shallower areas (M2.2 and M2.5) the median diameter of particles in the samples from a depth of 14–16 cm increases up to 120 µm and the dominating fraction is very fine sand. The LOI values in cores M2.2, M3.4 and M5.9 are higher (60–80%) in the lower part decreasing upwards (in surface samples 30–60%). In core M2.5 several cycles can be distinguished vertically in the distribution LOI values (Figure 3).

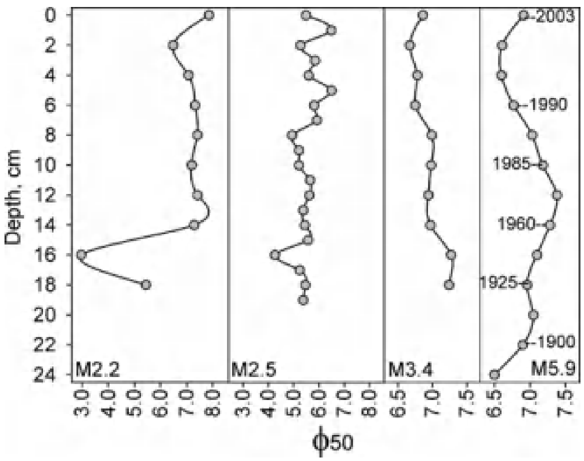


Figure 2. Grain-size in short cores in phi units (see Figure 1). Note that the Φ_{50} scale values for different cores are different.

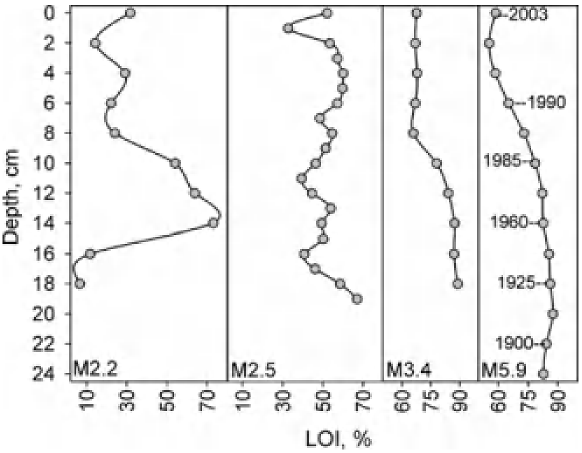


Figure 3. LOI values in short cores (see Figure 1).

4. Discussion

The LOI values and grain-size parameters in the surface sediment samples in the studied profile showed that the distribution of grain-size fractions depends on water depth at the sampling site (Figure 1d). As the topography of the lake basin is quite variable essential changes in the bottom topography took place in the course of lake-level fluctuations.

According to the monitoring data, three phases could be distinguished in the sedimentation process (see Figure 1c): (1) regression phase since the beginning of the 1960s; (2) minimum lake level in 1988–1992; (3) transgression phase since 1992 up to now.

The regression of the lake has resulted in extensive erosion and redeposition of sediments, changes in the distance to the shore and displacement of the erosion-transport-accumulation zones. During this period accumulated sediments originate in principal from two different sources: in-lake concurrently accumulated sediments (mainly atmospheric input, influx from the catchment, autochthonous organic matter) and matter eroded in the nearshore area from where water has retreated in the course of regression. The eroded matter consists of fine grain sands (limnoglacial sands embracing the lake), as well as of previously accumulated lacustrine sediments. In sites M3.4 and M5.9 lacustrine sedimentation took place during the whole regression phase. The ^{210}Pb chronology shows that during regression medium silt sediments from depths 14–16 cm up to 6–7 cm accumulated. Besides lake morphometry the lateral transport of sedimentary material was influenced by the change in the littoral vegetation. Although the water depth of site M3.4 was smaller than of M5.9, the Φ_{50} values are rather similar which might be explained by the gentler slope of the eastern shore (Figures 1c, 2). When the regressive lake level reached levels of –2.2 and –2.5 m the surface of sites M2.2 and M2.5 became above the lake level and erosion and accumulation of organic matter took place mainly as humic substance. As Figure 2 shows there is a very sharp short-lived increase in the coarser component of mineral matter (decline in the Φ_{50} values) in cores M2.2 and M2.5 at a depth of 16 cm from the sediment surface. In these cores the Φ_{50} values (2.3–2.5) are close to the values of bulk limnoglacial sands around the lake.

When the transgressive water level reached the surface of sites M2.2 and M2.5 sediment accumulation began there again. On the relatively badly sorted (average deviation 90.78 μm) and sandy sediments (Φ_{50}=2.9) well-sorted (average deviation 7–9 μm) mainly medium-grained silt accumulated (Figure 2). This means that the main source of mineral matter was well-sorted sediments accumulated before the water-level fall. Also the relatively stabile LOI values in core M2.2 (Figure 3) suggested homogeneity of the source material and depositional environment. The grain-size parameters of the deposits accumulated during this phase in sites M3.4 and M5.9 are relatively similar. At the beginning of transgression the flooding of the shores caused degradation of the vegetation and increasing shore erosion. Later, in course of the water-level rise the sedimentation regime stabilised and sediments became better sorted and finer in the direction of sediment transport. That regularity in the successive deposition during lake-level changes was pointed out also by McLaren and Bowles (1985). Thus, lake-level fluctuations were responsible for essential changes in the composition and structure of sediments and consequently in the biogeochemical matter cycling in the lake. The oil shale mining and processing nearby was responsible for emitting huge amounts of alkaline fly ash, characterised by a high concentration of several heavy metals and harmful organic compounds, into the atmosphere in 1960–1990 (Punning, 1994). In process of the erosion of older sediments, their resuspension, lateral transport and resedimentation, the pollutants were returned in the biogeochemical matter cycling in the lake.

Comparison of the fluctuations in the water level in some Estonian lakes with the lithological composition of the sediment, P content, carbon and nitrogen ratio, fossil pigments and diatom communities showed that in medium-term time scale (10^3 years) the decisive factor in the trophy of the lake was the depth of the water column above the sediment (Punning et al., 2004).

5. Conclusions

Well established history of the water-level fluctuations in L. Martiska during the last decades and its correlation with the lithological composition and grain-size parameters showed that: (1) the grain-size parameters of lacustrine sediments depend on the topography and reflect adequately changes in the sedimentary processes, first of all lake-level fluctuations; (2) the newly accumulated sediments during the regressive -transgressive period originate from two main sources: in-

This page intentionally blank

lake concurrently accumulated sediments and from the limnoglacial nearshore sands.

Acknowledgements

Financial support from the Estonian Ministry of Education (No 0282120s02) and Estonian Science Foundation (grant 5584) is gratefully acknowledged.

References

Appleby, P. G., Nolan, P. J., Gifford, D. W., Godfrey, M. J., Oldfield, F., Anderson, N. J., et al. (1986). ^{210}Pb dating by low background gamma counting. *Hydrobiologia, 141*, 21–27.

Beierle, B. D., Lamoreux, S. F., Cockburn, M. H., & Spooner, I. (2002). A new method for visualizing sediment particle size distribution. *Journal of Paleolimnology, 27*, 279–283.

Dearing, J. A. (1983). Changing pattern of sediment accumulation in a small lake in Scania, southern Sweden. *Hydrobiologia, 103*, 59–64.

Dearing, J. A. (1997). Sedimentary indicators of lake-level changes in the humid temperate zone: A critical review. *Journal of Paleolimnology, 18*, 1–4.

Digerfeldt, G. (1986). Studies on past lake-level fluctuations. In B. E. Berglund (Ed.), *Handbook of holocene palaeoecology and palaeohydrology* (pp. 127–143). Chichester, New York: Wiley.

Engstrom, D. R., Swain, E. B., & Kingston, J. C. (1985). A paleolimnological record of human disturbance from Harvey's Lake, Vermont: Geochemistry, pigments and diatoms. *Freshwater Biology, 15*, 261–288.

Folk, R. L. (1980). *Petrology of sedimentary rock*. Austin, Texas: Hemphill.

Håkanson, L. (1977). The influence of wind, fetch and water depth on the distribution of sediments in Lake Vänern, Sweden. *Canadian Journal Of Earth Sciences, 14*, 397–412.

Håkanson, L., & Jansson, M. (1983). *Principles of lake sedimentology*. Berlin Heidelberg New York: Springer.

Last, W. M. (2001). Mineralogical analysis of lake sediments. In W. M. Last & J. P. Smol (Eds.), *Tracking environmental change using lake sediments Vol. 2 – Physical and geochemical methods* (pp. 143–187). London: Kluwer.

McLaren, P., & Bowles, D. (1985). The effect of sediment transport on grain-size distribution. *Journal of Sedimentary Petrology, 55*(4), 457–470.

Punning, J.-M. (Ed.). (1994). *The influence of natural and anthropogenic factors on development of landscape, The results of a comprehensive study in NE Estonia*. Tallinn: Institute of Ecology, Estonian Academy of Sciences, Publication 2.

Punning, J.-M., Alliksaar, T., Terasmaa, J., & Jevrejeva S. (2004). Recent patterns of sediment accumulation in a small closed eutrophic lake revealed by the sediment records. *Hydrobiologia, 529*, 71–81.

Terasmaa, J. (2005). Bottom topography and sediment lithology in two small lakes in Estonia. *Proceedings of the estonian academy of sciences. Biology, ecology, 54*(3), 171–189.

Water, Air, and Soil Pollution: Focus (2006) **6:** 159–172
DOI: 10.1007/s11267-006-9036-3

MICROBIALLY MEDIATED REDOX CYCLING AT THE OXIC–ANOXIC BOUNDARY IN SEDIMENTS: COMPARISON OF ANIMAL AND PLANTS HABITATS

MARK E. HINES
Department of Biological Sciences, University of Massachusetts Lowell, Lowell, MA 01824, USA
(author for correspondence, e-mail: mark_hines@uml.edu; phone: +1-978-9342867;
fax: +1-978-9342071)

Abstract. Microorganisms are responsible for the bulk of transformations that occur in surficial sediments. They are most active at redox boundaries where they can benefit from access to various oxidants and reductants generated during redox cycling events. To illustrate the dynamics of microbially mediated processes, especially those involving sulfur and metal cycles, processes were compared in habitats either bioturbated by a capitellid worm or inhabited by a salt marsh grass. The presence of macrofauna and macroflora greatly altered the three-dimensional array of redox gradients in sediments, but the type and form of reductants and oxidants provided varied greatly; clastic sedimentary infauna subducted solid phase organic material and iron oxides, whereas plant roots released dissolved organic matter and oxygen. These differences resulted in a bioturbated system that exhibited a rapid sulfur cycle (residence time of minutes), but a slower iron cycle (days), whereas vegetation caused a slow sulfur cycle and rapid iron cycle. Alteration of sediments by higher life forms also greatly affected the composition and relative abundances of sedimentary bacteria, even on short time scales. Although redox cycling at interfaces can be somewhat predictable, variations in response to biological and physical perturbations demonstrated wide differences in the dynamics of redox-mediated processes.

Keywords: redox cycling, sulfate reduction, bioturbation, marine sediments, salt marsh, *Spartina alterniflora*, *Heteromastus filiformis*, iron, sulfur, bacteria

1. Introduction

Redox boundaries in sediments are sites of rapid microbial processes due to the overlap of reductants and oxidants. Overlying waters supply a variety of important oxidants that are utilized during organic matter oxidation, oxygen being the most important, but others also enter sediments as aqueous or solid phases including nitrogen oxides, oxidized metals such as Fe and manganese, and sulfate. Conversely, reduced compounds tend to accumulate in deeper anoxic sediments and these materials diffuse into surficial oxidizing sediments providing fuel for microbial metabolism and the use of the electron acceptors listed above. Hence, the overlap of these gradients results in intense redox cycling of a variety of elements and are sites of important geochemical transformations and microbial activities in sediments.

The distribution of redox gradients is affected by a variety of physical, chemical and biological processes. In undisturbed sediment, the vertical redoxcline can be rather uniform horizontally if sediment deposition is uniform, and it can be rather steep depending on the rate of organic matter deposition. In near-shore sediments that experience high rates of organic matter deposition, oxygen can be depleted within a millimeter or less of the sediment water interface.

This paper is a synopsis of a plenary lecture that was presented at the *10th International Symposium on the Interactions Between Sediments and Water*, which as held in Bled, Slovenia in August 2005. Here, I review two examples of redox processes in marine sediments that encompass several years of work in my own laboratory and with colleagues; one animal mediated and one plant mediated. Both cause dramatic and dynamic changes in redox cycling of elements, especially Fe and S in shallow marine sediments. The activities of these higher life forms, in consort with bacteria, result in changes in redox active elements over time and space in a manner that is opposite to what would be expected in the absence of these macroorganisms. These activities produce a three-dimensional array of redox processes in which redox cycling occurs well within sediments and over a vertical extent of several centimeters instead of over a vertical gradient of a few millimeters that would be expected in the absence of animal or plant disturbance. In addition, although both organisms greatly alter redox cycling, the mechanisms in which they do so differ greatly and the relative impacts on the Fe and S cycles also greatly differ.

2. Bioturbation by *Heteromastus Filiformis*

The marine capitellid polychaete *Heteromastus filiformis* is a very thin (~0.8 mm × 10 cm) conveyor-belt feeding worm that inhabits shallow and intertidal temperate marine sediments. It spends its adult life feeding on sedimentary particles by ingesting sediments below the surface, digesting organic material (bacteria) in its gut, creating a string of fecal pellets that stretches from the anterior to the posterior end, and then depositing these pellets at the sediment surface (Aller & Yingst, 1985; Neira & Hoepner, 1994). Unlike many polychaetes that create burrows that are ventilated with overlying oxic water, *H. filiformis* does not pump any water into sediments and lives and feeds within anoxic deposits. It aerates its anterior tissues by transporting oxygen from the tail to the head within its tissue. Hence, the worm does not oxidize sediments or its feces. In this way, the worm transports anoxic material from 10–12 cm in the sediments to the surface. The data described here were acquired from sediments in a mud flat in New Hampshire, USA with a population of *H. filiformis* of ~10,000 individuals per square meter. A population this size can completely turn over the upper ~10 cm of sediment every 14 days. *H. filiformis* was the only animal found in significant numbers below the upper 1–2 cm.

Although oxygen is not directly introduced into the sediments by *H. filiformis*, its feeding activities cause a dramatic sub-surface redox regime that greatly affects redox cycling below the surface. Figure 1 illustrates the feeding behavior of *H. filiformis* and how oxidants are introduced without pumping O_2 into the sediments. Despite the lack of molecular O_2 input at depth, subsurface sediments are constantly fed an oxidant, but in this case it is primarily Fe oxides that maintain subsurface redox cycling. Reduced sediments are packaged into fecal pellets within the worm gut and these are transported through the worm and deposited at the aerobic sediment surface. These pellets are black due to Fe sulfide minerals and these minerals are rapidly oxidized at the sediment surface where they become brown to orange in color due to the accumulation of Fe oxides during Fe oxidation at the surface. Pellets are rapidly buried into anoxic regions by newly deposited pellets. Once buried, fresh Fe oxides are readily metabolized anaerobically by Fe-reducing bacteria, which remobilizes Fe during Fe(II) dissolution. The burial of fecal pellets also causes a burial of fresh organic material since freshly deposited organic matter and organic matter produced at the sediment surface during benthic photosynthesis are rapidly subducted into anoxic sediments where it must undergo anaerobic decomposition rather than by aerobic process that would normally occur in the absence of conveyor belt bioturbation.

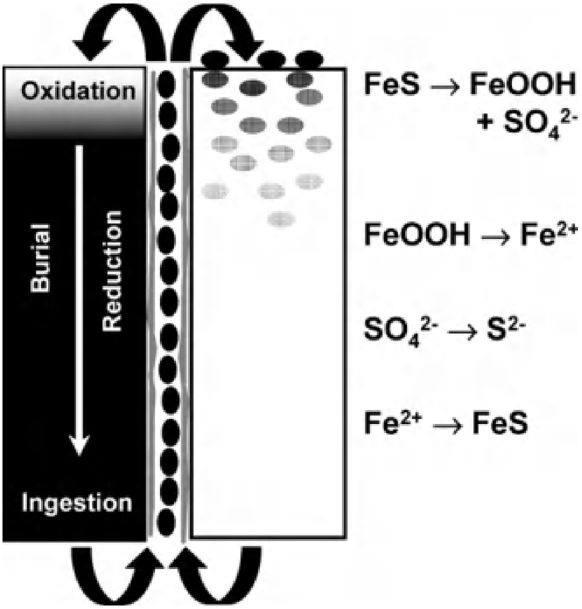


Figure 1. Conceptual model of feeding behavior by *Heteromastus filiformis* and its effect on particle transport, burial of iron oxide particles, and subsurface redox cycling of iron and sulfur. Fecal pellets (*ovoid bodies*) are passed through the gut and deposited at the surface where they oxidize and are then reburied and disintegrate.

Hence anaerobic metabolism is enhanced including bacterial Fe reduction. In addition, sulfate reduction is also stimulated by newly introduced organic matter, which leads to the rapid production of biogenic sulfide that rapidly precipitates the newly formed Fe(II) as FeS.

What are the consequences of this continual burial of oxidized particles into anoxic sediments? Figure 2 depicts depth profiles of dissolved Fe and rates of sulfate reduction (sulfide production) in sediments that are reworked by *H. filiformis*, and for comparison, sediments that are not inhabited by bioturbating fauna below 1–2 cm (Hines & Jones, 1985). In non-bioturbated sediments, maximum sulfate reduction is restricted to near-surface sediments where the freshest organic matter exists. Dissolved Fe is produced from the reduction of Fe oxides in surficial sediments (Tugel, Hines, & Jones, 1986) and this Fe is removed in deeper regions as FeS by sulfide produced during sulfate reduction (Hines & Jones, 1985). In the sediments bioturbated by *H. filiformis*, Fe and sulfate reduction co-exist because the former is occurring on buried fecal pellet material whereas sulfate reduction is occurring in adjacent sediments that are derived from disrupted fecal pellets in which Fe oxides have been largely exhausted. Fe dissolution is due to both Fe-reducing bacteria (Tugel et al., 1986) and reduction by reaction with sulfide. It was not clear to what extent each of these processes contributes to Fe dissolution. Moreover, the dissolution of Fe(II), after its reduction, is not instantaneous (Jones, Darah, & Kochian, 1996). Therefore, sediments with solid phase Fe(II) are buried further before the Fe is completely dissolved, so dissolved Fe(II) is supplied at depth even after Fe reduction is complete. Since Fe-reducing and sulfate-reducing bacteria compete for similar substrates, this delayed dissolution of Fe may explain the occurrence of high levels of dissolved Fe during sulfide production. The bioturbation process results

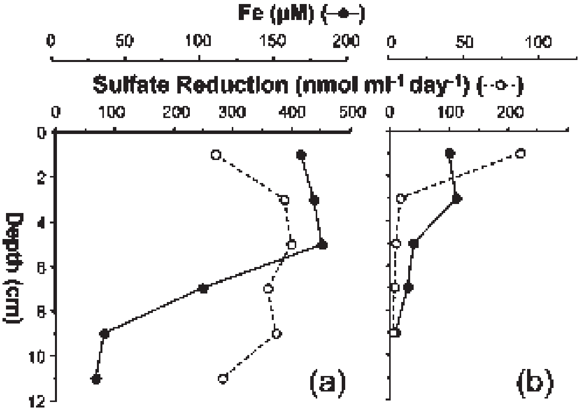


Figure 2. Depth profiles of dissolved iron and rates of sulfate reduction in sediments bioturbated by *Heteromastus filiformis* (**a**) and in sediments not bioturbated (**b**) (Hines & Jones, 1985).

in persistent high levels of dissolved Fe where it would not normally be expected to occur, i.e., in sediments experiencing high rates of sulfide production. Although sulfate reduction is quite rapid, these sediments do not contain any measurable dissolved sulfide (<2 µM) since it is titrated by the excess Fe(II) production (Hines, 1991; Hines, Lyons, Armstrong, Orem, Spencer, & Gaudette, 1984).

Bioturbation by *H. filiformis* does not occur all year and its onset in spring yields interesting changes in redox processes (Hines et al., 1984). It has been shown that this species seems to initiate rapid reworking activity in the spring after sediments reach ~12°C. Figure 3 illustrates how sulfate reduction and dissolved Fe change in the sediments from the winter into the spring and summer including what occurs before and after *H. filiformis* activity commences. Since Fe reduction can out-compete sulfate reduction, the former begins earlier in the spring as evidenced by increases in concentrations of dissolved Fe (Figure 3). However, sulfate reduction begins soon thereafter, which results in the removal of dissolved Fe as Fe sulfide minerals begin to precipitate. When bioturbation commences later, Fe again increases in solution despite an increase in sulfide production rate. In fact, within a few days after *H. filiformis* becomes active, there is a rapid stimulation in sulfide production and Fe dissolution (spikes in both), which attenuates some before entering the full summer season. Hence, pore water chemistry exhibits an oscillation in concentration due to temporal changes in Fe

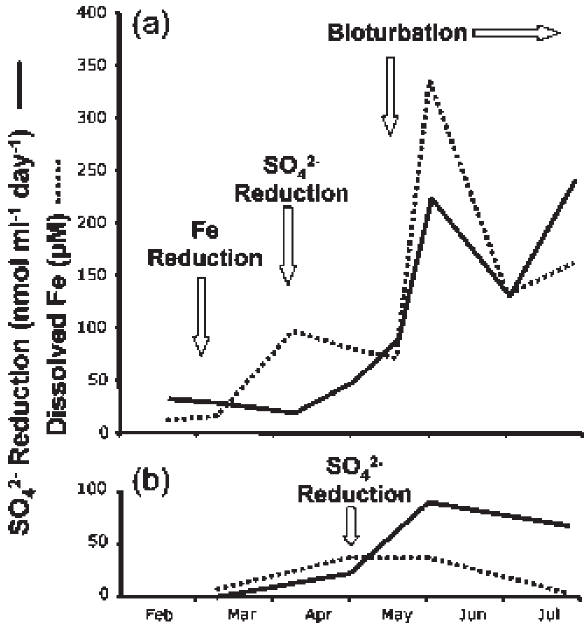


Figure 3. Seasonal changes in dissolved iron and sulfate reduction rates in sediments bioturbated by *Heteromastus filiformis* (**a**) and in sediments not bioturbated (**b**).

and sulfate reduction and the onset of bioturbation (Hines, Orem, Lyons, & Jones, 1982). The temporal changes in biological and redox conditions not only remobilize a great deal of Fe, but other trace metals such as copper, nickel, manganese, and molybdenum undergo dissolution as well and exhibit rapid changes in concentrations over time (Hines et al., 1984).

Bioturbation also greatly affects the exchange of materials between sediments and overlying waters. In the sediments bioturbated by *H. filiformis*, pore water nutrients like ammonium and phosphate turnover ~7-times more rapidly than in non-bioturbated sediments (Hines & Jones, 1985). Sedimentary DOC is also removed much more rapidly from these sediments (Hines & Jones, 1985; Hines et al., 1984).

3. *Spartina Alterniflora*

Plants can also greatly disrupt redox gradients in sediments (Hines, Knollmeyer, & Tugel, 1989; Hines et al., 1999). However, unlike *H. filiformis* that physically moves particles, plants deliver oxidants to sediments through roots. *Spartina alterniflora* is a salt marsh grass that is common in temperate environments, especially the east coast of the USA. It is found in two primary growth forms, the tall and short forms. The tall form is found primarily near creeks and can reach heights of 2.0 m. The data presented here were acquired from a marsh in southern New Hampshire USA at a site that is approximately 10 km upstream of the mud flat site described above for *H. filiformis*. *S. alterniflora* at this site, which is the tall form, displays a typical seasonal growth cycle for salt marsh plants. In the spring, when growth begins, carbohydrates stored in rhizomes over winter are remobilized and used to fuel early shoot growth (Hull, Sulluvan, & Lytle, 1976; Lytle & Hull, 1980a, b). Apparently a significant amount of this carbon is lost to the surrounding sediments through roots, which fuels microbial metabolism. After shoots are tall enough to support significant photosynthesis, organic carbon release from roots is derived from photosynthate that is transported from leaves to roots, again fueling microbial metabolism.

Another consequence of acquiring significant leaf area is that plants tend to transpire water at rates that are high enough to leave considerable salt deposits on leaves. During low tide when surface sediments are exposed, a great deal of water is removed from the sediments and this water most be replaced by air. The path of least resistance to air flow into the sediments is through air channels in shoots and rhizomes (aerenchyma) so that air enters the sediments through the root system (Dacey & Howes, 1984). Hence, the oxidizing ability of this air occurs at the root surface and the surrounding rhizosphere. This is convenient for the plant since it can use this oxygen to attenuate stresses due to the production of toxic compounds by bacteria such as sulfide. The release of dissolved organic carbon and O_2 into the root zone by *S. alterniflora* leads to competing processes similar to that shown above for *H. filiformis*. Release of DOC stimulates bacterial activity, and as will be shown below, much of this activity is attributed to sulfate-reducing bacteria (SRB) that produce sulfide.

Although O_2 is released into the rhizosphere, it is insufficient to completely aerate the rhizosphere and anaerobic metabolism tends to dominate bacteria activity. However, the O_2 does have a strong impact on the rhizosphere where it removes a great deal of reduced S. Since many SRB are capable of active nitrogen fixation, it is thought that plants may be attempting to stimulate this activity to acquire additional fixed nitrogen (Welsh, Wellsbury, Bourgues, De Wit, & Herbert, 1996). The cost for this nitrogen is the potential accumulation of toxic sulfide that the plant has to combat by introducing O_2.

These competing processes continue unabated for several weeks. However, near the end of July, *S. alterniflora* begins the reproductive stage of growth when it flowers and produces seeds. All of the culms of the tall form of *S. alterniflora* undergo reproductive growth. This differs from the short form that is found away from creeks in which only about 30% of the culms flower. This was a significant component of our studies since our primary goal was to determine the effects of changing growth stage on sedimentary microbial biogeochemistry (Hines et al., 1989). We were better able to observe these changes in plants in which all members underwent the reproductive process, so we purposely chose the tall form for more detailed study. The onset of reproduction results in drastic changes in the role of the plant as a provider of DOC and O_2 to the root zone. Immediately upon flowering, both DOC and O_2 release ceased, which resulted in extreme changes in belowground redox processes (Hines et al., 1989).

What are the consequences the plants ability to deliver DOC and O_2 to roots? Figure 4 depicts the seasonal growth of aboveground biomass of *S. alterniflora*, and its effect on sulfate reduction, dissolved Fe, and total reduced S in sediments (Hines et al., 1999). Grasses grew nearly 2 m before flowering commenced in late July and no additional growth occurred once flowering began. Growth was almost continuous except for a temporary slowdown in mid June. This year was the only one of four years studied that this temporary cessation of growth occurred. Sulfate reduction increased >10-fold as soon as plants began growing in early May. This increase was not due to increasing temperature, since the temperature over this period did not increase, but must have been due to the sudden release of DOC from leaky rhizomes as they began to promote early plant growth. The rate of sulfate reduction remained high throughout May, June and July, but also exhibited an additional increase when shoots re-established active growth following the brief slowdown in June. Once plants flowered in late July, sulfate reduction decreased significantly due to the cessation of DOC exudation.

Dissolved Fe displayed interesting changes over time (Figure 4) that were similar to those that occurred in the sediments inhabited by *H. filiformis*. Iron essentially disappeared from solution soon after sulfate reduction increased in May due to its removal as an Fe-sulfide mineral. However, once plants were tall

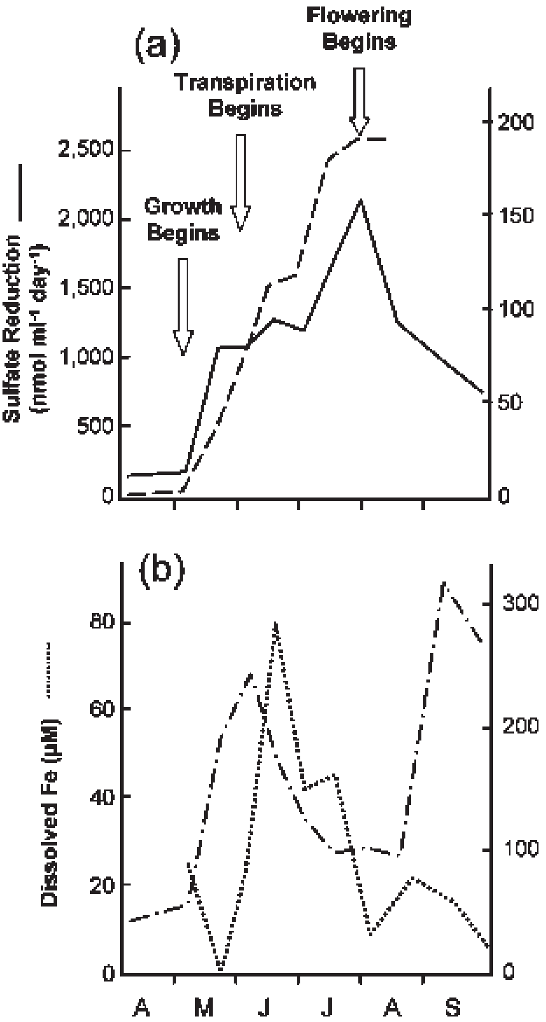


Figure 4. Temporal variations in plant height, sulfate reduction rates (**a**) and dissolved iron and total reduced sulfur (**b**) in sediment inhabited by the tall form of *Spartina alterniflora* (Hines et al., 1989, 1999).

enough to begin transpiring water, the introduction of O_2 into the sediments reversed the loss of Fe, which increased to nearly 300 µM despite the rapid production of sulfide (rapid sulfate reduction). Fe decreased to about 150 µM, but did not decrease to <50 µM until flowering commenced in late July. Once again, dissolved Fe changes over time were the opposite of what would be expected from sulfate reduction alone. Despite the extremely rapid rates of sulfide production, Fe was retained in solution since subsurface Fe and S cycles were maintained by the introduction of an oxidant into the sediments. Unlike the sediments bioturbated by *H. filiformis* in which Fe oxides were the primary oxidant, O_2 was responsible for subsurface oxidation in the *S. alterniflora* sediments.

Plant activities also affected reduced S in the sediments (Figure 4). The total reduced S data in Figure 4 are from a technique that measures essentially all reduced inorganic S species, including dissolve sulfide and Fe sulfide minerals such as Fe monosulfides and pyrite (Hines, Visscher, & Devereux, 2002). Hence, essentially the entire reduced S produced during sulfate reduction was determined. Once sulfate reduction increased rapidly in early May, reduced S increased as well. However, once O_2 was introduced into the sediments during transpiration, this material decreased greatly even though its production was very rapid and even increased in June. Plants were able to oxidize S species at a rate that exceeded its production. However, once reproductive growth began in late July and O_2 exudation ceased, reduce S increased rapidly even though its production decreased (Figure 4). Hence, plant activity and its change over time had profound effects on redox cycling belowground. In fact, when we used sulfate reduction rate data to calculate what the pore water chemistry should have been, the observed concentrations of sulfate and bicarbonate were much higher and lower, respectively than predicted in July, but identical to what was predicted in August just two weeks after flowering (Hines et al., 1989). Therefore, these sediments, after flowering, behaved biogeochemically exactly like unvegetated sediments since the plants did not affect the sediments at all after reproduction began (Hines, 1991). Studies that do not sample often will completely miss these important and dramatic changes.

We were interested in how these temporal changes might affect rhizosphere microbial populations. It seemed plausible that the composition of the sulfate-reducing population would change in response to dramatic temporal changes in DOC availability and O_2 exudation. This was certainly observed in terms of rates of sulfate reduction, but would these changes also affect the types of SRB inhabiting the sediments throughout these changes? To this end, we embarked on detailed studies that utilized traditional culturing techniques and molecular approaches to investigate SRB in bulk sediments and those inhabiting roots directly.

We utilized a variety of substrates to enumerate SRB in vegetated and unvegetated sediments using an anaerobic most-probable-number (MPN) technique (Hines et al., 1999). Vegetated marsh sediments harbored more than four orders of magnitude more SRB than did unvegetated estuarine sediments nearby (Table I). The marsh sediments exhibited sulfate reduction rates that were about 5–10 times more rapid than the estuarine sediments. The largest difference in abundances between the two sites was in MPN tubes containing ethanol as the electron donor. To further investigate this phenomenon, working with Irving Mendelssohn at the University of Louisiana, we incubated *S. alterniflora* roots hydroponically without O_2 and in the presence of antibiotics to inhibit bacterial utilization of root exudates. Ethanol rapidly accumulated under these conditions

TABLE I

Most-probable-number estimates ($\times 10^4$) of viable sulfate-reducing bacteria in sediments inhabited by *Spartina alterniflora* (marsh) and in unvegetated estuarine sediments (estuary)

	Substrates				
	Acetate	Ethanol	Benzene	Propionate	Butyrate
Marsh	640	6400	14	21	357
Estuary	0.18	0.20	ND[a]	0.12	0.09

The medium of Widdel and Pfennig (1981) was amended with the individual substrates (electron donors) listed.

[a] none detected

(Figure 5) indicating that roots conducted ethanol fermentation in the absence of O_2 and that this ethanol escaped into the rhizosphere. Roots collected from the field also exhibited active alcohol dehydrogenase activity underscoring their ability to exude ethanol as shown previously (Mendelssohn, McKee, & Patrick, 1981). Since ethanol is a substrate that can be used directly by SRB, it appeared that the large numbers of ethanol-utilizing SRB in the vegetated sediments occurred because ethanol was being supplied directly from plants instead of by fermenting bacteria that normally supply fermentation products to SRB. We also noted that *S. alterniflora* roots tended to produce acetate, which also may have supported sulfate reduction (Hines, Banta, Giblin, Hobbie, & Tugel, 1994).

Using molecular techniques, we noted that SRB in sediments inhabited by *S. alterniflora* were dominated primarily by members of the family *Desulfobacter-*

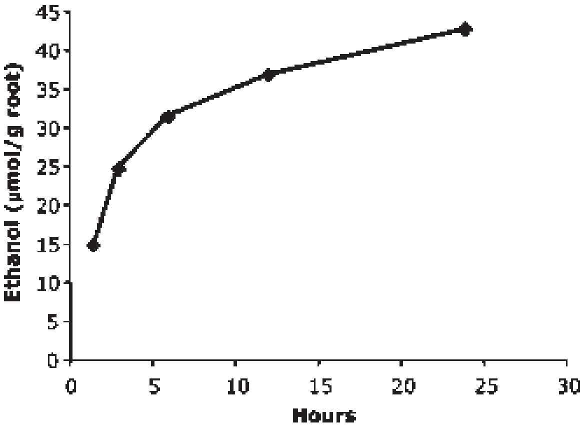


Figure 5. Accumulation of ethyl alcohol in hydroponic fluids during the anaerobic incubation of *Spartina alterniflora* roots.

iaceae, but members of the genus *Desulfobulbus* were also unusually high (Devereux, Hines, & Stahl, 1996; Hines et al., 1999; Rooney-Varga, Devereux, Evans, & Hines, 1997, Rooney-Varga et al., 1998). Members of the family *Desulfovibrionaceae* were almost non-existent, which differs from measurements of SRB populations in sediments without vegetation (Devereux et al., 1996). Later studies by others also demonstrated further that desulfovibrios are absent from salt marsh sediments (Klepac-Ceraj et al., 2004). Members of the *Desulfobacteriaceae* are extremely diverse and many are known to withstand wide changes in redox conditions, so they may be better adapted to the rapid changes that occur in the marsh rhizosphere (Widdel & Pfennig, 1981). When we isolated roots from bulk sediments, it was revealed that SRB of the *Desulfobacteriaceae* family increased in relative abundance (compared to total *Bacteria*) when *S. alterniflora* was exuding DOC, which closely correlated with seasonal changes in plant activity and other geochemical parameters (Figure 6). In fact, this bacterial group accounted for over 30% of the total bacteria present when plants were elongating aboveground (Rooney-Varga et al., 1997, 1998), a relative abundance that is >10-fold higher than what occurs in sediments in which substrates are provided to SRB by fermenting bacteria rather than plants (Devereux et al., 1996). Hence, root-associated bacteria responded rapidly to changes in plant activity.

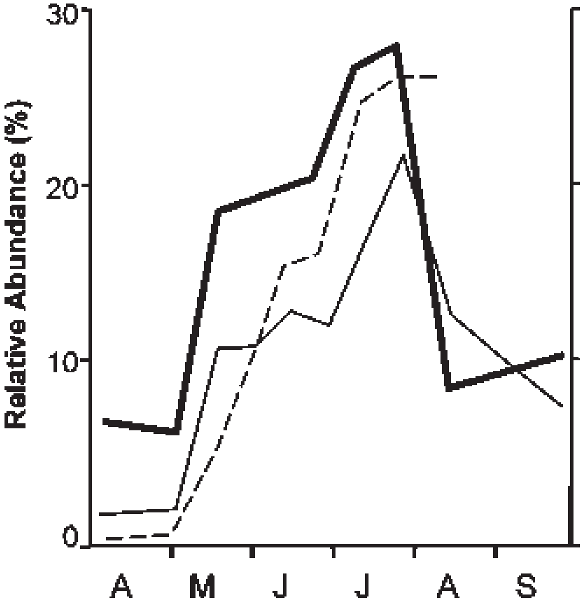


Figure 6. Temporal changes in the abundance of members of the *Desulfobacteriaceae* family relative to total *Bacteria* in terms of ribosomal RNA in sediments inhabited by the tall form of *Spartina alterniflora* (Rooney-Varga et al., 1997; Hines et al., 1999). *Light gray lines* represent plant height and sulfate reduction rates exactly as presented in panel **a** in Figure 4 for comparison.

4. Comparison of Effects of *H. Filiformis* and *S. Alterniflora* on Redox Cycling in Sediments

Both the bioturbating worm and the salt marsh grass greatly altered redox conditions and cycling of elements in the sediments from what would be expected in their absence. In both cases, concentrations of reduced S were much lower and dissolved Fe much higher. These anomalies were due to the introduction of oxidants into the sediments; oxidized Fe particles in the case of *H. filiformis* and O_2 in the case of *S. alterniflora*. However, redox cycling in both cases was exacerbated since labile organic matter was introduced into the sediments; solid organic matter in the case of *H. filiformis* as particles were buried, and as DOC in the case of *S. alterniflora* exudations including ethanol to some degree. Despite the similarities between the two systems in terms of creating three-dimensional redox gradients and stimulating subsurface bacteria, the sediments bioturbated by *H. filiformis* exhibited very high dissolved Fe levels, which exceeded 350 μM, while dissolved sulfide was <2.0 μM. Conversely, dissolved Fe in the *S. alterniflora* sediments reached only ~80 μM, but dissolved sulfide levels reached as high as 2,500 μM (Hines et al., 1989). This large difference was probably due in part to the fact that the *H. filiformis*-inhabited sediments received a constant supply of solid phase Fe from the surface while the salt marsh sediments simply recycled Fe *in situ*. The marsh also supported higher rates of sulfide production than the worm-inhabited sediments. Therefore, redox cycling was greatly stimulated in both cases, but the concentrations of redox-active elements varied greatly (Hines et al., 1989). The worm-inhabited sediments created a rapidly turning S cycle (dissolved sulfide residence time of <3 min) and much slower Fe cycle (dissolved Fe residence time of ~0.4 days). However, the marsh sediments created an opposite situation in which S turned over slowly (dissolved sulfide residence time of ~2 days) while Fe cycled rapidly (dissolved Fe residence time of <0.06 days; Hines, 1991).

5. Perspectives for Future Work

These studies illustrate the rapidity of microbially-mediated redox cycles when enhanced by macroorganism processes and underscore the importance of synergistic relationships between micro- and macroorganisms. These relationships occur along a continuum of spatial scales from micrometers to centimeters, and a further elucidation of micro-scale phenomena would improve our understanding of such biotic controls on redox processes. The combination of molecular and microscopic approaches has demonstrated the complexity of bacterial population compositions at small scales such as in worm burrow walls or on plant roots. A melding of these techniques with biogeochemical measurements within a framework of rapid temporal biochemical changes conducted by plants and animals should further clarify the intricacies of these important relationships.

Acknowledgements

I am grateful for the many colleagues and students who contributed to this work. In particular, I wish to thank Joyce Tugel, Berry Lyons, Steve Knollmeyer, Bob Evans, Bill Orem, Galen Jones, Rich Devereux, Stephanie Willis, and Juliette Rooney-Varga. This work was supported by grants from the US Environmental Protection Agency, the US National Science Foundation, and National Aeronautics and Space Administration.

References

Aller, R. C., & Yingst, J. Y. (1985). Effects of the marine deposit-feeders *Heteromastus filiformis* (Polychaeta), *Macoma balthica* (Bivalvia), and *Telling texana* (Bivalvia) on averaged sedimentary solute transport, reaction rates, and microbial distributions. *Journal of Marine Research*, *43*, 615–645.

Dacey, J. W. H., & Howes, B. L. (1984). Water uptake by roots controls water table movement and sediment oxidation in short *Spartina alterniflora* marsh. *Science*, *224*, 487–490.

Devereux, R., Hines, M. E., & Stahl, D. A. (1996). S cycling: Characterization of natural communities of sulfate-reducing bacteria by 16S rRNA sequence comparisons. *Microbial Ecology*, *32*, 283–292.

Hines, M. E. (1991). The role of certain infauna and vascular plants in the mediation of redox reactions in marine sediments. In J. Berthelin (Ed.), *Diversity of environmental biogeochemistry, Vol. 6* (pp. 275–286). Amsterdam, The Netherlands: Elsevier.

Hines, M. E., & Jones, G. E. (1985). Microbial biogeochemistry in the sediments of Great Bay, New Hampshire. *Estuarine, Coastal and Shelf Science*, *20*, 729–742.

Hines, M. E., Banta, G. T., Giblin, A. E., Hobbie, J. E., & Tugel, J. T. (1994). Acetate concentrations and oxidation in salt marsh sediments. *Limnology and Oceanography*, *39*, 140–148.

Hines, M. E., Evans, R. S., Genthner, B. R. S., Willis, S. G., Friedman, S., Rooney-Varga, J. N., et al. (1999). Molecular phylogenetic and biogeochemical studies of sulfate-reducing bacteria in the rhizosphere of *Spartina alterniflora*. *Applied and Environmental Microbiology*, *65*, 2209–2216.

Hines, M. E., Knollmeyer, S. L., & Tugel, J. B. (1989). Sulfate reduction and other sedimentary biogeochemistry in a northern New England salt marsh. *Limnology and Oceanography*, *34*, 578–590.

Hines, M. E., Lyons, W. B., Armstrong, P. B., Orem, W. H., Spencer, M. J., & Gaudette, H. E. (1984). Seasonal metal remobilization in the sediments of Great Bay, New Hampshire. *Marine Chemistry*, *15*, 173–187.

Hines, M. E., Orem, W. H., Lyons, W. B., & Jones, G. E. (1982). Microbial activity and bioturbation-induced oscillations in pore water chemistry of estuarine sediments in spring. *Nature*, *299*, 433.

Hines, M. E., Visscher, P. T., & Devereux, R. (2002). Sulfur cycling. In C. J. Hurst, G. R. Knudsen, M. J. McInerney, L. D. Stetzenbach, & M. V. Walter (Eds.), *Manual for Environmental Microbiology. 2nd edition* (pp. 427–438). Washington, DC: American Society for Microbiology.

Hull, R. J., Sulluvan, D. M., & Lytle, J. R. W. (1976). Photosynthate distribution in natural stands of salt water cordgrass (*Spartina alterniflora* Loisel.). *Agronomy Journal*, *68*, 969–972.

Jones, D., Darah, P., & Kochian, L. (1996). Critical evaluation of organic acid mediated iron dissolution in the rhizosphere and its potential role in root iron uptake. *Plant and Soil*, *180*, 57–66.

Klepac-Ceraj, V., Bahr, M., Crump, B. C., Teske, A. P., Hobbie, J. E., & Polz, M. F. (2004). High overall diversity and dominance of microdiverse relationships in salt marsh sulphate-reducing bacteria. *Environmental Microbiology*, *6*, 686–698.

Lytle, R. W., Jr., & Hull, R. J. (1980a). Photoassimilate distribution in *Spartina alterniflora* Loisel. II. Autumn and winter storage and Spring regrowth. *Agronomy Journal*, *72*, 938–942.

Lytle, R. W., Jr., & Hull, R. J. (1980b). Photoassimilate distribution in *Spartina alterniflora* Loisel. I. Vegetative and floral development. *Agronomy Journal*, *72*, 933–938.

Mendelssohn, I. A., McKee, K. L., Patrick, J. W. H. (1981). Oxygen deficiency in *Spartina alterniflora* roots: Metabolic adaptation to anoxia. *Science*, *214*, 439–441.

Neira, C., & Hoepner, T. (1994). The role of *Heteromastus filiformis* (Capitellidae, Polychaeta) in organic carbon cycling. *Ophelia*, *39*, 55–73.

Rooney-Varga, J. N., Devereux, R., Evans, R. S., & Hines, M. E. (1997). Seasonal changes in the relative abundance of uncultivated sulfate-reducing bacteria in a salt marsh sediment and rhizosphere of *Spartina alterniflora*. *Applied and Environmental Microbiology*, *63*, 3895–3901.

Rooney-Varga, J. N., Genthner, B. R. S., Devereux, R., Willis, S. G., Friedman, S. D., & Hines, M. E. (1998). Phylogenetic and physiologic diversity of sulfate-reducing bacteria isolated from a salt marsh sediment. *Systematic and Applied Microbiology*, *21*, 557–568.

Tugel, J. B., Hines, M. E., & Jones, G. E. (1986). Microbial iron reduction by enrichment cultures isolated from estuarine sediments. *Applied and Environmental Microbiology*, *52*, 1167–1172.

Welsh, D. T., Wellsbury, P., Bourgues, S., De Wit, R., & Herbert, R. A. (1996). Relationship between porewater organic carbon content, sulphate reduction and nitrogen fixation (acetylene reduction) in the rhizosphere of Zostera noltii. *Hydrobiologia*, *329*, 175–183.

Widdel, F., & Pfennig, N. (1981). Studies on dissimilatory sulfate-reducing bacteria that decompose fatty acids. I. Isolation of new sulfate-reducing bacteria enriched with acetate from saline environments. Description of Desulfobacter postgatei gen.nov., sp. nov. *Archives of Microbiology*, *129*, 395–400.

Water, Air, and Soil Pollution: Focus (2006) **6:** 173–181
DOI: 10.1007/s11267-006-9037-2

DISTRIBUTION OF REDOX-SENSITIVE ELEMENTS IN BOTTOM WATERS, POREWATERS AND SEDIMENTS OF ROGOZNICA LAKE (CROATIA) IN BOTH OXIC AND ANOXIC CONDITIONS

IRENA CIGLENEČKI[1,*], SRĐAN PICHLER[1], ESAD PROHIĆ[2] and BOŽENA ĆOSOVIĆ[1]
[1] *Department of Marine and Environmental Research, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia*
[2] *Department of Mineralogy and Petrography, Faculty of Science, University of Zagreb, Horvatovac bb, Zagreb, Croatia*
*(*author for correspondence, e-mail: irena@rudjer.irb.hr; phone: +385-1-4561148; fax: +385-1-4680242)*

Abstract. Geochemical, mineralogical and sedimentological analyses were carried out to contrast two different sites (respectively characterized by permanently oxic and anoxic conditions) in a small, meromictic, seawater lake. In fact, due to relatively high organic matter content, and reduced water exchange, the Rogoznica Lake has almost permanent anoxic conditions below the depth of 12 m, where sediment can be considered an anoxic–sulphidic sedimentary environment. Different water column and sediments redox conditions affect the distribution and speciation of major redox-sensitive metals (Fe, Mn, Mo), reduced sulphur species (RSS) and dissolved organic C (DOC). Trace metals, especially those that accumulate in anoxic–sulphidic environments (Fe, Mo) showed a marked enrichment in the solid phase, whereas the low solubility of sulphides leads to low porewater concentrations. The relatively high sedimentary enrichment of Mo (up to 81 mg/kg) also confirms highly anoxic conditions within the Rogoznica Lake sediments. Results clearly show that chemical species within the sediments will tend towards equilibrium between porewater and solid phase according the prevailing environment conditions such as redox, pH, salinity, DOC.

Keywords: anoxia, geochemistry, Fe, Mn, Mo, porewater, sulphide, sediment, Rogoznica Lake

1. Introduction

In aquatic systems, sediments are the final sink for pollutants. In fact, the interaction between dissolved species and suspended particles leads to the accumulation of materials onto bottom, eliminating them from the water column and reducing the potential toxicity to aquatic organisms (Salomons, De Rooij, Kerdijk, & Bril, 1987). In this process the water/sediment phase boundary has important role because in certain conditions metals can be release from sediments to porewater and then to bottom waters. In these circumstances, sediments become sources of pollutants to the aquatic environment.

Sulphides are considered the major solid phases controlling dissolved trace metal concentrations in most anoxic sediments (Jacobs, Emerson, & Skei, 1985; Huerta-Diaz, Tessier, & Carignan, 1998; Morse & Luther, 1999) because their low solubility results in low porewater metal concentrations. Upon resuspension of the sediment into an oxic water layer these metal sulphides may oxidize, thereby producing oxidized – more soluble – sulphur species and releasing the associated metals to the water column. Therefore, these sulphide minerals represent secondary sources when contaminants are remobilized in the water column under the effects of either resuspension events or changing environmental conditions (e.g., redox, pH, salinity, DOC) (Stuart, Apte, & Bately, 1998; Tang, Warneken, & Santschi, 2002).

The aim of this work was to investigate the distribution of major redox-sensitive metals (Fe, Mn, Mo), reduced sulphur species (RSS) and DOC between bottom, porewaters and sediments in two contrasting environments of Rogoznica Lake (Eastern Adriatic Coast).

Rogoznica Lake may be considered as a natural laboratory for studies of redox chemistry since it provides sites where the redox cline is situated in the sediment and in the water column (euxenic conditions). Comparison between those sites is a unique situation as both sites are situated in the same water body. The two locations chosen here represent permanently oxic and anoxic conditions.

The combined effects of sedimentological characteristics together with redox potential (Eh), pH, salinity, RSS and DOC of both sediment porewater and overlying water will be discussed.

2. Study Site

Rogoznica Lake is a karstic depression filled with seawater, situated on the eastern Adriatic coast, 40 km south from Šibenik, Croatia, on the Gradina peninsula (43°32′ N 15°58′ E) (Figure 1a). Its biogeochemical and geomorphological characteristics have been described by several authors (Barić et al., 2003; Ciglenečki, Carić, Kršinić, Viličić, & Ćosović, 2005; Ciglenečki, Kodba, Viličić, & Ćosović, 1998; Ćosović, Ciglenečki, Viličić, & Ahel, 2000; Kršinić, Carić, Viličić, & Ciglenečki, 2000; Mihelčić, Šurija, Juračić, & Branica, 1996; Stipaničev & Branica, 1996). The lake has an area of 10,276 m^2 and a maximum depth of 15 m. There is no visible connection with the surrounding sea but lake tides are detectable on the cliffs, although with a certain delay, indicating an underground water connection through porous karst over the coarse a year. The salinity of water varies between 24 (at the surface) and 39 (at the deepest parts), and changes seasonally with the amount of rainfall. Maximum summer salinity exceeds those in the Adriatic due to evaporation. The depth of oxic/anoxic boundary varies seasonally and usually is between 9 and 13 m, whereas almost permanent anoxic conditions exist below 12 m depth. Sediment is pore sorted silt and clay silt. Authigenic carbonates of mainly biogenic origin are the most important component. Major mineral is calcite (65%–92%) followed by aragonite, quartz, dolomite and pyrite (Table I). The accumulation rate, calculated

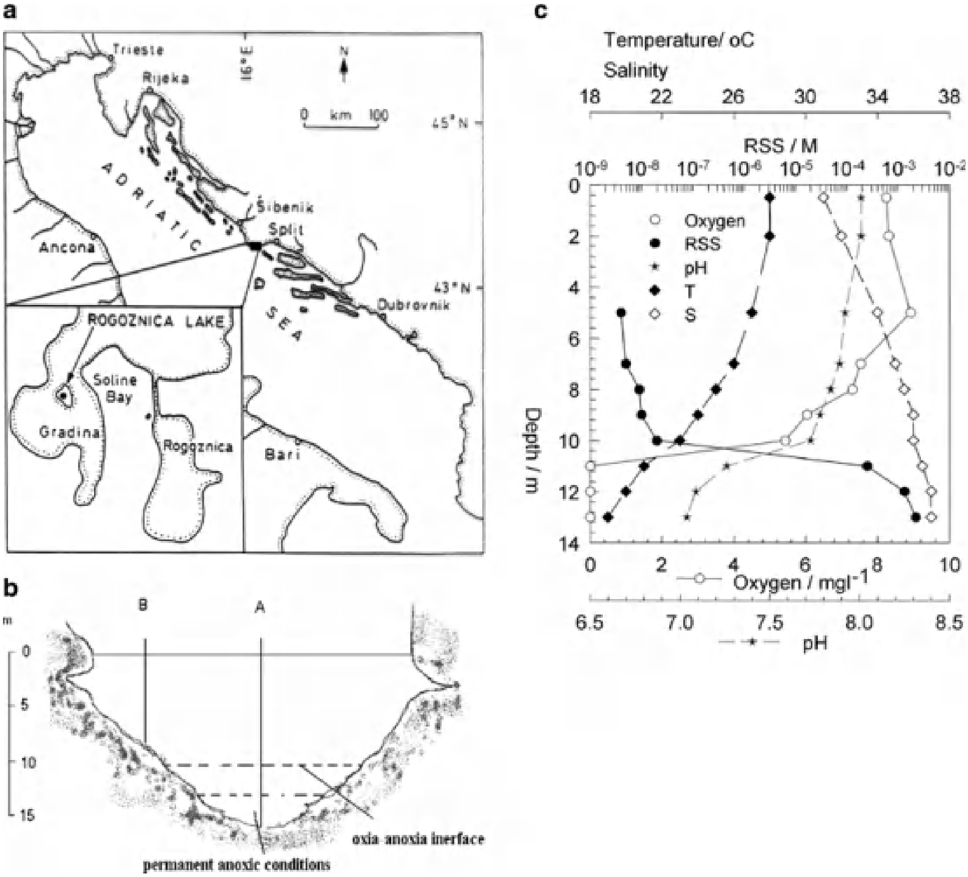


Figure 1. (**a**) map with the position of the Rogoznica Lake; (**b**) Vertical profile of the water column in the Rogoznica Lake with evident sediment sampling locations *A* and *B*; (**c**) Vertical profiles of RSS, oxygen, temperature, salinity and pH in the Rogoznica lake (June 1999).

by using the ^{137}Cs method is relatively high (0.45 cm/year) at site A, the deepest point, Figure 1b (Mihelčić et al., 1996). This implies that the 25 cm of deposition at A required about 50 years.

3. Materials and Methods

3.1. SAMPLING AND SEDIMENT MANIPULATION

Sediment samples were collected by scuba diving, using hand-driven Plexiglas corers (30–45 cm long, and 5–9 cm inner diameter). The samples were taken from two contrasting sites in the lake: A) at 14 m depth, where permanent anoxic conditions exist in the overlying water column and B) at 8 m depth, which is

TABLE I

Mineral composition of the Rogoznica Lake sediments[a]

	Site B (depth/cm)				Site A (depth/cm)					
Mineral	0–5	5–10	10–15	15–22	0–5	5–10	10–15	15–20	20–25	25–32
Calcite	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
Aragonite	++	++	++	++	++	++	++	++	++	++
Quartz	(+)	(+)	+	+	(+)	+	(+)	+	+	+
Dolomite	(+)	(+)	(+)	(+)	–	–	–	(+)	(+)	(+)
Pyrite	(+)	(+)	+	+	–	–	–	(+)	+	+

[a] Estimation from X-ray analyses data: +++, very abundant (>30%), ++, abundant (10%–30%), +, fairly abundant (5%–10%), (+), detected (>2%).

always exposed to the oxic water layer, Figure 1b. After sampling, the sediment was immediately frozen at −20 °C until further treatment. Before analysis, sediment was taken from the corer and cut in slices of 5 cm. These sample slices were put in PVC bottles for centrifugation. The porewater was collected from the sediment by centrifugation and squeezing through a cellulose nitrate filter, pore size 0.45 μm. To minimize sample oxidation artefacts, all sediment manipulation were performed in N_2 filled polyethylene ATMOS BAG.

Lake waters overlying sampled sediments were taken by 5 l Niskin sampler from 0, 2, 5, 7, 8, 9, 10, 11, 12 and 13 m depths in site A. The samples taken from anoxic conditions were also preserved under N_2 atmosphere. In collected lake water samples basic physico-chemical parameters such as salinity, temperature, pH, dissolved oxygen and RSS were measured (Figure 1c).

3.2. ANALYTICAL PROCEDURES

Temperature, salinity and pH were measured immediately after sampling with Hg-thermometer, refractometer (Atago, Japan) and pH meter Delta Ohm HD 8602, USA, respectively. Dissolved oxygen was determined by standard method by Winkler titration (Strickland & Parsons, 1972).

Trace metals were analyzed using inductively coupled plasma-mass spectrometer (ICP-MS) for porewater, bottom water, and sediment (fraction<63 μm) at the Activation Laboratories (Ontario, Canada).

RSS (sulphide, elemental sulphur, polysulphide) were determined electrochemically in the overlying lake water and sediment porewater by linear sweep voltammetry (LSV) (Ciglenečki & Ćosović, 1997).

DOC measurements were performed using a Shimadzu TOC-500 Analyzer that uses high-temperature catalytic oxidation.

Mineral composition and granulometric measurements were carried out following the work by Mihelčić et al. (1996).

Specific surface area (SSA) was measured by nitrogen adsorption (Micromeritics Flowsorb II 2300 surface area analyzer).

4. Results and Discussion

Vertical porewater profiles of redox-sensitive metals, RSS and DOC in sediments A and B (Figure 1b) are presented in Figure 2. The main differences reflect their different geomorphologic and biogeochemical characteristic. The water overlaying site A is permanently anoxic with relatively high concentrations of RSS and DOC (up to 10^{-2} M and 6 mg/l, respectively), while B always lies below oxic water column and the redox-transition zone is placed below the sediment–water interface. Redox potential of the surface sediments was 100 mV in B and −420 mV in A, whereas pH was 6.98 at both sites. Both sediments consist of silt and clay silt. Clayey silt prevails in A, where consequently SSA is higher (7.97–12.50 m^2/g) than at B (2.57–3.85 m^2/g).

Sediment redox conditions are closely related to the level of organic matter oxidation, RSS and DOC and drive metal distribution and speciation within sediment column. RSS and DOC accumulated in porewaters (Figure 2) indicate a very intense

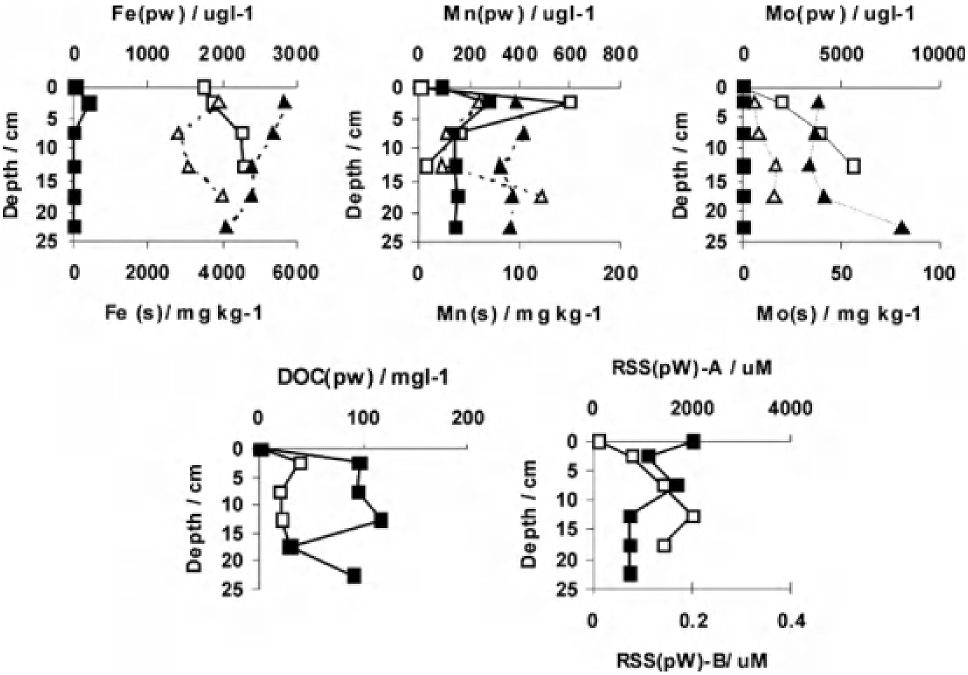


Figure 2. Porewater (*squares*) and sedimentary (*triangles*) profiles of Fe, Mn, Mo, RSS and DOC in sediment cores A (*full symbols*) and B (*open symbols*) in the Rogoznica Lake. Sediment was cut in slices of 5 cm. Water–sediment interface was denoted as 0 cm (*bottom water*).

sulphate reduction and pronounced organic matter mineralization at site A as compared to site B. RSS concentration at A changed from 2,000 μM in the lake bottom water to 750 μM in the sediment layer 20–25 cm. At B, RSS varied from 0.01 μM in the bottom water to 0.2 μM in the sediment layer at 10–15 cm, i.e., concentrations were lower than at A and increased with sediment depth. DOC in A increased from 3 mg/l in bottom water to the maximum value of 120 mg/l in the sediment layer at 10–15 cm, whereas in B, DOC increased from 3 mg/l in the bottom water to 38 mg/l in the layer at 0–5 cm depth (Figure 2). As expected, redox-sensitive metal (Fe, Mn, Mo) concentrations in porewaters, are much higher at B than at A. In contrast, sediment particles show the opposite relationship (Table II). For the considered metals several times higher concentrations were found in the porewater than in the bottom water which implies that diffusion is possible along the gradient from the sediment to the water column. Due to immobilization by RSS the metal enrichment is low or even negative for porewaters of site A (Table II). Metal distributions, as expected, seem to be controlled by redox potential profiles within both sediments. In anoxic sediment, sulphate reduction produces free reactive RSS which tend to form different soluble and precipitated metalsulphide species, depending on their solubility products (Thamdrup, Fossing, & Jorgensen, 1994; Henneke, Luther, de Lange, & Hoefs, 1997). High sulphate reduction rates produce sufficient amounts of sulphide to form very stable, insoluble metal sulphides and in particular pyrite crystals (FeS_2) via precipitation of FeS followed by its reaction with polysulphides and S^0. FeS can coprecipitate/adsorb trace elements and thus sedimentary pyrite appears to be an important sink for Mo, Mn, Co, Cu, Ni, Cr (Morse & Luther, 1999; Müller, 2002). In the Rogoznica Lake sediments, a similar mechanism may be responsible for the observed metal distributions. At site A, deposition of fine-grained sediments with high surface area (besides relatively high presence of RSS in the porewater) entailed the accumulation of both organic matter

TABLE II

Concentrations of Fe, Mn and Mo in porewater and sediments of the Rogoznica Lake at sites A and B

	A						B					
	Porewater ($\mu g\ l^{-1}$)			Sediment ($mg\ kg^{-1}$)			Porewater ($\mu g\ l^{-1}$)			Sediment ($mg\ kg^{-1}$)		
Depth/ cm	Fe	Mn	Mo	Fe	Mn	Mo	Fe	Mn	Mo	Fe	Mn	Mo
Bottom water	16.8	89	2.4				1,740	9	5.8			
0–5	204	278	2	5,700	97	38.4	1,890	597	2,015	3,900	59	5.71
5–10	5	142	3	5,400	103	36.4	2,280	162	3,950	2,800	26	8.05
10–15	5	149	5	4,800	81	34	2,295	30	5,635	3,100	23	17.2
15–20	5	153	5	4,800	92	41.3	–	–	–	4,000	121	15.9
20–25	5	147	47	4,100	91	81.4	–	–	–	–	–	–

and trace metals. It follows that sedimentary accumulation of all metals was about 50% higher at A than at B. Both sediments contained more Fe than Mn and Mo (in A about 60 and 150 times more, respectively). Fe enrichments coincide with the presence of the pyrite which was detected at both sites (Table I). Since elemental sulphur, polysulphide and sulphide ions are present at A above the sediment–water interface, pyrite can form even in the water column whereas in B it is expected to form only within sediment. Preliminary thermodynamic calculation of ion activity products (IAP) from measured concentrations of iron and sulphide in the bottom water, indicate that those ions are present at a sufficiently high concentration to make formation of pyrite feasible.

Fe and Mn in sediments and porewaters behave similarly at the same site. In A sedimentary Mn remains nearly constant, whereas in B due to reductive dissolution in the subsurficial sediments (indication of redox-transition zone) its concentration was decreased in the layers bellow (a similar profile was recorded for Fe). Consequently, increasing concentrations of dissolved Mn (Fe) in porewaters from the subsurficial layer were observed (Figure 2). In contrast to Fe and Mn, Mo increases in sediments and porewaters slowly with depth. Extremely high concentrations of Mo were detected in the porewater at site B. All measurements were checked for possible interferences and no visible artifacts were found. Since the measurements were done by high dilution (100 and 200 times) we assume that those results the most probably are overestimated. Similar measurements were repeated later in the porewater of the Rogoznica Lake and that time lower but still high concentrations for Mo were detected (N. Mikac, personal communication).This indicate that such high concentrations might be realistic even now it is hard to explain them. It is interesting that Mo, which is an indicator of sulphidic water (Zheng, Anderson, van Geen, & Kuwabara, 2000), increases with depth at site B. This might indicate that historically the sulphide interface in Rogoznica Lake was higher, and site B also was exposed to the sulphidic, anoxic water. Actually, there are two critical sulphide concentrations for autigenic Mo formation (Zheng et al., 2000). The first is the value of ~0.1 μM (reached in B) as threshold for the onset of Mo–Fe–S co-precipitation, the second of ~100 μM (reached even in the bottom water at A) where direct formation of molybdenum sulphide occurs. Both sediments show increased concentration of Mo (up to 20 mg/kg in the layer at 15–20 cm in B, and up to 81.4 mg/kg in the deepest layer in A) indicating that Rogoznica Lake is an extreme type of aquatic environment, characterized by all the anoxic features well known for the largest world anoxic systems such as the Black Sea, Framvaren Fjord and Lake Pavin.

5. Conclusions

The main geochemical processes influencing both distribution and speciation of redox-sensitive metals in the Rogoznica Lake appear to be transformations between their oxidation states, interaction with RSS and organic matter and/or formation of soluble and precipitated metalsulphide species. Results clearly indicate that chemical speciation within the sediments tends towards equilibrium between porewater and solid phase according the prevailing environment conditions such as redox, pH, salinity, DOC.

Acknowledgements

This work was supported by the Ministry of Sciences, Education and Sport of Republic of Croatia. Many thanks are due to Željko Kwokal for diving assistance, to Neda Vdović and Željko Grahek for their help during analyses. Authors are indebted with Nena Mikac, George R. Helz and anonymous reviewers for their valuable discussions and comments that improved the manuscript.

References

Barić, A., Grbec, B., Kušpilić, G., Marasović, I., Ninčević, Ž., & Grubelić, I. (2003). Mass mortality event in a small saline lake (Lake Rogoznica) caused by unusual holomictic conditions. *Scientia Marina, 67*(2), 129–141.

Ciglenečki, I., Carić, M., Kršinić, F., Viličić, D., & Ćosović, B. (2005). The extinction by sulphide – turnover and recovery of a naturally eutrophic, meromictic seawater lake. *Journal of Marine Systems, 56*, 29–44.

Ciglenečki, I., & Ćosović, B. (1997). Electrochemical determination of thiosulphate in seawater in the presence of elemental sulphur and sulphide. *Electroanalysis, 9*(10), 1–7.

Ciglenečki, I., Kodba, Z., Viličić, D., & Ćosović, B. (1998). Seasonal variation of anoxic conditions in the Rogoznica Lake. *Croatica Chemica Acta, 71*(2), 217–232.

Ćosović, B., Ciglenečki, I., Viličić, D., & Ahel, M. (2000). Distribution and seasonal variability of organic matter in a small eutrophicated salt lake. *Estuarine, Coastal and Shelf Science, 51*, 705–715.

Henneke, E., Luther, G. W. III., de Lange, G. J., & Hoefs, J. (1997). Sulphur speciation in anoxic hypersaline sediments from the eastern Mediterranean Sea. *Geochimica et Cosmochimica Acta, 61*(2), 307–31.

Huerta-Diaz, M. A., Tessier, A., & Carignan, R. (1998). Geochemistry of trace metals associated with reduced sulphur in freshwater sediments. *Geochimica et Cosmochimica Acta, 13*, 213–233.

Jacobs, L., Emerson, S., & Skei, J. (1985). Partitioning and transport of metals across the O_2/H_2S interface in permanently anoxic basin: Framvaren Fjord, Norway. *Geochimica et Cosmochimica Acta, 49*, 1433–1444.

Kršinić, F., Carić, M., Viličić, D., & Ciglenečki, I. (2000). Calanoid copepod *Acartia italica* Steuer, 1910 phenomenon in the small saline lake Rogoznica near Šibenik, Croatia. *Journal of Plankton Research, 22*, 1441–1464.

Morse, J. W., & Luther, G. W. III. (1999). Chemical influences on trace metal–sulphide interactions in anoxic sediments. *Geochimica et Cosmochimica Acta, 63*, 3373–3378.

Mihelčić, G., Šurija, B., Juračić, M., & Branica, M. (1996). History of accumulation of trace metals in sediments of the Rogoznica Lake (Croatia). *Science of the Total Environment, 182*, 105–115.

Müller, A. (2002). Pyritization of iron and trace metals in anoxic fjord sediments (Nordåsvannet

This page intentionally blank

fjord, western Norway). *Applied Geochemistry, 17*, 93–933.

Salomons, W., De Rooij, N. M., Kerdijk, H., & Bril, J. (1987). Sediments as a source for contaminants. *Hydrobiologia, 13*, 30–38.

Stipaničev, V., & Branica, M. (1996). Iodine speciation in the water column of the Rogoznica Lake (Eastern Adriatic Coast). *Science of the Total Environment, 18,* 1–9.

Strickland, J. H. D., & Parsons, T. R. (1972). A practical handbook of seawater analysis. *Bulletin - Fisheries Research Board of Canada, 167*, 1–310.

Stuart, L. S., Apte, S. C., & Bately, G. E. (1998). Effect of short-term resuspension events on trace metal speciation in polluted anoxic sediment. *Environmental Science & Technology, 32*, 620–625.

Tang, D., Warneken, K., & Santschi, P. (2002). Distribution and partitioning of trace metals (Cd, Cu, Ni, Pb, Zn) in Galveston Bay waters. *Marine Chemistry, 78*, 29–45.

Thamdrup, B., Fossing, H., & Jorgensen, B. B. (1994). Manganese, iron, and sulphur cycling in coastal marine sediment, Aarhus Bay, Denmark. *Geochimica et Cosmochimica Acta, 58*(23), 5115–5129.

Zheng, Y., Anderson, R. F., van Geen, A., & Kuwabara, J. (2000). Authigenic molybdenum formation in marine sediments: A link to pore water sulphide in the Santa Barbara Basin. *Geochimica et Cosmochimica Acta, 64*(24), 4165–4178.

Water, Air, and Soil Pollution: Focus (2006) **6:** 183–191
DOI: 10.1007/s11267-006-9038-1

TRANSFORMATION OF PARTICLE-BOUND PHOSPHORUS AT THE LAND–SEA INTERFACE IN A DANISH ESTUARY

HENNING S. JENSEN*, TINA BENDIXEN and FREDE Ø. ANDERSEN
Institute of Biology, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark
*(*author for correspondence, e-mail: hsj@biology.sdu.dk; phone: +45-6550-2223; fax: +45-6593-0457)*

Abstract. Danish rivers carry >50% of the phosphorus (P) transport as particulate P (PP). In five of six rivers sampled in November 1998 iron-bound P made up >59% of PP and loosely adsorbed P ranged between 2% and 13%. This fraction could potentially be released in 14‰ seawater. The behaviour of dissolved and particulate P fractions was studied during seven month in a 2 km long estuary with low freshwater retention time and low tidal range. The river carried ~10% of PP as loosely adsorbed P but increased concentrations of dissolved inorganic P (DIP) relative to the estuarine mixing line was only observed in the summer month with low freshwater flow and was more likely due to DIP release from the bottom sediment. Instead estuarine particles were always enriched with oxidized iron (ox.Fe) and iron-bound P as well as loosely adsorbed P and during May–September this coincided with increasing concentration of PP in estuary. We suggest that flocculation of ox.Fe and adsorption of DIP onto the particles with subsequent transport seawards is a major loss process for P during the summer month. During winter month where 85% of the run-off occurs the dominant process in the estuary is sedimentation of larger particles, however, a comparison of river particles with surface sediment clearly reveals that most PP is mobilized again from the bottom sediments.

Keywords: river, estuary, particles, phosphorus, salinity, sediment

1. Introduction

It has been estimated that 87% of the global riverine input of phosphorus (P) to the worlds oceans is transported as particle-bound P (PP). Some 20% of this is considered to be adsorbed phosphate, although, it is a matter of debate if phosphate bound to oxidized iron species (ox.Fe) can be considered as adsorbed (Fox, 1991; Froelich, 1988; Howarth, Jensen, Marino, & Postma, 1995). The high proportion of PP in the riverine load makes it important to understand the retention, transformation, and resulting bio-availability of PP in estuaries and coastal oceans. A number of studies have dealt with adsorption–desorption control of dissolved inorganic P (DIP) on suspended particles at increasing salinities (e.g., Chambers, Fourqurean, & Hollibaugh, 1995; Gardolinski, Worsfold, & McKelvie, 2004; Lebo, 1991; van Beusekom & Brockman, 1998; van Beusekom & de Jonge, 1998) and there is a general consensus that the binding capacity for DIP onto ox.Fe is reduced at increasing salinities. This a likely explanation for the, often observed, non-conservative behavior (here increase) of DIP relative to the estuarine mixing line (Howarth et al., 1995). Also clay and aluminum oxides contribute to the release of phosphate from river particles (Lebo, 1991) and some P is released from particles as dissolved organic P probably due to lysis of phytoplankton and bacterial cells at increasing salinities (Gardolinski et al., 2004). Processes that acts oppositely on the DIP concentration are flocculation of humic compounds and ox.Fe with adsorption and possible co-precipitation of DIP at low salinities (Forsgren & Jansson, 1992; Forsgren, Jansson, & Nilsson, 1996) and uptake by phytoplankton (e.g., Conley, Smith, Cornwell, & Fisher, 1995; Lebo & Sharp, 1993; Zwolsman, 1994). DIP concentration may also be affected by exchange with the bottom sediment where release from sub-oxic sediments is a dominating pattern in late summer in temperate estuaries (Jensen, Mortensen, Andersen, Rasmussen, & Jensen, 1995; van Beusekom & de Jonge, 1998; Zwolsman, 1994). Concentration of PP is mainly affected by precipitation, flocculation, growth of phytoplankton and, depending on the energy regime, by resuspension (e.g., Howarth et al., 1995).

Concentration of PP in river water and the distribution of PP-forms seems to differ markedly with land-use in the watershed and similarly is the contribution of DIP to the total P-transport increased in developed watersheds (Erntsberger, Edwards, & Balls, 2004).

Danish watersheds are in general dominated by agriculture (~75%) and recently (from 1988 to 1995) P-load from point sources has been reduced by 82% with reduction in river DIP as a consequence. The present estimate is that 50%–80% of the P-load in Danish rivers is carried as PP (Kronvang et al., 2005). It has therefore become increasingly important to understand the transformation of PP in estuaries bordering the agricultural watersheds. Suspended matter in the river, Vindinge Å, and the estuary, Holckenhavn Fjord, Denmark was analyzed by sequential P- and Fe- extraction during seven months in 1998 and sediment-water exchange of DIP was measured at four stations covering the length of the estuary. Concentrations and composition of all P-fractions were compared to the estuarine mixing line. In November 1998 phosphate desorption from river particles in P-free estuarine water was compared to similar measurements in five other Danish rivers.

2. Methods and Study Site

2.1. STUDY SITE

Vindinge Å drain a 221 km^2, mainly agricultural watershed with a run-off height of ~30 cm. It enters the 0.6 km^2, length 2 km, max. depth 2 m, Holckenhavn Fjord at 55°17′51″N, 10°45′51″E in the western end. The eastern end of the estuary is bordered by a road dam with an 8 m wide, 2 m deep opening to the sea. Average freshwater retention time in the estuary is 2–3 days and only 15% of the 1998 run-off took place during summer (May–September). Salinity rarely exceeds

14‰ and tidal range is 20 cm. Annual P-load in 1998 was 14 g m^{-2}. Primary production was dominated by the fast growing macro alga *Ulva lactuca*.

2.2. Sampling and Analytical Procedures

Water and suspended particles were sampled six times during March–October 1998 at six sites in the estuary, covering the range in salinity. The freshwater end-member was always sampled 4 km upwards in the river and the marine end-member was sampled outside the road dam at a site exposed to the open sea. Suspended sediment was retrieved by filtering (Whatman GF/C) and analyzed in duplicates for dry weight, Total P, total Fe, and P-binding sites. Filtered water was analyzed for DIP and total dissolved P (TDP) by standard seawater methods. Total P and total Fe was analyzed by combustion followed by extraction in 1 M hot HCl (see Jensen & Thamdrup, 1993). Seven different P fractions (loosely adsorbed inorganic P (*i*P), iron-bound P, *i*P adsorbed onto clay and aluminum oxides, calcium-bound P, P associated with humic acids, extractable organic P, and refractory organic P) were quantified by the sequential extraction scheme of Jensen and Thamdrup (1993) modified with an additional determination of humic-bound P (Jensen, Caraco, Hansen, & Christensen, 2005). The buffered dithionite solution used to extract iron-bound P, is also very specific for ox.Fe (Jensen & Thamdrup, 1993). Undisturbed sediment cores (5.2 cm clear acrylic tubes) were sampled from four fixed stations covering the length of the estuary. Five cores from each site were incubated with gently stirring of the overlying, oxygenated bottom water for measuring DIP exchange between sediment and water (method in Jensen et al., 1995). Flux measurements were conducted four times during the seven month. In October 1998, three sediment cores from each site were analyzed for P and Fe in solid fractions by methods of Jensen and Thamdrup. The cores were sliced in N2-atmosphere in 1-cm depth intervals and specific depth slices from the three cores were pooled before analyses. In November 1998 suspended particles were sampled in six Danish rivers by centrifugation of river water and freeze-drying of the particles. The particles were analyzed as above and further, desorption of phosphate in P-free, artificial seawater at 14‰ salinity was measured during 24 h of gently shaking.

3. Results

The suspended sediments from six Danish rivers in November 1998 showed higher total Fe for rivers draining iron-rich, organic soils (Brede Å, Skjern Å, Varde Å, Vidå) than for rivers draining clayey soils (Odense Å, Vindinge Å; Table I). Total P contents differed less when considering that the one sample for Vindinge Å with 111 μmol P gDW^{-1} was not representative for the annual average PP-concentration of 214 μmol P gDW^{-1} (Table II). Binding sites for P was quite

TABLE I

Total Fe, total P in µmol gDW^{-1}, and percentage distribution of seven P-fractions in particles from six Danish rivers sampled in November 1998

River	Total Fe	Total P	1 % of total	2 % of total	3 % of total	4 % of total	5 % of total	6 % of total	7 % of total	Desorption of DIP µmol gDW^{-1}
Brede Å	3,645	229	2.1	78	6.8	2.2	2.4	5.5	3.1	3, 9
Odense Å	948	223	12.7	61	4.3	4.2	3.5	7.9	5.8	23, 6
Skjern Å	3,182	183	2.1	38	36	4.7	4.4	9.2	5.4	3, 4
Varde Å	3,679	257	1.6	59	6.8	3.6	4.1	6.9	4.3	3, 9
Vidå	2,848	213	2.1	79	5.8	2.9	2.5	4.5	2.7	5, 0
Vindinge Å	688	111	11.2	59	4.4	5.3	3.6	9.8	6.6	10, 2

The P-fractions are 1: loosely adsorbed phosphate, 2: iron-bound P, 3: phosphate adsorbed onto aluminium oxides and clay, 4: calcium-bound P, 5: humic-bound P, 6: extractable organic P, and 7: refractory organic P. The column most to the right gives the measured desorption of DIP from river particles when suspended 24 h in P-free, artificial sea-water at 14‰.

similar in the iron-rich particles with low proportions of loosely adsorbed *i*P (<2.1%) and high proportions of iron-bound P (>59%) except for Skjern Å where iron-bound P was 38% and *i*P adsorbed onto clay and aluminum oxides was 36% (Table I). Iron-bound P was also the major PP fraction in River Odense Å (61%) and River Vindinge Å (59% in November and 45% as annual average), but in these two rivers loosely adsorbed *i*P made up 12.7% and 11.2% of PP. Sediment from these two rivers also released most DIP when suspended in P-free, artificial seawater (Table I) and for the whole data-set there was a strong correlation between loosely adsorbed *i*P and DIP desorption in artificial seawater ($R^2=0.99$; Table I). Correlation (negative) was also found between desorption and the ratio between ox.Fe and iron-bound P ($r=-0.80$ with log transformed Fe/P ratio; data not shown).

In River Vindinge Å the transport-weighed, annual average, suspended particle had much higher concentrations of Fe, P, ox.Fe, and iron-bound P than the surface sediment at any of the four sampling sites in the estuary (Table II). On each site the surface sediment was richer in iron-bound P than sediment layers down to 5 cm (data not shown) indicating release of iron-bound P in deeper, anoxic sediment as often observed in coastal marine sediments (e.g., Jensen et al., 1995). Iron-bound P contributed 36% to TPsed at station 1, 24% at station 2, and 6% and 8% at stations 3 and 4, respectively. Maximum concentrations of P, Fe, iron-bound P and ox.Fe were observed at station 2 which also was the station that showed diffusive influx of DIP (uptake from overlying water) at all sampling dates (Table II). Influx of DIP was observed at all stations in March and

TABLE II

Particle concentrations (μmol gDW^{-1}) of total P, total Fe, iron-bound P, and ox.Fe for and average annual (transport weighed average) suspended particle from River Vindinge Å, surface sediment (0–1 cm) for the four sediment sampling sites in Holckenhavn Fjord

	Annual average river particle	Station 1 0–1 cm	Station 2 0–1 cm	Station 3 0–1 cm	Station 4 0–1 cm
Total P	214	20.1	37.9	21.2	23.3
Total Fe	660	77.3	296	139	152
Iron-bound P	97	7.2	9.2	1.3	1.9
Ox.Fe	412	24.1	45.7	11.9	12.4
DIP flux					
March		−56	−63	−65	−57
May		111	−12	41	14
August		219	−45	35	11
October		−51	−170	−133	−19

Station 1 is closest to the freshwater inlet and station 4 is closest to the sea. The undermost four rows shows DIP flux (μmol m^{-2} d^{-1}) from undisturbed sediment to the overlying water (positive values) at the same four sites. Negative values represent uptake of DIP from the water into the sediment.

September but for stations 1, 3, and 4 efflux was observed in May and August with the highest values of 111 and 219 μmol P m^{-2} d^{-1} at station 1.

DIP in the estuarine water made up >90% of total dissolved P (TDP) at all times and mostly behaved conservatively relatively to the estuarine mixing line (Figure 1A). In April there was an uptake of DIP from the water and July and August DIP concentrations increased in the estuary. TP showed non-conservative behavior relative to the estuarine mixing line at all times (Figure 1B). The same was the case for PP except maybe for July. In March and April TP was retained in the estuary, seemingly due to sedimentation of PP, but for the rest of the period TP was mobilized in the estuary with increase in PP as a significant proportion of the excess TP.

Concentrations of iron-bound P (in μM) followed the tendency of PP (Figure 2A), and with similar amplitudes the indication is that iron-bound P was the fraction that contributed most to the observed enrichment in PP. Same conclusion may be reached when evaluated changes on a dry matter basis (μmol P gDW^{-1}; Figure 2B). Iron-bound P nearly always increased, especially, at low salinities (2‰–6‰). Loosely adsorbed *i*P (data not shown) followed the tendency of iron-bound P closely but made up a smaller proportion as in the river particle (Table I). Dry matter concentrations of extractable organic P increased some in July and August but otherwise, all other P-fractions behaved more conservatively. The enrichment of particles with iron-bound P and loosely adsorbed *i*P corresponded with enrichment in ox.Fe (Figure 2C), although, ox.Fe showed more variation.

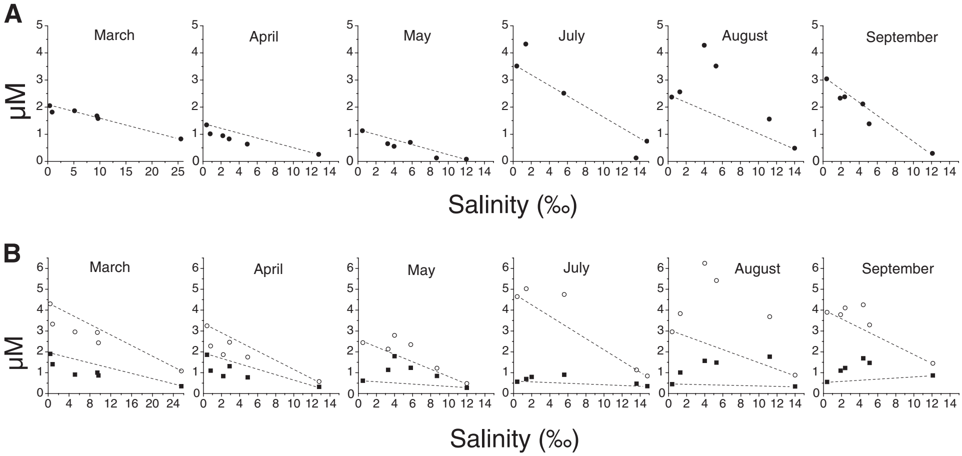


Figure 1. Concentrations of **A** dissolved inorganic P and **B** total P (*open circles*) and particulate P (*closed squares*) along the salinity gradient in Holckenhavn Fjord 1998. *Solid lines* indicate the estuarine mixing lines for the three parameters.

4. Discussion

Iron-bound P contributed more than 59% to PP in five of six Danish rivers in November and the seasonal study in River Vindinge Å confirmed the year-round dominance of iron-bound P. Such high proportions of iron-bound P has not been observed in other studies of PP entering estuaries that drain agricultural watersheds (Conley et al., 1995; Erntsberger et al., 2004) and may be due to iron-rich Danish soils as well as to the high application of P-fertilizer on the fields (up to 20 kg P ha^{-1} year^{-1}). Loosely adsorbed *i*P, on the other hand, was generally much smaller than the 20% suggested as a world average value (discussed in Howarth et al., 1995). The magnitude of DIP released in the desorption experiment with P-free seawater never exceeded the pool-size of loosely adsorbed *i*P, thus, this extraction step seems to provide valuable information on the potential DIP mobilization from suspended river sediments at the land–sea interface.

Even with a clear potential for DIP mobilization from the suspended sediment that entered Holckenhavn Fjord this process was only detected in March when evaluating PP fractions on a dry-matter basis. Thus, the DIP increase observed in July and August could only be explained by DIP efflux from the bottom sediment since PP concentrations increased along with the DIP increase. The (almost completely) absence of DIP desorption is in contrast to most of the investigations cited in the introduction, but it must be kept in mind that Holckenhavn Fjord only represents salinities up to ~14‰, which is only half of the maximum salinity reported in many other studies. We can therefore not exclude the possibility that desorption occurs further out in the sea. In Holckenhavn the general pattern was that particles became more P-rich when entering the estuary because of

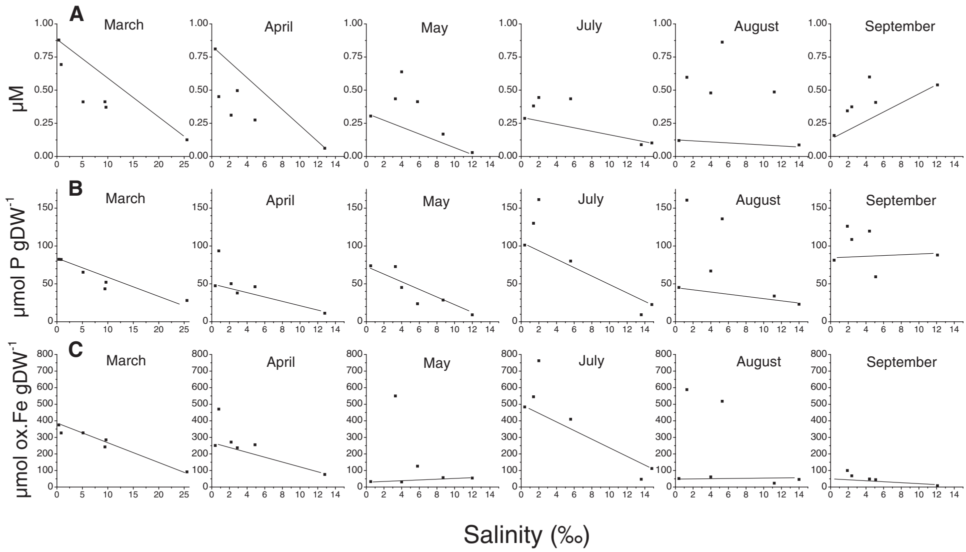


Figure 2. **A** Concentrations of particulate iron-bound P in the estuarine water, **B** iron-bound P in suspended particles, and **C** oxidized iron in suspended particles along the salinity gradient in Holckenhavn Fjord 1998. *Solid lines* indicate the estuarine mixing lines.

enrichment with iron-bound P and loosely adsorbed *i*P. Two mechanisms can be responsible for this. One is the preferential settling of larger, less iron-rich particles close to the river mouth. The remaining suspended particles will be small, iron-rich, and with large surface areas relative to dry weight. Preferential settling is likely dominating in March and April where PP concentrations per volume decline relative to the mixing line. Another mechanism is the formation of ox.Fe rich particles due to flocculation at low salinities as observed by Forsgren and Jansson (1992) in the study of Öre Estuary. This process seemed to dominate for the rest of the period where freshwater flow was lower and retention times higher. Dissolved iron for flocculation may to some extent be supplied from the river as in the Öre Estuary. This was not measured in the present study. It may also be released from the sediment along with DIP by upwards migration of dissolved Fe and P from anoxic sediment layers as it was observed in a seasonal study of Århus Bay (Jensen et al., 1995).

Phosphate was taken up by the bottom sediment in Holckenhavn Fjord from the estuarine water in March and October. This process, as well as the preferential sedimentation of larger particles, is probably dominating during winter when the major run-off occurs. However, when comparing the estuarine surface sediment with the annual average river particle it is clearly revealed that suspended river particles are not retained in the sediment without major mobilization of P from the solid fraction. The sulfide induced release of iron-bound P is one such mobilization mechanism and DIP efflux was most pronounced at the low-salinity site where also PP sedimentation seemed to be the largest. The DIP efflux, and maybe also the Fe-efflux, results in the formation P- and Fe-enriched particles which are carried to the sea during summer. This kind of seasonal pattern is also suggested for the Ems Estuary by van Beusekom and de Jonge (1998). PP increase due to algal DIP uptake as observed in Chesapeake Bay (Conley et al., 1995) seemed less important in Holckenhavn Fjord.

Acknowledgement

The study was supported by grant no. 272050408 from the National Danish Research Council for Nature and Universe.

References

Chambers, R. M., Fourqurean, J. W., & Hollibaugh, J. T. (1995). Importance of terrestrial derived particulate phosphorus to phosphorus dynamics in a west-coast estuary. *Estuaries, 18*(3), 518–526.

Conley, D. J., Smith, W. M., Cornwell, J. C., & Fisher, T. R. (1995). Transformation of particle-bound phosphorus at the land-sea interface. *Estuarine, Coastal, and Shelf Science, 40*, 161–176.

Erntsberger, H., Edwards, A. C., & Balls, P. W. (2004). The distribution of phosphorus between soluble and particulate phases for seven Scottish East Coast rivers. *Biogeochemistry, 67*, 92–111.

Forsgren, G., & Jansson, M. (1992). The turnover of river transported iron, phosphorus and organic carbon in Öre estuary, northern Sweden. *Hydrobiologia, 235/236*, 585–596.

Forsgren, G., Jansson, M., & Nilsson, P. (1996). Aggregation and sedimentation of iron, phosphorus and organic carbon in experimental mixtures of freshwater and estuarine water. *Estuarine, Coastal and Shelf Science, 43*, 259–268.

Fox, L. E. (1991). Phosphorus chemistry in the tidal Hudson River. *Geochimica et Cosmochimica Acta, 55*, 1529–1538.

Froelich, P. N. (1988). Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. *Limnology and Oceanography, 33*(4), 649–668.

Gardolinski, P. C. F. C, Worsfold, P. J., & McKelvie, I. D. (2004). Seawater induced release and transformation of organic and inorganic phosphorus from river sediments. *Water Research, 38*, 688–692.

Howarth, R. W., Jensen, H. S., Marino, R., & Postma, H. (1995). Transport to and processing of P in near-shore and oceanic waters. In H. Tiessen (Ed.), *Phosphorus in the global environment. Transfers, cycles and management. SCOPE 54* (pp. 323–346). Chichester: Wiley.

Jensen, H. S., Caraco, N., Hansen, J., & Christensen, K. K. (2005). Humic-bound phosphorus in soil and sediment. In H. L. Golterman & L. Serrano (Eds.), *Phosphate in sediments* (pp. 99–107). Leiden: Backhuys Publishers (202 pp).

Jensen, H. S., Mortensen, P. B., Andersen, F. Ø., Rasmussen, E., & Jensen, A. (1995). Phosphorus cycling in a coastal marine sediment, Aarhus Bay, Denmark. *Limnology and Oceanography, 40* (5), 908–917.

Jensen, H. S., & Thamdrup, B. (1993). Iron-bound phosphorus in marine sediments as measured by bicarbonate-dithionite extraction. *Hydrobiologia, 253*, 47–59.

Kronvang, B., et al. (2005). Nutrient pressures and ecological responses to nutrient loading reductions in Danish streams, lakes, and coastal waters. *Journal of Hydrology, 304*, 274–288.

This page intentionally blank

Lebo, M. E. (1991). Particle-bound phosphorus along an urbanized coastal plain estuary. *Marine Chemistry, 34*, 225–246.

Lebo, M. E., & Sharp, J. H. (1993). Distribution of phosphorus along the Delaware, an urbanized coastal plain estuary. *Estuaries, 16*(2), 290–301.

van Beusekom, J. E. E., & Brockman, U. H. (1998). Transformation of phosphorus in the Elbe Estuary. *Estuaries, 21*(4A), 518–526.

van Beusekom, J. E. E., & de Jonge, V. N. (1998). Retention of phosphorus and nitrogen in Ems Estuary. *Estuaries, 21*(4A), 527–539.

Zwolsman, J. J. G. (1994). Seasonal variability and biogeochemistry of phosphorus in the Scheldt Estuary, southwest Netherlands. *Estuarine Coastal and Shelf Science, 39*, 227–248.

Water, Air, and Soil Pollution: Focus (2006) **6:** 193–203
DOI: 10.1007/s11267-006-9039-0

USE OF AN *IN SITU* EROSION FLUME FOR MEASURING STABILITY OF SEDIMENT DEPOSITS IN HAMILTON HARBOUR, CANADA

BOMMANNA G. KRISHNAPPAN* and IAN G. DROPPO
Aquatic Ecosystem Impacts Research Division, Environment Canada, 867 Lakeshore Road, Burlington, ON, Canada L7R 4A6
*(*author for correspondence, e-mail: Bommanna.Krishnappan@ec.gc.ca; phone: +1-905-3364766; fax: +1-905-3364420)*

Abstract. An *in situ* erosion flume was used to measure the stability of sediment deposits in Hamilton Harbour, Ontario, Canada. The flume consists of a rectangular duct with an opening at the bottom. A submerged pump attached to the downstream end of the flume circulates the ambient water through the flume, thereby generating turbulent shear flows inside the flume. When the flume rests on a sediment deposit, the exposed part of the sediment deposit is subjected to the flow shear stress. By applying a continually increasing flow shear stress on the sediment deposit and by measuring the amount of sediment erosion, it is possible to assess the erosional stability of the sediment deposits. An under water video camera was mounted on the flume to get visual images of the sediment erosion process. The flume was used at two sites in the Harbour. The erosional resistances measured by the flume for the two sites were different. Measurement of dry density of the sediment deposits using an ultrasonic device was carried out to explain the differences in the stability of sediment deposits from the two sites.

Keywords: cohesive sediment, dry density, erosion stability, field testing, *in situ* erosion flume, shear strength

1. Introduction

Modelling cohesive sediment and associated contaminant transport in aquatic ecosystems requires knowledge of net sediment flux at the sediment water interface for a range of bottom shear stresses exerted by the flow fields. The net sediment flux is calculated as the difference between the upward erosion flux and the downward deposition flux. Our understanding of these erosion and deposition processes and the quantification of the corresponding fluxes is not complete. Previous studies (see e.g. Krone, 1962; Lick, 1982; Mehta & Partheniades, 1975; Parchure & Mehta, 1985; Partheniades, 1962), aimed at quantifying the erosion and deposition fluxes for the cohesive sediment transport, were only partially successful because the relationships that were developed from these studies were of semi-empirical nature and the coefficients involved in these semi-empirical relationships have to be determined by direct measurements either in the laboratory flumes or in the field.

In the case of cohesive sediment erosion, the determination of the empirical coefficients governing the erosion flux is further complicated by the fact that the presence of benthic organisms and biofilms in sediment deposits were found to influence the erosion behaviour of the cohesive sediments (see e.g. Daborn et al., 1993; Holland, Zingmark, & Dean, 1974; Lau & Droppo, 2000; Young, 1975). As the laboratory flumes may not be able to mimic the exact physical, chemical and biological sediment structure and operation, it is prudent to use *in situ* erosion flumes for the quantification of the erosion parameters. In this study, a simple *in situ* erosion flume is developed to measure the erosion parameters directly in the field. A detailed description of the flume and its performance in a field test are given in this paper.

2. Description of the Present *In Situ* Erosion Flume

The present *in situ* erosion flume is a rectangular duct measuring 3.5 m in length, 0.30 m in width and 0.08 m in depth. The bottom part of the flume is open over a length of 1.0 m and a width of 0.30 m (test section) and it begins at a distance of 1.75 m from the flume entrance. The entrance section of the flume consists of two segments. The first segment is a smoothly contracting section that accelerates the flow as it enters the flume. The second section is a flow establishment section and contains a set of straight acrylic tubes over the whole cross section to damp out any secondary circulation. Downstream of the test section, the flume contracts gradually into a circular cross section and connects to a pump that draws water through the flume and discharges to the ambient water. The flow rate of the pump is controlled electronically and a digital read out provides a measure of the flow rate. The flume is fitted with an observation window made up of Plexiglas on the top of the measurement section. When the flume is resting on the sediment bed properly, the surface of the bed will be in line with the bottom plate of the flume on both end-sections of the flume. Proper placement of the flume was confirmed by divers. A plan and an elevation view of the flume are shown in Figure 1.

2.1. INSTRUMENTATION

The flume is equipped with a Pitot tube to measure the flow velocity at a fixed point in the flow field. The difference between the dynamic and static pressure in the Pitot tube was measured using a Valedyne model DP-45 pressure transducer with a diaphragm having a pressure rating equivalent to 90 mm of water. The flume is also fitted with an optical instrument to measure the concentration of the eroded sediment. This instrument, known as OSLIM, was manufactured in the Delft Hydraulics Laboratory in Delft, the Netherlands. It consists of an infrared light emitting diode and a photodiode mounted on either side of a glass tube

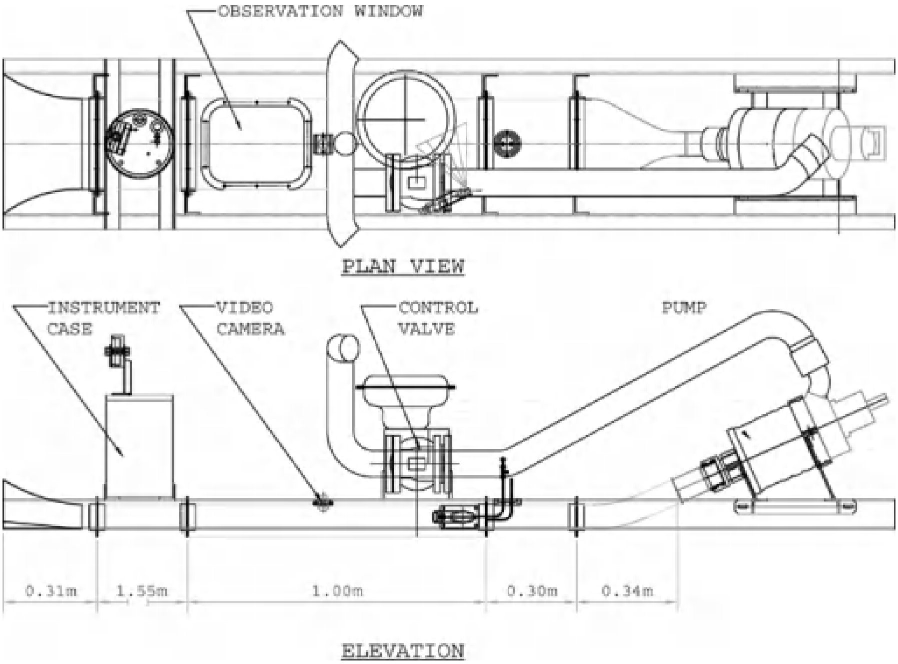


Figure 1. Plan and elevation views of the *in situ* erosion flume.

through which a sample containing the eroded sediment is pumped. The relationship between the photodiode output in volts and the concentration of the sediment is obtained by calibration. In addition, an OBS probe, which operates on the principle of back scattering of light was installed on the flume as a backup probe for measuring the concentration of the eroded sediment. The flume has two under water video cameras, one mounted on the top plate of the flume, and the other mounted on the side wall of the flume. The cameras focused on the eroding bed and served two purposes: (1) they help to locate the measurement site during the deployment of the flume and (2) they give a visual image of the sediment bed being eroded.

2.2. CALIBRATION

The relationship between the flow rate through the cross section and the bed shear stress induced by the flow on the exposed bed surface was obtained in a calibration in the laboratory. For measuring the bed shear stress, the Pitot tube was used as the Preston tube by positioning the tube against a 'false' flume bed made up of smooth plywood. By measuring the difference between the static and dynamic pressures at this position, the bed shear stress was calculated using a calibration equation that was established by Patel (1965) for Preston tube assemblies. The flow rate of the pump was controlled electronically and a digital display provided a read out that was proportional to the flow rate. The relationship between the display read out and the flow rate was obtained by laboratory measurement using a laboratory tank. The flume was operated at different flow rate settings and for each setting, the flow rate was measured by collecting the discharge from the pump into a pre-weighed tank for a known period of time. A calibration equation expressing the relationship between the bed shear stress and the flow rate was established for the flume as a result of the above calibration process, and the form of the equation obtained is as follows:

$$\tau = 0.005Q^2 \tag{1}$$

where τ is the bed shear stress in pascals and Q is the flow rate in liters per second. Full details of flume calibration can be found in Krishnappan, Taylor, Stephens and Biberhofer (2004).

3. Field Testing of the Flume

3.1. Test Locations

A field testing of the flume was carried out in Hamilton Harbour, Ontario, Canada. The flume was tested at two locations. These locations are shown on the map in Figure 2. Site 1 is a shallow water site, and the depth of water at the site is around 2.0 m. Site 2 is a deep water site with water depth of about 6 m. Sediment in this harbour is contaminated and remedial action plans are underway to clean up the harbour. Composition of the sediment (grain size distribution and percentage of organic material) at the two sites was measured and the results are tabulated in Table I.

3.2. Testing Procedure

The flume was deployed from a large boat (owned by Canadian Coast Guard). The boat was anchored at the site and the flume was lowered into the water. As the flume approached the sediment deposit, the video images were used to guide the speed of descent and placement of the flume on the sediment bed with minimum disturbance to the sediment deposit. Once the flume was in place, the pump was started and the flow rate through the flume was increased by operating the flow control device of the pump. The flow rate was increased in steps. Each flow rate step was maintained for a period of about 10 min. A total of 10 shear stress steps were generated for each site. The bed shear stress steps generated by the flume are as follows: 0.03, 0.15, 0.47, 0.82, 1.23, 1.73, 2.40, 3.15, 3.73 and 4.12 Pa. During each shear stress step, the signals from the pressure transducer of

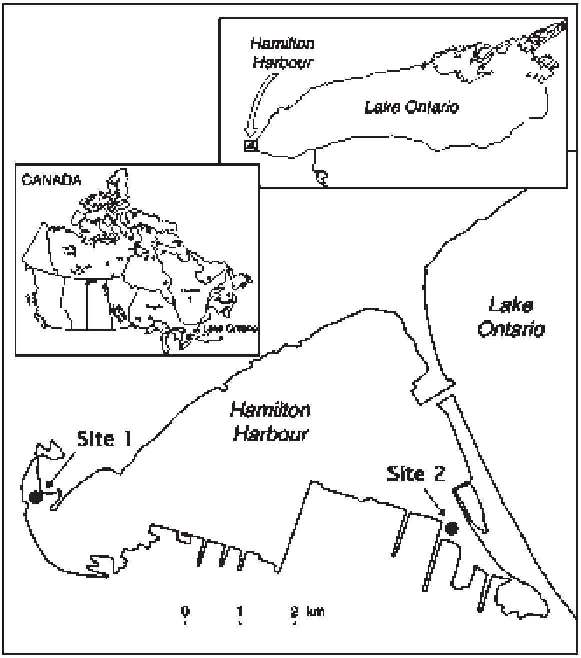


Figure 2. Location map showing sampling sites.

the Pitot tube and the signal processor of the OSLIM and OBS probes were acquired on a laptop computer. The video signal from the under water camera was viewed and recorded using a commercially available video monitor and a VCR assembly.

In addition to the erosion tests using the *in situ* erosion flume, sediment cores were collected at locations close to the flume deployment for measuring the density of sediment deposits. Dry density profiles near the top 3 cm were measured using an ultra sonic high concentration measuring device manufactured by the Delft Hydraulic Laboratory in the Netherlands.

TABLE I

Composition of sediment at the two sampling sites

	Percent of sand	Percent of silt	Percent of clay	D_{50} (μm)	Percent of LOI
Site 1	2.30	67.14	30.56	6.94	7.56
Site 2	3.19	63.78	33.04	7.42	11.6

4. Results and Discussion

4.1. CONCENTRATION OF ERODED SEDIMENT AND EROSION RATE

The concentration trace as measured by OSLIM for the two sites is shown for some selected bed shear stress steps (0.03, 0.15 Pa and 0.47, 0.82 Pa) in Figures 3 and 4. As can be seen from these figures, when the bed shear stress was increased, the sediment concentration in the water column increased due to the increase in the erosion and then the concentration drops to the background levels when the sediment that can be eroded at that particular shear stress is depleted. This normally took about 6 to 10 min Knowing the background concentration and the flow rate, concentration traces can be used to calculate the total amount of sediment that was eroded in each shear stress step as a product of the excess concentration and the flow rate. This allows one to calculate the erosion rate as given by the following relation:

$$E = Q(C - C_b)/(1.0 \times 0.30) \tag{2}$$

where E is the erosion rate in kilograms per square meter per second, C_b is the background concentration in kilograms per cubic meter and C is the concentration

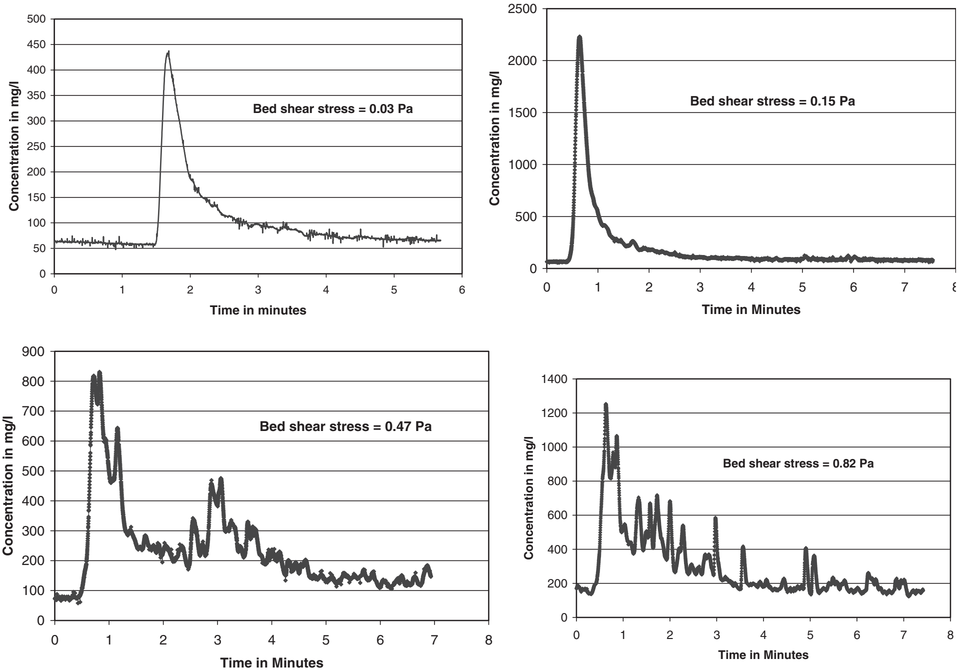


Figure 3. Concentration trace for Site 1 for selected bed shear stresses.

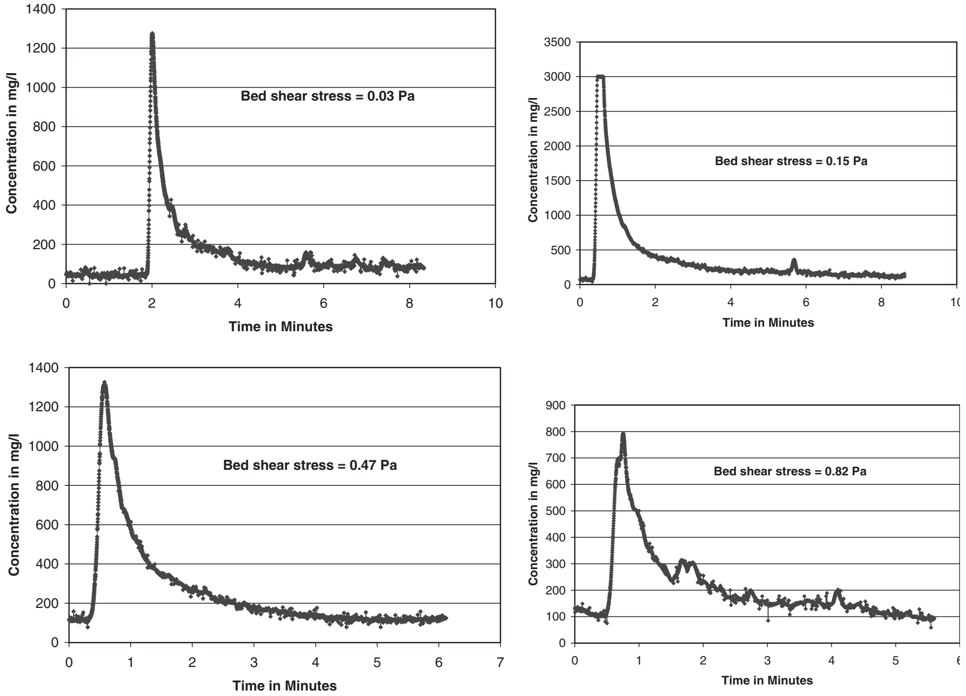


Figure 4. Concentration trace for Site 2 for selected bed shear stresses.

measured by the OSLIM probe in kilograms per cubic meter. Since the flow rate and the background concentration during a shear stress step are constant, the variation of erosion rate as a function of time is identical to the variation of concentration as a function of time.

An average value of the erosion rate was calculated for each bed shear stress step. The duration over which the average was calculated corresponds to the time when there was active erosion and hence the average erosion rates of different shear stress steps can be compared. The variation of the average erosion rate as a function of the bed shear stress steps for both sites is shown in Figure 5. From this figure, we can see that the erosion rate variation for the two sites shows different behaviour. For Site 1, the average erosion rate increases for lower values of the bed shear stress, and as the shear stress becomes large, the erosion rate levels off and shows slightly decreasing trend at the highest bed shear stress tested. In the case of Site 2, the behaviour is very different. In this case, the erosion rate is fairly constant at the lower bed shear stress steps, and as the bed shear stress increases the erosion rate shows a sudden increase and then it drops back to the levels observed at lower bed shear stress steps.

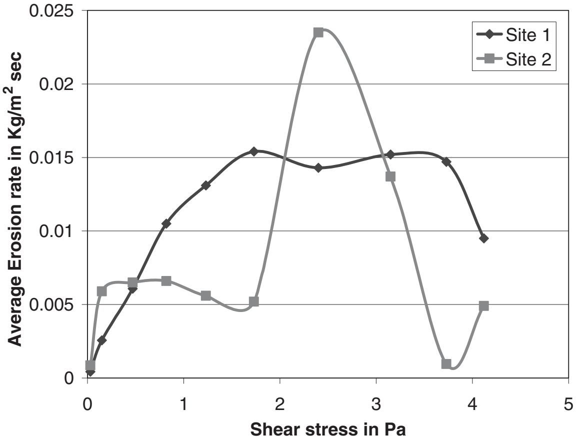


Figure 5. Average erosion rate as a function of bed shear stress for both sites.

4.2. DRY DENSITY PROFILES AND DEPTHS OF EROSION

The density profiles measured for the two sites are shown in Figure 6. From this figure, it can be seen that the dry density increases more or less linearly as a function of depth for Site 1, whereas it exhibits a more complex variation for Site 2. In the latter case, the density variation shows an increasing trend up to a depth of about 10 mm, and then it decreases before it starts to increase again resulting in a hump in the density profile. This means that there is a soft layer of sediment at a depth of about 15 mm. This soft layer can be attributed to bioturbation and/or accumulations of gases. Knowing the density of the sediment deposit and the amount of sediment eroded in each bed shear stress step, it is possible to calculate the depth of erosion at each bed shear stress step. Such a calculation was carried out and the results are tabulated in Tables II and III.

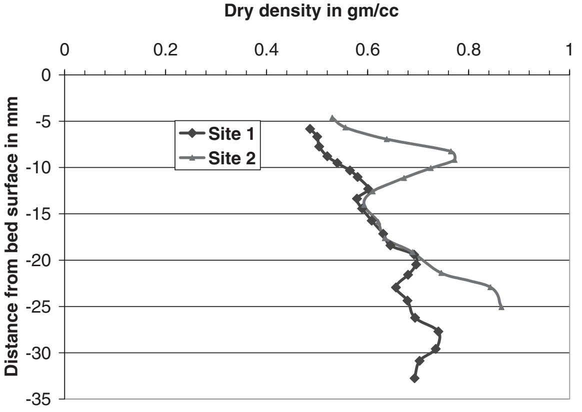


Figure 6. Density profiles of sediment deposits.

TABLE II

Summary of computed results for Site 1

Shear stress (Pa)	Duration of shear stress steps (min)	Amount of eroded sediment (g)	Average erosion rate (kg/m^2 s)	Dry density of eroded layer (g/cc)	Depth of erosion (mm)	Cumulative depth of erosion (mm)
0.03	4.193	32.8	0.00043	0.38	0.3	0.3
0.15	7.133	329.5	0.00257	0.38	2.9	3.2
0.47	6.477	708.4	0.00608	0.43	5.5	8.7
0.82	7.088	1341.2	0.01050	0.52	8.6	17.3
1.23	5.547	1312.5	0.01310	0.62	7.1	24.4
1.73	6.480	1792.8	0.01540	0.68	8.8	33.2
2.40	6.600	1699.8	0.01430	0.69	8.2	41.4
3.15	6.480	1778.5	0.01520	0.69	8.6	50.0
3.73	8.510	2256.8	0.01470	0.69	10.9	60.9
4.12	3.310	568.3	0.00950	0.69	2.8	63.7

4.3. SHEAR STRENGTH VARIATION OF THE SEDIMENT DEPOSITS

If we assume that the material eroded at each bed shear stress step possesses a shear strength equal to the applied shear stress, a shear strength variation curve can be established for the sediment deposits. Such variations are shown in Figure 7 for the two sites. From this figure, we can see that the shear strength

TABLE III

Summary of computed results for Site 2

Shear stress (Pa)	Duration of shear stress steps (min)	Amount of eroded sediment (g)	Average erosion rate (kg/m^2 s)	Dry density of eroded layer (g/cc)	Depth of erosion (mm)	Cumulative depth of erosion (mm)
0.03	6.442	99.4	0.00086	0.48	0.7	0.7
0.15	8.282	875.7	0.00590	0.49	6.0	6.7
0.47	5.790	681.7	0.00650	0.60	3.8	10.5
0.82	5.110	605.1	0.00660	0.73	2.8	13.3
1.23	6.347	640.0	0.00560	0.60	3.6	16.9
1.73	6.530	615.2	0.00520	0.63	3.3	20.2
2.40	6.473	2733.3	0.02350	0.70	13.0	33.2
3.15	7.863	1941.6	0.01370	0.87	7.4	40.6
3.73	2.557	56.3	0.00095	0.87	0.2	40.8
4.12	2.863	285.2	0.00490	0.87	1.1	41.9

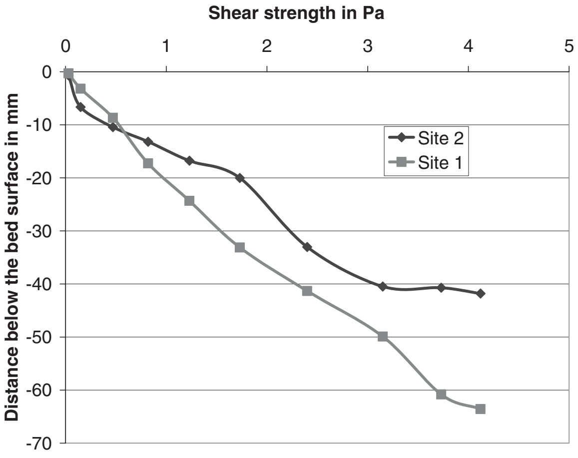


Figure 7. Shear strength variation as a function of depth *below* bed surface for both sites.

varies fairly linearly as the depth of deposit for Site 1, whereas the shear strength variation for Site 2 corroborates the presence of the softer layer discussed above.

5. Summary and Conclusions

A straight *in situ* erosion flume was used to measure the erosion characteristics of sediment deposits in Hamilton Harbour at two sites. Knowledge of erosion characteristics of Harbour sediments is useful for formulating remedial actions for cleaning of contaminated sediment deposits in the harbour. The results show that the erosion characteristics of the sediment deposit at two sites were different, and the difference can be explained on the basis of the density variation of the sediment deposits. Variation in density can result from bioturbation, gas accumulation, biofilm development/degradation etc. From the results of the flume experiments, it is possible to calculate erosion rates and depth of erosion at different bed shear stress conditions. The data was also useful to construct the shear strength variation of the sediment deposits in the Harbour.

Acknowledgments

The authors acknowledge the assistance of Mr Bruce Gray and Mr Ken Hill of the Technical Operations Services of the National Water Research Institute in the field testing of the flume. The flume and its accessories were fabricated in house with the technical skills of R. Reid, K. Davis and A. Tyler in the Machine Shop of the National Water Research Institute. Mr Robert Stephens and Mr Brian Trapp of National Water Research Institute provided the technical assistance for the study.

This page intentionally blank

References

Daborn, G. R., Amos, C. L., Brylinsky, M., Christian, H., Drapeau, G., Faas, R., et al. (1993). An ecological cascade effect: Migratory birds affect stability of inter-tidal sediments. *Limnology and Oceanography, 38(1)*, 225–231.

Holland, A. F., Zingmark, R. B., & Dean, J. M. (1974). Quantitative evidence concerning the stabilization of sediments by benthic diatoms. *Marine Biology, 27(3)*, 191–196.

Krishnappan, B. G., Taylor, W. B., Stephens, R. P., & Biberhofer, J. (2004). Use of an *in situ* erosion flume for testing stability of sediment deposits in St. Lawrence River near Cornwall, Ontario, Canada. In *Proc. 1st water and environmental specialty conference*, Saskatoon, Saskatchewan, June 2004 (WE-397, pp. 1–9).

Krone, R. B. (1962). Flume studies of the transport of sediment in estuarial shoaling processes. Final Report. Hydraulic Engineering Laboratory and Sanitary Engineering Research Laboratory, University of California, Berkeley, California.

Lau, Y. L., & Droppo, I. G. (2000). Influence of antecedent conditions on critical shear stress of bed sediments. *Water Research, 34(2)*, 663–667.

Lick, W. (1982). Entrainment, deposition and transport of fine grained sediments in lakes. *Hydrobiologia, 91*, 31–40.

Mehta, A. J., & Partheniades, E. (1975). An investigation of the depositional properties of the flocculated fine sediments. *Journal of Hydraulic Research, IAHR, 13*, 361–368.

Parchure, T. M., & Mehta, A. J. (1985). Erosion of soft cohesive sediment deposits. *Journal of Hydraulic Engineering, ASCE, 111(10)*, 1308–1326.

Partheniades, E. (1962). A study of erosion and deposition of cohesive soils in salt water. PhD thesis. Berkeley, California: University of California.

Patel, V. C. (1965). Calibration of the Preston tube and limitations on its use in pressure gradients. *Journal of Fluid Mechanics, 23*, part 1, 85–206.

Young, R. A. (1975). Flow and sediment properties influencing erosion of fine grained marine sediments: Sea floor and laboratory experiments. PhD dissertation. Woods Hole, Massachusetts: Woods Hole Oceanographic Institution.

Water, Air, and Soil Pollution: Focus (2006) **6:** 205–210
DOI: 10.1007/s11267-006-9041-6

BIOCHEMICAL COOPERATION BETWEEN *KLEBSIELLA OXYTOCA* SC AND *METHYLOBACTERIUM MESOPHILIUM* SR FOR COMPLETE DEGRADATION OF DIMETHYL ISOPHTHALATE

JIAXI LI[1] and JI-DONG GU[1,2,*]
[1]*South China Sea Institute of Oceanography, Chinese Academy of Sciences, 164 Xingang Road West, Guangzhou 510301, People's Republic of China*
[2]*Laboratory of Environmental Toxicology, Department of Ecology and Biodiversity, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, People's Republic of China*
*(*author for correspondence, e-mail: jdgu@hkucc.hku.hk; phone: +852-2299-0605; fax: +852-2517-6082)*

Abstract. *Klebsiella oxytoca* Sc and *Methylobacterium mesophilicum* Sr were isolated from enrichment cultures using dimethyl isophthalate (DMI) as the sole carbon and energy source and mangrove sediment as an inoculum. Complete degradation of DMI required both species of bacteria at different biochemical transformation steps. The biochemical degradation pathway was DMI to monomethyl isophthalate (MMI) by *K. oxytoca* Sc, MMI to isophthalate (IPA) by *M. mesophilium* Sr, and IPA by both *K. oxytoca* Sc and *M. mesophilium* Sr sequentially. The consortium comprising of *K. oxytoca* Sc and *M. mesophilicum* Sr was effective in complete degradation of DMI in eight days. Our results suggest that a consortium of microorganisms indigenous to the mangrove environment is responsible for mineralization of environmental pollutant DMI through biochemical cooperation.

Keywords: dimethyl isophthalate, mono-methyl isophthalate, isophthalic acid, biodegradation, biochemical cooperation, plasticizers

1. Introduction

Dimethyl isophthalate (DMI) is commonly used in the production of sodium dimethyl isophthalate-5-sulfonate (SIPM) for enhancing the chromaticity of polyethylene terephthalate (PET). Production wastewater of dimethyl terephthalate (DMT) contained high concentrations of DMI (Fajardo, Guyot, Macarie, & Monroy, 1997). Due to the limited awareness of ecological significance compared to other endocrine-disrupting phthalate esters (Kleerebezem, Look, Pol, & Lettinga, 1999), biodegradation of DMI has not been thoroughly studied.

Microorganisms showing an ability to degrade isomers of DMI were isolated from activated sludge (Aleshchenkova et al., 1997; Fan, Wang, Qian, & Gu, 2004; Wang, Fan, & Gu, 2003a, b, 2004) and mangrove (Gu, Li, & Wang, 2005; Gu, Wang, & Li, 2004; Li, Gu, & Pan, 2005a; Li, Gu, & Yao, 2005b; Xu, Li, & Gu, 2005). However, the complete mineralization of DMI appears to be more pronounced with mixed populations of selective microorganisms in consortium (Gu et al., 2004; Li et al., 2005a, b; Wang et al., 2003a, 2004).

The objectives of this study were to isolate microorganisms from mangrove sediment capable of metabolizing DMI, and to elucidate the biochemical pathway of degradation through identification of possible intermediates.

2. Materials and Methods

2.1. CHEMICALS AND SOURCE OF MICROORGANISMS

Dimethyl isophthalate (DMI), monomethyl isophthalate (MMI) and isophthalate (IPA) were purchased from Aldrich Chemicals (St. Louis, MI) with >99% purity. All other chemical reagents were also of analytical grade and solvents of HPLC grade. Mangrove sediment sample was collected from Mai Po Nature Reserve, Hong Kong. Information about the sediment is available elsewhere (Li et al., 2005a, b).

2.2. MEDIA AND ENRICHMENT CULTURE

The minimum salt medium (MSM) was used in enrichment experiments and the enrichment procedures were described by Li et al. (2005a, b).

2.3. DEGRADATION OF DMI BY PURE CULTURE OF BACTERIA

The degradation of DMI and MMI was studied in 100 ml of sterilized MSM inoculated with an initial culture containing each isolated strain and their different combinations into 250 ml Erlenmeyer flasks as previously described (Li et al., 2005a, b).

The microbial biomass in culture flasks was monitored spectrophotometrically using an UV 2100 spectrophotometer (UNICO Instrument, Shanghai, P.R. China).

2.4. ANALYSIS OF RESIDUAL SUBSTRATE

Chemical concentrations in the microcosms were quantified using high-performance liquid chromatograph (HPLC; Agilent 1100 series, Agilent Technologies, California) equipped with a diode array detector as detailed earlier (Li et al., 2005a, b).

2.5. MASS SPECTROMETRY

The intermediate peaks of DMI degradation were further characterized by a combination of techniques including mass spectrometry (LC/MS/MS), UV-visible spectra and their retention times (r.t.). Mass spectra were acquired in the negative ion mode using an API 2000 LC/MS/MS (Applied BioSystems). The full scan spectra were acquired by scanning 110–220 in 0.5 s. The data were an average of 20 scans.

3. Results and Discussion

3.1. CHARACTERIZATION OF BACTERIA

Each of the three bacteria isolated from DMI enrichment culture was tested for its ability to grow on minimal agar plates and in liquid culture media supplemented with each of the three chemicals – DMI, MMI and IPA as the sole source of carbon and energy. All three isolates were capable of utilizing IPA as sole sources of carbon and energy both on agar plates and in liquid cultures. However, strain Sc and Sr metabolized DMI and MMI, respectively, only in liquid cultures (Table I). Both Sc and Sr were gram-negative, and rod shaped, but strain Sw was gram-positive and rod shaped. Strain Sc was identified as *Klebsiella oxytoca* while strain Sr was *Methylobacterium mesophilicum*. Microorganisms from wastewater and activated sludge were previously shown capable of degrading DMI (Aleshchenkova et al., 1997; Kurane, 1997).

3.2. DEGRADATION OF DMI

DMI was rapidly metabolized in cultures of *K. oxytoca* Sc with DMI as the sole sources of carbon and energy and complete transformation of DMI was achieved in 36 h (Figure 1). One transformation intermediate was observed and accumulated without further transformation even after 40 days of incubation. A mass spectrum was obtained by negative ion electrospray mass spectrometry for the intermediate showing a parent ion mass of *m*/*z* 179.10 $[C_9H_8O_4\text{-}H]^-$ with fragment ions at *m*/*z* 135.10 $[M\text{-}H\text{-}CO_2]^-$ from MS/MS. These data confirmed that the intermediate was MMI based on the information available from the National Institute of Standards and Technology (NIST) database under identical analytical conditions.

TABLE I

Growth characteristics of bacterial strains Sw, Sc and Sr on various substrates

	Agar			Liquid		
Strain	DMI	MMI	IPA	DMI	MMI	IPA
Sw	+	–	+	–	–	+
Sc	+	–	+	+	+	+
Sr	+	+	+	–	+	+

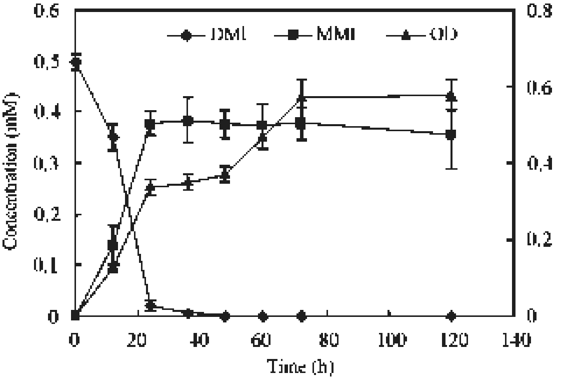


Figure 1. Degradation of dimethyl isophthalate (DMI) by *Klebsiella oxytoca* Sc in batch culture as the sole source of carbon and energy.

Subsequent experiment showed that *K. oxytoca* Sc MMI was not capable of degrading MMI, but *M. mesophilicum* Sr showed active growth after an initial two-day lag time. Further experiments also demonstrated that IPA was degraded by *M. mesophilicum* Sr and *K. oxytoca* Sc (Figure 2). In the sterile controls, DMI, MMI and IPA were not hydrolyzed for the entire duration of experiments (data not shown).

3.3. COMPLETELY DEGRADATION OF DMI

A mixed microbial population was suggested to be more efficient in converting the DMI isomer completely than by a pure culture of a single bacterium (Staples, Peterson, Parkerton, & Adams, 1997). Results of this investigation indicated that

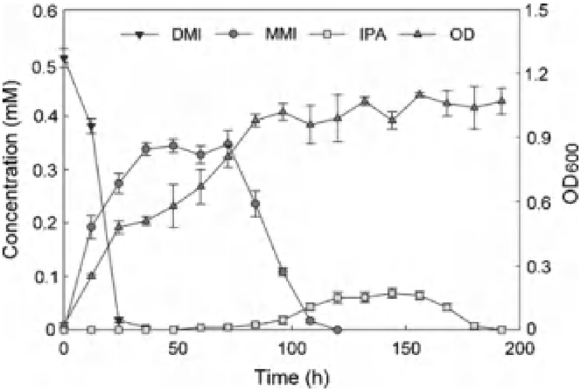


Figure 2. Degradation of dimethyl isophthalate (DMI) by co-culture of *Klebsiella oxytoca* Sc and *Methylobacterium mesophilicum* Sr in batch culture.

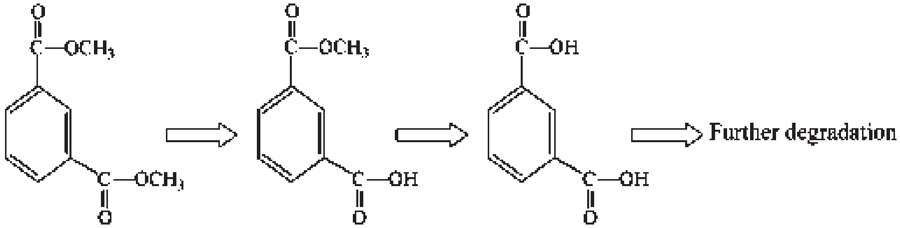


Figure 3. A proposed biochemical pathway for biodegradation of dimethyl isophthalate (DMI) by *Klebsiella oxytoca* Sc and *Methylobacterium mesophilicum* Sr forming monomethyl isophthalate (MMI) and isophthalic acid (IPA).

the association of two strains of bacteria was responsible for the complete mineralization of DMI, *K. oxytoca* Sc was able to initially degrade DMI rapidly but not the degradative intermediate MMI; on the other hand, *M. mesophilicum* Sr was able to metabolize MMI readily, but was not able to convert the parent compound DMI. However, both strains were capable of hydrolyzing another downstream product IPA. A biochemical degradation pathway of DMI by the two isolated strains is proposed in Figure 3. Degradation of DMI requires the first hydrolysis by *K. oxytoca* Sc and then subsequent hydrolysis by *M. mesophilicum* Sr.

The biochemical cooperation may have more important ecological significance because the co-existence of these bacteria allows utilization of one common substrate and will maximize the survival of members of the microbial community. Based on other investigations, enzymes responsible for hydrolyzing *o*-DMP and DMI could hardly have any effect on DMT (Wang & Gu, 2006). Such a mechanism may be more widespread in nature because of the low concentration of substrate and the wide spectrum of pollutants and natural organic compounds. Further elucidation of the biochemical and molecular basis of such biochemical process will provide insights into the evolutionary process in nature. Phthalate ester-hydrolyzing enzymes may have a high diversity in environmental microorganisms.

4. Conclusions

Complete degradation of DMI can be achieved by biochemical cooperation between the two bacteria *K. oxytoca* Sc and *M. mesophilicum* Sr isolated from mangrove sediment. The biochemical degradation processes involve initial hydrolysis of the ester bonds removing the two methyl groups forming MMI and IPA sequentially as degradation intermediates, but the hydrolysis was specifically carried out by two of the bacteria in different steps. High specificity of these hydrolytic reactions suggests the availability of different esterases in the natural environment.

Acknowledgements

This project was supported by the Chinese Academy of Sciences and additional financial support was by a knowledge innovation project of SCSIO (No. LYQY200306) and an 863 project (No. 2002AA601160).

References

Aleshchenkova, Z. M., Samsonova, A. S., Semochkina, N. F., Baikova, S. V., Tolstolutskaya, L. I., & Begelman, M. M. (1997). Utilization of isophthalate acid esters by rhodococci. *Microbiology, 66*, 515–518.

Fajardo, C., Guyot, J. P., Macarie, H., & Monroy, O. (1997). Inhibition of anaerobic digestion by terephthalic acid and its aromatic by products. *Water Science and Technology, 36*(6–7), 83–90.

Fan, Y., Wang, Y., Qian, P., & Gu, J.-D. (2004). Optimization of phthalic acid batch biodegradation and the use of modified Richards model for modeling degradation. *International Biodeterioration & Biodegradation, 53*, 57–63.

Gu, J.-D., Li, J., & Wang, Y. (2005). Biochemical pathway and degradation of phthalate ester isomers by bacteria. *Water Science and Technology, 52*(8), 241–248.

Gu, J.-D., Wang, Y., & Li, J. (2004). Degradation of the endocrine-disrupting dimethyl phthalate and dimethyl isophthalate by mangrove microorganisms. In W. Verstraete (Ed.), *European symposium on environmental biotechnology* (pp. 557−561). The Netherlands: A.A. Balkema Publishers.

Kleerebezem, R., Look, W., Pol, H., & Lettinga, G. (1999). Anaerobic biodegradability of phthalic acid isomers and related compounds. *Biodegradration, 10*, 63–73.

Kurane, R. (1997). Microbial degradation and treatment of polycyclic aromatic hydrocarbons and plasticizers. *Annals of the New York Academy of Sciences, 829*, 118–134.

Li, J., Gu, J.-D., & Pan, L. (2005a). Transformation of dimethyl phthalate, dimethyl isophthalate and dimethyl terephthalate by *Rhodococcus rubber* Sa and modeling the processes using the modified Gompertz model. *International Biodeterioration & Biodegradation, 55*, 223–232.

Li, J., Gu, J.-D., & Yao, J.-H. (2005b). Degradation of dimethyl terephthalate by *Pasteurella multocida* Sa and *Sphingomonas paucimobilis* Sy isolated from mangrove sediment. *International Biodeterioration & Biodegradation, 55*, 158–165.

Staples, C. A., Peterson, D. R., Parkerton, T. F., & Adams, W. J. (1997). The environmental fate of phthalate esters: A literature review. *Chemosphere, 35*, 667–749.

Wang, Y., Fan, Y., & Gu, J.-D. (2003a). Aerobic degradation of phthalic acid by *Comamonas acidovoran* fy-1 and dimethyl phthalate ester by two reconstituted consortia from sewage sludge at high concentrations. *World Journal of Microbiology & Biotechnology, 19*, 811–815.

Wang, Y., Fan, Y., & Gu, J.-D. (2003b). Microbial degradation of the endocrine-disrupting chemicals phthalic acid and dimethyl phthalate ester under aerobic conditions. *Bulletin of Environmental Contamination and Toxicology, 71*, 810–818.

Wang, Y., Fan, Y., & Gu, J.-D. (2004). Degradation of dimethyl phthalate ester by two reconstituted consortia and immobilization of bacteria on surfaces. *International Biodeterioration and Biodegradation, 53*, 93–101.

Wang, Y., & Gu, J.-D. (2006). Degradation of dimethyl isophthalate by *Viarovorax paradoxus* T4 isolated from deep-ocean sediment of South China Sea. *Journal of Human and Ecological Risk Assessment, 12*, 236–247.

Xu, X. R., Li, H. B., & Gu, J.-D. (2005). Biodegradation of an endocrine-disrupting chemical di-*n*-butyl phthalate ester by *Pseudomonas fluorescens* B-1. *International Biodeterioration and Biodegradation, 55*, 9–15.

Water, Air, and Soil Pollution: Focus (2006) **6:** 211–217
DOI: 10.1007/s11267-006-9042-5

BENTHIC INFAUNAL COMPOSITION AND DISTRIBUTION AT AN INTERTIDAL WETLAND MUDFLAT

PING-PING SHEN[1], HONG ZHOU[2], HO-YAN LAI[1] and JI-DONG GU[1,3,*]
[1]Laboratory of Environmental Toxicology, Department of Ecology and Biodiversity,
The University of Hong Kong, Pokfulam Road, Hong Kong, SAR, China
[2]College of Life Science, Ocean University of China, Qingdao, People's Republic of China
[3]The Swire Institute of Marine Science, The University of Hong Kong, Shek O, Cape d'Aguilar,
Hong Kong, SAR, China
*(*author for correspondence, e-mail: jdgu@hkucc.hku.hk; phone: +852-2299-0605;*
fax: +852-2517-6082)

Abstract. Benthic infaunal communities at Mai Po Inner Deep Bay mudflat, Hong Kong were investigated between August 2002 and August 2003. A total of 55 species belonging to 8 Phyla from more than 99,074 specimens were recorded. The species richness varied between 13 at Station B in August 2002 and 28 at Station D in August 2003 with an average of 21 across the mudflat and the species diversity was low [$H'(\log_2) = 0.7$–3.5 with an average $H' = 2.4$]. Seasonal variations were also observed through abundance and biomass across the mudflat among the seasons. The abundance density was between 8,977 individuals m^{-2} at Station D in February 2003 and 77,256 individuals m^{-2} at Station B in November 2002 and the overall average density was 25,274 individuals m^{-2} for the four stations. The benthic infauna were dominated by pollution tolerant species at this wetland mudflat.

Keywords: benthic infauna, composition, distribution, Mai Po mudflat, seasonal variation

1. Introduction

Mai Po Inner Deep Bay Ramsar Site of Hong Kong is located at the northwestern part of the New Territories. It comprises of inter-tidal mudflats, sub-tropical mangroves, as well as man-made fishponds and drainage channels. The inter-tidal mudflat, known as part of the Mai Po Nature Reserve, is an important natural feeding habitat for migratory waterfowl passing through Hong Kong along the East Asian/Australasian flyway and for wintering birds (Young & Melville, 1993). Between 49,000 and 68,000 individuals of waterfowl have been recorded utilizing different parts of the Nature Reserve in winter and more than 100,000 during the entire year (Tsim & Lock, 2002). Due to the high number and diversity of migratory birds, the wetland was officially listed as a Wetland of International Importance under the Ramsar Convention in September 1995 reflecting its high ecological and conservation values.

As a food source for the shorebirds, benthic infauna is a key structural and functional component of the ecosystem within Mai Po mudflat. Dynamics of their abundance and biomass could have significantly effects on the value of the site as a refueling station for the migratory birds. Furthermore, benthos can also be used as an important indicator for the ecological health of the ecosystem (Gray, 2000; Gray & Pearson, 1982). Pollution can cause significant adverse effects on benthos populations (Pearson & Rosenberg, 1978) and, thus structure of populations or communities can be used to deduce the unfavorable changes in the physical and chemical characteristics of habitat.

Therefore, the objectives of the present study were to establish reliable information about local benthos communities, and investigate the changes of composition and distribution across the mudflat and along the seasons.

2. Materials and Methods

2.1. STUDY AREA AND FIELD SAMPLING

The Mai Po mudflat lies within the Mai Po Nature Reserve Ramsar Site (22°30′N, 114°02′E) and is bounded by the Shenzhen River to the north and the Shan Pui River to the southwest. Detailed information about the site and sampling procedures are available (Hyder, 1998; Laboratory of Environmental Toxicology, 2003).

2.2. DATA ANALYSIS

Software PRIMER v5 (Plymouth Routines In Multivariate Ecological Research, Clarke & Warwick, 1994) was used for benthic data analysis. Biological properties included the following: total abundance and biomass, number of species (*S*), total number of individuals, Shannon–Wiener diversity index (*H*′). Faunal groups not properly sampled by the methods used, such as nematodes, bryozoans and fishes as well as juveniles, were not included in the data analyses.

Multivariate techniques included ordination of benthos samples by non-multidimensional scaling (nMDS) (Kruskal & Wish, 1978) and their classification by clustering using the hierarchical agglomerative method employing group average linking of Bray–Curtis similarities after square root transformation. Following clusters analysis, the species having the greatest contribution to the division of sites into cluster were determined using the similarity percentage program (SIMPER) (Clarke & Warwick, 1994).

3. Results and Discussion

3.1. SPECIES COMPOSITION

A total of 55 species belonging to 8 phyla and more than 99,074 specimens (a total biomass of 492.4 g wet weight of all specimens) were recorded during the study period. These samples included Annelida (11 polychaetes and oligochaete), Mollusca (6 bivalves and 19 gastropods), Arthropoda (8 crustaceans, 4 insects and 1 mite), Sarcomastigophora (1 foraminiferan), Nematoda, Nemertea, Playhelminthes (1 turbellaria) and Chordata (1 fish). Gastropods and polychaetes constituted the most dominant groups in term of abundance and number of species. Total species and abundance were 35 and 37% for gastropods, and 20 and 24% for polychaetes, respectively. Other important groups included oligochaetes, crustaceans and bivalves and each of them contributed to 23, 10 and 6% of the total abundance, respectively (Table I).

The species richness (SR_S) varied between 13 at Station B in August 2002 and 28 at Station D in August 2003 with an average of 21 across the mudflat. The abundance density was between 8,977 individuals m^{-2} at Station D in February 2003 and 77,256 individuals m^{-2} at Station B in November 2002 (Figure 1) and the overall average density was 25,274 individuals m^{-2} for the four stations. The species diversity index [H' ($\log_2$)] ranged between 0.7 and 3.5 (average $H' = 2.4$) and was higher than 2 on most sampling occasions (Figure 2). The highest diversity ($H' > 3$) was generally recorded at station with highest species number, e.g., Stations C and D. Both the lowest diversity and species number and the highest number of individuals occurred at Station B that was distinguished from other stations due to closer to the mangrove forest implying available high concentration of organic carbon. In this investigation, α diversity (Gray, 2000) of Mai Po intertidal mudflat was low and varied from 13 to 28 species with an average $SR_S=21$. It is much lower than that of a recent study by Shin and Ellingsen (2004) in sub-tidal Hong Kong waters. In spite of the sample scale,

TABLE I

The most common species found in the Mai Po mudflat

	Mean density (individuals m^{-2})		
Species	Group I	Group II	Group III
Polychaeta			
Neanthes glandicincta	347	116	539
Tharyx sp.	0	2,464	192
Capitella capitata	270	0	39
Potamilla acuminata	38	1,155	539
Oligochaeta	7,893	770	539
Mollusca			
Pseudopythina maipoensis	116	116	270
Sermyla riquetii	11,281	7,199	731
Stenothyra devalis	193	1,348	154
Crustacea			
Discapseudes mackei	38	1,425	192
Harpacticoida	39	1,771	77

Mean densities were calculated for the main groups from cluster analysis.

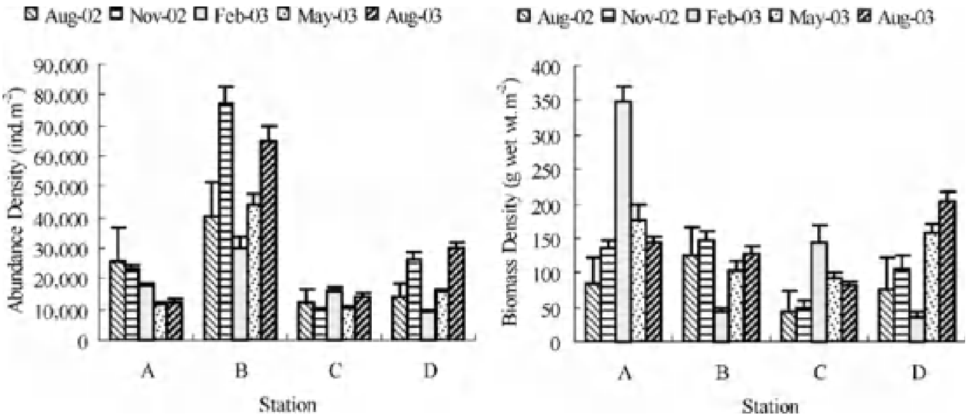


Figure 1. Mean abundance and biomass density of benthic infauna at Mai Po Inner Deep Bay mudflat between August 2002 and August 2003 (*vertical lines* show the standard deviation).

results of this study illustrated another example showing that the pattern of species richness increased from shallow water to deep sea (Gray, 2000).

3.2. SEASONAL CHANGES

Seasonal variation of benthic infauna in terms of abundance and biomass showed a clear pattern that samples were much more dissimilar to each others in August 2002 (most dissimilar in February or May 2003) and then became more similar to the starting time in August 2003 (Figure 3). Variations of the infauna abundance

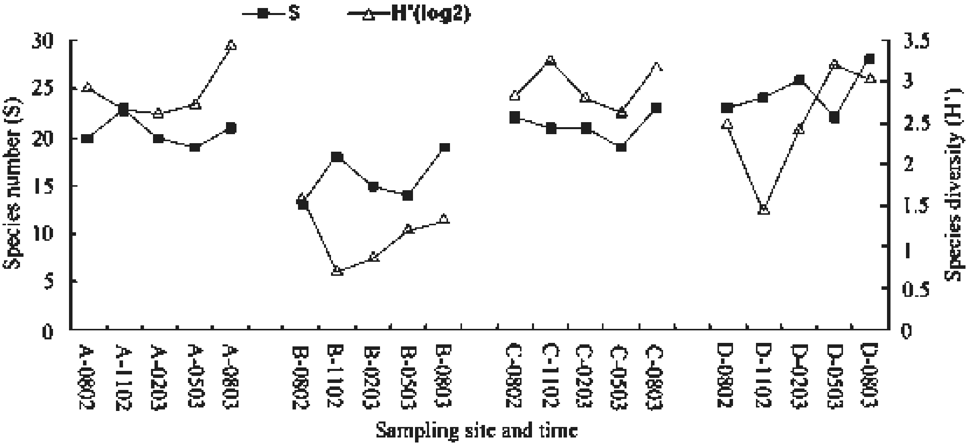


Figure 2. Species number and diversity of benthic infauna at Mai Po Inner Deep Bay mudflat between August 2002 and August 2003. Station codes are given with month and an extension for the year of sampling.

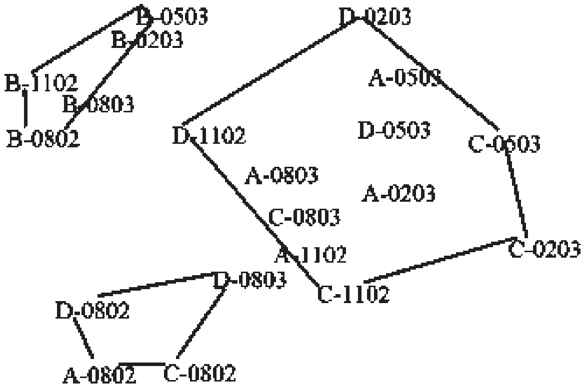


Figure 3. Multidimensional Scaling (MDS) ordination plot of the four stations at different seasons of sampling at Mai Po Inner Deep Bay (stress 0.14).

at Station B was much higher than those of the other three stations during the five seasons while the biomass changed very little except for Station A where substantial increase was evident in winter (Figure 3). During the five sampling events, two opposite trends of fluctuation were detected within the mudflat. At Stations B and D, both abundance and biomass of infauna decreased to the lowest level in winter of 2003, while at Stations A and C, both parameters reached the highest level except for the abundance of infauna at Station A.

3.3. COMMUNITY STRUCTURE ANALYSIS

Cluster analysis grouped the four stations of different sampling seasons into three main clusters. Group I consisted of all samplings from B mostly; Group II included various samples from stations excluding B; while Group III consisted of all samples from A, C and D. Similarly, distinctive assemblages could be identified from multi-dimensional scaling ordination plots for each infauna sample (Figure 3). It is apparent that the samples from Station B were more closely related to each other than those from the other stations indicated by the clustering of the sampling from the sites.

The organisms mainly responsible for the seasonal and spatial differences (SIMPER analysis, cut-off of 70%) were Oligochaeta, Gastropoda (*Sermyla riquetii*, *Stenothyra devalis*) and Polychaeta (*Neanthes glandicincta*, *Tharyx* sp., *Capitella capitata* and *Potamilla acuminata*). Most species were found at majority of the stations at different sampling times, but the mean densities of the three main clusters differed remarkably (Table I).

Another feature of the benthic community of the Mai Po mudflat was composed of high densities of small short-lived pollution-tolerant opportunistic species, a typical feature of impacted community by organic pollution and/or other disturbance (Pearson & Rosenberg, 1978). The global opportunist *C. capitata* and

Oligochaeta, for instance, may respond both to physical disturbance and organic pollution (Lai, 2004). *C. capitata* reached a highest density of 2,301 individuals m^{-2} at Station B in May 2003 and peak of Oligochaeta density was 28,484 individuals m^{-2}, indicating a severely polluted site compared to the others on the mudflat.

A major factor contributing to the seasonal changes in benthic infauna at Inner Deep Bay can be attributed to the freshwater discharge from Shenzhen River as well as freshwater outflow from the Pearl River delta, especially in summer. Unfortunately, no significant relationship could be detected between the salinity gradient and abundance and biomass of macrofauna on the mudflat during this monitoring period (Laboratory of Environmental Toxicology, 2003). The lowest number of species may be due to more widespread predation in this area as this site is in the vicinity of the bird feeding locations on Mai Po mudflat in particular during the winter–spring period (Hyder, 1998). However, the predation by birds is not likely to cause a reduction on the number of species, on the contrary the abundance of infauna increased at the same time in recent monitoring (Laboratory of Environmental Toxicology, 2003). The community changes can therefore hardly be explained by the predation by birds. On the contrary, the feeding behavior of over-wintering birds on Mai Po mudflat might contribute to the lowest abundance during the winter period at both Stations B and D.

4. Conclusions

The present investigation suggested that the Mai Po mudflat generally supported a poor benthic infauna community. The abundance and biomass of infauna at Mai Po mudflat showed seasonal changes, which involved shifts in the relative abundance of species and taxonomic group, but the changes were not large enough to alter the species composition of the fauna of the mudflat. Another feature of the community was that it was composed of high densities of a few pollution-tolerant opportunistic species: *C. capitata* and Oligochaeta, a typical feature of impacted community by organic pollution and/or other disturbance. Both low species diversity and high abundance of a few infaunal species as shown in the present study reflected the polluted condition at the Deep Bay and to protect the habitat of waterfowls.

Acknowledgement

This study is part of the Baseline Ecological Monitoring Programme for the Mai Po and Inner Deep Bay Ramsar Site supported by Agriculture, Fisheries and Conservation Department (AFCD) of the Hong Kong SAR Government. We would like to thank the team members in our Laboratory of Environmental

This page intentionally blank

Toxicology at The University of Hong Kong and the field-working group of AFCD at Mai Po for logistic support on sampling transport and assistance.

Any opinions, findings, conclusions or recommendations expressed in this publication do not reflect the view of the Government of Hong Kong Special Administrative Region.

References

Clarke, K. R., & Warwick, R. M. (1994). *Change in marine communities: An approach to statistical analysis and interpretation* (2nd ed.). Plymouth, UK: Plymouth Marine Laboratory.

Gray, J. S. (2000). The measurement of marine species diversity, with an application to the benthic fauna of the Norwegian continental shelf. *Journal of Experimental Marine Biology and Ecology, 250*, 23–49.

Gray, J. S., & Pearson, T. H. (1982). Objective selection on sensitive species indicative of pollution-induced change in benthic communities. I. Comparative methodology. *Marine Ecology Progress Series, 9*, 111–119.

Hyder (1998). Agreement no. CE 17/95—Deep Bay water quality regional control strategy study: Final Report. Environmental protection department water policy and planning group. Hyder Consulting, CES (Asia) Ltd. and Delft Hydraulics, Hong Kong.

Kruskal, J. B., & Wish, M. (1978). *Multidimensional scaling*. Beverley Hills, CA: Sage.

Laboratory of Environmental Toxicology (2003). Tender reference no. AFCD/SQ/28/01 ecological monitoring program for the Mai Po and Inner Deep Bay Ramsar Site (Oct. 2001–Sept. 2002). Final Report submitted to Agriculture, Fisheries and Conservation Department. Laboratory of Environmental Toxicology, The University of Hong Kong, Hong Kong SAR.

Lai, M. Y. (2004). *Fractionation, mobilization and bioaccumulation of heavy metals and mineralogical characteristics of the Mai Po inner deep bay mudflat*. M.Phil. Thesis. University of Hong Kong, Hong Kong SAR.

Pearson, T. H., & Rosenberg, R. (1978) Macrobenthic succession in relation to organic enrichment and pollution of the marine environment. *Oceanography and Marine Biology: Annual Review, 16*, 229–311.

Shin, P. K. S., & Ellingsen, K. E. (2004). Spatial patterns of soft-sediment benthic diversity in subtropical Hong Kong waters. *Marine Ecology. Progress Series, 276*, 25–35.

Tsim, S. T., & Lock, F. N. Y. (2002). *Knowing Ramsar wetland*. Hong Kong: Cosmos Books.

Young, L., & Melville, D. S. (1993). Conservation of the deep bay environment. In B. Morton (ed.), *The marine biology of the South China Sea, Proceedings of the first international conference on the marine Biology of Hong Kong and South China Sea, Hong Kong, 1990* (pp. 211–231). Hong Kong: Hong Kong University Press.

Water, Air, and Soil Pollution: Focus (2006) **6:** 219–227
DOI: 10.1007/s11267-006-9043-4

EFFECT OF SEDIMENT HUMIC SUBSTANCES ON SORPTION OF SELECTED ENDOCRINE DISRUPTORS

W. L. SUN*, J. R. NI and T. T. LIU
Department of Environmental Engineering, Peking University, The Key Laboratory of Water and Sediment Sciences, Ministry of Education, Beijing 100871, People's Republic of China
*(*author for correspondence, e-mail: sunweiling@iee.pku.edu.cn; phone: +86-10-62767014; fax: +86-10-62756199)*

(Received 1 September 2005; revised 16 April 2006; accepted 7 June 2006)

Abstract. Characterizing sorption processes is essential to understand the environmental distribution and toxicity potential of endocrine disruptors in terrestrial and aquatic systems. The sorption behaviors of three endocrine disruptors (bisphenol A (BPA), 17β-estradiol (E2), and 17α-ethynylestradiol (EE2)) on sediments were investigated using batch techniques. Samples were taken from some representative reaches in several major Chinese rivers. More attention has been paid to the effect of sediment organic components on the sorption of BPA, E2, and EE2. The results show that the sediment organic carbon-normalized partition coefficients (K_{oc}(sed)) for three endocrine disruptors are in the order of EE2 > E2 > BPA, which corresponds to the octanol-water partitioning coefficients ($\log K_{\mathrm{ow}}$) of the compounds. Moreover, the K_{oc} values for humic substances (K_{oc}(hs)) are comparable with the K_{oc}(sed) values and highly dependent on the physico-chemical properties of humic substances in sediments. The UV absorptivity at 272 nm (A_{272}), which suggests the abundance of aromatic rings in humic substance structure, correlates well with the K_{oc}(hs) values. In addition, the infrared spectra of the humic substances extracted from sediments show four strong bands centered at 3,400 cm^{-1}, 1,625 cm^{-1}, 1,390 cm^{-1}, and 1,025 cm^{-1}. The K_{oc}(hs) values have a positive linear relation with the peak area ratio for peak at 1,025 cm^{-1} and a negative linear relation with the peak area ratio between peaks at 1,625 cm^{-1} and 1,025 cm^{-1}. Hence, the hydrogen bonds play a critical role to the sorption of selected endocrine disruptors.

Keywords: 17α-ethynylestradiol, 17β-estradiol, bisphenol A, humic substances, sorption

1. Introduction

Steroid estrogens and endocrine-disrupting phenolic compounds (e.g., alkylphenols and bisphenol A) are of the similar classes of hydrophobic organics, and are ubiquitous in the environment. Such compounds have been linked to recent reproductive health problems reported in humans and wild animals (Kashiwada, Ishikawa, Miyamoto, Ohnishi, & Magara, 2002), and are widely found in wastewater treatment plant effluents and surface water (Kolpin et al., 2002; Vethaak et. al., 2005). Recently, alkylphenols, bisphenol A, and steroid estrogens have also been found in drinking water and surface water in China (Chang, Hu, Shao, & Xu, 2003; Zhang, Hu, Chang, & Wang, 2004).

Sorption of organic contaminants by soils and sediments has a critical influence on the fate of chemical pollutants in the environment, including a direct impact on bioavailability, transport by waters, and rates of transformation. Sorption of highly hydrophobic compounds such as PAHs, PCBs, and pesticides have been reported in literature (Gauthier, Seitz, & Grant, 1987; Hur & Schlautman, 2004; Spark & Swift, 2002), and sorption or partition of hydrophobic organic contaminants (HOCs) to dissolved and soil/sediment humic substances often governs their transport, reactivity, bioavailability, and ultimate fate in natural and engineered environmental systems. In most systems, organic carbon-normalized partition coefficient (K_{oc}) is a critical factor in determining HOC distributions. However, little is known about the effect of soil or sediment humic substances on the sorption of moderately hydrophobic compounds such as steroid estrogens and phenolic compounds.

Three representative endocrine disruptors were chosen in this study: natural female sex hormones 17β-estradiol (E2) with very potent endocrine disruptive activity, synthetic steroid 17α-ethynylestradiol (EE2) commonly used as growth promoter, and bisphenol A (BPA) widely used as industrial chemical. The sorption behaviors of BPA, E2, and EE2 by sediments were investigated using batch technique. Sediment samples were collected in different areas of China, and the humic substances in sediments were extracted and characterized to analyze their effects on sorption.

2. Materials and Methods

2.1. Reagents and Materials

HPLC-grade methanol and BPA (purity > 97%, ACROS ORGANICS, Geel Belgium) were obtained from J&K Chemical (Belgium). 17β-estradiol (E2, purity > 98%) and 17α-ethynyl estradiol (EE2, purity > 98%) were purchased from Sigma–Aldrich Co. (USA). Supelclean LC-18 solid phase extraction tubes (3 ml) packed with 500 mg of C18 materials were gained from Supelco Park Bellefonte (USA).

Surface sediment samples were collected from the lower reaches of the Liaohe River (LH, near Panjin), the Haihe River (HH, near Tianjin), and the Pearl River (PR, in Shenzhen), the middle reaches of the Yellow River (YR, at Hua Yuankou) and the Yangtze River (YTR, at Wuhan), and the sea near the Pearl River estuary (PRS). All samples were gathered during the wet season. The samples were air dried, grieved and screened into 0.063 mm. The mineral components and organic carbon of sediments (SOC) were analyzed using X-ray diffractometer (PE983G, America) and Muti 3000 TOC/TN analyzer (Analytik Jena, Germany) respectively, and the results are shown in Table I.

The humic substances (including humic and fulvic acid) in sediments were extracted using 0.1 M NaOH as recommended by International Humic Substance Society (IHSS) (Schnitzer, 1982). Then the humic substance contents in sediments were analyzed. Extracted sediments, obtained as the sediment residues after removal of humic substances, were equilibrated using de-ionized water until a pH

TABLE I

Mineral and organic carbon content of sediments

Sample	SOC (mg/g)	Mineral components (%)									
		Montmorillonite	Chlorite	Kaolinite	Illite	Quartz	Feldspar	Plagioclase	Calcite	Dolomite	Hopfnerite
LH	9.15	4.0	2.0	3.0	6.0	42.0	11.0	25.0	7.0	0.0	1.0
HH	5.83	5.0	3.0	4.0	13.0	39.0	9.0	20.0	6.0	0.0	1.0
YR	1.43	1.0	2.5	4.0	11.0	31.5	11.0	27.5	6.0	2.0	3.5
YTR	7.52	4.0	4.0	7.0	23.0	33.0	5.0	13.0	4.0	6.0	1.0
PR	5.70	3.1	0.0	11.5	24.0	47.9	6.3	5.2	2.1	0.0	0.0
PRS	2.19	0.0	0.0	2.0	8.0	68.0	9.0	12.0	1.0	0.0	0.0

of 7–8 was obtained. The absorptivity of each humic substance at 272 nm was calculated by dividing the absorbance at 272 nm by the TOC level of the solution. The absorbance was measured using an UV-visible spectrophotometer (SPECORD 200, Analytik Jena, Germany) in a 1 cm quartz cell. The infrared spectra were recorded using a VECTOR22 FTIR spectrometer (Bruker, Germany) scanning over the frequency ranged from 4,000 to 400 cm^{-1} at a resolution of 1 cm^{-1}.

2.2. BATCH SORPTION METHOD

All glassware was cleaned of any organic residues by combustion at 550 °C for 5 h. A 6 g sediment (or extracted sediment) sample was added into a 250 ml triangular flask, and 150 ml 4 mM $Ca(NO_3)_2$ solution and 10–50 μl BPA, E2, and EE2 mixing solution were added and mixed. The initial concentration range of BPA, E2, and EE2 is 2 to 16 μg l^{-1}; All the equilibrium experiments were carried out in water-bath shaker for 20 h at 25±1 °C. After equilibration, the suspensions were filtered through 0.45 μm glass fiber membrane. The filtrates (100 ml) were percolated through C18 SPE columns, conditioned with 6 ml methanol and 6 ml pure water, and subsequently washed with 6 ml methanol. Finally, the extraction samples were evaporated to dryness using a flow of N_2 and redissolved in 1 ml methanol. Control experiments were carried out using reactors containing no sorbent in order to assess the loss of solutes to the inside wall of the reactor during sorption tests. Duplicate or triplicate samples were considered with regard to repeatability, and the relative error found to be less than 10%.

2.3. LC-MS/MS ANALYSIS

A HP 1100 LC/MS^n Trap SL System consisting of a series 1100 HPLC and ion trap mass spectrometer equipped with electrospray interface (ESI) was used to separation and quantification of BPA, E2, and EE2. Chromatography was performed using a Zorbax Eclipse XDB-C18 (150 × 2.1 mm) reversed-phase HPLC column. BPA was eluted with 50% solvent A (100% water) and 50% solvent B (100% methanol), E2 and EE2 were eluted with 30% solvent A (100% water) and 70% solvent B (100% methanol) in 20 min, and the flow rate was 0.25 ml min^{-1}. The Optimum MS/MS conditions for BPA, E2, and EE2 analysis are referred to Sun, Ni, and Hao (2005), Sun, Ni, O'Brien, Hao, and Sun (2005).

3. Results and Discussion

3.1. K_{OC} VALUES FOR SEDIMENTS

Sorption of BPA, E2, and EE2 on sediment samples was tested. The experimental results were well described by the linear isotherm of $S=K_dC_e$. Herein S is the

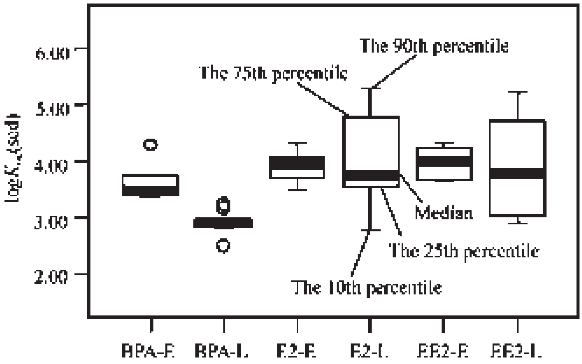


Figure 1. LogK_{oc}(sed) Values for BPA, E2, and EE2 (E-Experimental results, L-Literature results, $n \geq 6$).

concentration of a chemical adsorbed by the solid sample (mg kg^{-1}); K_d is the sorption coefficient (l kg^{-1}); C_e is the equilibrium solution concentration (mg l^{-1}).

With the organic carbon-normalized partition coefficients (K_{oc}) for sediments (K_{oc}(sed)$=K_d$/SOC), the order of EE2 > E2 > BPA was determined experimentally for the selected endocrine disruptors, which corresponds with the logK_{ow} order (4.15, 3.94, 3.32) by Ying, Kookana, and Dillon (2003). Figure 1 shows that the logK_{oc}(sed) values for E2 and EE2 are very close, whereas they are 0.5 greater than the logK_{oc}(sed) value for BPA.

Compared with results from other investigators, the calculated logK_{oc}(sed) values for BPA, as shown in Figure 1, are found to be 0.5–1.0 greater than those reported by Fent, Hein, Moendel, and Kubiak (2003) and Ying et al. (2003). The above discrepancy of BPA K_{oc} values may possibly result from lower adsorbate concentrations in the present experiments. Moreover, using the nonlinear Freundlich isotherm (Fent et al., 2003; Ying et al., 2003) could also result in a smaller K_{oc} (Cornelissen, Kukulska, Kalaitzidis, Christanis, & Gustafsson, 2004; Kang & Xing, 2005). Nevertheless, the calculated K_{oc}(sed) values for E2 and EE2 are comparable with those in previous studies (Lee, Strock, Sarmah, & Rao, 2003; Yamamoto, Liljestrand, Shimizu, & Morita, 2003; Ying et al., 2003).

3.2. EFFECTS OF SEDIMENT HUMIC SUBSTANCES ON K_{OC}(HS)

The humic substances account for 10%–21% of total organic carbon of sediment. Sorption of BPA, E2, and EE2 on extracted sediments was tested, and the experimental results were also described by the linear isotherm. Then the K_{oc} values for extracted sediments (K_{oc}(ex-sed)) were gained. The K_{oc} values for humic substances (K_{oc}(hs)) were calculated according to the K_{oc}(ex-sed) and its contribution to K_{oc}(sed). The results show that the K_{oc}(hs) values are comparable with K_{oc}(sed) values due to the lower concentrations of BPA, E2, and EE2. Moreover, the K_{oc}(hs) varies considerably (Figure 2) and is highly dependent on the physico-chemical properties of humic substances. In Figure 2, the K_{oc}(hs)

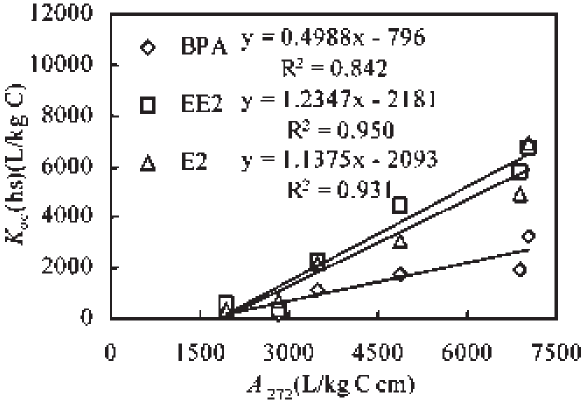


Figure 2. Correlation between K_{oc}(hs) and absorptivity of humic substances at 272 nm.

values of BPA, E2, and EE2 show a relatively strong positive correlation ($R^2 > 0.84$) with absorptivity of sediment organic matter at 272 nm (A_{272}). The result suggests that the abundance of aromatic rings in organic matter structure is of great importance to the sorption of selected endocrine disruptors. These relatively strong correlations for endocrine disruptors agree with Yamamoto et al. (2003) using three steroid estrogens (E2, estriol (E3), and EE2) with the selected DOM surrogates and Gauthier et al. (1987) using pyrene with marine and terrestrial humic acids. Furthermore, the correlation coefficient (R^2) increases with the rise of $\log K_{ow}$ values for BPA, E2 and EE2, which indicates that the role of aromatic ring in sediment organic matter is related to the $\log K_{ow}$ of selected endocrine disruptors.

Fourier Transform Infrared (FTIR) spectroscopy provides structural and compositional information on the functional groups presented in humic substances. As illustrated in Figure 3, the infrared spectra of the humic substances extracted from sediments show four typical broad transmittance bands in the region of 3,400 cm^{-1}, 1,625 cm^{-1}, 1,390 cm^{-1}, and 1,025 cm^{-1}. The band centered at 3,400 cm^{-1} (peak 1, from 3,700 to 2,600 cm^{-1}) probably arises from H-bonded OH groups including those of COOH, phenolic or NH groups; The band centered at 1,625 cm^{-1} (peak 2, from 1,850 to 1,580 cm^{-1}) may be attributed to the C=O stretch of COOH and aromatic or olefinic C=C vibration; The band centered at 1,390 cm^{-1} (peak 3, from 1,580 to 1,330 cm^{-1}) may be due to C-H deformation vibration from aliphatic $-CH_3$ and $-CH_2$, and polypeptide amide II band (N-H bending); The band centered at 1,025 cm^{-1} (peak 4, from 1,300 to 800 cm^{-1}) may result from the −CO stretch of poly-saccharides, and phenolic or alcohol groups (Davis, Erickson, Johnston, Delfino, & Porter, 1999; Gauthier et al., 1987).

To characterize the infrared spectra of the humic substances extracted from sediments in different rivers, the peak area ratio for peak *i* (i.e. the ratio of peak area for the *i*th peak over the total of all the peak areas, herein $i=1, 2, 3$, or 4) as well as

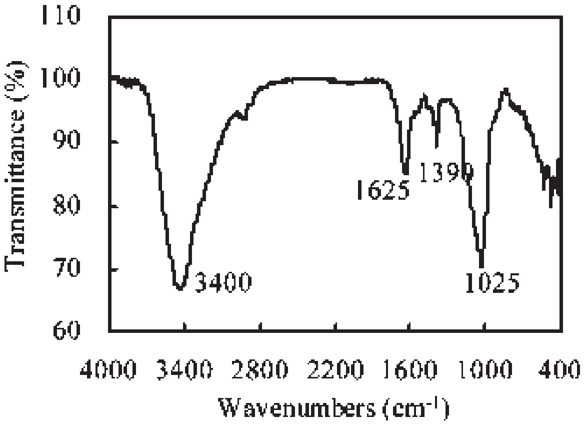


Figure 3. Infrared spectra of humic substances extracted from sediment (HH).

the peak area ratios between different peaks were calculated, and the relationship between K_{oc} and the peak area ratios was examined. As demonstrated in Figure 4 (a), the K_{oc}(hs) values of BPA, E2, and EE2 have a strongly positive linear correlation with the peak area ratio for peak 4 ($R^2 > 0.89$). The hydroxyl group content in humic substances increases with increasing peak area ratio for peak 4, thus the higher affinity resulted from hydrogen bonds between selected endocrine disruptors and sediment organic substances would have significant contribution to the sorption. This strong correlation is consistent with that observed by Yamamoto et al. (2003). On the other hand, the K_{oc}(hs) values are negatively related to the peak area ratio between peak 2 and 4 ($R^2 > 0.82$) (Figure 4b). The peak 2 is where carboxylic acid and aromatic carbon absorption occur, and the interaction between phenolic groups of endocrine disruptor and sediment organic substances may decrease with the rising of relative contents of carboxylic *versus* phenolic groups. Although FTIR spectroscopy has been used to characterize the humic substances in many studies (Davis et al., 1999; Gauthier et al., 1987), limited work has been

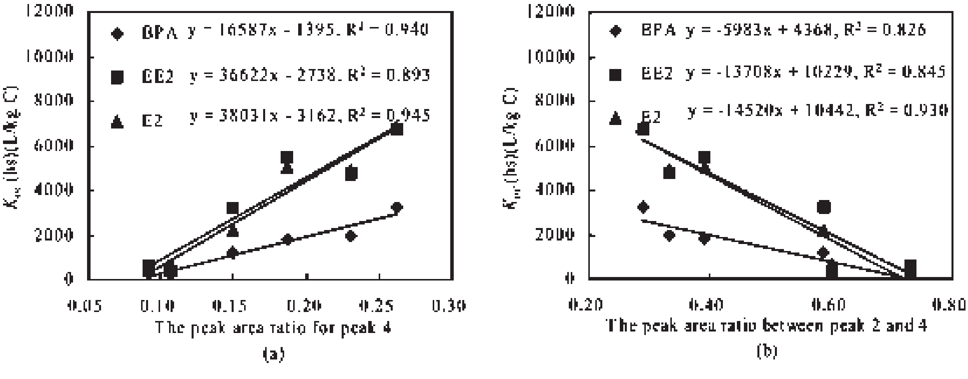


Figure 4. Correlation between K_{oc}(hs) and the peak area ratios.

reported to quantify the properties of humic substances using infrared spectra (Davis et al., 1999; Kang & Xing, 2005). Therefore, the relation between K_{oc} values and the area ratio of peaks should be further analyzed.

4. Conclusions

Sorption behaviors of three endocrine disruptors were investigated in terms of the organic carbon-normalized partition coefficients K_{oc}. The K_{oc} values for sediments (K_{oc}(sed)) are in the order of EE2 > E2 > BPA, which corresponds with reported (Ying et al., 2003) logK_{ow} values for the compounds (4.15, 3.94, 3.32, respectively). Moreover, the humic substances in sediments play a critical role in sorption of selected endocrine disruptors. The K_{oc} values for humic substances (K_{oc}(hs)) correlate with UV absorptivity at 272 nm (A_{272}), and this correlation relationship is related to the octanol-water partitioning coefficients (logK_{ow}) of selected endocrine disruptors. The infrared spectra of the humic substances extracted from sediments show four strong bands centered at 3,400 cm^{-1}, 1,625 cm^{-1}, 1,390 cm^{-1}, and 1,025 cm^{-1}. The K_{oc}(hs) values are positively related to the peak area ratio for peak at 1,025 cm^{-1}, and negatively related to the peak area ratio between peaks at 1,625 cm^{-1} and 1,025 cm^{-1}. The present study indicates that the aromatic carbon and hydroxyl group contents in the sediment humic substances are of great importance to the sorption of BPA, E2, and EE2.

Acknowledgements

Financial support is from National Natural Science Foundation of China (Grant no. 40501063) and the major state basic research program of the People's Republic of China (Grant no. 1999043603).

References

Chang, H., Hu, J. Y., Shao, B., & Xu, Y. (2003). Determination of trace estrogens in surface water using SPE-LC-MS. *Environmental Chemistry*, *22*(4), 400–403.

Cornelissen, G., Kukulska, Z., Kalaitzidis, S., Christanis, K., & Gustafsson, O. (2004). Relation between environmental black carbon sorption and geochemical sorbent characteristics. *Environmental Science & Technology*, *38*(13), 3632–3640.

Davis, W. M., Erickson, C. L., Johnston, C. T., Delfino, J. J., & Porter, J. E. (1999). Quantitation fourier transform infrared spectroscopic investigation of humic substance functional group composition. *Chemosphere*, *38*(12), 2913–2928.

Fent, G., Hein, J. W., Moendel, J. M., & Kubiak, R. (2003). Fate of ^{14}C-bisphenol A in soils. *Chemosphere*, *51*(8), 735–746.

Gauthier, D. T., Seitz, W. R., & Grant, L. C. (1987). Effects of structural and compositional

This page intentionally blank

variations of dissolved humic materials on pyrene K_{oc} values. *Environmental Science & Technology, 21*(3), 243–248.

Hur, J., & Schlautman, A. M. (2004). Influence of humic substance adsorptive fractionation on pyrene partitioning to dissolved and mineral-associated humic substances. *Environmental Science & Technology*, *38*(22), 5871–5877.

Kang, S., & Xing, B. (2005). Phenanthrene sorption to sequentially extracted soil humic acids and humins. *Environmental Science & Technology*, *39*(1), 134–140.

Kashiwada, S., Ishikawa, H., Miyamoto, N., Ohnishi, Y., & Magara, Y. (2002). Fish test for endocrine-disruption and estimation of water quality of Japanese rivers. *Water Research, 36*(8), 2161–2166.

Kolpin, W. D., Furlong, T. E., Meyer, T. M., Thurman, E. M., Zaugg, D. S., Barber, B. L., et al. (2002). Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: A national reconnaissance. *Environmental Science & Technology, 36*(6), 1202–1211.

Lee, S. L., Strock, J. T., Sarmah, K. A., & Rao, C. S. P. (2003). Sorption and dissipation of testosterone, estrogens, and their primary transfornation products in soils and sediment. *Environmental Science & Technology*, *37*(18), 4098–4105.

Schnitzer, M. (1982). Organic matter extraction. In A. L. Page (Ed.), *Methods of soil analysis*. (pp. 581). Madison, USA: WI.

Spark, K. M., & Swift, R. S. (2002). Effect of soil composition and dissolved organic matter on pesticide sorption. *Science of the Total Environment*, *298*(1–3), 147–161.

Sun, W. L., Ni, J. R., & Hao, P. P. (2005a). Analysis of endocrine in water by solid phase extraction-liquid chromatography-ion trap mass/mass spectrometry. *Journal of the Chinese Mass Spectrometry Society*, *26*(1), 22–26.

Sun, W. L., Ni, J. R., O'Brien, K. C., HAO, P. P., & Sun, L. Y. (2005b). Adsorption of bisphenol A on sediments in the Yellow River. *Water, Air and Soil Pollution, 167*(1–4), 353–364.

Vethaak, A. D., Lahr, J., Schrap, S. M., Belfroid, A. C., Rijs, G. B., Gerritsen, A., et al. (2005). An integrated assessment of estrogenic contamination and biological effects in the aquatic environment of The Netherlands. *Chemosphere*, *59*(4), 511–524.

Yamamoto, H., Liljestrand, M. H., Shimizu, Y., & Morita, M. (2003). Effects of physical-chemical characteristics on the sorption of selected endocrine disruptors by dissolved organic matter surrogates. *Environmental Science & Technology*, *37*(12), 2646–2657.

Ying, G.-G., Kookana, S. R., & Dillon, P. (2003). Sorption and degradation of selected five endocrine disrupting chemicals in aquifer material. *Water Research*, *37*(15), 3785–3791.

Zhang, H. F., Hu, J. Y., Chang, H., & Wang, X. L. (2004). Determination of bisphenol A in surface and drinking water in Hangzhou by SPE-LC-MS method. *Environmental Chemistry*, *23*(5), 584–586.

Water, Air, and Soil Pollution: Focus (2006) **6:** 229–239
DOI: 10.1007/s11267-006-9044-3

SOURCES, FATE AND DISTRIBUTION OF ORGANIC MATTER ON THE WESTERN ADRIATIC CONTINENTAL SHELF, ITALY

TOMMASO TESI[1,*], STEFANO MISEROCCHI[1], LEONARDO LANGONE[1],
LAURITA BONI[2] and FRANCA GUERRINI[2]
[1]ISMAR-CNR, Sede di Bologna – Geologia Marina, via P. Gobetti 101 40129 Bologna, Italy
[2]Laboratorio di Biologia e Fisiologia Algale, Sc. Ambientali, Università di Bologna,
via Sant'Alberto, 163 48100 Ravenna, Italy
*(*author for correspondence, e-mail: tommaso.tesi@bo.ismar.cnr.it; phone: +39-051-6398863;*
fax: +39-051-6398940)

Abstract. In the framework of the EUROSTRATAFORM projects, a multidisciplinary research was focused on processes that involve transport and deposition of riverine material in the Adriatic Sea. The aim of our contribution was to increase a more complete understanding of organic matter deposition on the Adriatic shelf, also taking into account the role of Apennine rivers beyond the Po influence. In order to characterize origin, fate and variability of sedimentary organic carbon we utilized elemental and stable carbon isotope data in surficial sediments along shallow cross-shelf transects on the western Adriatic shelf.

Keywords: organic matter, Adriatic Sea, Po and Apennine rivers, surface sediment, stable isotopes

1. Introduction

Burial of terrestrial and marine organic matter (OM) in marine sediments is an important reservoir representing the predominant long-term sink in the global biogeochemical cycle of organic carbon (OC) (Berner, 1982, 1989). Deltas and continental shelves receive large inputs from both autochthonous and allochthonous sources and account for ~90% OC burial in the ocean (Berner, 1982, 1989; Hedges & Keil, 1995). However, these same massive storage systems are often sites of efficient remineralization (Aller & Blair, 2004). Therefore despite their geochemical implications, the mechanisms controlling OM burial are not yet entirely understood (Gordon, Goñi, Roberts, Kineke, & Allison, 2001).

2. Background

The Adriatic epicontinental shelf exhibits an extensive and continuous mud-dominated regressive wedge formed after the attainment of the modern sea level high-stand under the combined influence of fluvial supply and marine processes (Cattaneo, Correggiari, Langone, & Trincardi, 2003; Correggiari, Trincardi, Langone, & Roveri, 2001). An important feature of the Adriatic basin is that its clastic sources are mainly located along the western side. The Po (Figure 1), which is the main river, is characterized by two annual floods associated with increased rainfall in autumn and snowmelt in spring. Along the eastern Italian coast an array of Apennine rivers (Figure 1) is characterized by high sediment yield and typical torrential regime (Cattaneo et al., 2003). The circulation is characterized by cyclonic movement driven by buoyancy effects and wind patterns (Malanotte Rizzoli & Bergamasco, 1983). During the winter the cyclonic currents steer Italian river plumes southward (Poulain, 2001). Fluvial sediments, initially deposited on the prodeltas, are resuspended and efficiently transported along the shelf following the general current circulation.

3. Materials and Methods

Sampling sites were located along shore-normal transects across the inner western Adriatic shelf. Surface sediments were collected at 5–74 m water depths utilizing a large diameter box corer. Box-cores were subsampled and only the uppermost

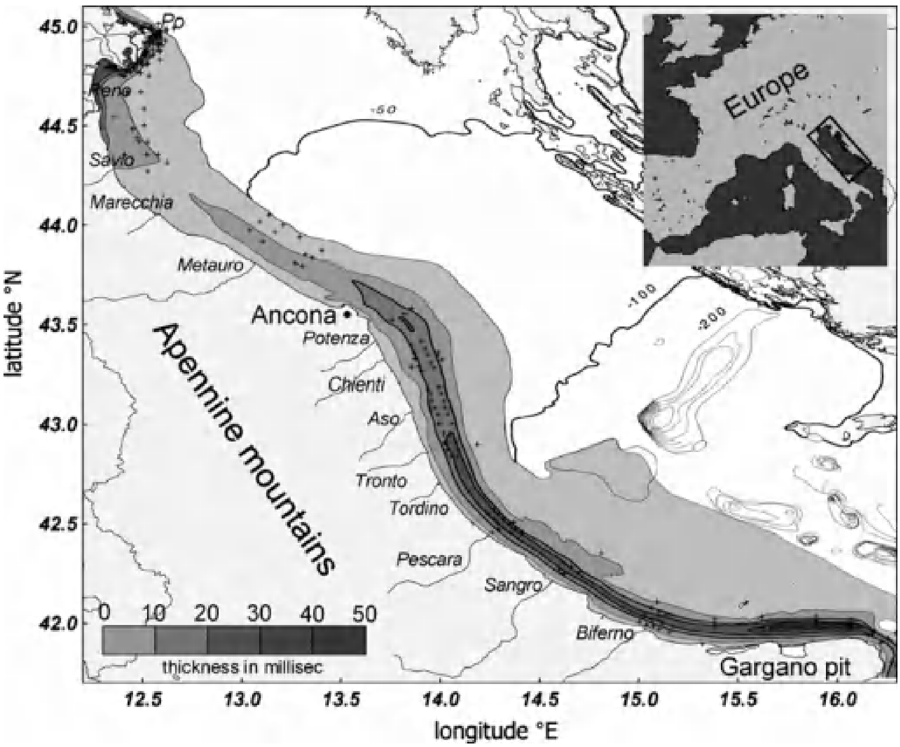


Figure 1. Map of study area in the Adriatic Sea. Each box core station is indicated by a *black crosshair*. Rivers and thickness of the Late Holocene mud-wedge (modified from Correggiari et al., 2001) are showed.

sediment slices (0–1 cm) are used in this study. Surficial sediments were collected during four cruises over one year (April and October 2002; February and May 2003). All samples were refrigerated during transport back to the laboratory where they were oven-dried (55°C). A portion of the dried sediment was ground to carry out elemental and isotopic analyses. In order to investigate the relative contribution of the terrestrial and marine sources, we also collected surface sediment in the lower part of the Po and Apennine rivers during July 2004. A portion of the dried riverine sediment was ground to pass a mesh (250 μm) sieve before elemental and isotopic analyses. Furthermore, two experiments with a common diatom (*Skeletonema costatum*) were carried out to define the isotopic fractionation during the photosynthesis. Algae were maintained in 18 dilute batch cultures (2.5 l): nine bottles contained oligotrophic water from the Adriatic Sea and the remaining nine bottles contained the same volume with 50% of eutrophic water from the Po River and 50% from the Adriatic Sea. The bottles were filled and closed without headspace. The Po and Adriatic water was filtered, with a method designed to protect the isotopic composition of the dissolved CO_2. Therefore the algae were grown in estuarine and marine conditions at different salinity, CO_2 isotopic composition and nutrient concentrations. The algae were inoculated at low concentration (~100 cells ml^{-1}). After two days, we filtered three bottles of both marine and estuarine water on precombusted (4 h, 500°C) GF/F glass fiber filters for elemental and isotopic analyses. The operation was repeated after 24 and 48 h. OC and total nitrogen (TN) contents were measured in silver capsules using a FISONS NA2000 Element Analyzer after removal of the carbonate fraction by dissolution in 1.5 N HCl. The average standard deviation of each measurement, calculated by replicate analyses of the same sample, was ±0.07% for OC and ±0.009% for TN. Stable isotopic analyses of OC were carried out on the same samples by using a FINNIGAN Delta Plus mass spectrometer, that was directly coupled to the FISONS NA2000 EA. The IAEA standard NBS19 was used as calibration material for carbon. Uncertainties were lower than ±0.2‰ as determined from routine replicate measurements of the IAEA reference sample CH-7.

4. Results and Discussion

The OC contents (Figure 2) in the Po prodelta area showed a wide range from 0.41% to 2.25%. South of 44.6°N, the OC content along shelf decreased drastically showing a narrower range between 0.50% and 0.98%. Mean values and standard deviations of OC for each cruise did not show significant differences (Table I), implying low seasonal variability that allowed combination of all elemental data in a single contour map (Figure 3a). In the Po prodelta, the high primary productivity (up to 10-fold the production calculated in southern portion, Giordani, Helder, Koning, Miserocchi, Danovaro & Malaguti, 2002) and the

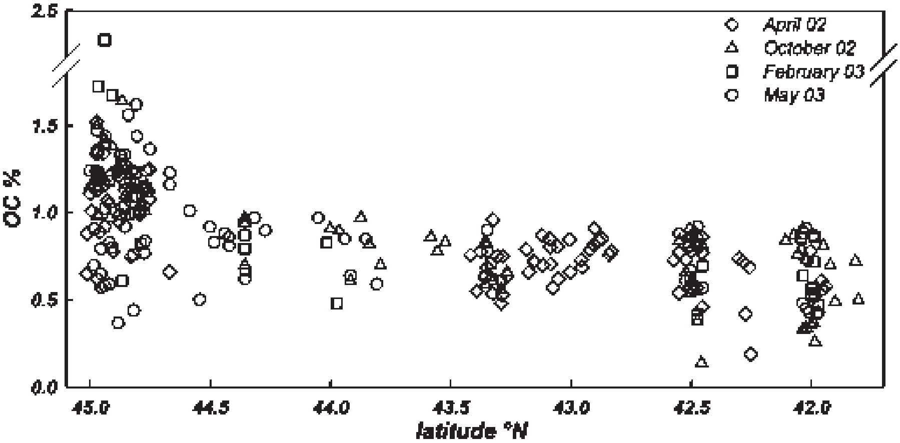


Figure 2. Organic carbon content of surface sediments along the western Adriatic shelf. Each cruise is indicated by *different symbols*.

considerable amount of OC delivered by the Po River (Pettine, Patrolecco, Camuso, & Crescenzio, 1998), directly affect the surface sediments off the Po mouth (Figure 3b). OC contents higher than 1% compose a concentrated depocenter developing around the delta, probably as a result of high and rapid sediment accumulation enhanced by large rapidly sinking flocs (Fox, Hill, Milligan, & Boldrin, 2004). Furthermore, four isolated smaller depocenters, just in front of each distributary, underline the key role of the river load on surface sediments. Going southward, the region between 44 and 44.5°N seems to be still under the influence of the Po River. Beyond this region, on the shelf, OC values increase offshore. This trend can be explained by material hydraulically sorted in grain size because of water dynamics, in accordance with the classic modern sedimentation pattern on continental shelves: coastal sands, mud and relict sand farther offshore (Brambati, Ciabatti, Fanzutti, Marabini, & Marocco, 1983). In contrast, in the Po region the rapid sinking of flocs prevents grain-size sorting. The deposition of fine sediment, which generally has elevated levels of associated OM relative to their coarse counterparts (Hedges & Keil, 1995), deeply influences the OC distribution in surface sediments. Indeed, using the map of grain-size surficial distribution of Brambati et al. (1983), it was possible to cluster samples in three broad classes characterized by different ranges of mud and OC contents. The positive correlation shown in Figure 3c confirms the preferential association of the organic material with the finest sediment fraction. Geochemical–isotopic investigations in the Adriatic have historically employed a two-end-member mixing model between marine phytoplankton and isotopically depleted vascular plants to quantify the terrigenous component of OM in marine sediments (Faganeli, Malei, Pezdič, & Malačič, 1988; Martinotti, Camusso, Guzzi, Patrolecco, & Pettine, 1997). Based on atomic ratio TN and OC (N:C) and

TABLE I

Summary statistics of OC content and isotopic composition, and C:N atomic ratio from superficial sediments collected in the western Adriatic shelf

Date	OC (%)			δ^{13}OC (‰)			C:N			Number
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	
April 2002	0.83 ± 0.24	0.19	1.52	−24.05 ± 0.59	−25.54	−23.08	8.68 ± 0.87	7.08	10.61	87
October 2002	0.83 ± 0.31	0.14	1.64	−23.92 ± 1.01	−26.09	−22.71	8.30 ± 0.69	5.64	9.65	62
February 2003	0.92 ± 0.41	0.41	2.25	−24.89 ± 0.84	−26.38	−23.63	9.23 ± 1.04	7.96	12.52	35
May 2003	0.90 ± 0.30	0.37	1.62	−24.83 ± 1.02	−26.85	−23.10	9.12 ± 0.79	7.53	11.02	92
Average	0.86 ± 0.30			−24.39 ± 0.97			8.80 ± 0.89			276

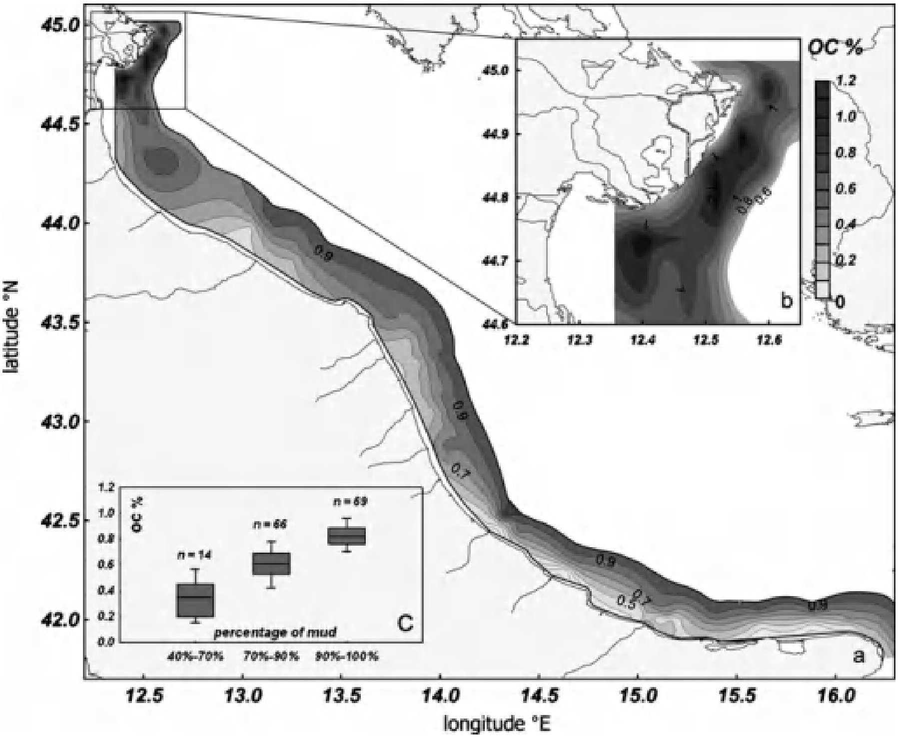


Figure 3. (a) OC distribution in surficial sediments along the western Adriatic shelf; (b) the Po prodelta is shown in detail; (c) relationship between contents of OC and mud.

δ^{13}OC values, Boldrin, Langone, Miserocchi, Turchetto, and Acri (2005) and Miserocchi, Langone & Tesi (in press) have identified the marine–estuarine algae as an additional important source of OC. In addition, in the Adriatic basin, ancient sedimentary OC represents a significant component of the terrestrial fraction supplied by many rivers (Ogrinc, Fontolan, Faganeli, & Covelli, 2005). Therefore, interpretation of the isotopic data and the reliability of a mixing-model depend on the choice of the end-members, which are usually defined according to sample distribution. To this target, surface sediment samples were collected also in the rivers and two experiments were carried out with different starting isotopic composition of dissolved CO_2 in cultures of *S. costatum*. Utilizing the data set of POC from the Po prodelta (Boldrin et al., 2005) and western Adriatic shelf (unpublished data), it has been possible to obtain a plot pointing out key indications of the origin and fate of OC (Figure 4); it was preferred to plot the N:C ratio to the C:N ratio because the first parameter behaves linearly in a mixing model (Goñi, Teixeir, & Perkley, 2003), even if the classical C:N ratio is better known. In the first place, the compositional variability among the rivers is reduced compared to algae; the same species of diatom, grown in identical nutrient and

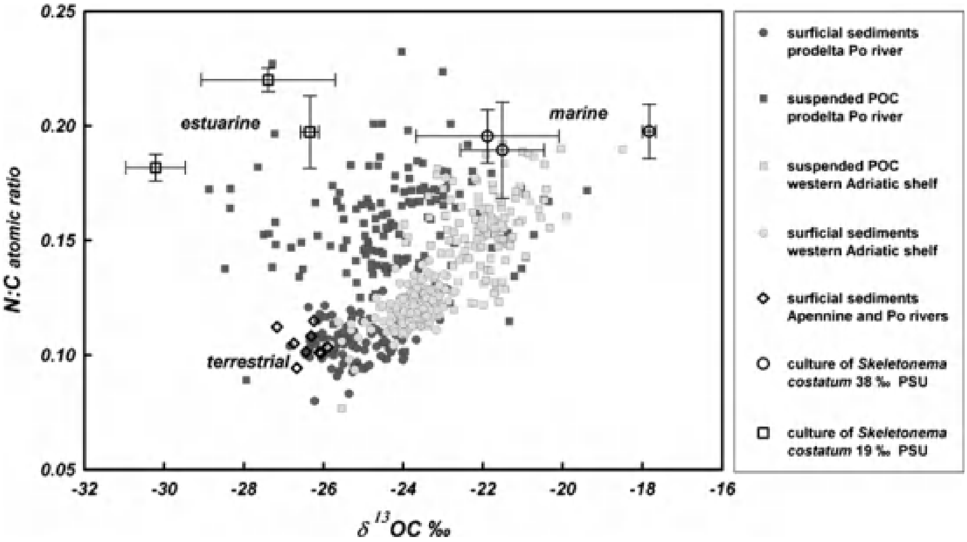


Figure 4. Plot of the carbon stable isotopic composition and nitrogen:carbon atomic ratio. The *open symbols* indicate three different sources: culture of marine and estuarine diatoms and riverine sediments. *Enclosed circles* indicate suspended particulate from the column and *enclosed squares* indicate surficial sediments, *dark gray* for the Po prodelta and *gray* for the western Adriatic shelf.

isotopic conditions, showed a wider variability in both δ^{13}OC and N:C values. The distribution of filtered suspended material, closer to algal values, shows a similar scattered distribution whereas the Adriatic surface sediments are more consistent. Marine–estuarine algae can exhibit a rather broad range of stable

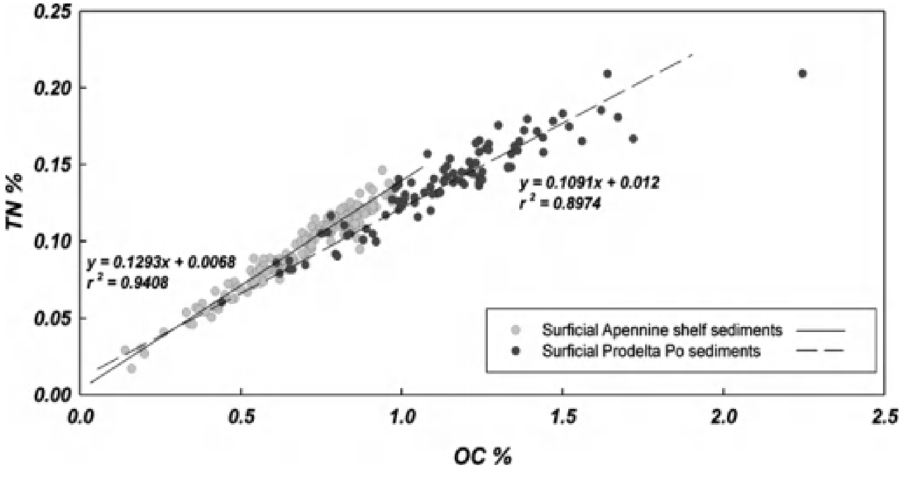


Figure 5. Relationship between OC and TN for surficial sediments for the Po prodelta and Apennine shelf area. The figure includes the *dashed* and *solid linear trend lines* for the Po prodelta and the Adriatic shelf, respectively.

carbon isotopic and N:C ratios that are related to the concentrations of nutrients and sources of the DIC (Fry & Sherr, 1984; Schneider, Schlitzer, Fischer, & Nöthig, 2003). Many authors explain the differences from the classical Redfield ratio in two ways: deviations during particle production and changes during subsequent remineralization processes. During particle production, variations in the elemental compositions may be related to ambient CO_2 concentrations and/or nutrient availability. Changes of elemental ratios during OM degradation are described as preferential remineralization of N with respect to C, or as existence of micro organisms, that could be responsible for the presence of nitrogen-rich biochemicals (i.e., proteins) (Goñi et al., 2003; Schneider et al., 2003). The variability of isotopic composition in the particulate matter depends on the species, growth rate and the shape of the algae, but the main factor is the isotopic composition of DIC (Fry & Sherr, 1984; Popp, Laws, Bidigare, Dore, Hanson, & Wakeham, 1998). For this reason the algae, which reside in environments where the isotopic DIC signature is variable, exhibit a wide range (from −22 to −28‰, Goñi et al., 2003). A strong, linear relationship was detected between the OC and TN contents in all surficial sediments (r^2 = 0.94 and 0.90 in the Apennine shelf and Po prodelta, respectively; Figure 5). The *x*-intercept of these regressions are close to zero, which indicates that the majority of nitrogen in these sediments is associated with OM (Goñi et al., 2003). The lower slope gradient (lower N:C values or higher C:N values) in the Po prodelta samples might indicate the major

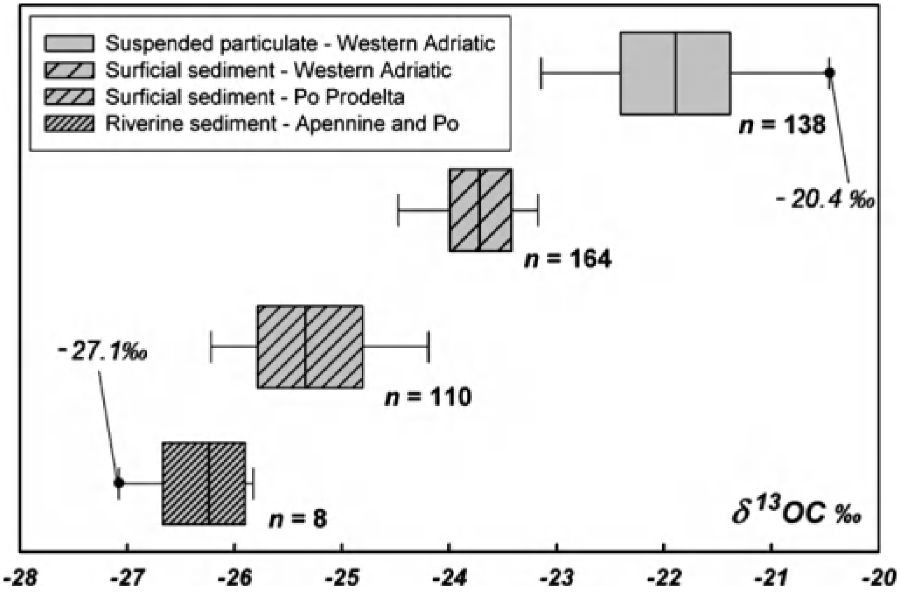


Figure 6. The whisker-plots show the inner OC isotopic variability for different data set. The lower value (−27.1‰, 10th percentile) and the higher value (−20.4‰, 90th percentile) indicate the terrestrial and marine end-member, respectively.

presence of woody debris (N:C < 0.071, C:N > 14; Goñi et al., 2003) compared to the Apennine sediments. Sand-sized plant fragments, rich in OC, hydraulically behave like very fine-sand (Leithold & Hope, 1999), and this might explain the four depocenters in front the main mouths of the Po. Indeed, the terrestrial end-member is generally considered as a single value, although in some cases this common simplification leads to underestimate the contribution of terrigenous OM, which in coastal sediments is complicated by the heterogeneous composition of the terrigenous end-member itself (Gordon & Goñi, 2003). Finally, the global burial flux of OC within modern marine sediments is estimated at 0.1–0.2 Gt year^{-1} (Hedges & Keil, 1995) while the marine plankton photosynthesizes about 50 Gt year^{-1} of OC. Based on this mass balance, the fresh marine particulate is efficiently recycled at least to 99.5%, throughout the ocean water column and the water/sediment interface (Hedges, Keil, & Benner, 1997; Mayer, 1994). An efficient algal degradation, in our case, could easily explain the decoupling between suspended POC and OC in surficial sediments, which are clearly more terrestrial (Figure 3). The 'refractory' organic material delivered by the rivers, being partially degraded, especially in the soil fraction, is more efficiently accumulated and preserved on the surficial sediment than 'labile' algal compounds. Considering both the influence of estuarine algae limited to the prodelta Po area and this highly efficient algal degradation, we propose for the rest of the Adriatic a two end-member mixing model between 'heavier' marine phytoplankton (−20.4‰, 90th percentile) and isotopically depleted vascular plant (−27.1‰, 10th percentile) (Figure 6).

5. Conclusions

In the Po prodelta, the content and distribution patterns of OC are principally related to the high *in situ* primary production and the high discharge of the Po, whereas the dispersion of fine material drives the surficial OC distribution on the western Adriatic continental shelf. Comparison between isotopic signature from sedimentary organic carbon and from filtered suspended material indicates an efficient degradation of the algal particulate matter. The 'lighter' terrigenous OC, especially in the Po prodelta, is preferentially accumulated and preserved on the surficial sediment relative to the 'labile' algal material.

Acknowledgments

This work was supported by the ONR–EUROSTRATAFORM project, grant no. N00014-03-01-0154 and by EU–EUROSTRATAFORM project, contract EVK3-CT-2002-00079. The authors would like to thank P. Giordani and G. Rovatti. This is contribution no. 1505 of ISMAR-CNR, Sede di Bologna – Geologia Marina.

References

Aller, R. C., & Blair, N. E. (2004). Early diagenetic remineralization of sedimentary organic C in the Gulf of Papua deltaic complex (Papua New Guinea): Net loss of terrestrial C and diagenetic fractionation of C isotopes. *Geochimica et Cosmochimica Acta*, *68*, 1815–1825.

Berner, R. A. (1982). Burial of organic carbon and pyrite sulfur in the modern ocean: Its geochemical and environmental significance. *American Journal of Science*, *282*, 451–473.

Berner, R. A. (1989). Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over phanerozoic time. *Palaeogeography*, *Palaeoclimatology*, *Palaeoecology*, *75*, 97–122.

Boldrin, A., Langone, L., Miserocchi S., Turchetto M., & Acri A. (2005). Po River plume on the Adriatic continental shelf: Observations on dispersion and sedimentation dynamics of dissolved and suspended matter during different river discharge rates. *Marine Geology*, *222–223*, 135–158.

Brambati, A., Ciabatti, M., Fanzutti, G. P., Marabini, F., & Marocco, R. (1983). A new sedimentological textural map of the northern and central Adriatic Sea. *Bollettino di Oceanografia Teorica ed Applicata*, *I*, 267–271.

Cattaneo, A., Correggiari, A., Langone, L., & Trincardi, F. (2003). The late-Holocene Gargano subaqueous delta, Adriatic shelf: Sediment pathways and supply fluctuations. *Marine Geology*, *193/1–2*, 61–91.

Correggiari, A., Trincardi, F., Langone, L., & Roveri, M. (2001). Styles of failure in late Holocene highstand prodelta wedges on the Adriatic shelf. *Journal of Sedimentary Research*, *Part B*, *71*, 218–236.

Faganeli, J., Malei, J., Pezdič, J., & Malačič, V. (1988). C:N:P ratios and stable C isotopic ratios as indicators of sources of organic matter in the Gulf of Trieste (northern Adriatic). *Oceanologica Acta*, *11*, 377–382.

Fox, J. M., Hill, P. S., Milligan T. G., & Boldrin, A. (2004). Flocculation and sedimentation on the Po River delta. *Marine Geology*, *203*, 95–107.

Fry, B., & Sherr, E. B. (1984). δ^{13}C measurements as indicators of carbon flow in marine and freshwater ecosystems. *Marine Science*, *27*, 13–47.

Giordani, P., Helder, W., Koning, E., Miserocchi, S., Danovaro, R., & Malaguti A. (2002). Gradients of pelagic–benthic coupling and carbon budgets in the Adriatic and northern Ionian Sea. *Journal of Marine Systems*, *33–34*, 365–387.

Goñi, M. A., Teixeir, M. J., & Perkley D. W. (2003). Sources and distribution of organic matter in a river-dominated estuary (Winyah Bay, SC, USA). *Estuarine*, *Coastal and Shelf Science*, *57*, 1023–1048.

Gordon, E. S., & Goñi, M. A. (2003). Sources and distribution of terrigenous organic matter delivered by the Atchafalaya River to sediments in the northern Gulf of Mexico. *Geochimica et Cosmochimica Acta*, *67*, 2359–2375.

Gordon E. S., Goñi M. A., Roberts Q. N., Kineke G. C., & Allison M. A. (2001). Organic matter distribution and accumulation on the inner Louisiana shelf west of the Atchafalaya River. *Continental Shelf Research*, *21*, 1691–1721.

Hedges, J. I., & Keil, R. G. (1995). Sedimentary organic matter preservation: An assessment and speculative synthesis. *Marine Chemistry*, *49*, 81–115.

Hedges, J. I., Keil, R. G., & Benner, R. (1997). What happens to terrestrial organic matter in the ocean? *Organic Geochemistry*, *27*, 195–212.

Leithold, E. L., & Hope, R. S. (1999). Deposition and modification of a flood layer on the northern California shelf: Lessons from and about the fate of terrestrial particulate organic carbon. *Marine Geology*, *154*, 183–195.

This page intentionally blank

Malanotte Rizzoli, P., & Bergamasco, A. (1983). The dynamics of the coastal region of the northern Adriatic Sea. *Journal of Physical Oceanography*, *13*, 1105–1130.

Martinotti, W., Camusso, M., Guzzi, L., Patrolecco, L., & Pettine, M. (1997). C, N and their stable isotopes in suspended and sedimented matter from the Po estuary (Italy). *Water, Air and Soil Pollution*, *99*, 325–332.

Mayer, P. A. (1994). Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chemical Geology*, *144*, 289–302.

Miserocchi, S., Langone, L., & Tesi, T. (in press). Content and isotopic composition of organic carbon within a flood layer in the Po River prodelta (Adriatic Sea). *Continental Shelf Research*.

Ogrinc, N., Fontolan, G., Faganeli, J., Covelli S. (2005). Carbon and nitrogen isotope compositions of organic matter in coastal marine sediments (the Gulf of Trieste, N Adriatic Sea): Indicators of sources and preservation. *Marine Chemistry*, *95*, 163–181.

Pettine, M., Patrolecco, L., Camuso, M., & Crescenzio, S. (1998). Transport of carbon and nitrogen to the northern Adriatic Sea by the Po River. *Estuarine*, *Coastal and Shelf Science*, *46*, 127–142.

Popp, B. N., Laws E. A., Bidigare R. R., Dore J. E., Hanson K. L., & Wakeham S. G. (1998). Effect of phytoplankton cell geometry on carbon isotopic fractionation. *Geochimica et Cosmochimica Acta*, *62*, 69–77.

Poulain, P.-M. (2001). Adriatic Sea surface circulation as derived from drifter data between 1990 and 1999. *Journal of Marine Systems*, *29*, 3–32.

Schneider, B., Schlitzer, B., Fischer, G., & Nöthig E. (2003). Depth-dependent elemental compositions of particulate organic matter (POM) in the ocean. *Global Biogeochemical Cycles*, *17-2*, 1–16.

Water, Air, and Soil Pollution: Focus (2006) **6:** 241–250
DOI: 10.1007/s11267-006-9045-2

SEDIMENTARY RECORD OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE GULF OF TRIESTE (NORTHERN ADRIATIC SEA)

ESTER HEATH[1,*], NIVES OGRINC[1], JADRAN FAGANELI[2] and STEFANO COVELLI[3]
[1]*Department of Environmental Sciences, »Jožef Stefan« Institute, Jamova 39,*
1000 Ljubljana, Slovenia
[2]*Marine Biological Station, National Institute of Biology, Fornače 41, 6330 Piran, Slovenia*
[3]*Department of Geological, Environmental and Marine Sciences, University of Trieste,*
Via E. Weiss 2, 34127 Trieste, Italy
*(*author for correspondence, e-mail: ester.heath@ijs.si; phone: +386-1-4773584;*
fax: +386-1-4235400)

(Received 2 September 2005; accepted 25 April 2006)

Abstract. To reconstruct a history of polycyclic aromatic hydrocarbon (PAH) pollution in the Gulf of Trieste, one of the largest urbanized areas in the Adriatic Sea, we analyzed three long sediment cores collected between 1996 and 1997. Concentrations of total PAHs, the sum of 16 PAH compounds and six of their methylated analogues, in all three cores show a decrease from 600–800 ng g^{-1}, at the surface, to levels below 250 ng g^{-1} in deepest layers (down to 3 m). The same trend was shown with separate representative pyrogenic PAHs (pyrene, benzofluoranthene and phenanthrene). Using Hg as a recent geochronological tracer, we observe an increasing input of PAHs since the beginning of the 20th Century and, especially, after the Second World War coinciding with increasing industrialization and urbanization of the region. This correlation is supported by PAH ratios that are indication of combustion processes and represent a marker for anthropogenic inputs. No correlation exists between PAHs and black carbon within the core profiles, indicating two different fractions of the 'black carbon continuum'.

Keywords: Gulf of Trieste, pollution, polycyclic aromatic hydrocarbons, sediment cores

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants being present in significant levels in the air, soil and water. Certain PAHs are among the most carcinogenic substances known and can be acutely toxic or genotoxic depending upon the number and configuration of the benzene rings and the presence and position of their substituents (Harvey, 1996). PAHs in the environment derive from several sources. Their introduction in the atmosphere is mainly from the combustion of fossil fuel in heat and power generation, refuse burning, coke ovens and vehicle emissions. Even though natural sources, such as forest fire and volcanic activity, contribute to the overall burden, anthropogenic sources are generally thought to be the most important source of PAHs in the atmosphere.

PAHs, arising from natural and anthropogenic sources, are also frequent contaminants in aquatic sediments. Natural sources include bush and forest fires, natural oil seeps and post-depositional transformations during early diagenesis of biogenic precursors (Blumer & Youngblood, 1975; Wakeham, Schaffner, & Giger, 1980). Anthropogenic sources include combustion and pyrolysis of fossil fuels and wood, and spillage of petroleum products (Blumer & Youngblood, 1975; Tolosa et al., 2004). Several studies reveal that historical records of PAH distribution in age-dated sediment cores reflect the increased anthropogenic inputs of pyrolytic PAHs that correspond to industrial and urban development and fossil fuel usage since the industrial revolution (Arzayus, Dickhut, & Canuel, 2002; Frignani, Bellucci, Favotto, & Albertazzi, 2003; Pereira et al., 1999).

The Gulf of Trieste is one of the largest urbanized areas in the Adriatic Sea. Organic contamination derived from urban, industrial, and agricultural activities have contaminated this area, making its sediments a likely repository for anthropogenic PAHs (Harvey, 1996; Notar, Leskovšek, & Faganeli, 2001). However, there are no reports on the concentrations of individual PAHs in sediments from the Gulf of Trieste prior the mid nineties (Guzzella & De Paolis, 1994; Notar et al., 2001) and little is known about the historical inputs of PAHs in the Gulf. Therefore, the main objective of the paper is to describe the PAHs distribution in three dated cores from the Gulf of Trieste and to construct a depositional history of combustion and petroleum derived PAHs.

2. Materials and Methods

2.1. SAMPLING

A 245 cm long core GT1, a 320 cm long core GT2 (both collected in 1996) and a 120 cm long core GT3 (collected in 1997) were sampled in the central part of the Gulf of Trieste (Covelli, Fontolan, Faganeli, & Ogrinc, 2006; Ogrinc, Fontolan, Faganeli, & Covelli, 2005) using a gravity corer (i.d. 10 cm) by research vessel OGS–Explora and sub-sampled at 1 cm intervals. For PAH analyses, all marine sediments were air dried at room temperature for five days, sieved (particles 0.02–0.05 mm) and homogenized. Samples were transferred to glass bottles and stored in a freezer.

2.2. ANALYSES

2.2.1. Extraction System

An ISCO (Lincoln, NE, USA) supercritical fluid extractor (SFX2-10) was adopted for our study. The solvents used for the ASE–SFE were methylene chloride and carbon dioxide. ASE–SFE was performed in static and dynamic mode, while SFE was applied only in dynamic mode. The ASE–SFE extraction procedure with a total extraction time of 30 min is presented in detail elsewhere (Notar & Leskovšek, 2000). Disposable high temperature crystalline polymer extraction cartridges (ISCO, Lincoln, NE, USA) of 10 ml packed with 5 g of sediment sample and 2 g (or the mass needed to fill up the cartridge volume) of wet support were used. Extracts were collected in glass-stopped 100 ml vials. Two grams of activated copper powder were added into sample vial to decrease the amount of sulphur. After 12 h reaction at room temperature, the sample was filtered and concentrated.

2.2.2. Gas Chromatographic and Mass Spectrometric Analysis

PAH analysis of marine sediment extracts was performed using a gas chromatograph equipped with a split/splitless injector port and a mass selective detector (Hewlett–Packard model 6890 GC/MSD) operating in the selected ion monitoring (SIM) mode. Separation took place on a ZB5-MS (Zebron, Phenomenex, Torrance, CA, USA) cross-linked 5% phenyl-methyl-siloxane capillary column (30 m×0.25 mm i.d., 0.25 μm film thickness). An internal standard mixture containing four deuterated PAHs (acenaphthene-d10, chrysene-d12, phenanthrene-d10, perylene-d12) was added directly to the sample prior to extraction. Response factors and retention times were determined relative to four deuterated internal standards and a standard PAH test mixture. The recovery data, precision, accuracy and method detection limits (MDL) of the whole method were evaluated statistically and are presented elsewhere (Notar & Leskovšek, 2000).

3. Results and Discussion

3.1. DISTRIBUTION OF PAHS

The depth distribution of total PAH content, the sum of 16 parent PAH compounds (Naphtalene, Acenapthylene, Acenaphthene, Fluorene, Phenanthrene, Retene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo (k)fluoranthene, Benzo(a)pyrene, Benzo(g,h,l)perylene, Dibenzo(a,h)anthracene, Indeno(1,2,3-c,d)pyrene) and six of their methylated analogues (2-Methylnaphthalene, 1-Methylnaphthalene, 2-Methylphenanthrene, 1-Methylphenanthrene, 1-Methylanthracene, 1-Methylpyrene), at all three sampling stations is shown in Figures 1, 2 and 3. In addition, concentrations of these compounds in core GT3 are presented in Table I. Concentrations of PAHs in our surficial sediments were intermediate between those observed in highly contaminated sediments and remote oceanic sediments (Wakeham, 1996; Yunker, Macdonald, Cretney, Fowler, & McLaughlin, 1993). Spatial differences in the surficial PAH content between the three cores suggests GT1 and, especially, GT3 locations to be as final ‘sinks’ for finer particles carrying PAH. Total PAHs in all three cores show a decrease

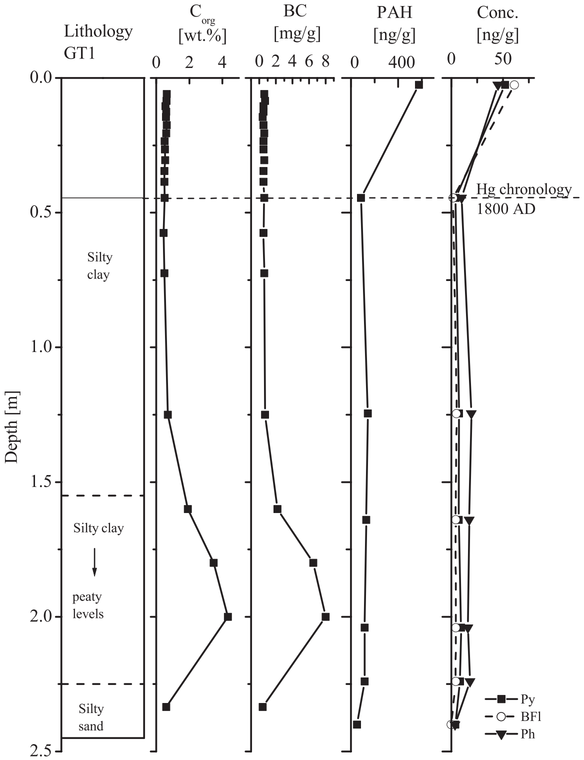


Figure 1. Sediment core GT1: Depth profiles of lithology, organic carbon concentrations (*C_{org}*) (Ogrinc et al., 2005), Black carbon (*BC*) (Muri, 2000), and concentrations of total polycyclic aromatic hydrocarbons (*PAHs*) and representative pyrogenic PAHs: pyrene (*Py*), benzofluoranthenes (*BFl*) and phenanthrene (*Ph*).

from 600–800 ng g^{-1} at the surface to levels of 250–100 ng g^{-1} at depths below 60 cm (Figures 1, 2 and 3). Concentration vs. depth profiles of three representative pyrogenic PAHs pyrene, benzofluoranthenes and phenantrene are similar to that of total PAHs (Figures 1, 2 and 3). Also fluoranthene, the amount of the major pyrogenic PAH used as an example, decreases from the surface to a depth of 55 cm in core GT2 (Figure 2). The onset of PAHs enrichment in core GT3 starts at about 10 cm depth while it is deeper (about 55 cm) in core GT2. Using Hg as a recent geochronological tracer (Covelli et al., 2006), which was previously correlated with sedimentation rates provided by ^{210}Pb analysis (Covelli, Faganeli, Horvat, & Brambati, 2001), it emerges that sediments located at a depth of 10 cm in core GT3 date just after the end of the Second World War (ca. 1946 A.D.). In the better resolved core GT2, sediments deposited at 55 cm depth are dated just before the First World War (ca. 1913 A.D.). The PAHs content in the lower sections of core GT1, GT2 and GT3 (i.e. below 150, 175 and 90 cm depth, respectively), dated by ^{14}C analysis to about 9,000 years BP (Ogrinc et al., 2005), is about three times lower than in the pre-industrial marine

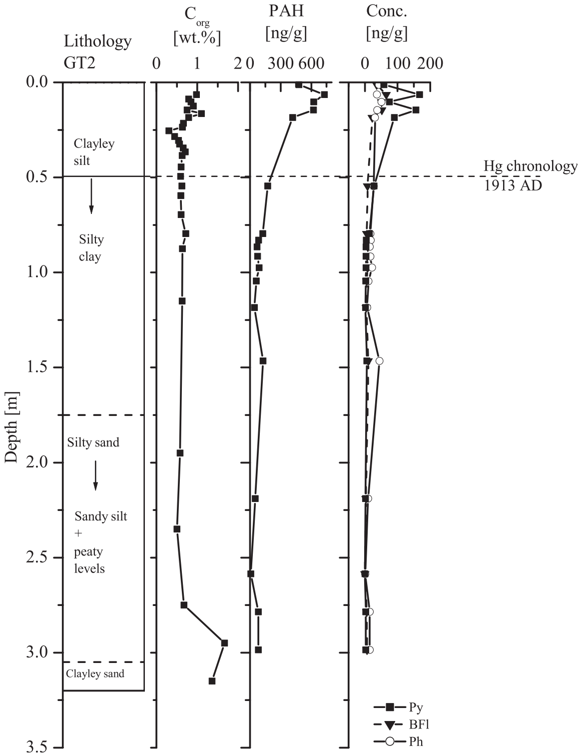


Figure 2. Sediment core GT2: Depth profiles of lithology, organic carbon concentrations (*C_{org}*) (Ogrinc et al., 2005), concentrations of total polycyclic aromatic hydrocarbons (*PAHs*) (top 80 cm of GT2 core are published in Notar et al., 2001) and representative pyrogenic PAHs: pyrene (*Py*), benzofluoranthenes(*BFl*), phenanthrene (*Ph*) and fluoranthene.

sediments. The lowest PAH concentrations observed at the top of the GT2 core, with the highest sedimentation rate (6 mm $year^{-1}$, Covelli et al., 2006), greater input of riverborne organic carbon and sampling resolution, are likely the consequence of a reduced atmospheric flux of combustion-derived PAH to sediments over the past decade. This reduced flux could be a result of a shift from coal-derived energy to the use of oil and gas (Fernandez, Villanova & Grimalt, 1999). Generally, coal combustion is more PAH-polluting than oil combustion (National Research Council, 1983).

Retene (Figure 3), a product of the burning of coniferous timber (Ramdahl, 1983), shows increased concentrations in the core GT3, and thus an increased fluvial input at the depth of 14.5 cm, i.e. about 1916 A.D., and at the depth of 23.5–49.5 cm, i.e. in the 18th and 19th Centuries. However, retene could also be formed during early diagenesis from abiotic acid, a common diterpenoid acid found in conifer resin and other higher plant lipids (Wakeham et al., 1980). No significant correlation between total PAH and organic carbon contents (C_{org}) in the

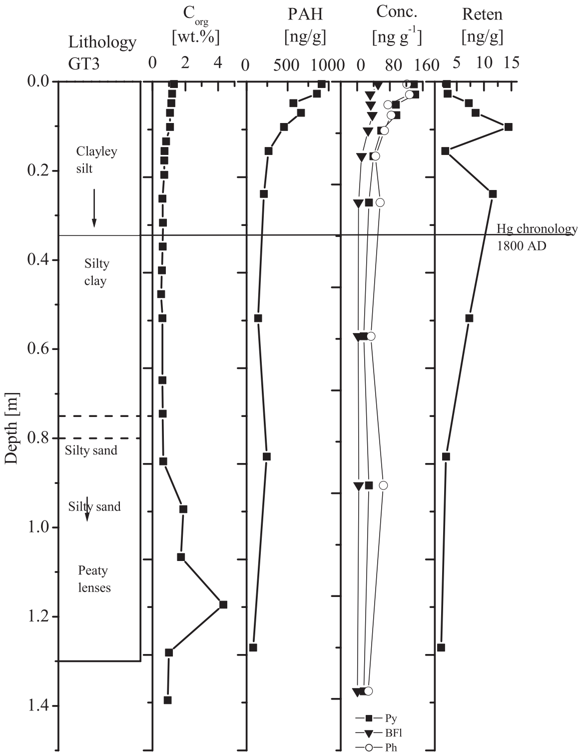


Figure 3. Sediment core GT3: Depth profiles of lithology, organic carbon concentrations (*C_{org}*) (Ogrinc et al., 2005), concentrations of total polycyclic aromatic hydrocarbons (*PAH*) and representative pyrogenic PAHs: pyrene (*Py*), benzofluoranthenes (*BFl*), phenanthrene (*Ph*) and retene.

cores was observed. However, Notar et al. (2001) found a significant correlation between PAHs and C_{org} in the recent surficial sediments of the Gulf of Trieste. In addition, there was no correlation observed between the vertical distributions of PAHs and black carbon (BC) in the core GT1 (Figure 1). Since BC covaries with C_{org}, no association could be suggested between PAHs and BC, both combustion-derived substances. This discrepancy is likely a result of analytical technique used to measure BC since it is known that the thermo-chemical method detects the most refractory BC fractions (Masiello, 2004; Schmidt et al., 2001). There are also complex factors involved in controlling the partitioning of PAHs in the sedimentary C_{org}. For example the Isonzo river mouth is acting as a ‘biogeochemical reactor’ including various microbial processes, flocculation, sedimentation and resuspension (Covelli, Piani, Faganeli, & Brambati, 2004) that influence the distribution of PAHs in sedimentary C_{org}. However, both substances are associated with the fine fraction, mostly riverborne clayey and silty particles, in surficial sediments of the Gulf of Trieste (Notar et al., 2001; Ogrinc et al., 2005).

From the present-day sedimentation rates (ϖ) of 2.3, 6.0 and 1.8 mm year^{-1} determined in cores GT1, GT2 and GT3, respectively (Covelli et al., 2006), surface PAH concentrations (C_{PAH}), sediment porosity (ϕ) and density (ρ), the PAH fluxes to sediments (F) can be estimated from the following equation:

$$F = C_{\mathrm{PAH}}(1 - \phi)\rho\varpi,$$

where ϕ=0.75 and ρ=2.6 g cm^{-3} (Covelli et al., 2001). The present-day PAH accumulation fluxes at GT1 and GT3 amount to about 1,000 μg m^{-2} yr^{-1} while it is approximately 1,800 μg m^{-2} yr^{-1} at GT2. Similar fluxes were obtained for coastal marine areas in the Mediterranean using sediment data (Saliot, Andrie, Ho, & Marty, 1985) and sediment trap experiment (Burns & Villeneuve, 1983; Lipiatou & Saliot, 1991). In contrast, the PAH fluxes were estimated to be <300 μg m^{-2} yr^{-1} in sediments deposited before the Second World War in cores GT1 and GT3 and before the First World War in the more resolved core GT2.

TABLE I

Concentrations of polycyclic aromatic hydrocarbons (PAH) in the core GT3 in the Gulf of Trieste (ng g^{-1}, dry weight)

	Depth (cm)									
Compounds	0.5	2.5	4.5	6.5	9.5	14.5	23.5	49.5	78.5	118.5
Naphthalene	55.1	43.3	37.4	37.8	34.2	21.7	20.5	21.9	33.1	7.4
2-Methylnaphthalene	20.9	23.6	20.4	20.9	16.7	11.3	12.5	7.0	20.0	1.6
1-Methylnaphthalene	5.0	4.9	3.5	3.5	3.6	2.3	2.1	1.7	4.3	0.3
Acenapthylene	11.9	8.1	4.4	4.4	3.9	2.7	2.0	2.1	1.7	1.1
Acenaphthene	3.6	2.6	3.2	2.6	1.8	1.4	1.5	1.0	1.8	1.0
Fluorene	2.2	8.4	6.2	4.9	4.5	3.2	2.6	1.9	6.7	0.7
Phenanthrene	121.9	128.4	74.9	82.8	66.2	44.6	56.5	33.0	63.9	27.1
2-Methylphenanthrene	17.2	14.9	12.6	12.5	9.3	6.2	4.9	3.6	7.6	0.9
1-Methylphenanthrene	8.9	7.6	6.4	6.4	4.9	3.6	2.5	1.7	4.1	0.4
Retene	3.2	3.3	7.2	8.5	14.5	2.9	11.6	7.3	3.1	2.2
Anthracene	22.3	18.4	9.4	9.6	10.5	5.2	5.6	2.7	6.0	2.4
1-Methylanthracene	6.7	6.1	5.9	4.6	3.9	2.6	1.9	1.4	4.0	0.3
Fluoranthene	152.7	135.8	77.5	78.7	52.2	30.9	19.8	11.0	18.3	9.9
Pyrene	138.1	141.6	94.5	95.6	58.8	39.7	29.0	16.3	28.8	15.8
1-Methylpyrene	4.9	5.4	3.4	4.0	3.4	1.8	0.9	1.0	1.9	u.d.l.
Benzo(a)anthracene	46.7	35.5	28.5	34.1	24.0	13.8	9.1	8.7	10.4	7.6
Chrysene	57.8	42.9	30.5	36.8	23.9	12.4	5.4	3.6	6.2	0.8
Benzo(k)fluoranthene	51.3	32.1	33.0	37.3	26.8	11.1	3.2	2.7	3.9	0.5
Benzo(b)fluoranthene	68.5	86.9	44.9	66.4	31.0	18.9	8.6	3.5	7.3	1.1
Benzo(a)pyrene	30.3	29.4	16.9	27.8	16.9	7.9	2.1	1.1	2.9	u.d.l.
Benzo(g,h,l)perylene	39.4	38.4	24.6	41.6	21.4	11.4	4.0	2.5	5.0	u.d.l.
Dibenzo(a,h)anthracene	0.7	0.6	0.7	1.1	0.4	0.2	0.1	0.1	0.1	u.d.l.
Indeno(1,2,3-c,d)pyrene	44.2	37.8	24.7	39.9	21.5	10.9	3.4	2.6	4.5	u.d.l.
Total PAH	913.7	855.9	571.0	661.6	454.2	266.6	209.8	138.7	245.6	81.2

u.d.l. under detection limit

3.2. SOURCES OF PAHS

The ratios of methylphenenthrenes to phenanthrene, as an indication of anthropogenic influences such as combustion of organic matter around the gulf (Pereira et al., 1999), were low (>0.5). These ratios indicate that combustion processes are the main source of PAHs in the gulf and not recent oil spills (Prahl & Carpenter, 1983). PAHs are introduced into the Gulf of Trieste through fresh water inflows, mainly by the Isonzo river (Notar et al., 2001), and through atmospheric inputs. Similar conclusions were reported for other coastal sediments, i.e. Chesapeake Bay (Arzayus, Dickhut, & Canuel, 2001), Narragansett Bay (Lake, Norwood, Dimock, & Bowen, 1979), San Francisco Bay (Pereira et al., 1999), Venice Lagoon (Frignani et al., 2003; Pavoni, Sfriso, & Marcomini, 1987). However, this ratio might also reflect the preferential loss of alkylated PAHs in the atmosphere (Simo, Grimalt, & Albaiges, 1997). The same conclusion can be drawn from the predominance of high molecular weight (four, five, six rings) over low molecular weight (two, three rings) PAHs in the upper layers of the cores (Table I). The low content of the more soluble low molecular weight PAHs could be a result of their faster degradation compared to high molecular weight compounds (Mac Rae & Hall, 1998). Their preferential loss during particulate lateral and vertical transport throughout the water column would lead to the sedimentation of particles depleted in low molecular weight PAHs (Lipiatou, Marty, & Saliot, 1993). In addition, phenanthrene/anthracene ratios of 10 and lower, and fluoranthene/pyrene ratios of 1 and lower suggest pyrolytic contamination of sediments. Lower phenanthrene/anthracene ratios in the surficial layer probably indicate that PAHs received by the sediment in the 20th century came from nearby sources.

4. Conclusions

This paper demonstrates that the PAH core profiles can be useful as a valuable historical record of past anthropogenic emissions of PAHs and the sediment dynamics in the Gulf of Trieste. The dominant sources of PAHs appear to be combustion. PAHs are introduced by freshwater, especially the Isonzo river, and by direct atmospheric inputs. Sediment chronologies of PAHs suggest that the Gulf of Trieste has been modified (polluted) by anthropogenic activities during the past century, especially in the period after the Second World War.

Acknowledgements

The financial support of the Ministry of Education, Science and Sport (Project P1-0143) are acknowledged. The authors are thankful to Mrs. Silva Perko for her technical support and assistance.

References

Arzayus, K. M., Dickhut, R. M., & Canuel, E. A. (2001). Fate of atmospherically deposited polycyclic aromatic hydrocarbons (PAHs) in Chesapeake Bay. *Environmental Science & Technology, 35*, 2178–2183.

Arzayus, K. M., Dickhut, R. M., & Canuel, E. A. (2002). Effects on the attenuation of polycyclic aromatic hydrocarbons in estuarine sediments. *Organic Geochemistry, 33*, 1759–1769.

Blumer, M., & Youngblood, W. W. (1975). Polycyclic aromatic hydrocarbons in soils and recent sediments. *Science, 188*, 53–55.

Burns, K. A., & Villeneuve, J.-P. (1983). Biogeochemical processes affecting the distribution and vertical transport of hydrocarbon residues in the coastal Mediterranean. *Geochimica et Cosmochimica Acta, 47*, 995–1006.

Covelli, S., Faganeli, J., Horvat, M., & Brambati, A. (2001). Mercury contamination of coastal sediments as the result of long-term cinnabar mining activity (Gulf of Trieste, Northern Adriatic sea). *Applied Geochemistry, 16*, 541–558.

Covelli, S., Fontolan, G., Faganeli, J., & Ogrinc, N. (2006). Anthropogenic markers in the Holocene stratigraphic sequence of the Gulf of Trieste (northern Adriatic Sea). *Marine Geology, 230*(1–2), 29–51.

Covelli, S., Piani, R., Faganeli, J., & Brambati, A. (2004). Circulation and suspended matter distribution in a microtidal deltaic system: the Isonzo river mouth (Northern Adriatic Sea). *Journal of Coastal Research, SI 41*, 130–140.

Fernandez, P., Vilanova, R. M., & Grimalt, J. O. (1999). Sediment fluxes of polycyclic aromatic hydrocarbons in European high altitude mountain lakes. *Environmental Science & Technology, 33*, 3716–3722.

Frignani, M., Bellucci, L. G., Favotto, M., & Albertazzi, S. (2003). Polycyclic aromatic hydrocarbons in sediments of the Venice Lagoon. *Hydrobiologia, 494*, 283–290.

Guzzella, L., & De Paolis, A. (1994). Polycyclic aromatic hydrocarbons in sediments of the Adriatic Sea. *Marine Pollution Bulletin, 28*, 159–165.

Harvey, R. G. (1996). Polycyclic aromatic hydrocarbons. New York: Wiley–VCH.

Lake, J. L., Norwood, C., Dimock, C., & Bowen, R. (1979). Origins of polycyclic aromatic hydrocarbons in recent sediments. *Geochimica et Cosmochimica Acta, 43*, 1847–1854.

Lipiatou, E., Marty, J. C., & Saliot, A. (1993). Sediment trap fluxes of polycyclic aromatic hydrocarbons in the Mediterranean Sea. *Marine Chemistry, 34*, 43–54.

Lipiatou, E., & Saliot, A. (1991). Fluxes and transport of anthropogenic and natural polycyclic aromatic hydrocarbons in the western Mediterranean Sea. *Marine Chemistry, 32*, 51–71.

Masiello, C. A. (2004). New directions in black carbon organic geochemistry. *Marine Chemistry, 92*, 201–213.

Mac Rae, J. D., & Hall, K. J. (1998). Biodegradation of polycyclic aromatic hydrocarbons (PAH) in marine sediment under denitrifying conditions. *Water Science and Technology, 38*, 177–185.

Muri, G. (2000). Black carbon in alpine lakes and coastal sea. M.Sc. Thesis, University of Ljubljana, 81 pp. (In Slovene).

National Research Council (1983). *Polycyclic aromatic hydrocarbons: Evaluations of sources and effects*. Washington, DC: National Academy.

Notar, M., & Leskovšek, H. (2000). Determination of polycyclic aromatic hydrocarbons in marine sediments using a new ASE–SFE extraction technique. *Fresenius' Journal of Analytical Chemistry, 366*, 846–850.

Notar, M., Leskovšek, H., & Faganeli, J. (2001). Composition, distribution and sources of polycyclic aromatic hydrocarbons in sediments of the Gulf of Trieste, Northern Adriatic Sea. *Marine Pollution Bulletin, 42*, 36–44.

Ogrinc, N., Fontolan, G., Faganeli, J., & Covelli, S. (2005). Carbon and nitrogen isotope compositions of organic matter in coastal marine sediments (the Gulf of Trieste, N Adriatic Sea): indicators of sources and preservation. *Marine Chemistry, 5*, 163–181.

Pavoni, B., Sfriso, A., & Marcomini, A. (1987). Concentration and flux profiles of PCBs, DDTs and PAHs in a dated sediment core from the lagoon of Venice. *Marine Chemistry, 21*, 25–35.

Pereira, W. E., Hostettler, F. D., Luoma, S. N., van Geen, A., Fuller, C. C., & Anima, R. J. (1999). Sedimentary record of anthropogenic and biogenic polycyclic aromatic hydrocarbons in San Francisco Bay, California. *Marine Chemistry, 64*, 99–113.

Prahl, F. G., & Carpenter, R. (1983). Polycyclic aromatic hydrocarbons in (PAH)-phase associations in Washington coastal sediments. *Geochimica et Cosmochimica Acta, 47*, 1013–1023.

Ramdahl, T. (1983). Retene – A molecular marker for wood combustion in ambient air. *Nature, 306*, 687–693.

Saliot, A., Andrie, C., Ho, R., & Marty, J. C. (1985). Hydrocarbons in the Mediterranean Sea: Their occurrence and fate in the sediment and in the water column, as dissolved and associated with small and large particles. *International Journal of Environmental Analytical Chemistry, 22*, 257–278.

Schmidt, M. W. I., Skjemstad, J. O., Czimezik, C. I., Glaser, B., Prentice, K. M., Gelinas, Y., et al. (2001). Comparative analysis of black carbon in soils. *Global Biogeochemical Cycles, 15*, 163–167.

Simo, R., Grimalt, J. O., & Albaiges, J. (1997). Loss of unburned-fuel hydrocarbons from combustion aerosols during atmospheric transport. *Environmental Science & Technology, 31*, 2697–2700.

Tolosa, I., de Mora, S., Sheikholeslami, M. R., Villeneuve, J.-P., Bartocchi, J., & Cattini, C. (2004). Aliphatic and aromatic hydrocarbons in coastal Caspian Sea sediments. *Marine Pollution Bulletin, 48*, 44–60.

Wakeham, S. G. (1996). Aliphatic and polycyclic aromatic hydrocarbons in Black Sea sediments. *Marine Chemistry, 53*, 187–205.

Wakeham, S. G., Schaffner, C., & Giger, W. (1980). Polycyclic aromatic hydrocarbons in recent lake sediments. I. Compounds having anthropogenic origins. *Geochimica et Cosmochimica Acta, 44*, 403–413.

Yunker, M. B., Macdonald, R. W., Cretney, W. J., Fowler, B. R., & McLaughlin, F. A. (1993). Alkane, terpene, and polycyclic aromatic hydrocarbon geochemistry of the Mackenzie River and Mackenzie shelf: Riverine contributions to Baufort Sea coastal sediment. *Geochimica et Cosmochimica Acta, 57*, 3041–3061.

Water, Air, and Soil Pollution: Focus (2006) **6:** 251–259
DOI: 10.1007/s11267-006-9046-1

QUANTIFYING FINE-SEDIMENT SOURCES IN PRIMARY AND SELECTIVELY LOGGED RAINFOREST CATCHMENTS USING GEOCHEMICAL TRACERS

W. H. BLAKE[1,*], R. P. D. WALSH[2], A. M. SAYER[2] and K. BIDIN[3]
[1]*School of Geography, University of Plymouth, Plymouth PL4 8AA, UK*
[2]*Department of Geography, University of Wales Swansea, Swansea SA2 8PP, UK*
[3]*School of Science and Technology, Universiti Malaysia Sabah, Kota Kinabalu, Malaysia*
*(*author for correspondence, e-mail: william.blake@plymouth.ac.uk; phone: +44-1752-233069; fax: +44-1752-233054)*

Abstract. Detailed information on post-logging sediment dynamics in tropical catchments is required for modelling downstream impacts on communities and ecosystems. Sediment tracing methods, which are potentially useful in extending to the large catchment scale and longer time scales, are tested in primary and selectively logged rainforest catchments of Sabah, Borneo. Selected nutrient (P and N) and trace metal (Ni and Zn) concentrations are shown to discriminate surface, shallow subsurface and deep subsurface sediment sources. Analysis of channel-stored fine-sediment samples and use of an unmixing model allow the relative importance of these vertical sediment sources to be estimated and erosion processes to be inferred for catchments of contrasting size.

Keywords: tropical rainforest, logging, sediment, tracing, nutrients

1. Introduction

Rotational selective logging (where trees above a threshold girth are extracted in annual coupes within a larger forest area, with each coupe left to recover before subsequent selective logging) is a relatively sustainable form of tropical forest exploitation (Marsh & Greer, 1992), but still has major erosional and hydrological impacts from elements of a post-logging disturbance mosaic such as skid trails and primary and feeder logging roads (Douglas et al., 1999; Sidle, Sasaki, Otsuki, Noguchi, & Nik, 2004). Work to date has focussed on direct monitoring of processes on slopes and in small catchments, with little attention given to the downstream transfer and storage of sediment, despite their importance to such issues as siltation, flooding, river pollution, water supply, fish stocks and offshore coral.

Long-term monitoring within the selectively logged Baru catchment in Sabah suggests a four-phase impact model (Douglas et al., 1999; Walsh et al., 2006). Phase 1 (during and years 1–2 post-logging) has high sediment loads related to erosion of disturbed surface soil. In phase 2 (years 3–6) sediment yield falls near to background levels with revegetation of slopes. In phase 3 (years 7–12+) a second sediment yield peak occurs with episodic landslides and channel re-excavation linked to log decay in road bridges/culverts and debris dams. Phase 4 sees a return to background erosion. Despite providing a quantitative picture of *part* of the *small* catchment system, these studies lack the integrated quantification of sediment sources incorporating channel storage dynamics needed to predict downstream impacts on large catchments. This study explores the potential for sediment tracing technology to fulfil this need.

2. Approach

2.1. Study Area

Work focussed on the Segama catchment draining the east of a 1 m ha forest area in Sabah under selective logging management by Yayasan Sabah. Within it lies the 438 km^2 Danum Valley Conservation Area (DVCA) of protected primary forest. Study catchments (Figure 1) included zero-order pipe-fed channels, termed W3 (catchment area: 5,300 m^2) and W7 (13,200 m^2); the third-order West (1.7 km^2) and Baru (0.44 km^2) catchments; and the Segama River at Danum (721 km^2) and Segama Bridge (1,720 km^2). West catchment is in primary forest; the Baru was selectively logged in 1988–1989. Part of the Segama catchment above Danum was logged in 1999–2000; the rest was logged in annual coupes

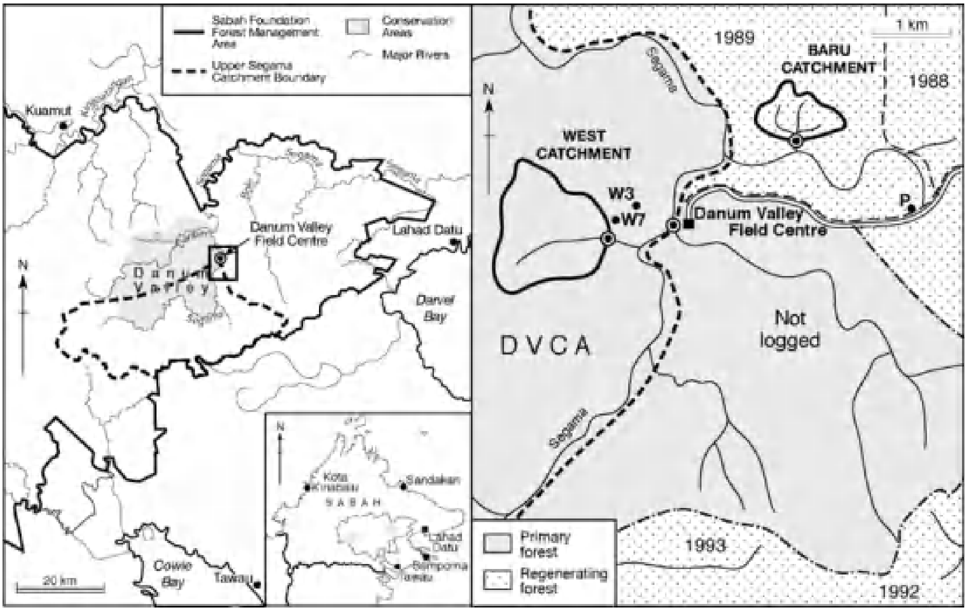


Figure 1. Map showing study area (*left*) and location of study catchments (*right*).

from the 1970s. The climate is equatorial and the annual rainfall at Danum (1985–2004) was 2,829 mm. The geology comprises a melange of interbedded volcanics and sedimentary mudstones and sandstones (Marsh & Greer, 1992). Topography is steep in headwaters, but moderate (10–25°) in the central/eastern sections. Loam and silty loam Ultisols are dominant, but sandy loams occur on steeper slopes (Chappell, Ternan, & Bidin, 1999; Clarke & Walsh, in press).

2.2. CHARACTERISING SOURCE SEDIMENT

In the primary forest, samples of soil were taken at depths of 0, 10, 20, 50, 70 and 110 cm from four pits (two in W3 and two in W7). Deeper material was sampled from recent landslide debris at three sites in the Baru catchment. The <125 μm of all samples was analysed for total P and N by spectrophotometry and a suite of acid-leachable trace metals by ICPMS for comparison of source and channel material.

2.3. CHARACTERISING CHANNEL-STORED FINE SEDIMENT

Composite samples of recently deposited fine sediment were derived from five bed-material samples from the outlet reach of each study catchment. Samples were sieved to <125 μm and analysed as for source material above.

2.4. DATA ANALYSIS

Signatures for each source type (see Table I) were assigned by calculating the mean value of each parameter with 95% confidence limits. After statistical comparison (cf. Collins & Walling, 2002) four tracer properties (TN, TP, Ni, and Zn) were selected for best discrimination of sources. Downstream sediment samples were quantitatively unmixed using a method based on Franks and Rowan (2000) which yields estimates of material derived from each source category.

3. Results

3.1. GEOCHEMISTRY OF SOURCE MATERIALS

TP levels in surface soil are 2.5 times higher than in subsoil and over 20 times higher than in deeper landslide material (Figure 2a). TN falls with depth likewise (Table I). Differences in metal levels with soil depth are neither consistent between profiles nor statistically significant (compare to Van Oort, Jongmans, Citeau, Lamy, & Chevallier, 2006), but Zn and Ni levels are four to five times higher in both soil categories than in landslide material (Figure 2b, Table I). Thus this suite of tracers distinguishes between surface (<10 cm) and shallow

TABLE I

Tracer values assigned to each source type (italics) and each channel-stored sediment location with associated confidence limits

Type	Sample	TN	TP	Ni	Zn
	Surface soil (0–10 cm)	*5,794±1,884*	*630±79*	*18±8*	*50±22*
	Subsurface soil (10–150 cm)	*1,010±190*	*256±38*	*20±6*	*63±13*
Source	*Deep-sourced material (<150 cm)*	*498±54*	*29±30*	*5±2*	*11±9*
	Pipe at West 3	2,017±43	601±±74	41±6	91±4
	Pipe at West 7	1,163±87	220±17	6±1	17±5
	West stream	816±221	289±42	33±7	30±2
	Baru Stream	379±171	148±22	18±7	53±53
	Segama at Danum Valley F.C.	133±59	131±9	35±7	99±13
Sediment	Segama at Segama Bridge	209±125	142±111	50±13	116±31

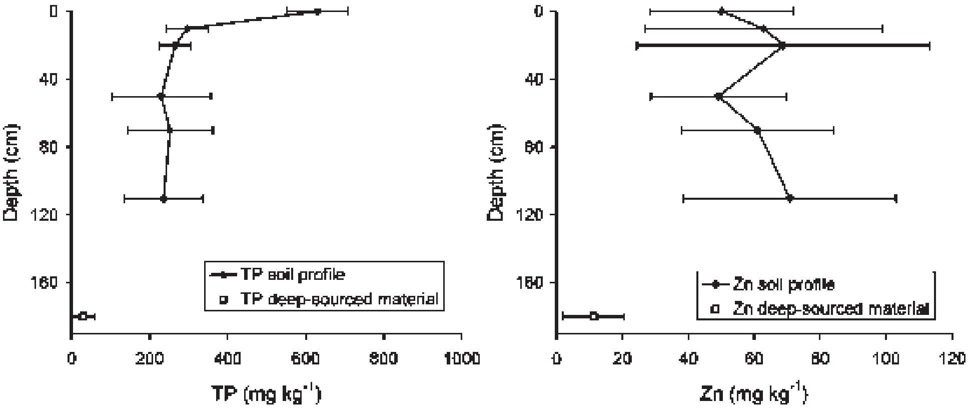


Figure 2. Plots of changing geochemical properties with depth in the soil profile.

subsurface soil (10–110 cm) largely on the basis of nutrient concentrations and between both soil levels and deeper material (>110 cm) on the basis of metal concentrations.

3.2. GEOCHEMISTRY OF CHANNEL-STORED FINE SEDIMENT

Geochemical properties of fine sediment from each channel site are shown in Table I. Samples from pipe outlets (notably W3) in primary forest have high nutrient levels intermediate between surface and shallow subsurface soil values, suggesting that much sediment is derived from surface soil in their upstream contributing areas. Metal concentrations are relatively high at W3, but low (typical of deep-sourced material) at W7. Sediment from the logged Baru catchment is deficient in nutrients relative to West Stream although metal concentrations are not fully in accord. At the larger scale, the Segama at Danum has lower nutrient and higher metal concentrations than the Baru. Nutrient levels increase somewhat at the Segama Bridge site, but metal levels remain high.

3.3. UNMIXING STORED SEDIMENT TO QUANTIFY SOURCES

Percentage contributions of each source to bed fine sediment at each study site are shown in Table II. The proportion of surface-sourced material is much higher for the W3 than for the W7 pipe-fed system. In contrast the deep-subsurface proportion was 3% for W3 but 72% for W7. Source contributions for the undisturbed West, selectively logged Baru and rotationally logged Segama

TABLE II

Model estimates of percentage source contributions to channel-stored sediment in each study catchment

	Pipe channel (W3)	Pipe channel (W7)	West Stream	Baru Stream	Segama at DVFC	Segama at Segama Bridge
Surface soil (0–10 cm)	34±2	22±2	18±2	16±3	6±3	16±7
Subsurface soil (10–150 cm)	64±1	5±6	38±9	40±8	42±5	41±10
Deep-sourced material (>150 cm)	3±1	72±8	43±8	44±9	52±6	43±16

at Segama Bridge were similar. In contrast, for the upper Segama at Danum the surface contribution was very low (6%) and the deep-subsurface input was high (52%).

4. Interpretation and Discussion

4.1. PIPE-FED CHANNELS

The high nutrient levels intermediate between surface and subsurface soil values accord with the 22%–34% surface soil contribution estimated by the model. The much higher surface and shallow subsurface contributions for W3 than for W7 may be due to the contrasting nature of the pipe-fed systems; piping in W3 is shallower and discontinuous with frequent roof collapses, whereas the W7 system above the site is entirely underground (Sayer, Walsh, Clarke, & Bidin, 2004) but with no known pipes below 1.5 m depth. The 72% deep-source contribution to W7 suggests either that part of the piping network is deeper than the visible network suggests or that the metal-deficient zone commences just below the 1.10 m maximum sampled depth of soil-pit material.

4.2. THE WEST, BARU AND SEGAMA SITES

Its similarity in relative source contributions to the primary forest West stream (Table II) would appear to suggest that the selectively logged Baru system has returned to a near-normal state in terms of sediment production and delivery dynamics. This would accord with Baru monthly sediment yields in 2003 being of a similar order to those of West Stream (Walsh et al., 2006). On the other hand, the 50% lower nutrient levels in Baru than in West Stream sediment suggests that Baru has not fully recovered from selective logging, but is actively reworking deeper-sourced material from landslide and logging road inputs of the late 1990s (Douglas et al., 1999) that have been stored in debris dams (Walsh et al., 2006). An alternative explanation of the similarity between Baru and West source contributions is that a recent natural landslide less than 200 m upstream of the sampled reach has temporarily elevated deeper subsurface inputs to West stream. The reduced importance of surface sources in favour of deep subsurface sources for the Segama at Danum may reflect landslide inputs caused by logging in the steep headwaters region in 1999–2000. This also helps to explain the low nutrient levels at this site. That the Segama at Segama Bridge exhibits a sources pattern similar to those of the West and Baru streams suggests either that recent sediment slugs from the headwaters are largely yet to arrive downstream or that headwater inputs are outweighed by shallower inputs from moderate terrain of downstream tributary systems covered by older regenerating forest.

4.3. LIMITATIONS AND FUTURE NEEDS

Some issues may affect the accuracy of the above results and their interpretation. These will need to be addressed by future work. First, confidence limits around source signatures are high (Table I). This may be due to contrasting tracer behaviour in minerogenic and organic material. Refinement of the nutrient and metal signatures could be attained by particle-size adjustment procedures (cf. Owens & Walling, 2002). Second, the model as adopted here assumes that source signatures of both nutrients and metals defined for a small part of the catchment are representative of the whole Segama catchment. Heterogeneous volcanic and sedimentary lithology and soils may complicate depth-related signatures (Walsh, Blake, Bidin, Sayer, & Thomas, 2004) and help to explain the poorer model performance and anomalous metal levels at the large catchment scale. More rigorous spatial sampling of the Segama catchment to explore spatial patterns in soil and sediment geochemistry would improve source definition and potentially enable relative contributions of sub-catchments to be assessed. Third, the model assumes that tracers are conservative and not preferentially stored or altered during transport. The reduction in nutrient levels in sediment up the catchment hierarchy may reflect losses en route (cf. Owens & Walling, 2002). The conservative nature of all tracer properties needs to be confirmed (cf. Motha, Wallbrink, Hairsine, & Grayson, 2002). Finally, information provided by the model on depth of sources can be ambiguous about the processes responsible and whether they have been enhanced by logging. Thus the deep subsurface category was inferred to be provided by pipes in the W7 primary forest zero-catchment, but mainly by landsliding (or reworking of landslip material in channels) in the logged catchments.

5. Conclusion

Against the apparent applicability of tracing methods at the smaller scale, detailed spatial analysis of sediment loads, storage and sources, i.e., a combined monitoring and tracing approach (cf. Walling, 2006), is urgently required to improve our knowledge of larger scale sediment dynamics in disturbed tropical basins.

Acknowledgements

The Royal Society SE Asia Rain Forest Research Programme – infrastructural and travel support (WHB/RPDW); NERC studentship NER/S/A/2001/06422 (AMS); Economic Planning Unit (Prime Minister's Office) & Danum Valley Management Committee – research permission; School of Geography, Plymouth University – analytical funding; J. Hanapi & J. Larenus – field assistance; K. Solman – geochemical analyses. This paper is number A/433 of the Royal Society SE Asia Rain Forest Research Programme.

This page intentionally blank

References

Chappell, N. A., Ternan, J. L., & Bidin, K. (1999). Correlation of physicochemical properties and sub-erosional landforms with aggregate stability variations in a tropical Ultisol disturbed by forestry operations. *Soil and Tillage Research*, *50*, 55–71.

Clarke, M. A., & Walsh, R. P. D. Long-term erosion and surface roughness change of rain-forest terrain following selective logging, Danum Valley, Sabah, Malaysia. *Catena* (in press).

Collins, A. L., & Walling, D. E. (2002). Selecting fingerprint properties for discriminating potential suspended sediment sources in river basins. *Journal of Hydrology*, *261*, 218–244.

Douglas, I., Bidin, K., Balamurugan, G., Chappell, N. A., Walsh, R. P. D., Greer, T., et al. (1999). The role of extreme events in the impacts of selective tropical forestry on erosion during harvesting and recovery phases at Danum Valley, Sabah. *Philisophical Transactions of the Royal Society of London Series B–Biological Sciences*, *354*, 1749–1761.

Franks, S. W., & Rowan, J. S. (2000). Multi-parameter fingerprinting of sediment sources: Uncertainty estimation and tracer selection. In L. R. Bentley, C. A. Brebbia, W. G. Gray, G. F. Pinder & J. F. Sykes (Eds.), *Computational Methods in Water Resources* (pp. 1067–1074). Rotterdam: Balkema.

Marsh, C. W., & Greer, A. G. (1992). Forest land-use in Sabah, Malaysia: An introduction to Danum Valley. *Philisophical Transactions of the Royal Society of London Series B–Biological Sciences*, *335*, 331–339.

Motha, J. A., Wallbrink, P. J., Hairsine, P. B., & Grayson, R. B. (2002). Tracer properties of eroded sediment and source material. *Hydrological Processes*, *16*, 1983–2000.

Owens, P. N., & Walling, D. E. (2002). The phosphorus content of fluvial sediment in rural and industrialized river basins. *Water Research*, *36*, 685–701.

Sayer, A. M., Walsh, R. P. D., Clarke, M. A., & Bidin, K. (2004). The role of pipe erosion and slopewash in sediment redistribution in small rainforest catchments, Sabah, Malaysia. In V. Gosolov, V. Belyaev & D. E. Walling (Eds.), *Sediment transfer through the fluvial system* (pp. 29–36). IAHS Publ. 288.

Sidle, R. C., Sasaki, S., Otsuki, M., Noguchi, S., & Nik, A. R. (2004). Sediment pathways in a tropical forest: Effects of logging roads and skid trails. *Hydrological Processes*, *18*(4), 703–720.

Van Oort, F., Jongmans, A. G., Citeau, L., Lamy, I., & Chevallier, P. (2006). Microscale Zn and Pb distribution patterns in subsurface soil horizons: An indication for metal transport dynamics. *European Journal of Soil Science*, *57*, 154–166.

Walling, D. E. (2006). Tracing *versus* monitoring: New challenges and opportunities in erosion and sediment delivery research. In P. N. Owens & A. J. Collins (Eds.), *Soil erosion and sediment redistribution in river catchments* (pp. 13–27). Oxfordshire: CABI.

Walsh, R. P. D., Blake, W. H., Bidin, K., Sayer, A. M., & Thomas A. D. (2004). Prospects for a sediment fingerprinting approach to unravelling changing upstream sediment sources in the rotationally selectively logged Segama catchment, Sabah. In R. C. Sidle, M. Tani, A. R. Nik & T. A. Taddese (Eds.), *Forests and water in warm, humid Asia* (pp. 223–226). Uji, Japan: Disaster Prevention Research Institute.

Walsh, R. P. D., Clarke, M. A., Bidin, K., Blake, W. H., Chappell, N. A., Douglas, I., et al. (2006). Changes in the spatial distribution of erosion within a selectively logged rain-forest catchment in Borneo 1988–2003. In P. N. Owens & A. J. Collins (Eds.), *Soil erosion and sediment redistribution in river catchments* (pp. 239–253). Oxfordshire: CABI.

Water, Air, and Soil Pollution: Focus (2006) **6:** 261–272
DOI: 10.1007/s11267-006-9047-0

RISKS FROM HISTORICAL CONTAMINATED SEDIMENTS IN THE RHINE BASIN

SUSANNE HEISE* and ULRICH FÖRSTNER
Department of Environmental Science and Technology, Hamburg University of Technology,
Eissendorfer Str. 40, 21071 Hamburg, Germany
*(*author for correspondence, e-mail: s.heise@tuhh.de; phone: +49-40-428782864;*
fax: +49-40-428782315)

(Received 30 August 2005; accepted 7 November 2006)

Abstract. The holistic river basin approach of the European Water Framework Directive (WFD) requires the combined assessment of ecological risks and the development of remediation measures. This paper presents a three-step strategy for the assessment of risks on Rotterdam harbour arising from historical contaminated sediment in the Rhine river basin, by the identification of (1) substances of concern, (2) areas of concern and (3) areas of risk with regard to the probability of polluting the sediments in the downstream reaches. The pragmatic approach provides initial evidence, that sediment-associated hexachlorobenzene (HCB) from the Higher and Upper Rhine has a significant effect on the quality of dredged material from Rotterdam harbour and that this HCB contamination is a candidate for the Category 1 of WFD Article 16 Source/Pathway S.11.1 'Historical Pollution from Sediments': This HCB source can contribute to a failure of the objectives of the WFD in the Rhine Basin and may require additional measures for its control.

Keywords: hexachlorobenzene, hydraulic processes, polycyclic aromatic hydrocarbons, priority substances, resuspension, risk assessment, Water Framework Directive (EU–WFD)

1. Introduction

A basin-scale framework for sediment management should be comprised of two principal levels of decision-making: the first for basin-scale evaluation (site prioritization) and the second for site-specific assessment. The Conceptual Basin Model for risk assessment, as presented by Apitz and White (2003), balances the mass flow of particles and contaminants, screening level assessment of sediment quality data, and basin-scale objectives, e.g., for source control. Information is still required about what type of measurements is needed and how to combine the various sets of quality and quantity data. In the following, a pragmatic approach will be presented exemplarily for the Rhine Basin, which is particularly needed for the harbours at the end of large catchment areas and – at the same time – respects the strategies for implementing measures under the Water Framework Directive (WFD).

2. Priority Substances in Historical Contaminated Sediments

With the action program 'Rhine' in 1987, extensive improvements of the water quality of the Rhine have been achieved by reduction of industrial and municipal point sources. In future, diffuse pollution and possibly pollution through secondary sources such as historic contaminated sites will gain in importance. Both will be more difficult to reduce than point sources – either because they are by definition 'highly dynamic spreaded pollution sources' (definition of diffuse sources, Vink, & Behrendt, 2001) or because their location and resuspension risk is not known as is often the case with historic contaminated sediments.

Even if water quality improves, sediment and floodplain soil contamination will remain a 'legacy of the past'. The owners of large 'sediment traps', such as the big ports, mostly at the end of navigable rivers, are put at a disadvantage as they have to pay the expenses of all former, actual and future shortcomings in emission control within their entire catchment areas.

This creates a situation in which environmental regulators and harbour managers (due to existing restriction in the handling of dredged material) share the common interests to reduce contaminating sources in the catchment area.

Nevertheless, risk due to erosion of contaminated sediments and their potential impacts downstream is not covered by *national* regulations. They focus on local impacts of the relocation of contaminated sediments and do not take the whole catchment into account. On the other hand, the *European* Water Framework Directive (WFD), which focuses on the catchment scale, also does not consider sediment quality and quantity as a major issue (Salomons & Brils, 2004). However, the strategies against chemical pollution of surface waters (WFD article 16), i.e., implementation of monitoring programs until 2006 and establishment of a program of measures until 2009, have to consider sediment quality at the catchment scale. With respect to the latter date, already the first step – screening of all generic sources that can result in releases of priority substances and priority hazardous substances – will include the specific source/pathway 'historical pollution from sediment.'

When sediments are acknowledged as sources of water contamination, key sources and pathways will need to be identified in accordance to WFD article 16[1]. A stepwise approach for source screening has been developed by an Expert Advisory Forum on Priority Substances and Pollution Control (Anonymous, 2004): The first step is the identification of potential sources and the second step assesses whether the source/pathway can contribute to a failure of the objectives of the

---

[1] WFD article 16 states: "measures against pollution for water aimed at the progressive reduction of discharges, emissions and losses of priority substances (PS) and at the cessation or phasing-out of discharges, emissions and losses of priority hazardous substances (PHS), at least to result in the achievement of good chemical status of surface waters."

WFD. The final steps 3 and 4 of the methodology deal with the development of measures. The key outcome of the process is to identify Category 1 sources, which may potentially require additional measures for their control. With respect to the source/pathway ‘historical pollution of sediments’, few Category 1 PS/PHS candidates – polycyclic aromatic hydrocarbons (from analogy ‘historical pollution from contaminated land’), cadmium, tributyltin – were mentioned (Anonymous, 2004); however, underlying data are still very insufficient.

3. Identification of Areas of Risk in the Rhine Catchment Area and its Tributaries for the Port of Rotterdam Due to Historic Contamination

In order to be able to effectively plan measures in the catchment area to improve river quality, those regions need to be identified, that represent not only a hazard but also have the potential to become a source and thus expose larger areas to an unwanted situation. These areas then need to be prioritized according to the risk that they pose (Babut et al., 2007).

The focus of port authorities necessarily lies on the harbour area and the risk that due to permanent contaminant emission from upstream sediments, their dredged material exceeds existing regulations and needs to be costly disposed in disposal sites rather than being allowed to being relocated to the environment. In the Port of Rotterdam, decisions on those management options for the 20 Mio m^3 that are annually dredged in the harbours and channels, are based on a system for assessing the acceptability of dredged material for dispersal in saline waters, the ‘chemical toxicity test’ (CTT), in which chemical target values are supplemented by biological effect considerations and the potential environmental risk of the contaminants present (Schipper & Schout, 2003).

3.1. THE CONCEPT: PRIORITIZATION OF SUBSTANCES AND AREAS OF CONCERN

The prioritization of sites in a catchment with regard to the risk that they pose for downstream areas should apply a three-step approach (Heise et al., 2004):

1. Identification of substances of concern and their classification into ‘hazard classes of compounds’. ‘Substances of concern’ are here defined as those compounds that frequently exceed regulatory criteria for suspended matter in downstream areas, indicating transport processes of contaminated sediment. Hazard classes are assigned depending on the chemicals’ persistence, their partitioning to sediment and their environmental risk. In this study, data were sampled directly upstream of the Rotterdam harbour area to identify these Rhine-relevant substances (Table I).

TABLE I

'Substances of concern' in the Rhine River and their assignment to hazard classes

Substances of concern	Hazard class
Cadmium	2
Chromium	1
Copper	1
Mercury	2
Nickel	1
Lead	1
Zinc	1
DDT + DDD + DDE (SUM)	2
Dioxins and Furans	2
HCB	2
PAH (z.B. Benzo(a) pyrene	2
PCB	2
TBT	1
Aldin (Dieldrin, Endrin)	1
γ-HCH	1
Nonyl–phenol compounds	1

2. Identification of areas of concern and their classification into 'hazard classes of sites'. Areas are defined to be of concern, if the surface sediment data at the site exceed the CTT levels for sediment. For the study, data from environmental authorities of the German 'Länder,' the Federal Institute of Hydrology, from the International Commission for the Protection of the Rhine (ICPR), from research reports, publications and scientific groups were gathered, resulting in information on 180 sites. Figure 1 depicts those sites and indicates the hazard classes, based on the extent of contamination, the hazard class of the contaminating compounds, and the degree on confidence in the conclusion, the latter being based on variability and amount of available sediment data per site.
3. Identification of areas of risk. The risk assessment for the harbour sediments due to those 'substances of concern' that could derive from the identified 'areas of concern' requires estimating resuspension, transport probabilities, and determination of transported quantities. As floods frequently occur in the main river and its tributaries, the final assessment of 'areas of risk' had to take into account the impact of event-related increased discharge levels. Monitoring data on water discharges, loads and concentration of suspended matter were used to look for evidence of event-related resuspension, combined with information on sediment erosion thresholds and measured current velocities where available.

An indication of the potential of an 'area of concern' to lead to an exceedance of the local threshold value (CTT value) in the Port of Rotterdam in case that its

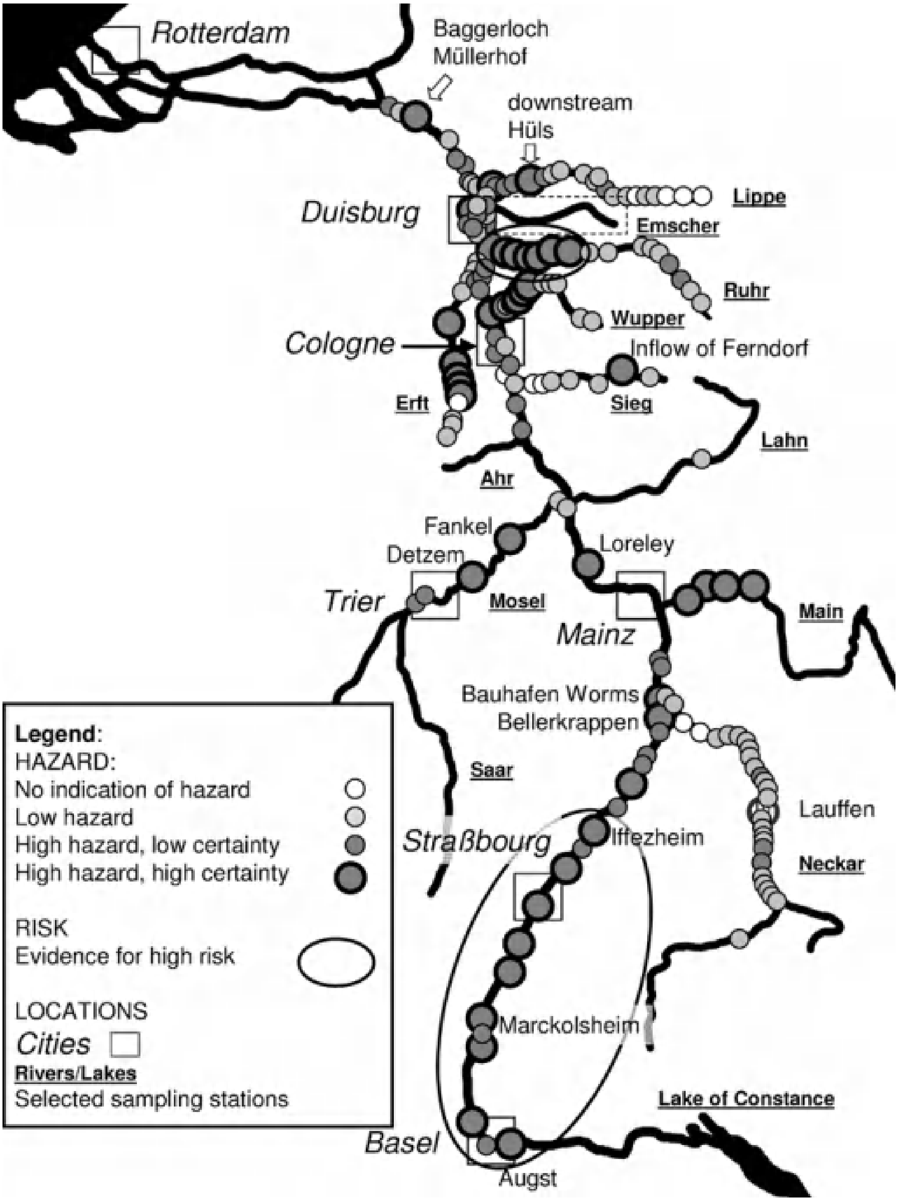


Figure 1. 'Areas of concern' and 'areas with a high certainty of high risk' for downstream river stretches at different discharge scenarios (Ruhr at HQ100 and Higher and Upper Rhine barrages at more than HQ1; Heise et al., 2004).

contaminated sediments become resuspended and transported downstream, is derived from taking into account dilution by suspended matter originating mainly from the tributaries:

$$X^{\mathrm{A}} = X^{*}\mathrm{SM}^{\mathrm{KB}}/\mathrm{SM}^{\mathrm{A}}$$

(where X^{A} is the concentration at location A which would be needed for the respective CTT value at Rotterdam to be exceeded; X is the CTT-value for the respective substance; '$\mathrm{SM}^{\mathrm{KB}}$' is the suspended matter load at Kleve-Bimmern (close to Dutch/German border); 'SM^{A}' is the suspended matter load at location A).

The different parts of information (hazard class, indication of sites where resuspension occurs, erosion thresholds in comparison with measured current velocities, indication of potentially effective contamination levels) were regarded as separate lines of evidence, from which at the end the final conclusions were drawn and sites classified as bearing 'no evidence of risk,' 'evidence for risk,' 'evidence for high risk,' or as those sites, for which a risk could not be excluded.

3.2. RESULTS AND CONCLUSIONS ON RISKS FOR THE PORT OF ROTTERDAM

The single data, classified into hazard classes (class 1: indication for a potential hazard, class 2: indication for a potential high hazard, class 3: high certainty that a high hazard is present), were aggregated into 12 large 'areas of concern' comprising the barrages in the Upper Rhine, harbours and flooded quarries in the Middle and Lower Rhine as well as the main tributaries. Table II that gives an overview over the 'substances of concern' at the different 'areas of concern', shows that patterns of contamination exist. These depend on (a) the historical emissions, (b) the dynamic of the system, and (c) the amount of data, that forms the basis of these results.

Similar contamination patterns in unconnected tributaries can be caused by similar economical situations, such as similar industries influencing the sediment quality. Comparing Mosel, upper and Erft, which are all areas under direct (Erft, Wupper) or indirect (Mosel via Saar) influence of the mining industry, all sediments are contaminated with nickel, lead and zinc. Exceptions are Ruhr and Neckar which show a similar pattern, having cadmium, copper and PCBs accumulated in the sediments despite differing industrial activities in these areas.

Similar patterns are also caused by transport of contaminants with sediment or suspended matter downstream, as it is the case with the locations from the barrages at the High Rhine till the harbours in the Middle Rhine such as Loreley and Worms Bauhafen. All show mercury, DDT and hexachlorobenzene contamination.

Also Wupper and the harbours in the Lower Rhine, like Hitdorf and the Duisburg harbours, share a similar pattern. The harbours are all located downstream of the confluence of the Wupper and especially Hitdorf is known to be affected by the tributary's effluents.

TABLE II

‘Areas of concern’, main hazard classes (‘H.C.’, classification see text) at their sites and the main contaminating compounds in sediments (‘X’)

Areas of concern		H.C.	Cd	Cr	Cu	Hg	Ni	Pb	Zn	DDT DDD DDE	Sum Dioxin Furan	HCB	Sum PAH	Sum PCB	TBT
High and Upper Rhine	Barrages	3				X				X		X		X	
Upper and Middle Rhine	Harbors e.g., Loreley	1–3				X				X		X			
Lower Rhine	Duisburg[a]	1–3	X	X				X	X		X				
	Harbours[b]	3	X	X	X	X	X	X	X			X		X	
Tributaries	Neckar	1	X		X									X	
	Main	3	X			X				nd	nd	nd	nd	nd	nd
	Mosel	2–3			X		X	X	X	nd	nd	nd	nd	X	nd
	Emscher	3											X	X	
	Wupper	3		X	X	X	X	X	X						
	Ruhr	3	X		X			X					X	X	
	Erft	3	X				X	X	X	nd	nd	nd	nd	nd	nd
	Lippe	2										X			X

nd No measurement or only single data on organic substances.

[a] Duisburg harbours.

[b] Harbours and flooded quarries in the Lower Rhine.

Evidence of risk for the Port of Rotterdam, was only found for five areas. Of these, two regions were classified as areas presenting a 'high risk with high certainty' under certain levels of water discharges (Figure 1; Table III).

The Ruhr was assessed to represent a risk at increased water discharges. High concentrations of polycyclic aromatic hydrocarbons (PAHs) but also of the other substances that are of concern in that river, especially cadmium, are likely to be resuspended and transported downstream under those circumstances.

The barrages in the Upper Rhine were the only sites in this study that may already present a risk during average annual flood events, at which increased concentrations of hexachlorobenzene (HCB) have been measured in suspended matter at Iffezheim. With increasing discharges, HCB becomes resuspended and transported downstream. With the continuous inflow of contaminated sediments from the barrages further south, the existing sediment disposal sites reaching their upper limits, with the continuously high HCB concentrations in the sediment and significant gaps in the understanding of its transport processes, this area becomes an important challenge for future sediment management.

TABLE III

'Areas of risk' in the Rhine Basin and selected tributaries, concluded from evidence of theoretical possibility to exceed the CTT level and indication of resuspension

Theoretical exceedance of CTT upon sediment resuspension		Indication of resuspension			Risk for the Port of Rotterdam
		Hydrological situation[b]	Erosion potential[c]	Increase in SPM load[d]	
Area/ Substance	Discharge level[a]				
Ruhr River					
Polycyclic aromatic hydrocarbons (PAHs)	MQ (~20 mg/l)	BAU	+		no risk
	MHQ (~150 mg/l)	HQ_{10}	++	+ (HQ_1)	risk
	HHQ (~250 mg/l)	HQ_{100}	+++		high risk
Higher and Upper Rhine barrages					
Hexachloro–benzene (HCB)	MQ (~20 mg/l)	BAU	+/−	+	risk
		$>HQ_1$	+	+++	high risk
		$>HQ_{10}$	++		high risk
		$>HQ_{50}$	+++		high risk

[a] Discharge level: MQ = mean water discharge, MHQ = mean flood discharge, HHQ = highest experienced discharge.

[b] Hydrological situation: BAU = business as usual conditions. HQ_x = flood return period; x indicates the frequency of years, with which such a high water is expected.

[c,d] +/− no obvious effect, + small effect, ++ significant effect, +++ large effect.

3.3. SOURCE OF HEXACHLOROBENZENE IN THE UPPER RIVER RHINE

HCB is a non-biodegradable, bioaccumulative micropollutant that belongs to the 12 persistent organic pollutants (POPs) that have been identified by the United Nations Economic Commission for Europe for international regulation. In 1975, a first study of fish for chlorinated aromatic hydrocarbons indicated values of to 150 mg HCB/kg fat in the Upper Rhine (Heise et al., 2004). Subsequently, the wastewater discharges of a company in Rheinfelden at Rhine – km 148.3 had been identified as the source of this HCB pollution. Since the 1960s this company operated a plant for the production of pentachlorophenol (PCP) and its sodium salt (PCP–Na). According to the first wastewater inventory in the year 1981, the emission was in the order of 10 kg HCB/day. Finally, the production of PCP–Na has been stopped in 1985 and of PCP in 1986.

However, the HCB pollution did not disappear. As compensation for the closed PCP/PCP–Na production, the company significantly increased the production of chlorosilanes; a big new plant went into operation in 1987. It has been shown, that during hydrochlorination of silicon, at high temperatures, HCB is unintentionally formed to a relevant extent. Until 1993, the company continued to discharge untreated rinsing and cleaning water; from 1994 onwards the discharged HCB load is practically zero. However, sediment samples still indicate high concentrations; even in 2003, HCB concentration in suspended matter up to 400 μg/kg have been determined in the Upper Rhine.

In the report of the WFD, the river section from the border to Switzerland up to the last barrage near Iffezheim is considered as ‘endangered’ (gefährdet) with regard to the chemical quality of the water due to the contamination of sediments with HCB (EG–WRRL, 2005).

Currently, the accumulation of this HCB contaminated material in the last barrage Iffezheim presents an example of different management objectives that – if in conflict with each other – can endanger sustainable management of a river basin.

3.4. THE MANAGEMENT OPTION: IFFEZHEIM IN THE CENTRE OF CONFLICTING INTERESTS

Until 2003, HCB-contaminated material that needed to be dredged at the Iffezheim barrage, the last barrage of the Upper Rhine, was disposed of near the barrage in containment facilities. These are now filled up and the responsible authority, the Waterway and Shipping Administration (WSA), had to look for a way to accommodate 130,000 m^3 of sediment that reach Iffezheim and accumulate there each year. The WSA followed the economic management objective and looked for the least expensive solution at the site. It was decided that this would be the relocation of the uppermost sediment layers, which show lower HCB concentrations, into the Rhine downstream of the barrage.

The Port of Rotterdam voiced its fears that any deliberate relocation of HCB-contaminated material into the Rhine may lead to an exceedance of the HCB concentration in sediments in the port, which would forbid the relocation of sediments at sea. The relocation at sea is for the Rotterdam port authorities the least expensive option.

According to the current discussion, the German decision to relocate the material complies with national regulations. In this case however, they contradict several EU principles and directives (non-deterioration principle, sustainability principle, SEA directive), and on April 27, 2005, a group of Dutch NGOs initiated a formal complaint to the Commission of the European Communities concerning failure to comply with community law against the national government of Federal Republic of Germany, the regional government of Baden-Württemberg, and the regional water manager WSA (Lycklama, 2005).

4. Outlook: Additional Information on Risk Assessment of Historical Contaminated Sediments

In the future, a significant increase of the weight of evidence for risks on downstream target areas could be expected from the precision of the term ‘indications that resuspension occurred’. Under favourable conditions – e.g., in areas exhibiting continuous sedimentation – the study of dated sediment cores has proven particularly useful as it provides a historical record of the various influences on the aquatic system by indicating both the natural background levels and the anthropogenic accumulation of substances over an extended period of time. Best locations for such historical records are within or close to the critical target areas (harbour basins, lakes, depressions, lowlands, flood plain soils and sediments, etc.). Additional information on the source areas of specific pollutants that are analyzed in the target sediment cores can be gained from indicator substances or from typical isotopes (e.g., lead isotopes) and patterns of congeners (e.g., for dioxins/furans; Götz & Lauer, 2003).

The pragmatic approach presented here can be supported by additional information from

1. Erosion stability test procedure (Witt & Westrich, 2003): The instrumental facilities allow one to measure not only the critical bed shear stress for erosion, but also the erosion rate for different sediment layers, using a special pressurized channel. The mobile, flume-like, calibrated testing equipment facilitates the simulation of local erosive events by applying high, near bed flow velocities and bed shear stress, respectively. The unique combination of laboratory and *in situ* experiments enables one to upscale and transfer sediment erosion and sedimentation criteria to nature, which is an essential prerequisite for numerical modeling of natural processes.

2. Ecotoxicological tests on old and freshly deposited material (Ahlf, Hollert, Neumann-Hensel, & Ricking, 2002). In order to assess environmental risks, derived from contaminated sediments, tests on effects should therewith be performed to cover potential changes in bioavailabilities during transport processes. This seems to be especially true for recently sedimented material, which, in addition, is prone to resuspension due to its low critical erosion thresholds. The specified layer is exactly the habitat where most benthic organisms live. The recommendation for an assessment strategy uses an integrated hierarchical approach combining toxicological, chemical and ecological information to assess and evaluate the quality of sediments.

Establishing a rough sediment dynamic model, building on tributary/main river dilution factors, sedimentation data, suspended, particulate-matter monitoring data and integrating a higher number of data on critical erosion thresholds that exist today, it should be possible to achieve a scientific site prioritization with detailed answers about what risks could be reduced by applying methods to a specific site (Förstner, 2003).

Acknowledgements

We would like to acknowledge the contribution of Dr. H. Schönberger, Prof. B. Westrich, T. Jancke, J. Karnahl and Prof. W. Salomons to the report on areas of risk in the Rhine, and the financial support of the Port of Rotterdam, the Netherlands.

References

Ahlf, W., Hollert, H., Neumann-Hensel, H., & Ricking, M. (2002). A guidance for the assessment and evaluation of sediment quality: A German approach based on ecotoxicological and chemical measurements. *Journal of Soils and Sediments*, *2*, 37–42.

Anonymous (2004). Concept paper on emission control from 8 June 2004. Expert Advisory Forum (EAF) on Priority Substances and Pollution Control. *7th EAF meeting*. Brussels, 14–15 (June 2004).

Apitz, S. E., & White, S. (2003). A conceptual framework for river-scale sediment management. *Journal of Soils and Sediments*, *3*, 132–138.

Babut, M., Oen, A., Hollert, H., Apitz, S. E., Heise, S., & White, S. (2007). Prioritization at river basin scale, risk assessment at site-specific scale: Suggested approaches. In S. Heise (Ed.), *Sediment risk management and communication*. Amsterdam, The Netherlands: Elsevier, pp. 107–152 (in press).

EG–WRRL (2005). Internationale Flussgebietseinheit Rhein. Internationales Bearbeitungsgebiet Oberrhein. Bericht zur Bestandsaufnahme. 10 März 2005, (158 pp.) http://www.iksr.org/fileadmin/user_upload/Dokumente/Bestandsaufnahme_Teilberichte/BAG_Oberrhein/or_gesamtbericht.pdf.

Förstner, U. (2003). Geochemical techniques on contaminated sediments – river basin view. *Environmental Science and Pollution Research International*, *10*, 58–68.

Götz, R., & Lauer, R. (2003). Analysis of sources of dioxin contamination in sediments and soils using multivariate statistical methods and neural networks. *Environmental Science & Technology*, *37*, 5559–5565.

Heise, S., Förstner, U., Westrich, B., Jancke, T., Karnahl, J., Salomons, W., et al. (2004). *Inventory of historical contaminated sediment in Rhine Basin and its tributaries*. Report on Behalf of the Port of Rotterdam, p. 223.

Lycklama, T., representing the NGOs Stichting Reinwater, Stichting De Noordzee, Waddenvereniging, Gelderse Milieufederatie, Natuur en Milieufederatie Utrecht, Rhein Kolleg. (2005). Complaint about Iffezheim. http://www.reinwater.nl/docs/Iffezheim.pdf.

Salomons, W., & Brils, J. (Eds.) (2004). Contaminated sediments in European River Basins. European Sediment Research Network SedNet, EC Contract No. EVKI–CT–2001–20002, Key Action 1.4.1 Abatement of water pollution from contaminated land, landfills and sediments. TNO Den Helder/The Netherlands, p. 80.

Schipper, C., & Schout, P. (2003). De weg naar implementatie van de Chemie-Toxiciteit-Toets. Werkdocument: RIKZ/2003.036. AKWA/RIKZ 04.005. ISBN: 36934761, p. 82.

Vink, R., & Behrendt, H. (2001). Present and future quality of sediments in the Rhine catchment area – heavy metals. In J. Gandrass & W. Salomons (Eds.), *Dredged material in the Port of Rotterdam – interface between Rhine catchment area and North Sea*. Germany: GKSS Research Centre Geesthacht.

Witt, O., & Westrich, B. (2003). Quantification of erosion rates for undisturbed cohesive sediment cores by image analysis. *Hydrobiologia*, *494*, 271–276.

Water, Air, and Soil Pollution: Focus (2006) **6:** 273–281
DOI: 10.1007/s11267-006-9048-z

CHANGES IN SEDIMENT SOURCES FOLLOWING WILDFIRE IN MOUNTAINOUS TERRAIN: A PAIRED–CATCHMENT APPROACH, BRITISH COLUMBIA, CANADA

PHILIP N. OWENS[1,*], WILLIAM H. BLAKE[2] and ELLEN L. PETTICREW[2]
[1]*National Soil Resources Institute, Cranfield University, North Wyke Research Station, Okehampton, Devon EX20 2SB, UK*
[2]*School of Geography, University of Plymouth, Drake Circus, Plymouth, Devon PL4 8AA, UK*
*(*author for correspondence, e-mail: owensp@unbc.ca; phone: +001-250-960-6177; fax: +001-250-960-5845)*

Abstract. This paper describes a study examining the potential of mineral magnetic, geochemical and organic properties to determine if a 2003 wildfire in a catchment in British Columbia, Canada, caused a change in the sources of the suspended sediment transported in the channel relative to a nearby unburnt (reference) catchment. The results show that some of the properties offer the potential to determine sediment sources in the unburnt catchment. However, the 2003 wildfire modified the concentrations of some properties and this can either compromise or enhance their ability as tracers in the burnt catchment. At present, the source tracing results are inconclusive. This has implications for the use of certain properties as fingerprints and raises important issues about approaches to sediment source identification.

Keywords: sediment sources, fingerprinting, wildfire, mineral magnetics, geochemistry

1. Introduction

Wildfires are a natural part of the behaviour of forest systems and are important for a variety of reasons. These include forest renewal and maintaining biodiversity. Wildfires are also important from a hydrological and geomorphological perspective, because they can alter soil hydrology and the rates of soil erosion, mass movement and channel bank erosion, which affect the delivery of water, sediment, carbon and chemicals to rivers. In turn, these changes have important implications for salmonid spawning gravels and other riverine habitats, and the chemical and ecological quality of freshwaters in forested catchments. While there is a reasonable amount of information available on the changes in soil hydrology and soil erosion rates at the plot and hillslope scales (e.g., Cerda & Lasanta, 2005) and on changes in sediment concentrations and fluxes at the catchment scale (e.g., Petticrew, Owens, & Giles, in press) to wildfires, there is much less information available on the linkage between hillslopes and channels in response to wildfires, and in particular on changes in the sources of the sediment being actively delivered to, and transported by, rivers. Such information is needed: to understand the landscape evolution of forested systems; for effective resource management; and for mitigating the effects of wildfire, especially given concerns over global climate change, such as the increase in the frequency of wildfires in many areas (Pausas, 2004).

Recent work (Blake, Wallbrink, Doerr, Shakesby, & Humphreys, 2006) has explored the use of mineral magnetic properties as sediment tracers in wildfire-impacted river basins since the Fe-mineralogy of soil can be altered during burning at high temperature (Rummery, Bloemendal, Dearing, Oldfield, & Thompson, 1979). Whilst the work demonstrated the occurrence of magnetic enhancement in burnt *versus* unburnt soil material, patterns were complicated by colluvial storage of previously burnt material and potential variability in background (pre-burn) magnetic assemblages. Blake et al. (2006) suggested that the inclusion of geochemical data may have reduced ambiguity in post-fire sediment source signatures, however, to date little work has focused on wildfire impacts on soil geochemistry in a tracing context. Work has chiefly been concerned with alteration of organic carbon, major nutrients (N and P) and exchangeable cations (e.g., Al, H, Ca, Mg, K, Na) in the context of forest recovery (Certini, 2005) where significant removal of C and mineralization of nutrients could offer tracing potential. Volatilisation of trace elements at high temperatures can also lead to changes in burnt soil chemistry as demonstrated by Marafa and Chau (1999) who observed a reduction in Mn, Fe and Zn following repeated burning of an upland soil in Hong Kong. The potential of these and other properties as post-fire sediment source tracers needs further exploration.

This paper describes some preliminary results of a field investigation into the effects of a wildfire event on sediment sources using a paired–catchment approach (i.e., a burnt and a nearby unburnt catchment) in British Columbia, Canada. This research had two objectives: (1) to use field observations to qualitatively determine any change in the main sediment sources due to the impacts of the wildfire; and (2) to explore *the potential* of sediment fingerprinting properties to provide a more quantitative indication of changes in sediment sources.

2. Study Area and Methods

2.1. STUDY AREA

In summer 2003, unusually severe wildfires burnt in many locations across British Columbia (BC). The McLure fire, in the central interior of BC, near the town of Kamloops, burnt an area of ca. 260 km^2 affecting erosion rates and sediment delivery into several rivers, including Fishtrap Creek. Fishtrap Creek has a forested (Pines, Firs, Spruce and Cedar) catchment of 170 km^2 (135 km^2 to the gauging station, see Petticrew et al., in press) and is drained by several gravel-bed streams that form an important habitat for salmonid species. The Jamieson Creek catchment is located ca. 15 km to the south of Fishtrap. As Jamieson has similar characteristics of vegetation cover, topography, climate and geology to Fishtrap, but was not affected by the 2003 McLure fire, it serves as a reference catchment for comparing the effects of the 2003 fire in the Fishtrap catchment. The underlying geology in both catchments is dominated by Palaeozoic (Pennsylvanian and Permian) volcanic and metamorphic rocks, with outcrops of Mesozoic (Triassic and Jurassic) and Cenozoic (Miocene and/or Pliocene) rocks in the headwaters of Fishtrap and Jamieson, respectively. The catchments have a distinct snowmelt regime with melting typically starting in early April and the main flood discharges occurring from late April to mid May (Petticrew et al., in press).

2.2. METHODS

Following reconnaissance surveys of the study catchments, samples of source materials and suspended sediment samples were collected in both catchments during 2004. Composite suspended sediment samples were collected using time-integrated samplers (Biickert, 1999). These consisted of cylindrical gravel-filled traps (45 cm long and 7.5 cm diameter) with each end enclosed by 0.64 cm wire mesh. The traps were fixed to the channel bed using rebar stakes, with the sampler's long axis parallel to the flow. This enables flow to percolate through the traps whilst suspended sediment is deposited within the gravel pores. In both Fishtrap and Jamieson, three suspended sediment samplers (the sediment from which were bulked together) were installed at both an upstream and a downstream site. In both catchments, samplers were installed in April 2004 and emptied in June 2004 and September 2004, thereby providing composite samples of the suspended sediment transported during the periods April to June 2004 and June to September 2004.

Samples of source material were collected during April and June 2004. In both Fishtrap (n=14) and Jamieson (n=11) catchments, samples of topsoil (0–2 cm) and subsurface (>5 cm depth) material were collected from active slopes (i.e., those likely to erode and supply sediment to channels), and also from actively eroding channel banks. Each source material sample represented a composite of 5–10 subsamples collected within an area of ca. 10 m^2 to encompass local spatial variability in soil properties. In the case of the topsoil samples collected from Fishtrap, material was collected from the upper soil layers likely to have been modified by the fire, which consisted of exposed soil material in areas devoid of vegetation. In places, the upper layer of material included layers of ash >1 cm in depth, and in these situations the surface ash layer was carefully removed prior to sampling the scorched mineral surface beneath for identification of sediment source signatures.

Suspended sediment and source material samples were air-dried at 30°C, and disaggregated prior to screening to <500 μm. This fine fraction was analysed for low (χ_{lf}) and high frequency (χ_{hf}) magnetic susceptibility (using a Bartington susceptibility meter), geochemical (by spectrophotometry and ICP-MS after acid extraction) and organic properties (by total combustion), and absolute particle size characteristics (by laser granulometry).

3. Results and Interpretation

3.1. QUALITATIVE APPRAISAL OF DIFFERENCES IN SEDIMENT SOURCES BETWEEN THE CATCHMENTS

Despite the recent quest for quantitative approaches to determine the sources of the sediment transported in rivers (Walling, 2005), it is desirable that tracer-based studies should be both steered by, and evaluated in the context of, field observations of hydrological and geomorphological processes operating in the contributing catchment. The effect of the wildfire in Fishtrap Creek on changing the type and potential of soil erosion and sediment delivery processes were clearly apparent following reconnaissance surveys of both study catchments. The wildfire in Fishtrap Creek significantly reduced the vegetation cover, thereby exposing hillslopes and channel banks to erosion and sediment transport processes. Observations (Figure 1) demonstrated the *potential* for an increase in both topsoil and subsoil erosion relative to the unburnt Jamieson Creek, thereby justifying the need for further investigation. Field observations also facilitated sample selection by identifying likely active sources and enabled more targeted sampling.

3.2. ASSESSMENT OF MINERAL MAGNETIC, ORGANIC AND GEOCHEMICAL PROPERTIES AS TRACERS

Having qualitatively confirmed that the wildfire has influenced erosion and sediment transfer susceptibility, the value of the proposed tracer properties as discriminators between sediment source types can be evaluated. An important first phase in this process is to determine which source material properties are able to differentiate between sources. Because this paper reports a reconnaissance field programme, source materials have been simply classified as either surface material (i.e., topsoil) or subsurface material (i.e., subsoil and channel bank material) for each of the burnt (seven topsoil and seven subsoil/channel bank samples) and unburnt (six topsoil and five subsoil/channel bank samples) catchments. The Mann–Whitney U test was used to examine which of the organic, geochemical and mineral magnetic properties were able to differentiate between the two source types. This was initially performed on the source material samples collected from Jamieson Creek, i.e., the unburnt samples. As there were no statistically significant differences in the particle size composition of the

Figure 1. Photographs showing exposed topsoil (a) and subsoil (b) material due to the wildfire in the Fishtrap catchment (photos taken by Phil Owens in July 2004).

surface and subsurface source material samples, no correction for particle size was undertaken at this stage. There were statistically significant (α=0.05) differences for certain organic (%C and %N) and geochemical (As, Co, Cu, Ni, P) properties, although there were no such differences in the basic mineral magnetic properties (χ_{lf} and $\chi_{\mathrm{fd\%}}$). For %C, %N and P, values were greater in surface compared to subsurface materials, reflecting the inputs of these to the soil surface from vegetation and atmospheric sources. Most of the significant geochemical properties (e.g., Co, Cu and Ni) were greater in subsurface samples reflecting the influence of bedrock sources and weathering. Other elements (Cr, K and Na) were also greater in subsoil materials, although were not statistically different. Therefore, as %C, %N, As, Co, Cu, Ni and P are able to distinguishing between topsoil and subsoil material, they are suitable for sediment source determination.

It is also useful to assess the impact of burning on source material properties, as this may enhance or compromise their ability for source identification. This was tested by comparing the surface source materials from Jamieson (unburnt) with those from Fishtrap (burnt) underlain by similar Palaeozoic geology, so as to remove the potentially confounding effects of geological variation. Again, as there were no statistically significant differences in the particle size composition of the surface source materials in both catchments, property concentrations were, therefore, not corrected for particle size at this stage. A number of organic (%C), geochemical (Co, Cu, K, Mn, Na, Ni, P, Pb, Zn) and mineral magnetic ($\chi_{\mathrm{fd}\%}$) properties were statistically different (α=0.05) between burnt and unburnt surface materials. In several cases (Co, Cu, K, Ni, P, Zn and $\chi_{\mathrm{fd}\%}$) values were enhanced in the surface materials collected from the burnt catchment which could be due to the mineralization of litter with further inputs of canopy ash. Other properties (%C, Mn and Pb) evidenced a decrease in concentrations in burnt samples which may be due to vaporisation from surface layers that experienced high temperatures or leaching to subsurface layers.

3.3. Quasi–Quantitative Determination of Changes in Sediment Sources

From the comparison of surface *versus* subsurface materials in Jamieson, some organic and geochemical properties were able to differentiate between the two source types and thus could be used as fingerprints. The two bulk mineral magnetic properties were not able to differentiate the source types, although as the concentrations of the surface materials in Fishtrap were enhanced by the wildfire, this suggests that mineral magnetic properties do possess the potential for discriminating material affected by fire (Blake et al., 2006). Due to the limited number of source material and suspended sediment samples collected we have not used an unmixing model to provide quantitative estimates of sediment sources (Walling, 2005). However, it is possible to use bi-variate plots to make some semi-quantitative inferences of the sources of the suspended sediment being transported in the study catchments and explore whether the wildfire event has caused a change in the relative dominance of surface and subsurface sources. As an example, Figure 2 presents plots of concentrations of C against N and Cu against Ni for the two catchments. For the plots of C against N, in Jamieson there is a clear distinction between the surface materials and the subsurface materials, with the two sets of suspended sediment samples in the domain space occupied by the surface materials suggesting that this is the dominant source of the sediment transported in Jamieson Creek. For Fishtrap Creek, there is a similar situation although C concentrations in surface soils are substantially reduced due to the fire. The suspended sediment samples collected in June appear to be from surface materials, although those collected in September, while still suggesting a surface source, are different. The high organic contents of the September samples may be due to either (a) in-stream processes as a result of the reduced canopy cover overhanging the channel and the increase in light, and thus the occurrence of biofilms on the sediments, or (b) the occurrence of 'black carbon' due to the fire. For the plots of Cu *versus* Ni, again there is a reasonably good distinction

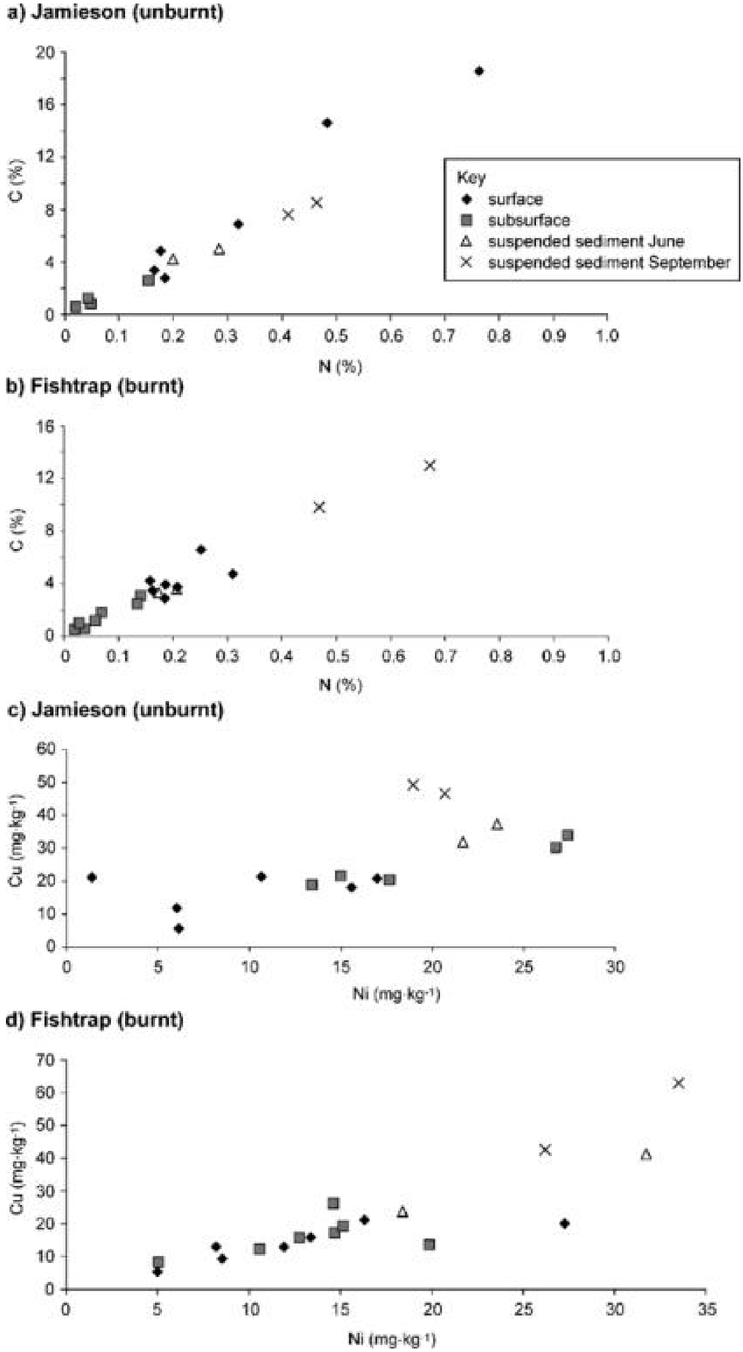


Figure 2. Plots of concentrations of C against N, and Cu against Ni for the source materials and suspended sediment samples (June and September 2004) collected from Jamieson (a, c) and Fishtrap (b, d) catchments.

between surface and subsurface source materials for Jamieson, with values for surface soils being lower for both properties. Although there is some overlap between the two groups, they are still statistically different. The suspended sediment samples are similar to subsurface samples, suggesting that this may be the main source. For Fishtrap, values of Cu and Ni for surface soils have increased due to the wildfire. There are also some subsurface soil samples with low values of Cu and Ni. These were collected from an area underlain by Mesozoic rocks. The effect of the wildfire in altering Cu and Ni concentrations, along with geological variations in Ni concentrations, means that it is not possible to distinguish between surface and subsurface materials, and thus it is not possible to determine with confidence the source of the sediment in Fishtrap.

4. Conclusion

The results show that some mineral magnetic, organic and geochemical properties offer the potential to distinguish sediment sources in unburnt catchments. However, the 2003 wildfire modified the concentrations of some properties and this can either compromise or enhance their ability as tracers in burnt catchments. The source tracing results presented above are to some extent contradictory and inconclusive. This underlines the fact that it is important to evaluate the controls on property concentrations and how these may change over time. It also raises important issues about source identification studies that use statistical approaches without detailed consideration of which fingerprint properties are being used in unmixing models, and if they are indeed appropriate.

Acknowledgements

Thanks are extended to Tim Giles (BC Ministry of Forests), Dan Moore (University of British Columbia) and Phillip Krauskopf (University of Northern British Columbia) for logistical support and assistance in the field, and to Richard Hartley and Kevin Solman (University of Plymouth) for undertaking laboratory analysis. NSERC, the Royal Society and the universities of Cranfield, Plymouth and UNBC are thanked for financial support.

References

Biickert, S. (1999). The effect of pulp mill effluent on fine-grained sediment morphology and storage in the Fraser River at Prince George, British Columbia. MSc Thesis, UNBC, Canada.

Blake, W. H., Wallbrink, P. J., Doerr, S. H., Shakesby, R. A., & Humphreys, G. S. (2006). Magnetic enhancement in wildfire-affected soil and its potential for sediment-source ascription. *Earth Surface Processes and Landforms, 31*, 249–264.

This page intentionally blank

Cerda, A., & Lasanta, T. (2005). Long-term erosional responses after fire in the Central Pyrenees. 1. Water and sediment yield. *Catena, 60*, 59–80.

Certini G. (2005). Effects of fire on properties of forest soils: A review. *Oecologia, 143*, 1–10.

Marafa, L. M., & Chau, K. C. (1999). Effect of hill fire on upland soil in Hong Kong. *Forest Ecology and Management, 120*, 97–104.

Pausas, J. G. (2004). Change in fire and climate in the eastern Iberian Peninsula (Mediterranean Basin). *Climate Change, 63*, 337–350.

Petticrew, E. L., Owens, P. N., & Giles, T. R. (in press). Wildfire effects on the quantity and composition of suspended and gravel-stored sediments. *Water, Air, and Soil Pollution*.

Rummery, T. A., Bloemendal, J., Dearing, J. A., Oldfield, F., & Thompson, R. (1979). The persistence of fire-induced magnetic oxides in soil and lake sediments. *Annales de Géophysique, 35*, 103–107.

Walling, D. E. (2005). Tracing suspended sediment sources in catchments and river systems. *Science of the Total Environment, 344*, 159–184.

Water, Air, and Soil Pollution: Focus (2006) **6:** 283–292
DOI: 10.1007/s11267-006-9049-y

WILDFIRE EFFECTS ON THE QUANTITY AND COMPOSITION OF SUSPENDED AND GRAVEL-STORED SEDIMENTS

ELLEN L. PETTICREW[1,*], PHILIP N. OWENS[2] and TIMOTHY R. GILES[3]
[1]*School of Geography, University of Plymouth, Plymouth, UK*
[2]*National Soil Resources Institute, Cranfield University, North Wyke, UK*
[3]*British Columbia Ministry of Forests and Range, Kamloops, British Columbia, Canada*
*(*author for correspondence, Present address: Geography Program, University of Northern British Columbia, Canada, e-mail: ellen@unbc.ca; phone: +1-250-960-6645; fax: +1-250-960-6533)*

Abstract. In August of 2003 a severe wildfire burnt the majority of Fishtrap Creek, a 170 km^2 catchment in central British Columbia, Canada. The objective of this study was to determine the short-term (15-month) influence of the wildfire on the amount and composition of fine sediment delivery and retention in the system and to compare it to a similar unburnt catchment. In the spring of 2004 automatic water samplers were installed at a gauging site on Fishtrap Creek to collect suspended sediments from the snowmelt runoff and gravel traps were deployed on the channel bed surface to collect composite samples of suspended fine sediment. Jamieson, the reference creek, exhibits similar geology and pre-burn vegetation and was sampled in the same manner for comparison. Composite suspended sediment collected in the traps was removed from the streams in mid-summer and early September. Quantitative estimates of the amount and particle size structure of the naturally stored fine sediment in, and on, the gravel creekbed were obtained in pre-melt, mid and late-summer conditions. Estimates of suspended sediment yields indicated that while the burnt system delivered 66% more material per unit area, the total seasonal suspended sediment yield was low (855 kg km^{-2}) compared to other fire-disturbed systems. While the burnt catchment was primed to deliver sediment, the hydrologic drivers were not of sufficient magnitude to generate a substantial response, suggesting that in this first post-fire year the system was transport-limited, not supply-limited. Differences were noted in the spatial and seasonal composition of the <500 μm composite suspended sediments, with the burnt catchment having significantly ($P \leq 0.05$) more OM%. Seasonally a significant increase of OM% in late summer samples was associated with instream biofilms and possible delivery of black carbon. The system's post-fire response was not geomorphically substantial but significant biological differences were noted in the short-term.

Keywords: organic matter, sediment yield, sediment response, suspended sediment, wildfire

1. Introduction

Recently, there has been an increase in the number of studies concerned with the effects of fires, both natural (e.g., wildfires) and human induced (e.g., prescribed burning) in forested catchments. This interest is due to a variety of reasons including the effect of fires on forest ecosystems and the implications for resource management, and concerns associated with the likelihood of increases in the number of wildfires in some areas due to climate change. Within a geomorphological context, much of the research on the response of catchments to fires, and particularly wildfires, has focused on the impacts of fire on (a) soil hydrology and river flows, and (b) soil erosion, mass movement events and sediment fluxes in rivers (Shakesby & Doerr, 2006). Research on the latter has been concerned primarily with how rates of soil erosion and fluxes of sediment in rivers have responded to fire events. Most of the available evidence suggests that these rates and fluxes increase after fires as the bulk of the surface vegetation cover is removed and soil hydrology changes (e.g., due to an increase in soil hydrophobicity); consequently the soil is more susceptible to erosion, mass movement and bank erosion processes (e.g., Cerda & Lasanta, 2005). Studies generally show that this is the typical behaviour immediately following a fire and that, after the initial response, values tend to return to those similar to pre-fire conditions, with the time required ranging from a few years to decades (Shakesby & Doerr, 2006). Recently, research has also focused on changes in the properties of the burnt soil and the material delivered to, and transported by, rivers (e.g., Certini, 2005). This interest has developed from the recognition that it is the type and quality of the material that is being eroded, and thus lost from the soil profile, and supplied to rivers (such as trace element, nutrient and organic matter/carbon content, and particle size composition), in addition to actual amounts of sediment, that are important for the future ability of soils to support vegetation and for water quality and aquatic ecology. Studies have tended to document a change in the nutrient, organic matter content and particle size content of mobilized and transported sediment following fire (Certini, 2005).

This paper presents preliminary (i.e., first 15 months) results from an investigation into the effects of a wildfire on a mixed coniferous catchment in British Columbia, Canada. The aims were to determine:

1) the post-fire response of a) suspended sediment fluxes and b) storage of fine-grained sediment within channels;
2) if there was a change in the compositional properties (e.g., organic matter content and particle size) of the transported and stored sediment due to the wildfire.

2. Materials and Methods

In August 2003, severe wildfires burnt in many locations across British Columbia (BC), Canada with the McLure fire, in the central interior of BC, burning an area of ca. 260 km^2. The Fishtrap Creek catchment, forested with Pines, Firs, Spruce and Cedar, was severely burnt in the lower reaches and moderately burnt in the headwaters. The Jamieson Creek catchment, located ca. 15 km to the south of Fishtrap, was not affected by the McLure fire and as it has similar vegetation cover, topography, stream slopes, precipitation regime and geology as Fishtrap, it serves as a reference catchment for comparing the effects of the McLure fire. The catchments have a distinct snowmelt regime with melt typically starting in early April and the main flood discharge occurring in mid May.

An automatic ISCO water sampler was installed on March 29, 2004 at Fishtrap Creek (~120°15′ WL: 51°10′ NL) to collect 1 L suspended particulate matter (SPM) every 4 h from 135 km^2 of catchment above this station. High frequency sampling continued until the snowmelt freshet was completed and on June 18 sampling was reduced to 8 h intervals. Collection continued until Oct 22, 2004. Another ISCO water sampler was installed on April 14, 2004 on the lower reaches of Jamieson Creek (catchment area of 215 km^2; ~120°15′ WL: 50°55′ NL) and water was collected on the same schedule as in Fishtrap. Continuous discharge was measured just downstream of the sample site on Fishtrap while for Jamieson it was calculated from the Fishtrap data set using areal proportions. Specific sediment yields (kg km^{-2}) were determined for the ~7-month sampling season. Precipitation data were obtained from the nearest Environment Canada meteorological station in Kamloops, approximately 30 km south of the sites.

Six gravel tube traps (Biickert, 1999) were installed in Fishtrap on April 13, 2004, with a set of three in an upstream riffle and a second set downstream. Another six were installed in two riffles in Jamieson on April 14. The upstream and downstream sites in each system were selected to have comparable flow regimes although several traps had to be moved to deeper water as the season progressed and discharge dropped. Each tube trap (45 cm long and 7.5 cm diameter) was filled with clean gravel which were contained by wire mesh at each end. Three tubes were fixed in place on the stream bed, parallel to each other and facing into the flow. They were left to collect any actively transported sediment smaller than the grid size of 0.64 cm, until June 23, 2004. When the tubes were retrieved the sediment <0.64 cm was washed from the trap gravels and collected in buckets for processing. The cleaned traps were replaced in the same locations and collected sediment until September 1, 2004.

In the field, the buckets containing both trap sediment and wash water were used to obtain an estimate of sediment less than approximately 500 μm. This size category was selected operationally as the triplicate 50 ml sub-samples were collected from the top few centimetres of the total sample a few seconds following stirring. The maximum size of sediment collected would be <500 μm, due to the settling speed of particles larger than this. These samples, in conjunction with the water volume, were used to calculate the mass of trapped sediment <500 μm. The material remaining in the buckets was transported back to a laboratory, air dried and amalgamated to obtain the total mass collected by the traps. Organic matter (OM) content of the total mass and <500 μm sub-samples was determined by ashing replicates in a muffle furnace at 550 °C. A sub-sample of the total mass was dry-sieved through a 500 μm mesh, the organic matter removed using hydrogen peroxide and particle size analyses of the inorganic trap sediments were undertaken using a Malvern laser particle sizer.

In April, June and September, when the gravel trap sites were visited, a quantitative estimate of the amount of naturally stored fine sediment was determined using a cylinder resuspension technique (Petticrew, Krein, & Walling, 2006). The mass of sediment stored on 531 cm^2 of gravel surface (as determined by the area of the cylinder base) was estimated by resuspending it with a gentle stirring of the water in the cylinder. Three 1 L samples of the mixed water were taken for analysis of resuspended sediment and organic matter content. Water volumes in the cylinder combined with the resuspended sediment concentration allowed an estimate of the areal load of surface-stored fine sediment. Mixing the gravel at the base of the cylinder to a depth of 15 cm, and sub-sampling the turbid water above allowed an estimate of the areal load of gravel-stored fine sediments. Resuspended sediment concentrations were obtained by filtering the water through pre-ashed and pre-weighed GF-F filters. Organic matter content was determined by ashing the dried filters at 550 °C in excess of 1 h. Due to small sample sizes (n=4–6), tests of significant differences were determined using the non-parametric Mann–Whitney test at 95% confidence limits.

3. Results and Discussion

3.1. SUSPENDED SEDIMENT LOADS AND YIELDS

Seasonal sediment loads, yields and denudation rates for both of the catchments are presented in Table I. The burnt basin has slightly higher SPM and inorganic seasonal loads even though the unburnt Jamieson is 80 km^2 larger. When the seasonal yields are compared the burnt basin contributes ~66% more sediment per unit area. The specific particulate sediment yields (kg km^{-2} day^{-1}), calculated from the average daily SPM (combined organic and inorganic) loads, are shown over the approximately seven month sampling period for both creeks in Figure 1. The spring-melt freshet in the burnt catchment (Fishtrap) carries the bulk of the seasonal material, with the maximum yield occurring on April 15 (day 106). In Jamieson this represented our second day of sampling, but a flush of sediment occurred 15–20 days later, in early May (days 121–126) likely reflecting delayed snowmelt in the unburnt basin (Figure 2). These differences in snowmelt timing are corroborated by comparisons of snowmelt patterns and rates between the burnt headwaters of Fishtrap Creek and an adjacent forested system (R.D. Winkler, personal communication) which indicated that the snowpack of the burnt area had 42% increased water equivalent on March 9, 2004 and that snowmelt was completed three weeks earlier in the burnt *versus* the forested

TABLE I

Estimates of seasonal loads, yields and denudation rates for both suspended particulate matter (SPM) and inorganic sediment for Fishtrap and Jamieson Creeks (2004). Values determined using an 18-day delay in springmelt discharge in Jamieson are presented to allow comparison

Parameter calculated	Fishtrap Creek (burnt)	Jamieson Creek (unburnt)	Jamieson Creek (18-day springmelt discharge delay)
Seasonal SPM load (kg)	115,360	110,952	108,025
Seasonal inorganic load (kg)	71,595	69,674	67,629
Seasonal SPM yield (kg km^{-2})	855	516	502
Seasonal inorganic yield (kg km^{-2})	530	324	314
Denudation (SPM[a]) (μm)	0.53	0.32	0.31
Denudation (inorganic[b]) (μm)	0.21	0.13	0.13

[a] Density of 1.6 assumed

[b] Density of 2.5 assumed

areas. As the suspended sediment concentrations (Figure 2) and visual field evidence suggest that the spring freshet occurred in Fishtrap approximately 18 days earlier, an underestimate of spring-melt discharge for Jamieson would result from the use of an areal discharge relationship between basins. Therefore another estimate of discharge, loads and yields were made using an 18-day delay for spring-melt discharge values for Jamieson. Results indicated that the seasonal estimates calculated both ways (Table I) are similar in magnitude, even though their timing would be slightly altered. In any case, for both scenarios the loads, yields and denudation rates for the unburnt basin are likely to be overestimates, as at pre-melt the burnt basin was observed to have a great water equivalent than unburnt areas. This means the range between the burnt and unburnt catchments noted in Table I are conservative estimates of the difference in the geomorphic response of the two systems.

While the values of the seasonal yield in the burnt catchment are larger than the estimates for the undisturbed, forested catchment, the magnitude of Fishtrap's yields are low in comparison to other burnt systems (Shakesby & Doerr, 2006). Helvey (1980) reported post-fire sediment yields of 500 kg km^{-2} over six months for a moderate burn and 12,000 kg km^{-2} yr^{-1} for an intense burn in mixed coniferous forests in Washington, USA. Given that the lower portion of Fishtrap was severely burned, as evidenced by a surface cover of ash, burnt debris and large areas of exposed topsoil (Owens, Blake, & Petticrew, this issue), the sediment yields are surprisingly low for a system so primed for erosion. Inorganic denudation rates of 0.2 (burnt) and 0.1 (unburnt) μm yr^{-1} are also low for

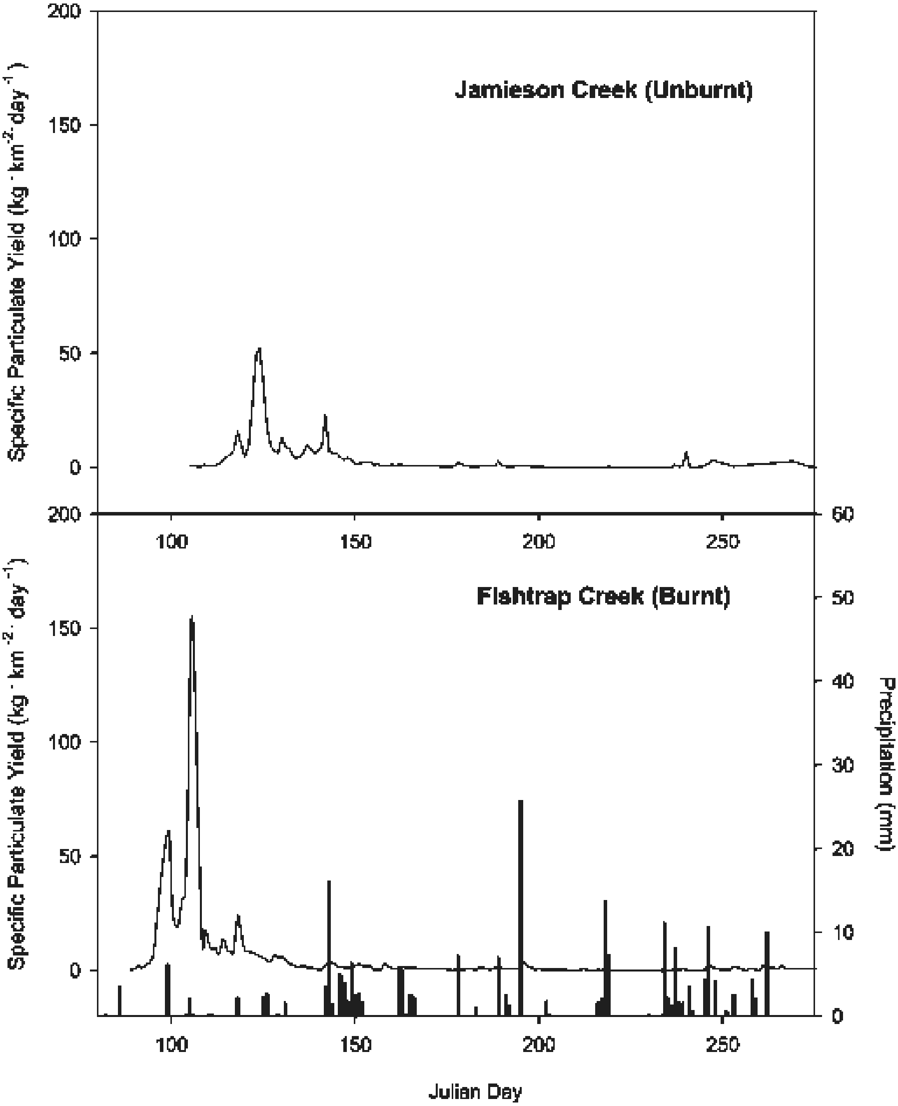


Figure 1. Specific particulate yields for the burnt (Fishtrap, 135 km^2) and unburnt (Jamieson, 215 km^2) catchments. The spring-melt yield for Jamieson has been calculated using an 18-day offset to account for the delayed snowmelt in the unburnt basin.

catchments of this size and are especially low for a disturbed system (e.g., Caine, 2004). These data all suggest that while a ready supply of sediment was available in the burnt catchment in 2004, the driving agents (precipitation and spring-melt discharge) did not move much material in the 15-month period following the McLure fire.

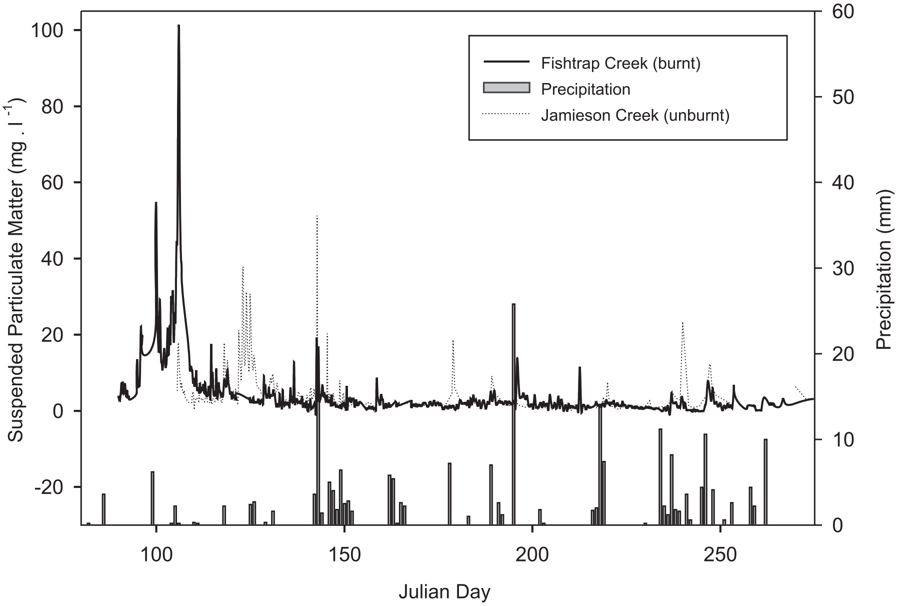


Figure 2. Total SPM in Fishtrap Creek (burnt), from March 30 to Oct 22, 2004 and SPM for Jamieson Creek, (unburnt) from April 14 to Oct 22, 2004. Daily precipitation data for Kamloops, British Columbia are shown.

3.2. SEDIMENT TRANSPORT AND COMPOSITION

The total mass of sediment collected in the gravel traps for both periods in the burnt catchment was almost double that of Jamieson (Table II) but these values should not be equated, as the total flow though the tubes varied between trap sites. However, the proportional composition of the sediment <500 μm can be compared and indicates a significantly ($P<0.05$) higher amount of OM% in the burnt system's traps for both seasons (Table II). As well, in both catchments the late summer traps exhibit significantly ($P<0.05$) higher percentage of OM values than the material collected over the spring and early summer. These spatial and temporal differences in OM likely reflect both instream and terrestrial processes. What was apparent in the streams when the gravel traps were being retrieved on June 23 and again on September 1 was an instream cover of benthic biofilms on the gravels in Fishtrap. The lack of canopy cover, due to the fire, allowed increased light which facilitated periphytic algae growth, as observed in recently harvested creeks (Fuchs, Hinch, & Mellina, 2003). These biofilms degrade and are flushed downstream episodically and likely represent a portion of the increased trap OM content. Another explanation for this OM increase in Fishtrap is the transport of 'black carbon' in the stream as suspended sediment. These particles are products of incomplete combustion of organics (Certini, 2005) and due to their low density

TABLE II

Mass of total and <500 μm sediment collected in surface traps and the proportion of organic matter in the burnt (Fishtrap) and unburnt (Jamieson) catchments (2004). The percentage of sand, silt and clay in the <500 μm fraction is also presented with one standard deviation (n=5 or 6) shown in brackets

	Total trap sediment (g)	Total trap organic matter (%)	Trap sediment <500 μm (%)	Trap organic matter <500 μm (%)	Absolute particle size <500 μm		
					% sand	% silt	% clay
Fishtrap							
June	991.8	8.3	39.0	18.0 (1.6)	34.6 (6.0)	60.6 (5.8)	4.8 (0.1)
Sept	592.8	14.3	39.7	29.9 (2.1)	36.1 (8.5)	59.2 (8.1)	4.7 (0.4)
Jamieson							
June	577.2	7.4	69.3	13.1 (1.8)	28.2 (3.7)	64.9 (3.2)	6.9 (0.5)
Sept	319.9	9.5	50.6	19.2 (2.2)	11.7 (3.0)	79.6 (2.3)	8.7 (0.7)

would be easily entrained as suspended sediment. Future microscopy and particle density analysis of the trap samples should elucidate these possibilities.

3.3. Fine Sediment Storage: Amounts and Composition

Table III represents the areal loadings of surface and gravel-stored (15 cm depth) fine sediments. There are no statistically significant differences in the seasonal patterns observed in either stream, and no major statistical differences in the amount of stored sediment between streams. While high variability exists in the OM% of these naturally-stored sediments, we do see a pattern of increasing OM (increases of >25%) in the surface sediments as the season progresses in Fishtrap, but not in Jamieson. June and September surface samples in Fishtrap have higher average and standard deviation values than the sediments stored in the top 15 cm of gravels, indicating the presence and the spatial patchiness of the benthic biofilms and/or the delivery of black carbon particles moved off the watershed in spring-melt and rainstorms in the burnt system.

4. Conclusions

The suspended sediment loads, yields and denudation rates of Fishtrap Creek, a burnt 135 km^2 catchment, were greater than those of unburnt Jamieson Creek, a larger (215 km^2) but biogeochemically similar, nearby catchment. While the differences in the response of the disturbed and undisturbed forested system were apparent, and potentially underestimated, the magnitude of the response to severe

TABLE III

Amount of sediments stored on and in the gravel bed, and the proportion of sediment organic matter for the burnt (Fishtrap) and unburnt (Jamieson) catchments (2004). $n=4$, standard deviation in brackets

	Areal load (mg cm^{-2})		Organic matter percentage	
	Surface	Top 15 cm gravel	Surface	Top 15 cm gravel
Fishtrap				
April	2.6 (1.3)	12.3 (9.1)	21.4 (2.1)	18.5 (4.5)
June	2.3 (2.1)	9.7 (9.3)	31.9 (23.3)	18.0 (4.8)
Sept	1.4 (1.5)	22.6 (16.5)	48.6 (23.3)	21.7 (5.3)
Jamieson				
April	2.4 (2.2)	7.7 (6.4)	24.4 (3.5)	12.8 (0.6)
June	1.6 (0.3)	20.0 (5.6)	26.2 (5.1)	12.4 (2.3)
Sept	3.7 (0.9)	23.0 (6.5)	22.0 (3.7)	15.6 (1.6)

wildfire was relatively small. Similarly, there were no significant differences in the amount of material stored on, or in, the channel bed. The lack of a significant first spring-melt response in sediment fluxes and channel storage in the Fishtrap catchment is somewhat surprising and suggests that there has been no major short-term response to the wildfire during the first 15 months, at least in terms of sediment flux. It is clear from visual observations that the catchment surface of Fishtrap was susceptible to surface erosion processes (Owens et al., this issue). However, the magnitude of response indicates that surface, channel and bank erosion was minimal during snowmelt and that the rainfall events over this time were not sufficient to initiate substantive erosive flows. Thus, while the catchment surface is primed for erosion and sediment transfers, the hydrological drivers required for significant inorganic sediment redistribution were not in operation. In a recent review paper Shakesby and Doerr (2006) indicate the need for a clear measure of the degradational significance of post-fire soil losses. In this case, the calculations for the burnt watershed indicate the first year response, seen in many other case studies, is muted due to transport-limiting factors rather than supply limitation. There is clearly a need for continued monitoring in these systems to determine when, and indeed if, Fishtrap will respond to the severe wildfire of summer 2003.

In contrast, the organic matter content of the smaller-sized sediment actively being transported in Fishtrap is significantly greater than in Jamieson. Thus, although there is a limited amount of available inorganic sediment being transported to, and in, the burnt river system, there is clearly a difference in the composition of sediment being mobilised and redistributed, reflecting processes on the land (e.g., an increase in exposed burnt soil that could contribute black carbon) and in the channel (e.g., biofilm growth and die-off). The temporal and spatial differences in the organic material and the lack of noteworthy transfers of inorganics suggests that this burnt system is biologically, but not geomorphically responsive in this short-term post-fire period.

Acknowledgements

Thanks are extended to R.D. Moore and R.D. Winkler who are collaborators on the larger fire project. P. Krauskopf assisted in the field and in the laboratory. Cartographic and laboratory support for particle size analysis was provided by University of Plymouth. Project funding was provided by NSERC Discovery Grants to ELP and RDM, a UNBC seed grant to ELP and RDM's FRBC Operating Grant.

References

Biickert, S. (1999). The effect of pulp mill effluent on fine-grained sediment morphology and storage in the Fraser River at Prince George, British Columbia. MSc Thesis in Environmental Science, University of Northern British Columbia.

Caine, N. (2004). Mechanical and chemical denudation in mountain systems. In P. N. Owens & O. Slaymaker (Eds.), *Mountain geomorphology* (pp. 132–152). London UK: Arnold.

Cerda, A., & Lasanta, T. (2005). Long-term erosional responses after fire in the Central Pyrenees. 1. Water and sediment yield. *Catena, 60*, 59–80.

Certini, G. (2005). Effects of fire on properties of forest soils: A review. *Oecologia, 143*, 1–10.

Fuchs, S. A., Hinch, S. G., & Mellina, E. (2003). Effects of streamside logging on stream macroinvertebrate communities and habitat in the sub-boreal forests of British Columbia, Canada. *Canadian Journal of Forest Research, 33*, 1408–1415.

Helvey, J. D. (1980). Effects of a north central Washington wildfire on runoff and sediment production. *Water Resources Bulletin, 16*, 627–634.

Owens, P. N., Blake, W. H., & Petticrew, E. L. (this issue). Changes in sediment sources following wildfire in mountainous terrain: A paired-catchment approach, British Columbia, Canada. *Water, Air and Soil Pollution*, DOI: 10.1007/S11267-006-9048-z.

Petticrew, E. L., Krein, A., & Walling, D. E. (2006). Evaluating fine sediment mobilization and storage in a gravel bed river using controlled reservoir releases. *Hydrological Processes*, DOI: 10.1002/hyp.6183.

Shakesby, R. A., & Doerr, S. H. (2006). Wildfire as a hydrological and geomorphological agent. *Earth-Science Reviews, 74*, 269–307.

Water, Air, and Soil Pollution: Focus (2006) **6:** 293–303
DOI: 10.1007/s11267-006-9050-5

USING FALLOUT LEAD-210 MEASUREMENTS TO ESTIMATE SOIL EROSION IN THREE SMALL CATCHMENTS IN SOUTHERN ITALY

PAOLO PORTO[1,2,*], DES E. WALLING[1], GIOVANNI CALLEGARI[3]
and FRANCESCO CATONA[1,2]
[1] *Department of Geography, University of Exeter, Exeter, United Kingdom*
[2] *Dipartimento di Scienze e Tecnologie Agro-Forestali e Ambientali, Università degli Studi Mediterranea di Reggio Calabria, Reggio Calabria, Italy*
[3] *C.N.R.-Istituto per Sistemi Agricoli e Forestali del Mediterraneo, Sezione Ecologia e Idrologia Forestale, Rende (Cs), Italy*
*(*author for correspondence, e-mail: P.Porto@exeter.ac.uk)*

(Received 2 September 2005; revised 8 March 2006; accepted 7 June 2006)

Abstract. Soil erosion and associated off-site environmental impacts have attracted increasing attention in recent decades, and there is a growing need for reliable information on rates of soil loss. The potential for using ^{137}Cs fallout to quantify rates and patterns of soil redistribution over medium-term timescales (ca. 45 years) has been successfully demonstrated in a wide range of environments around the world. The similar behaviour of fallout ^{210}Pb in soils offers potential for its use as an alternative to ^{137}Cs, in areas where ^{137}Cs inventories are low or are complicated by additional fallout from the Chernobyl accident. There have, however, to date been few attempts to validate the use of fallout ^{210}Pb measurements for assessing erosion rates. This paper reports an attempt to explore the use of fallout ^{210}Pb to estimate rates of water-induced soil erosion on uncultivated land. It focuses on three small forest/rangeland catchments located in Calabria, southern Italy, for which measurements of sediment output are available. Comparison of the estimates of net soil loss from the catchments derived from ^{210}Pb measurements with the measured sediment output, confirmed the validity of the ^{210}Pb approach. The soil redistribution rates estimated using ^{210}Pb measurements were also consistent with equivalent estimates obtained for the same study catchments using ^{137}Cs measurements.

Keywords: soil erosion rates, ^{210}Pb, ^{137}Cs, fallout radionuclides, sediment yield, Italy

1. Introduction

Soil erosion and the off-site impacts associated with increased fine sediment transport by streams and rivers have attracted increasing attention during recent decades, and sediment is frequently identified as a primary cause of degradation of aquatic habitats. In order to develop an improved understanding of sediment mobilisation and delivery to streams, there is a growing need for reliable information on rates of soil loss in different environments, to provide a basis for identifying the key controls and developing predictive tools. The potential for using nuclear weapon-produced ^{137}Cs fallout to quantify rates and patterns of soil redistribution over medium-term timescales (ca. 45 years) has been successfully demonstrated in a wide range of environments around the world (Walling, 1998; Zapata, 2003). There are, however, some important limitations to the ^{137}Cs technique, especially in areas where significant amounts of Chernobyl-derived fallout were received or where the levels of bomb-derived ^{137}Cs are low. The similar behaviour of fallout or excess ^{210}Pb (^{210}Pb$_{ex}$) in soils makes it a potential alternative to ^{137}Cs for soil erosion investigations in areas where ^{137}Cs measurements encounter problems and this potential has been recognised and demonstrated (e.g., Walling & He, 1999; Walling, Collins, & Sichingabula, 2003). There have, however, to date been few attempts to confirm more widely and validate the use of fallout ^{210}Pb measurements for assessing erosion rates. This paper reports an attempt to explore the use of fallout ^{210}Pb to estimate rates of water-induced soil erosion on uncultivated land. It focuses on three small forest/rangeland catchments, located in Calabria, southern Italy, for which measurements of sediment output are available. Comparison of the estimates of net soil loss from the catchments derived from ^{210}Pb$_{ex}$ measurements with the measured sediment output affords a means of validating those estimates.

2. The Study

2.1. THE STUDY CATCHMENTS

The investigation focussed on three small catchments (W1, W2 and W3) located near Crotone in Calabria, southern Italy (35 m a.s.l., 39°09′02″N, 17°08′10″E; Figure 1). The catchments ranged in size from 1.38 to 1.65 ha, and were characterized by mean slopes ranging from 24% to 53%. Further information on the catchments is provided in Table I. The catchments have never been cultivated and originally supported a rangeland vegetation cover (Avolio et al., 1980). Catchment W1 is still covered by rangeland vegetation, but catchments W2 and W3 were

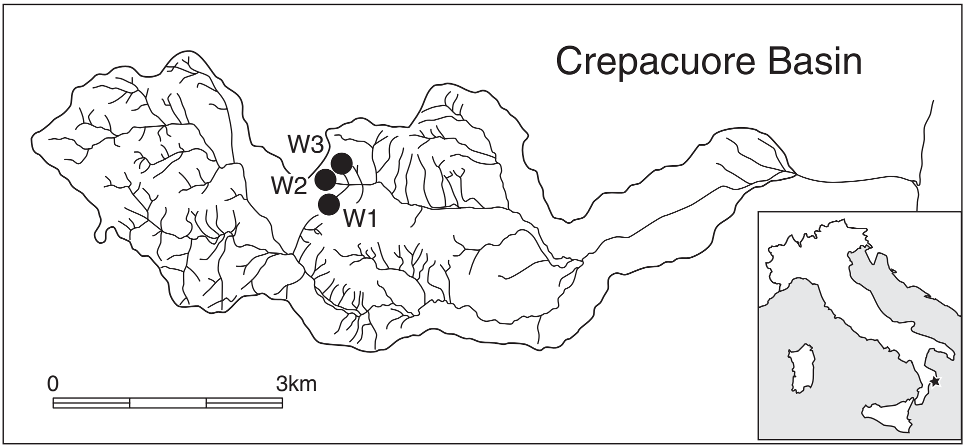


Figure 1. The location of the study catchments.

TABLE I

The characteristics of the study catchments

				Soil			Sediment yield			
Catchment	Drainage area (ha)	Mean altitude (m a.s.l.)	Mean slope (%)	Sand (%)	Silt (%)	Clay (%)	min (t ha^{-1} year^{-1})	max (t ha^{-1} year^{-1})	mean (t ha^{-1} year^{-1})	Estimated long-term sediment yield (t ha^{-1} year^{-1})
W1	1.473	122	53	14	44.5	41.5	5.1	38.4	11.6	12.4
W2	1.375	103	35	14.6	49.2	36.2	1.7	98.5	20.8	19.2
W3	1.654	98	24	20.7	45.5	33.8	2.9	25.7	7.6	7.8

planted with *Eucalyptus occidentalis Engl.* in 1968. These trees have been cut twice (in 1978 and 1990) in catchment W2 and once (in 1986) in catchment W3. The tree cover in catchment W2 is non-uniform, and about 20% of its area, located on south facing slopes, is characterized by discontinuous trees and grass cover. In catchment W3 the tree cover is almost continuous and only about 2%–3% of the area supports grass. The climate is typically Mediterranean with a mean annual rainfall of ca. 670 mm, most of which falls between October and March.

In 1978, each catchment was instrumented for measuring rainfall, runoff and sediment yield. Precipitation has been recorded using a tipping bucket rain gauge and runoff is measured at the outlet of each catchment using an H-flume structure, equipped with a mechanical stage recorder. The sediment load passing the gauging structure is measured using a Coshocton wheel sampler installed below the H-flume, which provides values of sediment load for individual events.

2.2. SEDIMENT YIELDS AT THE CATCHMENT OUTLETS

The sediment yield data used in this study cover the period from 1978 to 1994. Because of malfunctioning of the sediment sampling equipment, values of sediment yield are not available for some events. The sediment loads for these events were estimated using the sediment delivery distributed (SEDD) model (Ferro & Porto, 2000). Information on the range of the measured values of annual sediment yield values for each catchment is provided in Table I. In order to compare the measured sediment yields from the catchments with the estimates of longer-term net soil loss obtained from the $^{210}Pb_{ex}$ measurements, an estimate of the long-term (ca. 40 year) sediment yield from each catchment was generated by extrapolating the measured values, using the long-term rainfall record for the recording station at Crotone and the predicted temporal variation in canopy cover within the study catchments (see Porto, Walling, & Ferro, 2001; Porto, Walling, Ferro, & Di Stefano, 2003). The estimates of mean annual sediment yield for the 43 year period 1956 to 1998 for the three study catchments are also presented in Table I.

2.3. SOIL SAMPLING AND LABORATORY ANALYSIS

Soil sampling within the study catchments involved several campaigns undertaken in 1999 and 2001 (see Porto et al., 2003; Porto, Walling, & Callegari, 2004). Bulk cores were collected at the intersections of an approximately 20×20 m grid, with additional cores collected to take account of topographic variability. The cores were collected using a steel core tube (6.9 cm diameter) driven into the ground by a motorised percussion corer and subsequently extracted using a hand-operated winch. Where tree cover existed in the vicinity of the sampling points, care was taken to ensure that cores were collected from points located between the trees, rather than close to their trunks. Within the study, it has been assumed that the tree cover and associated timber harvesting has not significantly influenced the inventories documented for individual sampling points. The samples used to establish the reference inventory were collected from an area of undisturbed rangeland with minimal slope within catchment W1. In this case a scraper plate (cf. Campbell, Loughran, & Elliott, 1988) with a surface area of 652 cm^2 was used to collect samples at depth increments ranging from 1 to 4 cm to a depth of 50 cm. Six additional 8.6 cm diameter soil cores were collected from the reference site and sectioned into 2 cm depth increments, in order to assess the local spatial variability of the $^{210}Pb_{ex}$ inventories and the associated depth distributions. Because of the greater surface area associated with the scraper plate (652 cm^2), the inventory obtained from these samples was used as the reference inventory. All samples were initially oven dried at 45 °C, disaggregated and passed through a 2-mm sieve. A representative fraction of each sample was then placed into a plastic pot or Marinelli beaker for determination of its $^{210}Pb_{ex}$ activity. The samples were sealed for 20 days prior to assay in order to achieve equilibrium between ^{226}Ra and its daughter ^{222}Rn.

$^{210}Pb_{ex}$ activities in the samples were assayed by gamma-ray spectrometry, using a low-background, low energy, high-resolution coaxial HPGe detector coupled to an amplifier and PC-based data collection system and measurements of both the total ^{210}Pb and the ^{226}Ra (*via* ^{214}Pb) activity. Count times were typically ca. 30,000 s, providing results with an analytical precision of ca. 10% at the 95% level of confidence.

2.4. THE FALLOUT ^{210}Pb INVENTORY AND DEPTH DISTRIBUTION AT THE REFERENCE SITE

Figure 2 provides representative information on the depth distribution of $^{210}Pb_{ex}$ at the reference site in catchment W1. The $^{210}Pb_{ex}$ is found to a depth of about 40 cm in the soil profile, and shows evidence of an exponential decrease with depth, with the greatest concentration at the surface (47.7 Bq kg^{-1}). Based on this core, the reference inventory is estimated to be 5,266 Bq m^{-2} and this value is in close agreement with the mean value obtained from the six additional 8.6 cm diameter soil cores (5,440 Bq m^{-2}) Assuming a constant deposition flux, the annual atmospheric ^{210}Pb deposition flux rate in the study area, averaged over the last century (five half-lives), is estimated to be ca. 161 Bq m^{-2} $year^{-1}$.

2.5. ^{210}Pb$_{EX}$ INVENTORIES WITHIN THE STUDY CATCHMENTS

The range of values of $^{210}Pb_{ex}$ inventory obtained for the bulk cores collected from the three catchments are listed in Table II. Inventories are less than the local reference inventory (5,266 Bq m^{-2}) over a large part of each of the catchments, suggesting that their surfaces are characterized by net soil loss and that there is little or no storage of eroded sediment within the catchments. In order to explore the relationship between $^{210}Pb_{ex}$ inventories and topography, digital elevation models (3 × 3 m grid size) were created for the three catchments from the survey data provided by Avolio et al. (1980), using a kriging interpolation procedure. An interpolated map of $^{210}Pb_{ex}$

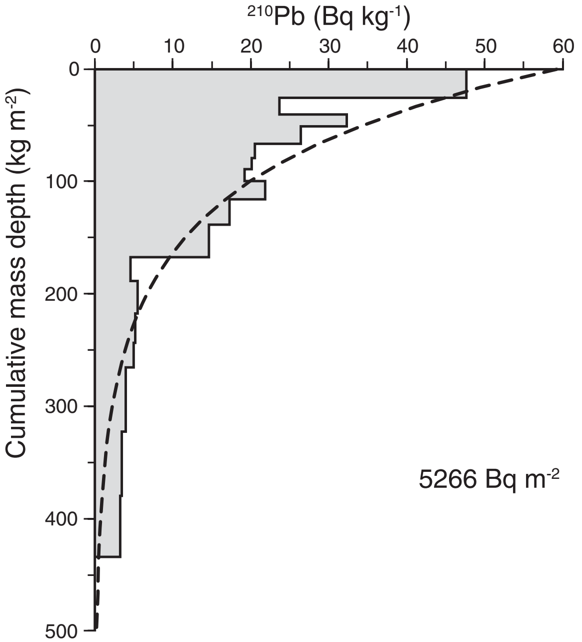


Figure 2. The $^{210}Pb_{ex}$ depth distributions documented for the reference site and the result of fitting the diffusion and migration model [Equation (1)] to this profile.

inventories, produced using the same kriging procedure, has been overlaid onto each DEM and an example is provided for catchment W1 in Figure 3a. The interpolated spatial patterns of $^{210}Pb_{ex}$ inventory for the study catchments show only limited dependence on topographic variability and appear to be more sensitive to variations in vegetation cover density. For example, the areas of discontinuous forest cover within the portions of catchment W2 facing south are marked by lower $^{210}Pb_{ex}$ inventories, which are in turn indicative of higher rates of soil loss.

2.6. USING $^{210}Pb_{EX}$ MEASUREMENTS TO ESTIMATE EROSION RATES

Estimation of rates of soil loss from $^{210}Pb_{ex}$ measurements is commonly based on a comparison of the inventory measured at a specific point with the reference

TABLE II

Excess ^{210}Pb inventories and estimates of soil erosion rates within the study catchments

Catchment	Min (Bq m^{-2})	Max (Bq m^{-2})	Mean (Bq m^{-2})	Total soil erosion (t ha^{-1} year^{-1})	Total deposition (t ha^{-1} year^{-1})	Net soil erosion (t ha^{-1} year^{-1})
W1	50.5	22,373	6,499	13.9	7.66	6.2
W2	11.6	11,117	2,868	15.7	3.63	12.1
W3	49.6	16,322	7,438	20.6	9.5	11.1

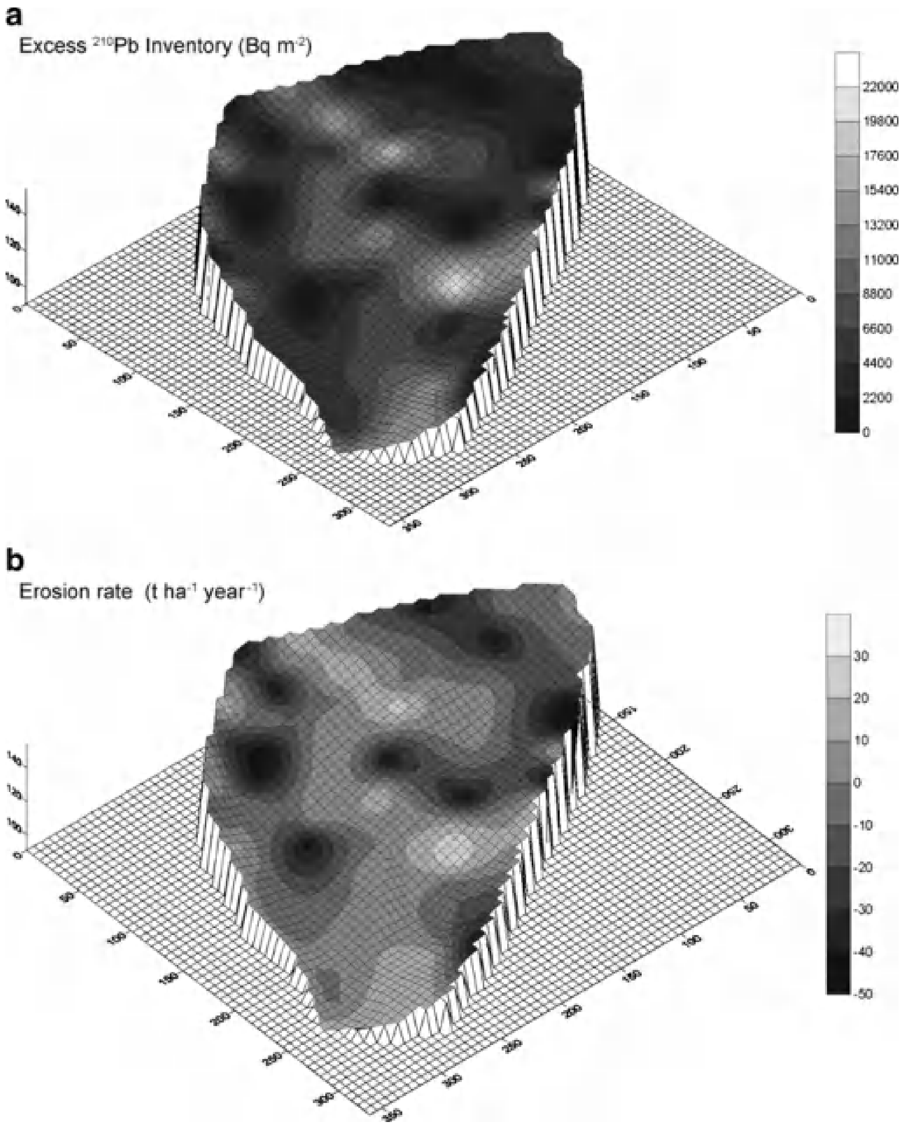


Figure 3. The spatial distribution of $^{210}Pb_{ex}$ inventories (Bq m^{-2}) **a** and the erosion rates estimated from these data (t ha^{-1} year^{-1}) **b** in catchment W1.

inventory and the degree of reduction of that inventory. The relationship used in this study to convert the magnitude of the reduction in the $^{210}Pb_{ex}$ inventory to an estimate of the rate of soil loss employs a theoretical diffusion and migration model to represent the vertical distribution of $^{210}Pb_{ex}$ within the soil.

According to He and Walling (1997), by treating the soil as a semi-infinite homogeneous porous medium, characterized by a constant effective diffusion coefficient and a constant migration rate, and assuming that fallout inputs are initially uniformly distributed at the soil surface, the vertical distribution of $^{210}\text{Pb}_{\text{ex}}$ activity from the surface downwards can be represented by the equation:

$$C(x) = C(0)e^{-\beta x} \tag{1}$$

where:

x mass depth from soil surface (kg m^{-2});
$C(x)$ concentration of $^{210}\text{Pb}_{\text{ex}}$ at depth x (Bq kg^{-1});
$C(0)$ concentration of $^{210}\text{Pb}_{\text{ex}}$ in the surface soil (Bq kg^{-1});
β constant (kg m^{-2}) defined as:

$$\beta = \frac{1}{2}\left(\sqrt{\frac{V^2}{D^2} + \frac{4\lambda}{D}} - \frac{V}{D}\right) \tag{2}$$

where:

D the effective diffusion coefficient (kg^2 m^{-4} year^{-1});
V the downward migration rate (kg m^{-2} year^{-1});
λ the radionuclide decay constant (year^{-1});

Equation (1) was used to simulate the fallout profile shown in Figure 2. The estimated value for β of 0.91 kg m^{-2} was obtained by varying the values of V and D to minimise the sum of the squares of the deviations between the modelled and observed depth distribution. The fitted result is depicted in Figure 2.

Integration of $C(x)$ over mass depth x gives the total $^{210}\text{Pb}_{\text{ex}}$ inventory A_u (Bq m^{-2}) for an undisturbed site at time t:

$$A_u(t) = \int_0^{\infty} C(x,t)\,\mathrm{d}x \tag{3}$$

At a location experiencing water-induced erosion, the rate of soil loss R_e (kg m^{-2} year^{-1}) can be estimated from the reduction in the $^{210}\text{Pb}_{\text{ex}}$ inventory ($A_{u,ls}(t)$ compared with the local reference value, in combination with information on the ^{210}Pb content of the eroded soil $C_e(t')$:

$$A_{u,ls}(t) = \int_0^{t} R_e C_e\left(t'\right)e^{-\lambda\left(t-t'\right)}\mathrm{d}t' \tag{4}$$

Alternatively, at a location experiencing water-induced deposition, the rate of sedimentation R_d (kg m^{-2} year^{-1}) can be estimated from the increase in the $^{210}\text{Pb}_{\text{ex}}$ inventory ($A_{u,ex}$ [Bq m^{-2}]) compared with the local reference value, coupled with information on the ^{210}Pb content of deposited sediment $C_d(t')$:

$$R_d = \frac{A_{u,ex}}{\int_0^t C_d(t')e^{-\lambda(t-t')}\mathrm{d}t'} \tag{5}$$

Assuming that the $^{210}Pb_{ex}$ concentration $C_d(t')$ of deposited sediment can be represented by the weighted mean of the $^{210}Pb_{ex}$ concentration of the sediment mobilized from the upslope contributing area, $C_d(t')$ can be calculated

$$C_d(t') = \frac{1}{\int_S R_d S} \int_S C_e(t') R_d S \tag{6}$$

where $C_e(t')$ (Bq kg^{-1}) is the $^{210}Pb_{ex}$ concentration of mobilised sediment and S is the upslope contributing area (m^2).

3. Results

3.1. COMPARING THE ESTIMATES OF NET SOIL LOSS DERIVED FROM THE ^{210}Pb MEASUREMENTS WITH THE MEASURED SEDIMENT YIELDS AT THE CATCHMENT OUTLETS

The $^{210}Pb_{ex}$ inventories measured for individual soil cores, were used with Equations (4) and (5) to provide estimates of soil redistribution rates (t ha^{-1} year^{-1}). These point values were then interpolated by using a kriging interpolation procedure to derive a map of soil redistribution rates for each catchment. As an example, the map produced for catchment W1 is presented in Figure 3b. The resulting estimates of soil redistribution rate were then spatially averaged to produce a sediment budget for each catchment, which comprised information on the total erosion, total deposition and the net soil loss. The estimates of net soil loss (t ha^{-1} year^{-1}) obtained for each catchment can be compared with the values of sediment yield based on the measurements at the catchment outlet, in order to provide a test of the validity of these estimates (see Table III). Taking account of the uncertainties associated with both the measured sediment yields and the procedure used to extrapolate those values to obtain an estimate of the longer-

TABLE III

Comparison of the estimates of net erosion rate obtained for the study catchments using ^{137}Cs and $^{210}Pb_{ex}$ measurements with the estimates of long-term sediment yield based on measurements at the catchment outlets

	Net soil erosion (t ha^{-1} year^{-1})		
Catchment	W1	W2	W3
^{137}Cs	8.6	14.0	11.3
^{210}Pb	6.2	12.1	11.1
Measured sediment yield	12.4	19.2	7.8

term sediment yield, as well as those associated with the estimates of net erosion rate obtained from the $^{210}Pb_{ex}$ measurements, the estimates of net soil loss reported in Table III, are in reasonable agreement with the equivalent measured values of sediment output. These results therefore provide a first-order demonstration that $^{210}Pb_{ex}$ measurements provide a viable means of estimating net erosion rates in the study catchments. Further work is, however, clearly required to explore the contrasts in both the absolute and relative values of net erosion rate obtained using the two approaches.

3.2. COMPARISON WITH ESTIMATES OF NET SOIL LOSS OBTAINED USING ^{137}CS MEASUREMENTS

In previous papers, Porto et al. (2001, 2003, 2004) explored the use of the ^{137}Cs technique to provide estimates of soil erosion rates within the same catchments. The results obtained from the $^{210}Pb_{ex}$ measurements are in close agreement with the values obtained from the ^{137}Cs measurements, in both absolute and relative terms (see Table III) and this comparison provides a further validation of the use of $^{210}Pb_{ex}$ measurements to estimate erosion rates in the study catchments. There are, however, some minor contrasts between the results obtained using the two radionuclides. Whereas, the ^{137}Cs results show evidence of significant deposition only for catchment W1, the soil redistribution rates derived from the $^{210}Pb_{ex}$ measurements, reported in Table II, show some deposition occurring in all the three catchments, although this is very limited within catchment W2. These apparently contrasting results may reflect the different behaviour of the two radionuclides in terms of their fallout and their distribution in the soil profile and the greater sensitivity of the $^{210}Pb_{ex}$ approach to recent erosion events, due to the continuous fallout input of $^{210}Pb_{ex}$ and its shorter half-life.

4. Conclusions

The results obtained from this investigation undertaken in three small catchments in southern Italy confirm the potential for using fallout ^{210}Pb to document soil erosion rates on uncultivated soils in this environment. The availability of information on the sediment output from the study catchments permits a direct comparison with an equivalent spatially averaged estimate of the erosion rate for the same areas, derived from $^{210}Pb_{ex}$ measurements. The results of the comparison show that the erosion rate estimates obtained from the $^{210}Pb_{ex}$ measurements are reasonably consistent with the measured sediment yields at the catchment outlets, when the various uncertainties associated with both data sets are recognised. In addition, the $^{210}Pb_{ex}$ results are in close agreement with those obtained from the same catchments using ^{137}Cs measurements. Further studies are clearly required to explore the potential for using fallout ^{210}Pb to estimate erosion rates on cultivated soils in the study area and in other

This page intentionally blank

environments, but the results reported in this paper provide further confirmation of the validity of the approach.

Acknowledgments

The study reported in this paper was supported by an EC Marie Curie Fellowship (MCF1-2000-00096) awarded to the first author, by grants from MURST, and by IAEA Technical Contract 12094. Thanks are also extended to Mr. G. Guarnaccia and Mr. D. Porcino for assistance with fieldwork and to Sue Rouillard for producing the diagrams.

References

Avolio, S., Ciancio, O., Grinovero, C., Iovino, F., Mirabella, A., Raglione, M., et al. (1980). Effetti del tipo di bosco sull'entità dell'erosione in unità idrologiche della Calabria–Modelli erosivi. *Annali Istituto Sperimentale Selvicoltura*, *11*, 45–131 (in Italian).

Campbell, B. L., Loughran, R. J., & Elliott, G. L. (1988). A method for determining sediment budget using caesium-137. In M. P. Bordas & D. E. Walling (Eds.), *Sediment Budgets* (Proceedings of the Porto Alegre Symposium), International Association of Hydrological Sciences Publication 174 (pp. 171–179). Wallingford, UK: IAHS.

Ferro, V., & Porto, P. (2000). Sediment delivery distributed (SEDD) model: Theoretical analysis and experimental validation. *Journal of Hydrologic Engineering*, *5*, 411–422.

He, Q., & Walling, D. E. (1997). The distribution of fallout ^{137}Cs and ^{210}Pb in undisturbed and cultivated soils. *Applied Radiation Isotopes*, *48*, 677–690.

Porto, P., Walling, D. E., & Callegari, G. (2004). Validating the use of caesium-137 measurements to estimate erosion rates in three small catchments in southern Italy. In V. Golosov, V. Belyaev, & D. E. Walling (Eds.), *Sediment Transfer through the Fluvial System* (Proceedings of a symposium held in Moscow, August 2004) International Association of Hydrological Sciences Publication 288 (pp. 75–83). Wallingford, UK: IAHS.

Porto, P., Walling, D. E., & Ferro, V. (2001). Validating the use of caesium-137 measurements to estimate soil erosion rates in a small drainage basin in Calabria, southern Italy. *Journal of Hydrology*, *248*, 93–108.

Porto, P., Walling, D. E., Ferro, V., & Di Stefano, C. (2003). Validating erosion rate estimates provided by caesium-137 measurements for two small forested catchments in Calabria, Southern Italy. *Land Degradation and Development*, *14*, 389–408.

Walling, D. E. (1998). Use of ^{137}Cs and other fallout radionuclides in soil erosion investigations: progress, problems and prospects. In *Use of ^{137}Cs in the Study of Soil Erosion and Sedimentation*, IAEA-TECDOC-102839-62. Vienna, Austria: IAEA.

Walling, D. E., Collins, A. L., & Sichingabula, H. M. (2003) Using unsupported lead-210 measurements to investigate soil erosion and sediment delivery in a small Zambian catchment. *Geomorphology*, *52*, 193–213.

Walling, D. E., & He, Q. (1999). Using fallout lead-210 measurements to estimate soil erosion on cultivated land. *Soil Science Society of America Journal*, *63*(5), 1404–1412.

Zapata, F. (2003). The use of environmental radionuclides as tracers in soil erosion and sedimentation investigations: recent advances and future developments. *Soil and Tillage Research*, *69*, 3–13.

Water, Air, and Soil Pollution: Focus (2006) **6:** 305–312
DOI: 10.1007/s11267-006-9052-3

SEDIMENT–WATER INTERACTIONS IN AN ERODED AND HEAVY METAL CONTAMINATED PEATLAND CATCHMENT, SOUTHERN PENNINES, UK

J. J. ROTHWELL*, M. G. EVANS and T. E. H. ALLOTT
Upland Environments Research Unit, School of Environment and Development, The University of Manchester, Mansfield Cooper Building, Oxford Road, Manchester M13 9PL, UK
*(*author for correspondence, e-mail: james.rothwell@manchester.ac.uk;*
phone: +44-161-275-3645; fax: +44-161-275-7878)

Abstract. Atmospherically deposited lead in the upper layer of the heavily eroded peatlands of the Peak District, southern Pennines, UK, reaches concentrations in excess of 1,000 mg kg^{-1}. Erosion of the upper peat layer in this region is releasing lead, associated with eroded peat particles, into the fluvial system. Understanding the process mechanisms that control dissolved lead concentrations in contaminated peatland streams is vital for understanding lead cycling and transport in peatland streams. Many headwater streams of the southern Pennines recharge drinking water reservoirs. Measurements in the Upper North Grain (UNG) study catchment show that mean sediment-associated and dissolved lead concentrations are 102±39.4 mg kg^{-1} and 5.73±2.16 μg l^{-1}, respectively. Experimental evidence demonstrates that lead can desorb from suspended sediments, composed of contaminated peat, into stream waters. In-stream processing could therefore account for the elevated dissolved lead concentrations in the fluvial system of UNG.

Keywords: peat erosion, lead, acidic water, desorption, in-stream processing

1. Introduction

Ombrotrophic peat bogs receive all their inputs from the atmosphere (Clymo et al., 1990). The nature of ombrotrophic peat, and the ability of peat to effectively sorb heavy metals, makes such environments excellent archives of atmospheric lead deposition. There is great spatial variability in lead concentrations in peatland environments around the globe (Table I). Peatland environments located near urban centres or close to industrial sites can be highly contaminated with lead. The peatlands of the Peak District, southern Pennines, UK, are situated in the heartland of the nineteenth century English Industrial Revolution, between the cities of Sheffield and Manchester. Consequently, very high concentrations of lead are stored in the upper peat layer in this region (e.g., Jones & Hao, 1993; Livett, Lee, & Tallis, 1979; Rothwell, Robinson, Evans, Yang, & Allott, 2005).

The peatlands of the southern Pennines are also the most severely eroded in the UK (Tallis, 1997), with approximately three quarters of the peatlands eroded or subjected to degradation (Anderson & Tallis, 1981). Erosion of contaminated land and subsequent transport of contaminated sediment to fluvial systems is

TABLE I

Maximum lead concentration in a selection of peatland environments

Location	Maximum Pb concentration (mg kg^{-1})	Reference
Gola di Lago, Switzerland	1,528	Shotyk (2002)
Upper North Grain, Derbyshire, UK	1,148	Rothwell et al. (2005)
Grassington Moor, North Yorkshire, UK	800	Livett et al. (1979)
Boží Dar, Czech Republic	479	Vile, Wieder, and Novak (2000)
Etang de la Gruère, Canton Jura, Switzerland	83	Shotyk (2002)

common in a variety of environmental contexts, and the role of suspended sediment as a vector for contaminants is widely recognised (e.g., Blake et al., 2003).

Pore water concentrations of heavy metals in peatlands are controlled by heavy metal loading, pH, the affinity of heavy metals for organic matter and dissolved organic carbon, and competition between heavy metals for binding sites (Lawlor & Tipping, 2003). Dissolved lead concentrations in upland peatland streams have been explained by leaching of dissolved heavy metals from catchments peats, as groundwater moves through contaminated layers of the peat into the fluvial system (e.g., Lawlor & Tipping, 2003; Vinogradoff et al., 2005). However, sediment-associated heavy metals in fluvial systems are subject to adsorption and desorption processes, where heavy metals can move between particulate and dissolved phases (Foster & Charlesworth, 1996). Chemical, physical, and biological conditions of stream waters control interactions of heavy metals between sediment and water (Kersten, 2002). Streams draining peatland catchments are often highly acidic, as organic acids and industrially-derived acid species are flushed out of the peats during stormflow (Evans, Jenkins, & Wright, 2000). Under such conditions, sediment-associated heavy metals in peatland streams may be desorbed from contaminated sediment into the water column.

The aims of this study are to assess the degree of lead contamination of the fluvial system at UNG, and to test empirically whether sediment-associated lead in streams draining contaminated peatlands is susceptible to desorption into the water column.

2. Materials and Methods

2.1. STUDY AREA

Upper North Grain (UNG) is a small headwater stream that drains a peat-covered catchment in the Peak District, southern Pennines, UK (Figure 1). UNG joins the

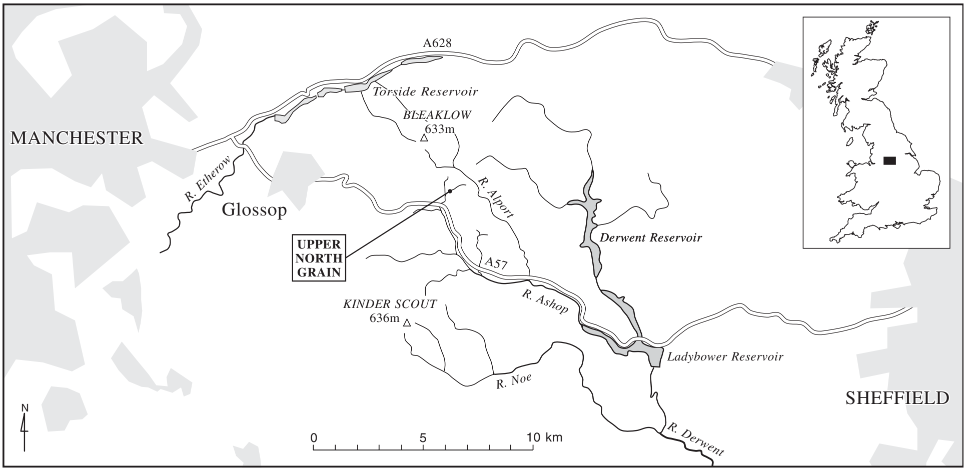


Figure 1. Location of study area.

River Ashop, which feeds Ladybower Reservoir in the Upper Derwent Valley. Ladybower Reservoir is one of ~200 drinking water supply reservoirs in the southern Pennines. The catchment has a drainage area of 0.38 km^2 and rises to an altitude of 520 m OD. The peats of the catchment are severely eroded.

2.2. CORING

During October 2002, eight peat cores were collected from intact peat areas within the UNG catchment. All cores were extracted with a 50 cm Russian corer, and subsequently wrapped in cling film. Seven of the peat cores were sliced at contiguous 1 cm intervals, disaggregated, dried at 105°C for 24 h, and then prepared for lead analysis as described below.

2.3. STORM WATER SAMPLES

Between June 2002 and November 2004, 205 stream samples were collected from UNG during 12 storm events. Stream water samples were taken at 15 min intervals from UNG by a Sigma 900 water sampler, triggered automatically by a rise in stage. Prior to use, all field and laboratory equipment was soaked in 10% Decon 90 detergent solution overnight, rinsed with distilled water (Elga Purelab Option R7), soaked overnight in 2 M HNO_3 (Analar, BDH), and then rinsed with distilled water. All storm water samples were filtered through pre-weighed glass microfibre filter paper circles (Whatman GF/C), in order to retain the suspended sediment fraction. Filter papers were then oven-dried at 105°C for 24 h, and the dry weight recorded.

2.4. SOLID PHASE LEAD

Peat samples and suspended sediments (including filter papers) were digested on a hot-plate at ~100°C for 4 h using 5 ml of 15.6 M HNO_3 (Analar, BDH). After digestion, all samples were made up to 25 ml with distilled water, filtered through Whatman GF/C filter paper, and stored at ~4 °C in polythene tubes prior to lead analysis. Lead concentrations in peat and suspended sediment samples were determined using AAS (Thermo Unicam S11), wavelength 217 nm. Lead standard solutions (Spectrosol, BDH), ranging from 7.5 to 15 mg l^{-1}, were used to calibrate the AAS. The sensitivity of the AAS was 0.1 ppm for lead. Certified Reference Material LGC6139 River Sediment (LGC Promochem) was digested and analysed along with the sediment samples, and a recovery of 105% was obtained for lead. A series of blank samples (digested, unused filter papers) were also analysed and were below the detection limit of the AAS.

2.5. DISSOLVED LEAD

Of the 12 storm events sampled, seven sets of storm water samples were filtered through 0.45 μm cellulose nitrate membrane filters (Whatman), acidified with 2% (v/v) HNO_3 (Ultrapur, BDH), and analysed for dissolved lead using ICP-MS(VG Elemental Plasmaquad 2 STE TM - Williamson Research Centre for Molecular Environmental Science, School of Earth, Atmospheric and Environmental Sciences, The University of Manchester). The ICP-MS is operated in a class 1,000 cleanroom. In sequential mode, the ICP-MS has a quantitation range of 1,000 ppb to 50 ppt. Duplicate measurements for all samples were undertaken, and analytical uncertainty was <2%. Duplicate blanks and standards were used during analysis to ensure accuracy and precision.

2.6. MIXING EXPERIMENT

On 1 October 2003, ~2 l of stream water was collected during a storm at UNG. The stream water was filtered through a 0.45 μm cellulose nitrate membrane filter (Whatman), and measured for pH using a Jenway 3320 pH meter (pH 3.68). The top 10 cm of the un-sliced peat core was homogenised whilst still moist. A sub-sample was dried at 105°C and analysed for lead content (694 mg kg^{-1}). A sub-sample of the homogenised moist peat (equivalent to ~6 g dry weight) was placed into a large polyethylene bottle with the filtered stream water. The approximate suspended sediment concentration (SSC) was 3 g l^{-1}, a SSC typical of large storm events at UNG (Rothwell et al., 2005). The bottle containing peat and water was mixed using a Stuart flask shaker for 20 min, 40 min, 1 h, 3 h, 6 h and 24 h. After each time period had elapsed, 10 ml of water was extracted, using a modified pipette. Five replicates were taken for each time interval, and all samples were filtered through 0.45 μm cellulose nitrate membrane filters, and analysed for lead using ICP-MS as described above.

3. Results and Discussion

The upper layer in the peat catchment of UNG is severely contaminated with lead. In a previous study at UNG by Rothwell et al. (2005), a maximum lead concentration of 1,148 mg kg^{-1} was recorded in the near-surface peat. In this study, a maximum lead concentration of 1,614 mg kg^{-1} was recorded in one of the peat cores analysed (Table II). The seven down-core lead profiles were similar to the downcore lead profile described by Rothwell et al., each with significant lead concentrations in the near-surface, with a lead peak at ~5 cm. Compared to other blanket peats from around the globe, the peatland catchment of UNG in the Peak District, southern Pennines, is amongst the most severely contaminated in the world (Table I).

Suspended sediment concentrations (SSC) for peatland catchments characterised by severe erosion are usually high, especially when there is good slope–channel linkage (Evans & Warburton, 2005). High SSC during storm events at UNG (Table II) are consistent with the severe erosion seen in the catchment. There are no established guidelines for the quality of sediment in UK rivers. However, in Canada, there are Sediment Quality Guidelines (CSeQGs) for the protection of aquatic life in the fluvial environment (CCME, 2002). For sediment-associated lead, there is a 'probable effect level' (PEL) to aquatic life of 91.3 mg kg^{-1} (CCME, 2002). The mean sediment-associated lead concentration of 102±39.4 mg kg^{-1} at UNG exceeds this PEL.

Dissolved lead concentrations in streams draining upland peatland catchments can be spatio-temporally variable. In a study of surface waters in the English Lake District by Lawlor and Tipping (2003), mean lead concentrations in three

TABLE II

Lead concentrations in system components at UNG

	Mean±SD	Range
[a, c]Peat	1121±312	713–1614
[b, d]SSC	163±435	2.89–4620
[c]Sediment-associated Pb	102±39.4	4.43–395
[e]Dissolved Pb	5.73±2.16	2.26–11.3

[a] Maximum lead concentration recorded for each peat core

[b] Suspended sediment concentration

[c] mg kg^{-1}

[d] mg l^{-1}

[e] μg l^{-1}

tributaries of the River Duddon, were 0.42, 0.23 and 0.70 μg l^{-1}. Vinogradoff et al. (2005) measured dissolved lead concentrations over a two-year period at an upland stream at Glensaugh, NE Scotland. Dissolved lead concentrations ranged from 0.08 to 7.53 μg l^{-1}, with a mean of 0.60±0.71 μg l^{-1}. At UNG the dissolved lead concentrations vary from 2.26 to 11.3 μg l^{-1}, with a mean of 5.73± 2.16 μg l^{-1} (Table II). When compared to dissolved lead levels reported by Lawlor and Tipping and Vinogradoff et al., dissolved lead concentrations are higher at UNG.

Results of the mixing experiment reveal that under laboratory conditions, lead bound to suspended sediment, which is composed of contaminated peat, can desorb from the sediment into stream water (Figure 2). The dissolved lead concentration in the stream water at the start of the experiment, prior to any addition of contaminated peat, was 5.63±0.14 μg l^{-1}. However, after only 20 min of mixing the dissolved lead concentration rose to 8.67±0.20 μg l^{-1} and after 24 h the concentration was 12.75±0.44 μg l^{-1}. Dissolved lead values from the mixing experiment are very similar to the range of values measured during storm events at UNG (Table II). Dissolved lead levels in upland peatland streams have often been explained by the leaching of lead from catchment peats (e.g., Lawlor & Tipping, 2003; Vinogradoff et al., 2005). Although the mixing experiment was conducted under a worst-case scenario basis, where a large sample of contaminated peat was mixed with acidic stream water, the study establishes empirically that in-stream processing may be important in controlling dissolved lead levels in peatland streams, and can potentially account for the elevated stream water lead concentrations in these systems. However, this would need to be validated in a field context. A thorough

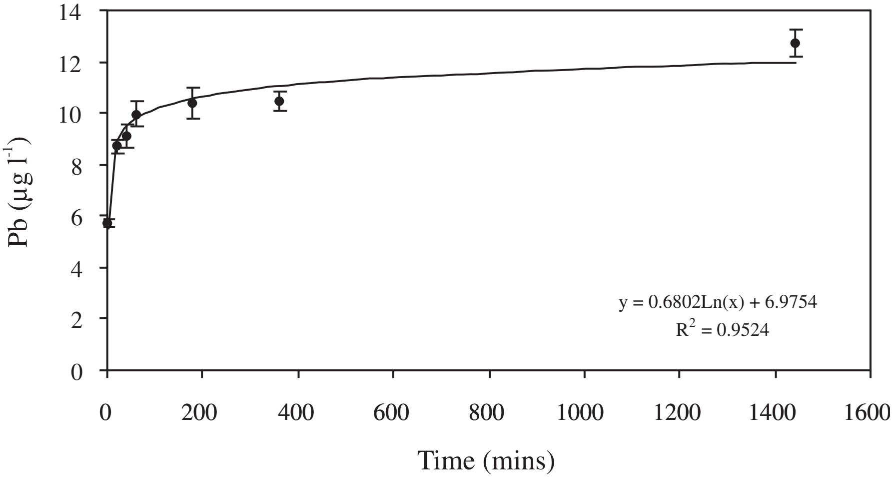


Figure 2. Dissolved lead as a function of time, measured in acidic stream water (pH 3.68) mixed with 3 g l^{-1} of peat contaminated with lead (694 mg kg^{-1}).

investigation of the relative importance of in-stream processing and leaching of lead from catchments peats in governing lead concentrations in peatland streams is therefore required.

4. Conclusion

Erosion of the upper peat layer at UNG is releasing large quantities of sediment-associated lead into the fluvial system and dissolved lead concentrations in the stream at UNG are higher than those of other upland peatland environments in the UK. An experimental approach demonstrates that the interaction of contaminated sediment and acidic stream water in peatland streams potentially explains elevated dissolved lead levels in such fluvial environments, but validation of the relative importance of this process is required. Erosion of contaminated peatlands in the southern Pennines, and elsewhere, may not only influence particulate heavy metal levels in streams, but sediment-associated lead may interact in a deleterious way with the water column.

Acknowledgements

The authors are grateful to The University of Manchester and Moors for the Future who provided funding for analytical costs. Thanks also go to Michael Clark for laboratory assistance and to Paul Lithgoe for ICP-MS analysis.

References

Anderson, P., & Tallis, J. H. (1981). The nature and extent of soil and peat erosion in the Peak District. In J. Phillips, D. Yalden & J. H. Tallis (Eds.), *Peak District moorland erosion study phase 1 report* (pp. 52–64). Derbyshire: Peak Park Joint Planning Board.

Blake, W. H., Walsh, R. P. D., Barnsley, M. J., Palmer, G., Dyrynda, P., & James, J. G. (2003). Heavy metal concentrations during storm events in a rehabilitated industrialized catchment. *Hydrological Processes*, *17*(10), 1923–1939.

CCME (2002). *Canadian environmental quality guidelines, National Guidelines and Standards Office*. Winnipeg: Canadian Council of Ministers of the Environment, 12 pp.

Clymo, R. S., Oldfield, F., Appleby, P. G., Pearson, G. W., Ratnesar, P., & Richardson, N. (1990). The record of atmospheric deposition on a rainwater-dependent peatland. *Philosophical Transactions of the Royal Society of London Series B-Biological Sciences*, *327*(1240), 331–338.

Evans, C. D., Jenkins, A., & Wright, R. F. (2000). Surface water acidification in the South Pennines. I. Current status and spatial variability. *Environmental Pollution*, *109*, 11–20.

Evans, M., & Warburton, J. (2005). Sediment budget for an eroding peat–moorland catchment in northern England. *Earth Surface Processes and Landforms*, *30*, 557–577.

Foster, I. D. L., & Charlesworth, S. M. (1996). Heavy metals in the hydrological cycle: Trends and explanation. *Hydrological Processes*, *10*, 227–261.

Jones, J. M., & Hao, J. (1993). Ombrotrophic peat as a medium for historical monitoring of heavy metal pollution. *Environmental Geochemistry and Health*, *15*(2/3), 67–74.

Kersten, M. (2002). Speciation of trace metals in sediments. In A. M. Ure & C. M. Davidson (Eds.), *Chemical speciation in the environment* (pp. 301–321). London: Blackwell Science.

Lawlor, A. J., & Tipping, E. (2003). Metals in bulk deposition and surface waters at two upland locations in northern England. *Environmental Pollution*, *121*, 153–167.

Livett, E. A., Lee, J. A., & Tallis, J. H. (1979). Lead, zinc and copper analyses of British blanket peats. *Journal of Ecology*, *67*, 865–891.

Rothwell, J. J., Robinson, S. G., Evans, M. G., Yang, J., & Allott, T. E. H. (2005). Heavy metal release by peat erosion in the Peak District, southern Pennines, UK. *Hydrological Processes*, *19*, 2973–2989.

Shotyk, W. (2002). Chronology of anthropogenic, atmospheric Pb deposition recorded by peat cores in three minerogenic peat deposits from Switzerland. *Science of the Total Environment*, *292*, 19–31.

Tallis, J. H. (1997). The Southern Pennine experience: An overview of blanket mire degradation. In J. H. Tallis, R. Meade & P. D. Hulme (Eds.), *Mires Research Group, British Ecological Society, Proceedings of the Manchester Conference* (pp. 7–15). April 1997.

Vile, M. A., Wieder, R. K., & Novak, M. (2000). 200 years of Pb deposition throughout the Czech Republic: Patterns and sources. *Environmental Science & Technology*, *34*(1), 12–21.

Vinogradoff, S. I., Graham, M. C., Thornton, G. J. P., Dunn, S. M., Bacon, J. R., & Farmer, J. G. (2005). Investigation of the concentration and isotopic composition of inputs and outputs of Pb in waters at an upland catchment in NE Scotland. *Journal of Environmental Monitoring*, *7*, 431–444.

Water, Air, and Soil Pollution: Focus (2006) **6:** 313–319
DOI: 10.1007/s11267-006-9053-2

THE EFFECT OF SEDIMENT SOURCE CHANGES ON POLLEN RECORDS IN LAKE SEDIMENTS

N. J. PITTAM[1], T. M. MIGHALL[2] and I. D. L. FOSTER[1,3,*]
[1]Geography, Faculty of Business, Environment and Society, Coventry University, Priory Street, Coventry CV1 5FB, UK
[2]Department of Geography and Environment, University of Aberdeen, Elphinstone Road, Aberdeen AB24 3UF, Scotland, UK
[3]Department of Geography, Rhodes University, Grahamstown 6140, South Africa
*(*author for correspondence, e-mail: i.foster@coventry.ac.uk; phone: +44-24-76888341; fax: +44-24-76888702)*

Abstract. A major focus of palynological research has been to assess the various pathways by which pollen is delivered to sedimentary archives. In open lake systems, the contribution of streamborne pollen to lake sediments is thought to be highly significant. Despite this, little research has attempted to identify changes in the pollen record that might be attributed to changing sediment pathways rather than to changes in vegetation. This research aims to partially redress this gap by examining a dated pollen sequence from Kyre Pool, Worcestershire, England. The results presented in this paper suggest that some changes in sediment source, as determined by a fingerprinting approach, can influence the pollen record reconstructed from a lake sediment profile.

Keywords: pollen, sediment fingerprinting, lake sediment, taphonomy

1. Introduction

There are a variety of pathways by which pollen can be incorporated into a lake sediment (Figure 1). Pennington (1979), however, suggests that in open lake systems (with inflows and outflows), streamborne pollen (Cs Figure 1) contributes between 85% and 93% of the preserved record. The contribution of streamborne pollen to a small lake with a large inflow will be significantly higher than the airborne contribution, in contrast to a larger water body with minor inflows, where the airborne component is likely to be much more important (Edwards & Whittington, 1993; Pennington, 1979).

Pollen could also be re-entrained by water erosion from secondary sources such as catchment soils (Cw Figure 1). Despite the early recognition of this as a potential source of pollen to a lake (Erdtman, 1943) there is still no consensus as to the relative contribution that this re-eroded pollen could make to the preserved record. Changes in sources, transport dynamics, deposition and preservation of pollen all impact upon the pollen record and the interpretations made. A greater understanding of the potential contribution of pollen transported via hydrological

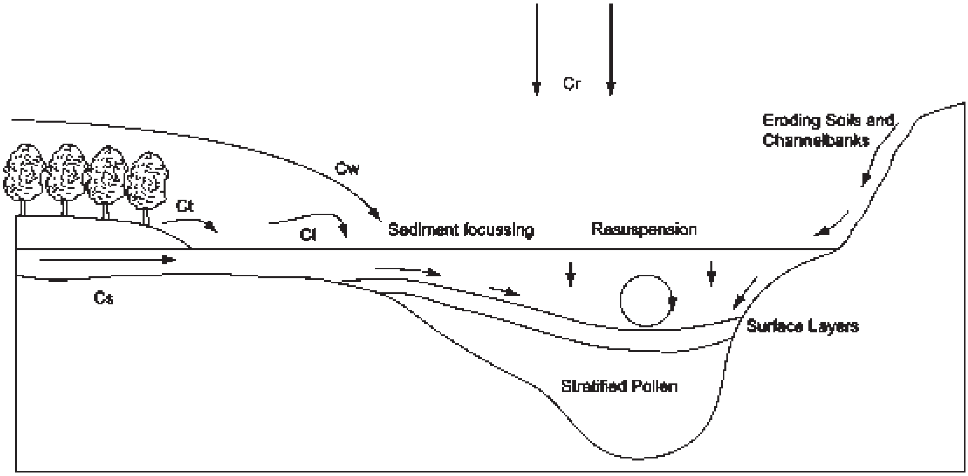


Figure 1. Modes of pollen transfer to lakes (modified from Moore, Webb, & Collinson, 1991).

pathways to the lake sediment would improve our ability to correctly interpret the record. Pathways through which secondary and streamborne pollen are transported are likely to be the same as those for the eroded soil that constitutes much of the lake sediment.

A range of methods have been employed to trace the origin of eroded soils delivered to a lake, including mineral magnetic, radionuclide and geochemical signatures (e.g., Foster & Lees, 2000). Thus fingerprinting could be used as an independent tracer of the sediment delivered to the lake and this can be compared with the reconstructed pollen record. This relationship will be examined in this paper by assessing the impact of changing sediment sources on the pollen record.

2. Site Description and Methods

Kyre Pool (Figure 2) is located in Worcestershire, England. It was formed by the damming of a tributary of Kyre Brook in 1584 A.D. The lake has 4.16 m of sediment and preserves a 419-year archive of landscape change. The catchment is mainly agricultural, with areas of woodland adjacent to the pool that extend up-valley into two streams that feed the lake (Foster et al., 2003; Foster, Lees, Jones, Chapman, & Turner, 2002).

Coring was undertaken in 2002 using Mackereth and Russian corers (Aaby & Digerfeldt, 1986). Between 5 and 10 catchment topsoils were sampled from each potential source using bulk density rings (5 cm diameter; 5 cm depth) to assess the pollen content. Samples were prepared for pollen analysis following Barber (1976). Five hundred terrestrial pollen grains were counted per sample. All pollen data from Kyre Pool are expressed as percentage of total land pollen (TLP). The

Lake and Catchment Properties	Kyre Pool	UK Location
UK Ordnance Survey Grid Reference	SO 633 638	 Kyre Pool Catchment in a regional context
Lake Area	$0.0534 km^2$	
Catchment Area	$2.73 km^2$	
Lake:Catchment Ratio	52:1	
Maximum altitude	262m	
Minimum altitude	90m	
Maximum lake depth	2.5m	
Mean lake depth	2.0m	
Lake Volume	$130\,000 m^3$	
Date of formation	1584	
Land Use		
Deciduous Woodland	27%	
Coniferous Plantation	6%	
Permanent Pasture	44%	
Arable	18%	
Soil Series	Bromyard Series	

Figure 2. Site characteristics and location.

lake sediment record is divided into zones using TILIA.GRAPH and CONISS (Grimm, 1991–1993). The zones are labelled KP1 (oldest) to KP6 (youngest). Dating of the sediment profile was undertaken using ^{210}Pb, ^{137}Cs and bio-stratigraphic markers (see Foster et al., 2002). Representative samples of soil were collected in an earlier research project to model source changes through time based on mineral magnetic and radionuclide signatures. Un-mixing models were used to estimate the changing source contributions over the history of deposition (see I.D.L. Foster, 2006; I.D.L. Foster, A.S. Chapman et al., 2003; I.D.L. Foster, J.A. Lees et al., 2002 for details).

3. Results and Interpretation

3.1. Pollen Content of Catchment Sources

The pollen content of the catchment soils varied significantly in relation to contemporary land use (Table I). The highest percentage of cereal pollen was found in arable topsoils, although there were still significant cereal counts in pasture topsoils. The proportion of arboreal pollen found in the soil samples was highly variable with the highest percentages in woodland topsoils (c.75%), although arboreal pollen contributed at least 29% TLP to all of the sources investigated. Even though channel bank sediments were collected under a woodland cover, their pollen spectra are remarkably similar to arable topsoils

TABLE I

Pollen percentage data for contemporary catchment sources

Source	Arboreal (%)	Dwarf shrub (%)	Herbs* (%)	Poaceae** (%)	Cereals (%)	Pollen concentration (grains cm^{-3})
Lake sediment	65.7	3.8	12.0	16.2	2.3	122,861
Wood' topsoil	73.3	1.0	10.9	12.1	2.7	226,556
Arable topsoil	31.9	4.8	25.3	35.2	2.8	7,186
Pasture topsoil	30.0	3.9	19.8	44.0	2.3	15,029
Channel banks	32.2	4.7	23.0	37.2	2.9	12,325
Tile drains	34.4	1.2	20.0	38.2	6.2	14,847

*Excluding Poaceae and cereals

**Excluding cereals

(Table I). The pollen content of catchment soils may have altered through time and may differ from the contemporary sources, and the extent of change cannot be fully known. The data do serve to demonstrate, however, that there are significant differences between contemporary sources and it has been assumed that similar differences have existed through time.

3.2. THE LAKE SEDIMENT RECORD

Part of the variation in the pollen record (Figure 3) could be caused by sediment source changes independently of vegetation change. Contemporary observations and historical documents show that woodland has always fringed the lake and this will provide a direct source of arboreal pollen irrespective of streamborne contributions from different parts of the catchment. Significant modelled subsoil contributions to the lake sediments are, however, coupled with high arboreal (tree and shrub) pollen percentages in the bottom half of pollen zone KP1. This represents the phase immediately following dam construction and the modelled source is consistent with a phase of subsoil disturbance during and immediately after dam construction. With the exception of the period straddling zones KP2 and KP3 (when channel banks are predicted to dominate sediment sources) the source modelling suggests that woodland topsoil makes the major contribution to the sedimentary record from the upper half of KP1 until half way through KP5. The contribution from channel banks at the junction of KP2 and KP3 is coincident with a fall in the oak (*Quercus*) and birch (*Betula*) percentages in the sediments. At the same time, alder (*Alnus*) increased, but this may reflect its preference for

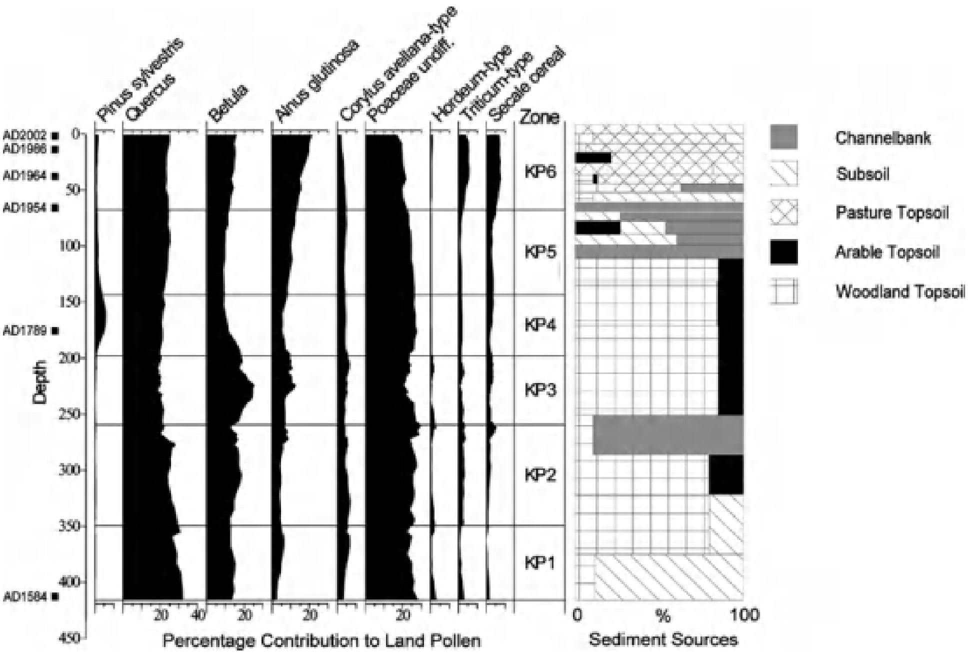


Figure 3. Patterns of vegetation change recorded in the pollen record of Kyre Pool, related to depth, age and modelled sediment sources. (Source contributions are given as percentages).

growing along stream margins, which appear to have been the dominant source of sediment at this time. If the pollen spectrum of Table I was similar to that at the time of the KP2/KP3 boundary, then the decrease in birch and oak pollen could simply reflect a source change rather than a change in vegetation because channel bank sources show higher levels of cereal pollen relative to arboreal pollen. As sediment sources again become dominated by woodland topsoil at the bottom of KP3, the birch percentage rises while the oak percentage remains relatively stable. Documentary records note that the region produced particularly tall and strong oak trees that were selectively used to construct the masts of warships and that this area was an important source of ships timber from the late sixteenth century onwards (Jones, 2001). The change in sediment source back to a woodland topsoil dominance is tentatively linked to disturbance due to selective timber harvesting that caused the change in sediment source. The rise of birch relative to oak would be consistent with the selective removal of oak at this time.

The emergence of pine (*Pinus*) within KP4 is probably due to a documented plantation in 1789. In the absence of a modelled sediment source change, the decline in birch and alder from KP4 to KP3 may reflect a real reduction in the number of trees in the local area, although similar trends are not observed for oak. The rise in alder from the KP3/KP2 boundary to the present day is consistent with the terrestrialisation of the inflow zones of the lake that can be identified on a range of maps of the catchment from the early nineteenth century that would have provided a larger area of wetland in which alder would thrive.

There is a significant increase in all cereal-type pollen coincident with major changes in predicted sediment source contributions, notably the dominance of pasture and arable topsoil, in the top 70 cm of the lake sediment (zone KP6). This change has been dated to the last ~50 years (Figure 3). Conventional palaeoecological interpretation of this change would be the intensification of agriculture in the post-war period (Rackham, 1986). It is known from independent farm records that the widespread intensification of agriculture was largely absent in the region surrounding Kyre Pool and that the balance of land use remained relatively stable (Pritchard, 1957). From Table I it is clear that the cereal contribution of arable and pasture topsoil is significantly higher than those of woodland topsoils and it is suggested that the increases in cereals during this period are due to increased connectivity in the hydrological system. Foster et al. (2002, 2003) demonstrated a fourfold increase in sediment yields entering Kyre Pool beginning in the early 1960s and extending through to the present day. These increases were attributed to the installation of land (tile) drains and it is suggested that the elevated cereal pollen percentages are the product of more efficient transportation through these underground linkages to the main catchment streams. This hypothesis is further supported by the presence of high levels of cereal pollen within the tile-drain sediments (see Table I) and demonstrates that the taphonomic process is impacting upon the pollen record of the lake sediment.

4. Conclusion

This paper has demonstrated that the pollen record of lake sediments is not only governed by aerial pollen but is also influenced by pollen transported via a number hydrological pathways and from different sources that dominate sediment yield contributions through time. By combining sediment source tracing techniques with pollen analysis, the results presented here suggest a better-informed palaeoecological interpretation of Holocene lake sediment records could be produced. In particular, land drainage is widely installed in the UK (Chapman, Foster, Lees, Hodgkinson, & Jackson, 2003), in many other areas of Europe, Canada and the United States (I.D.L. Foster, A.S. Chapman et al., 2003; I.D.L. Foster, J.A. Lees et al., 2002), and is likely to have significant consequences for pollen recruitment to lakes. It is not a recent phenomenon, and has been practiced since the early nineteenth century in parts of the UK. It is also conceivable that upland lake sediment records could be impacted by changes in hydrological pathways linking pollen sources to lakes (e.g., forestry drains). Further studies are required to establish whether changes in pollen records of lake sediments are attributable to land use changes, alterations to hydrological pathways or to broader changes in catchment vegetation.

Acknowledgements

Coventry University are thanked for funding a PhD studentship to undertake much of this work. Bob Hollyoak and Elizabeth Turner are thanked for laboratory support. Contributions from IDLF were made whilst in receipt of a Hugh Kelly Scholarship at Rhodes University, South Africa, which is gratefully acknowledged.

References

Aaby, B., & Digerfeldt, G. (1986). Sampling techniques in lakes and bogs. In B. E. Berglund (Ed.), *Handbook of holocene palaeoecology and palaeohydrology* (pp. 181–194). London: Wiley.

Barber, K. E. (1976). Pollen analysis. In S. B. Chapman (Ed.), *Methods in plant ecology* (pp. 5–83). Oxford: Blackwell.

Chapman, A. S., Foster, I. D. L., Lees, J. A., Hodgkinson, R. J., & Jackson, R. H. (2003). Phosphorus transfer from field to river via land drains in England and Wales. A risk assessment using field and national data bases. *Soil Use and Management, 19*, 347–355.

Edwards, K. J., & Whittington, G. (1993). Aspects of the environmental and depositional history of a Rock Basin Lake in Eastern Scotland. In J. McManus & R. W. Duck (Eds.), *Geomorphology and sedimentology of lakes and reservoirs* (pp. 155–180) London: Wiley.

Erdtman, G. (1943). *Introduction to pollen analysis, Chronica botanica*. Massachusetts: Waltham.

Foster, I. D. L. (2006). Lakes in the sediment delivery system. In P. N. Owens & A. J. Collins (Eds.), *Soil erosion and sediment redistribution in river catchments* (pp. 142–156). Wallingford: CAB International.

Foster, I. D. L., Chapman, A. S., Hodgkinson, R. M., Jones, A. R., Lees, J. A., Turner, S. E., et al. (2003). Changing suspended sediment and particulate loads and pathways in underdrained lowland agricultural catchments, Herefordshire and Worcestershire, UK. *Hydrobiologia, 494*, 119–126.

Foster I. D. L., & Lees, J. A. (2000). Tracers in geomorphology: Theory and applications in tracing fine particulate sediments. In I. D. L. Foster (Ed.), *Tracers in geomorphology* (pp. 1–20). New York: Wiley.

Foster, I. D. L., Lees, J. A., Jones, A. R., Chapman, A. S., & Turner, S. E. (2002). The possible role of agricultural land drains in sediment delivery to a small reservoir, Worcestershire, UK, a multiparameter fingerprint study. *IAHS Publication, 276*, 433–442.

Grimm, E. (1991–1993). *Tilia and Tiliagraph*. Illinois: Illinois State University.

Jones, A. R. (2001). A preliminary analysis of historic sediment flux in a rural catchment: Kyre Pool, Worcestershire, UK. Unpublished MSc Thesis, Coventry University.

Moore, P. D., Webb, J. A., & Collinson, M. E. (1991). *Pollen analysis* (2nd ed.). Oxford, UK: Blackwell Scientific.

Pennington, W. (1979). The origins of pollen in lake sediments: An enclosed lake compared with one receiving inflow streams. *New Phytologist, 83*, 189–213.

Pritchard, C. (1957). Great Kyre changes in the agricultural geography 1841–1951. (Public Records Office, Worcester, BA1572 s760/409).

Rackham, O. (1986). *The History of the countryside; the classic history of Britain's landscape, flora and fauna* (1st ed.). London: Phoenix.