BOREAL ENVIRONMENT RESEARCH 11: 383–388 ISSN 1239-6095
Helsinki 25 October 2006 

# Gulf of Bothnia receives high concentrations of potentially toxic metals from acid sulphate soils

Marcus Roos* and Mats Åström

*Department of Biology and Environmental Science, Kalmar University, SE-39182 Kalmar, Sweden (*e-mail: marcus.roos@hik.se)*

*Received 5 July 2005, accepted 10 Apr. 2006 (Editor in charge of this article: Timo Huttula)*

Roos, M. & Åström, M. 2006: Gulf of Bothnia receives high concentrations of potentially toxic metals from acid sulphate soils. *Boreal Env. Res.* 11: 383–388.

An estimated 460 000 ha of acid sulphate soil (AS soil) occur within the river catchments bordering the Gulf of Bothnia in Finland and Sweden. This soil type exists because extensive areas of sulphide-bearing Holocene sediments have been drained for agricultural purposes, resulting in oxidation of metal sulphides to sulphuric acid and the concomitant formation of these acidic, environmentally-unfriendly soils. The aim of this study was to compare median values of metal concentrations in rivers discharging into the Gulf of Bothnia and obtain a uniform picture of to what extent these rivers are affected by AS-soil leaching. Dissolved element concentrations for arsenic (As), cadmium (Cd), chromium (Cr), iron (Fe), nickel (Ni), lead (Pb), and zinc (Zn) were determined in 47 rivers (catchment size > 500 $km^2$) discharging into Gulf of Bothnia (a few into Gulf of Finland) along the coastline of Finland and Sweden. Water chemistry data was obtained from the Environmental Information System (HERTTA) database at the Finnish Environment Institute, the publicly available online database at Swedish University of Agricultural Sciences, Department of Environmental Assessment, and from a previous study of the authors. One area in central-western Finland proved to have highly elevated concentrations of Cd, Ni and Zn, and they all occurred with a similar spatial pattern and had the highest concentrations in rivers Teuvanjoki and Maalahdenjoki. This is caused by AS-soil leaching. The metalloid As and the metals Cr, Fe, Pb did not display this pattern and are, therefore, in line with previous studies, not leached abundantly from the AS soils, although they overall occur at somewhat higher concentrations in the Finnish as compared with those in the Swedish rivers. Thorough planning of land-use operations (e.g land reclamation through ditching, dredging of rivers and estuaries, etc.) in AS-soil landscapes should be necessary, which is currently not the case, to reduce the high concentrations of Cd, Ni and Zn in rivers.

## Introduction

Acid sulphate soils (AS soils) are developed from sulphide-rich marine sediments which occur in many coastal areas worldwide and contain acidic horizons (or layers) affected by oxidation of iron sulphides (actual AS soils) and/or sediments containing iron sulphides which have not been exposed to air and oxidized (potential AS soils) (Powell and Martens 2005). Hence, the term AS soil refers both to actual and potential AS soils (Fitzpatrik *et al*. 2003). According to meticulous work on recent survey data by Andriesse and van Mensvoort (2002), on a global level AS soils occupy an area of over 17 million ha, including large extensions in Africa (approx. 4.5 million ha, e.g. Nigeria, Senegal, Madagascar, Gambia and Guinea Bissau), Asia (approx. 6.5 million ha, e.g. Vietnam, Indonesia and Thailand), Australia (approx. 3.0 million ha, mainly Queensland) and Latin America (approx. 2.8 million, e.g. Brazil, Central America and Venzuela). In Europe the largest occurrences are found in Finland and Sweden, approx. 460 000 ha (Öborn 1989, Palko 1994).

Throughout the world where the water table has been dramatically and suddenly lowered, in sulphide-rich soils, the results have been a production of extreme acidity from sulphides and the transport of enormous quantities of acid and metals into the surrounding environment (Moormann 1961, Hart *et al*. 1963, Dost and Pons 1970, Bloomfield and Coulter 1973, Netherlands Delta Team 1973, Marius 1985). The negative environmental effects of this pollution have given rise to direct socioeconomic problems for local residents and settlers as the acidification of soils, pollution to water and damage to fisheries have occurred over wide areas, from the point of interference, over many years (Dent and Pons 1995). The acidification has both lethal and sub-lethal effects, which subsequently can lead to mass fish kills (Brown *et al*. 1983, Hart *et al*. 1987, Green 1993, Hudd and Leskelä 1998), and it increases the susceptibility of surviving fish to diseases and may leave them incapable of reproducing (Callinan 1997, Roach 1997, Hudd and Leskelä 1998). Bottom dwelling organisms that are stationary and trapped, such as mussels and oysters, can accumulate metals (Ke and Wang 2001) or become smothered by the formation of iron and aluminium flocs (Sammut 1998). Due to sulphide injury of roots, plants are found to decay (Mathew *et al*. 2000) and populations killed (Powell and Martens 2005). Where the leakage discharges into smaller water masses, the negative effects will immediately show up as low pH and high metal concentrations, while the leakage can be concealed in contact with large fresh-water masses (Roos and Åström 2005a) or where it discharges straight into the sea.

On the coastal plains of Sweden and Finland, AS soils are formed in fine-grained sulphide-rich Holocene sediments extensively drained for agricultural purposes (Öborn 1989, Yli-Halla 1997). An area especially rich in these soils is located in the central parts of the Finnish west coast (Palko 1994, Yli-Halla *et al*. 1999), in this paper referred to as CW Finland. A recent paper of the authors (Roos and Åström 2005b) presented hydrochemical data of 21 rivers in this area, and of the 35 variables determined as many as 24 were shown to be abundantly leached from the AS soils. A river ranking based on 11 potentially toxic metals (aluminium, beryllium, cadmium, cobalt, copper, manganese, nickel, thallium, thorium, uranium and zinc) leached from these soils showed that Sulvanjoki, Vöyrinjoki and Maalahdenjoki had the highest levels of these metals, and that Lestijoki, Lapväärtinjoki and Perhonjoki had the lowest.

When investigating an environmental problem, it is common to study only the contaminated/problem site and the reference material is often scarce. In this study, we deal with a few rivers which are affected by AS soils and with many others which are not. To demonstrate the AS-soil problem we chose to compare cadmium (Cd), nickel (Ni) and zinc (Zn) (associated with AS-soil leaching) and arsenic (As), chromium (Cr), iron (Fe) and lead (Pb) (not associated with AS-soil leaching). In this paper we highlight the dramatic difference in the concentrations of several elements between rivers draining AS soils and others which do not.

## Methods and material

Forty seven rivers with catchment sizes > 500 km$^2$ on the coastal plains of Sweden and Finland discharging into the Gulf of Bothnia, and a few into the Gulf of Finland, were included in the study.

For clarity three rivers with catchment sizes > 500 km$^2$ in Finland, discharging into the Gulf of Bothnia, were excluded from the study (Kuivajoki, Lapväärtinjoki and Kalajoki). Hydrochemical data for the potentially toxic metals As, Cd, Cr, Fe, Ni, Pb and Zn were obtained from the Environmental Information System (HERTTA) database at the Finnish Environment Institute (Finnish rivers), and from the publicly available online database at Swedish University of Agricultural Sciences, Department of Environmental Assessment (Swedish rivers). For CW Finland, where we wanted to include a higher number of rivers and elements than found in the HERTTA database, parts of data earlier presented in Roos and Åström (2005b) was used. All samplings were conducted 6–18 times in 2002, close to the outlet of each river. In this paper, only the median concentrations of each metal for each river were calculated and considered. The water samples were filtered (0.45 $\mu$m), acidified (pH < 2) and analysed with ICP-MS and hence reflect the dissolved element concentrations. The names of rivers, catchments sizes and data sources are listed in Table 1.

## Results and discussion

Of the examined elements, Cd, Ni and Zn clearly had elevated concentrations in CW Finland (Fig. 1) with highest concentrations in rivers 34 (Maalahdenjoki) and 33 (Laihianjoki). The highest concentrations of Cd, Ni and Zn in CW Finland were 0.29, 21.9 and 49.0 $\mu$g l$^{-1}$, respectively, while the highest concentrations in the remaining rivers were 0.038, 4.3 and 13 $\mu$g l$^{-1}$, respectively. The lowest concentrations in CW-Finland were 0.05, 1.27 and 8.65 $\mu$g l$^{-1}$ while the lowest concentrations in the remaining rivers were 0.005, 0.16 and 0.5 $\mu$g l$^{-1}$, respectively.

These three metals (Cd, Ni and Zn) are mobilised in large quantities and leached from boreal AS soils as shown by previous hydrochemical surveys (Lahermo *et al.* 1996, Eden *et al.* 1999, Åström 2001), geochemical studies of AS-soil profiles (Sohlenius and Öborn 2004) and laboratory oxidation experiments (Åström and Björklund 1997). The mechanism for liberation is weathering of sulphides (in Finland, only FeS and $FeS_2$ have been identified, but others certainly exist, and all can contain metals such as Cd, Ni and Zn) and possibly silicates that occur in these soils. Therefore these three metals are typical for drainage waters from AS soils, often referred to as AS waters.

The high concentrations in the river outlets in CW Finland as compared with those in others in Finland and all of the Swedish rivers are a con-

**Table 1**. Catchment areas and sources of hydrochemical data of the studied rivers.

| | Catchment size (km$^2$) | Data source |
|---|---|---|
| 1. Norrström Stream | 22650 | SLU |
| 2. Dal River | 28921 | SLU |
| 3. Gavle River | 2453 | SLU |
| 4. Ljusnan River | 19820 | SLU |
| 5. Delångersån River | 1992 | SLU |
| 6. Ljungan River | 12085 | SLU |
| 7. Indals River | 25767 | SLU |
| 8. Ångerman River | 30638 | SLU |
| 9. Gide River | 3442 | SLU |
| 10. Öre River | 2860 | SLU |
| 11. Ume River | 26567 | SLU |
| 12. Rickle River | 1648 | SLU |
| 13. Skellefte River | 11309 | SLU |
| 14. Pite River | 1285 | SLU |
| 15. Lule River | 25225 | SLU |
| 16. Råne River | 3781 | SLU |
| 17. Kalix River | 23845 | SLU |
| 18. Torne River | 34441 | LAP |
| 19. Kemijoki | 51000 | LAP |
| 20. Simojoki | 3160 | LAP |
| 21. Iijoki | 14191 | PPO |
| 22. Kiiminkijoki | 3814 | PPO |
| 23. Oulujoki | 22841 | PPO |
| 24. Siikajoki | 4318 | PPO |
| 25. Pyhäjoki | 3712 | PPO |
| 26. Lestijoki | 1372 | MM |
| 27. Perhonjoki | 2520 | MM |
| 28. Kruununpyynjoki | 746 | MM |
| 29. Ähtävänjoki | 2054 | MM |
| 30. Purmonjoki | 864 | MM |
| 31. Lapuanjoki | 4122 | MM |
| 32. Kyrönjoki | 1923 | MM |
| 33. Laihianjoki | 506 | MM |
| 34. Maalahdenjoki | 500 | MM |
| 35. Närpiönjoki | 992 | MM |
| 36. Teuvanjoki | 542 | MM |
| 37. Merikarvianjoki | 3438 | LOS |
| 38. Eurajoki | 1335 | LOS |
| 39. Aurajoki | 874 | LOS |
| 40. Paimiojoki | 1088 | LOS |
| 41. Kiskonjoki | 1046 | LOS |
| 42. Mustionjoki | 2045 | UYK |
| 43. Vantaanjoki | 1685 | UYK |
| 44. Mustijoki | 783 | UYK |
| 45. Porvoonjoki | 1270 | UYK |
| 46. Koskenkyläjoki | 895 | KAS |
| 47. Kyminjoki | 37158 | KAS |

SLU = Swedish University of Agricultural Sciences, Department of Environmental Assessment, LAP = Lapland Regional Environment Centre (Finland), PPO = North Ostrobothnia Regional Environment Centre (Finland), MM = Roos & Åström 2005b, LOS = Southwest Finland Regional Environment Centre, UYK = Uusimaa Regional Environment Centre (Finland), KAS = Southeast Finland Regional Environment Centre.

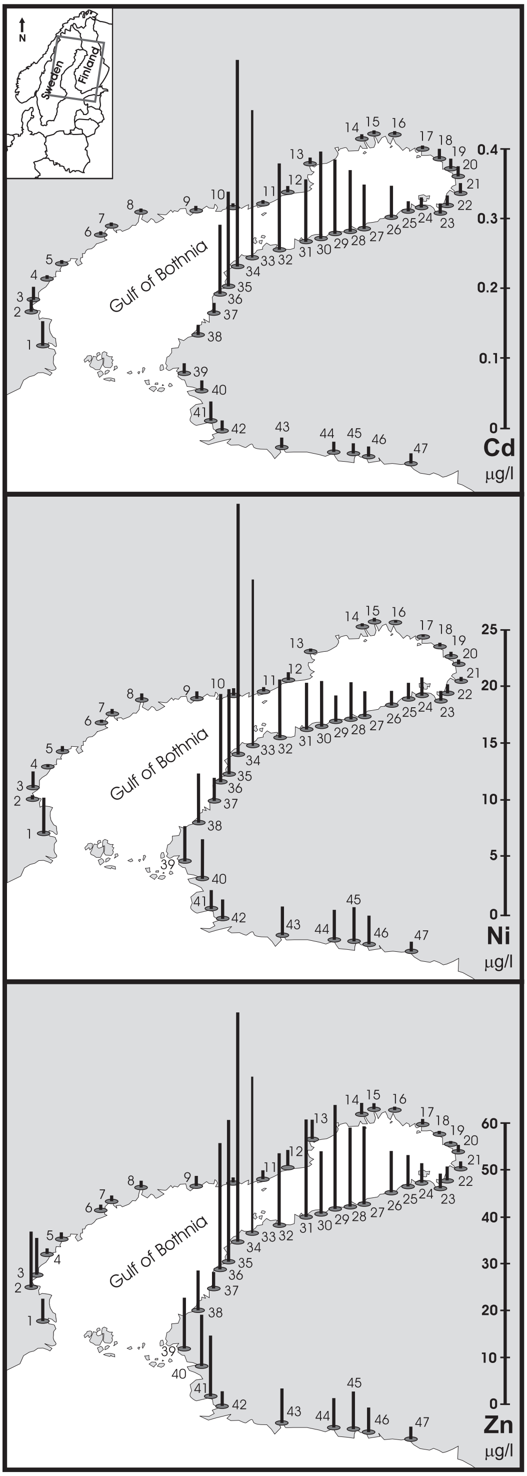


**Fig. 1**. Median concentrations of Cd, Ni and Zn in river waters. Names of rivers, sizes of their catchments (km$^2$) and data sources are listed in Table 1.

sequence of this area being highly enriched with AS soils. No thorough geochemical mapping of these soils has, however, been undertaken, but existing data indicate that 70% of the Finnish AS soils are located in this area. Consequently a larger part of the catchments in CW Finland consists of AS soils, as compared with others, and therefore in proportion leach more of these metals. Moreover, existing data show a correlation between high concentrations of these metals in river water and percentage arable land in the catchments, which strengthens since AS soils, in large quantities, exist under fields and arable land in CW Finland (Roos and Åström 2005b). The catchments in CW Finland are relatively small, 500–4122 km$^2$ (Table 1), which keeps dilution of the metal-rich AS waters low as compared with that in larger rivers. This contributes to the high concentrations. It is also possible that, due to some as yet unidentified geochemical characteristic, the AS soils in CW Finland are more potent and problematic than AS soils elsewhere along the Gulf of Bothnia (e.g. contains more easily dissolved metals or sulphides) and/or land use activity (catchments are more and/or deeper drained). Important potential anthropogenic sources of Cd, Ni and Zn are chemical industries, fertilizing, mining, paints, pigments and refining of petroleum (Siegel 2002). In CW Finland, where the high concentrations occur, there are no more (or larger) such anthropogenic metal sources than anywhere else along the Gulf of Bothnia. The highest concentrations of Cd and Ni in river waters do not e.g. occur close to the chemical industry in Kokkola City (Fig. 1, river 27). The contribution from anthropogenic sources with regards to river water Cd, Ni and Zn in CW Finland is thus of secondary importance. AS soils do however exist throughout the coastal plains of the Gulf of Bothnia, although precise locations are unknown due to insufficient mapping. Therefore, AS-soil affected rivers, with catchments < 500 km$^2$, possibly exist also elsewhere than in CW Finland. These were, however, not identified in this study.

The concentrations of metals As, Cr, Fe and Pb were not elevated in rivers in CW Finland, which is entirely in line with earlier studies which show that these metals are not part of the sequence of metals extensively liberated from boreal AS-soils (Eden *et al*. 1999, Sohlenius and Öborn 2004, Roos and Åström 2005b). These metals do, however, often occur in higher concentrations in the Finnish rivers as compared with those in the Swedish ones. The median concentration of As, Cr, Fe and Pb in Finnish rivers were 0.73, 1.27, 1450 and 0.50 $\mu$g $l^{-1}$, respectively, and in Swedish rivers 0.20, 0.22, 253 and 0.09 $\mu$g $l^{-1}$, respectively. The Swedish catchments are generally larger than the Finnish ones (Table 1) and thus can contain large areas of soil types that do not release particularly much metal which can lead to a greater dilution of the more metal-rich waters discharged from a variety of possible sources. It is particularly interesting that the concentration of Fe, which exists abundantly in AS soils, is not elevated in stream waters in CW Finland. The low level of Fe leaching from AS soils is believed to be a result of efficient Fe re-precipitation along semi-oxic soil cracks and in the drains (Österholm 2005). Precipitation and retention of Fe has also been found in AS-soils in Sweden (Öborn 1991) and Thailand (van Breemen and Harmsen 1975, Harmsen and van Breemen 1975).

## Conclusions

Potentially toxic metals (PTMs) in our environment originating from anthropogenic sources (e.g. discharge from industry, traffic, energy production) are often in focus when debating metal pollution, while PTMs originating from geological sources are more often forgotten or related to less seriously. Therefore it is exceedingly important that we hereby highlight CW Finland (rivers 24–36, Fig. 1) as having substantially increased concentrations of the PTMs Cd, Ni and Zn as a result of leaching from AS soils. Work to reduce the high metal concentrations in this "hotspot area" should be equally evident as counteracting discharge from anthropogenic point sources. This should include thorough planning, which is currently not the case, of all sorts of drainage operations (e.g land reclamation through ditching, dredging of rivers and estuaries, etc.) in AS-soil landscapes. Actions to lower the metal concentrations and counteract their negative effects on the aquatic environment will be facilitated by the fact that the most polluted rivers are relatively small. For the metalloid As and metals Cr, Fe and Pb, which are not leached abundantly from these soils, no immediate counteractions are needed.

We also want to emphasize that in this paper we present concentrations only and not loads, for which a flow-based study is needed. The biggest difference between these parameters is that the former have immediate and direct effect on aquatic life and water quality, while the latter is a parameter which contributes to the total metal loads on the estuaries and the sea (in this case the Gulf of Bothnia).

By combining our own data with different registers of water quality, spatially extensive hydrochemical patterns were identified. This is thus a good example of how different water-quality registers, composed of thoroughly performed and documented water samplings, are of great scientific value and are often underutilized for these purposes. By further decrease of costs and increase in availability, particularly on the Finnish side, these registers would find an even larger number of scientists and environmentalists.

*Acknowledgements*: The study was financially supported by Äspö Research School and Renlunds stiftelse. Asko Sydänoja, Jouni Näpänkangas, Jouni Törrönen, Karl-Erik Storberg, Leena Villa and Markku Örn kindly provided information regarding the catchment areas in Finland.

## References

Andriesse W. & van Mensvoort M.E.F. 2002. Distribution and extent of acid sulphate soils. In: Lal R. (ed.), *Encyclopedia of soil science*, Marcel Dekker Inc., New York, pp. 1–6.

Åström M. 2001. Effect of widespread severely acidic soils on spatial features and abundance of trace elements in streams. *Geochemical Exploration* 73: 181–191.

Åström M. & Björklund A. 1997. Geochemistry and acidity of sulphide-bearing postglacial sediments of western Finland. *Environmental Geochemistry and Health* 19: 155–164.

Bloomfield C. & Coulter J.K. 1973. Genesis and management of sulphate soils. *Advances in Agronomy* 25: 265–326.

van Breemen N. & Harmsen K. 1975. Translocation of iron in acid sulphate soils — Soil morphology, and the chemistry and mineralogy of iron in a chronosequence of acid sulfate soils. *Proceedings — Soil Science Society of America* 39: 1140–1148

Brown T.E., Morley A.W., Sanderson N.T. & Tait R.D. 1983.

Report of a large fish kill resulting from natural acid water conditions in Australia. *Journal of Fish Biology* 22: 335–350.
Callinan R.B. 1997. *Pathogenesis of red spot disease (Epizootic Ulcerative Syndrome) in estuarine fish in eastern Australia and the Philippines*. Ph.D. thesis, the University of Queensland, Brisbane.
Dent D.L & Pons L.J. 1995. A world perspective on acid sulphate soils. *Geoderma* 67: 263–276.
Dost H. & Pons L.J. 1970. *Provisional report on the soil conditions in the protected part of the Orinoco delta with a map of soil landscapes and some preliminary conclusions*. IRI Research Inst. Inc. Venezuela, Orinoco Delta Project.
Fitzpatrick R.W., Powell B., McKenzie N.J., Maschmedt D.J., Schoknecht N. & Jacquier D.W. 2003. Demands on soil classification in Australia. In: Eswaran H., Rice T., Ahrens R. & Stewart B.A. (eds.), *Soil classification: a global desk reference,* CRC Press, pp. 1–280.
Green D. 1993. Rivers of death. *Fishing World* April: 38–43.
Harmsen K. & van Breemen N. 1975. Translocation of iron in acid sulphate soils — production and diffusion of dissolved ferrous iron. *Proceedings — Soil Science Society of America* 39: 1148–1153.
Hart B.T., Ottaway E.M. & Noller B.N. 1987. Magela Creek system, Northern Territory, Australia. I. 1982–1983 wet season water quality. *Australian Journal of Marine and Freshwater Research* 38: 261–288.
Hart M.G.R., Carpenter A.J. & Jeffery J.W.U. 1963. Problems in reclaiming saline mangrove soils in Sierra Leone. *Agronomia Tropical* (Paris) 18: 800–802.
Hudd R. & Leskelä A. 1998. Acidification-induced species shifts in coastal fisheries off the River Kyrönjoki, Finland: a case study. *Ambio* 27: 535–538.
Ke C. & Wang W.-X. 2001. Bioaccumulation of Cd, Se, and Zn in an estuarine oyster (*Crassostrea rivularis*) and a coastal oyster (*Saccostrea glomerata*). *Aquatic Toxicology* 56: 33–51.
Lahermo P., Väänänen P., Tarvainen T. & Salminen R. 1996. *Geochemical atlas of Finland, part 3: environmental geochemistry — streamwaters and sediments*. Geol. Survey Finland, Espoo.
Marius C. 1985. *Mangroves du Sénégal et de la Gambie: écologie, pédologie, géochime, mise en valeur et aménagemaent*. Travaux et Documents, Paris, Orstrom.
Mathew E.K., Panda R.K. & Nair Madhusudan 2001. Influence of subsurface drainage on crop production and soil quality in a low-lying acid sulphate soil. *Agricultural Water Management* 47: 191–209.
Moormann F.R. 1961. *The soils of the Republic of Viet Nam*. Ministry of Agriculture, Saigon (separate map 1:1 million).
Netherlands Delta Team 1973. *Inventory of land resources, part 1. Mekong delta, South Vietnam*. Tech. Note 10, Committee for Co-ordination of Investigations of the Kowor Mekong Basin, Bangkok (separate land resource map 1:620 000).
Öborn I. 1989. Properties and classification of some acid sulphate soils in Sweden. *Geoderma* 45: 197–219.
Öborn I. 1991. Some effects of chemical weathering in three cultivated acid sulfate soils in Sweden. *Developments in Plant and Soil Sciences* 45: 55–63.
Österholm P. 2005. *Previous, current and future leaching of sulphur and metals from acid sulphate soils in W Finland*. Ph.D. thesis, Åbo Akademi, Finland.
Palko J. 1994. *Acid sulphate soils and their agricultural and environmental problems in Finland*. Ph.D. thesis, University of Oulu, Finland.
Powell B. & Martens M. 2005. A review of acid sulfate soil impacts, actions and policies that impact on water quality in Great Barrier Reef catchments, including a case study on remediation at East Trinity. *Marine Pollution Bulletin* 51: 149–164.
Roach A.C. 1997. The effect of acid water inflow on estuarine benthic and fish communities in the Richmond River, N.S.W., Australia. *Australian Journal of Ecotoxicology* 3: 25–56.
Roos M. & Åström M. 2005a. Seasonal and spatial variations in major and trace elements in a regulated boreal river (Esse River) affected by acid sulphate soils. *River Research and Application* 21: 351–361.
Roos M. & Åström M. 2005b. Hydrochemistry of rivers in an acid sulphate soil hotspot area in western Finland. *Agricultural and Food Science* 14: 24–33.
Sammut J. 1998. *Associations between acid sulphate soils, estuarine acidification and gill and skin lesions in estuarine and freshwater fish*. Ph.D. thesis, School of Geography, Faculty of Science and Technology, The University of New South Wales, Sydney.
Siegel F.R. 2002. *Environmental geochemistry of potentially toxic metals*. Springer, Berlin–New York.
Sohlenius G. & Öborn I. 2004. Geochemistry and partitioning of trace metals in acid sulphate soils in Sweden and Finland before and after sulphide oxidation. *Geoderma* 122: 167–175.
Yli-Halla M. 1997. Classification of acid sulphate soils in Finland according to soil taxonomy and the FAO/UNESCO legend. *Agricultural and Food Science* 6: 247–258.
Yli-Halla M., Puustinen M. & Koskiaho J. 1999. Area of cultivated acid sulfate soils in Finland. *Soil Use Manage*. 15: 62–67.