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## Science of the Total Environment

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# Weight-of-evidence approach in assessment of ecotoxicological risks of acid sulphate soils in the Baltic Sea river estuaries



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#### HIGHLIGHTS

- · Acid sulphate soils release high amounts of metals and acidity.
- Metals and acidity are transported to estuary sites.
- Acid sulphate soils impair the ecological status of several Baltic Sea estuaries.
- · More information is needed on low salinity estuaries.

#### ARTICLE INFO

# Article history: Received 6 October 2014 Received in revised form 31 October 2014 Accepted 23 November 2014 Available online 12 December 2014

Editor: C.E.W. Steinberg

Keywords: Acid sulphate soil Baltic Sea Metal Risk assessment WoF.

#### ABSTRACT

Acidity and leaching of metals from acid sulphate soils (ASSs) impair the water quality of receiving surface waters. The largest ASS areas in Europe are found in the coasts of the northern Baltic Sea. We used weight-ofevidence (WoE) approach to assess potential risks in 14 estuary sites affected by ASS in the Gulf of Finland, northern Baltic Sea. The assessment was based on exposure and effect profiles utilizing sediment and water metal concentrations and concurrent pH variation, sediment toxicity tests using the luminescent bacterium Vibrio fischeri and the midge Chironomus riparius, and the ecological status of benthic macroinvertebrate communities. Sediment metal concentrations were compared to national sediment quality criteria/guidelines, and water metal concentrations to environmental quality standards (EQSs). Hazard quotients (HQs) were established for maximum aluminium, cadmium and zinc concentrations at low pH based on applicable US EPA toxicity database, Sediment metal concentrations were clearly elevated in most of the studied estuaries. The EQS of cadmium (0.1 µg/l) was exceeded in 3 estuaries out of 14. The pH-minima were below the national threshold value (5.5) between good and satisfactory water quality in 10 estuaries. V. fischeri bioluminescence indicated toxicity of the sediments but toxic response was not observed in the C. riparius emergence test. Benthic invertebrate communities were deteriorated in 6 out of 14 sites based on the benthic invertebrate quality index. The overall ecotoxicological risk was assessed as low in five, moderate in three and high in five of the estuary sites. The risk assessment utilizing the WoE approach indicated that harmful effects of ASSs are likely to occur in the Baltic Sea river estuaries located at the ASS hotspot area.

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#### 1. Introduction

Acid sulphate soils (ASSs) are described as the nastiest soils in the world (Dent and Pons, 1995). This is due to their ability to generate sulphuric acid and extremely low pH to water phase. ASSs have developed in coastal areas mainly during Holocene as a result of microbial

activity which reduced sulphide rich sediments under anoxic conditions. Global area of ASSs is approximately 12 to 13 million hectares, mainly in tropical areas (Andriesse and van Mensvoort, 2006).

Finland has the largest ASS area in Europe (Roos and Åström, 2005). ASSs in Finland have been formed during Litorina period of Baltic Sea, approximately 4000–8000 bp (Palko, 1994). Area of ASSs has been estimated to cover 1600–3400 km² in Finland (Andriesse and van Mensvoort, 2006; Palko, 1994). The particular feature of Finnish ASSs is generally low sulphur content and buffering capacity in comparison to the tropical ASSs (Dent and Pons, 1995; Yli-Halla et al., 1999; Åström and Björklund, 1997).

When ASSs are exposed to oxygen, sulphides are rapidly oxidized and sulphuric acid is formed (Dent and Pons, 1995). Draining of ASSs

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for agriculture and other land use activities enhances oxidation of sulphide layers and consequent formation of sulphuric acid and leaching of metals. Thus acid runoff and high concentrations of dissolved metals have deteriorated ecological and chemical status of water bodies for centuries along the western coast of Finland. Massive drainage of ASSs for agricultural purposes occurred during 1960s and 1970s in Finland (Saarinen et al., 2010; Åström et al., 2005), and it has been estimated that metal loads from ASSs exceed the metal discharges of industrial effluents (Sundström et al., 2002). It is expected that climate change will increase acid runoff from ASSs (Saarinen et al., 2010).

Metals known to be abundantly leached from the Baltic ASSs include aluminium (Al), cadmium (Cd), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni) and zinc (Zn) (Boman et al., 2010; Nordmyr et al., 2008a; Åström and Björklund, 1997; Åström and Corin, 2000; Åström and Spiro, 2000). Acidity and high metal concentrations may have detrimental effects on biodiversity and community structure of fish, benthic invertebrates and aquatic plants (Fältmarsch et al., 2008). Occasional large fish kills are distinct effects of acidity and metal exposure. Acidity and high metal concentrations also impair reproduction, development and metabolism of fish (Hudd, 2000).

Concentrations, behaviour and speciation of metals in water bodies, especially estuaries, affected by runoff from ASSs are yet largely unknown (Fältmarsch et al., 2008; Nystrand et al., 2012; Åström and Corin, 2000). Therefore assessing hazardous effects of ASSs is challenging. Estuaries are considered as ecologically sensitive environments since their water chemistry, *e.g.* pH and salinity levels, varies according to rainfall, river discharge, tides and the overall climate conditions. In Finland, estuaries are unique environments since they locate in the coastal areas of Baltic Sea where tide is negligible and salinity is low (1–2‰) compared to tidal estuaries, and where salinity level fluctuations are mostly affected by the river discharge.

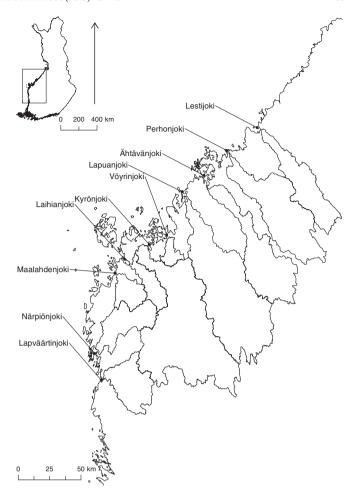
Weight-of-evidence (WoE) approach consists of multiple lines of evidence (LoE) (Chapman, 2007). Different LoE include screening of contaminant levels, evaluating their bioavailability and effects (Chapman, 2007; EPA, 1998). Laboratory and field toxicity tests are often included also. Different lines of evidence are weighed and based on the evidence, the risk of studied contaminants in the environment is determined. It is a flexible method, and WoE approach can be assembled individually to each studied subject area. WoE approach is suitable in comprehensive risk assessments, because evaluation of all the available data is by definition required (EPA, 1998), and it has been applied successfully in various subject areas (Chapman, 2007; Wolfram et al., 2012).

The objective of this study was to characterize ecotoxicological risks in 10 Baltic Sea river estuaries affected by ASS hotspot area based on their exposure and effect profiles using a WoE approach. Environmental quality objectives set by EU Water Framework Directive (WFD, Directive 2000/60/EC) call out for detailed information on the chemistry and biology of estuaries; hence, we addressed the following questions: 1) do the metal concentrations in water and sediment deviate from Environmental Quality Standards (EQSs) set by WFD and other applicable guidelines regulating metal pollution, 2) do the estuary sediments have toxic effects on biota, and 3) does the ecological status of estuaries reach the WFD quality objectives?

#### 2. Material and methods

#### 2.1. Study area

The study area is located in the Western coast of Finland and is comprised of 10 river estuaries in the Gulf of Bothnia (Fig. 1). All estuaries are affected by ASS runoff, but the exact area of ASSs in river catchments is unknown. River catchments ranged from 500 km<sup>2</sup> to 4923 km<sup>2</sup> and cultivated area upstream estuaries from 63 km<sup>2</sup> to 1160 km<sup>2</sup>.



**Fig. 1.** Study area, estuaries and their upstream river catchment areas. Base map: © MML, 2013 Catchment areas: © SYKE, 2013.

#### 2.2. Problem formulation

We followed the ecological risk assessment (ERA) procedure of US EPA (1998). Problem formulation included gathering the available information, evaluating nature and significance of the risk and developing a conceptual model for risk assessment (Fig. 2). Data and risk characterization plans were developed. Good ecological and chemical status of estuaries was defined as assessment endpoints, *i.e.* the environmental values to be protected.

#### 2.3. Exposure and effect assessment

#### 2.3.1. Water and sediment quality

Water quality data was obtained from the database of Finnish Environment Institute (HERTTA version 5.6). Water quality monitoring results for Al, As, Cd, Co, Cr, Cu, Pb, Ni, Zn, alkalinity, conductivity, total organic carbon (TOC), salinity and pH were collected from March 2009 to September 2010 to represent exposure conditions prevailing during the field work period of our study, and preceding time frame covering 19 months and three flood periods. Monitoring locations near river mouths were selected to represent estuary conditions in case no water quality measurements in the estuary area existed.

Sedimentation rates have been determined from the estuaries of R. Kyrönjoki and R. Vöyrinjoki, and they are approximately 1 cm/a and 4–5 cm/a, respectively (Heikkilä, 1999; Nordmyr et al., 2008a). Surface sediment samples (0–3 cm) were collected during the summer and autumn of 2010 from 10 different estuaries and 14 sample locations to

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