

## Environmental risks of metals mobilised from acid sulphate soils in Finland: a literature review

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Received 30 Mar. 2007, accepted 8 Oct. 2007 (Editor in charge of this article: Johanna Mattila)

Fältmarsch, R. M., Åström, M. E. & Vuori, K.-M. 2008: Environmental risks of metals mobilised from acid sulphate soils in Finland: a literature review. *Boreal Env. Res.* 13: 444–456.

The objective of this study was to review the available research information on the environmental risks and effects of metals leached from Finnish acid sulphate soils. The reason for carrying out this study was recent evidence demonstrating that much larger quantities of a number of metals are leached from these soils than from the entire Finnish industry taken together. Alarming few scientific studies on the actual biological impacts of acid sulphate soils have been published. However, they all indicate an extensive and serious effect on biota, including metal imbalance in crops and elevated concentrations of Al and Zn in the milk of cows. Acid sulphate soils have also significant, but spatially and temporally variable impacts on biodiversity and community structure of fish, benthic invertebrates and macrophytes, with numerous cases of mass fish kills along the Finnish coast. Furthermore, chronic exposure to high concentrations of metals may pose an actual threat on human health. The potential risks for Alzheimer's and Parkinson's disease in acid sulphate soil landscapes are discussed.

### Introduction

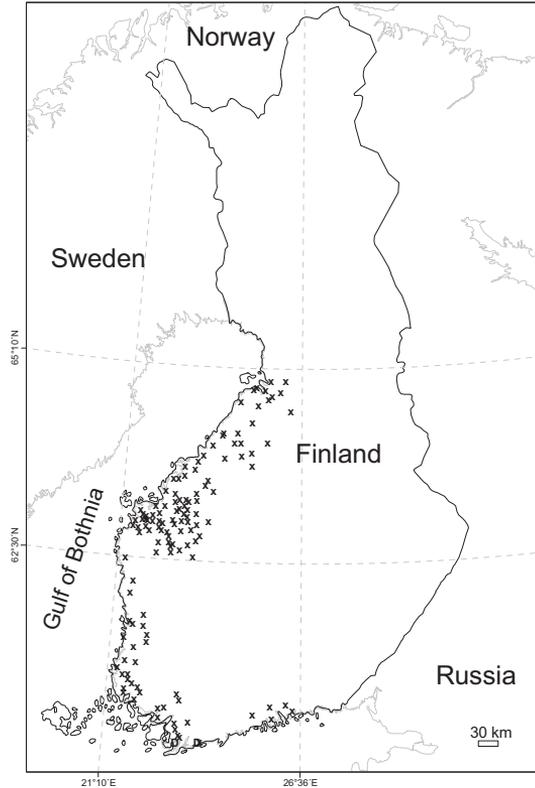
From an environmental point of view, acid sulphate (a.s.) soils are regarded as the most problematic soils in the world (Dent and Pons 1995). They develop where sulphide-rich sediments, low in carbonates, are exposed to atmospheric oxygen resulting in sulphide oxidation and thus formation of sulphuric acid. This lowers the soil pH to values between 2.5 and 4.5, and as a consequence, adjacent drains are often severely acidified. An associated problem is metals, which are released in the soils from both dissolving metal sulphides

and other minerals such as metal-bearing aluminosilicates, thus becoming available for transport and leaching. The a.s. soils occur mainly in coastal lowlands, where population and development pressures are as highest causing a need for reclamation and drainage of these sediments. The a.s. soils currently cover a total of approximately 17–24 million ha in the coastal regions worldwide, with major occurrences in Africa, eastern Australia, Asia and Latin America (Ritsemaa *et al.* 2000, Andriessse and van Mensvoort 2002).

In Europe, the largest a.s. soil occurrences are found in Finland (1600–3000 km<sup>2</sup>) (Palko

1994, Yli-Halla *et al.* 1999, Andriessse and van Mensvoort 2002) and Sweden (500–1400 km<sup>2</sup>) (Öborn 1994, Andriessse and van Mensvoort 2002) (Fig. 1). They have developed mainly on fine-grained sulphide-bearing sediments deposited during the Holocene in the brackish Baltic Sea and they are characterized by high sulphate concentrations, low pH, low volume weight and a high pore volume (Wiklander and Hallgren 1949, Palko 1994). The oxidation and weathering of these sulphide-rich sediments, which have risen above the sea level as a result of isostatic land uplift, have occurred as a result of artificial farmland drainage (Palko 1994, Österholm and Åström 2004, Österholm 2005). Intensification of this drainage, especially the utilisation of modern subsurface drainage techniques, have significantly increased mobility of metals and acidity (Erviö and Palko 1984, Palko and Yli-Halla 1988, 1990, Palko 1994, Öborn 1994, Dent and Pons 1995, Österholm and Åström 2002, Joukainen and Yli-Halla 2003, Sohlenius and Öborn 2004, Österholm 2005). This causes severe environmental problems in streams and rivers. However, the acidity and metal load from a.s. soils varies spatially, depending on the stage of development of the soil profile which in turn is controlled largely by drainage efficiency and inherent S abundance. Such spatial variations have not been mapped and can therefore not be considered in this review.

Despite the knowledge of the high amounts of metals and acidity mobilised in the a.s. soils on the coastal plains of Finland and Sweden, no comprehensive studies on the environmental risks of these soils, especially concerning metals, have been conducted. One reason for this is that while the acidity problems of these soils have been fairly well known for quite a time (Kivinen 1944, Wiklander and Hallgren 1949), the extensive pool of many metals mobilised in these soils has not been adequately understood until recently. The objective of this study was to review current available research information on the environmental risks and effects of metals mobilised in the Finnish a.s. soils. In the next chapter, before discussing the environmental and biological aspects, some important hydro-geochemical features of the boreal (Finnish) a.s. soils are discussed.



**Fig. 1.** Distribution of acid sulphate soils developed in Holocene fine-grained sediments in the coastal areas of Finland. The mapping survey covered a total of 740 randomly selected agricultural field sites along the coast, of which 20% was identified as an acid sulphate soil site. Each cross represents approximately 20 km<sup>2</sup> acid sulphate soil. (Modified from Palko (1994)). All acid sulphate soil studies referred to in this paper are located within 62°30'–65°10'N and 21°10'–26°38' E.

## Occurrence and behaviour of chemical elements in boreal acid sulphate soils

### Aluminium (Al)

Aluminium is not particularly abundant (in the order of a few percent) and it occurs as aluminosilicate and probably Al-hydroxide in the Finnish a.s. soils. It is, however, very mobile due to the characteristic acidic conditions (pH 2.5–4.5), which promote aluminosilicate weathering and Al-hydroxide dissolution and thus Al solubilisation and transport. The Al concentration in drainage water from a.s. soils correlates strongly with pH and concentrations up to 260 mg l<sup>-1</sup> has been

observed in small drains (Åström and Björklund 1995). Furthermore, due to Al hydrolysis, acidification increases and thus, additional metals are released and leached into the aquatic ecosystem (Palko 1994). Åström and Corin (2000) showed that Al exist mainly in cationic form in a.s. soil affected watercourses. Aluminium is one of the most enriched elements in drainage water from a.s. soils.

### **Cobalt (Co), Nickel (Ni), Zinc (Zn), Cadmium (Cd), Manganese (Mn)**

High total concentrations of Co, Ni, Zn, Cd and Mn do not normally exist in a.s. soils as compared with sulphide-free clay soils (Sohlenius and Öborn 2004). However, in the a.s. soils these metals are partly integrated in sulphides (Åström 1998a). Consequently, the oxidation and weathering of these sulphides, as a result of soil acidity and increasing redox potentials, increases the mobility of these metals (Palko and Yli-Halla 1988, 1990). Furthermore, weathering of other minerals (e.g. aluminosilicates) also contributes to the increased mobilisation of these metals (Sohlenius and Öborn 2004). This eventually results in extensive leaching of Co, Ni, Zn, Cd and Mn to nearby watercourses, in particular during heavy rainfall in summer and autumn and snow melting in spring, resulting in concentrations that are up to 50, 30, 20, 10 and 30 times higher, respectively, than typical background values of the region (runoff from areas covered by forests underlain mainly with till, peat and/or glaciofluvial material) (Åström and Björklund 1996, Åström 2001a, 2001b, Roos and Åström 2005, Österholm *et al.* 2005). Furthermore, the concentrations of Co, Ni, Zn, Cd, Mn and the above mentioned Al, are very high in streams affected by a.s. soils as compared with average values for Finnish and Fennoscandian rivers (Edén and Björklund 1993, Lahermo *et al.* 1996, Åström 2001a, 2001b). It has been estimated that the current amount of leakage of these metals from the Finnish a.s. soils is 10 to 100 times higher than the effluent discharges from the entire Finnish industry (Fig. 2). These metals are generally associated with the cationic fraction in the waters draining a.s. soils (Åström and Corin 2000).

### **Chromium (Cr)**

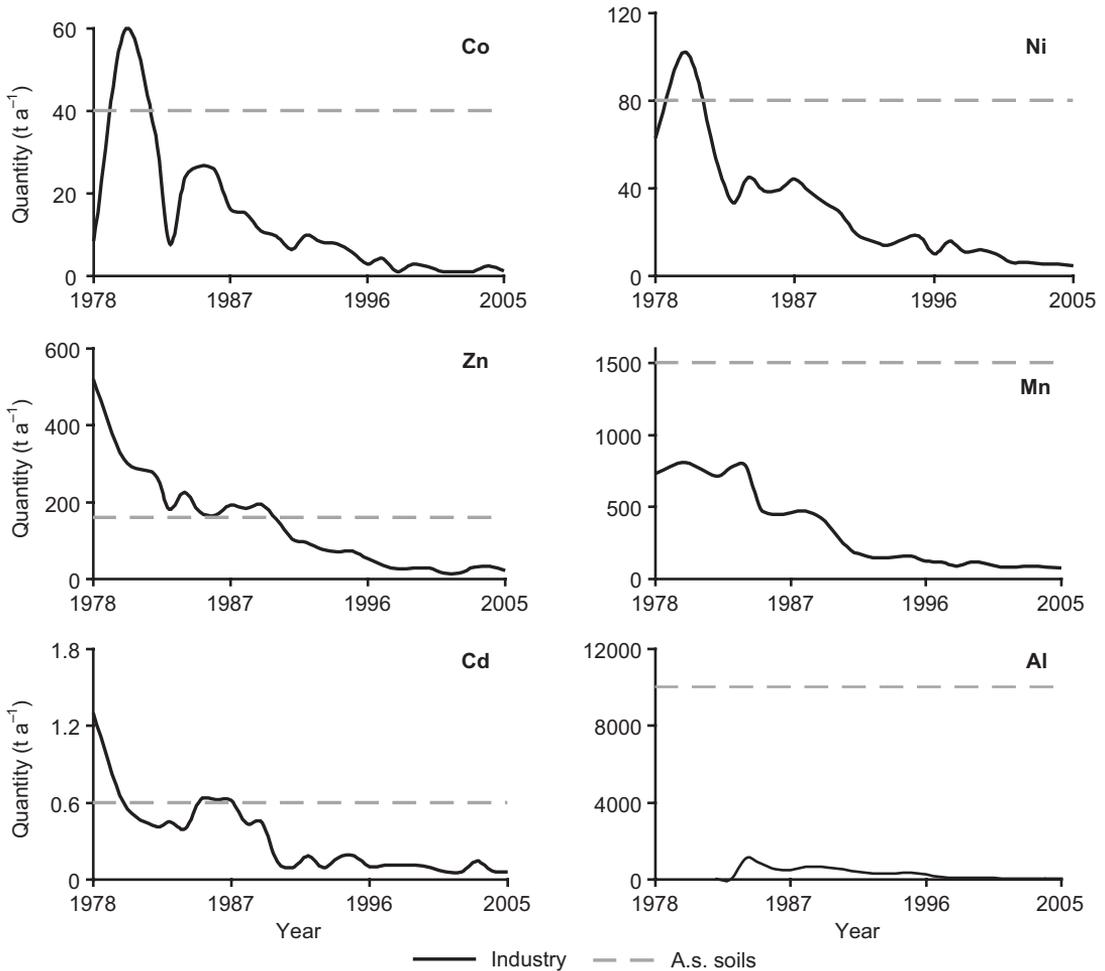
Chromium is generally less soluble than Zn, Co, Ni, Mn or copper (Cu) in a.s. soils (Palko and Yli-Halla 1990) and thus, only mobilised to a limited extent upon oxidation and acidification. According to Palko and Yli-Halla (1990), Cr responds only marginally to acidification. Consequently, Cr is commonly only weakly enriched in the a.s. soil affected waters (Åström and Björklund 1995). However, particularly acidic conditions (pH 2.5–3.5) in a.s. soils or affected ditches can mobilise Cr in relatively large amounts, nevertheless, not in the same quantity as Co, Ni and Zn (Åström 2001b). Chromium exists mostly as anionic species in a.s.-soil-affected surface waters and its distribution is governed to a large extent by formation of complexes with humic and fulvic acids (Lahermo *et al.* 1996, Åström and Corin 2000).

### **Iron (Fe)**

Iron is not particularly abundant in the a.s. soil, but it occurs as sulphide in the order of 0.5%–1.0%. After release from these minerals, it is largely precipitated as insoluble Fe hydroxides in the soil profile and in drainage pipes. Therefore, Fe is not leached more extensively from a.s. soils as compared with other types of nearby boreal soils (e.g. glacial till and peat) (Åström and Corin 2000) and therefore, leaching to adjacent watercourses is limited (Åström and Åström 1997, Österholm 2005). However, increased amounts (up to 100 mg l<sup>-1</sup>) of Fe have been observed in some particularly acidic a.s. waters (pH ~2.5–3.0). Iron is according to Åström and Corin (2000) predominantly associated with the anionic fraction in stream waters draining the a.s. soils.

### **Phosphorus (P), Magnesium (Mg), Potassium (K), Calcium (Ca)**

The concentration of P, K and Ca in cultivated a.s. soils are similar to Finnish average values (FAV) of cultivated soils, while Mg is found in higher concentrations in the former (Erviö and Palko 1984). Phosphorus and Mg are gener-



**Fig. 2.** Estimated metal discharges in effluent from the Finnish industry and in runoff from acid sulphate soils in 1978–2005, expressed as tonnes per year ( $t a^{-1}$ ). Data for Al during 1978–1980 do not exist. Figure modified and updated from Sundström *et al.* (2002).

ally associated with easily dissolved minerals (clay minerals, mica) and K and Ca with poorly dissolved minerals (feldspars). Furthermore, P and Ca are also enriched in the plough layer of cultivated a.s. soils due to liming and fertilisation, respectively (Österholm and Åström 2002). Magnesium, K and Ca are leached out in moderate to large amounts, while the leaching of P is limited (Åström 1998b). Several hydrogeochemical studies show that abundant amounts of Mg, Ca and K exist in a.s. soil affected watercourses (Åström and Björklund 1995, Åström and Åström 1997) and the concentration of the former two metals correlate significantly with the titrable acidity in acid rivers (Palko 1994). A significant portion of Mg, K and Ca in the waters

may originate as sea salts once trapped in the pores of the parent sediments of the a.s. soils.

### Metal accumulation in crop plant species

The only published papers involving metal concentrations in crops grown on a.s. soils in Finland are those by Palko (1986) and Yli-Halla and Palko (1987) who studied oat and timothy samples collected from a few selected a.s. soil fields ( $64^{\circ}50'N$ ,  $25^{\circ}30'E$ ) (Fig. 1). These agricultural fields were managed in a way typical for a.s. soils including normal drainage management, liming and fertilization. They compared their results

with FAV for timothy and oat, the latter representing background values of mineral elements in these crops grown on different soils and in different regions of Finland. For a more detailed description on the metal concentrations in timothy and oat, the reader is referred to Kähäri and Nissinen (1978), Paasikallio (1978) and Varo *et al.* (1980a). Palko (1986) found timothy samples enriched in Ni (a.s. soils 1.8 mg kg<sup>-1</sup> and FAV 0.34 mg kg<sup>-1</sup>), Co (0.27/0.06), Al (23/12), Mn (95/67) and Cr (1.1/0.23) and Yli-Halla and Palko (1987) found elevated concentrations of Fe (142/60), Mn (136/72), Co (0.50/0.08) and Ni (6.4/2.8) in oat grains. Consequently, timothy and oat were both enriched in Mn, Co and Ni, metals which are mobile in a.s. soils. The accumulation of Fe in oat indicates that even if the metal is generally immobile in the Finnish a.s. soil, the plant roots can still mobilise the oxide-bound Fe in the soil and subsequently absorb it. However, Fe was not enriched in timothy (Palko 1986).

The Cr concentrations in plants are generally governed by the soluble content of the element in the soil (Kabata-Pendias 2001), and it is quite immobile in a.s. soils in comparison with e.g. Ni, Co and Mn (Palko and Yli-Halla 1990). Timothy grown on a.s. soils have still significantly elevated Cr concentrations as compared to FAV (Palko 1986). This contradiction could be explained by elevated solubility of Cr-bearing primary minerals in the very acidic conditions (pH ~3, in rare cases < 3) liberating plant available forms of Cr in the soil. However, the major part of these plant roots is located in the plough layer, where pH conditions are not favourable for Cr solubilisation due to liming management. It has also been reported that Mn-oxides are capable of oxidizing Cr<sup>3+</sup> to Cr<sup>6+</sup>, the latter being the most plant available and mobile form of Cr (Kabata-Pendias 2001). This could explain the elevated absorption in timothy.

Zinc, which is mobile in the a.s. soils and abundantly flushed into drains, is in the same range in oat and even deficient in timothy compared to FAV (40/43 and 23/32 mg kg<sup>-1</sup>, respectively) (Palko 1986, Yli-Halla and Palko 1987). This shows that the plant's absorption of this metal is not correlated to its concentration and mobility in the soil and soil water. Antagonistic effects (other metals inhibit Zn absorption) and

genotypical differences in plants may contribute to the low Zn concentrations in these crops (Alloway 2005, Combs 2005).

No significantly deviating concentrations of Ca, Mg, K and P were found in oats (Yli-Halla and Palko 1987), but deficiency of these elements was observed in timothy (Palko 1986) when compared to FAV (1.6/2.6; 0.94/1.3; 18/24 and 1.9/2.9 g kg<sup>-1</sup>, respectively) (Kähäri and Nissinen 1978, Varo *et al.* 1980a). The inhibited accumulation of Ca, Mg, K and P in timothy may be due to acidity induced metal toxicities (e.g. Mn and Al), which may be reflected as competitive elemental interactions (antagonism, e.g. Mn vs. Ca) and reduced cation uptake by plants due to the high availability of Al<sup>3+</sup> in the a.s. soil (Foy *et al.* 1978, Kabata-Pendias 2001).

## Metal accumulation in dairy cattle

Published scientific studies on metal levels in animal feeding on a.s. soils are scarce. The only one which we are aware of is a two year investigation (sampling 1991–1992) of cow milk originating from a.s. soil farms located in the drainage basin of the Kyrönjoki (river outlet at 63°09'N, 21°52'E; Fig. 1) (Alhonen *et al.* 1997). In that study it was concluded that the metal concentrations in the milk samples ( $n = 16$ ) originating from a.s. soils were relatively high as compared with FAV from other dairies (Varo *et al.* 1980b). The Zn and Fe concentrations in the milk samples from cows with indoor-feeding was approximately two times higher (a.s. soils ~5300 µg kg<sup>-1</sup> and reference material 3500 µg kg<sup>-1</sup>; 500/250), respectively, and the Al concentrations in the milk samples from cows with outdoor-feeding up to 50 times higher (2400/50), in comparison to the reference material. Aluminium is, as shown above, highly mobile in the a.s. soils and enriched in plants (timothy) on these soils, so its occurrence in high levels in the cow milk is not surprising and indicates an important pathway for this potentially toxic metal, i.e. soil → plant → milk. It should be pointed out that inorganic Al (Al<sup>3+</sup>) is highly toxic and any association/complexation with e.g. dissolved humic matter and/or hydroxides detoxifies it. The speciation of Al in cow milk was not determined by

Alhonen *et al.* (1997).

As discussed above, also Zn is highly mobile in the a.s. soil, but in contrast to Al, it is not enriched in either of the plants investigated on the a.s. soil (previous chapter). However, the plant studies are very few so spatial variation and locally (regionally) high concentrations of Zn in a.s. soil-grown plants cannot be excluded. Zinc is, however, not generally associated with intoxication in animals and its enrichment in cow milk originating from a.s. soil farms was small. Iron is not leached abundantly from the a.s. soils, but it is still enriched in both oat and cow milk. Chromium, which was enriched in timothy (previous chapter), was not elevated in the milk samples originating from the a.s. soil farm. However, K, Mg and Ca, which are abundantly leached from a.s. soils, were deficient in timothy (previous chapter) and also in milk samples from cows with out-door feeding on a.s. soils, as compared with the reference material. This highlights the complex nature of the biogeochemical cycles of chemical elements in these settings. In the study by Alhonen *et al.* (1997), no attention was paid to the geochemistry of the a.s. soil, the elemental composition of the feedstuffs or the vegetation on the a.s. soil pasture-ground. This, in addition to the very limited number of data, makes the patterns outlined above indicative only, but they certainly highlight the need for more studies. In addition, it was suggested by Coni *et al.* (1995) that large or small variations in concentrations and the chemical form of elements in feedstuffs will affect the element content of cow's milk significantly. At present, therefore, we have very little knowledge as to what extent and how the a.s. soil affect metal concentrations in animals, except for the obviously high contents of Al in cow milk.

## Metal accumulation in aquatic plants and invertebrates

It is well known that e.g. aquatic roots of sedge (*Carex* species), meadowsweet (*Filipendula ulmaria*) and shoots of water moss (*Fontinalis antipyretica*) efficiently accumulate metals directly from the water, and rapidly respond to concentration fluctuations (Cenci 2000, Lax

2005). Therefore, these species were chosen for the biogeochemical mapping programme of Sweden, which today holds chemical data of these species from more than 30 000 small streams distributed throughout the country (Lax 2005). Because a.s. soils have a very large impact on stream-water metal concentrations in these northerly granitoid-dominated and sparsely populated regions, there has been an attempt to identify and map areas of a.s. soils using this extensive biogeochemical database. It has indeed been possible to locate a.s. areas (Lax 2005) which are poorly mapped over these regions, by using ratios between elements abundantly leached from a.s. soils (e.g. Ni, Y) to those not significantly leached from these soils (e.g. Pb), and by combining such ratios with existing Quaternary geological maps. The success with this approach shows basically three things: (1) biogeochemical data can be used to map pedological and geological features, (2) the above mentioned aquatic species efficiently accumulate metals in abundances correlating with those in the ambient aquatic phase, and (3) a.s. soils have a large impact on stream-water quality in Sweden, which in terms of climate, geology and topography is very similar to Finland.

Several studies were conducted dealing with metal accumulation in aquatic mosses as a direct cause by Finnish a.s. soils (Vuori and Sirén 1996, Vuori 2002). Aquatic mosses (*Fontinalis antipyretica*) were collected for a period of three years in three relatively large rivers (Kyrönjoki, 63°09'N, 21°52'E; Lestijoki, 64°03'N, 23°39'E and Perhonjoki, 63°49'N, 23°16'E, including upper and lower reaches) (Fig. 1) draining, to some extent, a.s. soils in western Finland (Vuori 2002). High concentrations of Al, Cu and Fe, but not of Zn, were found in these mosses (Vuori 2002). The enhanced liberation of Al and Cu in the a.s. soil and the subsequent leaching to adjacent waters is thus apparent as accumulation in these mosses. Consequently, the concentration of Al in the various media (stream water, aquatic moss, crops, cow milk) is an effect of the a.s. soil and its management. As discussed above, Fe is not leached out in large amounts from boreal a.s. soils, but it is enriched in oat and milk samples originating from these soils. The same trend is obvious in the aquatic mosses. Hence, Fe leach-

ing is not seen in the existing hydrochemical and geochemical data but, in contrast, this metal still seems to become enriched in several plant and animal species existing in areas underlain with these soils. This contradiction indicates that the physiochemical speciation and bioavailability of Fe in the a.s. soils and waters needs to be investigated in more detail. Zinc was not enriched in the moss species despite the fact that this metal is strongly elevated in the a.s. waters. It is assumed that e.g. Mg and Na, which are leached out in large quantities from a.s. soils to nearby waters, will reduce the bioavailability of Zn and thus are aquatic mosses not applicable as bioindicators for Zn in such waters (Vuori 2002). Other elements (e.g. Mn, Co, Ni) leached out in large quantities from Finnish a.s. soils to recipient waters have not, to our knowledge, been included in moss analysis of the a.s. soil impacted streams.

Aquatic insect larvae (e.g. Trichoptera, Hydropsychidae) have been used as bioindicators in a.s. soil drained watercourses because of their potential to efficiently accumulate metals, their low variation in inter-species accumulation, their tolerance to exposure (inter-specific) and their ability to accurately display both temporal and spatial variations of pollution in streams (Vuori 1993, 1996, 2002, Vuori and Kukkonen 1996). Vuori and Kukkonen (1996) postulated that Al, Cd, Cu and Zn are readily absorbed in the tissues of aquatic insect larvae (*Hydropsyche pellucidula*, sampling period of two years) and Fe is predominantly adsorbed on the larval exocuticle in the a.s. soil affected Kyrönjoki. Generally, good correlation exist between the metal concentration (e.g. Al, Fe, Zn) in lotic Trichopteran larvae (Hydropsychidae) and in the a.s. soil drained water. However, Cd is an exception, probably due to high concentrations of e.g. Mn, which prevent the bioaccumulation of the metal or competition between metals for the binding sites (Vuori 1993, 2002). The Fe adsorption on cuticles of larvae in a.s. soil waters might be a direct consequence of Fe precipitation associated with the pH variations during the hydrological events. The occurrence of morphological abnormalities in anal papillae and ion-regulatory organs in Trichopteran larvae (*Hydropsyche*) due to the deteriorated water quality in these streams,

can according to Vuori and Kukkonen (1996) be used as an effective estimator of metal contamination in the aquatic phase.

## Ecotoxicological effects in aquatic organisms

Several biological field surveys and experimental studies demonstrate adverse effects of a.s. soils on aquatic plant and animal communities and populations in stream and estuarine environments. Several fish species (burbot, smelt) in the coastal areas and lower reaches of the rivers of western Finland have, in some sites, been wiped out (Hildén *et al.* 1982, Hudd *et al.* 1984). Also numerous cases of mass fish kills have occurred in these a.s. soil areas, the first documented case dates back to the early 1830s (National Board of Waters 1973). Acid sulphate soils are related to these events, since low pH values and high concentrations of metals, typical of waters from these soils, were measured during variable hydrological periods (e.g. heavy rainfall in autumn). It is well known that these factors can cause a number of ecotoxicological effects in fish. Failure in reproduction because of disturbances in the yolk and sperm formation and spawning behavior, damage in ion regulation and respiration organs, growth reduction or retardation, and changes in the behavioural pattern are examples of the effects in fish exposed to metals and/or their mixtures in association with the low pH (Beamish *et al.* 1975, Mount *et al.* 1988a, 1988b, Van Dijk *et al.* 1993, Heath 1995, Hudd 2000, Vuorinen 2000, Vuorinen *et al.* 2003). However, fish responses to acidity vary in time and space according to the severity and duration of exposure conditions. This is demonstrated e.g. by Hudd (2000), Kjellman (2003) and Urho *et al.* (1990), who compiled results on studies involving recruitment and growth of burbot (*Lota lota*), perch (*Perca fluviatilis*) and smelt (*Osmerus eperlanus*) in the large Kyrönjoki and its estuary in W. Finland. The results demonstrate that acidification originating from a.s. soils often overlaps with hatching of juveniles of spring spawning fish species, which leads to decreased population sizes. This concerns especially burbot. On the other hand, in the late 1980s and early 1990s the

most acid periods took place prior to spawning and hatching of juveniles, and population sizes consequently increased. Further, the field experiments conducted by Hildén and Hirvi (1987) in the estuary of the Kyrönjoki indicated that the survival of larval perch during the acid periods is dependent on the complex combination of the degree and duration of acidity, salinity gradients, aluminium speciation and overall water chemistry.

Impacts of a.s. soils on aquatic macrophytes have been much less studied than impacts on fish or macroinvertebrates. Results of Meriläinen (1989) suggested that impacts of periodically acidic waters of the Kyrönjoki had no significant effects on the species richness of macrophytes. A total of 22 species of aquatic vascular plants and luxuriant growth of dominant species (e.g. *Phragmites australis*, *Scirpus lacustris*, *Nuphar lutea*, *Nymphaea candida*) were observed in the a.s. soil affected inner estuary, which is the part of the catchment that is affected the most of the a.s. soils and where the most acidic conditions (pH ~4–5) prevail. However, distribution of some sensitive species was considered to indicate growth inhibition due to acidity. The outer estuary, which is not heavily loaded by a.s. runoff, was characterized by a rather sparse vegetation. Meriläinen (1989) concluded that the high nutrient status in the inner estuary might have alleviated the detrimental effects of monomeric inorganic Al on the aquatic vegetation.

As compared with macrophytes, estuarine invertebrate communities demonstrated an opposite pattern: the innermost estuary had impoverished fauna and low biomasses prevailed. It was hypothesized by Meriläinen (1989) that the combination of both periodic pH changes during flood events and heavy rainfall, and high contents of detrimental  $Al^{3+}$  is the probable cause of the low abundance and species richness in the inner estuary. The species density was clearly higher in the middle and the outer estuary, despite the distinct influence of the poor river water quality in the shallow parts of the middle estuary, too. Meriläinen (1989) suggested that other factors (e.g. salinity, sediment quality) tend to determine composition and abundance of zoobenthos in those parts of the estuary where influence of river water remains low.

Macroinvertebrate studies in river sites affected by a.s. soils have demonstrated impoverished species richness and absence of sensitive species (Nyman *et al.* 1986). Translocation experiments with hydropsychid caddis larvae verified that the most sensitive species were unable to survive acute field exposure to low acidity and high metal concentrations (Vuori 1996). High incidence of morphological abnormalities in ion-regulation and respiration organs appeared to impede larval development and growth. For the more tolerant species (*Hydropsyche angustipennis*) origin of the exposed population significantly affected the mortality: individuals collected from the a.s. soil affected river sites survived better and did not show any morphological abnormalities. Further laboratory studies verified that damage in the ion-regulation and respiration organs are associated with exposure to high metal concentrations and low acidity (Vuori 1996). As with the fish responses, also macroinvertebrate responses depend on the severity and duration of the exposure to acidity and metals. For example, during the dry periods in 2002, when pH conditions remained favourable, no morphological abnormalities were observed (Lassila and Vuori 2005). Also long-term macroinvertebrate monitoring results of the period 1981–2002 indicate recovery of macroinvertebrate communities (Teppo *et al.* 2004).

In summary, existing research evidence indicates that a.s. soils have significant, but spatially and temporally variable impacts on biodiversity and community structure of fish, benthic invertebrates and macrophytes. Although recovery has been demonstrated, the fact that even a single short-term exposure to low pH and high metal concentrations can cause loss of sensitive fish and macroinvertebrate species stresses the importance for decreasing loading of acidity and metals from a.s. soils. There is a general lack of detailed knowledge of the short-term dynamics of water chemistry and metal speciation in both estuarine and river environments under variable hydrological conditions. Such information would enable prediction of fish survival (Hildén and Hirvi 1987) and overall responses of aquatic communities. Furthermore, our knowledge on ecotoxicological impacts of a.s. soils is based on few river and estuary sites only. A more com-

prehensive research on the effects of a.s. soils in coastal rivers and estuaries is needed.

## Potential impacts on human health

The etiology of the most common neurodegenerative disorder, Alzheimer's disease (AD), is still unknown, but many risk factors contributing to the disease have been put forward (Amaducci *et al.* 1986, Flaten 1990, 2001, Gauthier *et al.* 2000, Zatta *et al.* 2003, Brown *et al.* 2005). Epidemiological studies linking Al and AD have received much attention over the last two decades and nine out of fourteen epidemiological studies showed significant positive association between drinking water Al and the incidence of AD (McLachlan *et al.* 1996, Rondeau *et al.* 2000, Flaten 2001, Zatta *et al.* 2003), however, others found no significant relations (Forster *et al.* 1995, Martyn *et al.* 1997). The reasons for these conflicting results could potentially be due to study type design, bias, confounding factors, diagnostic errors, bioavailability of Al (Flaten 2001, Brown *et al.* 2005). Another difficulty interpreting these results is that Al in drinking water only represents a small portion of the total dietary intake ( $\leq 10\%$ ), in fact drugs (e.g. antacid, buffered aspirin) contain high concentrations ( $\sim 1$  g/dose) of Al as compared with drinking water ( $\sim 0.01$ – $0.1$  mg l<sup>-1</sup>) (Flaten 2001, Gillette-Guyonnet *et al.* 2005). However, Flaten (2001) suggested that the epidemiological evidence supporting the antacid-AD causality was chiefly negative/not significant. Moreover, the link between Al speciation in drinking water and AD was studied by Gauthier *et al.* (2000) who found an association between monomeric organic Al and AD, however, no other forms of Al in drinking water were related to AD. It should also be noted that Al present in drinking water could presumably be more bioavailable than in foodstuff, but this is still a matter of controversy (Flaten 2001, Gillette-Guyonnet *et al.* 2005). However, studies dealing with Al in foodstuff and AD incidence are scarce (Rogers and Simon 1999). A statistically significant relationship was found between AD and elevated amounts of Zn and Fe in the brain, but not in

the pituitary gland (Cornett *et al.* 1998a, 1998b) nor in the hair and serum for the latter element (Shore *et al.* 1984). As shown above, Zn and Fe are enriched in cow milk (Alhonen *et al.* 1997) and Fe in oat (Yli-Halla and Palko 1987) in a.s. soil areas. In western Finland, where these soils are particularly abundant (Fig. 1) and affect the metal concentration of stream waters (Fig. 2), crops and milk, it is reasonable to assume that, at least locally on some temporal scale, the metal (e.g. Al, Zn) uptake by humans is elevated. Therefore, it can not be excluded that chronic exposure to the abundantly available Al may have potential impacts on human health. Thus, an obvious risk group would consist of people deriving their food (e.g. vegetables, milk), raw products and drinking water from local farmland consisting of these soil types supplying abundant amounts of soluble Al to the environment. It should be stressed that a systematic epidemiological study on the potential health risks of a.s. soils in Finland is urgently needed. In addition, research on the speciation of potentially toxic elements in raw milk in a.s. soil areas should be conducted before any conclusive results can be drawn on their potential effects on human health. More research is also needed on the elemental composition of e.g. well water in a.s. soil landscapes.

The findings of Tanner *et al.* (1999) showed that genetic factors do not seem to play a major role in the majority of cases of Parkinson's disease (PD), the second most widespread neurological disorder. However, several environmental risk factors (e.g. metals, pesticides) have been implicated with PD (Gorell *et al.* 1997, 2004, Gorell and Checkoway 2001, Priyadarshi *et al.* 2001, Baldi *et al.* 2003, Zatta *et al.* 2003, Uversky 2004, Brown *et al.* 2005). Occupational exposure to Mn has been significantly associated with PD (Gorell *et al.* 1997, 1998, 1999), but others found no association between Mn exposure and the development of PD (Seidler *et al.* 1996, McDonnell *et al.* 2003, Jankovic 2005). Nevertheless, caution should be taken in interpreting the results since many of the studies may have suffered from low power to detect outcomes. The overall high concentrations and widespread dispersion of Mn in the crops and stream water draining a.s. soils have received

little attention, probably due to that no conspicuous impact on human health have hitherto taken place, which however does not mean that there is none. There are evidence linking exposure to combined metals (Fe-Cu, Pb-Fe, Cu-Pb) with PD (Gorell *et al.* 1997, 1998, 1999, Gorell and Checkoway 2001). However, no link was found between Fe exposure alone and PD (Gorell *et al.* 1999), and according to Brown *et al.* (2005) other studies showed variable results for the relationship between exposure to Al, Cu, Pb, Hg, and Zn and PD. Although the release and solubility of Pb, Hg and Fe in the Finnish a.s. soils are limited, Cu is mobilised in moderate and Al and Zn in very large amounts. Future studies providing information and knowledge on the exposure to elevated concentrations of potentially toxic metals in a.s. soil areas and surroundings and the possible health outcome should be undertaken. Moreover, other elements (e.g. Cr, Co, Ni) which are significantly mobilised in these soils and elevated in crops grown on them, but not generally associated with PD or AD, should be included to further define their individual and combined potential effects on human health. The overall high heavy-metal concentrations in the crops grown on these soils have received little attention, probably due to the fact that no serious negative effects have so far taken place, at least none that has been directly linked to an a.s. soil source.

## Conclusions

The review of the literature concerning environmental effects caused by the release of metals in Finnish a.s. soils clearly showed that the studies that were undertaken are alarmingly few. In addition, those few studies indicate an extensive and serious effect on biota, including metal imbalance in crops and elevated concentrations of Al and Zn in the milk of cows. Furthermore, a.s. soils have significant, but spatially and temporally variable impacts on biodiversity and community structure of fish, benthic invertebrates and macrophytes. Therefore, further research is urgently needed, and should include (i) the determination of all the a.s. soil derived potentially toxic metals and their speciation in dairy prod-

ucts, important raw materials (grain and cereal products), crops used in e.g. fodder and food and various fish and aquatic (e.g. *Carex*) species in a.s. soil landscapes, (ii) the short-term dynamics of water chemistry and metal speciation in both estuarine and river environments affected by a.s. soils under variable hydrological conditions in order to assess hydrobiological effects and risks, and (iii) a more comprehensive research on ecotoxicological impacts of a.s. soils on aquatic animal and plant communities. Additionally, a prominent aspect that should be of great concern for researchers and the general public, would involve interdisciplinary studies assessing possible relationships between the incidence of specific diseases (e.g. neurodegenerative and heart diseases) and abundances of potentially toxic metals (in combination with deficiencies of nutrients) in a.s. soil affected drinking water, dairy products and food.

*Acknowledgements:* We thank the following organizations for their financial support: Finska Vetenskaps-Societeten, Sohlbergska Delegationen, Stiftelsen för Åbo Akademi, Svenska Litteratursällskapet (Ingrid, Margit och Henrik Höijers Donationsfond II).

## References

- Alhonen P., Mantere-Alhonen S. & Vuorinen A. 1997. Preliminary observations on the metal content in some milk samples from an acid geoenvironment. *Bull. Geol. Soc. Finland* 69: 31–41.
- Alloway B.J. 2005. Bioavailability of elements in soil. In: Selinus O., Alloway B., Centeno J.A., Finkelman R.B., Fuge R., Lindh U. & Smedley P. (eds.), *Essentials of medical geology – impacts of the natural environment on public health*, Elsevier Academic Press, pp. 347–372.
- Amaducci L.A., Fratiglioni L., Rocca W.A., Fieschi C., Livrea P., Pedone D., Bracco L., Lippi A., Gandolfo C., Bino G., Prencipe M., Bonatti M.L., Girotti F., Carella F., Tavolato B., Ferla S., Lenzi G.L., Carolei A., Gambi A., Grigoletto F. & Schoenberg B.S. 1986. Risk factors for clinically diagnosed Alzheimer's disease: a case-control study of an Italian population. *Neurology* 36: 922–931.
- Andriess 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. 1998a. Partitioning of transition metals in oxidised and reduced zones of sulphide-bearing fine-grained sediments. *Appl. Geochem.* 12: 593–605.
- Åström M. 1998b. Mobility of Al, P and alkali and alkaline

- earth metals in acid sulphate soils in Finland. *Sci. Total Environ.* 215: 19–30.
- Åström M. 2001a. The effect of acid soil leaching on trace element abundance in a medium-sized stream, W. Finland. *Appl. Geochem.* 16: 387–396.
- Åström M. 2001b. Effect of widespread severely acidic soils on spatial features and abundance of trace elements in streams. *J. Geochem. Explor.* 73: 181–191.
- Åström M. & Åström J. 1997. Geochemistry of stream water in a catchment in Finland affected by sulphidic fine sediments. *Appl. Geochem.* 12: 593–605.
- Åström M. & Björklund A. 1995. Impact of acid sulfate soils on stream water geochemistry in western Finland. *J. Geochem. Explor.* 55: 163–170.
- Åström M. & Björklund A. 1996. Hydrogeochemistry of a stream draining sulfide-bearing postglacial sediments in Finland. *Water Air Soil Pollut.* 89: 233–246.
- Åström M. & Corin N. 2000. Abundance, sources and speciation of trace elements in humus-rich streams affected by acid sulphate soils. *Aquat. Geochem.* 6: 367–383.
- Baldi I., Lebaillly P., Mohammed-Brahim B., Letenneur L., Dartigues J.-F. & Brochard P. 2003. Neurodegenerative diseases and exposure to pesticides in the elderly. *Am. J. Epidemiol.* 157: 409–414.
- Beamish R.J., Lockhart W.L., Van Loon J.C. & Harvey H.H. 1975. Long-term acidification of a lake and resulting effects on fishes. *Ambio* 4: 98–102.
- Brown R.C., Lockwood A.H. & Sonawane B.R. 2005. Neurodegenerative diseases: an overview of environmental risk factors. *Environ. Health Perspect.* 113: 1250–1256.
- Cenci R.M. 2000. The use of aquatic moss (*Fontinalis antipyretica*) as monitor of contamination in standing and running waters: limits and advantages. *J. Limnol.* 60: 53–61.
- Combs G.F. 2005. Geological impacts on nutrition. In: Selinus O., Alloway B., Centeno J.A., Finkelman R.B., Fuge R., Lindh U. & Smedley P. (eds.), *Essentials of medical geology – impacts of the natural environment on public health*, Elsevier Academic Press, pp. 161–177.
- Coni E., Bocca A., Ianni D. & Caroli S. 1995. Preliminary evaluation of the factors influencing the trace element content of milk and dairy products. *Food Chem.* 52: 123–130.
- Cornett C.R., Markesbery W.R. & Ehmann W.D. 1998b. Imbalances of trace elements related to oxidative damage in Alzheimer's disease brain. *Neurotoxicology* 19: 339–345.
- Cornett C.R., Ehmann W.D., Wekstein D.R. & Markesbery W.R. 1998a. Trace elements in Alzheimer's disease pituitary glands. *Biol. Trace Elem. Res.* 62: 107–114.
- Dent D.L. & Pons L.J. 1995. A world perspective on acid sulphate soils. *Geoderma* 67: 263–276.
- Edén P. & Björklund A. 1993. Hydrogeochemistry of river waters in Fennoscandia. *Aqua Fenn.* 23: 125–142.
- Ervio R. & Palko J. 1984. Macronutrient and micronutrient status of cultivated acid sulphate soils at Tupos, Finland. *Ann. Agric. Fenn.* 23: 121–134.
- Flaten T.P. 1990. Geographical associations between aluminium in drinking water and death rates with dementia (including Alzheimer's disease), Parkinson's disease and amyotrophic lateral sclerosis in Norway. *Environ. Geochem. Health* 12: 152–167.
- Flaten T.P. 2001. Aluminium as a risk factor in Alzheimer's disease, with emphasis on drinking water. *Brain Res. Bull.* 55: 187–196.
- Forster D.P., Newens A.J., Kay D.W. & Edwardson J.A. 1995. Risk factors in clinically diagnosed presenile dementia of the Alzheimer's type: a case-control study in northern England. *J. Epidemiol. Community Health* 49: 253–258.
- Foy C.D., Chaney R.L. & White M.C. 1978. The physiology of metal toxicity in plants. *Ann. Rev. Plant Physiol.* 29: 511–566.
- Gauthier E., Fortier I., Courchesne F., Pepin P., Mortimer J. & Gauvreau D. 2000. Aluminium forms in drinking water and risk of Alzheimer's disease. *Environ. Res.* 84: 234–246.
- Gillette-Guyonnet S., Andrieu S., Nourhashemi F., de La Guéronnière V., Grandjean H. & Vellas B. 2005. Cognitive impairment and composition of drinking water in women: findings of the EPIDOS Study. *Am. J. Clin. Nutr.* 81: 897–902.
- Gorell J.A. & Checkoway H. 2001. Epidemiological studies: Risk factors session IV summary and research needs. *Neurotoxicology* 22: 837–844.
- Gorell J.M., Peterson E.L., Rybicki B.A. & Cole Johnson C. 2004. Multiple risk factors for Parkinson's disease. *J. Neurol. Sci.* 217: 169–174.
- Gorell J.M., Johnson C.C., Rybicki B.A., Peterson E.L. & Richardson R.J. 1998. The risk of Parkinson's disease with exposure to pesticides, farming, well water, and rural living. *Neurology* 50: 1346–1350.
- Gorell J.M., Johnson C.C., Rybicki B.A., Peterson E.L., Kortsha G.X., Brown G.G. & Richardson R.J. 1997. Occupational exposures to metals as risk factors for Parkinson's disease. *Neurology* 48: 650–658.
- Gorell J.M., Johnson C.C., Rybicki B.A., Peterson E.L., Kortsha G.X., Brown G.G. & Richardson R.J. 1999. Occupational exposure to manganese, copper, lead, iron, mercury and zinc and the risk of Parkinson's disease. *Neurotoxicology* 20: 239–247.
- Heath A.G. 1995. *Water pollution and fish physiology*, 2nd ed. CRC Press, Boca Raton.
- Hildén M. & Hirvi J.-P. 1987. The survival of larval perch (*Perca fluviatilis* L.) under different combinations of acidity and duration of acid conditions, analysed with a generalized linear model. *J. Fish Biol.* 30: 667–677.
- Hildén M., Hudd R. & Lehtonen H. 1982. The effects of environmental changes on the fisheries and fish stocks in the Archipelago sea and the Finnish part of the Gulf of Bothnia. *Aqua Fenn.* 12: 47–58.
- Hudd R. 2000. *Springtime episodic acidification as a regulatory factor of estuary spawning fish recruitment*. Ph.D. thesis, Finnish Game and Fisheries Research Institute, University of Helsinki, Finland.
- Hudd R., Hildén M., Urho L., Axell M.-B. & Jäfs L.-A. 1984. *Fishery investigations (in 1980–1982) of the Kyrönjoki River estuary and its influence area in the northern Quark of the Baltic Sea*. National Board of Waters, Report 242B. [In Finnish and Swedish with

- English summary].
- Jankovic J. 2005. Searching for a relationship between manganese and welding and Parkinson's disease. *Neurology* 64: 2021–2028.
- Joukainen S. & Yli-Halla M. 2003. Environmental impacts and acid loads from deep sulfidic layers of two well-drained acid sulfate soils in western Finland. *Agric. Ecosyst. Environ.* 95: 297–309.
- Kabata-Pendias A. 2001. *Trace elements in soils and plants*, 3rd ed. CRC Press, Boca Raton.
- Kivinen E. 1944. Sulfat- eller alunjordar, deras egenskaper och synpunkter på deras odling. *Svenska Vall- och Mosskulturforenings kvartalstidskrift* 6: 152–164.
- Kjellman J. 2003. *Growth and recruitment of Burbot (Lota lota)*. Ph.D. thesis, Dept. of Limnology and Environmental Protection, University of Helsinki, Finland.
- Kähäri J. & Nissinen H. 1978. The mineral element contents of timothy (*Phleum pratense* L.) in Finland. I. The elements calcium, magnesium, phosphorus, potassium, chromium, cobalt, copper, iron, manganese, sodium and zinc. *Acta Agric. Scand. Suppl.* 20: 26–39.
- Lahermo P., Väänänen P., Tarvainen T. & Salminen R. 1996. *Geochemical atlas of Finland, Part 3: Environmental geochemistry – stream waters and sediments*. Geological Survey of Finland, Espoo. [In Finnish with English summary].
- Lassila H. & Vuori K.-M. 2005. Applicability of aquatic mosses (*Fontinalis* sp.) and caddis flies (Trichoptera) in assessing impact of land use to the river ecosystems in Ostrobothnia: the role of flow conditions. In: Meriläinen P., Sivula L. & Oikari A. (eds.), *Proceedings of the 7th Finnish Conference of Environmental Sciences*, Koppijyvä Oy, Jyväskylä, Finland, pp. 233–236.
- Lax K. 2005. Stream plant chemistry as indicator of acid sulphate soils in Sweden. *Agric. Food Sci.* 14: 83–97.
- Martyn C.N., Coggon D.N., Inskip H., Lacey R.F. & Young W.F. 1997. Aluminium concentrations in drinking water and risk of Alzheimer's disease. *Epidemiology* 8: 281–286.
- McDonnell L., Maginnis C., Lewis S., Pickering N., Antoniak M., Hubbard R., Lawson I. & Britton J. 2003. Occupational exposure to solvents and metals and Parkinson's disease. *Neurology* 61: 716–717.
- McLachlan D.R.C., Bergeron C., Smith J.E., Boomer D. & Rifat S.L. 1996. Risk for neuropathologically confirmed Alzheimer's disease and residual aluminium in municipal drinking water employing weighted residential histories. *Neurology* 46: 401–405.
- Meriläinen J.J. 1989. *Impact of an acid, polyhumic river on estuarine zoobenthos and vegetation in the Baltic Sea, Finland*. Ph.D. thesis, University of Jyväskylä, Finland.
- Mount D.R., Hockett J.R. & Gern W.A. 1988a. Effect of long-term exposure to acid, aluminium and low calcium on adult brook trout (*Salvelinus fontinalis*). 2. Vitellogenesis and osmoregulation. *Can. J. Fish. Aquat. Sci.* 45: 1633–1642.
- Mount D.R., Ingersoll C.G., Gulley D.D., Fernandez J.D., LaPoint T.W. & Bergman H.L. 1988b. Effects of long-term exposure to acid, aluminium, and low calcium on adult brook trout (*Salvelinus fontinalis*). 1. Survival, growth, fecundity, and progeny survival. *Can. J. Fish. Aquat. Sci.* 45: 1623–1632.
- National Board of Waters 1973. *Selvitys Kyrönjoen ja sen edustan merialueen kalakuolemien syistä*. Internal Report, Vaasa.
- Nyman C., Anttila M.-E., Lax H.-G. & Sarvala J. 1986. *The bottom fauna of rapids as a measure of the quality of running waters*. Publications of the National Board of Waters and Environment 3, Finland. [In Finnish with English abstract].
- Öborn I. 1994. *Morphology, chemistry, mineralogy and fertility of some acid sulfate soils in Sweden*. Ph.D. thesis, University of Uppsala, Sweden.
- Österholm P. 2005. *Previous, current and future leaching of sulphur and metals from acid sulphate soils in W. Finland*. Ph.D. thesis, Åbo Akademi University, Turku, Finland.
- Österholm P. & Åström M. 2002. Spatial trends and losses of major and trace elements in agricultural acid sulphate soils distributed in the artificially drained Rintala area, W. Finland. *Appl. Geochem.* 17: 1209–1218.
- Österholm P. & Åström M. 2004. Quantification of current and future leaching of sulfur and metals from Boreal acid sulfate soils, western Finland. *Aust. J. Soil Res.* 42: 547–551.
- Österholm P., Åström M. & Sundström R. 2005. Assessment of aquatic pollution, remedial measures and juridical obligations of an acid sulphate soil area in western Finland. *Agric. Food Sci.* 14: 44–56.
- Paasikallio A. 1978. The mineral element contents of timothy (*Phleum pratense* L.) in Finland. II. The elements aluminium, boron, molybdenum, strontium, lead and nickel. *Acta Agric. Scand. Suppl.* 20: 40–52.
- Palko J. 1986. Mineral element content of timothy (*Phleum pratense* L.) in an acid sulphate soil area of Tupos village, northern Finland. *Acta Agric. Scand.* 36: 399–409.
- Palko J. 1994. *Acid sulphate soils and their agricultural and environmental problems in Finland*. Ph.D. thesis, University of Oulu, Finland.
- Palko J. & Yli-Halla M. 1988. Solubility of Co, Ni and Mn in some extractants in a Finnish acid sulphate soil area. *Acta Agric. Scand.* 38: 153–158.
- Palko J. & Yli-Halla M. 1990. Solubility of Al, Cr, Cu and Zn in soils from a Finnish acid sulphate soil area. *Acta Agric. Scand.* 40: 117–122.
- Priyadarshi A., Khuder S.A., Schaub E.A. & Priyadarshi S.S. 2001. Environmental risk factors and Parkinson's disease: A metaanalysis. *Environ. Res.* 86: 122–127.
- Ritsemaa C.J., van Mensvoort M.E.F., Dent D.L., Tan Y., van den Bosch H. & van Wijk A.L.M. 2000. In: Sumner M.E. (ed.), *Handbook of soil science*, CRC Press, Boca Raton, pp. 121–154.
- Rogers M.A.M. & Simon D.G. 1999. A preliminary study of dietary aluminium intake and risk of Alzheimer's disease. *Age Ageing* 28: 205–209.
- Rondeau V., Commenges D., Jacqmin-Gadda H. & Dartigues J.-F. 2000. Relation between aluminium concentrations in drinking water and Alzheimer's disease: an 8-year follow-up study. *Am. J. Epidemiol.* 152: 59–66.
- Roos M. & Åström M. 2005. Hydrogeochemistry of rivers

- in an acid sulphate soil hotspot area in western Finland. *Agric. Food Sci.* 14: 24–33.
- Seidler A., Hellenbrand W., Robra B.P., Vieregge P., Nischan P., Joerg J., Oertel W.H., Ulm G. & Schneider E. 1996. Possible environmental, occupational, and other etiologic factors for Parkinson's disease: a case-control study in Germany. *Neurology* 46: 1275–1284.
- Shore D., Henkin R.I., Nelson N.R., Agarwal R.P. & Wyatt R.J. 1984. Hair and serum copper, zinc, calcium, and magnesium concentrations in Alzheimer-type dementia. *J. Am. Geriatr. Soc.* 32: 892–895.
- 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.
- Sundström R., Åström M. & Österholm P. 2002. Comparison of the metal content in acid sulfate soil runoff and industrial effluents in Finland. *Environ. Sci. Technol.* 36: 4269–4272.
- Tanner C.M., Ottman R., Goldman S.M., Ellenberg J., Chan P., Mayeux R. & Langston J.W. 1999. Parkinson disease in twins: an etiologic study. *JAMA* 281: 341–346.
- Teppo A., Mäenpää E. & Paavola R. 2004. *Kyrönjoen pohjaeläimistö ja vesisammalten metallipitoisuudet-vesirakentamisen vaikutusten arviointi*. Alueelliset ympäristöjulkaisut 345, West Finland Regional Environment Centre, Vaasa.
- Urho L., Hildén M. & Hudd R. 1990. Fish reproduction and the impact of acidification in the Kyrönjoki River estuary in the Baltic Sea. *Env. Biol. Fish.* 27: 273–283.
- Uversky V.N. 2004. Neurotoxicant-induced animal models of Parkinson's disease: understanding the role of rotenone, maneb and paraquat in neurodegeneration. *Cell Tissue Res.* 318: 225–241.
- Van Dijk P.L.M., Van den Thillart G.E.E.J.M. & Wendelaar Bonga S.E. 1993. Is there a synergistic effect between steady-state exercise and water acidification in carp? *J. Fish Biol.* 42: 673–682.
- Varo P., Nuurtamo M., Saari E. & Koivistoinen P. 1980a. Mineral element composition of Finnish foods. III. Annual variations in the mineral element composition of cereal grains. *Acta Agric. Scand. Suppl.* 22: 27–35.
- Varo P., Nuurtamo M., Saari E. & Koivistoinen P. 1980b. Mineral element composition of Finnish foods. VIII. Dairy products, eggs and margarine. *Acta Agric. Scand. Suppl.* 22: 115–126.
- Vuori K.-M. 1993. Influence of water quality and feeding habits on the whole-body metal concentrations in lotic Trichopteran larvae. *Limnologica* 23: 301–308.
- Vuori K.-M. 1996. Acid-induced acute toxicity of aluminium to three species of filter feeding caddis larvae (Trichoptera, Arctopsychidae and Hydropsychidae). *Fresh. Biol.* 35: 179–188.
- Vuori K.-M. 2002. *Vesisammal- ja vesiperhosmetelmät jokivesistöjen haitallisten aineiden riskinarvioinnissa ja seurannassa*. Länsi-Suomen ympäristökeskus, Suomen Ympäristö 571, West Finland Regional Environment Centre, Kokkola.
- Vuori K.-M. & Kukkonen J. 1996. Metal concentrations in *Hydropsyche pellucidula* larvae (Trichoptera, Hydropsychidae) in relation to the anal papillae abnormalities and age of exocuticle. *Wat. Res.* 30: 2265–2271.
- Vuori K.-M. & Sirén O. 1996. Raskasmetallit. In: Huttula E., Nenonen M.-L., Koskenniemi E. & Suominen M. (eds.), *Tenojoen vesistön veden laatu ja biomonitorointi*, Alueelliset ympäristöjulkaisut 23, Lapland Regional Environment Centre, pp. 48–52.
- Vuorinen P.J. 2000. *Long-term reproductive and physiological effects of acidity and aluminium on three fish species studied in the laboratory and field*. Ph.D. thesis, Finnish Game and Fisheries Research Institute, University of Helsinki, Finland.
- Vuorinen P.J., Keinänen M., Peuranen S. & Tigerstedt C. 2003. Reproduction, blood and plasma parameters and gill histology of vendace (*Coregonus albula* L.) in long-term exposure to acidity and aluminium. *Ecotoxicol. Environ. Safety* 54: 255–276.
- Wiklander L. & Hallgren G. 1949. Studies on gytty soils. I Distribution of different sulfur and phosphorus forms and of iron, manganese and calcium carbonate in a profile from Kungsängen. *Ann. R. Agric. Coll.* 16: 811–827.
- Yli-Halla M. & Palko J. 1987. Mineral element content of oats (*Avena sativa* L.) in an acid sulphate soil area of Tuupos village, northern Finland. *Maataloustieteellinen Aikakauskirja* 59: 73–78.
- Yli-Halla M., Puustinen M. & Koskiahio J. 1999. Area of cultivated acid sulfate soils in Finland. *Soil Use Manage.* 15: 62–67.
- Zatta P., Lucchini R., van Rensburg S.J. & Taylor A. 2003. The role of metals in neurodegenerative processes: aluminium, manganese, and zinc. *Brain Res. Bull.* 62: 15–28.