Biogeochemistry in acid sulphate soil landscapes and small urban centres in Western Finland

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This work is dedicated to my
mother, Elisabeth Renvall,
the best mother in the world

Abstract

The overall purpose of this thesis was to increase the knowledge on the biogeochemistry of rural acid sulphate (AS) soil environments and urban forest ecosystems near small towns in Western Finland. In addition, the potential causal relationship between the distribution of AS soils and geographical occurence of multiple sclerosis (MS) disease was assessed based on a review of existing literature and data.

Acid sulphate soils, which occupy an area of approximately 17–24 million hectare worldwide, are regarded as the nastiest soils in the world. Independent of the geographical locality of these soils, they pose a great threat to their surrounding environment if disturbed. The abundant metal-rich acid drainage from Finnish AS soils, which is a result of sulphide oxidation due to artificial farmland drainage, has significant but spatially and temporally variable ecotoxicological impacts on biodiversity and community structure of fish, benthic invertebrates and macrophytes. This has resulted in mass fish kills and even eradication of sensitive fish species in affected waters. Moreover, previous investigations demonstrated significantly enriched concentrations of Co, Ni, Mn and Al, metals which are abundantly mobilised in AS soils, in agricultural crops (timothy grass and oats) and approximately 50 times higher concentrations of Al in cow milk originating from AS soils in Western Finland. Nevertheless, the results presented here demonstrate, in general, relatively moderate metal concentrations in oats and cabbage grown on AS soils in Western Finland, although some of the studied fields showed anomalous values of metals (e.g. Co and Ni) in both the soil and target plants (especially oats), similar to that of the previous investigations. The results indicated that the concentrations of Co, Ni, Mn and Zn in oats and Co and Zn in cabbage were governed by soil geochemistry as these metals were correlated with corresponding concentrations extracted from the soil by NH_4Ac-EDTA and NH_4Ac, respectively. The concentrations of Cu and Fe in oats and cabbage were uncorrelated to that of the easily soluble concentrations in the soils, suggesting that biological processes (e.g. plant-root processes) overshadow geochemical variation. The concentrations of K and Mg in cabbage, which showed a low spread and were strongly correlated to the NH_4Ac extractable contents in the soil, were governed by both the bioavailable fractions in the topsoil and plant-uptake mechanisms. The plant´s ability to regulate its uptake of Ca and P (e.g. through root exudates) seemed to be more important than the influence of soil geochemistry.

The distribution of P, K, Ca, Mg, Mn and S within humus, moss and needles in and around small towns was to a high degree controlled by biological cycling, which was indicated by the low correlation coefficients for P, K, Ca, Mg and S between humus and moss, and the low spread of these nutrients in moss and needles. The concentration variations of elements in till are mainly due to natural processes (e.g. intrusions, weathering, mineralogical variations in the bedrock). There was a strong spatial pattern for B in humus, moss and needles, which was suggested to be associated with anthropogenic emissions from nearby town centres. Geogenic dust affected the spatial distribution of Fe and Cr in moss, while natural processes governed the Fe anomaly found in the needles. The spatial accumulation patterns of Zn, Cd, Cu, Ni and Pb in humus and moss were strong and diverse, and related to current industry, the former steel industry, coal combustion, and natural geochemical processes. An intriguing Cu anomaly was found in moss. Since it was located close to a main railway line and because the railway line´s electric cables are made of Cu, it was suggested that the reason for the Cu anomaly is corrosion of these cables.

In Western Finland, where AS soils are particularly abundant and enrich the metal concentrations of stream waters, cow milk and to some extent crops, an environmental risk assessment would be motivated to elucidate if the metal dispersion affect human health. Within this context, a topic of concern is the distribution of multiple sclerosis as high MS prevalence rates are found in the main area of AS soils. Regionally, the AS soil type in the Seinäjoki area has been demonstrated to be very severe in terms of metal leaching, this area also shows one of the highest MS rates reported worldwide. On a local scale, these severe AS soil types coincide well with the corresponding MS clustering along the Kyrönjoki River in Seinäjoki. There are reasons to suspect that these spatial correlations are causal, as multiple sclerosis has been suggested to result from a combination of genetic and environmental factors.

Sammanfattning

Den övergripande målsättningen med denna avhandling var att öka kunskapen om biogeokemin i jordbruksmarker belägna på sura sulfatjordar och skogsekosystem nära småstäder i västra Finland. På basis av tidigare forskningsresultat och insamlad data bedömdes även det potentiella orskakssambandet mellan utbredningen av sura sulfatjordar och den geografiska förekomsten av sjukdomen multipel skleros (MS) i Finland.

Sura sulfatjordar, vilka globalt upptar en areal på ungefär 17–24 miljoner hektar, betraktas som en av de besvärligaste jordmånerna i världen. Oavsett det geografiska läget, utgör de sura sulfatjordarna ett stort hot för den omkringliggande miljön ifall de artificiellt torrläggs för uppodling. Den stora kvantiteten metallrikt surt avrinningsvatten från finländska sura sulfatjordar, en direkt påföljd av sulfidoxidation orsakad av dikning, har signifikanta, men spatiala och temporala varierande ekotoxikologiska effekter på biodiversiteten och samhällsstrukturen på fisk, bentiska invertebrater och makrofyter. Detta har bland annat resulterat i omfattande fiskdöd och utrotning av känsliga fiskarter. Metallerna Co, Ni, Mn och Al, vilka mobiliseras i stor omfattning i sura sulfatjordar, har i tidigare undersökningar visats vara kraftigt anrikade i grödor (timotej och havre) odlade på dessa jordar. Cirka 50 gånger högre koncentrationer av Al har också påvisats i komjölk härstammande från sura sulfatjordsområden i västra Finland. Resultaten som presenteras i denna avhandling påvisar dock relativt medelmåttiga metallkoncentrationer i havre och kål odlade på sura sulfatjordar i västra Finland, fastän några av fältena uppvisade kraftigt avvikande halter för bland annat Co och Ni i både mark och grödor (speciellt havre), i likhet med de tidigare undersökningarna. Resultaten indikerade att koncentrationerna av Co, Ni, Mn och Zn i havre, samt Co och Zn i kål, kontrollerades av markgeokemin eftersom metallhalterna uppvisade ett starkt samband med motsvarande koncentrationer extraherade från marken med NH_4Ac-EDTA respektive NH_4Ac. Koppar och Fe-halterna i havre och kål var opåverkade av de motsvarande lättlösliga koncentrationerna i jordarna, vilket antyder att biologiska processer (växt-rot mekanismer) överskuggar variationer i markgeokemin. Koncentrationerna av K och Mg i kål, som uppvisade en låg spridning samt ett starkt samband med de NH_4Ac-extraherbara halterna, var reglerade av både den biotillgängliga fraktionen i ytskiktet samt av växtupptagningsmekanismer. Växtens förmåga att reglera dess upptag av Ca

och P (genom exempelvis rotexudat) föreföll däremot vara mer betydande än inverkan av markgeokemin.

Fördelningen av P, K, Ca, Mg, Mn och S i humus, mossa och barr i närheten av småstäder kontrollerades till hög grad av biologiska kretslopp. Det här påvisades av de svaga korrelationskoefficienterna för P, K, Ca, Mg och S mellan humus och mossa, samt den låga spridningen av dessa näringsämnen i mossa och barr. Koncentrationsavvikelser för element i morän är i främsta hand beroende av naturliga processer (t.ex. intrusioner, vittring, mineralogiska variationer i berggrunden). I humus, mossa och barr uppvisade B ett starkt spatialt mönster, vilket antogs vara förknippat med antropogena emissioner från närbelägna städer. Geogent damm påverkade den spatiala fördelningen och det starka sambandet mellan Fe och Cr i mossa, medan naturliga processer associerades med den i barren förekommande Fe-anomalin. De starka och olikartade spatiala ackumulationsmönstren för Zn, Cd, Cu, Ni och Pb i humus och mossa förknippades med dagens industrin, den tidigare stålindustrin, kolförbränning och naturliga geokemiska processer. En intressant Cu-anomali påvisades i mossa och eftersom ackumulationsmönstret förekom i närheten av ett järnväggspår, vars elektriska kablar är Cu-baserade, föreslogs anomalin vara orsakad av korrosion av dessa kablar.

Sura sulfatjordar ger upphov till förhöjda metallkoncentrationer i ytvatten, mjölk och till viss grad grödor och med hänsyn till sulfatjordarnas omfattande förekomst i västra Finland skulle en miljöriskanalys vara motiverad för att klarlägga huruvida metallspridningen påverkar människans hälsa. I detta sammanhang kan utbredningen av multipel skleros vara av väsentlig betydelse eftersom höga frekvenser av MS förekommer i det huvudsakliga området där sura sulfatjordar påträffas. Sura sulfatjordstypen i Seinäjokiregionen har visats vara mycket extrem i avseende på metalläckage och i motsvarande område förekommer en av de högsta i världen rapporterade MS frekvenserna. Den lokala förekomsten av dessa extrema sura sulfatjordar sammanfaller även väl med den motsvarande omfattande utbredningen av MS längs Kyrö älv i Seinäjoki. Det finns anledning att misstänka att dessa spatiala samband är kausala eftersom sjukdomsutvecklingen av MS har föreslagits vara en påföljd av både genetiska och miljöbetingade faktorer.

List of publications

The main focus of this thesis was to study how the release of metals in Finnish acid sulphate soils were expressed in biota, mainly in crops as revealed by field studies (Paper **III** and **IV**), but also in other species as revealed by a literature review (Paper **II**). Additionally I have studied the distribution and behaviour of trace metals in biological, organic and inorganic materials in and around small urban centres (Paper **I**) and made an in-depth review on the potential causal relationship between the geographical distribution of acid sulphate soils and multiple sclerosis (Chapter 7). The thesis thus comprises five studies with three different but associated themes.

I. **Fältmarsch, R.**, Peltola, P., Åström, M. & Raitio, H. 2007. Abundance, correlations and spatial patterns of nutrients and metals in till, humus, moss and pine needles in a boreal forest, western Finland. *Geochemistry, Exploration, Environment, Analysis* 7: 57–69.

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

III. **Fältmarsch, R.**, Österholm, P., Greger, M. & Åström, M. 2009. Metal concentrations in oats (*Avena sativa* L.) grown on acid sulphate soils. *Agricultural and Food Science* 18: 45–56.

IV. **Fältmarsch, R.**, Österholm, P. & Jacks, G. Chemical composition of cabbage (*Brassica oleracea* L. var. *capitata*) grown on acid sulphate soils. *Journal of Plant Nutrition and Soil Science*, Accepted.

Rasmus Fältmarsch was predominantly responsible for Papers I-IV. Paper I is based on a multi-media, multi-element data set provided by the Finnish Forest Research Institute (METLA). In Paper II, Research Professor Kari-Matti Vuori, further developed and wrote part of the chapters "Metal accumulation in aquatic plants and invertebrates" and "Ecotoxicological effects in aquatic organisms". In Paper IV, soil and plant sampling was carried out by Dr. Peter Österholm. Papers I-III are reproduced in this thesis with the permission of the journals concerned. This work was supervised by Prof. Mats Åström and Dr. Peter Österholm.

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1. Introduction

1.1 Acid sulphate soils in Finland

Finnish acid sulphate (AS) soils, which have developed from fine-grained sulphide-bearing marine sediments that have risen above the sea level as a result of the postglacial land uplift (up to 9 mm/year), are today found to a large extent (1600–3000 km^2) (Palko 1994, Yli-Halla et al. 1999) on the coastal plains of Western Finland (Fig. 1a). These soils are very productive farmlands due to their favourable soil structure after drainage. Reclaimed AS soils require efficient drainage management for increasing the water outflow, hence keeping the ground water table well below the ground surface. Consequently, an aerated rooting zone, which is fundamental for the crops, is formed as excess water is rapidly discharged from the uppermost part of the soil profile. However, exposure of the formerly stable iron sulphides to air (as a result of drainage practise) trigger oxidation and consequently mobilisation of large quantities of sulphuric acid (H_2SO_4) and sulphide and silicate associated metals (e.g. Al, Cd, Mn, Ni) (Lin et al. 2001, Burton et al. 2006, 2008). The soil type that develops is an AS soil. There are significant spatial variations in the severity (e.g. pH and oxidation depth) of AS soils. Soils with high contents of sulphur that have only recently been drained (relatively little acidity has been leached) can in general be expected to be most severe, while, for example, high contents of organic matter may hamper the acidity (Österholm and Åström 2002). In the more severe Finnish AS soils pH drops below 3.5 (Yli-Halla et al. 1999, Österholm and Åström 2002). Moreover, intensification of drainage practises, especially the utilisation of modern subsurface drainage techniques, significantly increases the water outflow, thus maintaining a low water table and an aerated top- and subsoil, which in turn initiates large scale sulphide oxidation and increases the mobility of metals and acidity in these soils. Consequently, to enable cultivation on reclaimed AS soils efficient topsoil liming is required to counteract the acidity produced by sulphide oxidation.

The acidity problems of these soils have been fairly well known for quite some time (Kivinen 1944) and during the most recent decades conclusive evidence has been put forward regarding the acid-metal load and its devastating effects on surrounding aquatic environments (Callinan et al. 1993, Hyne and Wilson 1997, Hudd 2000, Gosavi et al. 2004, Powell and Martens 2005). Sundström et al. (2002) estimated that the current amount of metal leakage (e.g. Co, Ni, Zn, Cd, Mn, Al) from Finnish AS soils is 10 to 100 times higher than the effluent discharges from the entire Finnish industry (Fig. 2). This has caused severe environmental problems in streams and rivers (Hudd et al. 1984, Hildén and Hirvi 1987, Meriläinen 1989, Urho et al. 1990, Vuori 1996, Kjellman 2003, Teppo et al. 2004). While it is known that huge amounts of acidity and potentially toxic metals are leached from the Finnish AS soils, little is known about the metal uptake in crops grown on these soils. The present knowledge on the chemical composition of AS soil grown crops is mainly based on a few publications (Palko 1986, Yli-Halla and Palko 1987) only, which showed significantly elevated concentrations of a number of metals in timothy grass and oat grains. Exceptionally high concentrations of Al, a characteristic element mobilised in large quantities in AS soils, were also found in milk samples from cows grazing on AS soils (Alhonen et al. 1997). The lack of sufficient information on the biogeochemical pathways of mobilised metals within these soils is thus conspicuous. Such information would be of great importance since metal accumulation in AS soil derived food sources would serve as a direct link of metals to the human food chain and may thus pose a potential risk on human health.

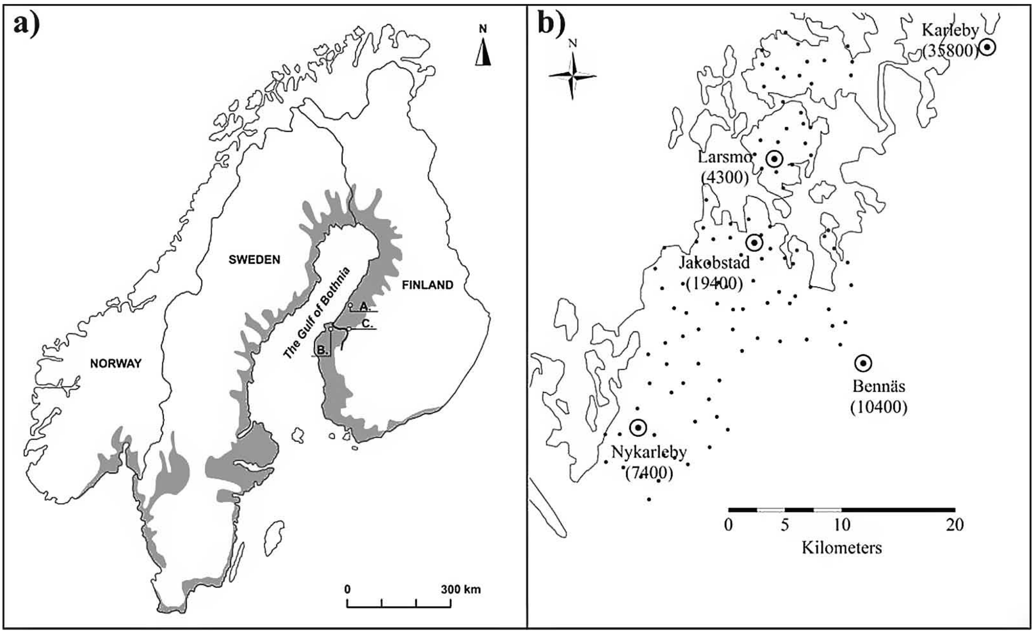


Fig. 1. a) Location of the study areas where (A.) represents the urban part consisting of forest sites near town centres (Paper I), (B.) the rural part consisting of eight agricultural fields located on AS soils within the Vaasa region (Paper III & IV) and (C.) part of the Kyrönjoki River located within the Vaasa and Seinäjoki area (Chapter 7). The shaded area represents the maximum extent of the former Litorina Sea, wherein AS soils can be found (Sohlenius 1996). **b)** Detailed map representing the sampling sites within the urban study area (A.), the location of town centres and number of inhabitants (in brackets) in corresponding towns.

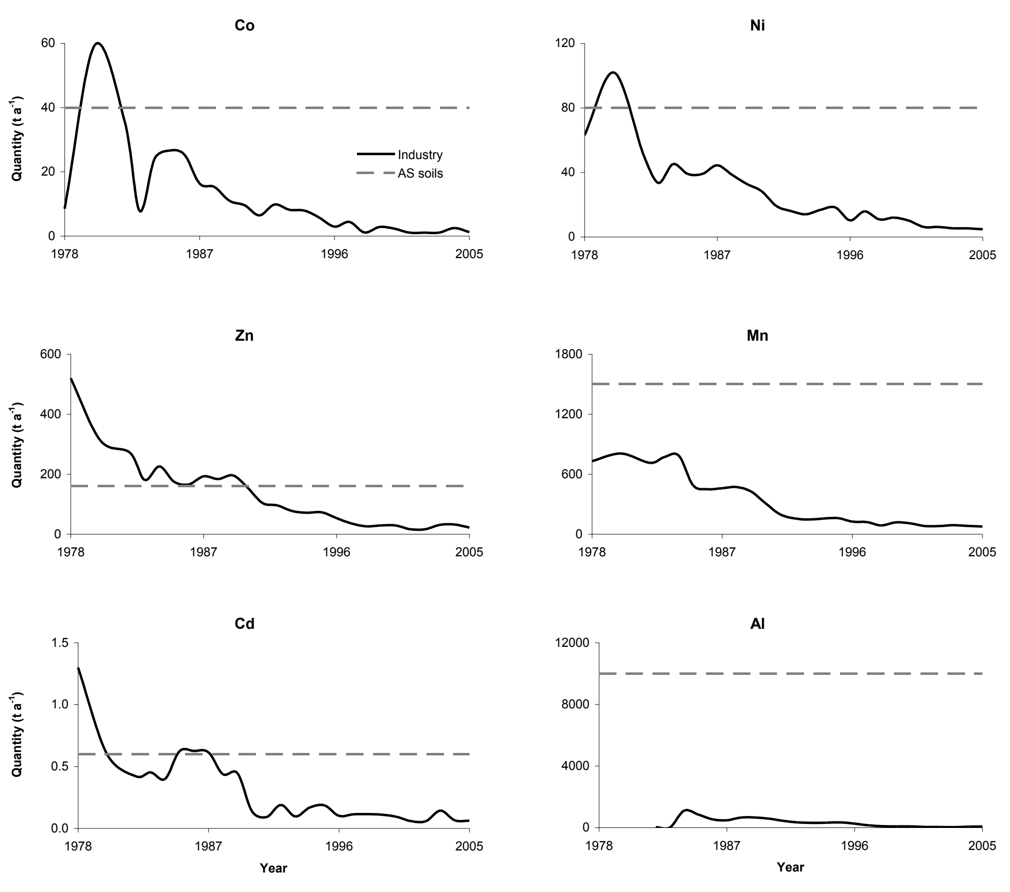


Fig. 2. Estimated metal discharges in effluent from the Finnish industry (continuous line) and in runoff from acid sulphate (AS) soils (broken line) in 1978–2005, expressed as tonnes per year (t a^{-1}). Data for Al during 1978–1980 do not exist. Figure modified and updated from Sundström et al. (2002).

1.2 Acid sulphate soils worldwide

Acid sulphate soils currently cover a total of approximately 17–24 million hectare in the coastal regions worldwide, with major occurences in Africa, Australia, Asia and Latin America (Ritsemaa et al. 2000, Andriesse and van Mensvoort 2002). The occurence of AS soils in the Mekong Delta of South East Asia is very extensive and because of the high population pressure in these productive agricultural regions (an estimated 2.4 million Cambodians and 17 million Vietnamese live on the delta), AS soils are being reclaimed for agricultural production (Minh et al. 1997a, b, Husson et al. 2000, Berg et al. 2007). The leaching of metal-rich acid drainage from AS soil farmlands in these areas is extensive during monsoonal rains (the mean annual precipitation ranging from 1500–2400 mm). Adjacent and downstream waterways are severely affected, making this contaminated surface water unsuitable for irrigation purposes and domestic uses (Minh et al. 1997a, b). Ground water pollution of the Mekong Delta is another serious environmental effect associated with metal-rich acid leakage from AS soils (Berg et al. 2007, Buschmann et al. 2007).

In other parts of the world, extensive drought periods, as was encountered in large parts of Australia in 2006, initiated development of AS soils. Earlier waterlogged sulphidic materials were oxidised due to the rapid drop of the ground water level (during a period of only 4 months), and as a consequence, ample sulphide oxidation and corresponding mobilisation of acidity and metals occurred (Fitzpatrick et al. 2008). The abundant amount of produced acidity and metals will eventually, as a result of heavy rains and/or tidal floods, be leached out to nearby waterways and/or be available for plant uptake at the upper soil profile.

In summary, independent of the geographical locality of AS soils, they pose a great threat to their surrounding environment if disturbed. This has globally been recognised and a large amount of work has been published on the environmental effects of AS soils (e.g. Klepper et al. 1992, Callinan et al. 1993, Lin et al. 1995, Sammut et al. 1995, 1996, Hyne and Wilson 1997, Wilson et al. 1999, Callinan et al. 2005, Powell and Martens 2005, Berg et al. 2007, Chu et al. 2008, Nuttal et al. 2008, Choongo et al. 2009).

1.3 Local and regional biogeochemical mapping

The number of geochemical studies in urban areas has increased in recent decades because of metal dispersion from different sources and/or human activities affecting the local ecosystem (Kohonen and Salminen 1993, Kelly et al. 1996, Salla 1999, Birke and Rauch 2000, Bityukova et al. 2000, Tijhuis et al. 2002, Peltola and Åström 2003, Cicchella et al. 2005, Fordyce et al. 2005). The purpose of these studies has been to assess metal accumulation in both urban and rural areas and to establish the origin and pathways of these pollutants. Sampling of top- and subsoil, and biological media (e.g. moss) has generally been used to determine the level of metal contamination and general pollution stress over longer periods of time in these areas (Kelly et al. 1996, Poikolainen et al. 2004, Salemaa et al. 2004). These type of geochemical mapping and/or environmental monitoring studies carried out on a local and/or regional scale with higher sample density (Raitio and Kärkkäinen 2002, Raitio et al. 2002, Niskanen et al. 2003), are, in contrast to wide-spaced, low-density sampling studies (Peltola and Åström 2003), more suitable for reflecting local contamination, human impact and the fate and origin of elements.

Large-scale regional geochemical surveys with low sampling density have been carried out in large extent. The most pronounced examples of typical ecogeochemical mapping and monitoring are the geochemical mapping of Europe, the Kola Ecogeochemistry- and Eastern Barents region projects (Niskavaara et al. 1996, Reimann et al. 1998, 2000, 2001a-c, de Caritat et al. 2001, Reimann and Melezhik 2001, Salminen et al. 2004, De Vos and Tarvainen 2006). The two latter surveys, which covered a total area of 188 000 km^2 and 1 550 000 km^2 at a sampling density of one site per 300 and 1000 km^2 respectively, included Finland, parts of Norway and Russia (see Salminen et al. 2004 and http://www.ngu.no/Kola for more detailed information). The purpose for carrying out these surveys was to develop geochemical baselines (and hence to obtain a consistent geochemical overview), and to elucidate how local pollution sources in the heavily industrialised parts of the Kola Peninsula in Russia affected the regional atmospheric deposition of heavy metals and the condition of the surrounding environment in the pristine parts of Northern Finland and Norway. Multi-media sampling, consisting of moss, needles, podzolic soil profiles, stream water and snowpack, was utilized in both surveys. The use of the multi-media approach gain insights into how the interplay between the atmosphere, biosphere, and lithosphere affect element cycling and distribution (Reimann et al. 2001b). It is therefore possible to determine the impact of anthropogenic pollution in relation to natural variations, and to map the extent of pollution in these various media on a regional scale.

2. Objectives of the research

The overall purpose of this thesis was to increase the knowledge on biogeochemical processes in agricultural landscapes (Paper II-IV) and urban areas in the boreal region (Paper I). The landscape-oriented studies focus on the impact and dynamics of AS soils in agricultural use, and the urban-oriented study on metal-distribution patterns in and around small towns. The objective of the urban study was to elucidate how a variety of human activities and natural processes have affected metal dispersion and accumulation in moss, humus, till and needle samples from coniferous forests near town centres in Western Finland (Paper I). The objective of the agricultural landscape studies was to review available research information on the environmental risks and effects of metal mobilisation in AS soil areas (Paper II), and to assess the role of soil chemistry on metal concentrations in oats and cabbage grown on AS soils with varying geochemical characteristics (Paper III & IV). Moreover, on the basis of existing data, a discussion on the potential connection between the distribution of AS soils and the geographical occurrence of multiple sclerosis (MS) disease in Finland is given (Chapter 7). The reason for the emphasis on geomedicine, defined as the science dealing with environmental factors influencing the geographical distribution of animal and human health (Låg 1980), is to establish a platform, not only intended for research and legislation purposes, but for public interest, discussion and further development.

3. Description of the study areas

The study areas, which are located at high latitudes and characterised as lowlands close to the present sea level, are situated in the boreal zone of Western Finland (Fig. 1a). The wind direction is highly variable with a slightly dominating (20%) SSW direction and the mean annual precipitation is ca. 500 mm. The mean annual temperature is approximately +3°C, with July and August as the warmest months (+15°C) and December to March the coldest (below 0°C) (Atlas of Finland 1987). Metamorphic granitoids, carbonate-poor mica gneisses and metasedimentary rocks (e.g. mica schists) are the primary bedrock types in these areas (Korsman et al. 1997). The different sampling sites within the study areas are divided into an urban (Paper I) and a rural (Paper III & IV) part consisting of forest sites near town centres and arable land located on AS soils, respectively (Fig. 1a, b). A more detailed description of the study sites is found in the corresponding papers (Paper I, III & IV) and only a brief overview is given below.

The towns of Jakobstad and Nykarleby and parts of Larsmo and Bennäs (the latter representing the administrative centre of the town Pedersöre) municipalities represents the urban part of the study area (a total size of ca. 500 km^2), which is located in Western Finland (Paper I; Fig. 1b). The main emitters (energy production-, metal-, pulp- and paper industries) are located in Jakobstad and Karleby (just outside the study area) whereas agriculture, forestry and fur farms are well established branches of business in Nykarleby and Bennäs. The forest vegetation is mainly made up of pine, spruce and to some extent of birch and mixed forest stands, typical of the boreal coniferous zone in the Northern Hemisphere.

The eight agricultural fields in the rural part of the study area, which are located close to each other within the Vaasa region in Western Finland (Fig. 1a), are found on fine-grained Holocene sediments (Paper III & IV). These fields are characterised as young since they relatively recently have emerged from the sea and thereafter been reclaimed (Nordmyr et al. 2006) and consequently developed into AS soils due to excavation works. Although these AS soils are at an early stage of development the soil profiles are still rather deep implying that soil forming processes have been swift. The quantity of anthropogenic pollution in this part of the study area is low since no big industries are located in the vicinity. However, diffuse leakage from reclaimed AS soils may be substantial as agriculture is common in these rural parts of the study area.

All the AS soil studies referred to in Paper II (literature review) have been conducted within 62°30′-65°10′ N and 21°10′-26°30′ E, which represents the coastal regions of Western Finland.

4. Material and methods

4.1 Existing multi-medium, multi-element data (Paper I)

In 2000, a bioindicator monitoring programme of the air quality in forest sites near town centres in Western Finland was carried out by the Finnish Forest Research Institute (METLA) (Paper I; Fig. 1b). Moss, humus, needle and till samples from coniferous forests at 87–103 sites within the 500 km^2 study area were analysed for P, K, Ca, Mg, Fe, S, B, Cu, Zn, Mn, Cd, Cr, Ni and Pb. The results of Paper I is based on this multi-media, multi-element data set provided by METLA. A brief overview of each medium, and the chemical analysis of these, is given below while a description of the sampling, sample preparation and quality control is given in the corresponding paper.

Terrestrial moss, which has been extensively used in bioindicator studies in Scandinavia over the last 30 years, was selected because of its relatively good reliability as a monitoring tool for atmospheric deposition (Reimann et al. 2001b). The element content in moss is apart from deposition fallout also affected by a multitude of other factors, such as ion exchange processes, element-specific processes (tendency of accumulation, natural cycling processes), climatic conditions, the mineral composition of soil dust, moss species etc. (Berg et al. 1995, Ford et al. 1995, Steinnes 1995, Reimann et al. 2001a). The humus horizon (organic layer of the forest soil), which reflects the interaction between the lithosphere, biosphere and atmosphere, normally acts as a sink for elements in northern ecosystems (Reimann et al. 2001b). The chemical composition of the humus layer is affected by the atmospheric addition of elements (geogenic and anthropogenic dust and emissions), the composition and productivity of the vegetation, the climate and the character of the bedrock or soil parent material (Reimann et al. 2000). Pine needles act as a nutrient reserve for the tree and concurrently take part in the cycling of elements in pine forest ecosystems (Lamppu and Huttunen 2003). The chemical composition of pine needles is to a great extent affected by root uptake and translocation processes and less by absorption of elements from atmospheric deposition (Čeburnis and Steinnes 2000). Chemical characterisation of needles makes it possible to assess the relationship between cause and effect in forest damage, trace changes of the nutrient condition in the ground and assess the condition of the forest (nutrient shortage and condition of toxicity) (Raitio and Kärkkäinen 2002). In addition to these three media above, till data from the corresponding area, but from different sample plots, were obtained from the Geological Survey of Finland (GTK). The till or the unsorted mineral soil consists of crushed bedrock material and superficial deposits developed on glacial drift (Koljonen 1992). The bedrock and natural geological processes (deposits, intrusions and weathering) are the main sources of the element accumulation and spread in till (Reimann et al. 2001b).

The humus samples were analysed for acidity (pH) on a water extract (15 ml powder/25 ml distilled water) according to the directives of the European programme on assessment and monitoring of air pollution effects on forests (ICP Forests Manual 2006). Samples of moss, humus and needles were digested in a mixture of HNO_3:H_2O_2 and P, K, Ca, Mg, Fe, S, B, Cu, Zn, Mn, Cd, Cr, Ni and Pb were determined by ICP-AES. The digestion, using 0.5 g of sample material, was carried out in a microwave oven using MDS 2000-equipment. The till samples were dry-sieved and the fine fraction (< 0.062 mm) was used in the analyses. The samples were dissolved in aqua regia at 90°C for one hour and afterwards diluted with distilled water to a 1:100 ratio. The solution was analysed by ICP-AES for P, K, Ca, Mg, Fe, Cu, Zn, Mn, Cr, Ni and Pb.

4.1.1 Data analysis

The application of various statistical analysis and GIS maps on this multi-medium, multi-element data facilitates the illustration of metal deviations through spatial accumulation patterns and establishment of origin of specific metals. On the basis of this, it was possible to elucidate how a variety of natural and anthropogenic processes had affected metal dispersion and accumulation within this boreal ecosystem. The utilization of box plot comparison of different media is a convenient way of displaying important information (e.g. spread) in data sets at a glance. The box plot shows the median and/or mean (marked with a line within the box), the quartiles/hinges (25% and 75%, the ends of the box), minimum and maximum values/whiskers (vertical lines outside the box), mild outliers (> 1.5 x hinge spread, marked as an unfilled dot) and extreme outliers (> 3.0 x hinge spread, marked as a filled dot). The use of percentiles (P_{25}, P_{50}, P_{75} and P_{90}) for class selection for each medium makes growing symbol maps directly comparable and independent of extreme values. These maps graphically display spatial variation and this mapping technique is an efficient tool for the interpretation of geochemical distribution patterns. Additionally, Spearman correlation analysis (significant at $P = 0.01$) was adopted in the present study for comparing element concentrations between and within media at the studied sites. Each significant element association was verified in XY-plots confirming these relationships were not artefacts.

4.2 Literature review (Paper II)

During the last decades a substantial amount of work has been published on Finnish AS soils and their associated environmental impacts (van Breemen 1973, National Board of Waters 1973, Hudd et al. 1984, Hildén and Hirvi 1987, Urho et al. 1990, Palko 1994, Vuori 1996, Åström 2001a, Sohlenius and Öborn 2004, Österholm 2005, Nordmyr et al. 2008a, b). This relatively scattered research information, which principally concerns metal uptake in biota and is compiled here to a literature review (Paper II), involves internal reports from Finnish regional environment centres and similar institutes (published in Swedish, Finnish and/or English), conference proceedings, PhD-theses and articles in scientific journals. The majority, if not all of these works have recognised the nuisance and environmental risks (e.g. serious damage on aquatic biota) related to the disturbance of AS soils. Moreover, these AS soil related problems have attracted much attention in the Finnish mass media, primarily through the recurring mass fish kills in affected streams. Despite the knowledge of the huge amounts of acidity and potentially toxic metals mobilised in and leached from these soils, little attention has been paid to metal accumulation in terrestrial crops. Only a few studies, focusing on metal concentrations in crops cultivated on AS soils, have been conducted and they all indicate significantly enriched concentrations of a series of metals (Palko 1986, Yli-Halla and Palko 1987). This subject is of public concern as enriched concentrations of potentially toxic metals in plants may pose negative effects on human health due to chronic exposure. Thus, the reason for carrying out this review was to compile relevant and essential literature on the environmental risks and effects (principally metal uptake in biota) of metals mobilised in Finnish AS soils and to discuss potential effects on human health. In addition, a literature study on AS soils has yet to be done, which in turn was a strong motive for this work. Finally, this compilation can be regarded as a contribution both to the general public, providing a better understanding of the complexity of problems related to AS soils, and to the science community for future research needs on geochemical and -medical related associations.

4.3 Soil sampling and chemical analysis (Paper III & IV)

During the late summer of 2005 and 2006, a total of 36 topsoil samples (0–20 cm) and 25 subsoil- (20–100 cm) and three whole soil profiles (~0–260 cm) were collected with an auger from 36 subsites from eight agricultural fields located on AS soils in the coastal areas of Western Finland (Paper III & IV; Fig. 1a). These soil profiles were subdivided into 20 cm section splits of which pH was determined afterwards in the laboratory with a Mettler Toledo inlab 426® sediment electrode, which was inserted in the soil. Deionised water was added to each subsample to assure contact with the electrode and the soil (Puustinen et al. 1994). These soil sample splits were dried at 40–60°C for five days and subsequently milled in a quartz mortar to a fine powder.

A 1.0 g portion of the top- and subsoil splits was analysed for Ca, Co, Cu, Fe, K, Mg, Mn, Ni, P and Zn by ICP-ES/MS after extraction in 10 mL ammonium acetate (0.5 N ammonium acetate 0.5 N acetic acid, below referred to as NH_4Ac) and acid ammonium acetate-EDTA (0.5 N ammonium acetate 0.5 N acetic acid 0.02 M EDTA, below referred to as NH_4Ac-EDTA) solution at pH 4.65 for one hour. The purpose of these methods was to extract the exchangeable and readily soluble fraction of chemical elements, thus simulating the easily available (bioavailable) fraction found in the soil. It has been shown that the extraction of Ca, K and Mg is suitable with either NH_4Ac or NH_4Ac-EDTA as the same amounts are extracted regardless of method used (Lakanen and Erviö 1971, Borgaard 1976), however, somewhat higher trace element concentrations might be extracted by the efficient complexing agent, EDTA, as to that of NH_4Ac alone (Menzies et al. 2007). Nevertheless, there is no universal single extractant suitable for perfectly assessing the easily available concentrations of multi-elements found in the soil.

A 0.5 g portion of soil samples, representing whole soil profile (Paper IV) and 40–60 cm section splits (Paper III), was analysed for the above mentioned elements plus S by ICP-MS after partial digestion in 3 mL 2:2:2 $HCl:HNO_3:H_2O$ (aqua regia extraction) at 95°C for one hour. The aqua regia digestion dissolves several phyllosilicates, organic material and metal sulphides, however, the most weathering resistant minerals, e.g. quartz, feldspars and crystalline oxides, are poorly dissolved (Räisänen et al. 1992).

A 1.0 g aliquot of the topsoil splits was analysed for Ca, Co, Cu, Fe, K, Mg, Mn, Ni, P and Zn after extraction in 10 mL 0.25 M hydroxylamine (NH_2OH) digested at 90°C for two hours followed by analysis with ICP-ES/MS. Fe-oxides are found in large proportions in these soils (Åström 1998b) and they are well known sinks for mobile trace elements in surface environments (Kabata-Pendias 2001). The metal fraction bound to Fe- and Mn oxides is mobilised through dissolution of these with the strong 0.25 M hydroxylamine reductant (Hall 1998, Filgueiras et al. 2002).

The organic matter content of the whole soil profile splits was estimated as loss on ignition (LOI) by combusting 1.0 g of dried sample for four hours in 500°C (Radojević and Bashkin 1999). LOI, which is a relatively rapid and accurate method for the estimation of the organic matter concentration present in a sample, is suggested to be proportional to the content of organic carbon (Ball 1964, Heiri et al. 2001).

4.4 Plant sampling and chemical analysis (Paper III & IV)

A total of 26 oat (*Avena sativa* L. cv. Fiia; Paper III) and 11 white cabbage (*Brassica oleracea* L. var. capitata; Paper IV) samples were collected adjacent to the soil sample pits in the late summer of 2005 and 2006 (Photo 1). Each oat sample (approximately 300 g) was collected from all cardinal points within a radius of 0.5 m from the centre of the soil sampling point. The oat samples were stored in plastic bags in a freezer at −18°C and dried at 60°C for 72 hours before pre-treatment. The oat leaflets and grains were separated with an aspirator at MTT Agrifood Research Finland in Jokioinen. The grains were sorted with a 2 mm sieve, thus obtaining an uniform grain size sample, and subsequently weighed and milled in a quartz mortar by hand. Similar to that of the oat samples, the outer leafs of the cabbage were cut off to avoid soil contamination of the samples. Subsamples were congregated from a transect representing the main inner part of the cabbage sample, thus obtaining an uniform bulk sample. These 11 bulk samples were stored in a refrigerator (5°C) until freeze-dried and analysed.

A 1.0 g portion of the oat and cabbage samples was digested with 2 mL HNO_3 for one hour following a 6 mL digestion in 3 mL 2:2:2 $HCl:HNO_3:H_2O$ (HNO_3 + aqua regia) at 95°C for one hour and analysed by ICP-MS for Ca, Co, Cu, Fe, K, Mg, Mn, Ni, P, and Zn. The HNO_3 + aqua regia digestion extracts near-total element concentrations bound in the plant material. Randomly selected replicates for each of the respective soil and plant extractions were determined for analytical reliability according to the method by Gill (1997) and are found in the corresponding papers (Paper III & IV).

Photo 1. Oats cultivated on AS soils in the typically flat landscapes of Western Finland, Ostrobothnia. Cabbage sample adjacent to AS soil sample pit.

4.5 Reference data for corresponding soil and plant material

In 1974 a total of 2015 topsoil samples (0–20 cm) were collected from cultivated soils representing 12 different soil types throughout the country (Sippola and Tares 1978). During 1972–1976, a multitude of different fresh vegetables (e.g. *Brassica oleracea*, n=5) from wholesale stores of five regional vegetable growers´ associations (Varo et al. 1980a) and oat samples (*Avena Sativa,* n=36) from 10 national granary stores and five commercial mills were collected (Varo et al. 1980b). The sampled crops originated from the main growing areas in the country and represented the vast bulk for Finnish consumption. These studies were a part of the general inventory of the mineral element survey of Finnish foods, and the aim was to gather background data on the mineral element concentrations of Finnish crops and cultivated soils (Sippola and Tares 1978, Varo et al. 1980a, b). While it is possible that AS soils and crops grown on them might be included in the reference data sets, their effect on the concentration levels will be of minor importance since the reference samples represent the whole of Finland (relatively small proportion of AS soils). The mean values of elements in these studies (Sippola and Tares 1978, Varo et al. 1980a, b) are used as a reference and termed Finnish average values (FAV) in this thesis (Paper III & IV).

The soil samples (n=2015) were analysed for Ca, Mg, P and K after NH_4Ac-extraction (0.5 N ammonium acetate 0.5 N acetic acid) (Vuorinen and Mäkitie 1955) and for Co, Cu, Fe, Mn, Ni and Zn after NH_4Ac-EDTA extraction (0.5 N ammonium acetate 0.5 N acetic acid 0.02 M EDTA) at pH 4.65 for one hour with a volume ratio of soil/extractant of 1:10 (Lakanen and Erviö 1971, Sippola and Tares 1978). Calcium and K were determined with flame photometry, P colorimetrically and Mg, Co, Cu, Fe, Mn, Ni and Zn with AAS (Sippola and Tares 1978). The oat grain samples (n=36) were analysed by AAS after dry ashing for 40 hours at 500°C following digestion in HCl-$HClO_4$- (Cu, Fe, Mn and Zn) and HNO_3-$HClO_4$ (Co, Ni) solution (Saari and Paaso 1980). The cabbage samples (n=5) were assorted, washed with tap water and in some cases peeled. The cabbage leaves, which were cut in small 0.5 cm pieces, oven dried and subsequently homogenised, were analysed with AAS after dry ashing for 40 hours at 500°C and 450°C following digestion in HCl-$HClO_4$- (Ca, Cu, Fe, K, Mg, Mn and Zn) and HNO_3-$HClO_4$ (Co, Ni) solution, respectively (Saari and Paaso 1980).

The same soil extraction methods were used for the reference material (FAV) and in the present studies to simulate the easily available concentrations of Co, Ni, Zn, Mn, Cu and Fe (NH_4Ac-EDTA, Paper III), and Ca, K, Mg and P (NH_4Ac, Paper IV) and hence, a comparison between results should be fairly applicable. In contrast, different extraction- and pre-treatment methods were used for the reference material for the analysis of the chemical composition of oats and cabbage. Nevertheless, the extraction methods used here and for the reference material are designed to provide near total concentrations bound in the biological material. Despite the analytical differences between these studies, it is reasonable to assume that these differences are not crucial in terms of element amounts extracted, and thus, the FAV is used here as a rough indicator of the total element concentrations in oats and cabbage and hence serves as a rough background estimate. All matters considered, direct comparisons of results obtained by different soil extraction methods, sampling methods, analytical techniques, time period between studies and inter-laboratory differences should be done with utmost discretion and without attention on fine details.

5. Extended abstracts of Paper I-IV

5.1 Paper I

High-density sampling of till, humus, moss and needles from coniferous forests at 87–103 sites was carried out by the Finnish Forest Research Institute (METLA) in a 500 km^2 area in Western Finland (Fig. 1a, b) to elucidate the effect of anthropogenic emissions and natural processes on accumulation patterns and spatial dispersion of P, K, Ca, Mg, Fe, S, B, Cu, Zn, Mn, Cd, Cr, Ni and Pb in the environment. The multi-medium, multi-element approach in connection with high-density sampling on a local and/or regional scale is useful in reflecting (i) element distribution affected by human activity and/or anthropogenic emissions and (ii) impact of natural processes on element cycling and -accumulation patterns, and is thus an essential tool explaining origin and pathways of pollutants. Furthermore, the utilization of box plots, correlation matrices and growing symbol maps is a convenient way of displaying and interpreting spatial variation, spread, natural processes and fate of elements.

No distinct spatial patterns were found for P, K, Ca, Mg, S and Mn in the four analysed media. The relative quantity (mg kg^{-1}) of these elements (except Mn) are generally found in the following order in all plants, K > Ca > Mg > P > S (Reimann et al. 2001c), which also is the case in this study for moss and needles, except Mg that was found in penultimate or last position. These elements showed low concentration variations in both moss and needles and low correlation coefficients between humus and moss, indicating effective biological recycling.

Distinctive spatial patterns were observed for B in humus, moss and needles, however, no significant correlation existed between these media. These accumulation patterns, which in humus was pronounced in the central part of the study area, around the town of Jakobstad, and in moss and needles in the northern rural parts of the study area, are attributed to anthropogenic emissions from the industrial towns of Jakobstad and Karleby (NE of the study area) (Fig. 1b, Fig. 3). The concentrations of B in humus, moss and needles were not correlated with the distance to the coast (brackish water), suggesting that these B patterns are unaffected by deposition of marine salts.

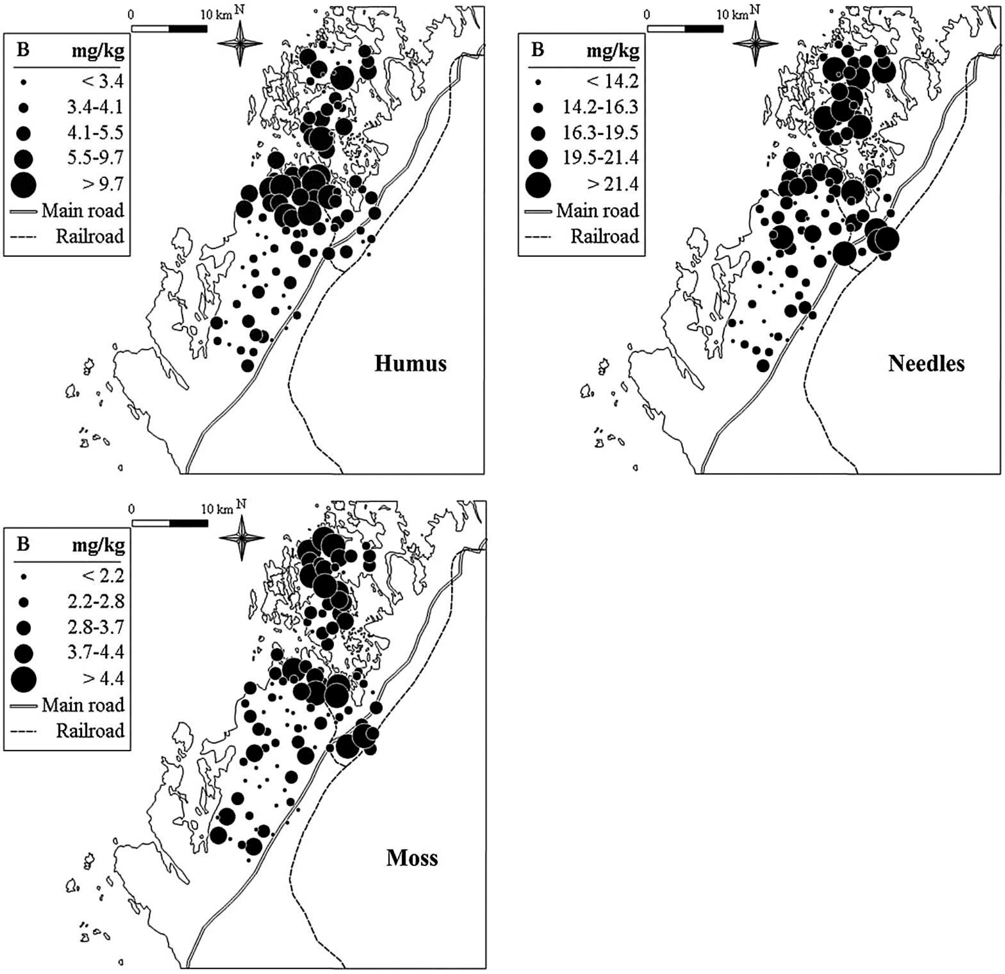


Fig. 3. Spatial distribution of B in humus, moss and needles.

Significant correlation existed between Fe and Cr in till, humus and moss, however, only the latter medium delivered a clear spatial pattern characterised by elevated concentrations of these elements in the central parts (the town of Jakobstad and Bennäs) (Fig. 4). It was argued that dust input governs the observed anomaly in moss for Fe and Cr, since a large spread of these elements in this medium is indicative of such a pathway (Reimann et al. 2001a, c). Similar to that of Fe and Cr in moss, a corresponding spatial accumulation pattern for Fe was observed in the needles (Fig. 4). This Fe pattern may partly be associated with the ability of the wax layer of the needles to retain the corresponding element (Čeburnis and Steinnes 2000).

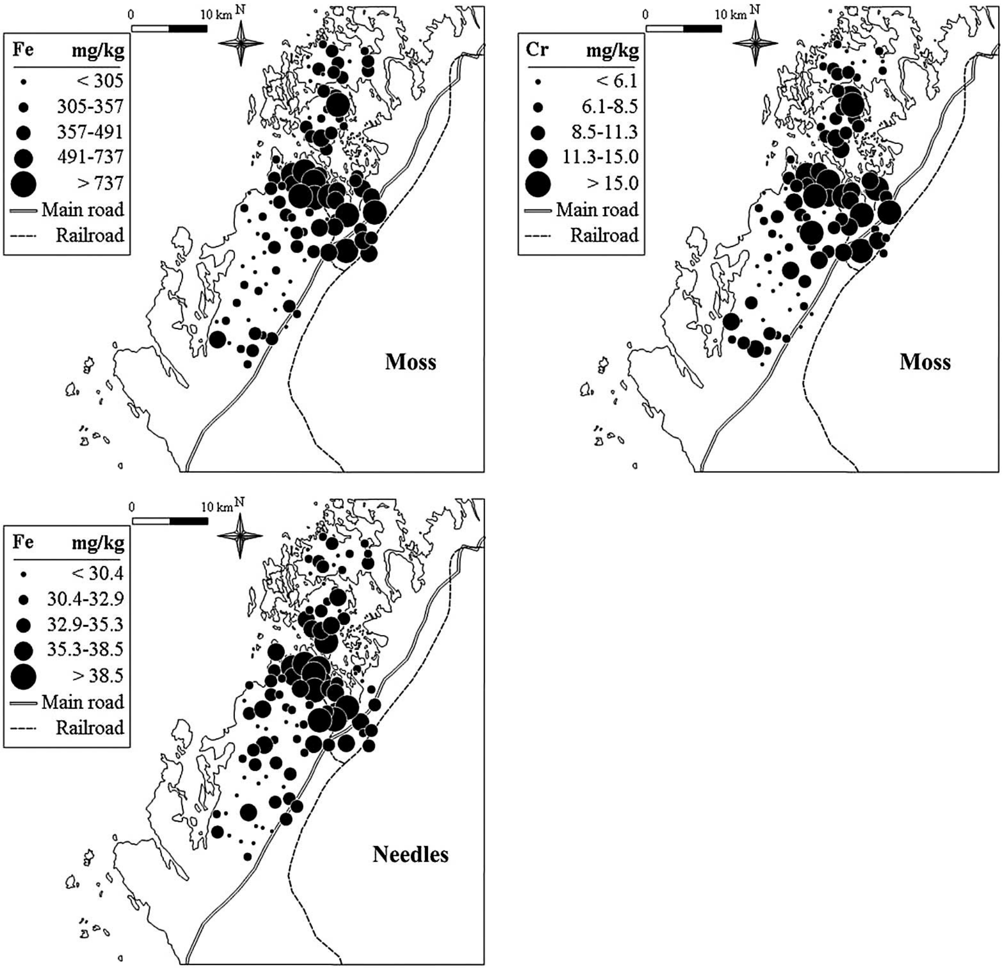
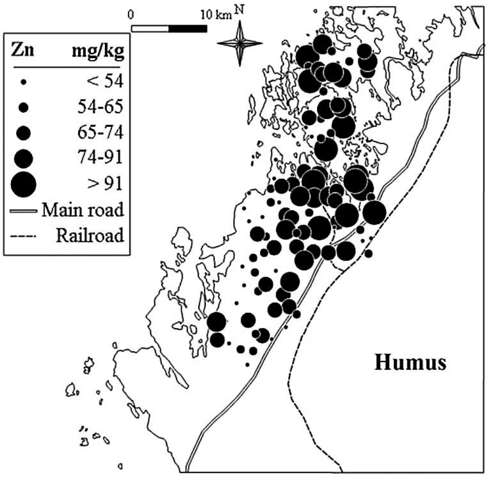


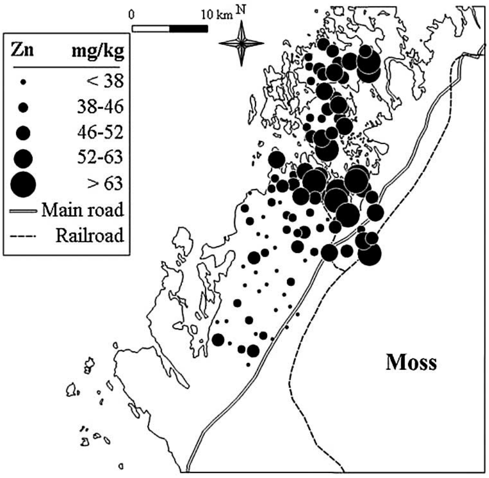
Fig. 4. Spatial distribution of Fe and Cr in moss and Fe in needles.

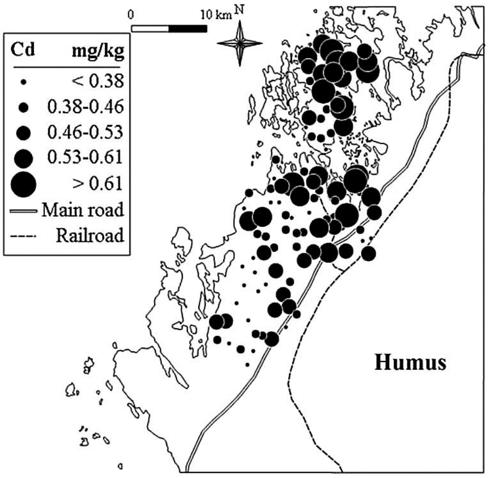
No spatial accumulation patterns were observed for Zn, Cd, Cu, Ni and Pb in till (not shown). However, the concentrations of these metals (except Pb) in humus were enriched in the northern part of the study area (Fig. 5). This accumulation pattern is partly associated with atmospheric deposition originating from the heavy industry in Karleby, where maximum concentrations of Zn, Cd, Cu and Ni in humus (Niskanen et al. 2003) exceed corresponding concentrations in this study up to 24 times, respectively. In humus, Pb showed a corresponding spatial pattern as to that of B with enrichment in and around Jakobstad (Fig. 5). This Pb anomaly could be due to deposition from a former metallurgic industry situated in the town. Furthermore, long-range transport from neighbouring countries as well as biologically and chemically related processes (e.g. organic complexing) may also to some extent explain this Pb pattern in humus (Reimann et al. 2001b).

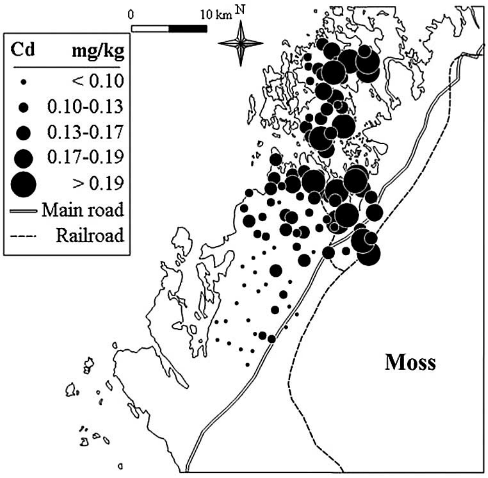
In moss, the low concentrations of Zn, Cd, Cu, Ni and Pb in the south are explained by the sparse establishment of industry in this particular part of the area (Fig. 5). The enriched concentrations of Cu, Ni and Pb in the central part of the study area, similar to that of Fe and Cr, can be attributed to increased dust and deposition levels from the iron and steel industry, coal combustion and traffic (Raitio and Kärkkäinen 2002, Peltola and Åström 2003). Additionally, an intriguing Cu anomaly (6.7–79 mg kg^{-1}) in moss, which showed approximately twice as high maximum concentrations as compared to corresponding Cu concentrations (40 mg kg^{-1}) close to the heavy industry in Karleby (Niskanen et al. 2003), was observed around the railway line in the SE of the study area (Bennäs) (Fig. 5). It was hypothesized that corrosion of the Cu-based railway line´s electric cables is the main cause for this spatial Cu anomaly.

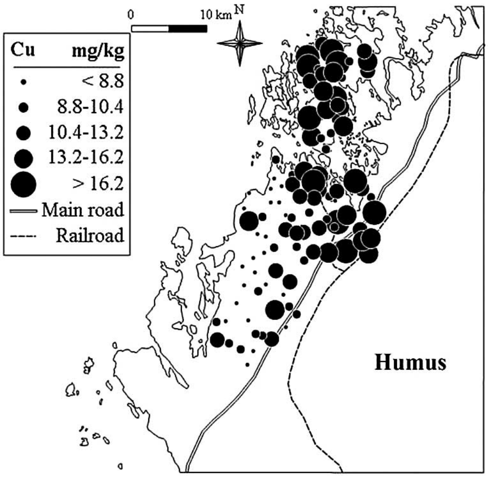
No clear spatial patterns were observed for Cu, Cd or Zn (Pb not analysed) in the needles, however, Ni displayed an apparent anomaly in the north (not shown). Natural biological processes (e.g. translocation) and antagonistic effects of Ni preventing root uptake of Cu, Cd and Zn (Rautio and Huttunen 2003) may partly explain these different spatial patterns observed in the needles.

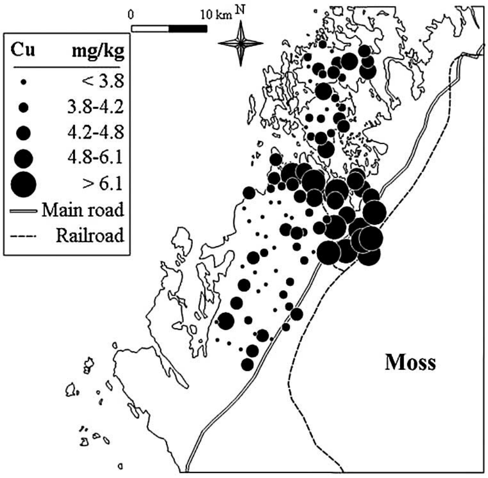


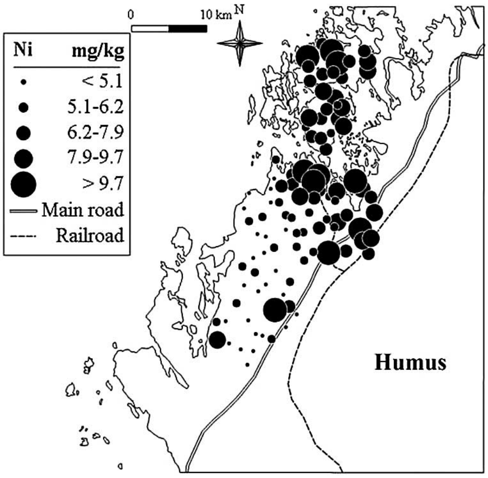


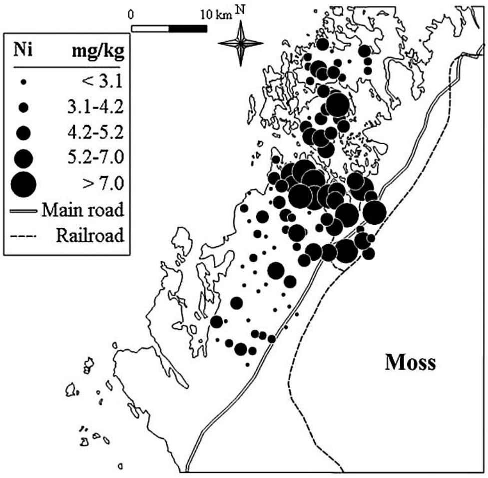

0
10 km
N
Cd mg/kg
< 0.38
0.38-0.46
0.46-0.53
0.53-0.61
> 0.61
Main road
Railroad
Humus


0
10 km
N
Cd mg/kg
< 0.10
0.10-0.13
0.13-0.17
0.17-0.19
> 0.19
Main road
Railroad
Moss


0
10 km
N
Cu mg/kg
< 8.8
8.8-10.4
10.4-13.2
13.2-16.2
> 16.2
Main road
Railroad
Humus


0
10 km
N
Cu mg/kg
< 3.8
3.8-4.2
4.2-4.8
4.8-6.1
> 6.1
Main road
Railroad
Moss


0
10 km
N
Ni mg/kg
< 5.1
5.1-6.2
6.2-7.9
7.9-9.7
> 9.7
Main road
Railroad
Humus


0
10 km
N
Ni mg/kg
< 3.1
3.1-4.2
4.2-5.2
5.2-7.0
> 7.0
Main road
Railroad
Moss

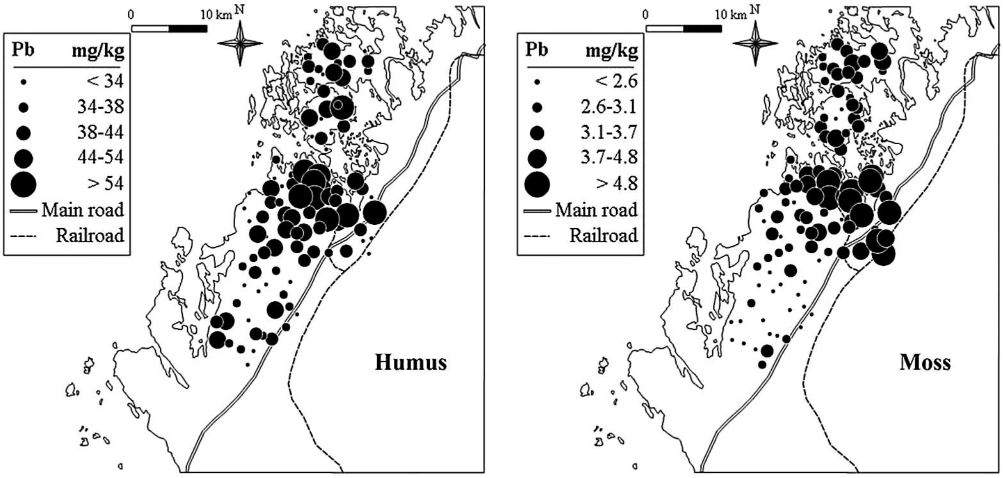


Fig. 5. Spatial distribution of Zn, Cd, Cu, Ni and Pb in humus and moss.

5.2 Paper II

The main aim of this study was to review the current available research information on the environmental risks and effects of metals mobilised in Finnish AS soils.

From an environmental point of view, AS soils are regarded as the most problematic soils in the world (Dent and Pons 1995). These soils currently cover a total of approximately 17–24 million hectare in the coastal regions worldwide. In Europe, the largest AS soil occurrences are found in Finland (1600–3000 km^2) with their major distribution along the coastal areas in the mid-western parts of the country (Fig. 1a) (Palko 1994, Yli-Halla et al. 1999, Andriesse and van Mensvoort 2002). Finnish AS soils develop where sulphide-bearing fine-grained sediments, deposited during the Holocene in the brackish Baltic Sea, are exposed to atmospheric oxygen, subsequently initiating sulphide oxidation and formation of sulphuric acid, resulting in low soil pH (2.5–4.5). The oxidation 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 2002, Österholm 2005). Soil acidification, which promote and consequently accelerate mineral weathering, abundantly mobilise metals bound in sulphides (e.g. Ni, Cd, Mn) and other minerals such as metal-bearing aluminosilicates (e.g. Al), thus making these potentially toxic metals available for transport and leaching. However, the quantity of metal-rich acid drainage originating from these soils, which vary in time and space, depend upon, for instance, the oxidation stage of the soil profile, inherent S content and drainage effectiveness.

Aluminium, which occurs in Finnish AS soils in the order of several percent as aluminosilicate and probably Al-hydroxide, is very mobile due to the acidic conditions promoting aluminosilicate weathering and Al-hydroxide dissolution and thus Al solubilisation and transport. Aluminium, which mainly exist in cationic form in AS soil affected waters (Åström and Corin 2000), is one of the most enriched elements in drainage water from typical soils and concentrations up to 260 mg l^{-1} have been observed (Åström and Björklund 1995).

The oxidation and weathering of sulphides, which results in soil acidity and increasing redox potentials, increases the mobility of Co, Ni, Zn, Cd and Mn in these soils (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 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, b, 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 AS soils as compared with average values for Finnish and Fennoscandian rivers (Edén and Björklund 1993, Lahermo et al. 1996, Åström 2001a, b). These metals are generally associated with the cationic fraction in waters draining AS soils (Åström and Corin 2000).

Chromium and Fe are generally mobilised to a limited extent upon oxidation and acidification, and thus only weakly enriched in AS soil affected waters (Åström and Björklund 1995, Åström and Åström 1997). However, high concentrations of both elements have been observed in some particularly acidic (pH 2.5–3.5) AS waters. These metals are predominantly associated with the anionic fraction (Åström and Corin 2000).

Phosphorus and Ca are enriched in the plough layer of cultivated AS soils due to recurring fertilisation and liming treatments, respectively (Österholm and Åström 2002). Magnesium, K and Ca are leached out from AS soils in moderate to large amounts (Åström and Björklund 1995, Åström and Åström 1997, Österholm and Åström 2002, 2004), while the leaching of P is limited (Åström 1998a). A significant portion of Mg, K and Ca in AS soil affected waters may originate as sea salts once trapped in the pores of the parent sediments of these soils.

Palko (1986) and Yli-Halla and Palko (1987) studied the chemical composition of timothy and oats grown on AS soils in Western Finland and compared these results to Finnish average values (FAV) for the corresponding crops (Paasikallio 1978, Kähäri and Nissinen 1978, Varo et al. 1980b). Palko (1986) found timothy samples enriched in Ni (AS soils 1.8 mg kg^{-1} and FAV 0.34 mg kg^{-1}), 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 grown on AS soils were both enriched in Mn, Co and Ni, metals which are mobile in these soils. Although Fe and Cr are only mobilised to a limited extent in these soils they were still enriched in both crops. Based on the above mentioned results, one could hypothesize that plant-root biochemistry is responsible for the Fe enrichment in oats, while Mn-oxides enhancing Cr solubility partly may explain the enrichment of Cr in timothy.

Only one study has been published on metal levels in cow milk originating from AS soil farms (Alhonen et al. 1997), and it revealed significantly elevated concentrations of Al to that of the reference material (AS soils 2400 μg kg^{-1} and reference material 50 μg kg^{-1}). It should be pointed out that no attention was paid to neither the geochemistry of the AS soils nor the chemical composition of the forage or vegetation on the pasture-ground, making interpretation of the origin of these elements difficult. Furthermore, the scanty number of data makes the Al pattern outlined above indicative only. Although shortcomings were encountered in the study by Alhonen et al. (1997) it certainly highlights the need for more studies on metal biogeochemistry in these landscapes. At present, therefore, we have very little knowledge to what extent and how the AS soil affect metal concentrations in animals, except for the obviously high contents of Al in cow milk.

Bioindicator studies, using aquatic mosses and -insect larvae in AS soil environments, demonstrated high concentrations of Al, Fe, Cu and Zn (the latter metal only in larvae) in these species (Vuori and Kukkonen 1996, Vuori 2002). Consequently, the accumulation of Al in crops, cow milk, stream-water, aquatic mosses and -insect larvae is an effect of the AS soil and its management. Iron, on the other hand, which is liberated and leached only to a limited extent from these soils according to existing hydrochemical and geochemical data, still seems to become enriched in several plant and animal species existing in areas underlain with these soils. This contradiction warrant further investigation to clarify the biogeochemistry of Fe in these settings.

Existing research evidence shows that AS soils pose adverse effects on aquatic plant and animal communities and populations in stream and estuarine environments. The abundant metal-rich acid drainage from these soils has significant, but spatially and temporally variable ecotoxicological impacts on biodiversity and community structure of fish, benthic invertebrates and macrophytes (Nyman et al. 1986, Meriläinen 1989, Urho et al. 1990, Vuori 1996, Hudd 2000, Kjellman 2003). Although recovery has been demonstrated, the fact that even a single short-term exposure to low pH and high metal concentrations can cause decreased population sizes and absence of sensitive fish and macroinvertebrate species stresses the importance for decreasing loading of acidity and metals from AS soils. Although the knowledge on ecotoxicological impacts of AS soils is based on a few river and estuary sites only, they highlight the need for more research on the effects of these soils on their surrounding aquatic environment.

A multitude of studies have been conducted during the last decade linking exposure to specific elements with the widespread neurodegenerative disorders, Alzheimer´s (AD) and Parkinson´s (PD) disease, respectively (Gorell et al. 1997, Rogers and Simon 1999, Rondeau et al. 2000, Flaten 2001, Zatta et al. 2003, Michalke et al. 2009). Significant positive association was observed in 9 out of 14 studies linking Al in drinking water with AD, however, others failed to find a significant relationship (Forster et al. 1995, Martyn et al. 1997). A statistically significant relationship was found with elevated amounts of Zn and Fe in the brain and AD, but not in the pituitary gland (Cornett et al. 1998a, b) nor in the hair and serum for the latter element (Shore et al. 1984). Epidemiological evidence point to a significant increase of PD for those occupationally exposed to Mn, increased risk was also observed for exposure to combined metals (e.g. Fe-Cu) (Gorell et al. 1997, 1998, 1999, Gorell and Checkoway 2001). Other studies showed no significant association with occupational exposure of metals or combination of these and PD (Seidler et al. 1996, McDonnell et al. 2003, Jankovic 2005).

These above mentioned studies show variable results for the association between exposure to metals and development of AD and/or PD, but they certainly highlight the need for further investigation linking chronic exposure of specific metals, or combination of metals, as risk factors implicated with these neurodegenerative diseases. Based on the literature review it is hypothesized that chronic exposure is plausible in areas in Western Finland where the occurrence of AS soils is abundant and affect metal concentrations in stream waters, crops and milk. Thus, an obvious risk group would consist of people deriving their food, raw products and drinking water from local farmland consisting of these soil types. The literature review also revealed that a systematic risk assessment on the possible health outcome in AS soil landscapes should be undertaken.

5.3 Paper III

The role of soil chemistry on the concentrations of Co, Ni, Zn, Mn, Cu and Fe in oats (*Avena sativa* L. cv. Fiia) grown on Finnish acid sulphate (AS) soils with varying geochemical characteristics was studied. A total of 22 soil profiles, which were sampled to a depth of 1 m at corresponding plant sample sites, were collected on five agricultural fields (F1-F5) in mid-western Finland and analysed for pH, S content and NH_4Ac-EDTA extractable (easily available) metal concentrations. The multi-element concentrations in soil and oats were compared with corresponding Finnish average values (FAV).

The pH, which decreased down the AS soil profile in all fields, were in the order: F5 < F3 = F1 < F4 < F2 (Table 1). The higher pH towards the surface is a result of heavy topsoil liming and a rather high organic matter concentration while the lower pH further down the soil profile is caused by oxidation of sulphides and low inherent carbonate concentrations (Palko 1994, Österholm 2005). The pH of the AS soil profiles (the upper meter) in this study can be considered relatively high as compared to that of other studies where pH can drop below 3.5 (Yli-Halla et al. 1999, Österholm and Åström 2002).

The aqua regia extractable S content differed significantly between the fields (not shown) with concentrations up to 7400 mg kg^{-1} in F4. The large S variation is explained by differences in inherent concentrations and extent of leaching.

The mean NH_4Ac-EDTA extractable concentrations of Co, Ni, Zn, Mn and Cu in F1-F5 were relatively similar between the top- and subsoil, with the exception of Fe, which was enriched in the subsoil (Table 1). The influence of the subsoil on the oats may have been relatively large due to the exceptionally dry growing season in 2006.

The variation of the NH_4Ac-EDTA extractable concentrations of Co, Ni, Zn and Mn in the soil profiles was much larger between-fields than within-fields (Table 1, Fig. 6). F3 was enriched in Co and Ni, while F5, in which pH was lowest, showed the highest concentrations of Zn and Mn (Table 1). All these metals are chalcophilic and in the AS soils thus associated with sulphides (Öborn 1994). However, in comparison with the FAV, F1-F5 showed relatively similar values of NH_4Ac-EDTA extractable Co, Ni and

Zn (except Ni in F3), and was even depleted in Mn (Table 1). This indicates that once released from sulphides, these four metals are not generally retained in the acidic soils but are flushed into drains. This is consistent with the abundance of these metals in streams draining AS soils (e.g. median concentrations of 110 μg l^{-1} Co, 180 μg l^{-1} Ni, 5700 μg l^{-1} Mn and 330 μg l^{-1} Zn reported by Åström and Åström 1997, Österholm et al. 2005) and accumulation close to the ground-water table (Åström 1998b, Österholm and Åström 2002).

The concentrations of Co, Ni, Zn and Mn in the oats were strongly correlated to those in both the top- (Fig. 7) and subsoil. This indicate that the uptake of these four metals in oats grown on Finnish AS soils is not efficiently regulated by the plant but largely controlled by the concentrations of easily available fractions in the soil. However, the concentrations of Co, Ni, Zn and Mn were not in general elevated in the soils nor grains, with the exception of the two former metals in F3, which showed up to four times higher concentrations as compared to the FAV (Table 2, Fig. 7). Yli-Halla and Palko (1987) found similar anomalous soil (NH_4Ac-EDTA extractable) and oat grain concentrations of Co and Ni, as compared to the FAV, in AS soils located in Western Finland. In F4, both the soil and oat concentrations of Co, Ni, Zn and Mn were low (Table 1, Fig. 7) while the aqua regia extractable S concentration in the soil was high. It is suggested that this particular field has undergone limited oxidation and leaching, and thus has the potential for future metal release and, as shown in this study, possible uptake in oats. These results indicate strong spatial variability between AS soils, hence, mobilisation of chalcophilic metals and subsequent bioaccumulation vary locally and is affected by soil geochemistry and most probably land-use practise.

Table 1. Mean and range of pH, LOI, NH_4Ac-EDTA- (Paper III) and NH_4Ac extractable (Paper IV) concentrations of elements (mg kg^{-1}) in top- (0–20 cm) respective subsoil (20–100 cm) in eight (F1-F5, F6-F8) AS soils and corresponding Finnish average values of topsoil in arable land (Sippola and Tares 1978). The subsoil (20–100 cm) represents the mean of four subsamples per site.

	Paper III														Paper IV													
	F1		F2		F3		F4		F5		F1-F5		FAV		F6		F7		F8		F6-F8		FAV	
	$(n_{ts}=2;\ n_{ss}=8)$		$(n_{ts}=5;\ n_{ss}=20)$		$(n_{ts}=5;\ n_{ss}=20)$		$(n_{ts}=5;\ n_{ss}=20)$		$(n_{ts}=5;\ n_{ss}=20)$		$(n_{ts}=22;\ n_{ss}=88)$		(nts=2015)		$(n_{ts}=5;\ n_{ss}=4)$		$(n_{ts}=2;\ n_{ss}=4)$		$(n_{ts}=4;\ n_{ss}=4)$		$(n_{ts}=11;\ n_{ss}=12)$		$(n_{ts}=2015)$	
	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R
pH (ts)	5.7	5.4-5.9	6.0	5.5-6.4	5.2	4.9-5.6	6.2	5.8-6.5	4.3	4.1-4.7	5.4	4.1-6.5	5.6	4.0-7.6	6.1	5.8-6.8	6.9	6.8-6.9	7.0	6.9-7.1	6.6	5.8-7.1	5.6	4.0-7.6
pH (ss)	4.6	3.7-5.3	5.4	4.5-6.4	4.7	4.2-5.4	5.0	3.9-6.0	4.1	3.9-4.4	4.8	3.7-6.4	-	-	3.8	3.6-4.2	4.1	3.9-4.6	4.2	3.5-5.5	4.0	3.5-5.5	-	-
LOI (ts)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6.2	5.9-6.6	5.1	4.5-5.7	5.8	5.3-6.2	5.8	4.5-6.6	-	-
LOI (ss)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6.0	5.6-6.2	3.9	3.9-4.1	5.1	4.4-5.9	5.0	3.9-6.2	-	-
Ca (ts)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2863	2664-3051	3661	3117-4204	4313	3813-4654	3535	2664-4654	1282	25-10250
Ca (ss)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	702	489-1011	748	340-1267	584	345-1197	678	340-1267	-	-
K (ts)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	85	78-97	137	134-139	61	57-68	86	57-185	97	10-1160
K (ss)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	157	118-192	102	98-109	80	48-111	113	48-192	-	-
Mg (ts)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	486	476-503	357	344-370	320	299-341	402	299-503	178	5.0-1250
Mg (ss)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	249	204-278	164	112-235	177	110-261	197	110-278	-	-
P (ts)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	18	15-23	83	79-87	75	67-84	51	15-114	9.3	0.4-343
P (ss)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	61	23-92	20	18-22	28	21-40	36	18-92	-	-
Co (ts)	0.62	0.45-0.79	0.24	0.20-0.31	0.93	0.50-1.3	0.10	0.083-0.11	0.49	0.36-0.62	0.46	0.083-1.3	0.52	0.02-14	0.26	0.17-0.50	0.04	0.03-0.05	0.14	0.12-0.16	0.18	0.033-0.50	-	-
Co (ss)	0.54	0.37-0.82	0.22	0.14-0.35	0.87	0.43-1.2	0.13	0.072-0.22	0.35	0.11-0.60	0.41	0.072-1.2	-	-	0.46	0.30-0.57	0.08	0.04-0.12	0.32	0.12-0.59	0.29	0.042-0.59	-	-
Ni (ts)	2.9	2.1-3.7	0.87	0.67-1.1	5.1	3.6-6.7	0.47	0.37-0.58	1.4	1.1-1.7	2.0	0.37-6.7	0.92	UD-18.8	0.78	0.49-1.3	0.22	0.17-0.26	0.44	0.42-0.46	0.55	0.16-1.3	-	-
Ni (ss)	2.5	1.9-4.6	0.91	0.54-1.2	4.3	3.1-6.0	0.60	0.38-0.82	1.2	0.62-1.6	1.8	0.38-6.0	-	-	1.1	0.78-1.3	0.21	0.11-0.35	0.72	0.47-1.1	0.66	0.11-1.3	-	-
Zn (ts)	2.9	2.1-3.6	4.9	3.2-6.6	4.4	3.0-6.6	0.80	0.60-0.90	6.3	4.0-10	4.0	0.60-10	5.0	0.35-89.2	2.0	1.4-3.3	3.1	2.6-3.6	0.86	0.70-1.0	1.8	0.70-3.6	-	-
Zn (ss)	3.8	2.7-4.7	3.9	1.4-6.0	4.6	2.9-6.7	1.2	0.70-1.8	4.6	0.90-8.1	3.6	0.70-8.1	-	-	4.3	2.7-5.7	0.89	0.55-1.1	2.4	0.75-4.5	2.5	0.55-5.7	-	-
Mn (ts)	11	10-11	13	11-15	18	15-21	3.6	3.0-4.0	37	31-48	17	3.0-48	59	0.6-8800	9.2	4.0-22	18	17-18	20	16-22	14	4.0-22	-	-
Mn (ss)	13	8.0-23	9.3	6.0-13	21	14-39	5.0	3.0-9.0	25	6.0-42	15	3.0-42	-	-	18	9.5-23	6.4	2.5-9.0	13	4.0-25	12	2.5-25	-	-
Cu (ts)	1.0	0.92-1.1	1.7	1.3-1.9	1.0	0.80-1.3	1.0	0.86-1.3	1.2	1.0-1.3	1.2	0.80-1.9	2.8	0.15-49.1	0.75	0.56-0.99	1.1	0.98-1.2	1.9	1.6-2.1	1.2	0.56-2.1	-	-
Cu (ss)	1.0	0.83-1.6	2.0	1.6-2.6	1.3	0.88-2.0	0.94	0.73-1.3	1.2	0.98-1.6	1.3	0.73-2.6	-	-	1.0	0.88-1.1	1.7	1.6-1.8	0.88	0.65-1.2	1.2	0.65-1.8	-	-
Fe (ts)	287	209-365	73	45-107	367	207-560	89	46-104	1553	1495-1602	499	45-1602	677	17-6300	102	38-233	44	42-46	33	29-38	66	29-233	-	-
Fe (ss)	849	354-1847	237	73-493	598	226-965	430	121-1174	1490	766-1804	703	73-1847	-	-	1366	709-1730	712	596-844	926	282-1394	1001	282-1730	-	-

FAV: Finnish average values
R: range
ts: topsoil
ss: subsoil
UD: under detection limit

Table 2. Chemical composition (dry weight) of oats (Paper III, F1-F5) and cabbage (Paper IV, F6-F8) in the eight studied fields and corresponding Finnish average values (Varo et al. 1980a, b).

	Paper III														Paper IV									
	F1		F2		F3		F4		F5		F1-F5		FAV		F6		F7		F8		F6-F8		FAV	
	(n=6)		(n=5)		(n=5)		(n=5)		(n=5)		(n=26)		(n=36)		(n=5)		(n=2)		(n=4)		(n=11)		(n=5)	
	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R	mean	R
Ca (g kg^{-1})	-	-	-	-	-	-	-	-	-	-	-	-	-	-	8.0	7.0-9.5	4.0	3.2-4.7	7.7	5.6-9.5	6.6	3.2-9.5	5.3	5.0-5.8
K (g kg^{-1})	-	-	-	-	-	-	-	-	-	-	-	-	-	-	41	39-44	51	42-60	36	35-39	43	35-60	40	36-43
Mg (g kg^{-1})	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.9	2.6-3.0	2.0	1.8-2.2	2.1	1.9-2.3	2.3	1.8-3.0	1.8	1.5-1.9
P (g kg^{-1})	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5.7	5.4-5.9	9.3	9.0-9.6	5.6	4.9-6.0	6.9	4.9-9.6	5.1	3.8-6.5
Co (mg kg^{-1})	0.070	0.040-0.10	0.016	0.010-0.020	0.23	0.13-0.31	0.048	0.040-0.060	0.068	0.040-0.10	0.086	0.010-0.31	0.081*	0.026-0.23*	0.12	0.070-0.23	0.030	0.020-0.040	0.065	0.060-0.070	0.073	0.020-0.23	0.063	0.013-0.13
Ni (mg kg^{-1})	3.6	2.2-4.4	1.6	1.4-2.0	11	5.9-16	2.1	2.0-2.3	4.0	2.7-5.7	4.5	1.4-16	2.8*	0.6-5.6*	0.86	0.3-1.5	0.70	0.4-1.0	0.78	0.5-1.1	0.78	0.3-1.5	1.3	0.25-3.8
Zn (mg kg^{-1})	65	56-74	54	51-59	63	50-77	39	34-43	66	61-72	57	34-77	43*	31-56*	31	25-36	64	59-68	22	18-25	39	18-68	26	19-36
Mn (mg kg^{-1})	40	31-47	38	32-41	60	48-72	37	33-39	63	55-69	48	31-72	72*	51-98*	8.4	5.0-11	15	14-15	14	9.0-18	12	5.0-18	30	14-45
Cu (mg kg^{-1})	6.9	6.1-8.2	6.5	6.2-7.4	7.2	6.3-7.9	6.5	5.8-7.3	7.4	7.0-7.8	6.9	5.8-8.2	5.6*	4.2-8.6*	3.9	3.2-4.3	5.5	4.9-6.0	2.6	2.4-3.0	4.0	2.4-6.0	4.5	3.8-5.5
Fe (mg kg^{-1})	63	50-80	74	70-80	64	50-70	92	70-110	92	80-100	77	50-110	60*	45-100*	48	40-80	70	69-71	40	40-40	53	40-80	48	44-51

FAV: Finnish average values

R: range

*Converted to dry weight.

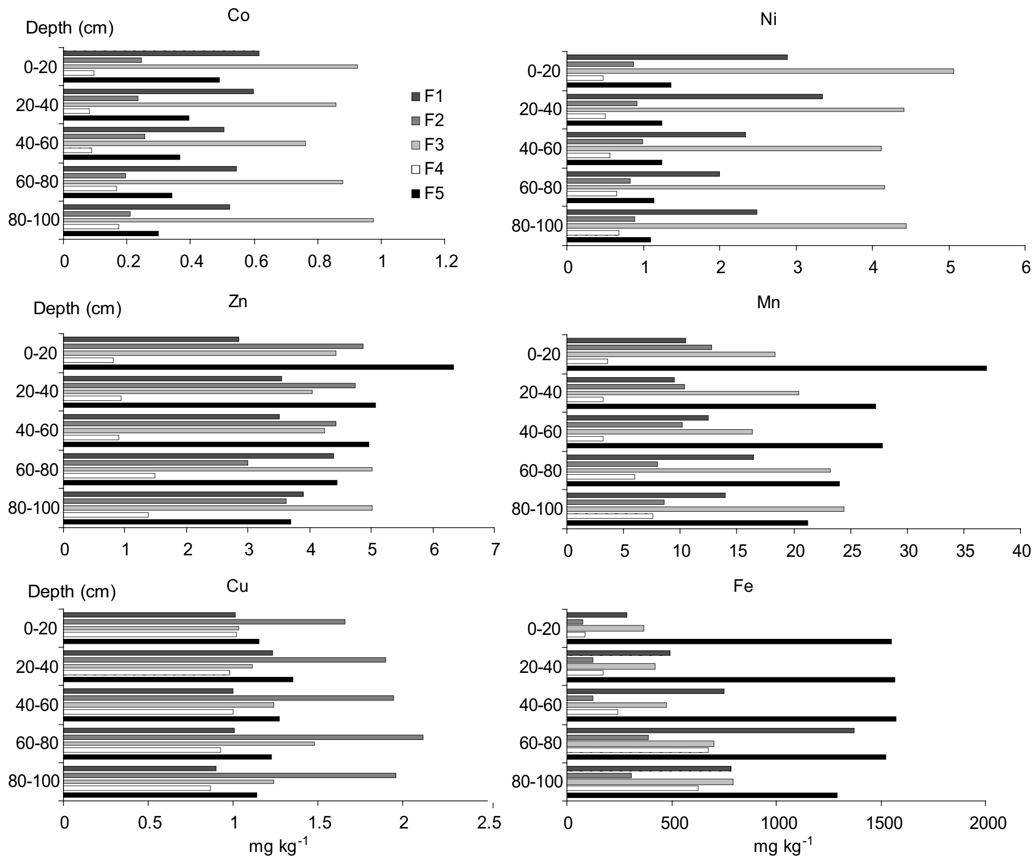


Fig. 6. Mean NH_4Ac-EDTA extractable concentrations (mg kg^{-1}) of elements in the soil profiles of F1-F5.

The NH_4Ac-EDTA extractable concentration of Cu was stable downwards the profile in all fields, whereas the Fe concentration increased slightly downwards in several profiles (Fig. 6). Overall, the concentration of Fe and Cu in F1-F5 were lower than the FAV (Table 1). The Fe concentration and pH were inversely correlated (not shown), indicating that the abundance of the NH_4Ac-EDTA extractable Fe fraction is controlled by soil acidity. It is however notable that although Fe is mobilised within the AS soil, it is only leached to a limited extent since it is abundantly reprecipitated on surfaces of oxic soil aggregates and cracks as amorphous oxide (Fe oxyhydroxides) coatings (Österholm and Åström 2002) to which Cu also is readily absorbed (Kabata-Pendias 2001). It has been suggested that plant roots are able to reduce Fe^{3+} to Fe^{2+} which is more readily absorbed by plants (Christ 1974, Kabata-Pendias 2001). Additionally, plant roots are capable of releasing Fe and Cu via the secretion of fytosiderophores, which enhance metal solubility through chelation (Shenker et al. 2001). The extraction of Cu and Fe with NH_4Ac-EDTA may therefore underestimate the easily available fraction due to the inability to dissolve the Fe(III) phases. Although Fe and Cu were not abundantly released by NH_4Ac-EDTA (except Fe in F5), they were somewhat elevated in the oats as compared to the FAV (Table 2), and it was therefore argued that biological processes (e.g. plant-root processes) overshadow geochemical variation. This in turn is consistent with the suggestion that NH_4Ac-EDTA is not an efficient extractant of Fe and Cu in these soils, and that oxides, which are abundant in AS soils, are a significant carrier of these metals from which they may be available for plant uptake.

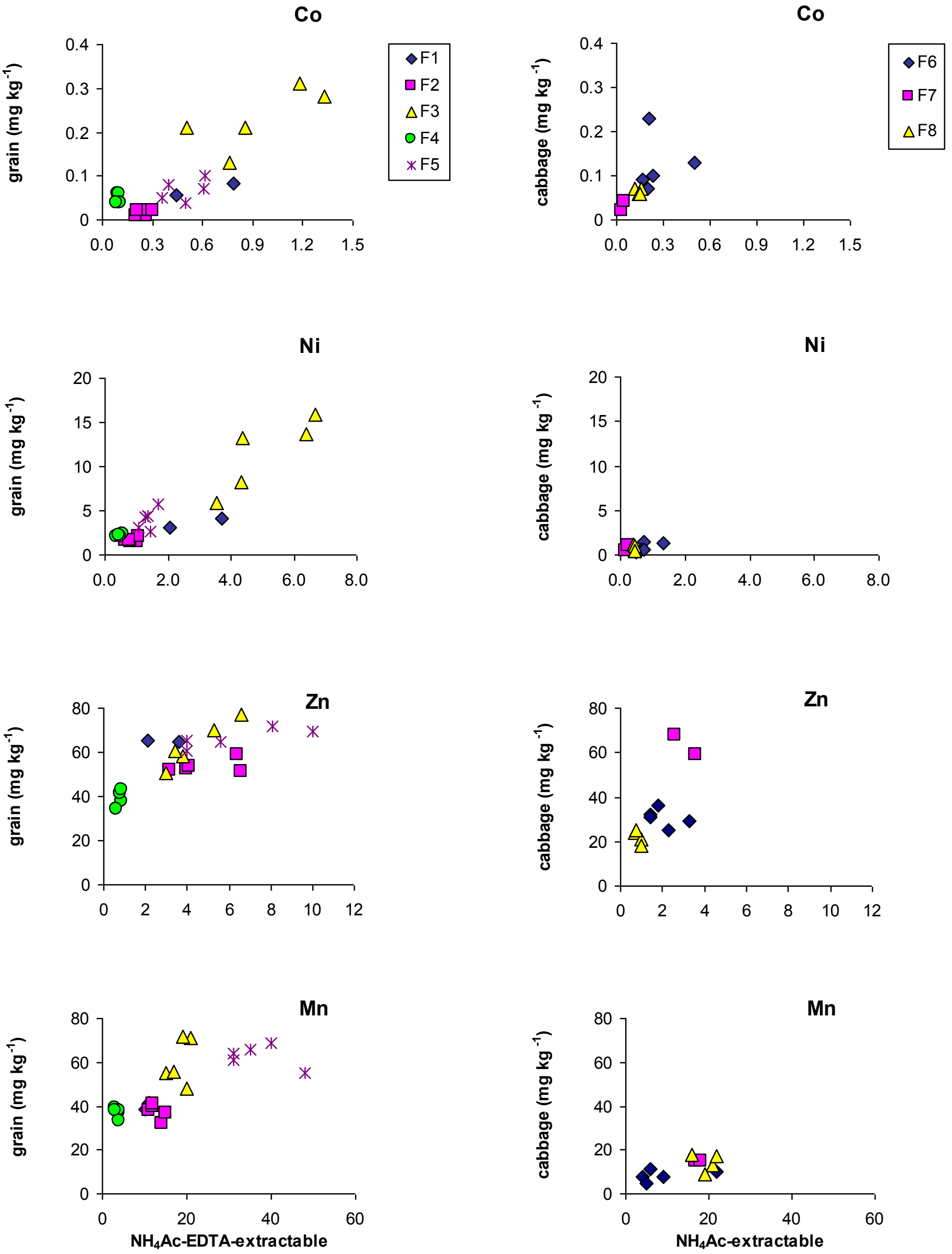


Fig. 7. NH_4Ac-EDTA- (Paper III) and NH_4Ac extractable (Paper IV) concentrations (mg kg^{-1}) of elements in topsoil (0–20 cm) in each of the studied fields (F1-F5, F6-F8) versus total concentrations (mg kg^{-1}) in oat grains and cabbage. All of the above presented element associations are significant ($P \leq 0.05$) except Ni and Mn in cabbage.

5.4 Paper IV

The purpose of this study was to investigate the influence of soil geochemistry on the concentrations of Ca, K, Mg, P, Co, Ni, Zn, Mn Cu and Fe in cabbage (*Brassica oleracea* L. var. capitata) grown on acid sulphate (AS) soils in mid-western Finland. A total of 11 topsoil samples (0–20 cm) and corresponding cabbage samples and three whole soil profiles (~0–260 cm) were collected from three agricultural fields (F6-F8). These soil samples were analysed for NH_4Ac (easily available)-, hydroxylamine (oxide-bound)- and aqua regia extractable metal concentrations. Additional soil characteristics determined were pH, LOI and oxidation depth. These results (metal content in cabbage and NH_4Ac extractable concentrations of Ca, K, Mg and P in topsoil) were compared with corresponding Finnish average values (FAV) of other soils.

Soil pH decreased and S content (aqua regia extractable) increased down the profile in all fields and eventually levelled off at the deeper section of the profile, respectively (Fig. 8). The almost neutral pH (~6–7) in the topsoil (0–20 cm), a necessity for the cultivation of cabbage, is attributed to efficient liming management and the strongly acidic conditions (~3.5–4.5) in the subsoil (~20–100 cm) is a feature of abundant sulphide oxidation. The transition zone, which is situated below the subsoil (>140 cm), is characterised by partly oxidized and reduced conditions and by a swift increase in pH (~6). The oxidation depth (boundary where pH exceed 6.5), which in these soils is located at ~160–200 cm and decreased in the order: F6 < F7 = F8 (Fig. 8), is mainly affected by the depth and efficiency of drainage system utilized within these agricultural fields. In the parent material (below 160–200 cm), where reducing conditions prevail, the pH is ca. 7–8. The low S concentration in the top- and subsoil (oxidized layer) compared to the sharp increase in the transition zone and parent material (mainly reducing conditions) (Fig. 8) is due to ample leaching (Österholm and Åström 2002). The inherent S concentrations of the parent material (0.9–2.0%) were notably higher, and pH similar, to that of other AS studies conducted in Western Finland (Åström and Björklund 1997, Österholm and Åström 2002, Joukainen and Yli-Halla 2003, Nordmyr et al. 2006, Boman et al. 2008).

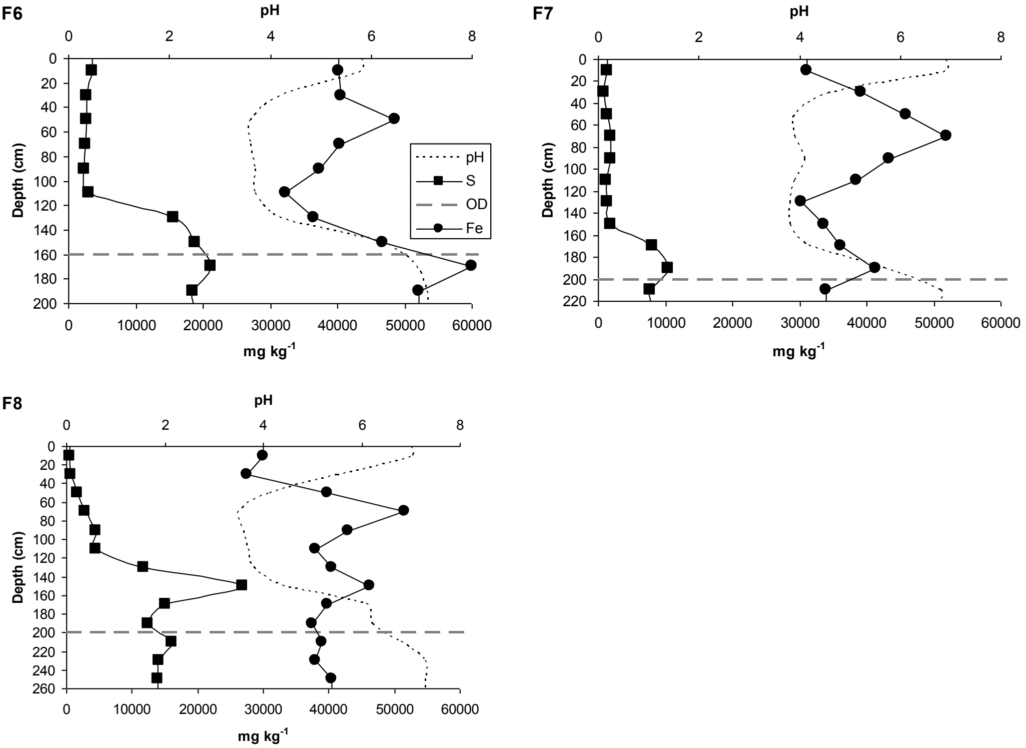


Fig. 8. Vertical variation of aqua regia extractable S and Fe concentrations, pH and oxidation depth (OD) in F6-F8.

The mean LOI concentrations of both the top- and subsoils were in the order: F7 < F8 < F6 (Table 1). The LOI contents recorded here are similar to those of other regionally representative AS soil studies (Nordmyr et al. 2006, Bärlund et al. 2004, Sohlenius and Öborn 2004). The higher LOI in F6 to that of F8 was unexpected since the latter had a remarkably brownish subsoil, indicating organic matter of different composition and origin.

The NH_4Ac extractable concentrations of Ca, Mg and P in F6-F8 were considerably higher and K similar to that of the FAV, respectively (Table 1). This indicate that input of easily available Ca, Mg and P through replenishment via fertilisation and liming is relatively high as compared to output through leaching and plant uptake (Åström and Björklund 1995, Åström et al. 2007).

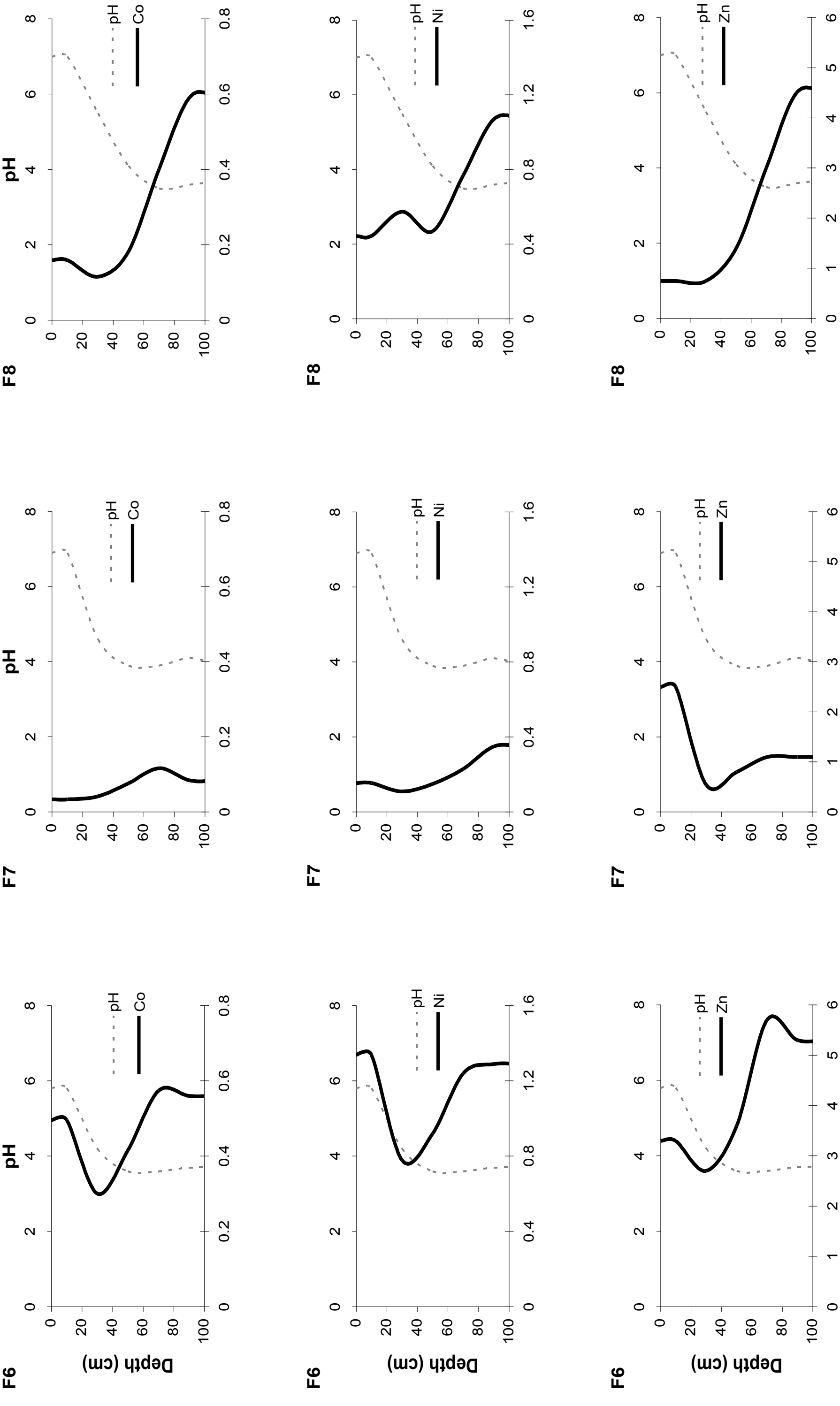
Cabbage grown on AS soils showed somewhat enriched concentrations of Ca, Mg and P and similar concentrations of K to that of the FAV, respectively (Table 2). Common for these macronutrients in cabbage was their overall low spread, which is indicative of biological processes controlling uptake (Reimann et al. 2001b). Moreover, the concentrations of Ca and P in cabbage were uncorrelated with corresponding NH_4Ac and hydroxylamine extractable concentrations in the topsoil. It has also been shown that cabbage (*Brassica oleracea* L. var. *capitata*) is efficient in increasing its P uptake through exudation of organic anions (e.g. citrate), which effectively dissolve phosphate bound on amorphous surfaces of Fe and Al (Dechassa and Schenk 2004, Schenk 2006). These results indicate that the plant´s ability to regulate its Ca and P absorption (through e.g. root exudates) seems to be more important than the influence of AS soil geochemistry. The concentrations of K and Mg in cabbage on the other hand, which were strongly correlated to that of the NH_4Ac extractable concentrations in the topsoil, are suggested to be governed by both the easily available fractions and plant-uptake mechanisms.

The variations of the NH_4Ac extractable concentrations of Co, Ni, Zn and Mn were relatively large between the fields. F6, in which pH was the lowest, was enriched in Co, Ni, Zn and Mn in the subsoil and the former two elements in the topsoil while F7 demonstrated remarkably low concentrations of Co and Ni throughout the profile (Fig. 9).

The concentrations of Co and Zn in cabbage were correlated to those in the topsoil of F6-F8 (Fig. 7), indicating that uptake of these elements in cabbage is largely governed by soil geochemistry. Yet, the concentrations of Co and Zn in cabbage were not in general elevated to that of the FAV, although some AS soils showed enriched concentrations of these metals in both soil and cabbage. This is consistent with the results of Paper III, which showed generally similar mean micronutrient concentrations in oat grains cultivated on five AS soils, but clearly enriched contents in oats in one of these fields as compared to the FAV. The concentrations of Ni and Mn in cabbage were uncorrelated to those in the topsoil of F6-F8 and lower to that of the FAV (Fig. 7, Table 2). On all fields, the mean Ni concentrations in cabbage were exceptionally similar although the corresponding NH_4Ac extractable concentrations differed markedly (Table 1, 2). This may imply that the plant effectively can regulate its relative uptake through rejection of this potentially toxic metal and is thus independent of the easily available Ni concentrations in the soil. On the contrary, an "on demand" mechanism by exudation of organic acids could be initiated by the plant when the concentrations of easily available Ni are low (Kabata-Pendias 2001). Oxidation depth affected neither the easily available concentrations of Co, Ni, Zn and Mn in the topsoil nor the concentrations in cabbage. Nevertheless, the subsoil with a lower oxidation depth, which is to a smaller extent affected by leaching, may partly be enriched in these metals, however, these were not reflected as enriched concentrations in cabbage.

The NH_4Ac extractable concentrations of Fe in F6-F8, which were depleted in the heavily limed topsoil and enriched in the acidic subsoil, were inversely correlated with soil pH (Table 1, Fig. 9). Iron (as well as Cu) is in general only leached to a limited extent upon mobilisation in boreal AS soils, however, the depletion of Fe in the topsoil of each field may, except pH, be an indication of efficient downward leaching and subsequent reprecipitation as immobile oxyhydroxides (Österholm and Åström 2002). A vertical translocation of easily soluble Fe from the topsoil to a less soluble fraction (e.g. amorphous Fe oxide) in the subsoil was indicated as a concentration peak of aqua regia extractable Fe in the 50–70 cm section of the profile in F6-F8 (Fig. 8). The NH_4Ac extractable Cu concentrations, which showed differing vertical patterns in each of the three soil profiles (not shown) and were uncorrelated with pH, showed a significant inverse relationship with the LOI concentrations, indicating that the Cu bioavailability is controlled by the organic matter content (Kabata-Pendias 2001). Consequently, the organic-rich F6 showed an overall low concentration of easily available Cu (Table 1).

The variations of the hydroxylamine extractable concentrations of Cu and Fe in the topsoil were relatively large between the fields. F6, which was enriched in Fe, showed low concentrations of Cu while F8 demonstrated two times lower and three times higher contents of Fe and Cu to that of F6, respectively. The relatively high extent of hydroxylamine extractable Fe in F6, indicating enriched contents of Fe oxyhydroxides, may trap abundant amounts of metals and thus serve as a possible sink of metals. The hydroxylamine extractable concentrations of Cu and Fe in the topsoil of F6-F8 were strongly correlated with the easily soluble fraction, which was observed as an abundance of bioavailable and hydroxide-bound Fe in F6 and Cu in F8, respectively (Table 1). However, neither the hydroxylamine- nor NH_4Ac extractable concentrations of Fe and Cu in the topsoil of F6-F8 were correlated to those in cabbage, indicating that uptake is not to a significant extent governed by the oxide- bound- or easily soluble content of these elements in the soil. Interesting to note was the rather low spread of these metals in cabbage, similar to that of the macronutrients, and their comparable concentrations to that of the FAV (Table 2). Based on these findings it is suggested that cabbage can regulate, and thus optimize its concentrations of Cu and Fe and is independent of the soil extractable contents of these metals. Consequently, the large amounts of metals mobilised in Finnish AS soils seem to be easily lost to drains, subsequently contaminating nearby waterways and estuaries (Åström and Åström 1997), and only partly enriched in cabbage grown on typical AS soils.


F6
F7
F8
pH
Depth (cm)
mg kg^{-1}
pH
Co
Ni
Zn
0
2
4
6
8
0.2
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1.6
1
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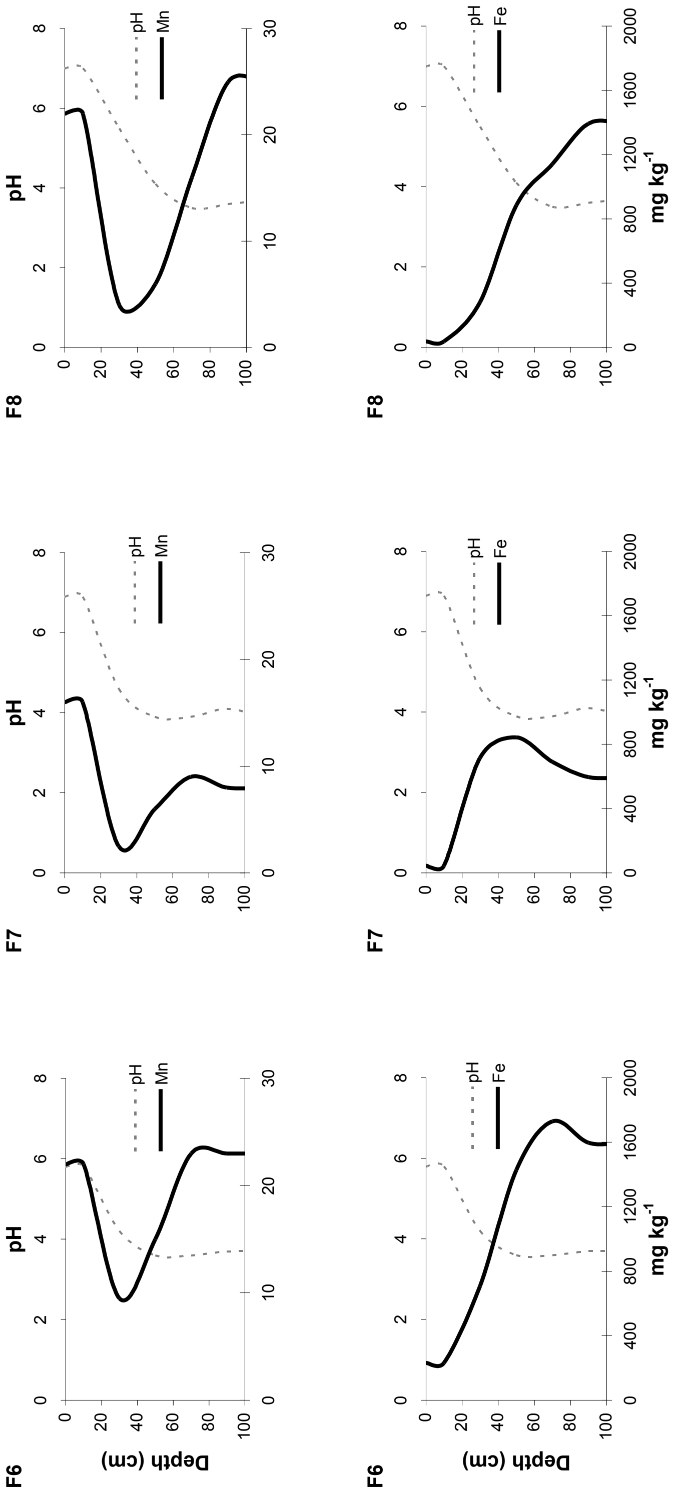

Fig. 9. Vertical variation of NH_4Ac extractable element concentrations (mg kg^{-1}) and pH in F6-F8.

6. Biogeochemical pathways of metals released in acid sulphate soils – integration of results from Paper II-IV

The above discussion shows that regional and local transfer pathways of metals in the urban and rural study area are governed by a multitude of different processes. Metal anomalies observed in moss in and around town centres (Paper I) are predominantly governed by anthropogenic point sources, dust input and biological processes. The abundant quantity of mobilised metals in AS soils is, on the other hand, a direct consequence of artificial drainage management (Paper II-IV). The main difference between these two settings is that the disturbance of these soils for agricultural purposes by reclamation, which results in abundant amounts of mobilised acidity and potentially toxic metals, has widespread major impacts on the surrounding environment (e.g. mass fish kills) compared to that of local metal pollution by diffuse industrial emissions in these western parts of Finland. The main biogeochemical pathways, and thus potential human exposure routes, of the large pool of potentially toxic metals (e.g. Ni, Mn, Cd and Al) released in AS soils are depicted below in a conceptualized model (Fig. 10).

As the soil substrate is the main source of chemical elements to plants, the large proportion of mobilised metals in AS soils can induce excessive metal uptake in cultivated crops grown on typical soils. Previous investigations have demonstrated anomalous concentrations of Al, Co, Ni and Mn in both oats and timothy grass grown on AS soils in Northern Ostrobothnia, Western Finland (Palko 1986, Yli-Halla and Palko 1987). However, the results presented here (Paper III & IV) demonstrated in general relatively moderate metal concentrations in oats and cabbage grown on AS soils in Western Finland, although some of the studied fields showed anomalous values of metals (e.g. Co and Ni) in both the soil and target plants (especially oats), similar to that of the results by Palko (1986). It is hypothesized that differences in AS soil geochemistry and plant uptake (species-specific and part of the plant used for analysis) are contributing factors explaining these variations in plant chemistry. Therefore, it would be ill-advised to generalize about metal uptake in agricultural crops grown on Finnish AS soils as our knowledge still is limited and the results presented here are partly contradictory to that of earlier investigations (Palko 1986, Yli-Halla and Palko 1987).

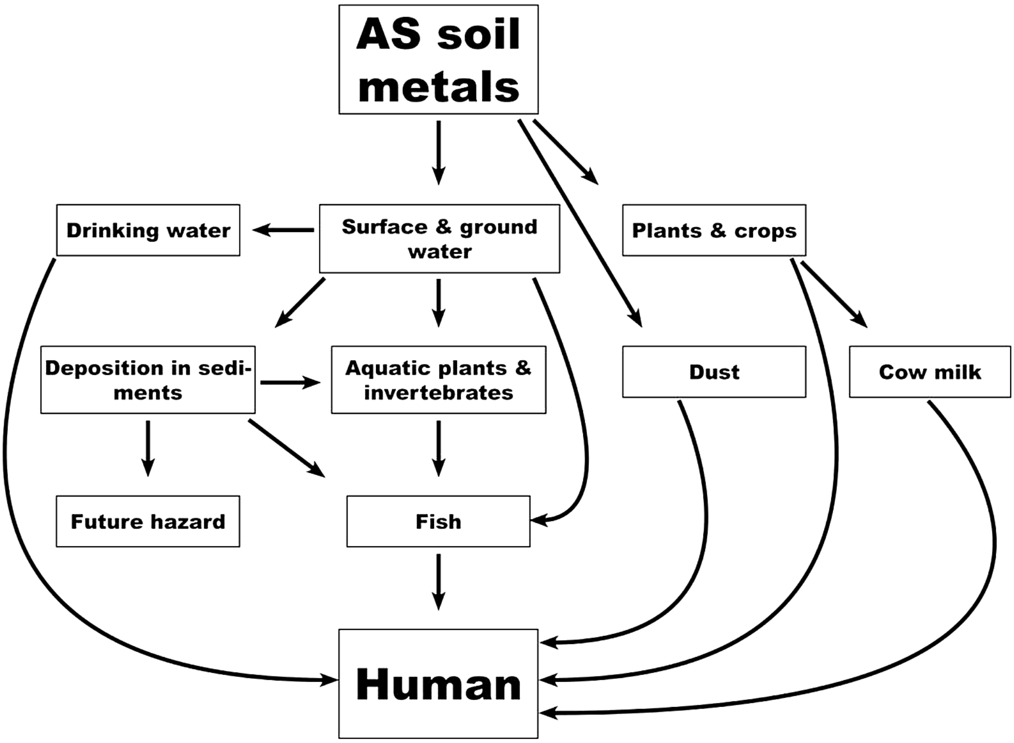

Fig. 10. A simplified conceptual model illustrating the main biogeochemical pathways of metals released in AS soils and potential routes of human metal exposure.

A previous investigation on cow milk originating from AS soil farms in the drainage basin of Kyrönjoki River in Western Finland revealed up to 50 times higher Al concentrations in milk samples from cows with outdoor feeding as compared to reference concentrations (Alhonen et al. 1997). Aluminium is highly mobile in these soils so its occurrence as high levels in cow milk is not surprising and indicates an important pathway for this potentially toxic metal, i.e. soil → plant → milk (Fig. 10). It should be pointed out that inorganic Al (Al^{3+}) is highly toxic and association with, for example, hydroxides detoxifies it. The speciation of Al in cow milk was not determined by Alhonen et al. (1997).

Although these mobilised metals are to some extent absorbed in cultivated crops and cow milk, it is obvious that an abundant quantity is readily flushed out to nearby drains and waterways. Previous AS soil studies have shown that extensive leaching of

Co, Ni, Zn, Cd and Mn to nearby watercourses has resulted in 10 to 50 times higher concentrations 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, b, Roos and Åström 2005, Österholm et al. 2005). The concentrations of Co, Ni, Zn, Cd, Mn and the above mentioned Al, are also very high in streams affected by AS soils as compared to average values for Finnish and Fennoscandian rivers (Edén and Björklund 1993, Lahermo et al. 1996, Åström 2001a, b). The extensive leaching from these soils has resulted in deposition of significant amounts (up to 100 times higher compared to background levels) of these above mentioned metals in sediments of rivers and estuaries (Nordmyr et al. 2008a, b). Hence, one could assume that aquatic bottom-feeding organisms (e.g. fish, benthic invertebrates) are likely to be subject to bioaccumulation of these sediment-bound contaminants. Furthermore, the ongoing isostatic land uplift (up to 9 mm/year) of the coastal regions of Finland causes fresh Holocene sediments and these metal-rich depositions to rise above the sea level, thus making them a future environmental nuisance (Fig. 10). The massive metal-rich acid load from these AS soils, which is most severe after heavy rains and snowmelt, causes ecotoxicological effects in aquatic plants, macroinvertebrates and fish in affected watercourses (Nyman et al. 1986, Meriläinen 1989, Urho et al. 1990, Callinan et al. 1993, Kjellman et al. 1994, Vuori 1996, Hudd 2000, Powell and Martens 2005). Numerous cases of mass fish kills, but even eradication of species (burbot, smelt), have occurred in these AS soil affected waters (Hildén et al. 1982, Hudd et al. 1984). Consequently, one could assume that fish originating from AS soil affected waters may demonstrate elevated levels of associated metals (e.g. Al, Ni, Mn), however, no investigations to my knowledge, on metal concentrations in fish, have yet to be conducted. Hence, the soil → water → fish pathway may constitute a route of human metal exposure (Fig. 10).

Clearly elevated metal concentrations (e.g. Al, Cd) were found in ground water derived from AS soil landscapes in Western Australia (Hinwood et al. 2006). The ground water was mainly used for irrigation of home grown produce indicating potential bioaccumulation, which in turn, may result in human exposure through dietary intake. Similarly, As and Mn pollution of ground water, which mainly is used for drinking water needs, derived from the Mekong Delta area of South East Asia containing an abundance of AS soils, was identified (Husson et al. 2000, Berg et al. 2007, Buschmann et al. 2007). Chronic exposure to elevated As concentrations in drinking water pose a serious health threat to people living in these regions. Similar studies focusing on the potential effect of metal leakage from Finnish AS soils to ground water aquifers are limited. One could speculate that shallow aquifers may be more easily affected by these soils as the dilution effect of water passing through the soil would be less pronounced, and the ground water could thus contain larger amounts of metals. Moreover, the abundance of acidity produced within these soils, as a consequence of sulphide oxidation, could drastically lower the pH in the ground water aquifer, which in turn could result in higher concentrations of mobile, inorganic metals (e.g. Ni^{2+}, Cd^{2+}). This is supported by Åström and Corin (2000), who suggested that Co, Ni, Zn, Mn, Cd and Al are generally associated with the cationic fraction in AS soil affected acidic waters. The amount of private wells are, however, less common today and these are possibly to some extent utilized for irrigation of farmlands and drinking water for livestock. In areas were ground water aquifers are uncommon, drinking water generally originates from surface water of rivers, which before distribution to the municipal waterworks, undergoes several purification treatments (e.g. chlorination, flocculation with aluminium sulphate). Water samples (n=10), which originated from areas with AS soil affected waters in Western Finland, were taken at different municipal water treatment facilities after purification (unpublished data, Österholm et al.). The results showed no deviating metal concentrations of the tested water, thus assuming purification and/or dilution of the AS soil affected surface water had been significant. Due to the limited knowledge on ground water quality in AS soil landscapes more detailed investigations on metal composition and speciation of well water should be conducted.

Another possible human exposure route, which may be of minor importance, would consist of dermal contact (and subsequent absorption through the skin and/or lungs) via dust exposure from AS soil farmlands (Fig. 10). However, recreational activities, for instance swimming in AS soil affected waters, can not be considered to expose individuals to excess metals.

Due to the large flow of mobilised metals in these soils, which are transferred to different biological compartments in various extent, an environmental risk assessment would be motivated to elucidate if metal concentrations are enriched in people residing in these areas and in livestock grazing on AS soils. As the most significant exposure route of metals for the general population is through dietary intake (Adriano

2001), metal imbalances in AS soil derived produce and/or milk could be of concern for people with unbalanced diet habits relying abundantly on local food sources originating from these landscapes (Fig. 10). Consequently, in Western Finland, where these soils are particularly abundant and affect the metal concentrations of stream waters, milk and to some extent crops, it is reasonable to assume that, at least locally on some temporal scale, metal (e.g. Al, Ni) uptake by humans could be elevated. However, strong variations in the metal concentrations of crops grown on typical soils are likely to be demonstrated as a result of AS soil heterogeneity, differences in metal uptake by plant species and part of plant analysed. Therefore, future research is needed and should include: (i) chemical composition of other food sources (e.g. edible parts of crops and vegetables, forage, cow milk, fish) originating from AS soil landscapes, (ii) other toxic chemical elements (e.g. Cd, As) potentially enriched in these products and (iii) differences between drainage techniques in AS soil farmlands and metal concentrations in target plants. More research is also needed on metal concentrations and speciation of potentially toxic elements in ground water (utilized for e.g. irrigation) in these areas.

7. Acid sulphate soils, a predisposing environment in the development of multiple sclerosis?

It is well known that chronic exposure to Al and Mn, which affect brain development, can induce neurotoxicity (Bjertness 1994, Oliver 1997, Zatta et al. 2003, Jankovic 2005, Michalke et al. 2009). Research on environmental risk factors (e.g. metal exposure) implicated in the etiology of different type of diseases (e.g. Alzheimer´s- and Parkinson´s disease, multiple sclerosis, amyotrophic lateral sclerosis) has gained considerable interest the last decades (Kurtzke 1977, Häsänen et al. 1986, McLachlan et al. 1996, Gorell et al. 1997, Flaten 2001, Sumelahti et al. 2001, Zatta et al. 2003, Roos et al. 2006, Michalke et al. 2009). Although results connecting metal exposure as a contributing cause for disease development are conflicting, they certainly highlight the need for further investigation on the role of chronic exposure of specific metals, or combination of these, in the etiology of multifactorial diseases. The etiology of multiple sclerosis (MS) is considered multifactorial, with both genetic and environmental factors involved in disease development. It is assumed that genetic susceptibility to MS and the interaction with still unknown, exogenous environmental factors trigger the onset of the disease (Ebers 2008). A brief geomedical overview of the distribution of AS soils in relation to the geographical occurrence of MS in Finland is presented below.

7.1 General characteristics of MS

MS is an autoimmune disorder affecting the central nervous system by damaging the nerve-insulating myelin sheath, subsequently affecting nerve signalling negatively. The disease is common among young adults with an age of onset between 20 to 30 years and it has been reported to occur more frequently in women than men (Sadovnick et al. 1997). The frequency of a disease (in this case MS) is often presented as *prevalence*, which is the total number of MS cases in a population at a given time and/or as *incidence*, referring to the number of new MS cases in a population at a given time. Furthermore, depending on study design, the relative MS incidence or prevalence rate is often adjusted for specific age groups, sex and/or disease course and calculated, for instance, with confidence intervals and age standardisation. MS prevalences below $5/10^5$ (the numerator corresponds to the total number of MS cases, the denominator the population) are mostly found in Latin America, Africa and Asia, and they are characterised by a low risk of developing MS. The distribution reflecting high risk areas (>30/10^5) include Northern Europe, especially the Nordic countries, other high risk zones include Northern United States, southern parts of Canada, Australia, New Zeeland, Ireland and Scotland (Kurtzke 1977, Marrie 2004). The uneven geographical distribution of MS, which is considered to be the epidemiological hallmark of the disease, and the risk reduction with migration from high to low risk areas indicate that environmental causal factors exist and genetic factors can only to some extent explain MS epidemiology (Marrie 2004, Ascherio and Munger 2007, Ebers 2008).

7.2 Prevalence and incidence rates of MS in Finland

Numerous MS studies conducted the last 40 years all point to high prevalence rates and marked regional and temporal differences between the western and southern parts of Finland (Rinne et al. 1966, Wikström 1975, Kurtzke 1977, Kinnunen et al. 1983, Sumelahti 2002). The Seinäjoki district, located in Western Finland (ca. 50 km southeast of the rural study area in Fig. 1a), showed the highest rates of MS whereas the neighbouring Vaasa region and parts of Southern Finland, the Uusimaa district (the latter used as a reference), showed significantly lower prevalence rates (Fig. 1a, Table 3) (Sumelahti 2002, Sumelahti et al. 2001). Significant temporal and regional incidence fluctuations were also observed in these areas. During the period 1979–1993 the incidence rate (age-adjusted, 10–69 years) more than doubled in Seinäjoki (11.6) compared to Vaasa (5.2) and Uusimaa (5.1), and in the early 1990s a significant increase was observed in Seinäjoki (13/10^5 person-years) compared to the two other areas, which showed figures of 3/10^5 and 5/10^5, respectively. The significant variation in incidence during the 15 year period was partly explained by the increased incidence rate among men in Seinäjoki, a decrease for both men and women in Vaasa and a stable trend for both genders in Uusimaa (Sumelahti 2002, Sumelahti et al. 2000, 2003). These incidence and prevalence rates in the high risk area of Seinäjoki are amongst the highest reported worldwide (Sumelahti et al. 2001). Although the MS frequency has increased in Finland during the last decades, and is still today increasing (personal communication with Marja-Liisa Sumelahti), improved case recognition and diagnostics (e.g. availability of MRI) may to some extent positively affect incidence and prevalence rates. Swift regional and temporal variations in MS incidence and prevalence can not solely be associated with genetics, as such changes in populations are slow, but would further support the hypothesis of an exogenous factor(s) involved in disease etiology.

Table 3. The prevalence (per 100 000) of definite MS cases for men and women in Uusimaa, Vaasa and Seinäjoki during 1964–1993 (Rinne et al. 1966,Wikström 1975, Sumelahti 2002).

Year	Uusimaa	Vaasa	Seinäjoki
1964	13	23	36
1972	44	61	-
1983	69	102	116
1993	93	107	188

7.3 Regional and local distribution of AS soils and MS

During the last decades, a great deal of research has been conducted on AS soils located in the Vaasa and Seinäjoki district of Western Finland (Erviö 1975, Heikkilä 1991, Åström 1998a, b, Österholm and Åström 2002, Joukainen and Yli-Halla 2003). The extensive occurrence of typical soils in these areas coincide relatively well, at least on a regional scale, with the high MS frequency in these corresponding districts, respectively. The AS soil type in the Seinäjoki area has been demonstrated to be very severe in terms of metal leaching (Österholm and Åström 2002, 2004). This particular region also show one of the highest MS rates reported worldwide (Sumelahti et al. 2001). Further evidence, which may support the hypothesis of a causal relationship between AS soil environments and MS occurrence, are those by Häsänen et al. (1986) who compared regional geochemistry with MS prevalence in Finland. Topsoil samples from arable land in the rural communes of Western (Seinäjoki- and Vaasa region) and Southern Finland (Uusimaa district) were analysed for pH, organic carbon, electrical conductivity, easily soluble content of macro- (NH_4Ac extractable) and micronutrients (NH_4Ac-EDTA extractable) (Sippola and Tares 1978), and compared with prevalence figures of clinically definite MS cases. Lower pH, higher organic carbon content and electric conductivity, elevated concentrations of easily soluble Fe, Cr, Zn, Al, but decreased amounts of Ca, K and Mg was observed in the high prevalence rate area of Western Finland compared to that of the lower prevalence rates in Southern Finland, respectively. The association between soil geochemistry and MS frequency gives reason to suspect the influence of AS soils as they liberate abundant amounts of metals (e.g. Al, Zn) and acidity to that of other soil types in the country. The sparse distribution of AS soils in the south may, at least partly, be explained by the smaller land area covered by the former Litorina Sea in these parts to that of the coastal parts of Western Finland (Fig. 1a). Consequently, as these fine-grained sulphide-rich sediments once have emerged from the former Litornia Sea, one can assume that the occurrence of AS soils in the northern and eastern parts of Finland is significantly lower (Fig. 1a), which also corresponds to the lower MS frequency in these parts of the country (Rinne et al. 1966). Apart from Finland, abundant occurrence of AS soils is also found in other areas of high MS prevalences, these include: NE Sweden, Southern Canada and Australia (e.g. Hammond et al. 1988, Warren et al. 2008), other high-risk regions of MS with potential for AS soil occurrence include NW United States.

Regional MS mapping provides an excellent basis for supplementary investigations on the distribution of the disease on a local scale. Local mapping is therefore effective in pinpointing MS clusters within high-risk areas, and can in this sense be utilized as a high resolution tool reflecting potential contributory environmental factors involved in MS etiology. Results from a local mapping study on MS distribution, which represented the high-risk area of the Seinäjoki district, showed that villages with a high MS frequency were located along the Kyrönjoki River (Fig. 1a) and its branches. It was hypothesized drinking water being a possible exogenous factor associated with the pronounced MS clustering along the Kyrönjoki River (Wikström 1975). Similar to that of Wikström (1975), Sumelahti et al. (2001) found the highest MS prevalence (200–300/10^5) in the western and southern part of the high-risk area of Seinäjoki, where the Kyrönjoki River and its branches is located. Previous (hydro) geochemical investigations have shown that large areas of the Kyrönjoki catchment consist of AS soils. Disturbance of these soils through efficient drainage practise has resulted in exceptionally high concentrations of Al, Cd, Co, Ni, Zn, Mn, Tl and acidity in drains and tributaries and thus elevated concentrations of these metals also in the Kyrönjoki River (e.g. Erviö 1975, Österholm and Åström 2004). It seems that these severe AS soil types, which are found in the Kyrönjoki catchment area, coincide rather well with the corresponding local MS clustering along the river.

The above outlined results show there are indications of noticeable associations between regional and local distribution of AS soils and the geographical occurrence of MS in Finland, however, as the severity of these soils vary both locally and temporally, a potential causal connection between AS soils as a predisposing environment and MS frequency could be difficult to corroborate. Consequently, future studies should focus on locally occurring severe AS soils within MS clusters, which have been well-studied (e.g. the Kyrönjoki area; Fig. 1a), to confirm a probable association between typical soil type and disease. Furthermore, if a potential association could be confirmed, follow-up studies should elucidate: (i) the possible metal exposure source(s)/hazard(s) and route(s) (e.g. ingestion and/or inhalation) in these settings, (ii) locality and distribution pattern of this potential source(s)/hazard(s), and (iii) the group at highest risk of chronic metal exposure. One way of indirectly assessing the potential effects of environmental exposure sources on MS frequency could be by retrospective birth cohort studies. The purpose of such a study would be to identify potential differences between MS incidence rates in certain age groups within the Kyrönjoki area. Pinpointing the age group most susceptible to developing MS in this given area would, in follow-up studies, facilitate the potential determination of local environmental exposure source(s)/hazard(s) (e.g. single and/or multi-metal exposure through contaminated ground water) among these people. In this context, some important questions should be addressed: which exposure source(s) can be linked to this group of people? Are they dependent on local food sources and/or drinking water? Can occupational exposure be a mutual risk factor? Is this group of people mainly exposed to one kind of metal or mixtures of metals? What are the effects of and difference between single metal and/or multi-metal exposure? For instance, can chronic exposure to low concentrations of multi-metals give rise to toxic effects as a result of synergistic interactions? How can such effects of metal-mixtures be recognised and predicted? There are several uncertainties involved in the assessment of hazard, exposure and risk influencing the outcome and quality of significant geomedical observations (Ramsey 2009, Stewart and Carter 2009). One of the most important criteria required for undertaking such an interdisciplinary study is the broad knowledge and expertise from different scientific fields, including, geochemists, medical geologists, epidemiologists, statisticians, public health scientists and toxicologists.

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