

Metal levels and microbial effects in forest soils at the Avesta and Oxelösund steelworks

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Keywords

Miljö, metall, mark, effekt, järn- och stålindustri

SUMMARY

Syftet med studien har varit att samla information om historiska utsläpp av metaller från stålverk och undersöka deras biologiska effekter i skogsmark. Områden kring två stålverk har undersökts, Avesta som har en skrotbaserad tillverkning av rostfritt stål och Oxelösund som tillverkar låglegerat stål i en malmbaserad process.

Emitterade metaller har deponerats i omgivande skogsmarker och upplagrats i marken. De biologiskt aktiva humusskikten, de s.k. mårskikten, tar emot och kvarhåller en stor del av metallföroreningarna. SLU har under 2002 och 2003 undersökt haltförhöjning av Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, V och Zn i mårskikt, skadliga mikrobiologiska effekter och metallers löslighet i samma skikt samt metallers fördelning i markprofilen.

Undersökningarna har genomförts inom två skogklädda provytor i närområdet kring stålverken samt i en avlägsen referensyta. En viktig undersökningsmetod har varit att analysera småskaliga rumsliga samband mellan metaller och mikrobiell respiration samt mellan metaller inbördes i provytorna. Dessa analyser har gjorts i mårskiktets övre del (O_F -skikt). Den stora rumsliga variation som finns i skogsmarken har utnyttjats för att söka samband som kan tolkas som toxisk effekt. Den småskaliga metallvariationen kan härledas från den heterogena uppfångningen i trädskronorna som leder till heterogen deposition på marken. Med denna ansats har i vissa fall negativ inverkan av metaller vid lägre nivåer än med traditionell storskalig gradientundersökning kunnat registreras. Det är dock problem att entydigt kunna fastställa samband mellan en viss metall och respiration. Många metaller och andra variabler samvarierar i fältsituationen och man kan ej alltid utpeka den påverkande faktorn enskilt.

Som komplement har gjorts experiment med tillsats av metaller till mårprover för att mer entydigt finna enskilda metallers inverkan på mikrobiell aktivitet. Experiment har emellertid den nackdelen att effektkoncentrationerna inte direkt kan översättas till haltvärden i fältsituationen även om experimenten har utformats för att ge realistiska förhållanden.

Metoderna har kombinerats till en samlad riskbedömning där startpunkten är observation om halterna förhöjts mer än 3 gånger. Då anses det generellt finnas risk för mikrobiella störningar.

Resultaten presenteras separat för Avesta och Oxelösund i rapportens två delar och det finns en separat sammanfattning för respektive del.

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SAMMANFATTNING

Stålverket i Avesta flyttades 1949 till sin nuvarande position söder om staden från ett historiskt läge nära Dalälven. Verksamheten har expanderat efter denna tid, inledningsvis med ökad luftförorening som följd. Kraftfulla åtgärder att minska utsläppen har genomförts efterhand. Den nuvarande produktionen av rostfritt stål baseras på nedsmältning av skrot inköpt på en internationell marknad. Innehållet av olika metaller i råvaran varierar från tid till annan. Emitterade metaller har deponerats i omgivande skogsmarker och upplagrats i marken. De biologiskt aktiva humusskikten, de sk mårskikten, tar emot och kvarhåller en stor del av metallföroreningarna. Vi har under 2002 och 2003 undersökt haltförhöjning av Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, V och Zn i mårskikt, skadliga mikrobiologiska effekter och metallers löslighet i samma skikt samt metallers fördelning i markprofilen.

Undersökningarna har genomförts inom två skogklädda provytor 0.6 km respektive 3 km från stålverket samt i en avlägsen referensyta 29 km bort. En viktig undersökningsmetod har varit att analysera småskaliga rumsliga samband mellan metaller och mikrobiell respiration samt mellan metaller inbördes i provytorna. Dessa analyser har gjorts i mårskiktets övre del (O_F -skikt). Vi utnyttjar den stora rumsliga variation som finns i skogsmarken för att söka samband som kan tolkas som toxisk effekt. Den småskaliga metallvariationen kan härledas från den heterogena uppfångningen i träd Kronorna som leder till heterogen deposition på marken. Med denna ansats har vi i vissa fall kunnat registrera negativ inverkan av metaller vid lägre nivåer än med traditionell storskalig gradientundersökning. Det är dock problem att entydigt kunna fastställa samband mellan en viss metall och respiration. Många metaller och andra variabler samvarierar i fältsituationen och man kan ej alltid utpeka den påverkande faktorn enskilt.

Som komplement har vi gjort experiment med tillsats av metaller till mårprover för att mer entydigt finna enskilda metallers inverkan på mikrobiell aktivitet. Experiment har emellertid den nackdelen att effektkoncentrationerna inte direkt kan översättas till haltvärden i fältsituationen även om experimenten har utformats för att ge realistiska förhållanden.

Metoderna har kombinerats till en samlad riskbedömning där startpunkten är observation om halterna förhöjts mer än 3 gånger. Då anses det generellt finnas risk för mikrobiella störningar.

Mo, Cr and Ni hade betydligt högre förhöjning än så i mårskiktet i Kyrkbyn, 3 km från industrin. I AGA-ytan, 0.6 km från industrin, var Mo, Cr, Ni, Fe, Cu, V och Cd förhöjda mer än 5 gånger, Mo och Cr ända upp till cirka 100 gånger.

De förhöjda metallerna i Kyrkbyn, Mo, Cr and Ni, korrelerade med varandra i provytan och alla hade negativt samband till respiration. Alla tre kan anses som troliga effektvariabler på denna yta, vilket också stöds av experimentresultat. För AGA-ytan kunde vi knappast finna några samband med respiration, trots mycket starkt förhöjda halter. Endast Fe uppvisade ett negativt samband. Avsaknaden av biologisk effekt kan härledas till extremt högt pH på AGA-ytan och påföljande immobilisering av vissa metaller. pH-värdet beror förmodligen på alkaliskt damm.

Genom att jämföra metallhalter i undre och övre del av mårskiktet, O_H/O_F -kvoter, utvärderades om metallhalter ökat eller minskat under tidsperiod av flera decennier. Ni, Cu, V Cd och Zn befanns ökande i AGA liksom Ni i Kyrkbyn. Mo var enda ämnet som visade tecken på minskad halt i mårskiktet. Observation av metaller i markprofilen inkluderande mineraljorden visade stark allokering av Cr, Ni och Mo till mårskiktet i AGA-ytan medan V hade utlakats till mineraljorden.

ABSTRACT

Investigations were carried out in the surroundings of the Avesta steelworks in 2002 and 2003. Metal concentrations and elevation above reference levels were determined in forest humus layers in two soil plots 0.6 and 3 km from the industrial site. Possible microbial effects, metal solubility in humus layers and metal distribution in soil profiles were studied. Small-scale spatial relationships between metal contents and microbial respiration were determined. This was the most important way to look for microbial metal effects, although co-variation between a large number of factors makes it difficult to distinguish individual effects. Complementary experiments with added metals were carried out, although effect levels were not directly comparable to field situations.

Risk assessments for soil microbial activity in humus layers were carried out with a combined use of the methods. Metals that were elevated more than threefold were considered to constitute risks. At the site Kyrkbyn, 3 km from the industrial pollution source, Mo, Cr and Mo were elevated to that level. At AGA, at 0.6 km, Mo, Cr, Ni, Fe, Cu, V and Cd were sufficiently elevated, with Mo and Cr being elevated up to 100-fold.

Mo, Cr and Mo were correlated to each other at Kyrkbyn and all were negatively correlated to microbial respiration. It could be concluded that all three have harmful effects at that site. Experimental results support this. At the AGA site, only Fe showed indication of harmful effects in spite of high metal levels. Immobilisation due to high pH was the probable cause.

Comparison of horizons within the mor layer showed that Ni, Cu, V, Cd and Zn had increased at AGA in the time span of several decades, as had Ni at Kyrkbyn. Mo showed signs of decline. Cr, Ni and Mo were strongly allocated to the mor at AGA, while V was leached to a large degree.

1. AIMS

The principal aim of our assessment was to obtain information on the presence of historically emitted metals and their biological effects in forest soils. We dealt with the following metals: Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, V, Zn. This list of potential pollutants was agreed by a reference group for the project consisting of representatives from *Jernkontoret* (Swedish Steel Producers' Association) and some metal producing industries. Unfortunately, Co and W should also be dealt with but had to be excluded from the present report (see Section 5.5). The soil sampling took place in 2002 and 2003.

More specifically, the following questions on the status of forest soils were asked:

- * Are the metals in our list present at elevated levels in the soils?
- * Are there harmful effects of anthropogenic metals on soil microbial activity?
- * To what degree are metals available in soluble fractions?
- * To what degree have metals migrated from humus layer to mineral soil?

Biological assessments were aimed at identifying indicators for individual metals in our list. We also looked for signs of recovery in soils in the current situation of successfully reduced emissions. However, as soils have a very large capacity to retain heavy metals, improvement of the environmental situation is expected to be slow.

In the following two chapters there will be some general remarks on forests and soils and on the investigation strategy.

2. FOREST AND SOIL

2.1. Forest as receptor of metal pollution

Forest stands are very effective receptors of particulate and wet air pollution since large leaf areas with adsorptive properties ensure their interception. Metals adhering to the leaves are transferred to the soil surface by the processes of litterfall and throughfall, the former being the fall of plant debris, the latter being wet deposition. The usually completely organic layer covering forest soils has a very large capacity to retain metals. Metals accumulate in that layer, which is also a site for intensive biological activity. This concentration of both metals and organisms to the same layer poses an obvious risk for biological disturbance.

Microbial decomposition of litter from vegetation is one of the processes that might be disturbed by pollutants, with impacts on the cycling of nutrients as a consequence. The quality and quantity of shed plant material are major factors controlling the decomposition, with inhibition by pollutants as an additional factor. During the ageing of organic material the quality gradually decreases, which makes the uppermost part of the organic layer most vital and also most vulnerable to toxic impacts. Our biological investigations were restricted to that layer.

2.2. The podsol

The most common soil type in coniferous forests in Sweden is the podsol. It is characterised by clearly separated soil layers (**Fig. 1** in 2.2). In this soil type mixing activity by soil animals or root penetration is weak, so a layered structure can develop due to other soil forming processes. On top of the profile there is an organic cover of more or less humified material of

plant origin, called the *mor layer* or O-horizon. The mor layer, typically of 3-8 cm thickness, has low pH. In our study we further subdivided the *mor layer* into an upper O_f- and a lower more humified O_h-layer. The mineral soil below the mor layer is also layered in a greyish 5-15 cm eluvial horizon (E-horizon) on top, and a red-brown illuvial horizon (B-horizon) below. At 50-100 cm, the latter gradually fades into the pale beige colour of the unaffected mineral sub-stratum. The soil forming process, the podsolisation, constitutes leaching of organic acids and Fe- and Al-hydroxides from O- and E-horizons, and precipitation in the B-horizon by organic complex formation. The mineral soil has low organic content and higher pH than the overlaying mor, due to mineral weathering. pH increases further in deep soil layers. Metals accumulate mainly in the O-horizon but to some extent also in the B-horizon. Although concentrations of organic material and metals are low in the mineral soil, there are large pools of these substances.

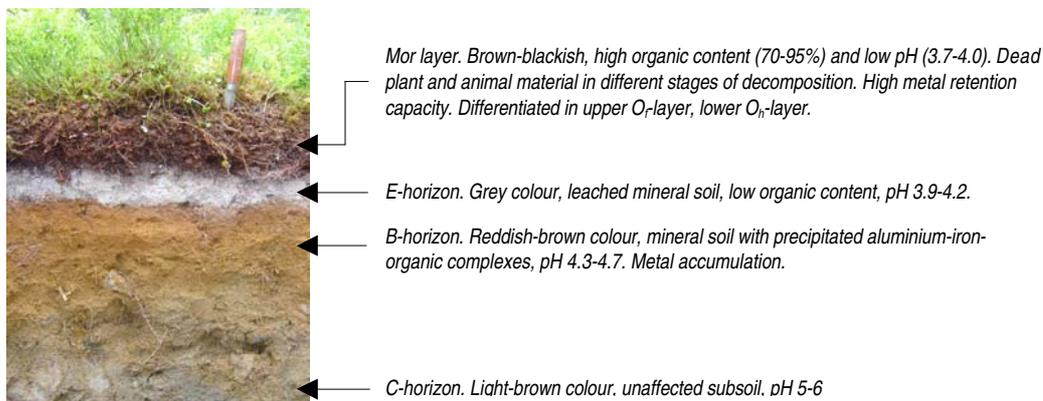


Figure 1. Podsol profile of coniferous forest soil (copyright Åke Nilsson, SLU).

We restricted sampling for biological effects to the upper part of the mor layer, the O_f. However, metal contents were determined in the O_f, the O_h and throughout the mineral soil profile.

3. INVESTIGATION STRATEGY

3.1. Previous studies at smelter industries

The metal impact zone around smelter industries has been extensively used to obtain knowledge on the distribution and effects of heavy metals in ecosystems. In fact, the full scale 'experiments' thus provided were instrumental in the development of metal ecology in the 1970s. From well-defined point sources, distinct gradients of heavy metal deposition can often be found emerging from smelter sites. An example of an intensely studied site is the brass mill at Gusum in Southern Sweden. The metal gradient of Cu and Zn in the humus layer was found to be very steep, with contents falling by a factor of 500 within 6 km. A battery of methods applicable in environmental metal studies was developed (Tyler 1984).

Investigations included microbial processes, soil enzymes, soil fauna, fungi, lichens, etc. Most of the variables are sensitive ecological indicators of metal effects showing similar responses, although with different sensitivities. Soil enzymes can show specific reactions to certain metals. A peculiarity is that an absence of microbial effects is sometimes found close to

smelters, where the heavy metal levels are highest. The sigmoid form of the toxic response curve can explain this, since at very high metal levels additional loads have little additional influence (Haanstra et al. 1985). A large number of case studies of similar design have been performed worldwide in impact areas around industries.

More recently, variables showing the composition of the microbial community have been introduced, using e.g. phospholipid analysis. In studies performed by Pennanen et al. (1998) the microbial community was assessed around the smelters at Rönnskär and Harjavalta. Altered microbial composition was observed in association with metal contamination, although in that case not with higher sensitivity than for microbial activity. These measurements broadened the ecological interpretation, but easily measured respiration still remains a good and sensitive indicator of the ecological status of the soil.

A drawback with gradient studies is that comparable sites have to be found, preferably forest sites. This may be difficult in a diverse landscape such as at Avesta. Homogeneous forest stands are rare and there may be large scale gradients in the landscape in addition to the pollution gradient. As described in chapter 4.2, the northern part of the Avesta region has poorer soils than the vicinity of the town, which would certainly affect the gradients of several soil variables. An earlier study of respiration in mor layers at Avesta by the large-scale gradient approach revealed weak metal effects (Rühling & Tyler 1979, cited in Waltersson 1999). Phosphatase enzyme tests were considered more sensitive in that study.

3.2. Homogeneous soil plots

To improve sensitivity in interpreting spatial patterns in terms of metal effects, we utilised the variability found within limited ‘homogeneous’ soil plots. The plots were homogeneous in the sense that they had no major breaks in soil characteristics over the area of the plots and tree stands were even. However, there still remained substantial soil variability, which in fact is utilised for the effect assessments. Due to heterogeneous interception of pollutants in tree canopies, subsequent deposition to the forest floor creates small-scale patterns of metal contents. Metal variation within plots can be quite substantial. Measuring microbial activity as well as metal contents in the same mor samples provides the potential to look for correlations between metals and microbial activities. The samples in our method were taken at the nodes of regular grid systems measuring 50 x 50 m (**Fig. 2** in 3.2).

This method has been successful in investigations of metal effects caused by long-range pollution (Bringmark & Bringmark 2001a). It was demonstrated that internal negative correlations between microbial activities and metal contents in soil plots were present at sites with high metal loads and absent at low loads. The absence is important, as it means that the metal variables are very probably causal factors. Should the correlations be caused by some irrelevant third factor affecting both metal levels and microbial activities, the correlations would be expected at all sites.

The increased probability of finding metal effects using our method compared to the large-scale gradient method is due to three factors in the methods. As already described, the choice of the limited ‘homogeneous’ plot eliminates some irrelevant variations. The allocation of the measurement to the more active upper O_F-layer of the mor layer rather than the organic layer as a whole improves sensitivity. The third factor is that small-scale variability is preserved and observed, while gradient studies aim to eliminate such variation by making composite

samples for each site. The significant effects on respiration found for the soil plot at Kyrkbyn were recorded at lower metal levels than effects found in the older gradient study at Avesta.

The effects are described for each site as a case study. Although we compare metal levels between sites to give information on elevation above background, we make no attempts to use comparison of respiration levels between sites as indicative of metal effects. That would require a larger number of sites according to the principles of gradient studies.

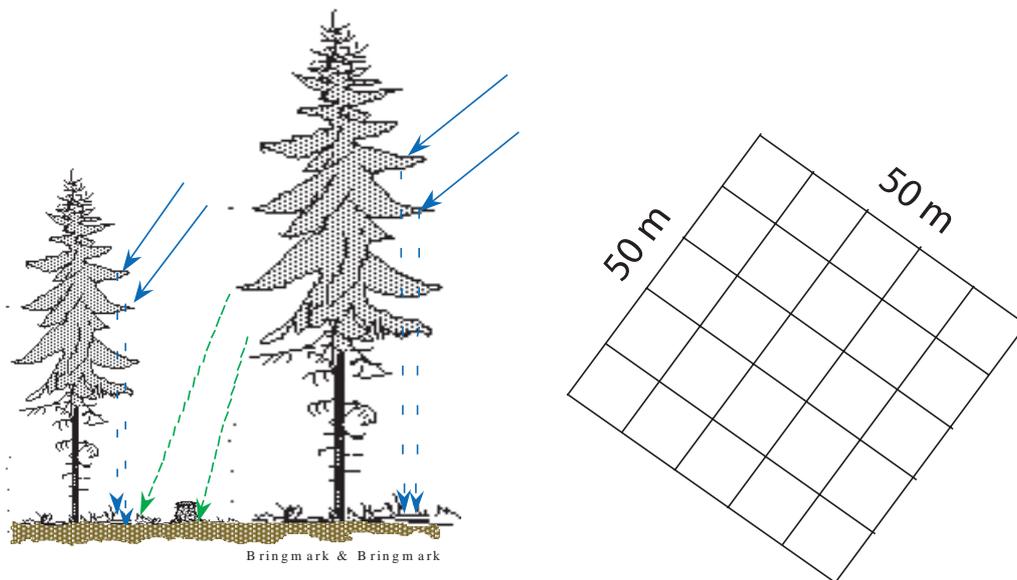


Figure 2. Principles of sampling for spatial patterns in forest mor layers. Metals intercepted by trees are heterogeneously deposited on the forest floor.

3.3. Experimentally added metals

Soil samples taken from field situations have been subject to metal inputs in the slow chronic realistic way. This is the great advantage of field studies compared to experiments. However, there are drawbacks with the field observations. It is difficult to single out effects of an individual metal, as metals tend to show co-variation. Another problem is irrelevant variation that cannot be ascribed to variables under investigation. Other factors control the biological processes, such as physical (temperature, moisture) and chemical (pH, nutrient status) factors, and also the composition of the microbial community. The difficulty in environmental effect studies in soil is to find weak signals in a large noise. These difficulties can be overcome by adding metals experimentally to soil materials to distinguish single factors.

By adding metals at different levels and measuring the activity in samples over time, an evaluation of metal effects is possible. The metal dose is expressed on a logarithmic scale. Toxicity thresholds can be determined as illustrated for copper in **Fig. 3** in 3.3. The concentration resulting in a reduced microbial activity is denoted *effect concentration* (EC). A suffix 10 stands for 10% reduction compared to control samples, e.g. EC₁₀.

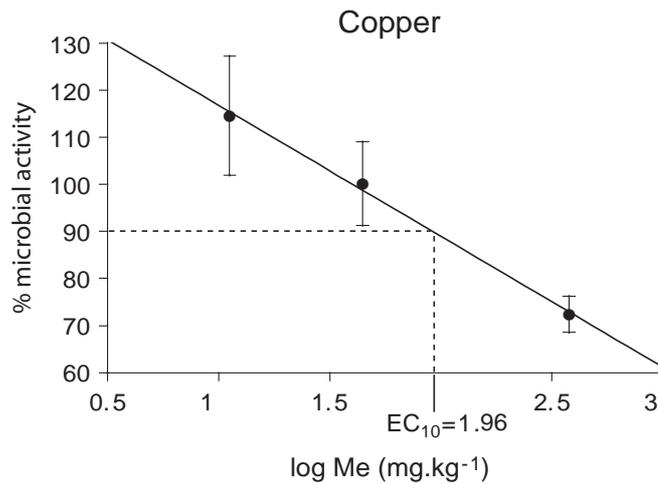


Figure 3. Experimental derivation of the effect concentration at 10% reduction of microbial activity (EC_{10}), with copper as an example. Microbial activity expressed as % of activity in control samples.

To avoid initial shock effects, we performed the experiments during a long time period, during which respiration was monitored. The duration was several months, including a resting period. Nevertheless, we cannot be certain that we have obtained equilibrium of processes such as metal immobilisation and microbial adaptation. In fact, our experience is that effects recorded by spatial patterns in field plots are found at lower effect levels than in long-term experiments (Bringmark & Bringmark 2001a, 2001b). For this reason, experimental effect levels should be compared with soil contents only with great caution. It is the relationship between toxicity levels rather than absolute values that should be the outcome of the experiments. Nevertheless, the experiments are important as a way to single out effects of individual metals.

3.4. Bioavailability of metals

The soluble fraction is considered more biologically available than the total acid-digestible fraction. Furthermore, within the soluble fraction, only the free metal ions are seen as biologically active. This means that very minute portions of the total metal contents are responsible for biological effects at a given time. Of course there is a rate of transfer from the larger pools to consider as well. These matters are getting increasing attention in environmental metal assessments. There have been great achievements recently in describing bioavailability of Cu, Zn, Pb and Cd in general ways involving large numbers of measurements (Lofts et al 2004). Although bioavailability of Cr, Ni, Mo and others have also been studied, more needs to be done, especially for organic soils and for generalised practical models. One important motive for assessing bioavailable fractions is to help bridge the gap between experiments and field observations.

We measured and reported metal solubility in our soil plots. This is a research activity intended to continue beyond the project period. However, within a limited system such as the organic mor layer of a forest site, more or less close relationships between total metal contents and biological active fractions are expected. Factors of importance for bioavailability, such as pH and organic content, have rather limited variation within the sites. This means that in the search for spatial relations with biological activity within sites, total acid-digestible metal contents are acceptable as proxies for soluble metal or free ion contents.

4. AVESTA REGION

4.1 Some history

Avesta was a pioneering site in the development of stainless steel production, which started in the 1920s, and today Outokumpu at Avesta is a major world producer. Initially the location was a historical industrial site at the river Dalälven near the city centre. Copper and iron production had been going on at that site since the 17th century with variable intensity. The factory moved to its present location south of the city to start operations in 1949. The time of relocation is of importance for judging the accumulated impact at our investigation sites. At present the process is based on smelting of scrap-metals, which are re-used for steel products. Raw materials imported from international markets have very variable origin over time. This means that the composition in terms of different metals entering the smelter is also variable.

Metals and other substances are released to the environment as dust from the smelting process. Heavy metals in forest soils around the smelter site originate to a large degree from industrial air dust emissions. Data from the Avesta Works on dust emissions from the steel plant and other internal sources show 90% reduction of emissions between 1986 and 2000 (Fig. 4 in 4.1). This is largely due to the effect of installation of filters in the factory.

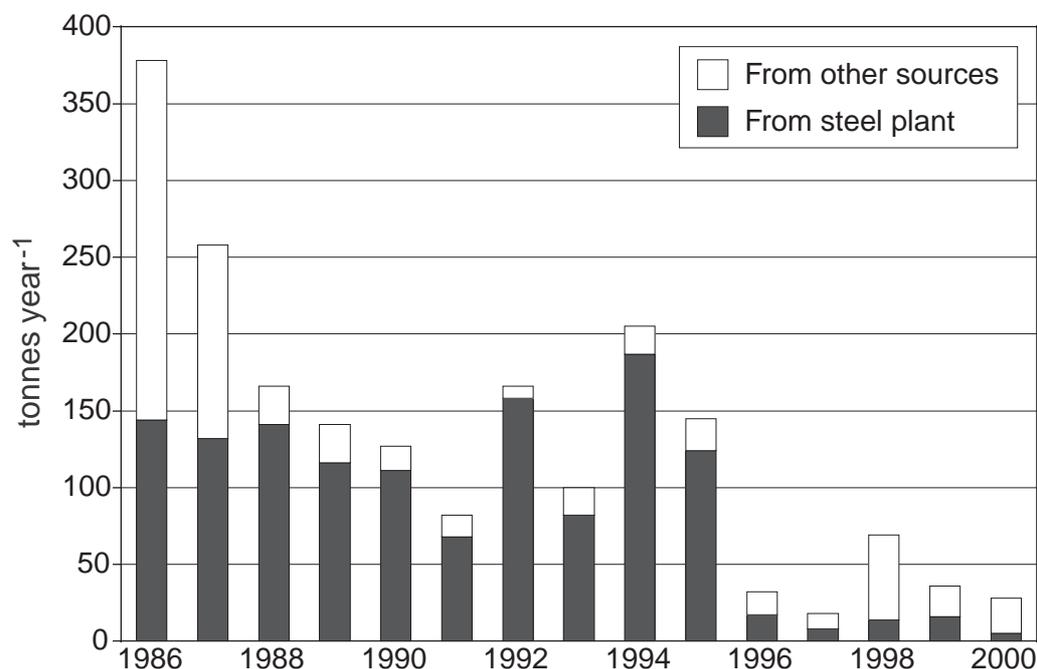


Figure 4. Dust emissions to air from the Avesta Works from 1986 to 2000. Data provided by Outokumpu at Avesta (Christer Manngård, pers. communication).

4.2 Avesta region and investigation sites

The region of Avesta is situated at the so-called *Limes Norrlandicus*. This is a pronounced climatic and biological border zone between the harsh boreal North and a milder nemo-boreal South Sweden. Oak and ash have their northern limits just to the South, while the Avesta area has mainly purely coniferous spruce and pine forests of a northern character. The river Dalälven, which originates in alpine areas, flows near the city. There is a mosaic of agricultural land and forest surrounding the city and its steel industry. The quaternary substrate is sedimentary plains with sandy-loamy materials. Along the river there is a mighty esker of coarse material traversing the plains. In the northern parts of the Avesta region there are coarse till soils rich in boulders, the type of soils typical for vast forest regions in Sweden. Spruce-pine forests appear on all these substrates, but nutrient status and forest productivity would be higher on the sediment areas. The area is part of Bergslagen, a region of historical metal-mining in Sweden.

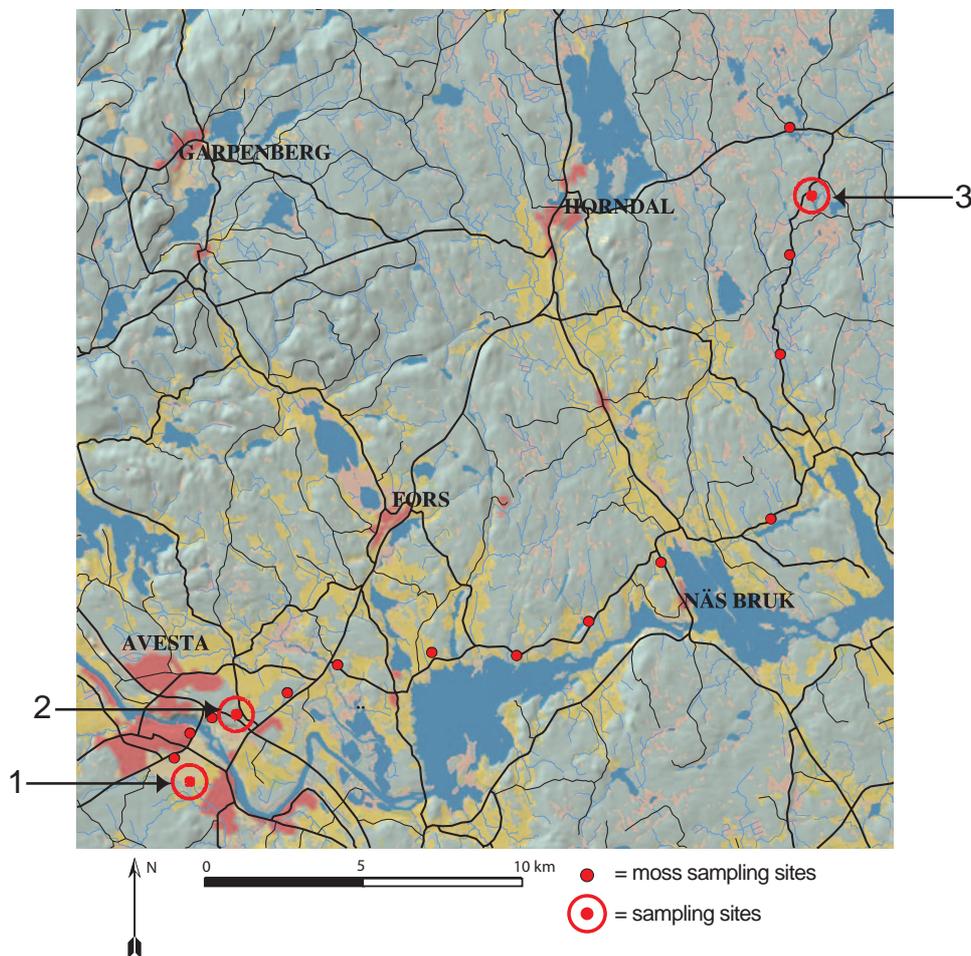


Figure 5. Soil sampling sites (circles) of this study and earlier moss sampling sites used by Rühling (dots). 1=AGA-factory ; 2= Kyrkbyn ; 3=Grönsinka.

According to the weather station at Folkkärna, the primary wind directions are both north-east and south-west. Consequently, these are the main directions of pollution transport from point sources. Our two sampling sites near the smelter are situated in spruce stands in the sedimentary plain areas (**Fig. 5** in 4.2). One site, AGA-factory, is just at the fence of the present-day industrial area, 600 metres south-east of the main emission source in the steel plant.

The site Kyrkbyn is situated across the river to the north-east, at a distance of 3.0 km from the main point source. As the site is only 2 km from the old industrial location near the city it might have received pollution in historic times. Some metal distribution from a major national road 500 metres away cannot be ruled out, although a dense protective forest in between should intercept almost all of it. The reference site Grönsinka is in a spruce forest 29 km away to the north-east in the forested till areas. **Table 1** (page 11) some properties of soil and tree stands at the sampling sites.

Table 1. Soils and tree stands at sampling sites around Avesta smelter factory

	AGA-factory		Kyrkbyn		Grönsinka
Thickness of mor layer (cm) CV	14.4	38%	10.2	29%	9.9 41%
Stem thickness (cm) CV	25.8	46%	24.2	43%	
	Stand composition	Stem thickness	Stand composition	Stem thickness	Stand composition
Spruce Scotch pine Birch Rowan	83% 7% 4% 6%	25.2 42.8 25 6	80% 17% 3%	22.5 34.9 11.5	Small, old spruces, variable stand density
Other site information	No lichens on stems Field and bottom layer of blueberry /lingonberry with herbaceous plants Loam, no stones Soil profiles podsol / cambisol Gleyic stains below 25 cm indicate water-logging		Lichens on stems sparse Field and bottom layer of mosses, blueberries and herbaceous plants Loam, no stones Soil profile iron-podsol Some gley stains below 30 cm		Lichens on stems occur Field and bottom layer of blueberries and mosses Coarse till with stones and boulders Soil profile iron-podsol

5. METHODS

5.1 Sampling, spatial correlations in mor layer of soil plots

The theoretical rationale for our sampling for small-scale spatial patterns in soil plots is described in chapter 3. Spatially variable patterns of metal contents have developed in the humus layer as shown by standard deviations in **Tables A2-A4** (in Appendix, pages 32-34) and in **Table 5** (page 15). The main intention was to search for correlations between metal contents and microbial activity in soil samples from individual sample points. Metals tend to be mutually correlated in the spatial patterns due to similar deposition mechanisms, but a few metals proved to have independent distributions. From earlier experience we know that the upper, more active part of the humus layer (O_f -layer) rather than the whole organic layer has to be sampled to obtain significant relationships to microbial activity.

Sampling in November 2002 at the AGA-factory and Kyrkbyn sites was performed in regular grids within 50 by 50 metre squares in ‘homogeneous’ forest stands (**Fig. 2** in 3.2). The number of O_f-layer samples from each grid was 36, with 10 metre spacing between sampling points. A humus auger of 95 mm diameter equipped with a sawing edge to cut roots was used. Cores of the mor layer were horizontally divided into two halves of equal sizes, the upper one considered to represent the O_f-layer. Six samples of the lower, more humified layer (O_h-layer) were also sampled. At the reference site Grönsinka a simpler scheme with fewer samples was employed, since correlation analysis was not the aim.

Field-moist samples were sieved through a stainless steel net of 4 mm mesh size to remove roots and large pieces. pH and respiration measurements were initiated within a week of sampling. Samples were subsequently dried awaiting metal analysis.

Correlation matrices for heavy metals were constructed by Pearson correlation coefficients. In the calculation of relationships between metals and respiration rates, all variables were corrected for mineral content by calculation of residuals for correlations to mineral content. Metal variables were expressed in logarithmic form when related to respiration.

5.2 Sampling in soil pits and moss sampling

At the AGA-factory and Kyrkbyn sites, two soil pits were dug in each soil plot in September 2003 (**Table 2**, page 12) for metal analysis were sampled in adjacent areas. In and at each pit the following soil samples were taken: O_f- and O_h-layer, mineral soil layers at 0-5 cm (E-horizon), 5-15 cm (B-horizon), 40-50 cm (B/C-horizon) and 70 cm (C-horizon). Two samples for each pit made four samples in each layer for each soil plot. Soil samples were sieved in stainless steel nets (4 mm mesh size for humus layer, 2 mm for mineral soil layers) and dried. Chemical characteristics of soil layers and vertical metal distribution were determined by the following parameters: %OM (organic matter), pH, exchangeable acidity, CEC (cation exchange capacity), carbon, nitrogen and metals. The bulk density of mor layer and mineral soil was determined on separate samples with the purpose of calculating metal stores.

Moss samples were of the species *Hylocomium splendens*, a species with identifiable annual shoot segments. Segments representing three years were cut off and used for metal analysis.

Table 2. Soil sampling scheme for the sites at AGA-factory and Kyrkbyn. Number of samples per site (n) and chemical variables analysed (Chem=%OM, pH, exchangeable acidity, CEC, C%, N%; M=pH and acid-extractable metals Mo, Cr, Ni, Fe, Cu, V, Zn, Mn, Pb, Cd, Hg). Additional O_f -samples were taken for dissolved metals.

	Grid	Pits	n	Chemical variables	Respiration at 20°C
Upper mor layer (O _f)	x		36	M	x
Lower mor layer (O _h)	x		6	M	
Upper mor layer (O _f)		x	4	Chem	
Lower mor layer (O _h)		x	4	Chem	
0-5cm (E-horizon)		x	4	Chem, M	
5-15cm (B-horizon)		x	4	Chem, M	
40-50 cm (B/C-horizon)		x	4	Chem, M	
70 cm (C-horizon)		x	4	Chem, M	

5.3 Long-term experiment

Experiments with added metals were performed according to Bringmark & Bringmark (2001b). Field-moist sieved and homogenized O_f-layer material with background metal contents was collected near Östervåla, in the same forest type and biogeoclimatic region as our reference site at Grönsinka. It was amended with 7.5% by dry weight of powdered Scots pine needles. The amendment is natural feed for microorganisms. Moist samples of defined dry weights were placed in small pots. Chloride solutions of heavy metals were added to the samples and vigorously mixed. The treatments were three dose levels each of Cd, Ni, Cu, Zn, Pb, Cr(III) and Mo(V), with four replicates for each treatment and twelve control samples. In a first period samples were incubated for 67 days at 20°C with adjusted water content. Then samples were frozen for an inactive period of 240 days and a second incubation period at 20°C was initiated by adding 7.5% powdered needles. It was continued for 107 days. Microbial respiration was measured weekly during the first and second incubation periods. An almost identical experiment for vanadium effects was conducted later with newly taken O_f-layer samples from the vicinity of Östervåla. The number of days in period 1 and 2 of that experiment was 65 and 91 days respectively.

Cumulative CO₂-losses for the whole period were calculated for each separate sample by linear interpolation between days of respiration measurement. Results for different treatments were evaluated by single factor analysis of variance followed by the Dunnett test for comparison with control. Linear regressions with logarithmic metal concentration as independent variable were used for determination of effect concentration at 10% inhibition of microbial activity (EC₁₀). Initial positive microbial effects usually appear at low-level treatments, but in our cases such effects remained throughout the measurements. For that reason EC₁₀-values were calculated only in declining segments of dose-response curves.

Chloride effects at very high salt additions were estimated in a separate test by adding NaCl. Metal treatments with chloride levels corresponding to >3% inhibition of microbial activity in the experiment with NaCl were excluded from calculations of EC₁₀.

5.4 Pore water sampling

Within sampling grids at the AGA-factory, Kyrkbyn and Grönsinka sites, 4 large mor soil samples of approximately of 1 kg of O_f-layer material were taken. Sampling was performed in spots where appropriate amounts of soil were to be found. Sieved samples wetted to 100% of WHC were thereafter stored in 1-L glass beakers with plastic covers. Ceramic porous probes (P60) with plastic tubing were attached to the centre of the soil samples. Pore water was extracted by applying -0.5 bar suction and analysed for pH and for Mo, Cr, Ni, Co, Cu, V, and Cd by ICP-MS. Organic matter and metal contents were determined on the soil samples.

5.5 Chemical and biological determinations

- *Organic matter (OM%)* by weight loss on ignition at 550°C
- *pH* in water extract
- Exchangeable acidity (EA), 1M KCl extraction, titration with NaOH, calculation of titrated acidity per unit of dry soil
- *Cation exchange capacity (CEC)*, 1M NH₄Cl-extraction, determination of Ca, Mg, Na and K by ICP, calculation of CEC = EA + Ca +Mg +Na +K, all expressed as equivalents per unit of dry soil
- *Base saturation (%)*, calculation as 100*EA / CEC

- *Carbon and nitrogen* with LECO analyzer
- *Metals semi-total content*, digestion in conc. HNO₃ at 155°C for 1 h. Analysis by ICP-MS or for Hg by cold vapour AAS in acetylene flame. Further details on metal analysis below
- *Respiration rate*. Moist soil samples allowed to rest for 12 days in humid atmosphere and 20°C, measurement by incubation with NaOH at 20°C overnight to trap CO₂, exact recording of incubation time, interruption by precipitation of carbonate with BaCl₂, titration of excess NaOH with HCl, difference to blanks with no soil samples corresponds to entrapped CO₂, express evolved CO₂ per hour and unit of dry soil
- *Metals in pore water*. Analysis by ICP-MS. Further details on metal analysis below.

Semi-total soil concentrations and pore water concentrations of Mo, Cr, Ni, Fe, Cu, V, Pb, Cd, Zn and Mn were determined using Inductively Coupled Plasma-Mass Spectroscopy, ICP-MS (Perkin Elmer ICP-MS 6000). Hg content in soil samples was analysed using cold vapour Atomic Absorption Spectroscopy (Cold Vapour-AAS) in acetylene flame (LDC-Analytical). Prior to analysis soil samples were digested in conc. HNO₃ at 155°C for 1 h. Digestion and analysis were performed at the Department of Environmental Analysis, SLU, Uppsala. Limits of detection and uncertainty in the analysis of metals are presented in **Table 3**, page 14.

Table 3. Limits of detection and uncertainty in analysis of concentrations in solid and water samples

	Limits of detection (mg/kg)		Uncertainty in analysis (%)	
	Solid(mg/kg)	Water (µg/L)	Solid	Water
Mo	0.1		10	
Cr	0.8	0.05	20	16
Ni	1.5	0.05	15	14
Fe	150	2	20	10
Cu	0.8	0.04	15	12
V	0.1	0.03	25	10
Pb	0.5	0.02	15	15
Cd	0.1	0.005	20	20
Zn	2.5	0.2	15	16
Mn	3	0.06	15	10
Hg	0.02		25	

Control samples with standardised metal content (IAEA SL-1 Lake sediment; VKI QC Loam soil A; EC IMEP-14) for each metal were digested and analysed at regular intervals together with the soil samples. Calibration solutions of metals were used during water analysis to accurately determine concentration in pore water samples.

Comparisons with other investigations in background areas led to the conclusion that the data quality for Co and W needed further evaluation and these two metals were thus excluded from this report. A comprehensive national inventory of contents in moss and mor samples, useful as reference, has been reported by Lithner & Holm (2003).

6. RESULTS AND DISCUSSION (AVESTA)

6.1 Atmospheric deposition to forests

As mentioned previously, statistics on dust emissions from the steel mill at Avesta 1986-2000 show a steady reduction by about 90% in the period (**Fig. 4** in 4.1). Moss inventories were used to estimate the metal deposition taking place in the forest sites. Metal contents in mosses were converted to quantities of Cr, Mo and Ni in bulk deposition using an empirical equation by Rühling & Tyler (2001). The deposition data from three repeated moss inventories 1993-2003 (**Table 4**, page 15) showed temporal variation. The fluctuations were especially large for Cr but evident for the other two elements as well.

Table 4. Deposition of Cr, Mo and Ni by the moss method calculated according to Rühling & Tyler (2001). Metal measurements in 1993 and 2001 unpublished by Tyler & Rühling, 2003 this investigation

Site, year	Cr, mg/m ² /yr	Mo, mg/m ² /yr	Ni, mg/m ² /yr
Kyrkbyn, 1993	9.6	2.3	8.5
Kyrkbyn, 2001	19.0	2.4	12.0
Kyrkbyn, 2003	8.6	2.8	10.0
AGA-factory, 1993	41	13	51
AGA-factory, 2001	422	27	184
AGA-factory, 2003	125	15	78

6.2 Metal increments in mor layers

Metal contents and coefficients of variation (CV%) for mor layers of investigated sites are presented in **Table 5** (page 15). The elevation ratios (ER) of the mean metal contents at the AGA-factory and Kyrkbyn sites to metal contents at the reference site Grönsinka show the metal elevation caused by pollution.

Table 5. Elevation ratios (ER) describing elevation of metal contents in soil plots above contents at reference site Grönsinka. All data from upper part of organic mor layers (O_f).

	AGA-factory (600 m)			Kyrkbyn (3000 m)			Grönsinka (29 km)	
	Ratio to reference ER	Mean (mg/kg)	CV%	Ratio to reference ER	Mean (mg/kg)	CV%	Mean (mg/kg)	CV%
Mo	113	277	59%	13	31.0	44%	2.4	38%
Cr	98	733	38%	11	83.3	36%	7.4	27%
Ni	45	560	28%	10	129	31%	12.4	50%
Fe	8.8	10550	28%	2.3	2800	25%	1197	38%
Cu	6.1	47.3	19%	1.9	14.5	17%	7.8	18%
V	5.6	26	32%	1.6	7.5	29%	4.6	28%
Cd	5.3	2	25%	1.0	0.4	25%	0.4	25%
Zn	3.3	210	24%	0.9	61	17%	64	17%
Mn	2.6	1120	35%	0.4	183	47%	427	74%
Pb	2.3	79	36%	1.4	48	28%	34	36%
Hg	1.5	0.45	29%	0.8	0.24	25%	0.31	32%

Metals are sorted in order of decreasing relative increments at the polluted sites with the most elevated metal (highest ER) presented at the top of the table and the least elevated metal at the bottom (lowest ER). This order of the metals is also maintained in other tables throughout this report. Metals are considered elevated if the metal content is more than 3 times higher than the level at the regional reference site. Molybdenum, chromium and nickel showed highly elevated contents. The National Forest Survey, based on a larger number of sites, was used to estimate a background value of 2.1 µg/g for chromium in mor layers at the latitude of Avesta (Andersson et al. 1991). With this as a reference value, the chromium content in the forest mor layers near the Avesta factory is even more elevated than proposed in **Table 5** (page 15).

6.3 Spatial patterns of metals and microbial respiration in soil plots

Many of the metals are highly correlated in the mor layer. This is a result of similar patterns of interception in tree canopies and similar mechanisms of deposition to the ground. The correlation matrices in soil plots are reported in **Table A1** (in Appendix, page 31) provide an overview, the correlation matrices are also graphically depicted in **Fig. 6** (in 6.3). Highly elevated molybdenum, chromium and nickel are strongly correlated. Iron, vanadium, cadmium, copper, zinc, mercury and lead are included in the correlation webs to a greater or lesser extent. These patterns are expected when pollution is the main source rather than internal sources and when the metals have similar degrees of sorption to plant litter. Correlations between metals within sampling plots have consequences for interpreting microbial effects, as individual metals cannot be distinguished in correlations with respiration.

It is of interest to observe metals that were more or less independent of the others. At the Kyrkbyn site, Cu was loosely correlated only to a few metals, while Zn and Mn were fully independent (**Fig. 6** in 6.3). At the AGA-factory site, Hg and Mn were more or less left outside correlations.

Small-scale spatial correlations in soil plots between respiration and metals are presented in **Table 6** (page 18). All variables were cleared from influences of mineral soil contents in the humus material. In the ideal field study the effect variable (i.e. the metal) and the response variable (respiration) would be the only variables that show variability. Furthermore, only one effect variable should have an influence on the response variable. However, in reality the effect variable is controlled by a vast amount of chemical factors and so is the response variable. Often the same factors control both the response and the effect variable. Drastic pH changes such as those resulting from forest liming have a clear effect on the solubility of metals in soil, but pH also controls the microbial activity to some degree. The same is true for the organic matter content. The ideal situation never exists in field investigations. Thus complementary experimental studies in the laboratory are also motivated. The great advantage of field observations is direct observation of real situations developed over a long time. Under favourable conditions the field assessment of toxic effects has proved to be very sensitive.

When analysing internal relations, microbial respiration was negatively correlated to the most elevated metals at Kyrkbyn (**Table 6**, page 18). These are metals of the main correlation cluster; Mo, Cr, Ni and Fe. There are also relationships with Pb and Hg of the cluster, but as these are hardly elevated relative to background levels, they are probably not of biological consequence. In summary, we can conclude from the spatial relations at Kyrkbyn probable adverse biological effects by Mo, Cr, Ni and Fe and no effects of the other metals. The

positive relation for Mn is another story. Mn is a nutrient essential in enzymes involved in lignin degradation with a stimulatory effect on decomposition (Berg 2000).

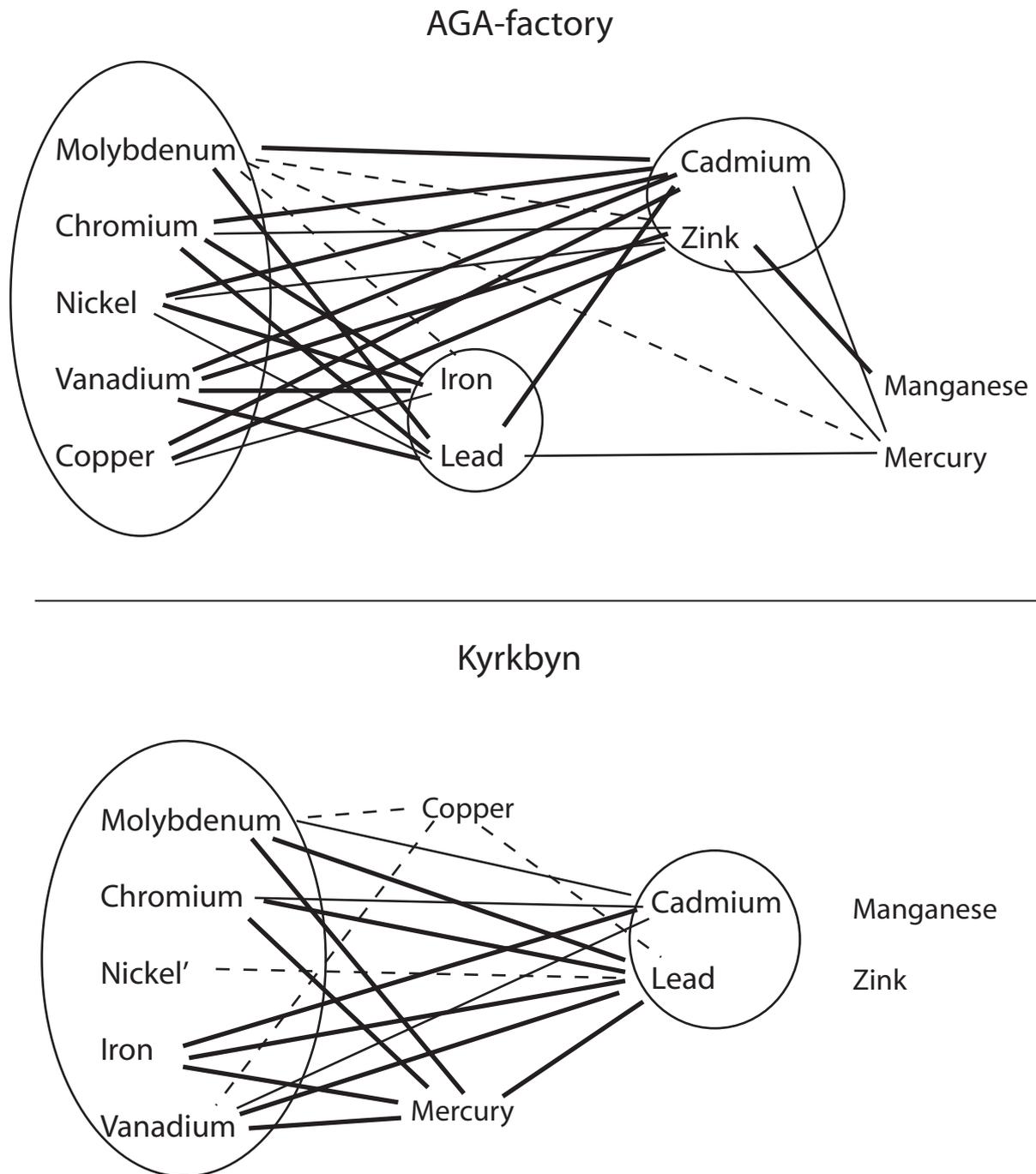


Figure 6. Spatial correlations between metals in mor layers of the sites at the AGA-factory and at Kyrkbyn. Metals within ovals are correlated at level of confidence $p < 0.001$, bold lines indicate correlations at $p < 0.001$, thin lines at < 0.01 and dotted lines $p < 0.05$.

Table 6. Spatial correlations between respiration rate and metal contents of mor layers within forest plots at 2 plots at the Avesta smelter. Coefficients of correlations were calculated for residuals of the relationship of the variables with minerogenic content

	AGA-factory (n=36)		Kyrkbyn (n=36)	
	r	Level of significance, p	r	Level of significance, p
Mo	-0.14	ns	-0.40	<0.05
Cr	-0.16	ns	-0.47	<0.01
Ni	-0.14	ns	-0.41	<0.05
Fe	-0.49	<0.05	-0.57	<0.001
Cu	-0.21	ns	0.09	ns
V	-0.10	ns	-0.30	ns
Cd	0.04	ns	-0.18	ns
Zn	0.26	ns	0.14	ns
Mn	0.41	<0.05	0.46	<0.01
Pb	-0.31	ns	-0.49	<0.01
Hg	-0.09	ns	-0.43	<0.01

The absence of toxic indications on microbial respiration at the AGA-factory site was striking. Possible explanations can be the following. Metals might have had such large impact that further biological effects are unlikely. In other words, we are in the upper tail of a sigmoid response curve (Haanstra et al. 1985). Another explanation is that high pH characteristic of the AGA-factory site might have immobilised some metals. This is further discussed in the section on solubility (6.6). Fe is known to specifically immobilise Mo under aerobic conditions (Alloway 1995), Fe being high at the AGA-factory site.

6.4 Metal effects in long-term respiration experiments

Experiments with metals added as salts are complements to field investigations. There is need to isolate effects of single metals among all factors appearing in field situations, especially to single out individual metals among correlated metals. It is common practice even in large recent assessments to compare field concentrations with experimentally obtained effect levels (Scott-Fordsmand & Pedersen 1995, Jensen et al. 1997). However, today there is increasing awareness that experiments cannot very well represent real situations with long-term chronic pollution loads. In our experience with forest mor layers, field observations of spatial patterns have been more sensitive than experiments in indicating possible metal effects (Bringmark & Bringmark 2001a, 2001b).

In our experiments all metals were added as cations of chloride salts to an O_f-layer material of background metal levels collected at Östervåla in the wider Avesta region. Chloride was chosen as counter-ion in its capacity as the major anion in acid forest soils. Inorganic Cu, Pb, Cd and Zn mainly occur as divalent cations in soil as they likewise did in the added salts. For Mo there is probably rapid oxidation to anionic Mo(VI)O₄²⁻ in the experimental arrangement (Alloway 1995). Cr has different oxidation states in nature, especially Cr(III) and Cr(VI). However less soluble and less toxic Cr(III), the form added, is prevalent in acid soils (Alloway 1995).

We tried to create conditions of some realism by monitoring microbial respiration during long periods of time, 174 or 156 active days in different experiments plus a freeze period. Then, metal immobilisation, biological adaptation and other processes would have time to proceed. After addition of metal salts and vigorous mechanical homogenization of soil samples microbial activity is stimulated initially, a stimulation that can be enhanced by the metal salt treatments. In the present experiments we found that at low dose levels positive effects often persisted throughout the whole experiment. Thus, inhibitory effect levels were calculated within that part of the dose-response curves that had negative slope.

Significant inhibitory effects on microbial respiration were recorded for all metals selected for the experiments (ANOVA). Selected metals were Mo, Cr, Ni, Cu, Pb, Cd, Zn and V. The resulting sequence of metal toxicities expressed by EC_{10} values was (**Fig. 7** in 6.4):

$$Mo \approx Cr \geq Cu > Zn \approx Ni > Cd \gg V > Pb$$

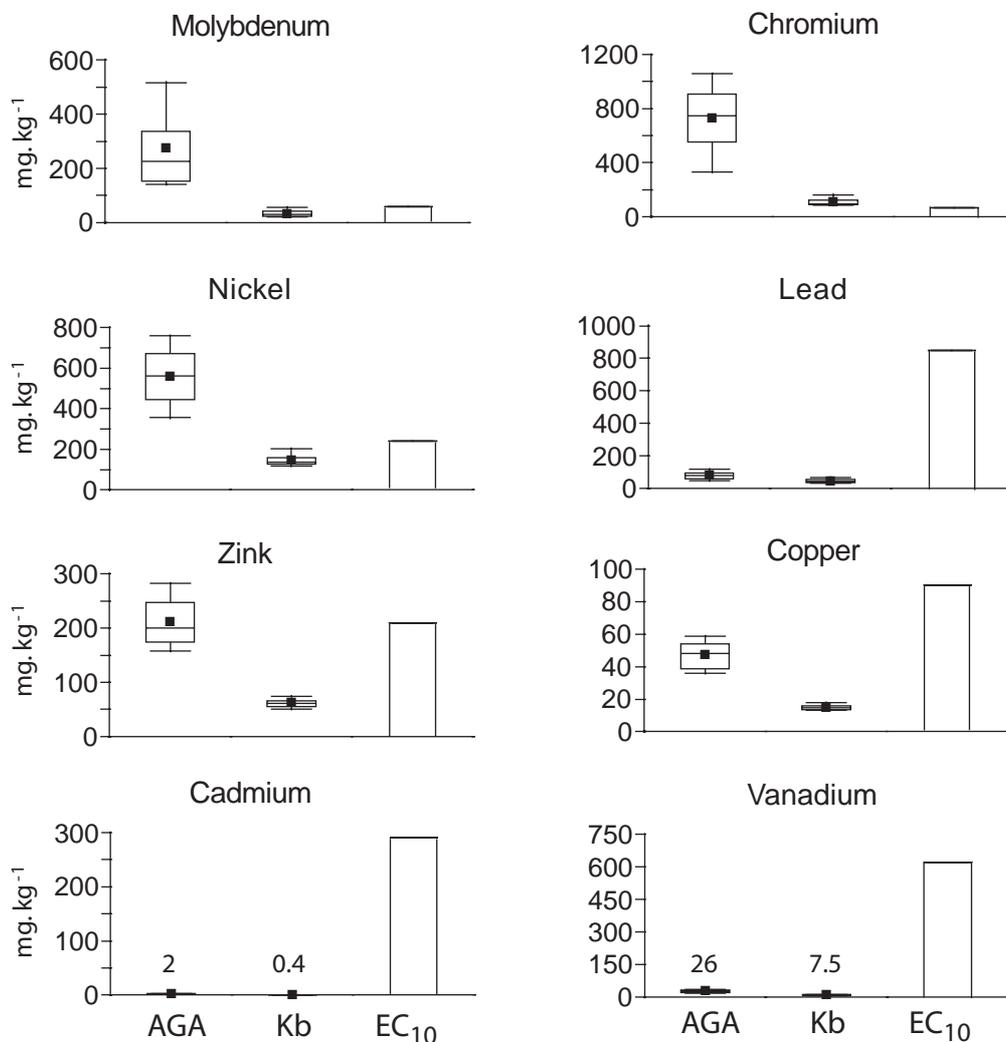


Figure 7. Inhibition of microbial activity by 10% (EC_{10}), determined in mor layer material (O_r -layer) by metal additions in long-term experiments and metal levels at AGA-factory and Kyrkbyn (O_r -layers) shown by box-and-whisker symbols depicting 10-, 25-, 50-, 75- and 90-percentiles.

This is similar to other metal-toxic sequences for soils reported in literature (Stadelmann & Santschi-Führmann 1987, Bååth 1989, Tyler 1992, Scott-Fordsmand & Pedersen 1995, Welp 1999). There were some notable differences. Cd was relatively less toxic and Zn more toxic than is usually reported. The reason for the deviations is probably the organic nature of our soils. Cr and Mo, two of the most elevated pollutants at Avesta, were found in the toxic end of the metal sequence. High toxicity for these two has been reported by other authors too, although low toxicity for Cr(III) and high toxicity for Cr(IV) have also been reported (Scott-Fordsmand & Pedersen 1995, Welp 1999). Ni, the third major pollutant, was of relatively low toxicity in our experiment.

In line with cautiousness of interpretation, experimental EC₁₀-values should not be translated numerically to effect levels in field situations. Instead, we suggest that the toxicity sequence gained by EC₁₀-values should be combined with information on field concentrations in a qualitative way. We can see from **Fig. 7** (in 6.4) that experimental effect levels were very roughly in parity with metal contents at Kyrkbyn for Cr, Ni, Mo, while EC₁₀ for Cu, Cd, Zn Pb and V were much higher than levels at Kyrkbyn. The conclusion is that effects at Kyrkbyn are more likely for the former metals than the latter. At the AGA-factory site, several metal levels were very much higher than experimental effect levels, but the absence of correlations with respiration at AGA-factory was considered more important in evaluation of the high pH situation of that site.

For Hg we have EC₁₀-values from earlier research. The EC₁₀-value was determined as 0.9 µg/g in a Northern Swedish O_T-material (Bringmark 2003). It was higher, 2 µg/g, in a Southern Swedish material of higher Hg content (Bringmark & Bringmark 2001a). Field concentrations are lower than these values.

6.5 Chemical properties of soil profiles

Some general notes on the soils at the AGA-factory and Kyrkbyn sites are appropriate as background to vertical metal distributions. The soil type, the so-called podsol, was described in the common introduction. The soils have been formed on loam of sedimentary origin with a distinct mor layer on top. They are dense soils with slow movement of water and air. Stones are absent. Deeper layers show signs of temporary anaerobic conditions in the form of gleyic stains. These layers are probably affected by ground water at least at AGA. Some chemical soil properties of importance for metal-holding and metal availability are shown in **Table 7** (page 22) and **Fig. 8** (in 6.5).

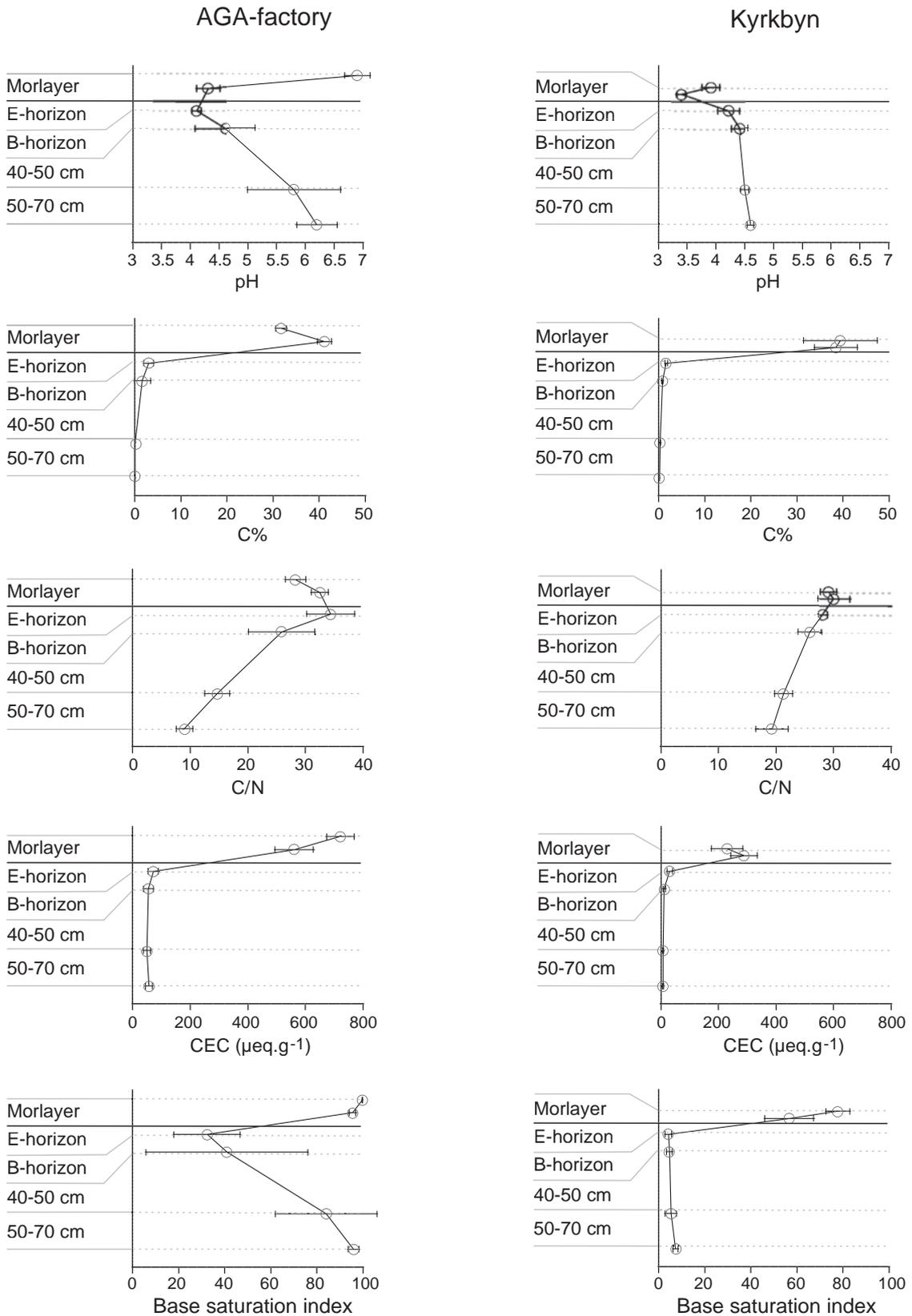


Figure 8. Soil chemistry; pH; Carbon content (C%); Carbon-to-nitrogen ratio (C/N); Cation exchange capacity (CEC); Base saturation index (%) in soil profiles at AGA-factory and Kyrkbyn. Mean values and standard deviation as bars.

Calculated on an areal basis, i.e. per square meter, about one third of the cation exchange capacity (CEC) and half of the organic material are allocated to the humus layer. CEC and organic material are of importance for the metal holding capacity, whether it is by strong metal-organic complexation or by cation adsorption. In general the soils at Avesta have substantial metal retention capabilities. Anaerobic conditions and slow water percolation are also important factors for metal migration. Sulphides of low solubility might be formed for some metals, while reduction might make some cationic metals such as Fe more mobile.

Table 7. Some soil chemical parameters in soil profiles at Kyrkbyn and AGA-factory. C stands for carbon, N for nitrogen, CEC for cation exchange capacity. N=4

Site	Horizon (cm)		pH-H ₂ O	Tot C %	C/N	CEC μ eq/g	Base saturation %		
Kyrk	O _f	Mean	3.9	39	29	230	78		
		Cv%		20	5	24	7		
Kyrk	O _h	Mean	3.4	39	30	281	57		
		Cv%		12	9	16	19		
Kyrk	0-5	Mean	4.2	1.6	28	30	4.2		
		Cv%		16	3	31	34		
Kyrk	5-15	Mean	4.4	0.80	26	12	4.6		
		Cv%		20	8	35	27		
Kyrk	40-50	Mean	4.5	0.32	21	7.4	5.3		
		Cv%		14	7	21	47		
Kyrk	70	Mean	4.6	0.15	19	7.1	7.3		
		Cv%		12	15	23	14		
AGA	O _f	Mean	6.9	32	28	721	100		
		Cv%		4	6	7	0,1		
AGA	O _h	Mean	4.3	41	33	565	96		
		Cv%		4	5	12	2		
AGA	0-5	Mean	4.1	3.0	34	71	32		
		Cv%		36	12	25	44		
AGA	5-15	Mean	4.6	1.6	26	55	41		
		Cv%		107	22	31	86		
AGA	40-50	Mean	5.8	0.09	15	49	84		
		Cv%		25	15	26	26		
AGA	70	Mean	6.2	0.07	9.0	56	96		
		CV%		10	16	21	2		

At the AGA-factory site, there is very high pH and base saturation at the soil surface, but these conditions are restricted to the top half of the mor layer (**Table 7**, page 22 and **Fig. 8** in 6.5). Exchangeable Ca is also much elevated in that layer at AGA-factory. This alkalization limited to the superficial layer makes deposition of dust a very probable cause. Similar soil reactions due to dust emissions are known from other metal industries (Rühling & Tyler 1979, Tyler 1984). The high pH has led to higher cation exchange capacity throughout the profile at AGA-factory compared to Kyrkbyn. At the bottom of the AGA-factory soil profile, there is again high pH and very high base saturation (**Fig. 8** in 6.5). Alkaline groundwater is a possibility at the bottom.

Our reference site at Grönsinka had soils formed in sandy till material, i.e. unsorted glacial deposits. Contents of stones and boulders were very high. This site would have more rapid

water percolation than the soils of the investigation sites near the steel smelter at Avesta. Only the mor layers were investigated for metal contents at Grönsinka.

6.6 Metal solubility

Defining the biologically most relevant metal fraction is a matter of major concern for assessment of metal effects in soils. The relevance of the total acid digestible fraction has been disputed and the soluble fraction considered more biologically available. This fraction exerts the largest effects on soil microorganisms (Geiger et al. 1996; Welp and Brummer, 1997; Sauvé et al. 1998). Recently the biological relevance to speciate metals within the soil solution has also been demonstrated, with the purpose of determining free ions (Lofts et al. 2004).

The present study uses a method to extract existing pore water from soil samples using lysimetric suction. Although the method is laborious, the solution obtained is more biologically and chemically relevant for real soil solutions than extracts obtained by other methods, e.g. from soil suspended in salt solution (i.e. 10 mM CaCl₂). However the extractions could only be performed on a few samples and with results relevant for the soil plots.

Application to individual soil samples would require a modelling approach, which could not be performed within the project. However, soluble portions of metals are known to be strongly correlated with total contents (Sauvé et al. 1997, Sauvé et al. 1998, Welp 1999). Other factors controlling fractionation of metals are pH and organic matter. Within mor layers of the sites, the variation in pH and organic matter is not as large as the variation in total metal contents. Therefore it is reasonable to expect a linear relationship between dissolved and total metal contents in soil samples within the sampling grids.

The three most elevated metals in the polluted sites (Mo, Cr and Ni) show different patterns of solubility. The dissolved content of Cr and Ni at the site Kyrkbyn is as high (Cr) or almost as high (Ni) as at the AGA-factory site, although the total metal contents are much higher at the latter site (**Fig. 9** in 6.6). Mo on the other hand shows a higher solubility at the AGA-factory site than at Kyrkbyn. This pattern can partly be explained by chemical characteristics of the plots. pH in the O_F-layer is much higher at the AGA-factory site than at Kyrkbyn (**Table 7**, page 22). In anaerobic conditions Mo is mainly in the form of MoO₄⁻. Due to the negative charge of this ion, in contrast to positively charged Cr and Ni, an exchange process with hydroxyl ions occurs at high pH, which makes MoO₄⁻ more soluble (Alloway 1995). The cation sorption in organic mor layers is governed by the negatively charged groups on the humus particles, mostly carboxyl and hydroxyl groups. The amount of dissociated groups increases with pH. As these negatively charged groups have a large affinity for positively charged ions in solution, Cr and Ni is more strongly bound to the organic matrix than MoO₄⁻ at pH > 7. Cr is almost insoluble at pH > 5.5 as Cr(OH)₃ precipitates (Alloway 1995).

Regarding the other metals, some conflicting trends were uncovered. The solubility of Cu and Cd behaved mutually differently. The solubility of Cd is known to be affected by pH (Berggren 1992a), whereas the solubility of Cu is controlled to a higher extent by organic matter (Berggren 1992b). The pH-dependence of Cd should result in decreased solubility at AGA-factory, but the opposite was the case (**Fig. 9** in 6.6). For V, we found lowered solubility at AGA-factory, although anionic forms would be expected to increase solubility at high pH similarly as for Mo.

Another result in **Table 6** (page 18) in need of more discussion is the strong negative correlation between Fe and respiration at both the AGA-factory and Kyrkbyn sites. Solubility of Fe was not investigated, but biological Fe effects might be due to lowered supply of dissolved organic substances that constitute energy source to microorganisms. Marschner & Kalbitz (2003), and Miltner & Zech (1998) made studies on factors controlling decomposition of litter in soil. They came to the conclusion that aluminium, iron and manganese oxides in soil have a strong influence on the stabilisation of organic matter, making organic matter in soil less available for degradation. Such observations on iron effects would have important consequences for the iron-enriched surroundings of steel industries. In addition, the fact that Fe-oxides are strong chelating agents to heavy metals might be important for control of bioavailability of other metals in this study (Venditti et al. 2000a, Venditti et al. 2000b).

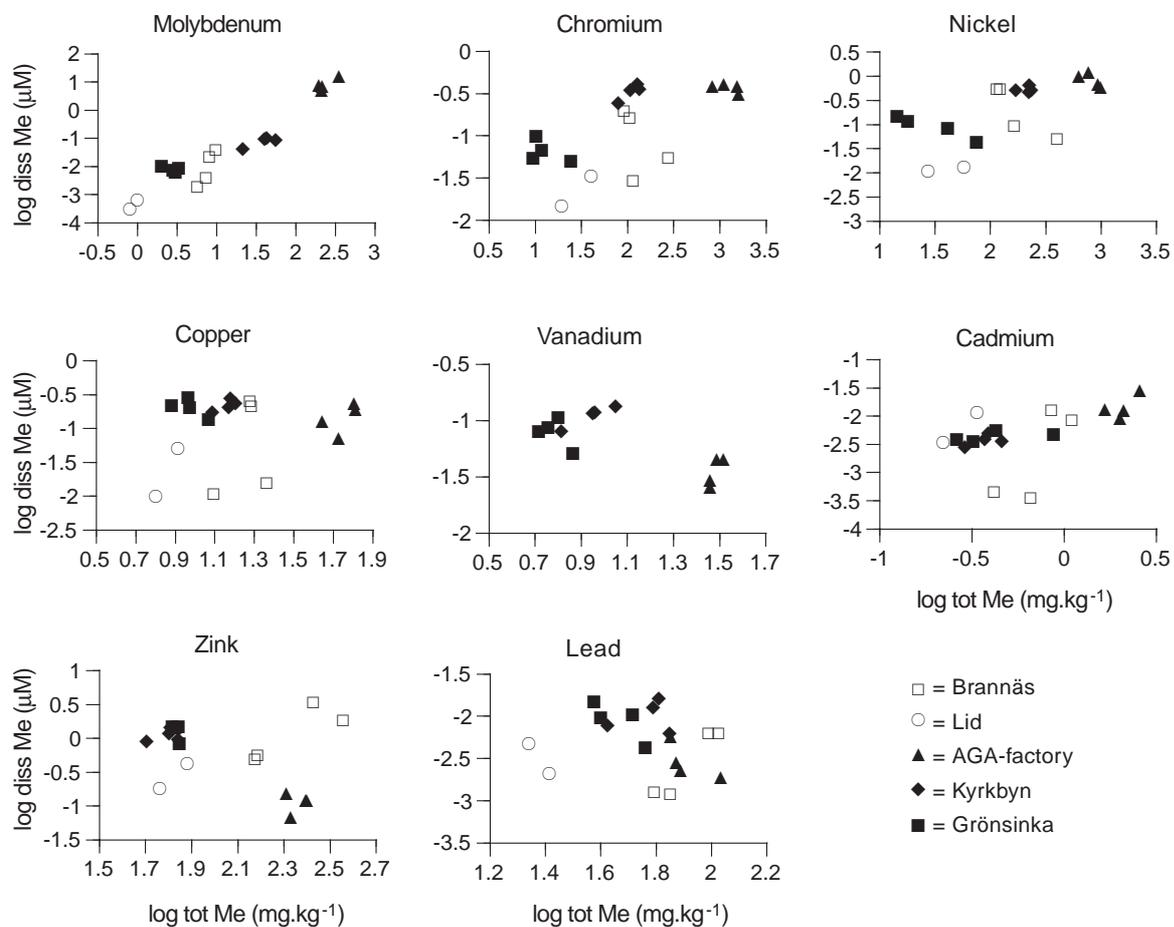


Figure 9. Correlations between total acid-digestible metal content and dissolved metal fraction at sites in Avesta (filled) and Oxelösund (unfilled) for Mo, V (not Oxelösund), Cr, Zn, Pb, Ni, Cu, Cd.

6.7 Vertical metal profiles in soils

Metal quantities in the upper part of the mineral soil (0-15cm) were related to the mor layer stores in a semi-quantitative way. Quantities in the mor layer and in the upper part of the mineral soils (0-15 cm, from top of mineral soil) were compared by taking into account that at

Kyrkbyn the weight of the 0-15 cm layer is about 25 times the weight of the mor layer per unit area. At AGA-factory, the same weight ratio is 15. With this knowledge, concentration ratios can be transformed into quantity ratios, which is done in the lower rows of **Tables A2 and A3** (in Appendix, pages 32-33). Values much larger than one indicate larger quantities in the upper part of the mineral soil than in the overlying mor, whilst low values indicate allocation to the mor layer.

Under the assumption that the dominant metal source was deposition, the quantity ratios on an areal basis at Kyrkbyn show that Mo and to lesser degree Ni were retained in the mor layer (**Table A3** in Appendix, page 33). The reason could be that high pollution loads occurring relatively recently did not have sufficient time to be redistributed to lower soil layers. Cr showed no strong preference, while other metals were not elevated pollutants. The AGA-factory site (**Table A2** in Appendix, page 32) showed effective retention of Mo, Cr and Ni in the mor layer. V was excessively allocated to the mineral soil, as were Cu and Zn to more moderate degrees. The distributions reflect different affinities to organic and inorganic components of the soil matrix. Fe and Mn were excepted from the analysis due to large internal sources.

Vertically cumulative distributions of the soil stores of Mo, Cr and Ni on an areal basis are shown in **Fig. 10** (in 6.7). The whole soil profile down to 70 cm is taken into account. For Mo the dominance of the mor layer stores was quite pronounced and mineral soil stores diminutive at both sites. For Cr and Ni the mor layers contain minor parts of the total although mor layer stores are proportionally much larger at AGA-factory than at less polluted Kyrkbyn. The total soil stores that can be read from the cumulative curves in **Fig. 10** (in 6.7) are much larger at AGA-factory than at Kyrkbyn.

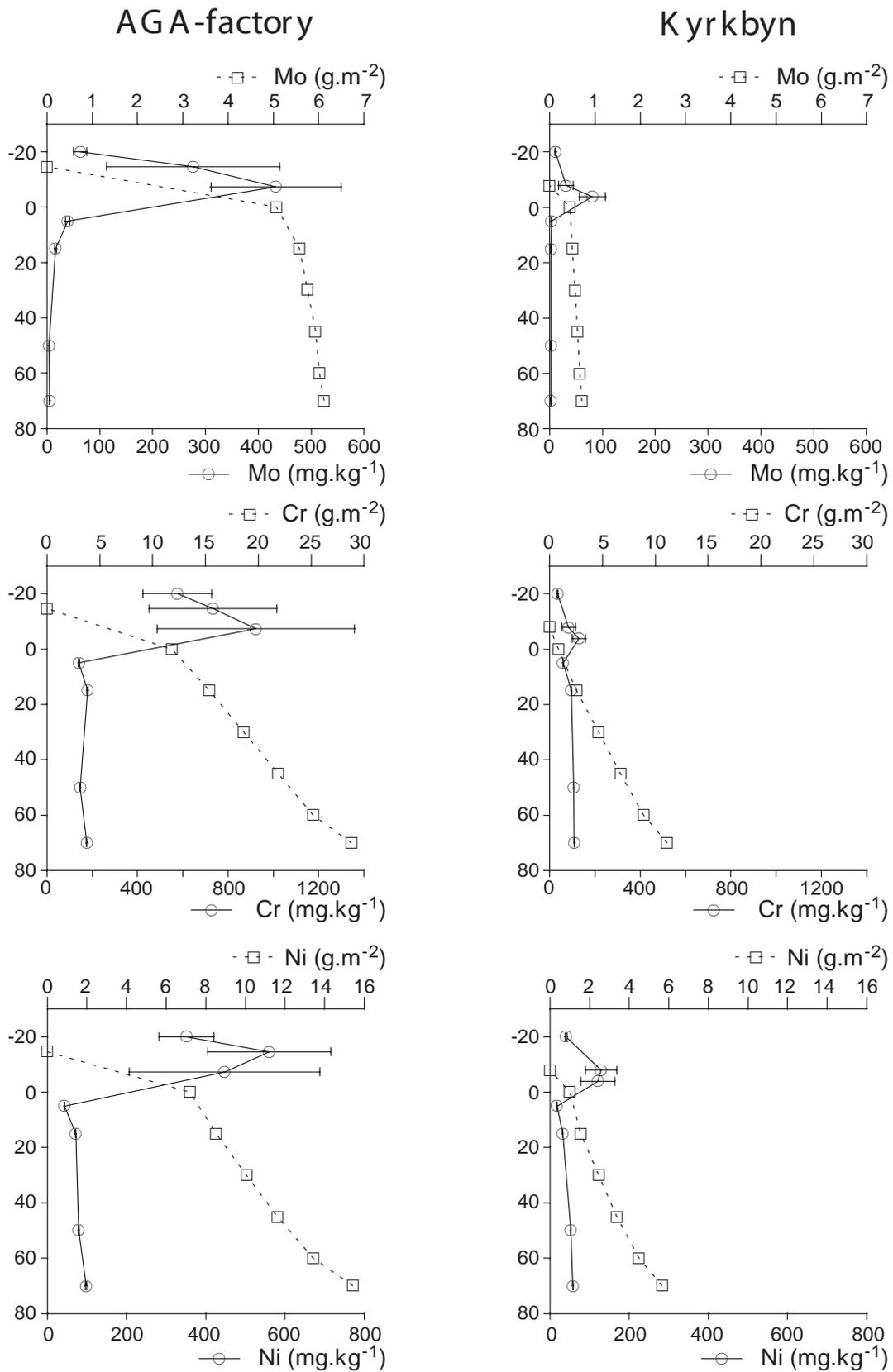


Figure 10. Contents of Mo, Cr and Ni (solid lines, mg/kg) in soil profiles and cumulative amounts with depth (hatched lines, g/m²). Values for metal contents (mg/kg) in organic layers denoted on lower x-axis. Contents in mineral soil layers (E-horizon to 70cm) enhanced by a factor ten in relation to the lower x-axis, roughly compensating for soil layer densities. Values of cumulative amounts are denoted on upper x-axis. They are in mineral soil layers calculated for each 15 cm consecutive layer by linear interpolation between layers sampled.

6.8 Metal distribution within mor layers (O_h / O_f)

Vertical metal relationships within the organic mor layers were also measured in our investigation. The upper O_f -layer is a younger material than the lower O_h -layer, which has been subject to carbon loss for a longer time and to a further degree of decomposition. Air-borne metals remain fixed in the humus spite of carbon loss and to a large degree remain in the ageing material on its transfer to the lower O_h -layer. With regard to carbon loss, O_h / O_f metal ratios approximately in the range 1.3 to 1.6 indicate conservative metal contents. Markedly lower values show a history of increased deposition, while high values indicate reduced pollution under the assumption that losses as well as inputs from other sources to the mor layer are small. This assessment is valid for the time span of O_f -layers, i.e. a few decades.

Among metals having most elevated levels, Ni showed a situation of increasing pollution load by having low O_h / O_f ratios at AGA-factory and Kyrkbyn (**Table A2 and A3** in Appendix, pages 32-33). The high O_h / O_f ratio for Mo at Kyrkbyn indicates lowered Mo pollution load at that site, with weak evidence of such lowering at the heavily polluted AGA-factory site. Cr contents were in the conservative range at both sites indicating neither increase nor decline. At AGA factory Cu, V, Cd and Zn with elevated levels also had rather low O_h / O_f ratios increased pollution load in the time span of decades (**Table A2** in Appendix, page 32). Mn and Fe were excluded from the discussion due to internal sources.

7. CONCLUSIONS

7.1 Metal risks in mor layers

Toxicity levels for individual metals in the upper part of the organic mor layers were evaluated by combining different observations. Mo, Cr and Ni, major components of alloy steel, were highly elevated in the mor layers, i.e. up to 45-113 times background levels near the Avesta smelter, 10-13 times at a distance of 3 km. Other elevated metals were Fe, Cu, V, Cd and Zn; elevated 5-12 times near the smelter, 1-4 times at 3 km. Pb, Hg and Mn were close to regional 'background' levels at the 3 km site and no more than 3 times elevated near the smelter. A general observation from various studies on heavy metals in soils is that a 3-5-fold increase in the level results in biological effects (Tyler 1992). This means that Mo, Cr and Ni would very likely affect soil microbiology at the metal levels encountered at Kyrkbyn 3 km from the steel works. Moderately elevated Fe, Cu, V and Pb and hardly elevated Pb, Zn, Hg and Mn at Kyrkbyn would not cause any disturbance. At the AGA site Mo, Cr, Ni, Fe, Cu, V and Cd are elevated more than 5-fold, which is to potential risk levels.

Metals were interrelated in the soil plot at Kyrkbyn, obstructing individual evaluation. As a collective group there was negative correlation to microbial activity for several metals (Mo, Cr, Ni, Fe, Pb and Hg). The spatial patterns show that there are certainly metal effects of some kind at Kyrkbyn. The experimental toxicity levels (**Fig. 3** in 3.3) compared with observed metal contents support the assumption that for the metals negatively correlated to respiration Cr, Ni and Mo are the likely biological culprits, while Pb and Hg most likely are not. This is consistent with the observed elevations of the respective metals. In this assessment EC_{10} -values are used in a cautious way, ranking the effect levels, while the spatial correlation is the hard evidence that effects do exist. For Fe, which was also negatively correlated to respiration, we did not have experimental information, but Fe was not very elevated at Kyrkbyn.

Several metals were highly elevated at AGA-factory, but high pH, low solubility of Ni and Cr and absence of metal/respiration correlations seem rule out biological effects at that site. For elevated Fe, which showed a negative correlation to respiration at AGA-factory, a biological effect cannot be ruled out.

In summary, Mo, Cr and Ni are clearly having adverse effects on microbial respiration in the mor layer of the Kyrkbyn site. Cu, V, Cd, Zn, Mn, Pb and Hg constitute no risks. At the AGA-factory site, alkaline dust immobilised the toxic metals. Some question marks remain for Fe.

7.2 Metal distribution in soil profiles

Judging from stores in different soil layers of elevated pollutants, Mo and to a lesser degree Ni were retained in the mor layer at Kyrkbyn. Cr showed no strong preference between organic and mineral layers. At the alkaline AGA-factory site elevated Cr, Ni and Mo were effectively retained in the mor layer, while V was more located to the mineral soil.

7.3 Are metal levels decreasing in mor layers?

O_h / O_f ratios indicate that Ni have been increasing in the mor layers of both sites, also Cu, V, Cd and Zn at AGA-factory, while Mo at Kyrkbyn shows signs of a decrease. Thus, the only indication of an improved situation is for Mo at Kyrkbyn. This would be a development in recent decades. Very effective metal retention in the organic mor layer necessitates reduction of metal loads to very low levels. For the major pollutants Cr and Mo at AGA-factory, inputs to the mor seem to have been roughly the same for a longer time. The moss analysis shows that some metal deposition is still ongoing.

7.4 How available are metals?

Measurement of soluble fractions shows that only a very small proportion of metals is dissolved. Alkaline conditions at AGA-factory immobilised some metals such as cationic Cr and Ni but not others such as anionic Mo. Absence of biological effects at the AGA-factory site could perhaps be explained by lower availability of Cr and Ni. High levels of Fe, which occur at the steel factory in Avesta, would probably diminish the availability of other metals, although this difficult problem was not studied. For individual mor samples within soil plots, we believe that our acid-digestible fraction reflects the soluble fraction, making the correlations to respiration at field sites a relevant biological assessment.

7.5 How serious are the disturbances?

The strategy of this investigation was to focus on the most sensitive compartment of the forest ecosystem, the organic layer in the topsoil in which metals accumulate. Very high metal levels as well as very probable toxic effects on microbial respiration were recorded. The occurrence of high levels of toxic metals is in itself an infringement of the national environmental aim of a toxin-free environment. The soil microbiota is doing the important work of decomposing organic material and recycling nutrients. This means that a major ecosystem process becomes disturbed. Thick organic layers at our investigation sites were manifestations of disturbed carbon recycling.

However, a superficial observation of trees, fields and bottom layer vegetation showed that plant growth is thriving. Only epiphytic lichens on the trees were visibly affected. Bearing in mind that vegetation was not subject to investigation, it is still appropriate to say that ecosystems have not deteriorated in their capacity to sustain plant life. Similar conclusions were drawn at Falun, where the many centuries of heavy metal and sulphur pollution from the copper production industry do not seem to have affected present-day forest vegetation (Lindeström 2002). On the other hand there are other potential risks with large metal stores in soils. For example, the microbial community could be genetically impoverished or in the future, metals stored to high levels in soils might be mobilised by activities of forestry or building, although the capacity of soils to retain metals is indeed very large.

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9. APPENDIX

Table A1. Correlation matrix between metals within sampling plots at AGA-factory and Kyrkbyn (Pearson correlation coefficient). *** = $p < 0.001$; ** = $p < 0.01$; * = $p < 0.05$

Mo											
Mo	1.000	Cr									
Cr	0.612***	1.000	Ni								
Ni	0.598***	0.955***	1.000	Fe							
Fe	0.379*	0.558***	0.557***	1.000	Cu						
Cu	0.784***	0.739***	0.773***	0.487**	1.000	V					
V	0.742***	0.618***	0.629***	0.614***	0.717***	1.000	Cd				
Cd	0.764***	0.591***	0.626***	0.219	0.877***	0.600***	1.000	Zn			
Zn	0.372*	0.428**	0.463**	0.056	0.571***	0.537***	0.714***	1.000	Mn		
Mn	-0.204	-0.124	-0.012	-0.385	0.036	0.031	0.199	0.570**	1.000	Pb	
Pb	0.813***	0.576***	0.522**	0.555***	0.803***	0.712***	0.720***	0.330	-0.181	1.000	Hg
Hg	0.384*	-0.096	0.009	0.095	0.442**	0.318	0.498**	0.459**	0.289	0.455**	1.000

Mo											
Mo	1.000	Cr									
Cr	0.777***	1.000	Ni								
Ni	0.593***	0.677***	1.000	Fe							
Fe	0.780***	0.733***	0.638***	1.000	Cu						
Cu	0.351*	0.258	0.055	0.271	1.000	V					
V	0.908***	0.684***	0.644***	0.705***	0.391*	1.000	Cd				
Cd	0.492**	0.461**	0.243	0.680***	0.146	0.444**	1.000	Zn			
Zn	0.174	-0.062	0.009	0.100	0.068	0.270	0.224	1.000	Mn		
Mn	-0.132	-0.082	-0.012	-0.102	0.023	-0.046	0.141	0.272	1.000	Pb	
Pb	0.816***	0.577***	0.379*	0.839***	0.403*	0.772***	0.594***	0.287	-0.165	1.000	Hg
Hg	0.636***	0.603***	0.285	0.606***	0.303	0.541***	0.414	-0.057	0.032	0.614***	1.000

Table A2. Metal concentrations ($\mu\text{g/g}$) in different soil layers at the AGA-factory site. Number of measurements 36 in O_f -horizon, 6 in O_h -horizon and 4 in mineral soil horizons.

		Mo	Cr	Ni	Fe	Cu	V	Pb	Cd	Zn	Hg	Mn
<u>AGA-factory</u>												
O_f -horizon	Mean	277	733	560	10600	47	26	79	2.0	212	0.46	1122
	<i>Sd</i>	164	282	155	2900	9.0	8.3	28	0.46	50	0.13	391
O_h -horizon	Mean	433	923	448	16500	48	22	116	2.0	125	0.45	255
	<i>Sd</i>	123	435	240	3300	7.4	6.7	25	0.37	39	0.07	157
0-5cm	Mean	3.9	14	4.3	7600	9.0	22	27	0.07	16	0.019	109
	<i>Sd</i>	3.9	2.7	1.0	4000	7.2	5.7	3.0	0.03	4.8	0.011	40
5-15cm	Mean	1.6	18	7.2	19100	10.4	30	13	0.11	31	0.011	257
	<i>Sd</i>	1.7	3.4	0.8	3400	5.8	4.4	3.1	0.06	1.8	0.001	85
40-50cm	Mean	0.38	15	7.9	16700	9.8	28	12	0.06	28	0.038	371
	<i>Sd</i>	0.09	1.9	1.2	2460	0.8	3.2	1.2	0.01	2.7	0.011	63
70 cm	Mean	0.48	18	9.8	19300	11.1	32	12	0.08	31	0.016	448
	<i>Sd</i>	0.14	2.9	2.0	2800	1.2	3.6	1.6	0.03	4.5	0.002	125
O_h / O_f		1.6	1.3	0.8	1.6	1.0	0.8	1.5	1.0	0.6	1.0	0.2
15 * min / mor ^{*)}		0.10	0.3	0.2	17	3.1	17	1.6	0.7	2.3	0.45	4.5

*) ratios of metal quantities on area basis in upper 0-15cm of the mineral soil and metals in mor layer ($O_h + O_f$). Factor 15 accounts for the weight ratio of the layers, 0-15 cm being fifteen times heavier per m^2 than the mor layer at the site.

Table A3. Metal concentrations ($\mu\text{g/g}$) in different soil layers at the Kyrkbyn site. Number of measurements 36 in O_f -horizon, 6 in O_h -horizon and 4 in mineral soil horizons.

		Mo	Cr	Ni	Fe	Cu	V	Pb	Cd	Zn	Hg	Mn
<u>Kyrkbyn</u>												
O_f -horizon	Mean	31	83	129	2800	15	7.5	48	0.38	61	0.24	183
	<i>Sd</i>	14	30	40	720	2.4	2.2	13	0.10	10	0.06	86
O_h -horizon	Mean	81	129	121	6300	15	14	91	0.57	69	0.34	112
	<i>Sd</i>	25	29	43	1850	1.9	2.8	17	0.22	13	0.12	73
0-5cm	Mean	0.32	5.9	1.8	6500	6.6	17	14	0.038	12	0.029	66
	<i>Sd</i>	0.14	1.0	0.4	1250	1.0	2.1	1.4	0.007	2.0	0.007	13
5-15cm	Mean	0.28	10	3.2	12500	3.3	27	7.2	0.048	19	0.017	108
	<i>Sd</i>	0.005	0.2	0.4	1150	0.3	0.1	0.7	0.004	1.2	0.003	5.6
40-50cm	Mean	0.25	11	5.2	10700	2.5	27	7.0	0.033	18	0.030	121
	<i>Sd</i>	0.012	0.7	0.8	2200	0.6	1.5	0.3	0.005	1.6	0.011	17
70 cm	Mean	0.24	11	5.8	12500	3.4	23	7.1	0.027	18	0.009	251
	<i>SD</i>	0.073	0.8	0.5	2300	0.3	4.6	0.6	0.003	1.1	0.001	73
O_h/O_f		2.6	1.6	0.9	2.2	1.0	1.9	1.9	1.5	1.1	1.4	0.6
25 * min / mor ^{*)}		0.13	2.0	0.55	58	7.3	55	3.4	2.4	6.4	1.8	16

*) ratio of metal quantities on area basis in upper 0-15cm of the mineral soil and metals in mor layer ($O_h + O_f$). Factor 25 accounts for the weight ratio of the layers, 0-15cm being twenty-five times heavier per m^2 than the mor layer at the site.

Table A4. Metals in soil layers of reference sites. Concentrations ($\mu\text{g/g}$) in upper and lower part of mor layer at Grönsinka. Number of measurements 12 in O_f -horizon, 6 in O_h -horizon at Grönsinka.

		Mo	Cr	Ni	Fe	Cu	V	Pb	Cd	Zn	Hg	Mn
<u>Grönsinka</u>												
O_f -horizon	Mean	2.4	7.4	12	1200	7.8	4.6	34	0.38	65	0.31	427
	<i>SD</i>	0.9	2.0	1.2	450	1.4	1.3	12	0.08	11	0.10	317
O_h -horizon	Mean	3.2	6.7	7.7	2000	7.7	5.7	59	0.50	65	0.40	116
	<i>SD</i>	1.6	3.1	1.9	860	2.6	2.3	32	0.20	3.3	0.15	71
O_h/O_f		1.3	0.9	0.6	1.7	1.0	1.2	1.7	1.3	1.0	1.3	0.3

Metal levels and microbial effects in forest soils at the Oxelösund steelworks

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SAMMANFATTNING

Stålverket i Oxelösund byggdes ut kraftigt under 1950-talet. Större delen av metallutsläppen till luft har skett efter denna tid, men kraftfulla åtgärder för att minska utsläppen har genomförts efterhand. Det är att notera att järnmalmen har innehållit höga halter av vanadin vilket speglas i utsläppen. Metallföreningar har deponerats i omgivande skogsmarker och upplagrats där. De biologiskt aktiva humusskikten, de s k mårskikten, kvarhåller till stor del metallföreningen. Vi har under 2003 undersökt haltförhöjning av Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, V och Zn i mårskikt, skadliga mikrobiologiska effekter och metallers löslighet i samma skikt samt metallers fördelning i markprofilen.

Undersökningarna har genomförts inom två skogklädda provytor 1-2 km från stålverket. En viktig undersökningsmetod har varit att analysera småskaliga rumsliga samband mellan metaller och mikrobiell respiration samt mellan metaller inbördes i provytorna. Dessa analyser har gjorts i mårskiktets övre del (O_1 -skikt). Vi utnyttjar den stora rumsliga variation som finns i skogsmarken för att söka samband som kan tolkas som toxisk effekt. Därvid har det gällt att entydigt kunna fastställa samband mellan en viss metall och respiration. På grund av de många metaller och andra variabler som inverkar i fältsituationen kan man ej alltid utpeka den påverkande faktorn.

Vi har gjort experiment med tillsats av metaller till mårprover för att entydigt finna enskilda metallers inverkan på mikrobiell aktivitet. Experiment har emellertid den nackdelen att effektkoncentrationerna inte direkt kan översättas till haltvärden i fältsituationen även om experimenten har utformats för att ge realistiska förhållanden, bl a har de följts under lång tid.

Metoderna har kombinerats till en samlad riskbedömning där startpunkten är observation om halterna förhöjts mer än 3 gånger. Då anses det generellt finnas risk för mikrobiella störningar. Mo, V, Cr, Zn, Ni uppvisade denna förhöjning i en eller båda ytorna nära Oxelösund, men inga negativa samband till respiration kunde fastställas. Fe i hög grad och Mn i mindre grad var också förhöjda men anses inte giftiga. Dock, för de mycket höga Fe-nivåerna fanns viss misstanke genom påverkan av humus, men det fanns inga samband till respiration i provytorna. Experimentella resultat indikerade att negativa mikrobiella effekter kunde misstänkas för Cr, Ni och Zn vid de halter som fanns i provytorna. Men avsaknaden av samband i provytorna ansågs väga tyngre som bevis.

Pb, Cd, Cu, Al and Hg var endast svagt eller ej alls förhöjda. Toxiska effekter bör ej misstänkas av dessa metaller även om det fanns ett negativt samband mellan Pb och respiration i en provyta.

Frågan om metallhalter har ändrats analyserades genom att jämföra metallhalter i undre och övre del av mårskiktet, O_1/O_2 -kvoter. Om dessa kvoter var låga (<1.3) ansågs metalldeposition ha ökat under loppet av några decennier. Detta var fallet för de flesta av metallerna. Dock visade jämförelse av undersökning av Å. Rühling 1980 att halter sjunkit sedan dess. Upprepade depositions-mätningar med mossanalys visar också på minskande belastning.

Sammanfattningsvis kan sägas att halterna av Fe, Mo, V, Cr, Zn, Mn och Ni är starkt förhöjda i mårskiktet vid Oxelösund men biologiska effekter kan knappast påvisas. Det finns någon form av skydd mot skadlig inverkan på markbiologin. Möjligen kan de mycket höga halterna av Fe ha betydelse.

ABSTRACT

Investigations were carried out in the surroundings of the Oxelösund steelworks in 2003. Metal concentrations and elevation above reference levels were determined in forest humus layers in two soil plots 1-2 km from the industrial site. Possible microbial effects, metal solubility in humus layers and metal distribution in soil profiles were studied. Small-scale spatial relationships between metal contents and microbial respiration were determined. This was the most important way to look for microbial metal effects, although co-variation between a large number of factors makes it difficult to distinguish individual effects. Complementary experiments with added metals were carried out, although effect levels were not directly comparable to field situations.

Risk assessments for soil microbial activity in humus layers were carried out with a combined use of the methods. Only metals that were elevated more than threefold were considered to constitute risks. Fe, Mo, V, Cr, Zn, Mn and Ni were elevated to that level, while Pb, Cd, Cu, Al and Hg were not. No negative relationships with respiration were found for any of the elevated metals, of which Mn were not expected to be toxic in any case. Experiments indicated possible effects of Cr, Ni and Zn, but the absence of correlations in field plots was considered to be more important. In summary, although some metals were highly elevated, no microbial effects could be clearly detected. Some protective factor appears to be operating.

Comparing the ratios of metal concentrations in upper and lower parts of humus layers made it possible to evaluate whether metal contents had increased in the time span of decades. This was the case for a large number of the metals, although repeated inventories in the past two decades indicate declining concentrations.

1. BACKGROUND

The reader is referred to the report on our investigations at Avesta (Bringmark & Åkerblom 2005) for a general introduction. The aims of the investigations, some notes on forest systems and soils as metal recipients, and an explanatory discussion on investigation strategies can be found in the introductory chapters 1-3 of that report. However, a more specific introduction to the investigations at Oxelösund, some relevant notes on the industrial history, earlier investigations and the character of the sites investigated are included here.

1.1 Brief industrial history and earlier investigations at Oxelösund

The steelwork at Oxelösund was radically expanded in the 1950s from a small iron-producing plant and a glassworks in preceding decades. The main raw materials brought into the facility over the years have been iron ores and coal. A large blast furnace, a coke works and a huge rolling-mill have been operating since the 1950s. A notable fact is that the iron ores used contain high levels of vanadium. The industrial activity has led to high loads of metals in the surroundings. Measures to reduce emissions have been implemented at various points in time, with good results.

Metal deposition and metal concentrations in humus layers at Oxelösund were investigated in 1978 (Rühling 1980). Rühling identified iron and vanadium and to lesser degree chromium and nickel as the most important pollutants at Oxelösund. Mosses were sampled again in 1994 and 2000.

The main object of our investigations was humus layers of the forest floor. These layers are called mor layers in podzol soils.

1.2 Oxelösund region and sites investigated

The city of Oxelösund and its steelworks is situated on the Baltic coast, in a region famous for its beautiful archipelago of small islands. Numerous fractures in the resistant gneiss-granite bedrock have formed these islands. The land along the coast is a broken landscape formed from the same fractured bedrock and formerly also washed by the sea before the rising of the land. Areas of exposed rock carrying coniferous forest alternate with depressions with deep marine clay sediments used for agriculture. Adjacent to the rocky areas there are usually shallow till soils under mixed forest. Our two investigation sites near the industry were located in these latter fringe soils, while the remote reference site at 32 km to the north was in a landscape of thick tills.

The city of Oxelösund occupies the area immediately to the west of the steelworks, while forest, some agriculture and a recreational nature reserve cover a peninsula to the north. Our two investigation sites close to the industry were located on this peninsula. The primarily westerly winds at Oxelösund tend to carry much of the air pollution from the industry towards the eastern sea. However, substantial pollution has been intercepted over the years in forests situated in other wind directions.

Our investigation site closest to the industry was placed just outside the perimeter fence towards the north-west (**Fig. 1** in 1.2). This site, called 'Fence', was on a rocky outcrop carrying a meagre

pine forest approximately 1.0 km from the steel producing plant (**Table 1**, page 5). A second site was at a distance of about 2.0 km due north in the peninsular area. This site, called ‘Brannäs’, carrying mixed spruce-pine forest, was situated in a small section of deep soil in the rocky landscape. The inland reference site ‘Lid’, 32 km to the north, carried well-grown spruce forest growing on deep soil.

Table 1. Characteristics of soil, vegetation and tree stands at the three sampling sites

	Fence		Brannäs		Lid
Thickness of mor layer (cm)	19.1		9.1		7.6
CV%	43.8		29.0		33.7
pH in water extract of O _f -layer	4.9		4.9		3.9
SD	0.42		0.40		0.22
Stem thickness (cm)	17.4		29.1		
CV%	35.1		23.7		
	Stand composition (%)	Stem thickness (cm)	Stand composition (%)	Stem thickness (cm)	Stand composition
Norway spruce	14	9.8	61	30.1	Mature spruce, some birch.
Scotch pine	78	19.0	26	28.6	
Birch	4	18.3	13	24.9	
Oak	4	11.7			
Other site information	<p>Rocky hilltop. Meagre forest dominated by Scotch pine and some deciduous trees.</p> <p>Blueberry, lingonberry, heather, crowberry, mosses (<i>Hylocomium splendens</i>, <i>Pleurozium schreberi</i>). Some grasses (<i>Dechampsia flexuosa</i>).</p> <p>Undeveloped shallow soil profile. Thick organic mor layer. 20 cm of coarse sandy material below mor layer.</p>		<p>Pocket of thick soil among rocks. Mature forest dominated by spruce, with some Scotch pine and deciduous trees.</p> <p>Blueberry, lingonberry, mosses and grasses (<i>Dechampsia flexuosa</i>). Old arable land.</p> <p>Podsolized soil, partly moist. Organic mor layer. Mineral soil with a sandy layer of 30 cm thickness carrying small stones. Dense layer of clay sediment at bottom.</p>		<p>Hill country with deep till soils. Mature spruce, some birch.</p> <p>Blueberries and mosses (<i>Hylocomium splendens</i>).</p> <p>Sandy material. Weakly podsolized soil. Dense organic mor layer.</p>

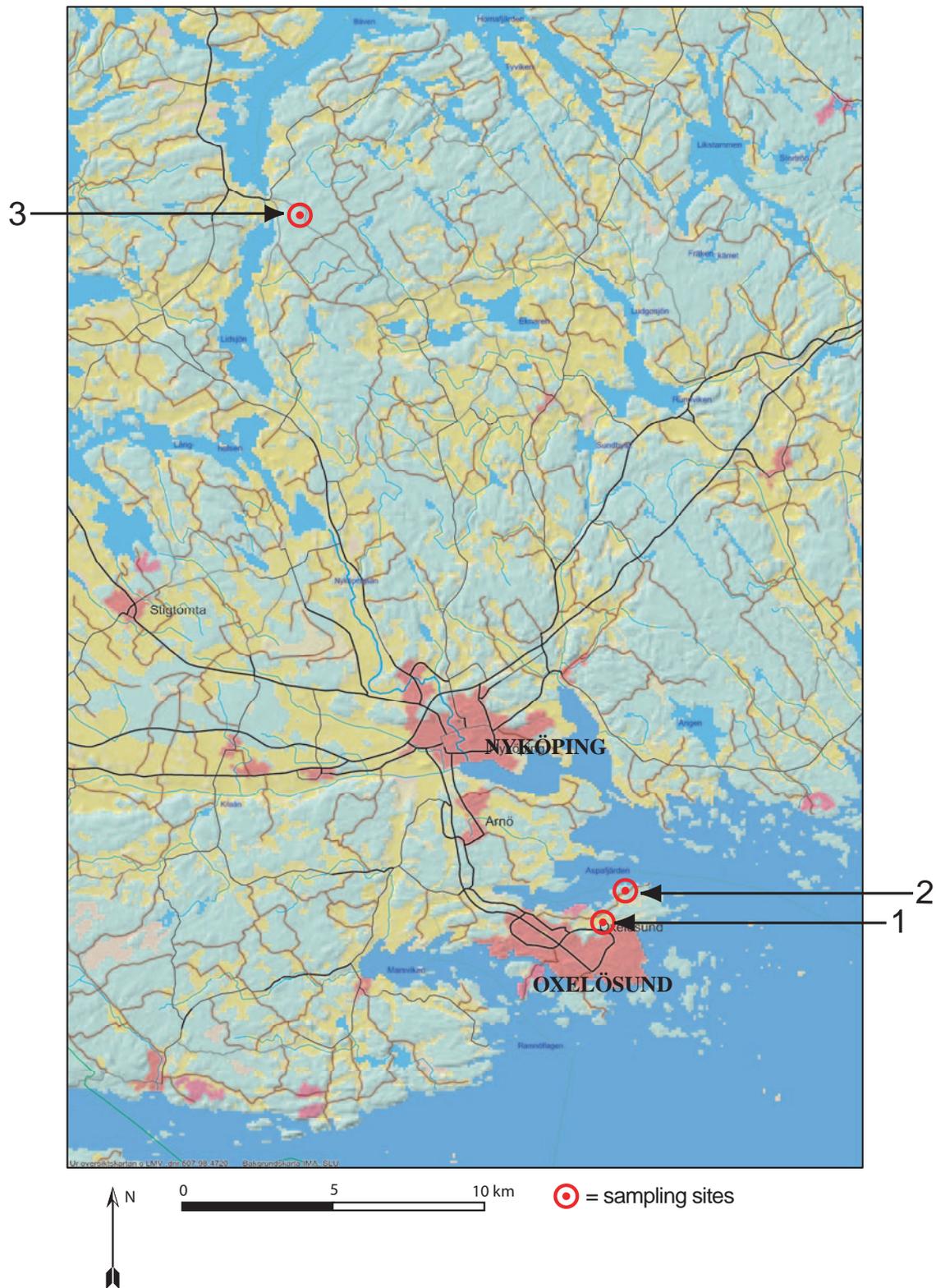


Figure 1. Location of the three soil sampling sites at Oxelösund. 1= Fence; 2=Brännäs; 3=Lid.

2. METHODS

2.1 Investigation of mor layers for risk assessment

The investigations at the steel industry at Oxelösund were performed using the same methods as at Avesta, see Bringmark & Åkerblom (2005) for a more thorough description. The ideas behind our investigation strategy are discussed in the introductory chapters of the Avesta report.

The assessments are mainly based on chemical and biological determinations in ‘homogeneous’ soil plots at different distances from the industry. Metal levels and spatial correlations between metals and microbial activity were determined within those soil plots and presented as case studies. The complex pollution history gave rise to the problem that several metals and other environmental factors were correlated to each other. Therefore, the effects of individual metal species were not distinguishable from the field method alone.

Laboratory-derived toxicity data were also part of the analysis. Those experiments resulted in effect levels for individual metals, but it must be stressed that they should be interpreted with caution for field situations. These experiments were similar to those presented in the Avesta study (Bringmark & Åkerblom 2005).

Soil sampling was performed in November 2003 at the Fence, Brannäs and Lid sites. Methods of chemical and biological measurements are described in the Avesta report.

2.2. Sampling in soil pits

At Brannäs, two soil pits were dug and soil layers were sampled and taken for analysis. The layers sampled were O_r- and O_h-layer, 0-5 cm (E-horizon), 5-15 cm (B-horizon), and 40-50 cm (B/C-horizon). At the Fence site, soil layers was very thin and the bedrock was found at a depth of about 20 cm below the mor horizon. Therefore mineral layer samples were taken only at two depths (0-5 cm and 5-15 cm). Two samples were taken from each depth and pit for chemical analysis of %OM (organic matter), metals, pH, etc.

3. RESULTS AND DISCUSSION

3.1 Deposition

Metal analysis of mosses sampled at Oxelösund in 1994 and 2000 in unpublished investigations commissioned by the steelworks showed that metal deposition had been reduced to very low levels. In 1994, there were clear gradients with distance from the industry in concentrations of Cd, Cr, Cu, Ni, Pb, V and Zn determined in the mosses. These gradients had virtually disappeared by 2000, with only weak tendencies remaining for Cr and V. This shows that measures to reduce emissions have been very successful.

3.2 Metal increment in mor layers

Increments of metal concentrations in mor layers relative to the reference site at Lid were taken as a measure of the long-term metal load at the sites. The organic mor layer has a large capacity

to retain deposited metals for long times. Increments are presented for O_F -layers as elevation ratios (ER) in **Table 2**, page 8. To facilitate presentation of the results, metals have been tabulated in order of decreasing elevation observed at the Fence site in **Table 2**, and in other tables in this report.

It was shown that iron had accumulated to a high degree in the humus layers of the two sites near the industry. Molybdenum and vanadium were also elevated, although to a somewhat lesser degree. The increments well exceeded the range 3-5, above which increments of hazardous metals are generally regarded to constitute risks (Tyler 1992). Further down the metal list (Table 2), elevation of Cr and Ni barely exceeded the range 3-5 at one or both of the sites near the industry, Brannäs and Fence. However, the elevations of Cr and Ni might be underestimated as the background levels at the site Lid were high compared to other background sites. The two sites near the industry can be regarded as roughly equally polluted. The surroundings of Oxelösund were less polluted by the toxic metals Cr and Ni than was the case at Avesta.

Table 2. Elevation ratios (ER) for metals in O_F -layers. Elevation above level at reference site Lid is presented. Distance from steel mill shown after name of site

	Fence (1.0 km) N=31			Brannäs (2.0 km) n=34			Lid (32 km) n=30	
	Ratio to reference ER	Mean (mg/kg)	CV %	Ratio to reference ER	Mean (mg/kg)	CV %	Mean (mg/kg)	CV %
Fe	23	39903	17	18	30321	35	1717	48
Mo	9.6	7.6	17	9.4	7.4	42	0.79	23
V	9.4	142	20	8.9	135	50	15	52
Cr	4.4	51	34	6.5	76	55	12	74
Zn	3.7	236	21	3.4	216	53	63	34
Mn	3.3	1302	43	4.0	1563	89	395	95
Pb	2.9	108	24	2.5	92	46	37	28
Ni	2.8	61	54	5.8	126	67	22	65
Cu	2.5	20	14	2.1	17	36	7.9	27
Cd	2.3	0.90	25	1.9	0.74	51	0.39	40
Al	2.2	3560	23	3.7	6063	55	1654	57
Hg	1.2	0.38	8	0.9	0.31	30	0.33	11

There was an opportunity to compare present day levels for some metals with 1978 metal levels measured by Rühling (1980) (**Table 3**, page 8). The comparison had to be conducted for the organic mor layer as a whole investigated by Rühling. Values were calculated for the whole mor layer from our determinations in O_F - and O_h -layers in **Tables A2 and A3** in the Appendix, pages 15 and 16. The levels had decreased substantially, except for Cr and Ni at one site. However, the most highly elevated metals, Fe and Mo, were not included in the comparison.

Table 3. Comparison of current concentrations of some metals with concentrations measured in 1978 in mor layers of sites adjacent to the present sites Brannäs and Fence (Rühling 1980). Whole layers (O_F+O_h) were compared

	V	Zn	Cd	Cr	Ni
Rühling 1978 ($\mu\text{g. g}^{-1}$)	210	710	1.9	95	120
Brannäs 2003, ratio to sites of 1978	0.5	0.3	0.3	0.9	1.2
Fence 2003, ratio to sites of 1978	0.5	0.3	0.4	0.4	0.4

3.3 No indication of metal toxicity in soil plots

As is illustrated by **Fig. 2** in 3.3, most metals in the mor layers investigated were highly inter-correlated at the polluted sites, forming spatial clusters. Nickel, aluminium and chromium formed a cluster independently of the others at both sites. However, there were no general correlations between any of these metal clusters and soil respiration (**Table 4**, page 9). Respiration determined under standard conditions in the laboratory is a measure of the potential microbial activity that can be sustained by the soil substrate. Metals are suspected to be negative factors for substrate quality. However, the only significant correlations found for the respiration were with a few individual metals at one or other of the sites. Pb had a negative correlation to respiration at the Fence site, while Mn and V showed positive correlations. However, Pb was not very elevated at the Fence site, making toxic effects unlikely for that metal. None of the highly elevated metals showed a negative correlation to microbial activity.

Table 4. Spatial correlations between respiration rates and metal concentrations in mor layers within forest plots at the Fence and Brannäs sites, near the Oxelösund steel mill. Correlations were calculated for residuals of the correlation of each variable to minerogenic content

	Fence (n=34)		Brannäs (n=31)	
	r	Level of significance, p	r	Level of significance, p
Fe	-0.098	ns	-0.152	ns
Mo	0.203	ns	0.007	ns
V	0.551	<0.01	0.153	ns
Cr	0.096	ns	0.262	ns
Zn	0.280	ns	-0.020	ns
Mn	0.504	<0.01	0.206	ns
Pb	-0.452	<0.05	-0.261	ns
Ni	-0.066	ns	0.240	ns
Cu	-0.216	ns	-0.254	ns
Cd	0.084	ns	-0.053	ns
Al	0.037	ns	-0.367	<0.05

It seems that the major pollutants at Oxelösund did not affect soil biology. There was no drastic increase in pH by industrial dust that would explain the lack of metal toxicity (**Table 1**, page 5), as we found for one site at Avesta. However, the sites at Oxelösund were under the influence of very high levels of iron, which dominate the chemical environment. As was remarked in the Avesta report (Bringmark & Åkerblom 2005, chapter 6.6), high levels of iron might have negative effects on the microbial decomposition of soil organic material by stabilising the humus. However, the very high Fe levels at Oxelösund did not generate negative correlations to microbial activity within soil plots. As an example of possible iron effects, availability of Mo is known to be reduced in the presence of iron, which could obliterate the effects of that metal at Oxelösund (Alloway 1995). The absence of effects could also be attributed to the unavailability of metals in the particles deposited.

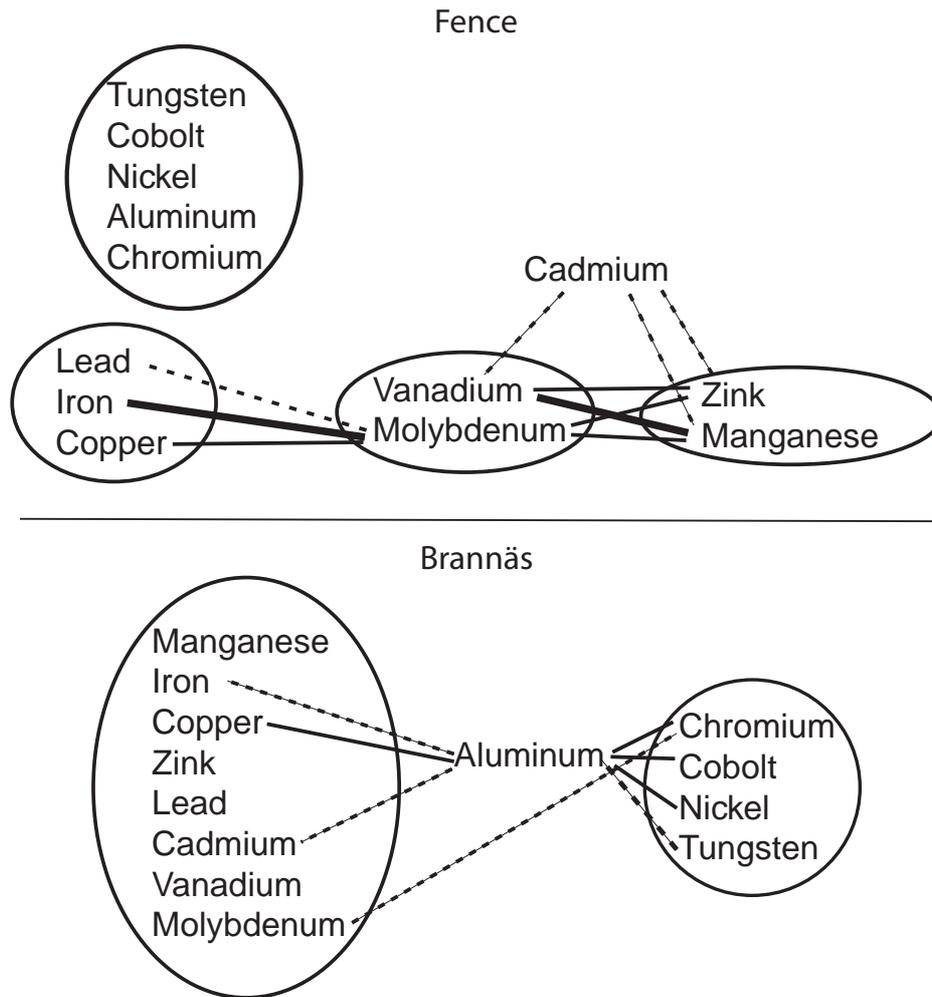


Figure 2. Spatial correlations between metals in mor layers (O_F -layers) of the Fence and Brannäs sites. Metals within ovals are correlated at a level of confidence $p < 0.001$, bold lines indicate correlations at $p < 0.001$, thin lines at $p < 0.01$, and dotted lines < 0.05 . Correlations were calculated for residuals of the correlation of each variable to minerogenic content.

The fact that humus layers were thick at the polluted sites investigated could be taken as some indication of impeded decomposition (**Table 1**, page 5). It might be that there is a general impact of the very high iron levels that are not generating detectable within-site patterns of microbial activity. Rühling (1980) showed possible weak effects on soil respiration activity in his comparison of sites, as opposed to our within-site comparisons.

3.4 Long-term respiration experiments

The results of experiments with added metal salts are described in our Avesta report (Bringmark & Åkerblom 2005). These experiments were performed on a mor layer material with low metal concentrations. Added metal concentrations ($\mu\text{g. g}^{-1}$) resulting in a 10% reduction of microbial activity (EC_{10} values) were 66 for Cr, 59 for Mo, 240 for Ni, 210 for Zn, 90 for Cu, 850 for Pb and 290 for Cd (total concentrations including initial contents). We do not believe that laboratory-derived EC values should be translated numerically to field situations but rather be

used to qualitatively indicate the possibility of effects of individual metals (see chapter 6.4 in Bringmark & Åkerblom (2005)). Bearing this in mind, it could be concluded that median metal levels of O_F -layers at the Brannäs and Fence sites were such that Cr and Zn just exceeded or were close to the EC_{10} values and Ni reached half of EC_{10} at one site (**Figure 3** in 3.4). The other metals investigated in the experiments were well below EC_{10} levels. Some biological risk is a possibility but the absence of negative correlations in soil plots is taken as stronger evidence.

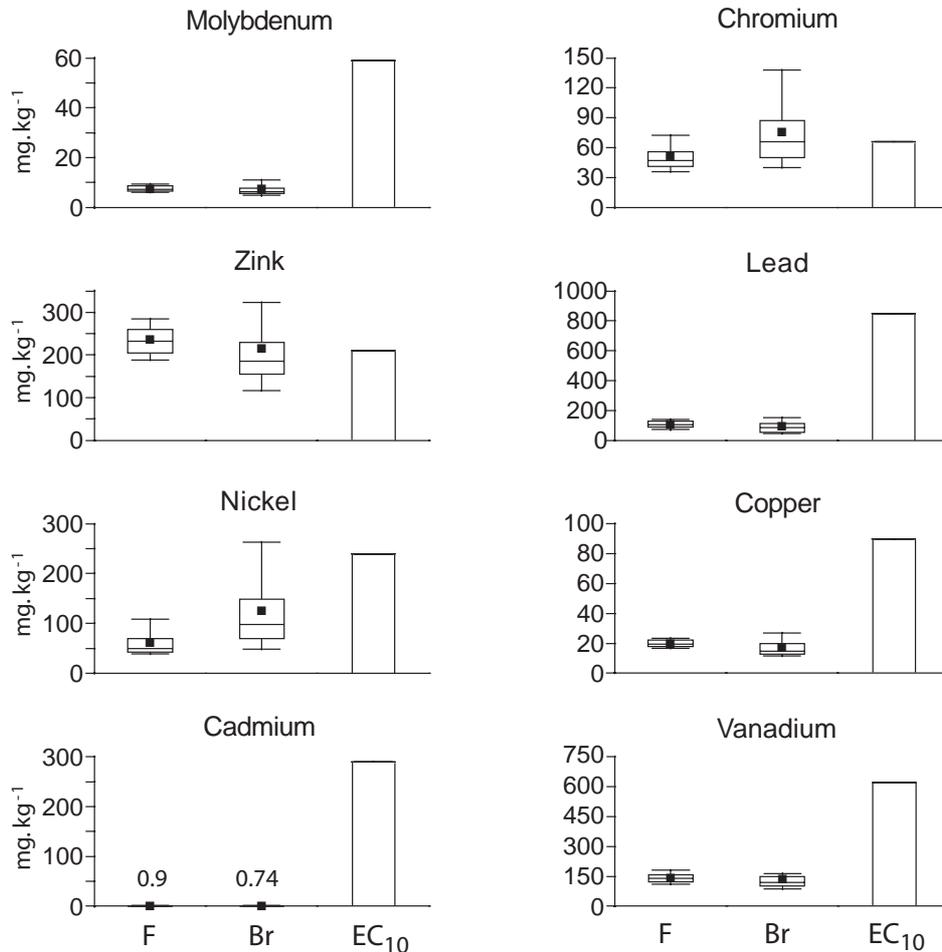


Figure 3. 10% inhibition of microbial activity (EC_{10}), experimentally determined in mor layer material (O_F) compared with field metal levels at Fence and Brannäs (O_F -layer). Box-and-whisker symbols depict 10-, 25-, 50-, 75- and 90-percentiles of concentrations.

3.5 Metal solubility

The discussion in the Avesta report (Bringmark & Åkerblom 2005) is relevant in the case of Oxelösund as well. In the present study, we used a method to extract existing porewater in soil samples using lysimetric suction applied on ceramic cells inserted in soil materials. This is a very labour-consuming method whose success depends on the presence of water in the samples. The resulting solutions represent the real soil solutions more closely than other extractions. At

Oxelösund, it was only possible to extract a small number ($n=6$) of samples. This had an influence on the interpretation of the solubility data. Furthermore, vanadium could not be analysed in water samples from the extractions at Oxelösund (**Figure 4** in 3.5).

A comparison was made between porewater extracts of soils from Avesta and from Oxelösund (**Figure 4** in 3.5). Cr, Ni, Cu and Cd had in some samples at Oxelösund lower solubilities than at sites at Avesta at equivalent total contents. Lower solubility can partly explain the lack of spatial correlation to biological activity in the sampling grid at Brannäs. We can only speculate on the reason for this, but we have already discussed the influence of high levels of iron at Oxelösund (see chapter 3.3 and Bringmark & Åkerblom 2005, chapter 6.6).

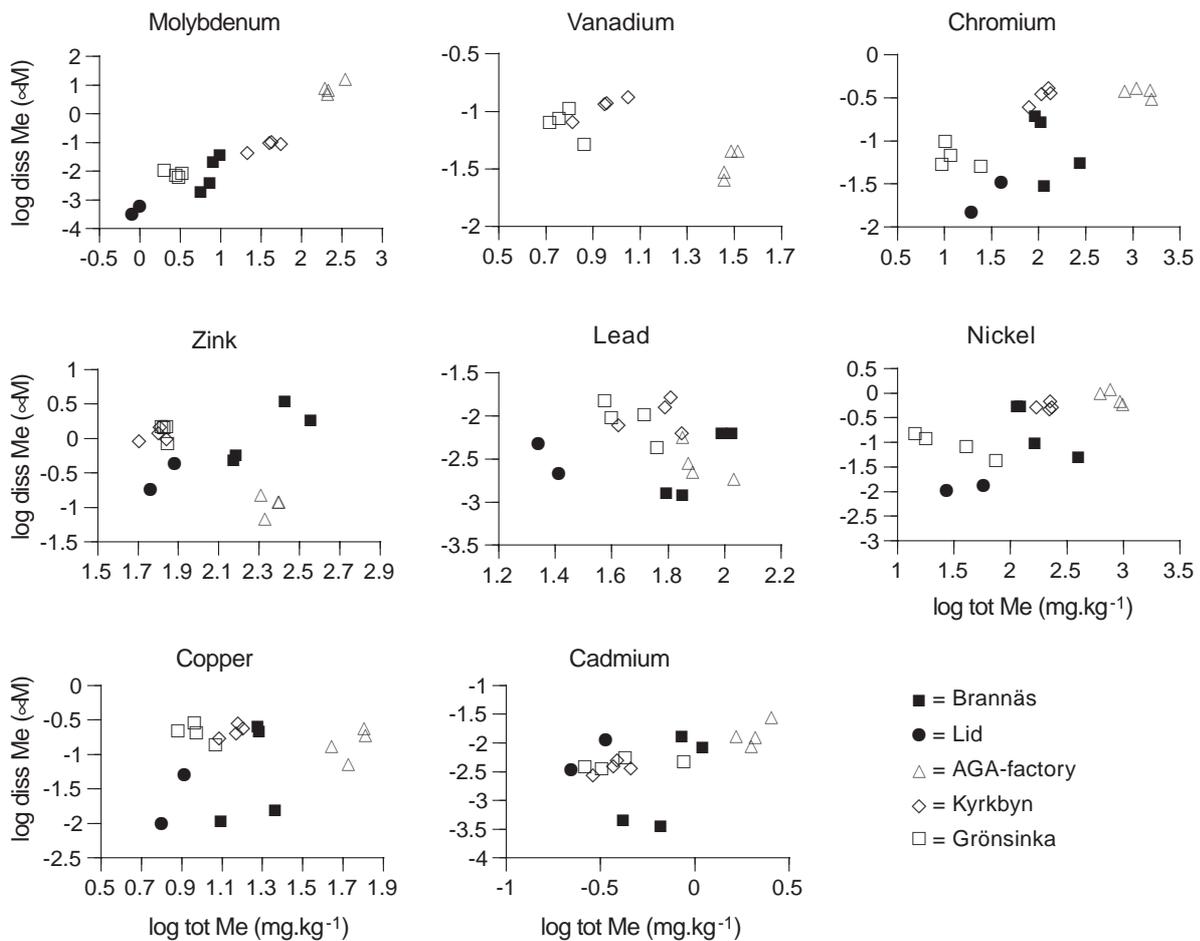


Figure 4. Dissolved metal fractions versus total metal contents at sites in Avesta (unfilled) and Oxelösund (filled). Vanadium shown for Avesta only.

3.5 Vertical metal distributions in mor layers

Within the mor layer, the upper O_f -layer is a younger material than the lower O_h -layer, which has decomposed to a further degree. Metals remain in the ageing organic material on its transfer to the lower O_h -layer irrespective of the carbon loss taking place. O_h/O_f metal concentration ratios in the range 1.3 to 1.6 roughly indicate conservative metal contents. Markedly lower ratios reflect a history of increased deposition, while higher ratios indicate reduced pollution loading. The assessments are valid for the life span of O_f -layers, i.e. a few decades. This is under the assumption that both losses and inputs from other sources to the mor layer are small. Fe, Mn and Al had to be excluded from the analysis for that reason, while O_h/O_f ratios of other metals were evaluated.

The O_h/O_f ratios were found to be low for Fe, Mo, V, Cr, Zn, Pb, Ni, Cu, Cd and Hg at Brannäs (**Table A2** and **Table A3** in the Appendix, pages 15 and 16). Ratios were low at Fence also but less pronounced for Cr, Pb, Ni and Hg. This would indicate generally increased metal loads during the course of some decades. This is in contrast to the reduced loads revealed in the past two decades when different investigations were compared (chapter 3.2).

4. CONCLUSIONS

4.1 Metal risks in mor layers

Mo, V, Cr, Zn, Ni were elevated in the O_f -layers of at least one of the two sites investigated to such levels (>3-fold) that negative effects on soil biology are possible according to general experience. Experimental EC_{10} -values also indicated the possibility of effects for Cr, Ni and Zn. However, the absence of negative relationships to microbial respiration in soil plots is taken as stronger evidence of an absence of microbial effects.

Pb, Cd, Cu, Al and Hg were less highly elevated and should not be suspected as toxic risks, although a negative correlation to respiration was actually found for Pb in one field plot.

Fe and Mn, which were highly elevated, are usually not considered to be toxic, although some suspicions of effects on the degradability of humus might apply to the highly elevated Fe at Oxelösund. However, no effect was recorded as Fe showed no negative correlation to microbial respiration in field plots.

In summary, a number of metals were found to be highly elevated in mor layers at Oxelösund, but there was no evidence of effects on soil biology in the present study. Detrimental effects are apparently being counteracted for some reason. The weak respiratory effects observed by Rühling (1980) and the presence of a thick mor layer near the industrial site are weak evidence of some effects.

4.2 Are metals decreasing?

Our analysis of concentration profiles within the mor layers showed that the loads of Mo, V, Cr, Zn, Pb, Ni, Cu, Cd and Hg have increased over a time span of several decades. There is evidence

of reduced soil levels in the past two decades when repeated investigations were undertaken. Deposition measurements by moss analysis also show decreasing loads.

4.3. How available are metals?

Metal solubility is generally low in organic soils. There is some evidence of lowered metal solubility at Oxelösund. Very high iron levels are a possible cause.

4.4 How serious is the situation?

The same general discussion as ended our Avesta report (Bringmark & Åkerblom 2005) applies to Oxelösund. In Oxelösund, we did not have clear evidence of negative effects on soil biology, only of elevated metal concentrations in the mor layer. Other aspects of ecosystem function, such as forest growth, are probably even less affected.

5. REFERENCES

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6. APPENDIX

Table A1. Correlation matrix between metals of O_r-layers within sampling plots at Fence and Brannäs (Pearson correlation coefficients). ***=p<0.001; **=p<0.01; *=p<0.05

Fence (n=31)

Fe	1.000	Mo																			
Mo	0.817***	1.000	V																		
V	0.438*	0.670***	1.000	Cr																	
Cr	0.232	0.286	0.017	1.000	Zn																
Zn	0.276	0.517**	0.555***	0.251	1.000	Mn															
Mn	0.251	0.532**	0.666***	0.344	0.741***	1.000	Pb														
Pb	0.702***	0.445*	-0.001	0.278	0.316	0.081	1.000	Ni													
Ni	0.069	0.119	-0.143	0.964***	0.233	0.312	0.268	1.000	Cu												
Cu	0.598***	0.475*	0.042	0.001	0.122	0.098	0.649***	-0.046	1.000	Cd											
Cd	0.034	0.191	0.455*	-0.201	0.366	0.374	0.035	-0.217	0.024	1.000	Al										
Al	0.086	0.123	-0.061	0.709***	0.234	0.346	0.241	0.731***	0.195	-0.088	1.000										

Table A3. Metal concentrations ($\mu\text{g. g}^{-1}$) in different soil layers at the Brannäs site. Number of measurements: 34 in O_f -horizon, 6 in O_h -horizon and 4 in mineral soil horizons. Dense sedimentary clay below 30 cm has high metal levels.

		Fe	Mo	V	Cr	Zn	Mn	Pb	Ni	Cu	Cd	Al	Hg
BRANNÄS													
O_f -horizon	Mean	30321	7.4	135	76	216	1563	92	126	17	0.74	6063	0.31
	CV%	35	42	50	55	53	89	46	67	36	51	55	30
O_h -horizon	Mean	30657	6.7	79	104	155	432	106	171	16	0.47	6602	0.37
	CV%	27	28	32	50	32	61	36	56	27	33	44	27
0-5 cm	Mean	11173	0.83	26	15	30	102	26	5.8	8.2	0.12		0.078
	CV%	39	3.6	18	37	24	13	19	33	22	46		4.5
5-15 cm	Mean	19755	0.73	36	27	44	176	9.3	9.5	6.8	0.065		0.021
	CV%	12	17	11	16	0.5	21	9	11	17	3.3		47
40-50 cm	Mean	28213	0.37	51	39	55	304	12.6	16.3	17.0	0.043		0.004
	CV%	42	13	48	48	40	42	55	46	25	1.7		83
70 cm	Mean	45090	0.30	82	63	93	562	20	29	27	0.059		0.005
	CV%	2.5	13.8	2.5	2.5	1.9	0.9	1.4	4.2	1.1	4.8		47
O_h/O_f		1.01	0.90	0.58	1.37	0.72	0.28	1.16	1.36	0.96	0.65	1.09	1.29

Table A4. Metal concentrations ($\mu\text{g. g}^{-1}$) in different soil layers at the reference site (Lid). Number of measurements: 30 in O_f -horizon and 3-5 in O_h -horizon

		Fe	Mo	V	Cr	Zn	Mn	Pb	Ni	Cu	Cd	Al	Hg
LID													
O_f -horizon	Mean	1717	0.79	15	12	64	395	38	22	7.9	0.39	1654	0,33
	CV%	48	23	52	74	34	95	28	65	27.4	40	57	10.7
O_h -horizon	Mean	2851	1.2	11.0	14	55	69	65	26	6.8	0.42	3373	0.41
	CV%	47	27	39	16	38	32	19	27	23	38	54	41
O_h/O_f		1.74	1.53	1.65	1.68	0.67	0.30	1.68	1.95	0.99	1.03	2,36	1.22

DEN SVENSKA STÅLINDUSTRINS BRANSCHORGANISATION

Organisationen grundades 1747 och ägs sedan dess av de svenska stålföretagen. Jernkontoret företräder stålindustrin i frågor som berör handelspolitik, forskning och utbildning, standardisering, energi och miljö samt skatter och avgifter. Jernkontoret leder den gemensamma nordiska stålforskningen. Dessutom utarbetar Jernkontoret branschstatistik och bedriver bergshistorisk forskning.

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