

Trace Metals in Urban Soils – Stockholm as a Case Study

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Abstract

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Urban areas can be considered risk areas as regards trace metals and will continue to be so for a long time, according to predictions. The present work started as a sub-project in the urban part of the multifaceted research project Metals in Urban and Forest Environments. The overall aim of the work was to gain systematic knowledge about the amounts and behaviour of trace metals in urban soils, with Stockholm (the capital of Sweden) as the study area. The concentrations of trace metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn) and arsenic (As) were surveyed and the metal pools estimated in soils in Stockholm Municipality. The results showed a wide range in trace metal concentrations, as well as in other soil properties. The city centre soils constituted a rather homogeneous group, whereas outside this area no soil geographical zones could be distinguished. These soils were instead grouped based on present land use, i.e. undisturbed soils, public parks, wasteland (mainly former industrial areas), and roadside soils. The city centre and wasteland soils generally had enhanced Cu, Hg, Pb and Zn concentrations compared to the other soil groups and rural soils in the region. The Guideline values for sensitive land use (set by SEPA) are exceeded by the mean concentrations of Hg and Pb and maximum concentrations of Cd, Cu and Zn in the city centre soils. The average soil pools (0-30 cm depth) of Cu, Pb and Zn in city centre soils were 21, 38 and 58 g m⁻² respectively, which for Pb was 3-4 times larger and for Cu and Zn 1.5-2 times larger than that in park soils outside the city centre. The total amounts accumulated in city centre soils were calculated at 40, 1.1, 120 and 80 t for Cu, Hg, Pb and Zn respectively. Solubility and mobility of the trace metals were studied with sequential extraction and column leaching extraction. In the sequential extraction, four steps (1M NH₄NO₃, 0.1 M NaCl, 1M NH₄Ac pH 4,8 and 0.5 MH₄Ac+0.02 M EDTA) were used. Four different treatments aimed at imitating the effect of specific urban activities were used in the leaching extraction (i.e. rain, acid rain, salt and bark). The sequential extractions were not found to be useful for quantitative prediction of metal mobility. The column extraction experiment showed that contaminated soils might be one possible explanation for the enhanced concentrations of Cd, Cu, Pb and Zn in Stockholm groundwater. Leachate solutions from all treatments showed that most Cd, Ni and Zn was mobilised in the salt treatment and that the concentrations of Cu, Cr, and Hg were strongly positively correlated to the DOC concentration. The positive correlation between Pb and DOC and the negative correlation between Cd and pH were weak. The computer model SHM was used to evaluate the leaching results. For Cd and Zn simulated values corresponded rather well with measured values, but for Cu and Pb the results were more contradictory.

Key words: Biogeochemistry, contaminated soil, heavy metal, leaching extraction, sequential extraction, Stockholm, trace metal, urban soil

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Till Erik och Anna

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Appendix

Papers I – IV

This thesis is based on the following papers, which are referred to in the text by their Roman numerals:

I. Linde, M., Bengtsson, H. and Öborn, I. 2001. Concentrations and pools of heavy metals in urban soils in Stockholm, Sweden. *Water, Air and Soil Pollution: Focus* 1(3-4) 83-101.

II. Linde, M. and Gustafsson, J. P. 2005. Concentrations and distribution of trace metals in park soils in Stockholm, Sweden. (Manuscript)

III. Öborn, I. and Linde, M. 2001. Solubility and potential mobility of heavy metals in two contaminated urban soils from Stockholm, Sweden. *Water, Air and Soil Pollution: Focus* 1(3-4) 255-265.

IV. Linde, M. Gustafsson, J. P. and Öborn, I. 2005. Effects of changed soil conditions on the mobility of trace metals in two moderately contaminated urban soils (Manuscript)

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Introduction

Impacts on both human health and the environment have been documented from almost the entire history of man's use of metals, even if the precise relationships have not always been fully understood (e.g. von Linné, 1889; Brännvall *et al.*, 1999; Ek & Brennberg, 2001; Hylander & Meili, 2005; Pyatt *et al.*, 2005). The most severe medical and ecological effects have been observed in areas with intense mining and metallurgy industries. During processing of the ore, the toxic metals, which often naturally occur at very low concentrations (trace metals), are released to the environment, resulting in high concentrations at a local scale. As a consequence, until the 1980s such metal pollution was generally considered to be a local problem mainly occurring around an easily identified point source. However, even on a global scale, anthropogenic activities are the most important source of the potentially toxic metals found in the environment (Campbell *et al.*, 1983). Around 15 times more cadmium (Cd), 100 times more lead (Pb), 13 times more copper (Cu) and 21 times more zinc (Zn) are emitted to the atmosphere by human activities than by natural processes (Ross, 1994a).

In most industrial countries, heavy polluters like metallurgy industries have been forced to improve their techniques and to radically reduce the discharge of toxic trace metals to the atmosphere and water. Over the same period, the production, transformation and use of these metals in society, sometimes referred to as metal metabolism, has increased (Bergbäck, 1992). This development can for example be illustrated by how the import of chromium (Cr) to Sweden changed from 1920 to 1980 (Figure 1). The consequence of the increasing use of metals is an ongoing diffuse release of metals to the environment. In Sweden, lead from traffic (Rühling & Tyler, 1968; 1971) and cadmium from fertilizers (Andersson & Nilsson, 1974) were two of the first pollutants of this type to receive attention.

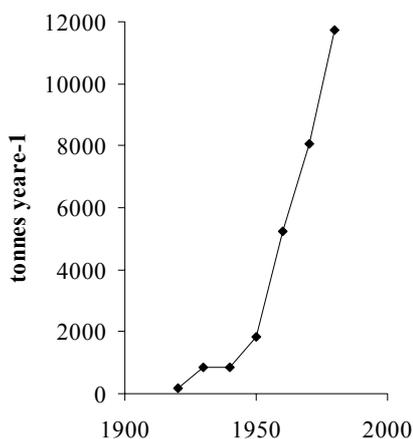


Figure 1. Imports of chromium to Sweden in tonnes year⁻¹. (modified from Bergbäck, 1992)

There are of course no well-defined boundaries between different sources of metal emissions, but the diffuse release resulting from the total metal metabolism in society generally differs in some aspects from point source emission. Over time, point source emission is directly related to the degree of activity at the source, whereas metal release from constructions and industrial products typically continues for a very long time. Through calculation of the future contamination factor (FCF), Wallgren (1992) argued that trace metals will be an important environmental problem in the future (Figure 2). The FCFs were calculated by dividing the accumulated amount of a metal in the Swedish technosphere by the original amount of the metal in Swedish urban area (original amount is calculated for the top 20 cm of urban land of Sweden, representing 3.1% of the total area). This calculation is theoretical and based on the somewhat extreme assumption that all accumulated metals sooner or later will be released into the environment, but even so it gives an idea about the dimension of the problem and the relative importance of the metals.

Another typical characteristic of pollution emanating from one dominant source is that the environmental effects show a decrease with increasing distance from the source (Burkitt *et al.*, 1972; Låg, 1978; Rieuwerts *et al.*, 1998; Ek *et al.*, 2001), whereas accumulation of metals and trace metal-containing products, and thus emission from these products, generally corresponds to the population distribution and is most pronounced in urban areas. On a national scale Bergbäck (1992) have illustrated this by calculation of a Swedish immission landscape, *i.e.* the calculated amounts of cadmium, chromium and lead accumulated in soils and sediments (Figure 3). In a study in the UK, Culbart *et al.* (1988) show the same positive correlation with empirical data on high population density and on metal concentrations (Cu, Pb, Zn) in garden soils.

All over the world, urbanisation is a rapidly ongoing process and approximately half the total world population and two-thirds of people in developed countries live in urban areas (United Nations, 2004). Consequently, the urban environment has a great impact on public health and from this point of view, knowledge about the outdoor environment in urban areas is crucial.

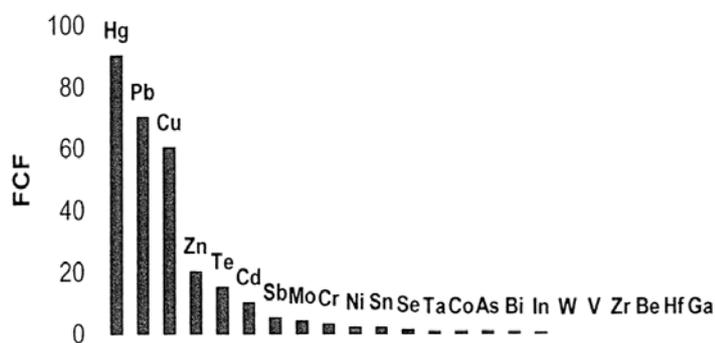


Figure 2. Future contamination factor (FCF) for some elements in Sweden (adapted from Wallgren, 1992)

As in all ecosystems, soils in urban areas act as collectors and reservoirs of substances, including pollutants. Much is understood about how different substances are bound in soil but much also remains unknown about the long-term fate of pollutants in soil and how they react when the environmental conditions change in different ways. Urban soils are not as well characterised as soils found in forest and agricultural ecosystems. Properties and processes typical for these soils are also less well studied.

Furthermore, in Sweden and in many other industrialised countries, political decisions have been made on compulsory rehabilitation of contaminated soils. Many of these most contaminated soils are found within urban areas, and need to be remediated or sometimes even excavated at a high financial cost to landowners and to society.

Thus from an environmental point of view, urban areas can be considered as risk areas with regard to trace metals and will continue to be so for a long time, according to predictions. There is a need to improve understanding about pollutant behaviour in soils in general and in soils in urban environments in particular. Such knowledge could be used for making accurate risk assessments concerning human health and long-term ecological effects, for setting limit values and for identifying priorities concerning the remediation of contaminated sites.

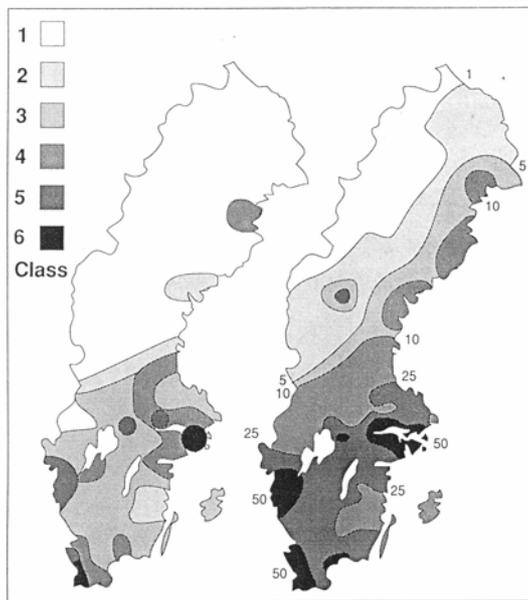


Figure 3. A. Calculated total immission landscape (amount of metals km⁻²) of Cd, Cr and Pb. Low average soil metal content (Class 1) to high average soil metal content (Class 6). B. The distribution of population (inhabitants km⁻²) in Sweden, 1980 (adapted from Bergbäck 1992).

Context of the work

This work started as a sub-project in the urban part of the multifaceted research project *Metals in Urban and Forest Environment*. The overall objective of the urban part of the project was to obtain knowledge about the environmental consequences and long-term fate of the enormous amount of metals accumulated in the urban technosphere. The research within the project was focused on identifying and quantifying flows and pools of potentially toxic trace metals in an urban area, with the administrative unit Stockholm municipality as a study object. Soil was recognised as one important sub-system of the main system, Stockholm municipality. The size of metal pools, the changes in pool size over time and extent to which the size of the soil metal pools were a result of anthropogenic activities were identified as major research questions. During the project period, questions concerning both urban soils and trace metals were formulated. To enable the amounts of substances in the soils to be calculated, the sub-system 'soil' had to be defined and the soils analysed had to be classified with respect to the area represented by each identified soil group. To assess the ecological or health risks associated with trace metals in soils, knowledge about the concentrations and pools of metals is not enough. An assessment of the mobility and bioavailability of the metals is even more important.

Stockholm as urban study object

Stockholm, the capital of Sweden, represents one of the most densely populated areas in Sweden with approximately 4000 inhabitants per km² (Stockholms stad, 2005). In total, the City of Stockholm covers 187 km² of land and has approximately 750 000 inhabitants. The city was mentioned in text for the first time in the middle of the 13th century (Harrysson, 2002). From early in its history, Stockholm became an administrative and commercial centre due to its strategic position with respect to both trade and military defence. Since the city lacks heavily polluting industries, the environmental situation in Stockholm could be seen as a result of urbanisation as such. A typical feature of the City of Stockholm is that outside the city centre, there is almost no correlation between distance from the city centre and type of settlement, land use or vegetation. This is a result of a conscious effort to preserve large green areas but is also due to the heterogeneous landscape. From the beginning, Stockholm was built on a small island and one-third of the inner city still consists of open water. In addition to this open water, three elements dominate the natural landscape in Stockholm, namely fault scarps of granite, open valleys formed by the bedrock and an esker (Stockholmsåsen) running from north to south through the city (De Geer, 1932). The floors of the valleys are mostly covered with a thick layer of calcareous glacial clay and noncalcareous post-glacial clay. In higher parts of the landscape, the bedrock is mostly covered by glacial till. The natural soil material thus comprises glacial and water drift deposits and does not derive directly from the bedrock of the region.

Objectives

The overall aim of the work presented in this thesis was to gain a better understanding of the behaviour of trace metals in urban soils, with Stockholm as a study area.

Specific objectives were to:

1. Calculate the trace metal pools in urban soils of Stockholm and estimate the urban contribution to these pools.
2. Investigate the solubility of trace metals in the Stockholm soils and test whether the leaching of trace metals from soil could explain the metal concentrations found in groundwater.
3. Study the effects of specific urban activities on trace metal solubility and potential mobility.

The thesis is divided into three different parts, I) the soils in urban areas, II) the trace metals concentrations in urban soils and III) the binding and mobility of trace metals in contaminated soils. The results of the thesis work are presented in relation to the background given in each part.

Methods

Soils and soil sampling

The sampling sites in the survey of Stockholm soils (Paper I) were selected in order to provide a representative geographical distribution within the entire City of Stockholm. The City was divided into three zones based on the distance to the centre of Stockholm (defined as the square 'Sergels torg'); 0-3 km, 3-9 km and more than 9 km. The sites were distributed among the zones with the aim of ensuring that each zone had an approximately equal number of sites and to get a variation with regard to historical and present land use. This sampling scheme resulted in a higher sampling density in the central zone than in the outer parts of the City, which was actually the intention.

In a more detailed study of trace metal distribution in park soils (Paper II), two parks (Humlegården, Fatbursparken) were chosen for soil sampling. Both parks are situated within the city centre of Stockholm but they represent two totally different histories of development and thereby two extremes amongst the Stockholm inner city green area soils. For the metal solubility/leachability studies (Papers III and IV), two of the soils from the survey with enhanced concentrations of trace metals were used. Soil C was sampled at a well-drained small green area located close to a busy road in the city centre of Stockholm. Metal concentrations in soil C were of the same magnitude as the average of the city centre soil group and, compared to the rural soils, 16 and 8 times higher in Hg and Pb, threefold

higher in Cu and Zn and twice as high in Cd (Table 1 in Paper IV). Soil W represents a grass-covered poorly drained area on the shore of the Baltic Sea that is used for storage of small boats during winter. The Hg concentration was about 70 times larger than in arable soils. The Pb and Cu levels were elevated 20- and 10-fold, respectively, whereas Zn was three times higher.

Stainless steel corers and spades were used for soil sampling. In both the survey (Paper I) and the park study (Paper II), the sampling depth varied depending on what was technically possible. The soil samples (except for material used in the column leaching experiment) were dried at 30-35 °C and the analyses were conducted on the fine earth fraction. In the leaching experiment, fresh soil material with a particle size less than 4 mm was used.

Soil analysis

Electric conductivity (EC) and pH were measured in water suspensions (Paper I) or in 0.01 M CaCl₂ (Paper II). In soils with a pH around and above pH 7, the CaCO₃ content was determined by HCl treatment of the soil and subsequent measurement of the released amount of CO₂ (International Organisation of Standardisation, 1995). The clay content was determined by sedimentation analysis using a hydrometer after dispersion in sodium polyphosphate. The soil content of total C was determined on finely ground samples by total elemental analysis and the organic C content (C_{org}) was calculated as the difference between total C and carbonate C.

To determine the trace metal content, the soils were digested with boiling (120 °C) 7 M HNO₃ (*p.a.*) (Swedish Standards Institute, 1997) (Papers I and II) and in addition separate samples were extracted with acid EDTA-NH₄OAc solution (0.5 M NH₄OAc+0.02 M EDTA at pH 4.65) (Paper II) (Lakanen & Erviö, 1971; Sillanpää & Jansson, 1992). Concentrations of Pb, Zn and Cu in the extracts were analyzed with AAS (acetylene air flame). For Cd the AAS-graphite furnace technique (Perking Elmer Zeeman 3030, HGA-600 graphite furnace) with addition calibration was used. For As, the hybrid AAS method and for Hg the cold vapour AAS-technique after reduction with SnCl₂ were used. The ICP-MS (Perking Elmer Elan 6001) technique was used to determine all metals in the HNO₃ extracts in the study presented in Paper II.

Sequential extraction

Sequential extractions (Paper III) were performed on air-dried soil with four extractions 1 M NH₄NO₃ (Symeonides & McRae, 1977), 0.1 M NaCl, 1 M NH₄Ac (pH 4.8) (Andersson, 1975) and 0.5 M NH₄Ac + 0.02 M EDTA (pH 4.65) (Sillanpää & Jansson, 1992). The soil was shaken for 1 h with the respective extractants, except for NH₄Ac (pH 4.8), which was shaken for 16 h, and centrifuged for 20 min at 2000 rpm. In the following the fractions of metals extracted with the different solutions are referred to as F1 (NH₄NO₃ extractable), F2 (NaCl soluble), F3 (acid NH₄Ac extractable) and F4 (EDTA extractable). The analyses of Cd and Cu (F1-F3) and Pb (F1-F2) were carried out after addition of a matrix modifier (NH₄H₂PO₄), using atomic absorption spectrophotometry (AAS)

with a graphite furnace (Perkin Elmer Zeeman 4100ZL). Copper (F4), Pb (F3-F4) and Zn (F1-F4) were determined by AAS with air-acetylene flame (IL 551, background correction).

Leaching experiment

For the column leaching experiment (Paper III & IV), the two soils C and W were resampled, sieved fresh at 4 mm and stored cold until the start of the experiment. Four different treatments were included in the study. In all treatments, artificial rain water (ARW) was added to the columns. The chemical composition of the ARW was similar to the average rain water chemistry measured in central Stockholm ($\text{SO}_4\text{-S}$ 0.77 mg L⁻¹, Cl 0.43 mg L⁻¹, $\text{NO}_3\text{-N}$ 0.37 mg L⁻¹, $\text{NH}_4\text{-N}$ 0.30 mg L⁻¹, Na 0.22 mg L⁻¹, K 0.03 mg L⁻¹, Mg 0.04 mg L⁻¹, pH 4.45; Vattenprogram för Stockholm, 1994). The *rain* treatment was subject to leaching with ARW only and can be considered as a reference. In the *acid* treatment, the inflow water consisted of ARW that had been acidified with H_2SO_4 to pH 3.1. In the *bark* treatment, 20 g of bark pieces were applied on top of the columns, and subjected to leaching with ARW. The material used was a slightly composted bark of coniferous trees (mainly pine and spruce) which is commonly used as soil coverage in various types of park plantations. In the *salt* treatment, 50 mM NaCl were added to the ARW used to irrigate the columns. The NaCl concentration was similar in magnitude to that of runoff water from roads during winter (Bäckström *et al.*, 2003; Blomqvist, G. 2004) and for the Stockholm groundwater (Miljöförvaltningen, 1997).

Glass columns of 2 cm \varnothing and 20 cm length were used in the experiment. To these columns, 30 g of field-moist soil were added and in the bark treatments 20 g of moist bark were applied on top of the soil. All treatments except the *acid* treatment were conducted in triplicate for both soils; the *acid* treatment was applied only to soil W. Three additional columns were filled with bark, but with no soil, and these were leached with ARW to investigate the possible contribution of metals from the bark as such. One empty column was also included. In total, this gave 25 columns in the experiment. An overview of the 25 columns included in the experimental set-up is given in Table 1.

Table 1. An overview of treatments, soil material and number of columns in the experimental set-up. In total 25 columns were used in the experiment

Material	Treatment			
	<i>Rain</i> (artificial rainwater)	<i>Acid</i> (artif. rainwater + acid)	<i>Salt</i> (artif. rainwater + salt)	<i>Bark</i> (artif. rainwater over bark)
Soil C	3 columns		3 columns	3 columns
Soil W	3 columns	3 columns	3 columns	3 columns
Bark	3 columns			
None	1 column			

Before the start of the leaching experiment, de-ionized water was added to the columns to bring the soil to field capacity. During a three-week period, 5 portions of 20 mL inflow solution were added slowly (2 h) as droplets to the top of the columns. This was equivalent to an L:S (liquid to solid) ratio of approximately 5 (100 ml solution and 21.6 g dry matter) for soil C and 7 (100 ml solution and 14.1 g dm) for soil W. In total the volume corresponded to 320 mm, about two-thirds of the average total annual precipitation and 1.5-2 times the average annual recharge in the region (Alexandersson, 1991).

Column leachate was analysed for pH, EC, DOC and for seven trace metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn). Metals and DOC were determined on filtered samples (0.2 µm washed membrane filter), whereas EC and pH were measured on unfiltered samples. DOC was determined by a TC-IC method (Shimadzu TOC-5000) and all metals except Hg were determined as in the F1 extract in the sequential extractions above. The concentration of total Hg (only soil W leachate 4) was determined at the Swedish Environmental Research Institute with cold vapour atomic fluorescence spectroscopy (CVAFS) after BrCl Oxidation (Bloom & Fitzgerald, 1988; Fitzgerald & Gill, 1979).

Modelling of metal solubility

The equilibrium modelling of metal concentrations in the leachates (Paper IV) was carried out with the the Stockholm Humic Model (SHM) implemented in Visual MINTEQ (2005) (Gustafsson, 2001; Gustafsson & van Schaik, 2003; Gustafsson & Berggren Kleja, 2005). A definition of variables and parameters used in the modelling and the values used in the parameterisation of the model is given in detail in tables 3, 4 and 5 in Paper IV. More generally the parameterisation of the model was based on the following assumptions:

1. For soil C, which had a relatively low organic C content (3.4 %), 25 % of the total organic C was assumed to consist of 'active' humic acid whereas an additional 25 % was assumed to be 'active' fulvic acid. These figures were based on a simple average of the low-organic C soils studied by Gustafsson et al. (2003).
2. For soil W, which contained 17 % organic C, 18.8 % of the total organic C was assumed to be 'active' humic acid whereas 6.2 % was 'active' fulvic acid, in accordance with results for Swedish mor layers (Gustafsson and Berggren Kleja, 2005).
3. The soils were assumed to be in equilibrium with an $\text{Al}(\text{OH})_3$ phase with a log $*K_s$ of 8.8 at 20°C. Competition from Fe^{3+} was not considered.
4. The geochemically active concentrations of heavy metals were obtained from the sequential extractions including the EDTA step (extractions F1-F4).
5. Because dissolved base cations were not measured in the extracts, apparent charge balances were corrected by adding an appropriate amount of Ca^{2+} to the Visual MINTEQ simulations.

6. Proton and metal binding could be described by generic proton-binding parameters for humic and fulvic acids, in combination with metal complexation constants recently optimized for mor layer material.
7. Dissolved organic carbon was assumed to consist of 65 % fulvic acid, whereas the rest was inert with respect to metal binding (Bryan et al., 2002).
8. The model was applied in a one-cell “batch” mode, assuming an L:S ratio of 1 (The exact value of the L:S ratio was of minor importance for the result)

Soils in the Urban Environment

Soils in urban environments differ in several respects from soils in rural environments (Craul, 1985; Hollis, 1991, Agarkova *et al.*, 1994; Kuehn, 2002). The climate in built-up areas is warmer and groundwater recharge more complex (Landsberger, 1981; Lerner, 1990; Tapper, 1990). The history of the soil material is highly variable and often unknown as a result of temporal differences in land use, transfer between sites and mixing in connection with excavations, addition of new materials, *etc.* The vertical and horizontal variation in soil properties is also greater and less predictable because of these human activities.

Even though it is possible to find more or less undisturbed ‘natural’ old soils in protected green areas, urban soils in general are young from a pedological point of view. Young soils are by definition undeveloped and unstable and their properties could be expected to be in a state of relatively rapid change. The organic matter in soils is particularly labile and in a young soil both the content and quality of organic matter are continually changing. For example, in Sweden the organic matter content in constructed topsoils is often higher than 5% by weight (AB Svensk Byggtjänst, 1983), a level that is rarely stable. An organic matter content of 5% corresponds to the carbon concentration of fertilized grassland soils and needs a high biomass production to be maintained (Sindhøj, 2001). If the biomass production of urban vegetation and thus the input of organic material to the soil is not high enough to support such a high organic matter content, it will decrease over time until it reaches a steady state (Killham, 1999).

The continuously ongoing building and reconstruction activities in urban areas also have a great influence on the soil structure and the groundwater level (Burghardt, 2002), site properties that regulate the gas and water permeability and the soil moisture regime of the soil and thus the redox conditions.

Classification of urban soils

The term 'urban soil' has no pedological significance in the strict sense but is a pragmatic concept used for soils that occur within built-up areas. It is a soil classification based on land use. In scientifically stricter systems, classification is based on measurable and observable soil features. These systems have mostly been developed to categorise soils as a resource base for biomass production related to their original parent material and genesis. The classification soils found in the urban environment are usually not very well developed in the systems. According to a review of Hollis (1991) only the FAO/UNESCO and the German soil classification systems had exclusive groups for strongly man-influenced or modified soils. In the World Reference Base for soil resources (WRB) which has replaced the FAO/UNESCO-system, classification of these soils has been further developed (FAO, 1998; Driessen *et al.*, 2001). In the WRB system, most strongly man-influenced soils are classified as either Anthrosols or Regosols. Anthrosols are soils where the parent material has been changed as a result of long-term agricultural practices, whereas soils that are constructed or a result of landfilling and with a minimum soil development belong to Regosols. The subdivisions/soil units Anthropic, Garbic, Spolic and Urbic, which can be used for Regosols, are all soils built up with so-called anthropogeomorphic soil materials. Burghardt (2002) suggests that in addition to the origin of the soil material, structure should also be used as a diagnostic character in soil taxonomy to differentiate urban soils. Therefore, some work has been done concerning classification of 'urban soils' but a generally accepted system for classification and description of those soils is still needed. Such a system would at least theoretically make it easier to generalise and compare results from different studies of urban soils. Because of the lack of a generally accepted classification system, land use is probably the most common way of classifying or grouping soils in the urban environment also on a smaller scale. Studies on roadside soils, parkland soils, playgrounds, home gardens, industrial land, *etc.* are frequently reported in the literature.

The objectives of the survey of trace metals in Stockholm soils presented in Paper I were not only to describe the metal concentration in the soils but also to calculate the amounts or pools of different metals in the Stockholm soil. To enable us to calculate metal pools, we first had to stratify the sampled soils. Ideally the soil strata should be homogeneous as regards metal concentration and easy to identify. Studies on trace metal concentrations in lake sediments and in topsoil (0-5 cm) from playgrounds in the Stockholm region had reported a decreasing metal concentration with increasing distance from the centre of the city (Berglund *et al.*, 1994; Sternbeck & Östlund, 2001). Based on the hypothesis that concentrations of metals in soils have the same geographical distribution pattern, the soil sampling for the survey was initially based on distance from the centre. Nevertheless, observations during soil sampling and analytical data showed that outside the city centre, no geographical zones based on distance from the centre could be distinguished. This can most probably be explained by the lack of relationship between distance to the centre and type of settlement, industrial activities or landscape features.

The first hypothesis on how the soils should be grouped was thus falsified and, like many other studies of urban soils, we found it more useful to ‘classify’ the soils according to land use. The most important criteria for distinguishing soil groups were that they should be possible to identify concerning land use and that they should represent different levels of metal enrichment. We finally decided to ‘classify’ the soils as *city centre*, *undisturbed*, *park*, *roadside* and *wasteland soils*. The *city centre soils* were treated as a single group representing the areas that had been exposed to urban conditions for the longest period of time. The group *undisturbed soils* represented areas with semi-natural vegetation and the group *park soils* other green areas. *Roadside soils* were sampled at sites situated within a few metres from a roadway and *wasteland soils* were taken mainly from former industrial ground, both categories presumed to represent areas with larger metal loads. The *city centre soils* turned out to be the most useful group for calculation of metal pools since it was possible to estimate the total area represented by the soil group.

Trace metal concentrations in urban soils

The concentration of any substance in soil is a result of the inherited mineral/chemical composition of the parent material and the weathering, leaching, erosion and fallout history of the specific site. As stated in the introduction, a significant part of the potentially toxic trace metals found in soil derive from anthropogenic activities but there are also important natural sources. On a global scale, volcanic activity gives an important input of some metals, *e.g.* Hg, Pb and Ni, but at most sites the bedrock is the natural source of almost all metals (Ross, 1994a). It is not possible to specify the type of mineral that is generally the most important for the soil concentration of trace metals. There are higher quantities of the several trace metals in igneous rocks than in sedimentary rocks (Table 2), but on a global scale, sedimentary rocks are more important as precursors of soil parent material. The metals are released from the bedrock to the soils and the ecosystems by mineral weathering. Thus, weathering ability is another important factor which determines how much a certain mineral has contributed to the trace metal concentration in soil.

Table 2. *Typical trace metal concentrations in major rock types ($\mu\text{g g}^{-1}$) (Ross, 1994a)*

Element	Igneous rocks			Sedimentary rocks		
	Ultramafic	Mafic	Granite	Limestone	Sandstone	Shale
Cd	0.12	0.13-0.2	0.09-0.2	0.028-0.1	0.05	0.2
Cu	10-42	90-100	10-13	5.5-15	30	39-50
Cr	2000-2980	200	4	10-11	35	90-100
Hg	0.004	0.01-0.08	0.08	0.05-0.16	0.03-0.29	0.18-0.5
Pb	0.1-14	3-5	20-24	5.7-7	8-10	20-23
Zn	50-58	100	40-52	20-25	16-30	100-120

The importance of anthropogenic versus natural influence on the concentration of Cd, Cr and Pb in Swedish soils is illustrated by comparing Bergbäck's (1992) maps showing calculated total immissions (Figure 3) with maps of geographical distribution of concentrations of the same metals in Swedish soils (Figure 4 and 5). These latter maps have been adapted from a survey of forest soils (Markinfo, 2005) and another survey of arable soils (Eriksson *et al.*, 1997). The general impression is that most of the areas with a high soil concentration may also be recognised as areas with a high calculated immission, but the pattern is not completely the same. The only surface soil concentrations given in the survey reports is the plough layer (0-20 cm) maps in Figure 4. These maps are the most relevant ones for a comparison between soil concentrations and immissions on a national scale. Discrepancies between soil concentration and immissions can for example be seen around Lake Storsjön in central Sweden and south of Lake Vänern in south-west Sweden. In the former example the soil concentration is large and the immissions low, while in the latter the situation is the reverse. These discrepancies could most probably be explained by that fact that the influence of human activities is overshadowed by the mineralogy and natural chemical composition of the parent material at the respective sites. Accepting that subsoil horizons in undisturbed soils reflect parent material composition, this explanation is also supported when

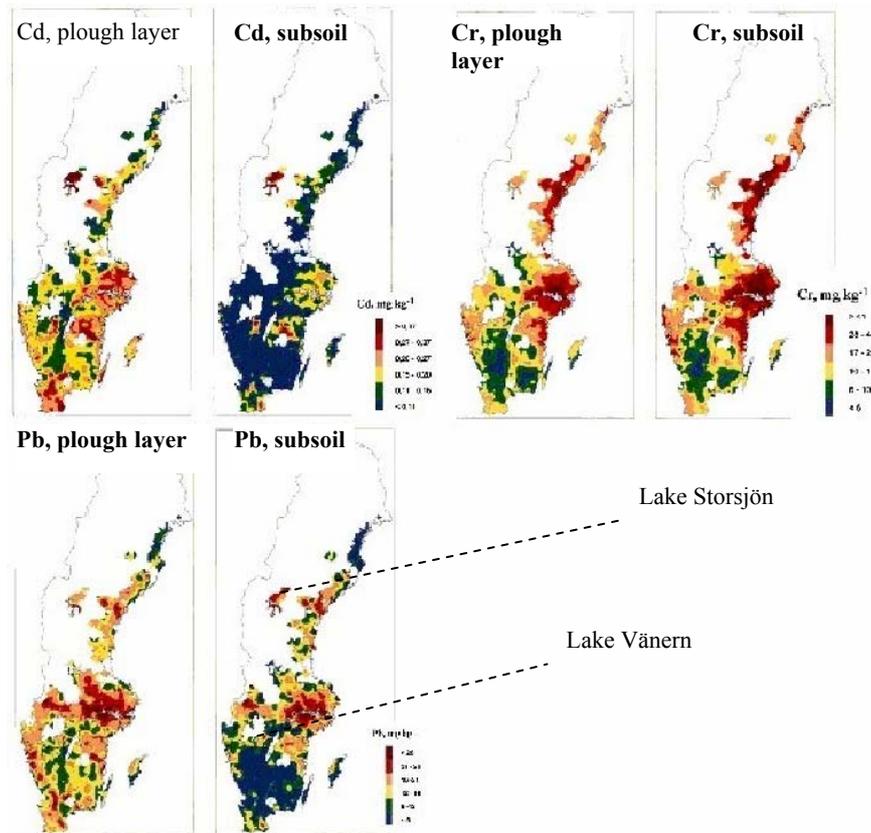


Figure 4. Cd, Cr, and Pb concentration in agricultural soils (Eriksson *et al.* 1997)

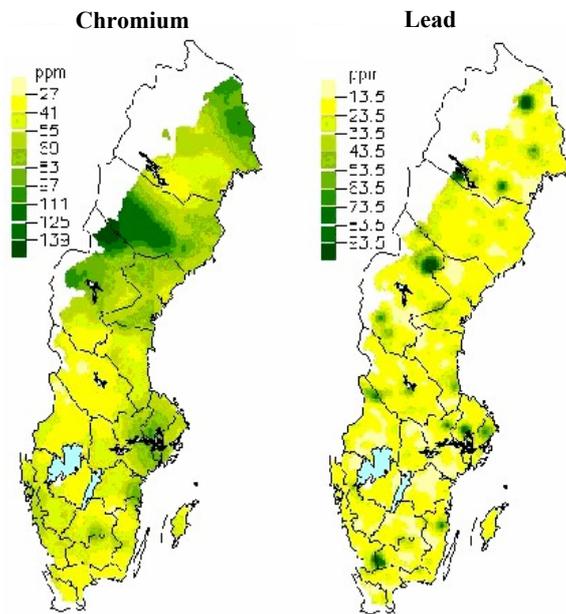


Figure 5. Cr and Pb concentration in forest soils at 50 cm depth (n=1585) (Melkerud et al., 1992).

comparing the plough layer map in Figure 4 with the subsoil maps in Figures 4 and 5. In the areas where the surface soil concentrations do not correspond with the calculated immission, the concentrations are at the same level in the subsoil as in plough layer.

Background values of trace metal concentrations in soils

In order to assess the extent to which metal concentrations in soils have been altered by human activities, it is necessary to determine what the concentration would have been without these influences (Crockett, 1998; Al-Chalabi & Hawker, 2000; Paterson *et al.*, 2005). A baseline or background value has to be established to understand the dynamics of the soil metal concentration or to give quantitative answers to questions such as: Is there an ongoing accumulation of metals in the soil, or how much has a single environmental factor contributed to the metal concentration?

Theoretically the definition of background value is clear and simple: A true background concentration of a trace metal in a soil is the sum of the concentration in the parent material plus the natural inputs minus natural losses of the metal in question. Besides the philosophical question concerning what is natural, difficulties arise when we want to establish a background value for an area, a single site or a restricted time period. In the literature on studies of trace metals in soils, a number of different approaches for measuring or at least estimating background values are suggested. In the following some of these approaches,

including that used in Paper I, are evaluated and discussed in relation to the specific difficulties associated with soil investigations in the urban environment.

Probably the most common way of setting background values for trace metals in urban soils is to use concentrations of the metals in soils outside the city. Examples of such studies are reported by Paterson *et al.* (1996), and Sanchez-Martin *et al.* (2000) who use concentrations in soil built up from a similar parent material as background values for soils within cities and along roads. In a study on the accumulation of contaminants in soils in three cities in north-eastern USA, Bradley *et al.* (1994) used published general data for soils in the region as a background. Another closely related approach is to use the concentration of an undisturbed soil within a city to establish baseline values (Madrid *et al.*, 2002). In Paper I, the accumulation of trace metals in the city centre soils of Stockholm due to local urban activities were estimated using a combination of both approaches. The similarity of the pools (0-5 cm) for all metals analysed except Hg in the park soils outside the city centre and arable soils in the region (table 3) was taken as an indication that the levels found in the park soils could be used as reference values in comparison with the city centre soils. The differences between the metal concentrations in the park soils and the city centre soils were calculated to provide a rough estimate of the amount of metals accumulated in the city centre due to local emissions.

Table 3: Calculated average pool (g m^{-2}) of trace metals down to 5 and 30 cm depth in arable soil, City centre soil and Park soil outside central Stockholm.

Metal	Arable soil		Park soil		City centre soil	
	Average pool		Average pool		Average pool	
	g m^{-2}		g m^{-2}		g m^{-2}	
	0-5 cm	0-5 cm	0-30 cm	0-5 cm	0-30 cm	
As	0.20	0.20	1.55	0.21	1.65	
Cd	0.02	0.01	0.08	0.02	0.13	
Cr	1.85	1.45	13.4	1.11	9.50	
Cu	1.22	1.18	11.9	1.91	20.7	
Hg	0.003	0.02	0.05	0.03	0.29	
Ni	0.99	0.72	6.90	0.36	3.54	
Pb	1.16	1.19	11.9	4.15	38.3	
Zn	4.68	6.43	39.5	6.29	57.9	

Another fairly well-established and accepted approximation of background values relies on the hypothesis that the whole soil profile initially had a homogeneous chemical composition and that differences in natural accumulation/leaching history within the profile are negligible. Thus, differences in chemical composition, *e.g.* metal concentration, are seen as a result of human impact. This approach was used by Colbourn & Thornton (1978) in a study of Pb pollution in agricultural soils. In this study the extent of Pb contamination in soil was expressed as the Relative Topsoil Enhancement (RTE), which was defined as the ratio of metal concentration in topsoil to the concentration in subsoil. In Sweden, the RTE approach is also used in urban areas on geochemical

environmental maps issued by the Geological Survey of Sweden (Selinus, 2001). Judging from the data on how trace metal concentration varied with depth in two park soils in Stockholm presented in Paper II, the use of the RTE approach in the heterogeneous urban environment could be questioned. Mellors & Bevans (1999) discussed the spatial pattern of Pb concentration in topsoil in an urban catchment and how it was related to the history of the soil material. Their study is another example of the complex relationship between topsoil and deeper soil horizons, even on a very local scale. They point out the varying thickness of the topsoil layer as a probable explanation for the variation in Pb concentration within the sampled area. Turer *et al.* (2001) have also demonstrated that even if the metal concentration in soils close to urban highways declines rapidly with depth, the correlation with organic C is stronger than the correlation with depth.

In the literature on urban soils, other less common methods can be found. One method was introduced by Yun *et al.* (2000). These authors write that anthropogenic contamination can be calculated as the ratio of the measured concentration to a normalising factor whose value is affected to a minor degree by human activities. In their study, they chose the aluminium concentration as the parameter for normalising the trace metal concentrations because of its high natural concentration and minimal anthropogenic contamination.

One statistical method for calculation of background values is the Probability Graph method proposed by Sinclair (1974) and used by Rundquist *et al.* (2001) in a survey of soils in Gothenburg. In this method, data on trace metal concentrations are plotted in a cumulative frequency diagram. Boundaries between different populations, *e.g.* trace metals from different sources, appear in the diagram as distinct changes in data distribution. The 90th percentile is traditionally meant to be the upper limit for background values. In an urban environment not dominated by one single source of pollutants or one specific soil material, the usefulness of the method is questionable. Most of the soils sampled in a city may very well be contaminated to some extent and the reason for a sharp change in the data distribution could just as well be differences in parent soil material as in degree of contamination.

None of the methods mentioned above could be said to be right or wrong. The parameters used for approximation of background values (differences in concentration between soils, ratio between elements, extractability of a substance, *etc.*) are influenced by degree of contamination (*i.e.* Wilcke *et al.*, 1998) but also by other factors. All methods have to be used with care and their limitations should be kept in mind, especially for soils in urban areas where the material often has been mixed and moved. A true background value may often be impossible to establish.

Urban versus rural soils in Sweden

Until the late 1990's, systematic knowledge on trace metal concentrations in urban soils was rather lacking in Sweden, as well as in other countries. Since then the situation has totally changed. Soils in cities all over the world have been surveyed with respect to trace metals or studied in specific projects and the results have

been published. Data from some of these studies are compiled in Table 5 (Sweden) and Table 6 (other countries). For comparison, data on rural soils in Sweden are also presented (Table 4).

The data concerning rural soils were taken from Markinfo (2005), Eriksson *et al.* (1997), a geochemical survey of sub-surface soils (Naturvårdsverket, 1997) and from an older study on 361 rural surface soils made by Andersson (1977). The Swedish urban soil data (Table 5) are from a study of 19 cities made by the Swedish Environmental Protection Agency (Naturvårdsverket, 1997), geochemical surveys made by the Geological Survey of Sweden (SGU) together with a consultant company (AB Jacobson & Widmark) and the local authorities in the Gothenburg (Rundquist, 2001) and Västerås urban regions (Andersson, 2005), one study on metal concentrations in playground topsoils in Stockholm carried out by Berglund *et al.* (1994), one on roadside soils (Norrström & Jacks, 1998) and finally the survey of all types of soils in Stockholm (Linde *et al.*, 2001) presented in Paper I. Data in Table 6 are chosen to represent urban environments from various parts of the world. Even if neither the sampling nor the extraction technique is precisely the same in the different studies, a rough comparison between soils in different environments is still possible. Data on Swedish forest soils (Markinfo, 2005) are true total concentrations, which may explain extremely large maximum concentrations of Cr and Cu. In all the other studies, soil metal concentrations have been determined by strong acid (*i.e.* boiling HNO₃ or *aqua regia*) extraction. The difference between the HNO₃ and the *aqua regia* extractable concentrations are relatively small (0-15% of *aqua regia*-extractable) for most metals (Lax, 2005).

Cd and Cr have been measured in all studies of urban and rural soils with the exception of the limited study on six roadside soils (both metals missing) and the survey of forest soils (Cd missing). The maximum values for these metals are measured in rural soils and even if the Stockholm soils have the largest mean values, it could be concluded that there is typically no urban induced accumulation of Cd and Cr in soils. The soil concentrations of Cd and Cr seem to be at the same level in rural as in urban areas in Sweden.

Cu, Pb and Zn are included in all studies in the tables. For Cu and Pb, the highest maximum value is measured in urban soils. For Zn, extremely large concentrations are found in forest soils developed on till material. Even so, for all three metals the mean/median concentration is larger in the urban soils and the difference between the lowest and the largest mean/medium value is also larger for the urban soils. With the reservation that Hg concentrations are presented only in one study of rural soils, the same relationships concerning maximum and differences between largest and lowest mean/medium values but even more pronounced could be seen for Hg concentrations in the different soil groups. These relationships indicate that the concentrations of Cu, Hg, Pb and Zn in soils in built-up areas are enhanced as a result of the specific situation of urban pollution.

Table 4. Concentrations (mg kg^{-1} dry weight) of strong acid-extractable Cd, Cr, Cu, Hg, Pb, and Zn in Swedish soils in rural areas

Soil	Value	Metal					
		Cd	Cr	Cu	Hg	Pb	Zn
		mg kg^{-1}					
<i>All soils</i> ¹ , 0.6-1.2 m (n = 15844; aq. reg.)	Median	---	---	12	---	9	35
	Max	---	---	229	---	925	2197
<i>All soils</i> ² , surface soil (n = 361; 2 M HNO ₃ extract.)	Mean	0.22	15.7	14.6	---	15.9	59
	Median	0.19	12.2	12.0	---	14.5	50
	Max	2.3	57	190	---	364	310
<i>Forest, non cultivated</i> ³ till, 0.5 m (n = 1892, total digestion)	Mean	---	59	31	---	12	60
	Median	---	46	23	---	0	50
	Max	---	626	1006	---	389	1933
<i>Agriculture</i> ⁴ plough layer, 0-0.20 m (n = 3067; 7 M HNO ₃)	Mean	0.23	20.5	14.6	0.04	17.1	59
	Median	0.20	17.3	11.4	0.04	15.9	54
	Max	2.83	71.9	102.1	0.59	402.5	223
subsoil, 0.6 m (n = 1720; 7 M HNO ₃ extract.)	Mean	0.14	23.8	14.9	0.02	13.5	53
	Median	0.10	20.3	12.1	0.01	12.5	48
	Max	3.58	84.6	97.0	0.24	77.4	246
All studies	Mean/ median	0.10- 0.23	12.2- 59	11.4- 31	0.01- 0.04	0-17.1	35-61
	Max	3.58	626	1006	0.59	925	2197

¹Naturvårdsverket, 1997

³Markinfo, 2005

²Andersson, 1977

⁴Eriksson *et al.*, 1997

Stockholm soils versus soils in other urban areas

A comparison of Stockholm with other Swedish cities shows that the trace metal concentration is largest in Stockholm (Table 5). The differences between Stockholm and Gothenburg (the second largest city in Sweden) could partly be explained by larger natural concentrations in the soil material in the region around Stockholm (Andersson, 1979; Eriksson *et al.*, 1997). Even so, the differences are too large to just be inherited from the parent material. Furthermore, the concentrations in the Gothenburg topsoils are at the same level as in the topsoils in other Swedish cities including Västerås, situated within the same region as Stockholm. The trace metal concentrations in Stockholm are larger than in other Swedish cities, reflecting a more pronounced influence from urban activities.

Table 5. Concentrations (mg kg^{-1} dry weight) of strong acid-extractable Cd, Cr, Cu, Hg, Pb, and Zn measured in urban soils in Sweden

Soil	Value	Metal					
		Cd	Cr	Cu	Hg	Pb	Zn
							mg kg^{-1}
19 Swedish cities ¹ 0-0.2 m, till/sediment (n = 58, 60, 93 or 108)	Median	0.27/0.16	17/22	15/20	0.05/0	23/36	58/83
	Max	1.35/0.58	50/52	76/94	1.58/0.85	143/409	236/719
0.60-0.7 m till/sediment (n = 58, 60, 93 or 108)	Median	0.10/0.07	20	13	0/0	10	48
	Max	0.69/0.28	76	65	0.10/0.17	34	151
Stockholm ² , playgrounds surface soil (n = 30)	Median	<0.5	23	46	---	100	160
	Max	0.9	43	120	---	330	610
Stockholm ³ , roadside surface soil (n = 6)	Max	---	---	57	---	542	140
							67
Göteborg ⁴ 0-20 cm (n = 73)	Median	0.19	9.9	17	0.21	37.8	69
	Max	0.62	22.7	400	1.61	184	279
0.7-1.2 m till/sediment (n = 28/49)	Median	0.04/0.05	7.5/12.2	6.7/7.7	0.03/0.03	3.3/6.1	16/30
	Max	0.10/0.33	19.4/37.2	13/271	0.06/0.35	6.7/57	41/141

Table 5. Continued

Soil	Value	Metal					
		Cd	Cr	Cu	Hg	Pb	Zn
		mg kg ⁻¹					
<i>Västerås</i> ⁵ 0-20 cm (n = 36)	Median	0.22	18.1	20	---	27.8	88.1
	Max	1.14	52.8	189	---	86.1	529
0.7-1.2 m till/sediment (n = 17/20)	Median	0.10/0.14	17.7/30.4	13/22	---	12.3/21.4	85.9/46.5
	Max	0.30/0.70	53.4/46.7	32/35	---	31.6/24.0	83.1/120
<i>Stockholm</i> ⁶ 0-0.05 m (n = 42)	Median	0.34	30	34	0.16	37	111
	Mean	0.40	34	71	0.59	101	171
	Max	1.11	145	1315	6.52	1279	965
0.30 m (n = 40) ;	Median	0.21	33	32	0.12	24	112
	Mean	0.27	33	55	0.41	79	142
	Max	1.00	52	533	2.89	606	527
All studies	Mean/Median	0.04-0.40	7.5-34	13-71	0.0-0.59	3.3-101	16-171
	Max	1.35	145	1315	6.52	1279	965

¹Naturvårdverket 1997

²Berglund *et al.*, 1994

³Norrström & Jacks, 1998

⁴Runquist, 2001

⁵Anderson, 2004

⁶Paper I

Unfortunately, rather few studies on urban soils outside Sweden include sub-surface soils. Even if some authors (Madrid, 2004) argue that sampling down to 0.1 m is enough, our results from Stockholm (Papers I and II) have clearly shown the need for deep soil sampling in urban areas in order to calculate the 'total' amount of metals accumulated in soils. The limited amount of information about mercury concentration is also unsatisfactory since Hg is highly toxic and large concentrations of Hg could be expected in urban areas since.

Data in Table 6 show a partly different picture of the trace metal situation in urban areas from around the world compared to Swedish urban areas. Whereas data from Sweden supports the finding by de Miguel *et al.* (1997) and Madrid *et al.* (2004) that Cu, Pb and Zn are typical 'urban' elements, this pattern can not be seen in Table 6. Very large maximum concentrations and large mean/median-intervals are reported for all metals including Cd and Cr. A probable explanation is that some studies include areas with very intense industrial activity. Such areas are not included in the Swedish studies since the goal of the investigations has been to determine more typical trace metal concentrations in the cities studied and in one case in roadside soils. The large mean/median-interval in the international dataset is due to the fact that the data represent such a heterogeneous material. The city areas in the studies have very different histories and represent widely different conditions in various parts of the world.

The only investigations from cities outside Sweden including all trace metals in the tables are the extensive survey of Berlin soils (Birke & Rauch, 2000) and the study from Jakobstad (Peltola & Åström, 2003). Comparing the results from these three studies, the overall impression is that the differences between the cities are surprisingly small. Despite the differences in history and number of inhabitants, the median metal concentrations are very similar in Berlin (approx 3.5 million inhabitants) and Jakobstad (approx. 20 000 inhabitants). Moreover, the mean concentrations in the Stockholm and Berlin soils are also of the same magnitude. The only exception is that the concentration of Hg is larger in soils in Stockholm and Berlin than in Jakobstad. One possible explanation could be that Hg found in soils to a rather significant extent originates from the technical and medical uses of the metal in the 19th Century, when Jakobstad was a very small town. To conclude, the concentrations of Cd, Cr, Cu, Hg, Pb and Zn measured in Stockholm soils correspond with the concentrations in other similar (north European) urban areas whereas it partly differ when compared to more distant urban areas.

Table 6. Concentrations (mg kg^{-1} dry weight) of strong acid-extractable Cd, Cr, Cu, Hg, Pb, and Zn measured in soils in 15 urban areas from all over the world.

Soil	Value	Metal					
		Cd	Cr	Cu	Hg	Pb	Zn
		mg kg^{-1}					
<i>Bangkok</i> ¹⁴ , 0-0.5 m (n = 30)	Median	0.15	25.4	26.6	---	28.9	38
	Mean	0.29	26.4	41.7	---	47.8	118
	Max	2.53	57.4	283	---	269.3	814
<i>Hong Kong</i> ³ , surface soils, (n = 10)	Mean	0.94	---	16	---	89.9	58.8
	Max	---	---	---	---	---	---
<i>Uberlândia, Brazil</i> ⁵ 0-20 cm (n = 18)	Max	0.47	60.9	154	---	25.5	107
	Min	0.11	12.5	6	---	3.5	4.5
<i>Chanchun</i> ⁸ (n=7)	Max	---	---	---	0.14	---	---
<i>Glebe</i> ⁹ , surface soils (n = 36)	Max	14	---	4141	---	20278	200
	Min	0	---	2	---	22	3000
<i>New Orleans</i> ¹¹ (n = 4026)	Median	3.2	---	---	---	120	131
	Max	87	---	---	---	191000	26600
<i>Sevilla</i> ¹ , surface soils (n = 62)	Mean	---	40	73	---	150	138
	Max	---	64	698	---	1080	611
<i>Madrid</i> ² surface soils (n = 55)	Median	---	62	71	---	150	205
	Mean	---	75	72	---	161	210
	Max	---	211	211	---	463	82
<i>Turin</i> ¹ , surface soils (n = 24 or 40)	Mean	---	229	111	---	158	242
	Max	---	356	293	---	565	550
<i>Berlin</i> ¹² surface soils (n = 2182)	Median	0.35	25	31	0.19	77	129
	Mean	0.92	35	79	0.42	119	243
	Max	131	1840	12300	71.2	4710	25210
<i>Rostock</i> ⁶ , garden soils topsoil (n = 13)	Median	0.7	---	38	---	151	207
	Mean	0.6	---	34	---	186	271
	Max	1.5	---	71	---	756	33
subsurface soil (n = 17)	Median	0.1	---	10	---	35	31
	Mean	0.2	---	7	---	16	34
	Max	0.7	---	33	---	102	99

Table 6. *Continued*

Soil	Value	Metal					
		Cd	Cr	Cu	Hg	Pb	Zn
		mg kg ⁻¹					
<i>Warsaw</i> ⁷ , surface soils (n = 36)	Mean	1.0	12.9	25	---	---	134
	Max	5.5	69.6	65	---	---	426
<i>Glasgow</i> ¹ , surface soils (n = 62)	Mean	---	93	140	---	971	364
	Max	---	217	484	---	7051	1004
<i>Aberdeen</i> ¹⁰							
Parkland soils (n = 29)	Mean	---	24	27	---	94	58
Roadside soils (n = 46)	Mean	---	23	45	---	173	113
<i>Jakobstad, Finland</i> ¹³ 0-0.15 m (n = 32)	Median	0.25	23	22	0.09	59	82
	Max	2.52	388	2612	2.3	3439	2368
0.15-0.30 m (n = 32)	Median	0.09	20	12	0.04	33	35
	Max	2.3	30	10249	0.5	2113	2293
All studies	Mean/ Median	0.1- 3.2	12.4- 229	13- 71	0.04- 0.19	16- 971	31- 364
	Max	131	1840	1315	71.2	191000	26600

¹Hursthouse et al., 2004²de Miguel, 1998³Chen et al., 1997⁴Wilcke et al., 1998⁵Wilcke et al., 1999⁶Kahle, 2000⁷Pichtel, 1997⁸Fang et al., 2004⁹Marcus & McBratney, 1996¹⁰Paterson et al., 1996¹¹Mielke et al., 1999¹²Birke & Rauch, 2000¹³Peltola & Åström, 2003

Trace metal binding and solubility

The environmental risk arising from potentially toxic trace metals in soils depends on the bioavailability and the mobility of the metal, factors that are only partly related to the total amounts of the metals in soil (Figure 6). Risk assessment of metal-contaminated soils or sites also has to include evaluation of metal binding and solubility in the actual soil.

Trace metals bound in soils are either incorporated as a building brick in the solid mineral material or attached to the surface of soil particles. If a trace metal is one of the cations in a solid compound it could be the solid fraction that regulates the soil solution concentration, but more commonly it is the surface-bound fraction that interacts directly with the soil solution. Trace metals from an external source trapped in a soil are primarily bound to the surface of soil particles and the surface-bound fraction could also most easily be released to the environment. Consequently, processes regulating surface binding of metals in soil are crucial from an environmental perspective and in the following, trace metal binding in soil only refers to particle surface binding.

There are of course differences between trace metals but generally the important soil characteristics influencing trace metal binding in soil are the clay content and mineralogy, content of iron (Fe), aluminium (Al) and manganese (Mn) oxides, organic matter quality and quantity, pH and concentration of other ions in soil solution (Ross, 1994b; Gustafsson *et al.*, 2003). The minerals that dominate in the clay fraction in most soils (*i.e.* secondary aluminosilicates or clay minerals) have a net charge due to electrical imbalances in the mineral structure (structural or permanent charges) and from dissociating surface groups (pH-dependent or variable charges) (Sposito, 1989). The charge properties of the clay fraction in a specific soil thus depend on the relative fraction of permanent versus variable charges and on pH. Even so, looking at the clay fraction as a metal binding component, it could be considered to be a negatively charged surface, which attracts metal cations electrostatically.

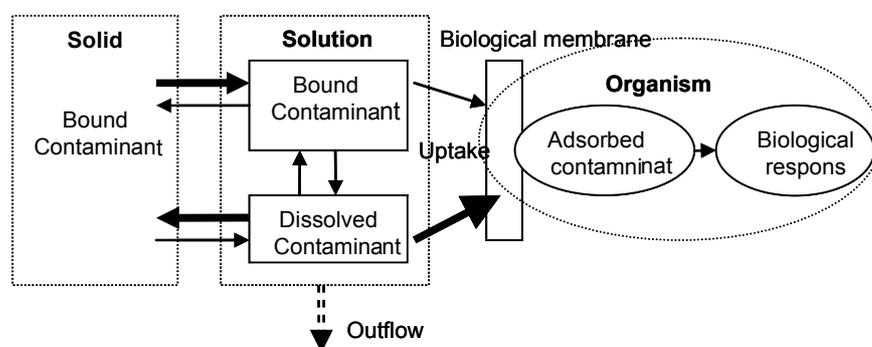


Figure 6. Processes (arrows) influencing the leaching and biological response of a toxic contaminant in a soil (modified from National Academy of Sciences, 2003).

The influence of iron, aluminium and manganese oxides on trace metals binding is twofold. The oxides have a pH-dependent surface charge attracting ions but they are also a source of free Fe, Al and Mn ions. The free ions, Fe^{2+} and Al^{3+} in particular, act in competition with other metal cations for binding sites on soil minerals and organic material (Tipping, 2002). The concentration of free Al in soils with Al-oxides is determined by pH and the equilibrium concentration of Fe and Mn by both pH and redox potential being higher at lower pH and redox potential. The PZC:s of the Fe and Al oxide surfaces are high and the binding capacity of metal cations at neutral to weakly acid pH-values is quantitatively usually of minor importance whereas it could be important for metals forming anions, such as chromium, vanadium and molybdenum (Anderson & Sposito, 1992). At high pH, however, oxide adsorption may be important for metals such as Pb^{2+} and UO_2^{2+} . For trace metals forming cations, Al-oxides in particular can also be considered as a source of a binding site blocker (Al^{3+}), which increases the solubility of the trace metals.

Soil organic matter (SOM) is a complex mixture of different organic compounds with a detailed composition not fully understood, but some properties important for heavy metal adsorption, desorption and solubility are well known. SOM consists of large molecules which are traditionally divided into humin, humic acids (HA) and fulvic acids (FA). Humic acids have a molecular weight of 10000 to 2000 g mol^{-1} and fulvic acids 2000 to 500 g mol^{-1} . Both types of SOM have acid properties and, like oxides, SOM has pH-dependent unbalanced charges. In the organic molecules these charges are localised to specific sites or chemical groups with specific binding properties. The binding properties for a single site also very much depend on the chemical ‘surroundings’, electropotential and steric factors. Metal ion binding to these groups is generally very strong, especially for di- or trivalent ions and ions capable of covalent binding. An example of a steric factor is when two charge groups are situated so close together that they can bind to the same metal ion, creating a bidentate complex (Figure 7). There are only a limited number of sites for strong or specific binding and their relative importance for the binding of a specific metal is very much dependent on the total concentration of the metal. The lower concentrations of the metal the greater proportion of the metal ions are specifically bound. The strong binding of metal ions to SOM does not necessarily mean that the metals are insoluble. Some of the lower molecular weight dissolved organic matter (DOM) binds metals and acts as a carrier that makes the metals even more ‘soluble’. The total effect of SOM on metal solubility depends on the relative amount of DOM, which in turn depends on other soil factors such as pH and total ion strength (Bloomfield *et al.*, 1976; Strickland *et al.*, 1979; Bergkvist *et al.*, 1989).

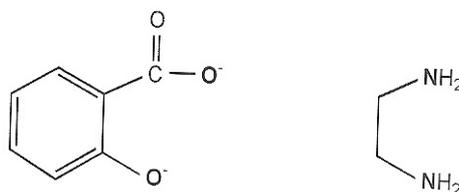


Figure 7. Functional groups with a possible bidentate binding site (adated from Tipping, 2002).

As can be understood from the above, pH has a significant and complex influence on metal binding in soil by regulating both the surface binding properties of the soil particles and the solubility of important substances. Other important chemical factors are the redox situation and the occurrence of other ions in soil solution. Anions such as Cl^- and SO_4^{2-} can form soluble complexes with trace metals such as Cd and Pb, which increases the solubility of these metals. At high ionic strengths, DOM flocculates easier; this may reduce the solubility of metals that form strong complexes with DOM. Redox processes influence trace metal binding indirectly by influencing the pH value and by governing the balance between Fe^{2+} and Fe^{3+} . The oxidation state of Cr, and thereby the binding properties of this element, are directly determined by the redox potential.

The metals studied in this thesis discussion on solubility are Cd, Cr, Cu, Hg, Pb and Zn. In the survey (Paper I), As and Ni were also analysed but they are not included in this discussion. For all the studied metals, binding to organic substances and to oxides is most important under normal (*i.e.* neutral to weakly acid, oxidised) soil conditions. The weakest complexes are formed by Cd and Zn, which for these metals make electrostatic binding to clay minerals relatively more important and overall binding more dependent on the concentration of competing ions (*e.g.* Ca^{2+} and Al^{3+}). Copper and lead on the other hand form strong complexes with both organic molecules and oxides. The strongest bonds to binding sites on organic molecules are formed by Hg. The most common forms of chromium in soil are Cr^{3+} and CrO_4^{2-} . Like other metal cations, Cr^{3+} binds to negatively charged groups on both organic material and oxides whereas chromate (CrO_4^{2-}) is strongly bound to positively charged oxide sites.

Even if the different processes discussed above are fairly well understood, the complex interactions between the processes make prediction of trace metal solubility and mobility a challenge. Focusing on the urban environment, the difficulties are even larger. Compared to soils in other ecosystems, soils in urban areas are more exposed to human activities that drastically change the soil chemical environment. Most obvious is building and reconstruction activities creating changes to soil structure and groundwater level (Burghardt, 2002), factors that greatly influence redox conditions and thereby also pH. Another less dramatic activity is the application of high amounts of organic material (*e.g.* bark, compost or peat) to topsoil, which could be expected to release soluble organic acids. A third example is application of de-icing salt on roads during winter, which causes large concentrations of Na^+ and Cl^- in soils and groundwater (*e.g.* Miljöförvaltningen, 1997; Norrström & Bergstedt, 2001; Johansson Thunqvist, 2003). In Papers III and IV, two experimental methods (sequential extractions and soil column leaching) and one simulation model to assess the potential solubility of the trace metals in soils were tested. In the experimental set-up, particular emphasis was placed on how the solubility was affected by changes in soil chemistry likely to occur in an urban environment in Sweden.

Sequential extraction

When sequential extraction was introduced as a method in soil chemistry, the main purpose was to determine the relative amount of different species of metals in the soil. The different extracting solutions were chosen with the intention that each solution should extract one species of the metal under analysis. For example, the NH_4Ac pH 4.8 solution used in this work is presumed to extract the fraction of the metal bound to the surface sites of oxides and organic matter. The use of sequential extractions has shown that the overlap between fractions extracted by the different solutions is large and that the method can scarcely be used for metal speciation. Even so, sequential extraction can be useful to estimate the solubility of metals in soils and quite recently it has been suggested as a method for assessment of potential mobility of metals in contaminated soils (Anderson *et al.*, 2000; Pueyo *et al.*, 2003). Testing and development of sequential extraction procedures is still ongoing (Davidson *et al.*, 2004). The extraction schema used in

this study is a combination solutions suggested by a number of different authors as described in the Method section above.

Cadmium was mainly found in the easily extractable fractions (F1-F3) in both soils (Table 7). In soil C, Cd was mainly soluble in acid NH₄ Ac (F3), whereas in soil W the dominant part was extractable with 1M NH₄NO₃ (F1) and 0.1 M NaCl (F2). The low natural pH (4.8) was probably the main reason for the higher solubility of Cd in soil W compared to soil C (pH 6.1). In both soils only a minor part of the Cd was found in the residual fraction. There was a big difference between the two soils with respect to Zn solubility. In soil C, 82% of the Zn was recovered in the residual fraction (Table 7), whereas in soil W Zn was mainly easily soluble, with 63% extracted in the F1-F2 fractions. Copper and lead showed a similar pattern in both soils, and in total 7-13% of Cu and 16-19% of Pb was extracted by F1-F3, whereas about 40% of Cu and Pb was extracted by EDTA (F4), confirming that these metals are strongly bound in soils, presumably in surface complexes of organic substances and oxides. The residual fraction constituted a substantial part (40-50%) of HNO₃-extractable Cu and Pb. None of the solutions in the sequence was effective in releasing Cr. For both soils almost all Cr was found in the residual fraction. This most of all illustrates that the sequence of solutions was not designed and is not useful for fractioning metals appearing in anionic form.

Table 7. Concentration (mg kg⁻¹ dw) of four different fractions of trace metals (Cd, Cu, Pb, and Zn) extracted by different solutions in a sequential extraction procedure. The amount of each metal is also expressed as % of total HNO₃-extractable fraction (%_{HNO3})

Extraction	Cd		Cu		Pb		Zn	
	µg kg ⁻¹	% _{HNO3}	mg kg ⁻¹	% _{HNO3}	mg kg ⁻¹	% _{HNO3}	mg kg ⁻¹	% _{HNO3}
<i>Soil C</i>								
F1	40	6	0.91	2	0.17	0	12.8	5
F1-F2	50	8	2.32	4	0.35	0	22.5	9
F1-F3	390	67	7.18	13	22.0	16	26.7	11
F1-F4	530	91	30.1	54	76.8	57	47.9	19
Residual	50	9	26.2	46	57.1	43	212	82
<i>Soil W</i>								
F1	90	37	2.55	1	6.89	2	66.6	29
F1-F2	140	56	4.07	2	8.59	3	144	63
F1-F3	190	75	14.7	7	65.4	19	146	64
F1-F4	240	94	93.9	47	208	59	161	70
Residual	10	6	106	53	153	42	67.8	30

a) F1= extractable with 1M NH₄NO₃; F2= extractable with 0.1 M NaCl; F3= extractable with 1M NH₄Ac pH 4.8; F4=extractable with 0.5M NH₄Ac + 0.02M EDTA pH 4.65; Residual = 7M HNO₃-extractable - (F1+F2+F3+F4)

Column leaching

Column leaching tests have been an important tool for soil scientists from the very beginning of soil research (Way, 1850; Thomas, 1977). The soil columns are often used as small experimental models of real soils. This is of course an approach with limitations, especially the difficulties of scaling up the results. Still, a lot has been learned about soil processes from leaching experiments and the method is useful for studies on how soil and the soil solution are affected by environmental changes. In this work, column leaching experiments (Papers III and IV) were used to describe and quantify the leaching behaviour of Cd, Cu, Hg, Zn and Pb in typical urban situations discussed above.

For both soils, the *salt* treatment (and not the *acid* treatment) produced the lowest pH values, 5.0 for soil W and 5.7 for soil C in the 5th leachate. This could probably be explained by the release of exchange acidity from the soils due to the high Na^+ concentration, or, alternatively, by the salt-dependent proton binding by soil organic matter (Gustafsson & Berggren Kleja, 2005). The lowest pH measured in the *acid* treatment for soil W was 5.4 (5th leachate) but extrapolation of the curve suggests that the value would have decreased even more if the experiment had continued. The DOC concentration did not reflect the initial content of soil organic matter; rather it was a result of the different treatments. The largest DOC concentration was measured in the first leachate in the *bark* treatment (soil C 135 mg L^{-1} , soil W 89 mg L^{-1}) but decreased thereafter during the experiment as a result of the limited source of DOC (20 g bark and soil organic matter). The fifth leachate in the *salt* and *acid* treatment gave the smallest DOC concentrations (soil C: 12 mg L^{-1} , soil W: $7\text{-}9 \text{ mg L}^{-1}$), also illustrating the pH dependent solubility of organic molecules.

The Cd concentration was largest in the solutions from the *salt* treatment columns, being $10\text{-}12 \text{ } \mu\text{g L}^{-1}$ in the first leachate (sampled after approx. 1 pore volume). The Cd concentration decreased to about $3 \text{ } \mu\text{g L}^{-1}$ in the fifth leachate (Figure 8). In the other treatments, the Cd concentration was small, $0.1\text{-}0.3 \text{ } \mu\text{g L}^{-1}$ in the *rain* and *bark* treatments, and $0.5 \text{ } \mu\text{g L}^{-1}$ in the *acid* treatment. Zinc was also mainly mobilised in the *salt* treatment for soil W, whereas small effects were encountered for the other treatments (Table 8). Although the treatment-specific effects were seen most clearly for soil W, the effects could be seen also for soil C. The ‘acid rain’ caused a small but steadily increasing concentration of both Cd and Zn, probably as a result of the decreasing pH. Approximately 5 times more Cd and 2 times more Zn were released in the *acid* treatment, compared to the *rain* treatment (Table 8).

Table 8. The total amounts of Cd, Cu, Pb and Zn leached during five leaching events, with different extraction solutions (Treatments) in relation to soil mass (dry weight) in the columns. The means, minimum and maximum values of three replicates are given. The mean values are also calculated as % of total HNO₃-extractable fraction (%_{HNO3}). For each metal, mean values marked with the same letter are not significantly different ($p < 0.05$)

Treatment	Cd		Cu		Pb		Zn		
	$\mu\text{g kg}^{-1}$	% _{HNO3}	mg kg^{-1}	% _{HNO3}	mg kg^{-1}	% _{HNO3}	mg kg^{-1}	% _{HNO3}	
Soil C Rain	Mean	2.69 ¹ a	0.5	0.31 ¹ a,b	0.6	0.14 ¹ a	0.1	1.45 ¹ a	0.6
	Min	2.40		0.31		0.12		1.43	
	Max	2.93		0.32		0.16		1.49	
Bark	Mean	3.79 a	0.7	0.38 a	0.7	0.22 a	0.2	1.98 a	0.8
	Min	3.69		0.36		0.20		1.91	
	Max	3.92		0.39		0.25		2.08	
Salt	Mean	58.9 b	10	0.14 b	0.2	0.09 a	<0.1	9.05 b,d,f	3.5
	Min	54.8		0.13		0.09		8.86	
	Max	61.4		0.15		0.09		9.29	
Soil W Rain	Mean	3.72 ¹ a	1.5	3.81 ¹ c	1.9	0.84 ¹ c	0.2	5.94 ¹ b,c	2.6
	Min	3.34		3.70		0.81		5.76	
	Max	4.18		3.97		0.88		6.23	
Bark	Mean	4.58 a	1.8	4.57 d	2.3	1.45 d	0.4	7.99 c,d	3.5
	Min	4.43		4.49		1.44		7.65	
	Max	4.85		4.66		1.46		8.19	
Salt	Mean	149c	60	1.68 e	0.8	0.96 c	0.3	74.7 e	33
	Min	143		1.57		0.84		70.6	
	Max	156		1.75		1.06		76.8	
Acid	Mean	17.8 d	7.1	2.17 f	1.1	0.28 b	<0.1	12.0 f	5.2
	Min	13.9		2.08		0.26		11.0	
	Max	22.6		2.31		0.32		12.9	

The *rain* and *bark* treatments produced the largest leachate concentrations of Cu and Cr, while the smallest concentrations were seen in the *salt* treatment (Figure 8). For Pb the largest concentrations were observed in the *bark* treatment. The total amount of Pb leached was 1.5 times larger in the *bark* treatment than the *rain* and *salt* treatments. From the 2nd leachate and onwards, the concentration was approximately 2 times larger. The smallest Pb concentrations were found in the acid treatments. Reduced solubility of organic substances due to the lower pH might provide an explanation for these results. The concentrations measured in leachates are at the same level as maximum concentration of Cd ($1.1 \mu\text{g L}^{-1}$), Cr ($7.8 \mu\text{g L}^{-1}$), Cu ($93 \mu\text{g L}^{-1}$), Pb ($5.5 \mu\text{g L}^{-1}$) and Zn (0.4mg L^{-1}) in groundwater in Stockholm (Aastrup & Thunholm, 2001) (Figure 8, For illustrative purpose are maximum Cd and Zn concentration not included in the figure). Thus, the soils can not be excluded as a possible source of the metals found in groundwater.

The mercury concentration was measured only for one soil and in the 4th leachate, but effects of the different treatments could be observed. In comparison with the *rain* treatment, the concentration in the *bark* leachate was 1.5 times larger, whereas the concentration in the *salt* leachate was only one tenth of that in the *rain* treatment, 0.01 and $0.10 \mu\text{g L}^{-1}$ respectively. The concentrations in *rain* and *bark* leachates were somewhat larger than the median concentration ($0.02 \mu\text{g L}^{-1}$) but much smaller than the maximum concentration ($4.6 \mu\text{g L}^{-1}$) in groundwater in Stockholm reported by Aastrup and Thunholm (2001) (Figure 8).

Metal concentrations and leachate chemistry

The effect on metal behaviour of the different treatments in the leaching experiment showed some surprising results as the large *salt* effect and small effect of *acid* treatment. With the purpose of better explaining the leaching behaviour of each single metal, the statistical correlation between the measured metal concentrations and pH, EC and DOC for all leachates was calculated. Overall there was no obvious relationship between metal concentrations and the pH or EC measured in the leachates. The only linear relationship with r^2 values above 0.2 was found for Cu, Cr and Hg concentration versus pH (not shown). For the same metals the concentration was negatively correlated to EC. The well-documented correlation between pH and solubility of Cd and Zn could be seen for most samples (Figure 9) but the statistical correlation was weak for both soils when all leaching events were included in the calculations. When the 'outliers' in first leaching event were excluded in the calculations the correlation between pH and metal concentration was as expected, strong and negative. For the leachates from

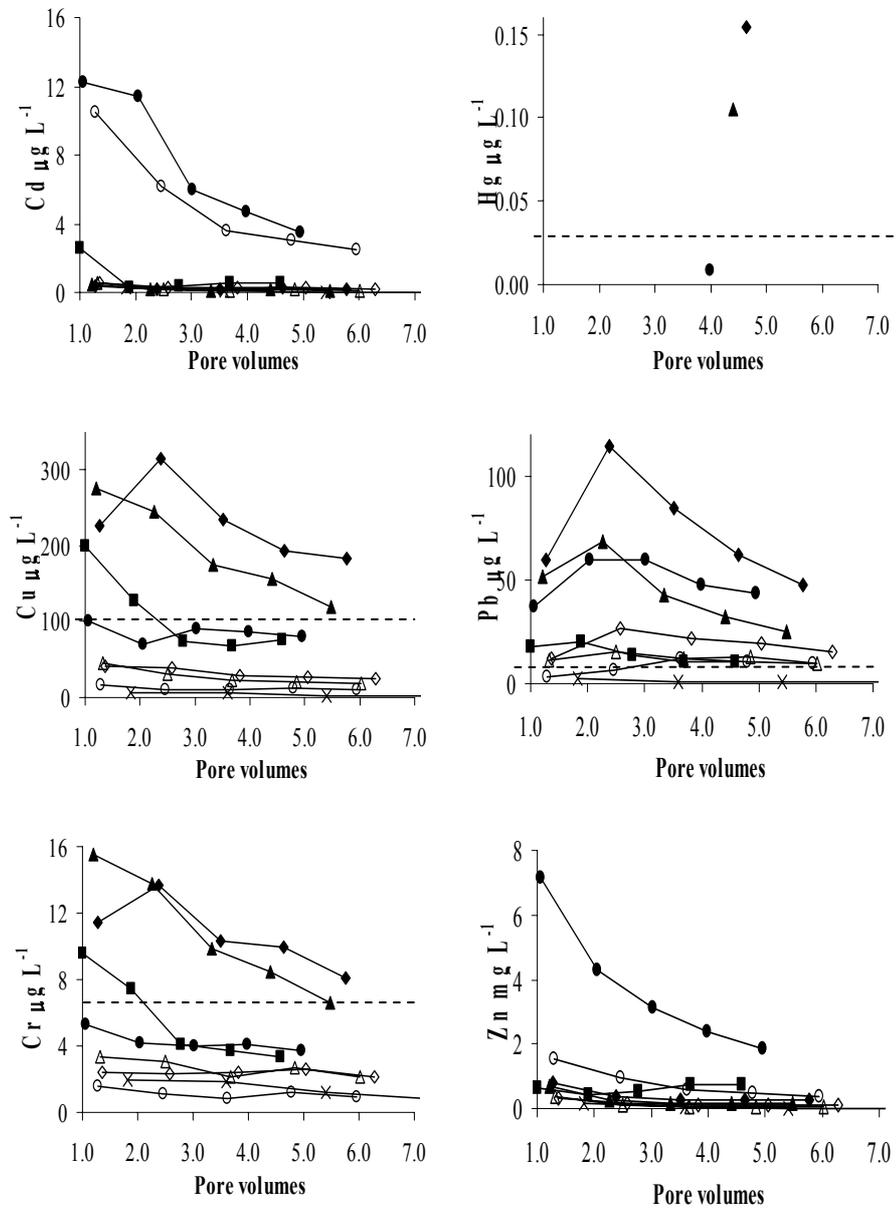


Figure 8. Metal (Cd, Cr, Cu, Hg, Pb and Zn concentration (mg L^{-1}) in leachates (\blacklozenge = soil W bark; \diamond = soil C bark; \bullet = soil W salt; \circ = soil C salt; \blacktriangle = soil W rain; \triangle = soil C rain; \blacksquare = soil C acid; \times = only bark; --- = median (Hg) or maximum (Cr, Cu and Pb) concentration in Stockholm groundwater from Aastrup & Thunholm (2001).

both soils, there was a strong and positive correlation between the DOC concentration and the Cu, Cr, and Hg (only measured in soil W) concentrations (Figure 10). A fairly strong and positive correlation was also expected between dissolved Pb and DOC in the solutions. There was also a correlation but it was much weaker ($R^2 = 0.36$ for soil C and 0.44 for soil W) than for copper and chromium, partly due to deviating results in the *salt* treatment (Figure 10).

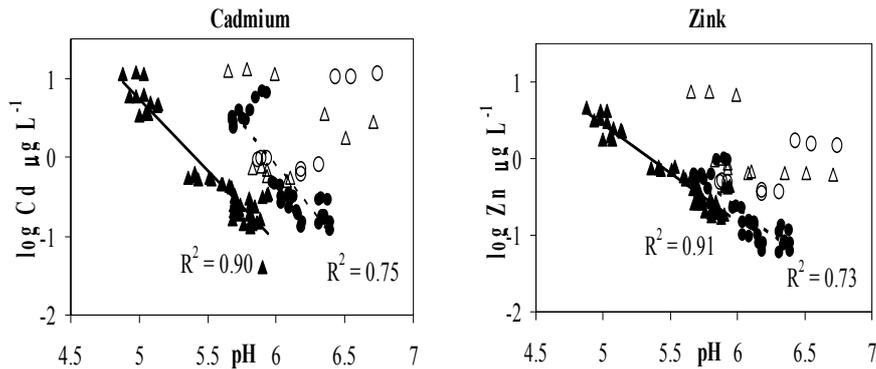


Figure 9. Correlation between log Cd respectively log Zn concentrations ($\mu\text{g L}^{-1}$) and pH in leachates solutions. Both soils (W and C), all treatments (rain, salt, bark and acid), leaching events (1-5) and replicates ($n=3$) included. (Δ = soil W leaching event 1; \blacktriangle / $---$ = soil W leaching event 2-5; \circ = soil C leaching event 1; \bullet / $---$ = soil C leaching event 2-5).

Sequential extraction and potential metal mobility

Since the same soil material is used in the sequential and leaching extractions, the usefulness of the sequential extraction for prediction trace metal leachability at different soil chemical situations could be evaluated. Comparing data in Table 7 with the amount of metal (mg kg^{-1} dw soil) leached in the different treatments in the column experiment (Table 8), it could be seen that for Cd the NaCl-extractable fraction (soil C $50 \mu\text{g kg}^{-1}$, soil W $140 \mu\text{g kg}^{-1}$) corresponded very well with the amount leached in the *salt* treatment (soil C $58.91 \mu\text{g kg}^{-1}$, soil W $149.2 \mu\text{g kg}^{-1}$). For Zn the best agreement was between the amount leached by the *salt* treatment (soil C 9.05 mg kg^{-1} , soil W 74.7 mg kg^{-1}) and the NH_4NO_3 -extractable fraction (soil C 12.8 mg kg^{-1} , soil W 66.6 mg kg^{-1}), whereas the NaCl-extractable fraction of Zn was approximately double that (soil C 22.5 mg kg^{-1} , soil W 144 mg kg^{-1}). For all four metals the fractions extractable with acid NH_4Ac and NH_4Ac with EDTA

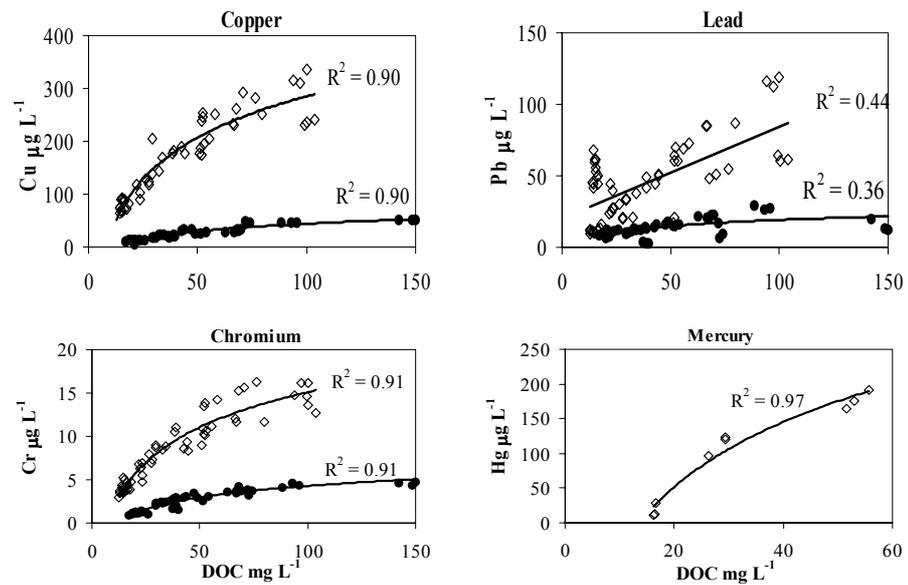


Figure 10. Correlation between metal concentration and DOC in leachates. Both soils (C and W), all treatments (rain, salt, bark and acid), leaching events (1-5) and replicates (n = 3) included. (\diamond = soil W; \bullet = soil C)

were much larger than the amount leached by any of the treatments in the column experiment. For all four metals, the fractions extractable with $\text{NH}_4\text{Ac} + \text{EDTA}$ were much larger than the amounts leached by any of the treatments in the column experiment. The metals extracted by EDTA are, most probably, the fraction complex bound to insoluble SOM and oxides.

Modelling metal behaviour in soil

In recent decades, numerous models of the fate of metals in soils have been presented in the literature. Such models are developed for different purposes and using different approaches. Mechanistic models are developed as research tools to better understand governing of processes, while functional, less mechanistic, models are developed from a management perspective (Addiscott & Wagenet, 1985). The approach may also differ in scale, as well as in the part of the system considered most important. The following is only a brief glimpse into the world of soil metal modelling and by no means an attempt to cover the whole subject.

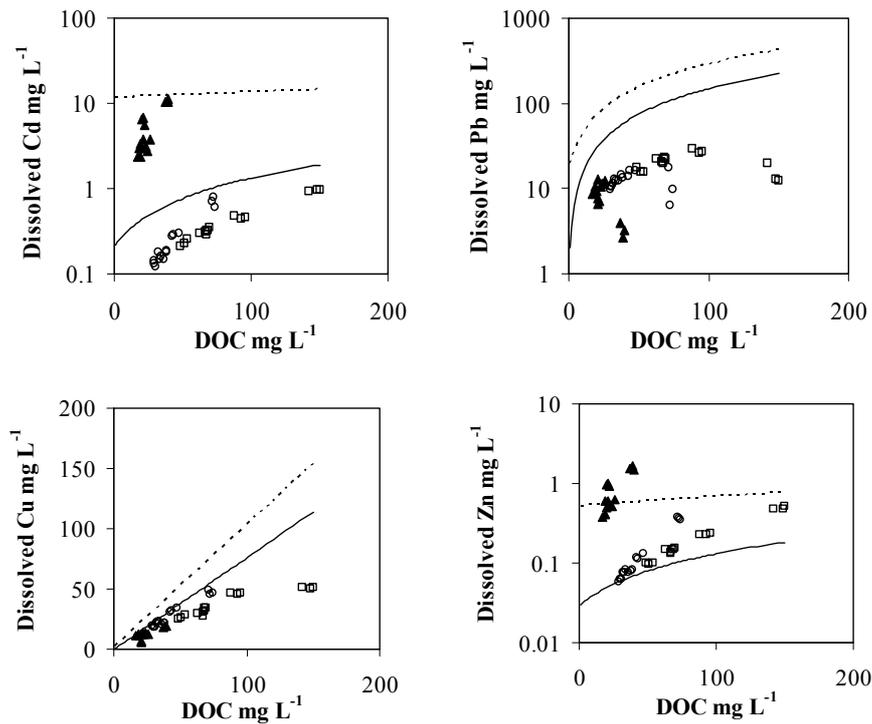
Davis et al. (1998) discuss different modelling approaches for describing the adsorption of inorganic contaminants, *e.g.* metals, to natural materials. According to those authors, all such models have some basic assumptions in common:

1. The mineral surface is composed of specific functional groups that react with dissolved solutes to form surface species analogous to complexation in homogeneous solution.

2. The equilibria of metal sorption or surface complexation and surface acidity can be described by mass action equations.
3. The apparent binding constants determined for the mass action equations are empirical parameters related to thermodynamic constants by the rational activity coefficients of the surface species.
4. The electrical charge at the surface is determined by the chemical reactions of the mineral functional groups, including acid-base reactions and the formation of ion pairs and coordinative complexes.

Davis *et al.* (1998) also compare what they term the component additivity (CA) approach and the generalised composite (GC) approach. In the former, binding to different sorbing components (*e.g.* Fe oxide, humic substances, clay) is treated separately with different sub-models and the results are summed for a description of the overall metal sorption. It is assumed in this approach that the wetted surface of complex mineral assemblage is composed of a mixture of one or more mineral (or organic) phases whose surface properties are known from independent studies

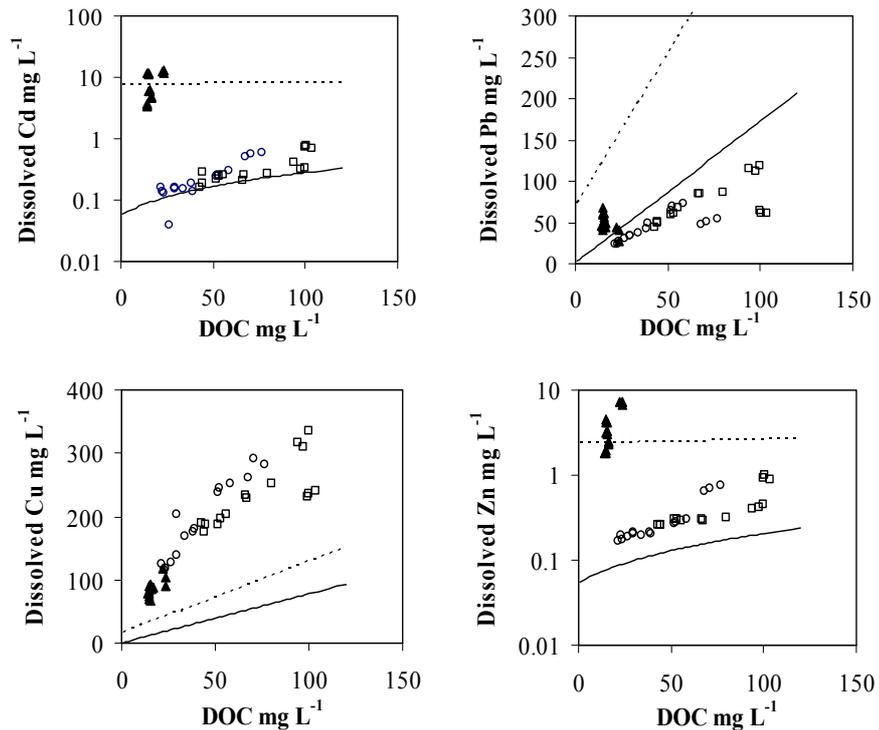
Figure 11. Measured and simulated metal concentrations in relation to DOC concentration in leachates from soil C. (— = rain and bark simulated; --- = salt simulated; □ = bark measured; ○ = rain measured; ▲ = salt measured). See text for details



of individual phases. In the generalised composite approach, it is assumed that the surface composition of the mineral assemblage is too complex to be quantified in terms of the contributions of individual phases to adsorption. Instead, the adsorptive reactivity of surfaces can be described by fitting experimental data for the specific soil (sorbent mixture).

From their comparison, Davis *et al.* (1998) concluded that the GC approach is far preferable because the important linkage between surface and aqueous species is retained in the modelling and the number of surface equilibria that must be considered can be minimised. Furthermore they found that the GC approach requires less information and laboratory data and is more useful for immediate and practical applications. One recent example of a model using a functional GC approach for metal adsorption in an applied context is the SLAM model (Bergkvist & Jarvis, 2004). The model was constructed to describe the fate of metals, *e.g.* cadmium, applied to arable land with sewage sludge, using empirical extended Freundlich adsorption isotherm to describe Cd adsorption in sludged soil.

Figure 12. Measured and simulated metal concentrations in relation to DOC concentration in leachates from soil W. (— = rain and bark simulated; --- = salt simulated; □ = bark measured; o = rain measured; ▲ = salt measured). See text for details.



Despite the arguments put forward by Davis *et al.* (1998) for a GC approach, the AC approach has also proved popular. One example is the Stockholm Humic Model (SHM) originally developed as a research tool for studying proton and metal binding to humic substances (Gustafsson, 2001). When using SHM in combination with the Gaines-Thomas equation for simulation of the ion exchange to the clay fraction, it was possible to simulate the acid-base characteristics and metal binding properties in soils (Gustafsson & Schaik, 2003; Gustafsson *et al.*, 2003). The results indicate that CA-type models including only two sorbing components could be useful for predicting metal solubility in practical applications such as environmental risk assessment but much work remains, not only in the model development but also on making better speciation of the metals bound in soils.

In this thesis work (Paper IV) SHM was used to evaluate whether the observed statistical correlation between metal concentration and leachate chemistry corresponded quantitatively with our mechanistic understanding of the system. Stockholm Humic Model, as implemented in Visual MINTEQ, was considered to be a useful tool since DOC was statistically the single most important factor regulating the leachate concentration of several metals. Results from the simulations are presented in Figure 11 (soil C) and Figure 12 (soil W). The simulated values for Cd and Zn corresponded rather well with measured data for all treatments. In contrast to what was concluded from the measured data alone, this illustrates that the Cd and Zn solubility at small (*i.e.* normal) salt concentrations was governed by binding to humic substances. For Cu, Ni and Pb the SHM simulations gave more contradictory results. In the measured data representing all leachates from all treatments (including the *salt* treatment), the correlation between DOC and especially Cu but also Pb concentrations was strong and positive. However, for Pb SHM tended to overestimate the dissolved concentrations, whereas dissolved Cu in soil W was underestimated. The model fit for Cu in soil C was fairly good and this is the only case where the simulations for Cu and Pb were in agreement with the measurements. The poorer fits for Pb indicate that something else, presumably iron oxide, is also quantitatively important for the Pb solubility in these cases. The results from the simulations are not unambiguous but quite encouraging and illustrate the potential of SHM as a tool to improve interpretation of experimental results.

Concluding remarks

Metal concentrations in the Stockholm soils were determined using a standard method, namely digestion with boiling 7 M HNO₃. Risk assessments of metal-contaminated soils in Sweden were, and still are, generally based on this particular fraction of extractable metals (Naturvårdsverket 1997; 1999). Strong acid digestion (*e.g.* by boiling HNO₃ or *aqua regia*) is often claimed to yield the total metal concentration or sometimes the quasi- or pseudo-total concentration (*e.g.* Anderson *et al.* 2000; Madrid *et al.*, 2002). These terms are particularly used in an applied context. However, this is not an adequate terminology since the soil

particles will be far from metal exhaustion when using strong acid procedures. Andersson (1976) demonstrated that HNO₃ (2 M 100 °C) only extracted 57-92% of the total amount (the latter determined after HF-treatment) of trace metals in soil material. Similar results have been obtained in a comparison between HNO₃ (7 M, boiling), *aqua regia* extraction and XRF analysis (the latter method being supposed to yield the total amount) conducted on 162 soil samples (Lax, 2005). Another fairly well established manner to classify metal fractions is simply to refer to the extractant used for analysing concentrations by either AAS, ICP or ICP-MS. The analytical method must of course be mentioned when the results of a study are reported but this does not necessarily say anything specifically about a metal fraction extracted from soil. However, to minimise the risk of misconceptions, the best (and probably most correct) way to name the fraction of a metal is still to refer to the extractant used.

The overall conclusion from the urban project with the objective to identify and quantify flows and pools of metals in Stockholm, was that trace metal-containing goods had accumulated in Stockholm and the metal stocks were still growing for Cr, Cu, Ni, Pb and Zn (Bergbäck *et al.*, 2001; Sörme *et al.*, 2001a). The use of Cd, Pb and Hg should be stepwise reduced according to legislation. However, Hg was the only metal for which a decreasing use could be documented. For the majority of the trace metal containing goods, the emissions were more or less negligible and only a minor fraction of the stock might cause environmental problems under prevailing conditions (Sörme *et al.*, 2001b). However, there were goods whose use did yield significant emissions. The importance of the traffic sector for emissions of Cu, Zn, Cr, Ni and Pb was very obvious. Results from studies of the Stockholm outdoor environment also demonstrated that the concentrations of several trace metals in soil, groundwater and sediments were enhanced compared to those in rural areas (Paper I; Aastrup & Thunholm, 2001; Sternbeck & Östlund, 2001). Moreover, according to our results, the mean concentrations of several metals in the Stockholm soils were larger than in other Swedish cities. This was still the case even when soils from the non-built-up areas within the Stockholm municipality were included in these comparisons. In the soils in the central part of Stockholm, the guideline values for sensitive land use launched by the Swedish Environmental Protection Agency were exceeded by the mean concentrations of Hg and Pb (Table 9). This situation most probably reflected the historical use of Hg for technical and medical purposes and of Pb in petrol. As illustrated in this work, contaminated soils might be one possible explanation for the enhanced trace metal concentrations in the Stockholm groundwater. To conclude, from an environmental perspective the trace metal situation in Stockholm was not alarming but there was a need for special attention and for initiating activities to stop the ongoing accumulation of metals in Stockholm soils and reduce the threat against the groundwater quality. This should be done in two ways, I) already highly contaminated sites should be remediated to protect ground water and reduce future risks and II) the diffuse leakage from the technosphere should be reduced by recycling of rejected trace metal containing goods. New technical solutions should be encouraged especially in the transport sector.

Table 9. Trace metal concentration (mg kg^{-1} dw, 7 M HNO_3 extractable) in Stockholm city centre soils. For comparison, data from arable land in the region and guideline values for land with sensitive use are given

Soils		Cd	Cr	Cu	Hg	Ni	Pb	Zn
		——— mg kg^{-1} ———						
Stockholm City centre ¹								
0-5 cm	Mean	0.4	27	47	0.9	9	104	160
	Max	0.8	39	105	3.3	14	444	410
30 cm	Mean	0.3	27	67	1.0	11	135	190
	Max	0.6	42	153	2.9	21	339	530
Guideline values ²		0.4	120	100	1	35	80	350

¹From Paper I

²Fom Naturvårdsverket (1997)

A better implementation of what is known about trace metal behaviour in soils in applied risk assessments is desirable. Most studies on contaminants in urban soil focus on surface soils, which is unsatisfactory. The values from the Stockholm city centre in Table 3 clearly illustrate that the deeper soil horizons are just as contaminated as the topsoil. The concentrations throughout the whole soil profile should be analysed to get a full documentation of the contamination situation in an area. For reasons discussed earlier the HNO_3 extractable fraction of metals is not optimal for assessment of metal bioavailability, solubility or mobility and alternative or complementary methods should be introduced.

The concentration of acid EDTA-extractable metals has long been known to correlate fairly well with plant uptake (Lakanen & Erviö, 1971; Sillanpää & Jansson, 1992). However, the direct uptake of metals by organisms is of minor concern for the urban environment, since the risk of potentially toxic trace metals entering into circulation in ecosystems or human food through plant uptake is small. However, EDTA pH 4.8 is also suggested as an alternative to 7 M HNO_3 or *aqua regia* in risk assessments of contaminated soils or sediments (Tack & Verloo, 1996). This is not fully supported by the results from the sequential and column leaching experiments in this work but if it is correct that EDTA pH 4.8 extracts most of the complex bound fraction of a metal it could probably be useful for quantification of a potentially labile pool of metals.

In the search for complements to strong acid extraction of metals for assessment of contaminated sites there has been an increasing interest in standardised leaching tests. The tests are primarily developed for risk classification of waste material and have been adopted for soil material. The standardisation work has been done within the European Union (Halm & Grathwohl, 2003). The leaching solutions used in these tests are basically pure (demineralised) water (*e.g.* CEN/TC 14405 and EN 12457) and pH is the only chemical parameter that is altered in the tests (PrEN 14429). There is no doubt that the pH of the extraction/leaching solution is an important factor, if not the most important one (Andersson, 1975; van der Sloot *et al.*, 1996; Halm & Grathwohl, 2003; Dijkstra *et al.*, 2004), but to assess the risks associated with changing soil conditions, other parameters such as DOC should be included as well. The only cost-effective way to predict metal leaching in different chemical situations is probably to use computer-based user-friendly

models. Promising results on modelling the solubility and leachability of trace metals in contaminated soils have been presented with both the generalised composite approach (Bergkvist & Jarvis, 2004) and the component additivity approach (Gustafsson & Schaik, 2003; Djikstra *et al.*, 2004; Lumsdon, 2004), but the models available for practical use do not include the DOC effect in an adequate way and there is a need for further refinement of the tools. The development of x-ray based methods *i.e.* Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near-Edge Structure (XANES) for metal speciation might facilitate this work within just a few years time.

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