

# **Metals in Urban Playground Soils**

## **Distribution and Bioaccessibility**

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## Abstract

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Urban soils generally have elevated metal contents originating from both point and diffuse pollution sources. Urban areas designated for children, who are most susceptible to any negative health effects of soil metals, may therefore have elevated soil metal contents. Children ingest soil both directly and by putting dirty hands and objects in their mouths. The soil ingested involuntarily mainly comprise very fine particles that have a larger surface area for sorption and may therefore hold higher metal contents than the bulk soil. However, only a fraction of the total soil metal content is generally bioaccessible, *i.e.* can be released from the soil and absorbed in the body.

This thesis presents studies on total and bioaccessible metal contents in soils collected from playgrounds in urban Uppsala. *Aqua regia* digestion was used for total metal analysis while bioaccessibility was investigated for As, Cd, Cr, Ni and Pb using an *in vitro* digestion model simulating three ingestion scenarios: pica (compulsive ingestion of large amounts of soil), deliberate and involuntary ingestion.

While mainly natural sources were found to contribute to soil contents of As, Al, Fe, Cr, Ni, Mn and W, the main sources of Cd, Cu, Hg, Pb and Zn were anthropogenic. Clay content and construction year of the playgrounds were more important factors for the soil metal content than past and present land use in the surrounding areas. The fine soil particles (<50 µm) had on average 150% higher metal contents than larger size fractions. Up to 250% enrichment was found in the fine fraction of sandy soils. The effect of particle size and soil mass on bioaccessibility was found to depend largely on soil texture, with the effects diminishing in soils with high clay content. Lead bioaccessibility was largely affected by gastrointestinal pH, which in turn was affected by particle size fraction and soil mass.

The results emphasize the importance of soil analysis beyond only assessment of total metal content of bulk soil for a correct risk assessment of soil metals. The results also show the difficulties associated with generic soil metal guideline values in risk evaluation of soil contamination.

**Keywords:** urban soil, metal, bioaccessibility, *in vitro* test, particle size distribution, geochemical origin, biogeochemistry, risk assessment

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Sola dosis facit venenum

(The dose alone makes the poison)

*-Paracelsus (1493-1541)*

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## Preface

### Papers I-IV

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

- I. Ljung, K., Otabbong, E. & Selinus, O. 2006. Natural and anthropogenic trace metal inputs to soils in urban Uppsala, Sweden. *Environmental Geochemistry and Health* 28, 353-364.
- II. Ljung, K., Selinus, O. & Otabbong, E. 2006. Metals in soils of children's urban environments in the small northern European city of Uppsala. *Science of the Total Environment* 366, 749-759.
- III. Ljung, K., Selinus, O., Berglund, M. & Otabbong, E. 2006. Metal distribution in soil particle sizes relevant to soil ingestion by children. *Applied Geochemistry* 21, 1613-1624.
- IV. Ljung, K., Oomen, A., Duits, M., Selinus, O. & Berglund, M. Metal bioaccessibility of urban playground soil. *Journal of Environmental Science and Health, Part A*. *Accepted*.

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I am the first author on all papers, and thus primarily responsible for the field and laboratory work, statistical analysis, data interpretation, illustrations and text. The co-authors have contributed with field and laboratory work, data interpretation, method development and discussion.

## Introduction

There is increasing awareness that metals present in soil may have negative consequences on human health and on the environment, demonstrated by the many books and articles that are published on soil metal bioaccessibility and risk assessment (see for example Ruby *et al.*, 1993; Berglund *et al.*, 1994; 2000; Berglund, Sörensen & Vahter, 1995; Lanphear & Roughmann, 1997; Lanphear *et al.*, 1998; Mielke & Reagan, 1998; Mielke *et al.*, 1999; 2005; Abrahams, 2002; Schroeder *et al.*, 2003; 2004; Selinus *et al.*, 2005). Industrial sites have been subjected to point pollution, which often results in elevated soil metal contents within a limited area. The type of contaminant is also often known. However, a large proportion of the metals present in soil originate from diffuse emission sources such as long- and short-range atmospheric deposition. This is especially apparent in urban soil, where there are more diffuse emission sources, for example traffic and building material, than in rural areas, resulting in short-range atmospheric deposition and a more general increase in metal contents (Paterson, Sanka & Clark, 1996; Filippelli *et al.*, 2005).

Since metals are largely immobile in the soil system, an accumulation occurs over time which may result in levels that are harmful to humans upon both acute and chronic exposure (Thornton, 1991; Brinkmann, 1994; Sheppard, 1998). Because of the diffuse emission in urban areas and the accumulation of soil metals with time, even residential areas located away from point pollution sources may have elevated soil metal contents.

Most children are exposed to metals present in soil because of their hand-to-mouth behaviour, which puts them in more frequent contact with soil than most adults. Children practise both deliberate ingestion of soil and involuntary ingestion through mouthing dirty hands and objects (ATSDR, 2000). Children are also more susceptible than adults to any potential negative health effects of metal ingestion. While their smaller body mass increases the relative exposure to a given quantity of contaminants (per kg body mass), they also have a higher gastrointestinal absorption of metals (Schütz *et al.*, 1997). Moreover, because their nervous system is not fully developed, they are more sensitive to neurotoxic metals such as Pb and Hg (Klaassen, 1996).

The potential risks from soil metal intake depend on the amount of metal ingested and the bioaccessibility of that metal, which in turn depends on variables both in the soil and in the gastrointestinal environment. Metals are present in soil in different chemical and physical forms with different solubilities, affecting bioaccessibility. Metals from anthropogenic emission sources are commonly present in a more reactive form than those naturally occurring in minerals. This is because while added metals are sorbed on surfaces in initial stages, metals of natural origin may be incorporated into soil particles, which slows down the desorption process considerably (Ruby *et al.*, 1996). The sorption of metals in soil is, however, a continuum of different processes, occurring simultaneously and at different rates (Sparks, 1999). Soil characteristics such as pH, organic matter and

clay content affect the sorption strength of metals. Lowered pH increases the mobility of metals, while presence of organic matter and clay generally lowers the mobility and increases the metal content because more attractive binding sites are provided (Alloway, 1990; Citeau & Lamy, 2003).

The form in which metals are present in soil also determines their ability to dissolve in the gastrointestinal system and be accessible for uptake (Ruby *et al.*, 1996). The low pH in the stomach renders metals more mobile, but as metals differ in pH dependence of their solubility, the effect of the low pH differs among elements. This has consequences for risk assessment of soil, since the bioaccessible fraction determines the uptake and hence the potential negative health effect. Bioaccessibility studies have been conducted *in vivo* on test animals, but as these methods are time-consuming and expensive, *in vitro* studies have been developed that simulate the gastrointestinal system. In order to be realistic, the *in vitro* system takes into account enzymes and acids present in the stomach and intestine as well as transit times and pH of both compartments, and the gastric and intestinal solutions are mixed at body temperature. While the method does not permit analysis of the fraction that is taken into circulation in the body, it gives an idea of a worst case scenario and the maximum fraction that is accessible for uptake, *i.e.* the fraction that remains dissolved after dissolution, complexing and re-adsorption (Grøn & Andersen, 2003).

## Context of the current work

The work reported in this thesis formed part of the EU-funded research project 'URBSOIL - Urban soils as a source and sink for pollution: *Towards a common European methodology for the evaluation of their environmental quality as a tool for sustainable resource management*'. Six cities across Europe (Aveiro, Glasgow, Ljubljana, Seville, Turin and Uppsala) participated in the project and urban soils in different land use areas were investigated in each city. The overall aim of the project was to identify and document soil quality parameters and their use in urban areas, in order to provide local, national and European authorities with decision support tools for correct planning and sustainable management of the soil resource in cities. While the URBSOIL project focused on urban soil in general, the current thesis specifically investigated soil in children's urban environments and children's exposure to soil metals in Uppsala. Two MSc theses have been published within the URBSOIL project regarding soils in Uppsala. Johansson (2003) focused her thesis on particle size distribution of metals in playgrounds selected from the current study, but used different particle size fractions than those used in this thesis. Franco (2005) studied the origin of metals in roadside soils. Other previous studies in Uppsala have investigated agricultural soils (Klang & Eriksson, 1997) and determined background values of metals (Andersson, unpublished).

Soils from twenty-five playgrounds in Uppsala were sampled in the current work. Sand boxes at the playgrounds were not investigated, since the sand material is replaced frequently. Instead, soil material was collected from eroded



surfaces where children may come into direct contact with soil. The sampled playgrounds were located in five different land use areas, with the aim of collecting soils from sites with varying degrees of metal input. While playgrounds located in industrial and traffic-intense areas and those located on abandoned industrial land were assumed to have elevated metal contents, moderate contents were expected from playgrounds located in public parks, and low contents were expected from playgrounds in forested and residential areas on the outskirts of the city.

The playground soils were fractionated into particle sizes of relevance for children's soil ingestion. Deliberate soil intake was represented by a particle size <4 mm, while involuntary ingestion was represented by a particle size <50 µm. The choice of the smaller size fraction was based on studies investigating soil adherence to hands (Sheppard & Evenden, 1994). The different soil fractions were passed through an *in vitro* gastrointestinal test to obtain values on bioaccessibility of the different metals investigated. Previous *in vitro* studies have mainly investigated contaminated soils from mines, hazardous waste sites, historically contaminated sites and reference materials (Ruby *et al.*, 1993; 1996; Williams *et al.*, 1998; Rodriguez *et al.*, 1999; Ellickson *et al.*, 2001; Schroeder *et al.*, 2003; 2004). This investigation is to my knowledge the first to evaluate metal bioaccessibility in non-point polluted soils using an *in vitro* digestion model. It is also the first to investigate metal distribution in the selected particle size fractions. Since bioaccessibility differs between soils due to the origins of metals and soil chemical parameters, the current study adds valuable information to on-going research on bioaccessibility and potential risks of soil metals. It also provides useful information for ongoing improvement work regarding risk assessment.

## Objectives

The overall aim of the work reported in this thesis was to contribute to the understanding of metal distribution and bioaccessibility in non-point polluted urban soil. The initial idea was that because children are more susceptible than adults to any potentially adverse health effects of metals, both for physiological and behavioural reasons, it was considered relevant to look at metal contents in soils of children's urban environments.

The main objective was to evaluate soil metal content with regard to children's exposure. The specific objectives were to:

- (1) Investigate the origin of metals in non-point polluted soils of urban Uppsala (Paper I)
- (2) Investigate which factors affect the soil metal distribution in non-point polluted urban soil (Paper II)
- (3) Evaluate the difference in metal content between soil particle size fractions of relevance for children's deliberate and involuntary soil ingestion (Paper III)

- (4) Assess the bioaccessibility of As, Cd, Cr, Ni and Pb in non-point polluted urban soil (Paper IV)

The hypotheses of the investigation were:

- ☐ Metals present in urban soil can be identified according to their main natural or anthropogenic origin
- ☐ Present and past land use affects the soil metal content in urban areas
- ☐ The distribution of metals in soil is related to soil particle size distribution
- ☐ The bioaccessibility of soil metals varies with ingested particle size fraction and soil mass.

The elements aluminium (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), tungsten (W) and zinc (Zn) were analyzed in order to obtain information on both essential elements and those that have no biological function or only adverse effects on biological functions. For the bioaccessibility study, the selection of elements was restricted to As, Cd, Cr, Pb and Ni for analytical reasons. Although As is not a metal by definition, but a metalloid, it will be referred to in the text as a metal for simplicity.

## Background

The Papers on which this thesis is based regard two main issues. While Papers I and II regard the origin and present distribution of metals in Uppsala soils, Papers III and IV focus on the exposure of children to metals and evaluate whether the present methods of risk assessment and application of guideline values are viable. The following sections describe the background to the issues underlying the research.

### Urban soils and soil metals

The composition of urban soils differs from that of rural soils, especially with regard to the probability of it having originated from several different locations, and having been mixed with non-soil material (Bullock & Gregory, 1991; Linde, Bengtsson & Öborn, 2001). In an urban area, the term 'soil' therefore includes a wide spectrum of compositions and stages of development, ranging from areas that appear to lack any soil cover, such as demolition sites and brick rubble, to well developed soils with natural profiles, such as the types found in parks and gardens. According to Linde, Bengtsson & Öborn (2001), most city soils contain more coarse-grained material than rural soils. They also include more building waste and other waste materials (Bridges, 1991). Urban soil also often has a different vertical variability than rural soil, resulting from excavation and backfilling, as

well as a more pronounced horizontal variability due to different land uses (Effland & Pouyat, 1997). The most common waste material found in urban soil is building waste (broken bricks, tiles, glass, timber, piping, cable and insulation materials, discarded masses of cement, concrete and plaster). Other sources of waste material in the urban environment include various industries, power stations, oil spills, organic and chemical waste spills, transport systems, scrap yards and waste disposal sites. Other than the solid soil phase, materials derived from the decomposition of wastes may also be found in the gaseous and liquid phases of the urban soil (Bridges, 1991). Even in soils with a seemingly naturally developed profile, remnants of human activity may be found lower down in the profile. According to Mullins (1991), large dense objects tend to sink into the soil at a surprising speed in areas with a high earthworm population. He refers to Darwin's (1882) study of stone slab sinkage rates in a graveyard, which states that dense objects only sink to the depth of earthworm activity (0.5-1.0 m).

In addition to altered composition, urban soils also differ from rural soils with regard to physical properties, with a more compact structure due to treading and soil compaction by vehicles and heavy machinery (Mullins, 1991). Compaction and trampling, together with pollution and construction, also disturb processes carried out by soil organisms. Since soil organisms are responsible for incorporation and decomposition of organic matter in soil, they together with plants play a major role in developing and maintaining a stable soil structure. The altered composition and structure of urban soils can result in decreases in population and diversity of species, which in turn adversely affects certain processes, for example litter incorporation (Harris, 1991). Concomitantly, impermeable surfaces in the urban environment result in scarce vegetation. As a result, urban soils commonly contain less organic matter than the corresponding rural soils (Harris, 1991).

### *Metals in urban soils*

The difference in metal contents between urban and rural soils is the anthropogenic addition to the former from pollution sources both within and outside the urban area. While point-pollution sources spread metals to a restricted and sometimes easily identified area, diffuse sources including long- and short-range atmospheric deposition spread metals to areas located at some distance from their source. Contaminated urban soils are often the result of point pollution, such as industrial activity, where remediation may be necessary to avoid unwanted effects on humans and the environment. The largest sources of diffuse emissions in the urban environment include traffic (including corrosion of road materials and vehicles) and buildings (including paints and different construction materials). A study of the Stockholm area showed that the metal emissions from point sources have decreased markedly since the 1970s, leaving diffuse metal emission as an increasingly important metal source (Sörme, Bergbäck & Lohm, 2001). Other sources of metals to urban soils include buried waste and applications of fertilizers and pesticides (McBride, 1994).

Table 1. Median metal contents ( $\text{mg kg}^{-1}$ ) in urban soils worldwide. All samples are collected from non-contaminated soil

	Population	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	W	Zn
Playgrounds													
Stockholm <sup>1</sup>	760 000			<0.5	23	46	17000		325	13	100		160
Göteborg <sup>2</sup>	481 000		3.6	0.03	3	7				2	2		14
Bergen <sup>3</sup>	239 209		7.7	0.05	11	26		0.01		9	3		51
Swedish cities													
Stockholm <sup>4</sup>	760 000			0.40	30	34		0.16			37		111
Gothenburg <sup>5</sup>	481 000		2.6	0.19	10	18		0.21		6	38	0.05	69
Falun <sup>6</sup>	55 000		13.8	0.59	4	95		0.42	138	3	338		152
Nordic cities													
Oslo <sup>7</sup>	630 260	17200	4.5	0.34	29	24	21100	0.06	438	24	34		130
Bergen <sup>8</sup>	239 209		3.2	0.30	21	29		0.20		13	81		128
Jakobstad <sup>9</sup>	20 810	4400	2.7	0.25	23	22	11600	0.09		8	59	6.90	82
Worldwide cities													
Berlin <sup>10</sup>	3 388 477		4.3	0.41	27	37		0.34		9	109		163
Damascus <sup>11</sup>	1 394 322				51	30				35	10		84
Naples <sup>12</sup>	1 000 449				8	54					184		180
Seville <sup>13</sup>	704 104				39	68	20100		471	22	137		145
New Orleans <sup>14</sup>	469 032			3.60	3	32			134	10	656		373
Tallinn <sup>15</sup>	397 150				33	35			320	15	50		114
Aberdeen <sup>16</sup>	212 125	13897			24	27	18469		286	15	94		58
Gaborone <sup>17</sup>	186 007			1.30	79	35				51	50		175

<sup>1</sup> Berglund et al, 1994

<sup>2</sup> Lax, unpublished

<sup>3</sup> Ottessen et al., 2000

<sup>4</sup> Linde, Bengtsson & Öborn. 2001

<sup>5</sup> Rundquist & Johansson, 2000

<sup>6</sup> Sandberg, 1995

<sup>7</sup> Tijhuis, Brattli & Sæther, 2002

<sup>8</sup> NGU, 1999

<sup>9</sup> Peltola & Åström, 2003

<sup>10</sup> Birke & Rauch, 2000

<sup>11</sup> Möller et al. 2005

<sup>12</sup> Imperato et al, 2003

<sup>13</sup> Madrid, Diaz-Barrientos & Madrid, 2002

<sup>14</sup> Mielke et al., 2004

<sup>15</sup> Bityukova, Shogenova & Birke, 2000

<sup>16</sup> Paterson, Sanka & Clark, 1996

<sup>17</sup> Zhai et al, 2003

In large industrial cities, the number of emission sources is greater than in smaller cities but this does not necessarily lead to higher soil metal contents. Peltola & Åström (2003) reached this conclusion after findings of elevated trace metal contents in a small town in Finland (Jakobstad). They claim that the soil metal content of large cities is not necessarily higher than that of small cities, but that the areas containing elevated metal contents are usually larger. Designated industrial areas are usually located closer to the city centre in small cities, while redundant central industrial areas are often changed into residential areas in large cities, thereby removing or covering contaminated sites, and thus limiting human exposure to contaminated soil.

Metal contents of topsoil from selected cities in different parts of the world are presented in Table 1. The sampling sites were located in residential areas and the metal contents were analyzed using similar digestion methods. Although somewhat different sampling and measurement techniques were used for the results in Table 1, it gives an idea of metal contents in urban soil. The variation in metal contents between the cities shows the complexity of urban soils, and supports Peltola & Åström's (2003) suggestion that the size of the city is not always related to its metal content. For example, Table 1 shows that Berlin, a city with over 3 million inhabitants, has significantly lower Pb contents than New Orleans, a much smaller city with a population just below half a million. Both the Berlin and the New Orleans studies were based on samples from residential areas where children could play. It is apparent that there are several factors that influence the metal contents in urban soil, such as the industrial history of the city, traffic intensity, geochemical background contents, and also the choice of sampling sites.

In a study of metal pollution in Stockholm City, metal contents were found to vary greatly between locations. This was explained by long-term emission of metals to the soil and a variation of land uses over time, which had resulted in soil being mixed and/or moved and polluted soil being mixed with 'clean' soil (Berglund *et al.*, 1994). In a study by Linde, Bengtsson & Öborn (2001), land use was found to be a more significant factor affecting soil metal contents than geographical distance to the city centre in the Stockholm urban area. Wasteland and city centre areas showed elevated levels in their study, while a study of Hong Kong by Li, Poon & Liu (2001) reported elevated metal contents in commercial districts with high traffic emissions, as well as in industrial areas. The Berlin study also found a clear correlation between soil metal contents and types of land use and industry (Birke & Rauch, 2000).

#### *Natural and anthropogenic origin of metals in urban soil*

Metals in urban soil originate from both natural and anthropogenic sources. While all soil metal inputs initially originate from igneous rock formation, the natural pathway is through weathering of minerals where the metal content in soil reflects the metal content in the parent material. The anthropogenic input is through human activity, releasing metal compounds both near and far from their original source. Since anthropogenic activities releasing metals are more concentrated in

the urban environment, urban soils receive a higher load of metals from the immediate surroundings than the corresponding rural soil (Thornton, 1991). Metals are rather immobile once they enter the soil system, which indicates that any transport is likely to be physical (by removing soil mass) rather than chemical (Brinkmann, 1994; ATSDR, 2002). This results in the presence of metal residues originating from discontinued activities in the present soil and an ongoing accumulation of metals in undisturbed soils of the urban environment (Bridges, 1991; Brinkmann, 1994; Mielke & Reagan, 1998; ATSDR, 2002).

Senesi *et al.* (1999) report that metropolitan regions show annual increases in concentrations of Mn, Co, Cr, Be, V, Cd, Cu, Zn and Pb due to atmospheric deposition. Several studies have tried to differentiate between anthropogenic soil metal load and the natural geochemical backgrounds of elements in urban areas. Studies have been carried out in Berlin (Birke & Rauch, 2000), Tallinn (Bityukova, Shogenova & Birke, 2000), Mieres (Loredo *et al.*, 2003) Oslo (Tijhuis, Brattli & Sæther, 2002) and Madrid (De Miguel *et al.*, 1997). All studies concluded that the present soil Cd, Cu, Hg, Pb and Zn contents mainly originated from anthropogenic sources. While all soils were analyzed for Pb and Zn, the Tallinn study did not analyze Cd and Cu, and Hg was only analyzed in three of the studies. Chromium and Mn were concluded to mainly originate from natural sources in Oslo, Madrid (only Mn analyzed) and Mieres, while these metals were concluded to be of mainly anthropogenic origin in Tallinn and Berlin. The Tallinn, Berlin and Mieres studies also concluded that soil As and Ni originated from anthropogenic sources, while these elements were concluded to be of mainly natural origin in Oslo. Arsenic and Ni were not analyzed in the remaining studies.

### **Soil metals and children**

Children are more susceptible to the potential negative health effects of metals in soil than adults, both for physiological and behavioural reasons (Schütz *et al.*, 1997; ATSDR, 2000). It is therefore especially important that soil contents of potentially harmful substances are kept low in areas frequented by children. A child's environment determines the level of exposure to a certain metal. Lead, for example, can be present in the paint of residential houses, day-care centres and the facilities at playgrounds. Even though such paints are now banned, they have been used in the past, with residues left in the soil. Another example is As, which is a component of chromated copper arsenate (CCA) used as a wood preservative. Arsenic-containing wood was previously used for playground equipment, but has today been replaced and must no longer be used for that purpose (KIFS, 1998). A study on playground soil and sand in Bergen, Norway, found elevated concentrations of As from the use of impregnated wood (Ottesen *et al.*, 2000).

Contaminated urban soils have been clearly identified by several authors as a significant source of metal exposure to children (McKone & Daniels, 1991; Berglund *et al.* 1994; Sheppard, 1995; Lanphear & Roughmann, 1997; Mielke & Reagan, 1998; Mielke *et al.*, 1999; 2005). Soil ingestion has been recognized as an equally important exposure route for contaminants in children as water and food

ingestion (McKone & Daniels, 1991), especially for children up to the age of six due to their hand-to-mouth behaviour (Mielke & Reagan, 1998). For Pb, inhalation is a minor exposure route, and after the elimination of Pb from water pipes and tanks, Pb from soil has become a major source of exposure (Filippelli *et al.*, 2005; Laidlaw *et al.*, 2005). Several studies have investigated the relationship between soil metal contents and blood metal contents in children, mostly for Pb (Dugan, 1980; Dugan & Inskip, 1985; Schilling & Bain, 1989; Berglund *et al.*, 1994; 2000; Schütz *et al.*, 1997; Lanphear *et al.*, 1998; Mielke *et al.*, 1999). A study focusing on the contribution of soil Pb to childhood Pb exposure carried out by Mielke *et al.* (1999) concluded that a significant correlation existed between soil Pb levels and blood Pb levels in children aged six years and younger. In a study carried out on blood Pb in Uruguayan children, a negative correlation was found between blood Pb levels and age and was concluded to most likely be due to a more pronounced hand-to-mouth activity, as well as a higher gastrointestinal absorption in younger children compared to older ones (Schütz *et al.*, 1997). In a study on children in Pb-contaminated areas in Sweden, Berglund *et al.* (1994) found that the blood Pb level increased considerably from the age of one, when a child becomes more mobile. The blood Pb level then reached peak values between the ages of 2 and 3 and decreased at the ages of 4 to 5. These studies all suggest that presence of metals in soil can be reflected in children's blood metal levels and that hand-to-mouth behaviour is a significant exposure route to Pb.

Children's small bodies result in a greater contaminant intake per kg body weight, compared to the same contaminant intake in adults. Children also have a developing nervous system that is more sensitive to contaminants. The rapid cell division and growth in children's bodies also present opportunities for genotoxic effects (Klaassen, 1996). Moreover, children have a higher gastrointestinal absorption than adults. Laquatra (2001) reports that while adults absorb 10-20% of ingested Pb, the absorption by children is between 30 and 50%. Children between the ages of 13 and 36 months are also known to have Fe deficiency, which increases gastrointestinal absorption of ingested Pb (Laquatra, 2001).

### *Health effects of metals*

Most metals affect multiple organ systems, but each metal has a critical effect in a specific organ or tissue (Klaassen, 1996). Acute effects of metals are uncommon in the urban environment, but there are several subtle, chronic and long-term effects, such as lowered IQ, that are of great concern. Children's exposure to Pb has received the greatest attention because of its negative effects on the central nervous system (Osman, 1998, ATSDR, 2002). Ingestion of large amounts of Pb may cause anaemia, kidney damage, colic, muscle weakness and brain damage (ATSDR, 2002). After ingestion of smaller amounts of Pb such as Pb containing dust, effects on blood, development and behaviour may occur. Low blood Pb levels may cause fatigue, insomnia, irritability, hyperactivity and effects on hearing, vision and motor functions (Brinkmann, 1994; Osman, 1998). Schütz *et al.* (1997) also report indications of slight hearing impairment and slight renal effects in children having moderately elevated blood Pb levels. Long-term effects of low doses of Pb exposure also include effects on physical and mental growth

including intellectual functioning (ATSDR, 2002; Centeno *et al.*, 2005). Environmental exposure to Pb has decreased significantly over the past twenty years with the removal of Pb from petrol, food cans and other sources, resulting in a reduction in population blood Pb levels of over 80% (Davies *et al.*, 2005). At the same time, the blood Pb level regarded as safe for children has progressively been lowered, from 60  $\mu\text{g dL}^{-1}$  in 1978 to 10  $\mu\text{g dL}^{-1}$  in 1991 (Osman, 1998). In fact, recent research suggests that there may be no safe level of Pb for children (Abrahams, 2002). The present Swedish guideline value for Pb in soil has been set at 80  $\text{mg kg}^{-1}$ . In a risk assessment study conducted by Victorin *et al.* (1990), an even lower guideline value of 30  $\text{mg Pb kg}^{-1}$  soil was recommended, considering children's behaviour and absorption rate.

Health effects from metal exposure other than Pb include neurological damage (Cd, Mn, Hg), kidney damage (Cd, Cu, Hg), stomach ache, nausea, vomiting and diarrhoea (As, Cd, Cu, Zn), allergies (Ni, Cr), skin lesions (As), pancreas damage (Zn), mobility dysfunction (Cd, Mn), liver damage (As, Fe, Cu) and cancer (As,  $\text{Cr}^{\text{VI}}$ , Ni, Cd) (ATSDR, 2002; Centeno *et al.*, 2005; Nordberg & Cherian, 2005). There is evidence of links between stomach cancer incidence and soil Co, Cr and Zn (Davies *et al.*, 2005). A recent study in Nevada, USA, suggests that W and Co may be added to the list of possible carcinogens (Sheppard *et al.*, 2006). They found evidence suggesting that high airborne exposures of W and Co particulates, most likely originating from a nearby hard-metal facility, may be related to childhood leukaemia.

#### *Children's exposure to soil metals*

Children are more susceptible to the negative health effects of soil contaminants not only because of physiological factors, but also because their exposure is greater as they are close to the ground when playing. This may result in soil ingestion as children put dirty hands and objects into their mouths. They may also consume soil directly and eat dropped food (ATSDR, 2000).

Soil ingestion resulting from child hand-to-mouth behaviour is most common in children aged 18 months to 2 years and is considered developmentally inappropriate in children above this age (Ellis & Schnoes, 2005). Stanek *et al.* (1998) performed a study on soil mouthing/ingestion among healthy children aged 1 to 6 in the USA, and found that 38% of the one-year-olds ingested soil at least monthly, while 11% put soil in their mouths daily. The incidence then decreased rapidly with age. The study distinguished between sand/stones and soil/dirt, and the incidence of mouthing sand and stones was greater than that of mouthing soil and dirt (54% monthly and 17% daily).

Several attempts have been made to estimate the amount of soil that children ingest per day, using calculations based on assumptions regarding soil loading on hands, frequency of hand-to-mouth transfer and efficiency of transfer. Estimates have varied between 20-250  $\text{mg}$  soil ingested per day (Kissel *et al.*, 1998). Measurements in faeces and soil of trace elements that are believed to be poorly absorbed in the gut have resulted in similar average daily intakes of between 39



and 271 mg soil per day, with upper percentile values ranging from about 100 to 1400 mg day<sup>-1</sup> in children. Most studies using tracer elements have not been able to successfully differentiate between ingestion of soil and ingestion of dust (Moya, Bearer & Etzel, 2004). However, Calabrese & Stanek (1992) compared faecal tracer ratios from a child with excessive soil intake behaviour and concluded that the predominant proportion of the faecal tracers was of outdoor soil and not indoor dust origin.

Calabrese, Stanek & Barnes (1998) investigated the main soil particle size ingested by children by comparing intertracer variability between a backyard soil sieved to <250 µm and to <2 mm, respectively. They found that the variability was markedly diminished in the smaller size fraction and concluded that the children in the study tended to mainly ingest soil of a smaller particle size. The United States Environmental Protection Agency (USEPA, 2002) has summarised studies of soil ingestion by children by several authors and has set guideline values for estimated soil ingestion rates at a mean of 100 mg day<sup>-1</sup> for children between 1 and 6 years and an upper percentile of 400 mg day<sup>-1</sup>. As a conservative measure they propose a mean value of 200 mg day<sup>-1</sup>.

Deliberate soil ingestion may likely result in ingestion of a larger soil mass as well as a larger soil particle size range than involuntary ingestion. For children who ingest large soil masses, soil metals may be a significant source of the daily metal intake (Filippelli *et al.*, 2005). Pica is a term used for describing deliberate ingestion of large amounts of non-nutritive substances, including soil, and is common in children aged 18 months to two years (Ellis & Schnoes, 2005). USEPA (2002) suggests that a reasonable ingestion rate for children with soil pica behaviour is 10 g soil day<sup>-1</sup>. However, this value was primarily based on one study and one child displaying soil pica behaviour, where the soil intake ranged from 10 to 14 g day<sup>-1</sup> during the second week of observation (Calabrese *et al.*, 1989).

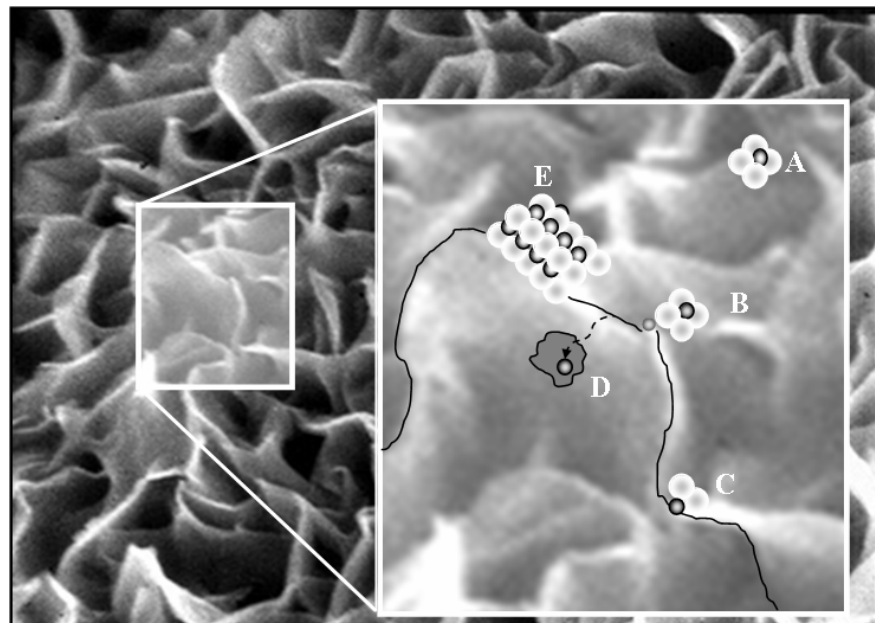
The soil particles ingested involuntarily by children through putting objects and hands into their mouths are usually of a smaller diameter than the average original soil. Small particles have a greater reactive surface area per unit mass and those finer particles may therefore have higher concentrations of contaminants than the original larger soil particles (Sheppard, 1995). It has been found that Pb in small particles is more soluble than Pb in larger particles due to this relatively large surface area. For example, Barltrop & Meek (1979) found that in particle sizes <100 µm, Pb adsorption decreased with increased particle size. This fraction is also easily transported by suspension, and can remain airborne for a long time and enter organisms, including humans, by inhalation (De Miguel *et al.*, 1997).

Sheppard & Evenden (1994) found in studies of the characteristics of soil adhering to skin that the adhesion process tended to exclude particles larger than 50 µm in diameter when dry, regardless of soil type. In addition to small particle size, contaminant enrichment was also found to be associated with high organic matter and extractable Fe content. Up to a 10-fold contaminant enrichment was found when comparing the original soil with the adhering soil. The greatest enrichment was associated with sandy soils, since the bulk of the sorbed

contaminant is on the fine particles that adhere readily to skin but make up only a small fraction of the total soil mass. Lower soil loads on the skin showed greater enrichment, with a marked increase at soil loads below levels that would call for obvious hand washing. Through microscopic inspection it was apparent that clay sized soil particles ( $<2\ \mu\text{m}$ ) fitted in size with the roughness characteristics of the skin, implying that the finest particle sizes may be resistant to washing of hands. This particle size may not be ingested, but may be of greater importance for dermal absorption.

### Soil metal chemistry and bioaccessibility

Understanding sorption processes in soils is necessary to understand the occurrence, mobility and behaviour of metals in soils. When metals enter the soil, either from natural or anthropogenic sources, they are retained and can be rendered relatively immobile because of sorption reactions with the soil constituents (Brinkmann, 1994). However, the mobility and availability of metals in soils differs depending on different sorption and desorption mechanisms. These mechanisms depend on the soil material as well as characteristics of the sorbing metal. Plants can readily take up ionic or soluble complexed forms present in the soil solution (Alloway, 2005), while the acid environment in the stomach can dissolve metals more strongly bound. Figure 1 shows the different sorption mechanisms of a metal ion at the mineral water interface.



*Figure 1.* Sorption mechanisms of metals onto soil minerals: A = diffuse ion swarm; B = outer sphere complexation; C = inner sphere complexation; D = diffusion into mineral lattice; E = precipitation. The black circles are metal ions and the white oxygen ions. The larger picture shows a  $2\ \mu\text{m}$  section of a montmorillonite surface (Eick & Burgholzer, 2005). Adapted from Sparks (1999) and Sposito (1989).

The most mobile metal cations (A) are free to move about in the soil solution, but nevertheless remain near enough to solid surfaces to neutralize their surface charge (Sposito, 1989). Ions can also bind to the surfaces of minerals, organic matter and oxides via a water molecule and form an outer-sphere complex (B) or directly, forming an inner-sphere complex (C). These two processes also neutralize surface charges. Processes (A) and (B) are non-specific with regard to dependence on surface charge and mainly involve electrostatic bonding (Sposito, 1989). The exchange process is rapid, reversible, diffusion-controlled, stoichiometric and there is usually some preference for one ion over another by the sorbent. In general, for a group of elements with the same valence, ions with the smallest hydrated radius are preferred and if the elements have different valence, the higher charged ion is preferred (Sparks, 2003). Reactions with direct bonds (C) are slower, usually non-reversible, more selective and result in metal ions being adsorbed more strongly and to a far greater extent. This type of sorption is also more dependent on pH (Alloway, 2005). Since the adsorbing metal ion bonds directly to the sorbent surface, the tendency for adsorption is dictated by the properties at the surface and the nature of the sorbing metal (McBride, 1994). Inner-sphere complexes are the most common sorption mechanisms for As, Cd, Cr, Cu and Pb on soil minerals (Sparks, 2003).

Metal ions can also diffuse into the mineral lattice (D) or precipitate on the mineral surface (E). Precipitation only occurs when the soil metal load is high, either from natural sources or from pollution (McBride, 1994), and is likely to be less important in the moderate metal content soils of the current study. However, co-precipitates can be formed at lower metal loads where dissolution products of mineral and organic phases catalyze the nucleation step. The formation of co-precipitates is limited by mineral dissolution, so these reactions are often much slower than inner-sphere complexation reactions. Time-dependence is therefore characteristic for precipitation in soils (Sparks, 1999). Solid-phase humic material in the soil can also retain metals by forming complexes, in addition to serving as a charged surface for ion exchange (Alloway, 1990). In addition, soluble organic compounds can form soluble complexes with many metals, preventing sorption onto solid surfaces and enabling leaching down the soil profile. However, the sampling strategy of the current study resulted in samples of low organic matter contents, so these two latter retention mechanisms are likely to be less important in the investigated soils.

There is a continuum of processes between surface complexation reactions and surface precipitation depending on the ratio between sorption sites and number of ions in solution, on the strength of the metal oxide bond and degree of undersaturation of the bulk solution. At low metal loadings, outer- and inner-sphere complexation dominate (Sparks, 2003). These types of reactions are most likely present in non-point polluted soils in the urban environment, such as the soils sampled in the current study. With increased metal loading surface aggregates are formed through nucleation while surface precipitation dominates as metal load increases further (Sparks, 2003).

In soils, which are heterogeneous systems with a range of particle sizes, porosities and multiple retention sites, metal ions are transported and sorbed by the different mechanisms described above simultaneously and at different rates (Sparks, 1999). The type and quantity of the components and the charge and radius of the ion determine the rate of sorption. The rate is rapid for minerals with only external exchange sites while the reaction rate is slower for minerals containing both internal and external exchange sites because of slow diffusion into partially collapsed interlayer spaces. Sorption in the latter type of minerals then involves three different reaction rates with high rates on the external sites, intermediate rates on edge sites and slow rates on interlayer sites (Sparks, 2003). Increased ion charge generally decreases the rate of exchange where ions with small hydrated radius fit well in the interlayer spaces of clay minerals. The often instantaneous ion exchange reaction is usually followed by a slow reaction limited by the transport of the ion to the sorbing surface. This rate-limiting process for ion exchange can result in quite slow reactions where the time scales for soil chemical reactions range from a few milliseconds to years (see Figure 2) (Sparks, 1999).

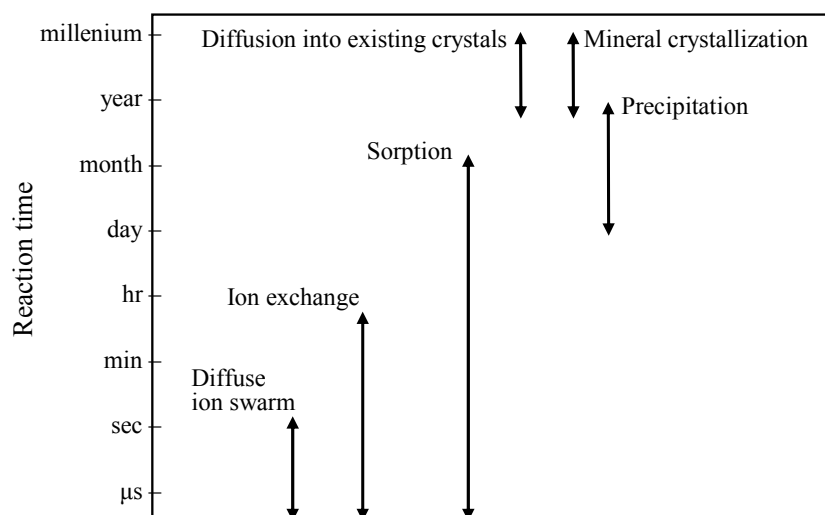


Figure 2. Time ranges needed to reach equilibrium by different soil reactions (after Sparks, 1999).

The majority of ion or organic chemical sorption occurs within a few hours and these fast reactions are usually attributed to high affinity sites. Metal sorption reactions on oxides, hydroxides and humic substances depend on the type of surface and metal but the chemical reaction appears to be rapid (Sparks, 2003). According to Sparks (1999), metal sorption on clay minerals and oxides increases with time. These slow and time-dependent reactions are not yet fully understood but are likely attributable to surface precipitation, interparticle diffusion (diffusion into pores), intraparticle diffusion (diffusion into crystal defects and into the soil particle) and a change in the type of complex (Sparks, 1999, 2003; Glover, Eick & Brady, 2002). Metal sorption on minerals thereby results in a continuum of

processes, from adsorption to precipitation to solid phase transformation (Sparks, 2003).

### *Soil metal bioaccessibility*

Only a fraction of the total metal content of soil is generally bioavailable (the fraction that reaches the blood compartment) and bioaccessible (the fraction available for uptake in the gastrointestinal tract) (Versantvoort, Rempelberg, & Sips, 2000). Whether ingested metals pose a health risk to children or not therefore depends on metal solubility, both in the soil environment and in the gastrointestinal environment. Absorption of ingested elements in humans occurs mainly in the gastrointestinal tract, and can take place along the entire route, including the mouth and the rectum. However, dissolution generally occurs in the acid stomach environment, while uptake takes place in the more neutral intestinal tract (Grøn & Andersen, 2003). Figure 3 shows the processes that take place when soil has been ingested.

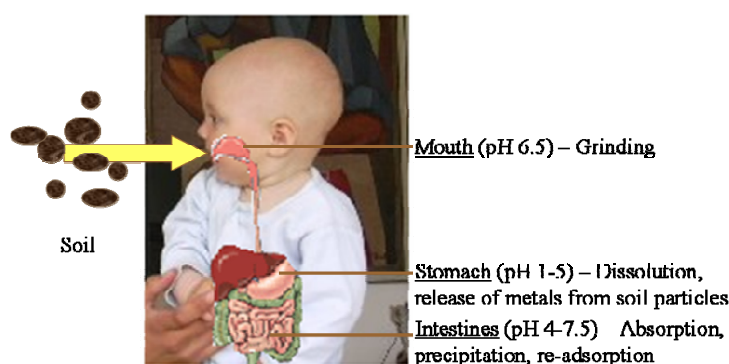


Figure 3. Processes in the gastrointestinal tract following ingestion of soil (Grøn & Andersen, 2003).

### *Solubility in the gastrointestinal tract*

When soil enters the acid stomach environment, labile mineral oxides, sulphides and carbonates release metals and adsorbed organic compounds (Grøn & Andersen, 2003). The dissolution in this phase determines the bioaccessible fraction and depends on the characteristics of the metal itself, the soil matrix in which it is incorporated and the composition of the gastrointestinal fluid. Water-soluble metal ions can be transported into body tissues quite easily, since water is continuously passed through the cell by transport activities. Free ions and small particles are more easily absorbed in the stomach due to their ability to pass through the gastrointestinal walls, while insoluble particles can be absorbed by active transport by binding to transport proteins (Ahlgren, 1996). Active transport can occur if the metal has a similar structure and size to a required element. One example is Cd, which is taken up by the same metal transporter as Fe at low body Fe stores (Gunshin *et al.*, 1997; Tallkvist, Bowlus & Lonnerdal, 2001; Leazer, Liu & Klaassen, 2002).

In the intestinal phase, the speciation of the metal and the gastrointestinal motility are limiting factors for absorption into the human body (Grøn & Andersen, 2003). The absorption of metals in the intestine requires that the metals are dissolved (free or bound to a dissolved carrier such as bile), transported to the gastrointestinal wall and, if bound to a carrier, released at the surface of the gastrointestinal membrane for absorption. The higher pH of the intestinal phase dissolves organic matter, and contaminants bound to it are released. Cationic metals are solubilized by complexation with bile acids and some metals are precipitated by the high pH or by phosphate (Grøn & Andersen, 2003). A re-adsorption of solubilized ions on charged surfaces such as clay mineral and organic matter also occurs at this higher pH. Ruby *et al.* (1996) found that Pb (cation) was removed from the solution by neutralization in the intestinal phase to a greater extent than As (anion), due to adsorption and precipitation reactions occurring for Pb but not for As at neutral pH values.

A main variable in the gastrointestinal environment that affects bioaccessibility is the pH. The pH of the stomach varies with fed and fasting conditions, and is generally lower in the stomach of a child than of an adult (Grøn & Andersen, 2003). According to Ruby *et al.* (1996), paediatric gastric pH under fasting conditions is 1.7-1.8. Following ingestion of food, pH rises to >4 and returns to basal values within two hours as food is emptied from the stomach. The pH in the small intestine is around neutral. Schroeder *et al.* (2003) found bioaccessibility values of 63% for Cd in contaminated soil when simulating gastric extraction without food. When food was added, the bioaccessibility was 38% in the same compartment. For the intestinal phase, the fed and fasting conditions resulted in 13% and 39% Cd bioaccessibility, respectively. Ruby *et al.* (1996) found that the extent of Pb dissolution decreased by 65% when stomach pH was increased from 1.3 to 2.5. The dissolution of As also decreased, but only by 16%. Yang *et al.* (2003) also found greater pH dependence (stomach, intestine and soil pH) of Pb bioaccessibility than As, with lower bioaccessibility at increased pH. A comparison of five different *in vitro* studies also concluded that the differences in bioaccessibility between the different methods were due to differing pH, with low pH producing high bioaccessibility values (Oomen *et al.*, 2002).

The standard procedures for estimating soil Pb exposures in children recommended by the USEPA assume that 30% of ingested soil Pb is bioavailable (Ruby *et al.*, 1996). According to an investigation carried out by the Norwegian Geological Survey (Ottesen *et al.*, 2000) up to 60% of ingested Pb may be absorbed depending on the solubility in the gastrointestinal tract. In the comparison of different *in vitro* methods carried out by Oomen *et al.* (2002), the bioaccessibility of Pb varied from 1-96% depending on soil type and gastrointestinal pH. As stated above, the bioaccessibility, particularly of Pb, is dependent on pH and feeding conditions. It is also dependent on transit time and soil composition. If the transit time through the stomach is fast, dissolution may not be complete. The presence of dissolved phosphate, either from digested food or from the soil, results in very rapid precipitation of Pb as chlorolead phosphate, limiting absorption in the intestinal phase (Grøn & Andersen, 2003).

### Soil variables affecting bioaccessibility

The occurrence and distribution of an element among the various phases present in soil (mineral phases, co-precipitated, sorbed, dissolved and complexed species) determines its bioaccessibility. Changes in distribution and thereby bioaccessibility occur over time, from physical and chemical weathering, biological processes, infiltration of water and anthropogenic activities (Ruby *et al.*, 1999). In order for metals to become bioaccessible in the gastrointestinal tract, they have to dissolve within a specified time and the bioaccessibility is therefore dependent on processes limiting the rate of dissolution. The larger surface area ratio of smaller particles generally enables a more rapid solubilization resulting in greater bioaccessibility. While less soluble minerals are dissolved by surface-reaction controlled kinetics limited by the surface detachment of ions, more soluble minerals dissolve by transport-controlled kinetics where the dissolution rate is limited by the transport of ions away from the saturated layer at the particle surface. While the former reaction is sensitive to transit time in the gastrointestinal tract, the latter is sensitive to the extent of mixing. A combination of both reactions above is limiting for intermediately soluble minerals (Ruby *et al.*, 1999).

As pollutants of anthropogenic origin, metals may enter the soil either in organically complexed form or as metal salts. In the latter case, the metal cations adsorb on mineral and organic surfaces, and are more exchangeable than metals of natural origin. In general, metals from anthropogenic sources are therefore more bioaccessible than metals from natural sources (Grøn & Andersen, 2003). Lead particles in paint, for example, are of a small particle size that renders them more bioaccessible, while coatings of highly bioavailable lead oxide are formed from Pb in batteries, cable coverings, ammunition and solder (Ruby *et al.*, 1999). Metals contained in natural minerals are more stable in the environment and hence they tend to be less soluble and less bioaccessible (Ruby *et al.*, 1996).

Soil properties and metal origin thus influence the bioaccessibility of metals by affecting their form and solubility (Ruby *et al.*, 1996). Studies on the relationship between soil Pb and blood Pb have been carried out in the cities of Falun, Sala and the Stockholm districts of Södermalm and Sundbyberg (Berglund *et al.*, 1994; 2000; Berglund, Sörensen & Vahter, 1995; Bjerre *et al.*, 1998;). These studies show diverse results, implying that bioavailability differs in the respective areas. Although Falun and Sala showed greater soil Pb levels than Södermalm and Sundbyberg, the blood Pb levels in children of Sala were considerably lower than blood Pb levels in both of the Stockholm districts. The blood Pb levels of Falun children were higher than in Sala, although the difference in soil Pb in the two cities did not show a corresponding difference. This is explained by Ahlgren (1996) to be the result of a difference in Pb bioavailability in the cities. Soil Pb in Falun and Sala, both old mining towns, is believed to be strongly bound to different crystalline minerals, while soil Pb in the Stockholm districts mainly originates from traffic. Traffic emissions of Pb are in the form of small particles and are thereby more soluble.

### *In vitro* digestion models

*In vitro* models have been developed in order to try to measure bioaccessibility of soil metals in the laboratory. The technique has been adapted from nutritional studies on uptake of iron from food, and has been applied to investigate gastrointestinal metal uptake from soil (Ruby *et al.* 1993). The *in vitro* techniques are relatively inexpensive and easy to use compared to *in vivo* techniques. Validations against *in vivo* data from studies of pigs and children's blood have shown that the method can predict bioaccessibility (Ruby *et al.*, 1999; Schroeder *et al.*, 2004).

The *in vitro* models simulate the release of contaminants from soil in the acid gastric environment and the neutral intestinal environment and assess the metal content available for absorption (bioaccessibility). Since the model assumes that all metals that are dissolved in the intestinal environment are available for uptake, it simulates a worst-case scenario. The *in vitro* digestion procedure takes into account variables such as human body temperature, soil-to-fluid and digestive juice ratios, pH and transit times in the different compartments, chemical composition of the digestive juices and the mixing that occurs in the human body in order to best simulate soil ingestion with regard to child physiology (Oomen *et al.*, 2003). Most studies have investigated the bioaccessibility of As and Pb. Table 2 shows the results from a number of studies that have assessed bioaccessibility in different materials using *in vitro* tests.

Table 2. *In vitro* study results on bioaccessibility (%) of As, Cd and Pb from different types of soil, measured in the intestinal phase

Soil origin	As	Cd	Pb
Hazardous waste sites <sup>1</sup>		15 – 55	
Hazardous waste sites <sup>2</sup>			1.06
Mining/smelter sites <sup>3</sup>	2.7 - 42.8		
Mine tailings <sup>4</sup>			1.1 - 3.0
Mine waste <sup>4</sup>			4.6 - 8.3
Mine waste <sup>5</sup>	14 - 21		
Mine waste <sup>6</sup>			0.5 – 6
Potteries <sup>7</sup>			28 – 73
Residential/Zn, Pb smelter areas <sup>4</sup>			29 – 54
Residential/Cu smelter areas <sup>4</sup>	44 - 50		
Standard reference material <sup>8</sup>	10.7		65.9

<sup>1</sup> Schroeder *et al.*, 2003

<sup>2</sup> Schroeder *et al.*, 2004

<sup>3</sup> Rodrigues *et al.*, 1999

<sup>4</sup> Ruby *et al.*, 1996

<sup>5</sup> Williams *et al.*, 1998

<sup>6</sup> Ruby *et al.*, 1993

<sup>7</sup> Oomen *et al.*, 2003

<sup>8</sup> Ellickson *et al.*, 2001

As can be seen from Table 2 there is a great variation in metal bioaccessibility between different types of soil. The mine waste soils have relatively low bioaccessibility values compared to those found in residential areas located in the



vicinity of smelters. This difference could perhaps be attributed to similar factors determining the difference found between Stockholm and Sala in the example above. While the metals in the residential areas mainly originate from atmospheric deposition from the nearby smelter sites, which is relatively bioaccessible, the metals found in mine waste originate from stable natural minerals.

### **The Fourth Environmental Quality Objective – a non-toxic environment**

In 1999, Sweden set up fifteen Environmental Quality Objectives (a sixteenth was added in 2005) of which the fourth is a Non-Toxic Environment (Environmental Objectives Portal, 2006a). The objective states that: “The outcome within a generation for this environmental quality objective should include the following:

- ☐ The concentrations of substances that naturally occur in the environment are close to the background concentrations.
  - ☐ The levels of foreign substances in the environment are close to zero and their impacts on the ecosystems are negligible.
  - ☐ All fish in the seas, lakes and watercourses in Sweden are fit for human consumption with regard to the contents of foreign substances.
  - ☐ Overall exposure in the work environment, the external environment and the indoor environment to particularly dangerous substances is close to zero and, as regards other chemical substances, to levels that are not harmful to human health.
  - ☐ Polluted areas have been investigated and cleaned up where necessary.”
- (Environmental Objectives Portal, 2006b)

Several interim targets have been set up to reach the overall goal of a non-toxic environment. Interim targets 6 and 7 consider remediation of contaminated soils and state that “studies will have been carried out and, where necessary, appropriate action will have been taken by the end of 2010 at all contaminated sites that pose an acute risk of direct exposure, and at contaminated sites that threaten important water sources or valuable natural environments, today or in the near future” and “between 2005 and 2010, measures will be implemented at a sufficiently large proportion of the prioritized contaminated sites to ensure that the environmental problem as a whole can be solved by 2050 at the latest.” (Environmental Objectives Portal, 2006c).

At present (2006), 80 000 polluted sites have been identified, of which half may pose risks to humans and the environment (Naturvårdsverket, 2006a). The next step after the identification phase is to classify the polluted sites according to risks regarding humans and the environment into four different risk classes. It is estimated that 1 500 sites will be graded as Risk class 1 and 15 000 sites as Risk class 2 (very high and high risks to health and environment, respectively) (Naturvårdsverket, 2006a). So far, 7000 sites have been classified. Almost half (45%) of the prioritized sites requiring remediation are contaminated by metals. Half of these sites are contaminated primarily with regard to As and Pb, making

up 27 and 23% each, followed by Cr and Hg at 15% each and Cd at 10% (Nahlin & Strid, 2003).

In order to reach the objective of a non-toxic environment within forty years, polluted sites need to be remediated, not only identified and classified. The committee that formulated the environmental objective had assumed that 7000 sites would fall into Risk class 1 and 2. In November 2001, the Riksdag (Swedish Parliament) therefore approved a changed interim target and stated that remedial actions would be initiated at 100 polluted sites and terminated at 50 of these sites by the end of 2005. At present (2006), remedial actions have been initiated at 59 sites and terminated at 31 of these sites (Naturvårdsverket, 2006a). Costs for remedial actions have so far reached 2.5 billion Swedish crowns (SEK). The Swedish Environmental Protection Agency (EPA) has calculated that a further 45 billion SEK will be needed in order to remediate the most polluted sites (Naturvårdsverket, 2006a).

## **Risk assessment**

Risk assessment of contaminated soil is an important tool for evaluating risks to human health and the environment, for prioritizing remediation efforts and techniques, and for evaluating the need for risk reducing actions (Naturvårdsverket, 2005). The two main questions that are targeted in risk assessment of contaminated soil are: 1) What risks do the current contaminant situation pose at present and in the future and; 2) what extent of risk reduction measures is needed to eliminate potential hazards to humans and the environment (Naturvårdsverket, 2005). The difference between human health risk assessment and environmental risk assessment is that the former concerns only one species, humans, and the protection of all individuals, while the latter focuses on protection of many species but not all individuals (Campbell, Chapman & Hale, 2006). The following sections mainly focus on human health risk assessment.

Contaminated soils contain metal contents that exceed the local or regional background value (Naturvårdsverket, 2005). Background values are therefore used to estimate the load from anthropogenic sources in metal-enriched areas. Since metals pose a potential health risk to the environment and humans, especially children, guideline values have been developed to set levels in soil that will not result in any negative effects. The guideline value for use in risk assessment for humans has been developed from calculated maximum tolerable daily intake values (TDI). The following sections describe the background, guideline and tolerable daily intake values and how they were established. Table 3 presents the current background and guideline values used in Sweden.

### *Background values*

The definition of a metal's background level in soil can be synonymous with the metal content in non-polluted soils where the metal content is determined only by the soil's parent material (Welp & Brümmer, 2003). However, it is difficult to

define general background levels because of the regional variation in metal contents due to differences in bedrock composition and the local variation due to soil type. Moreover, the defined level depends on the soil constituent collected, the particle size fraction analyzed and the analytical method used (Salminen & Tarvainen, 1997).

It is not realistic to set background levels at levels corresponding to the soil's level prior to the industrial age, since atmospheric transport has resulted in metal additions to areas located far from the pollution source. An example of this is the 200-fold increase in the Pb content of the Greenland ice-sheet compared to the pre-industrial content (Klassen, 1998). The Swedish EP has therefore included the normal diffuse addition of natural and anthropogenic metals to soil in addition to the metal content originating from the soil's parent material in their definition of background levels (Naturvårdsverket, 1997a). Welp & Brümmer (2003) provide a similar definition, and it should be pointed out that the anthropogenic metal addition is diffuse, and separates the background level from metal contents found in point-polluted sites.

Background levels do not, however, always equal desired levels of metals. Natural levels of metals in soil, even if unaffected by diffuse metal input, can sometimes exceed the guideline values set up by authorities for contamination of soils, as can be seen in Table 3 (Lax, 2002). In Finland, the action limits for soil metals have been revised with regard to natural variations but are still lower than the natural metal contents in large areas (Salminen & Tarvainen, 1997). Arsenic, Cd and Ni are known examples of elements that exceed guideline values in some Swedish soils for geological reasons (Lax, 2002).

Although elevated soil metal contents may result in unwanted effects, an increased metal background level in soil does not necessarily indicate a health risk or a negative impact on the environment. Again, the effect is related to the bioavailability of the soil metal, as many metals occur in non-soluble minerals or oxidation states with low toxicity, where the bioavailable fraction is much smaller than the total metal content. However, there are several examples worldwide of high natural contents that cause severe negative health effects in millions of people. One example is arsenic of geological origin. According to Centeno (2006), the number of people that are exposed to toxic levels of arsenic may equal the total number of people that suffer from cancer, stroke, coronary heart disease, HIV/AIDS and diabetes throughout the world (287 million). Much attention has been given to the increased As contents in the drinking water of Bangladesh and India, but dangerously high levels have also been reported in 22 countries across Africa, Asia, Europe and South and North America (Centeno, 2006).

### *Guideline values*

The Swedish EPA has set up generic guideline values for soil pollutants with regard to three main land uses: 1) Sensitive land use (to be used for crops, residential areas, playgrounds, parks, forestry *etc.* as well as groundwater

Table 3. *Generic guideline values (GV) and background values set by the Swedish EPA. The guideline values are presented with the human toxicological value (HT) and the ecotoxicological value (ET) used in the calculations of the GV. Background values are presented for urban areas nationally as well as for Uppsala's urban area (mg kg<sup>-1</sup>)*

	Sensitive land use <sup>1</sup>			Less sensitive land use <sup>1</sup>			Less sensitive land use without ground water abstraction <sup>1</sup>			Background values					
	HT	ET	GV	HT	ET	GV	HT	ET	GV	Uppsala <sup>2</sup>			Sweden <sup>3</sup>		
										min	med	max	min	med	max
As	0.08	20	<b>15</b>	0.18	40	<b>15</b>	40	40	<b>40</b>	n.d.	8	17	n.d.	3	21
Cd	0.4	6	<b>0.4</b>	0.9	12	<b>1</b>	250	12	<b>12</b>				n.d.	0.23	2.7
Cr	1500	120	<b>120</b>	3000	250	<b>250</b>	-	300	<b>250</b>	10	35	49	4	20	54
Cu	5000	100	<b>100</b>	30000	200	<b>200</b>	-	200	<b>200</b>	2	24	48	1	12	66
Hg	2	5	<b>1</b>	5	10	<b>5</b>	25	10	<b>7</b>				n.d.	n.d.	0.1
Ni	40	100	<b>35</b>	130	200	<b>150</b>	900	200	<b>200</b>	4	21	51	2	14	65
Pb	80	150	<b>80</b>	290	300	<b>300</b>	8000	300	<b>300</b>	1	22	39	n.d.	11	59
Zn	5000	350	<b>350</b>	42000	700	<b>700</b>	-	700	<b>700</b>	30	85	173	7	41	182

<sup>1</sup> Naturvårdsverket, 1997a

<sup>2</sup> Andersson, unpublished

<sup>3</sup> Naturvårdsverket, 1997b

abstraction); 2) less sensitive land use (to be used for industrial and office buildings, roads, *etc.* as well as groundwater abstraction at some distance from the contaminated site); and 3) less sensitive land use without groundwater abstraction (Naturvårdsverket, 1997b). The generic guideline values consider different exposure routes for humans including soil intake, dermal exposure, inhalation of dust particles and intake of drinking water, vegetables and fish, while the protection of the environment considers effects in the area and in nearby surface water. Environmental effects are considered by securing the soil functions with regard to flora and fauna, while surface water is protected by securing all life forms of the aquatic life cycle. Two different values, one regarding the environment and one regarding humans, are calculated, and the lowest of the two is used as a guideline value (see Table 3).

The generic guideline values are intended to be used for assessment of polluted sites and are valid for the whole country. The values regard a level that should not be exceeded in order to avoid unwanted effects of soil pollution and are not levels up to which it is warranted to pollute. They are, however, recommendations and not legally binding. The values are set for the mineral soil layer, above the watertable, analyzed by the methods described within the report or similar methods, and are calculated on an assumption that the total contaminant content is available for spread and uptake. However, synergy effects are not considered (Naturvårdsverket, 1997b).

The generic guideline values have been calculated to be applied to most, but not all, polluted sites in the country. A questionnaire is available to help determine whether the generic guideline values can be used at a specific site. If these values cannot be used because of differences in toxicity, risk of leaching or sensitivity of the area, an extended risk assessment has to be carried out and site-specific guideline values have to be calculated (Naturvårdsverket, 1997b). The site-specific guideline values are calculated in the same way as the generic values, but based on site-specific information including bioavailability of the contaminant(s), exposure routes and the risk of spreading to nearby sensitive biotopes or leaching into groundwater. However, the extended risk assessment should also include risk for presence of undetected contaminants, synergy effects, time aspects regarding spreading, land use, *etc.* Information on soil characteristics such as chemical form, particle size distribution and adsorption pattern of the pollutant also have to be included in order to assess bioavailability and health risks to humans (Naturvårdsverket, 1997b).

#### *Tolerable Daily Intake values*

The human toxicological guideline value is calculated from the maximum tolerable daily intake (TDI) which in turn is derived from toxicological studies. The toxicological studies involve administering a soluble metal salt in feed or water to a test animal. The calculations assume that the bioavailability and bioaccessibility of metals in soil are equal to that of the soluble metal form used in the test matrix (Sips *et al.*, 2001). Since soil includes less soluble metal forms and

there are interactions between dissolved metals and the soil constituents, the risk from soil intake with regard to metals may be overestimated (Ruby *et al.*, 1999).

For human risk assessment, the different exposure routes described above are weighted equally. A reference soil metal content is calculated for each of the exposure routes (including drinking water) which corresponds to an acceptable risk level from each exposure route independently. An integrated guideline value is then calculated from the reference soil content. Because drinking water guideline values are often set to a specified percentage of the TDI, the integrated guideline value is often considerably lower than the TDI and an adjustment is therefore made. Simultaneously, an adjustment is made for elements with high background exposure so that the background exposure and the estimated exposure from the site collectively do not exceed the TDI (Naturvårdsverket, 1997b).

### *Difficulties with the present guideline values*

Many difficulties have been identified in using the current generic guideline values. One problem is that the ecotoxicological values that were used for calculations of the Swedish generic guideline values were in large based on studies carried out in the Netherlands (RIVM), and were thus not specific for Swedish conditions (Naturvårdsverket, 2006b). The aim of the Dutch guideline values was to protect 75% of species. Sweden adopted this value for less sensitive land use and used half the value for sensitive land use (Elert, 2002).

The difficulties with using a generic guideline value also include site-specific characteristics such as main exposure routes and spreading patterns as well as soil characteristics that may differ substantially between sites (Elert, 2002). For example, some generic guideline values for soil have been set to ensure safe drinking water standards, in case the pollutant spreads to a nearby aquifer. At a specific polluted site, this exposure route may not be relevant, and the generic guideline value is therefore lower than necessary for that site.

The authors of the report on guideline values acknowledge that for some elements, the guideline values may be set with excessive caution because of the high level of uncertainty and lack of knowledge at the time of setting the values. As can be seen from Table 3, some unpolluted sites used for sampling for the determination of background values in urban areas exceed the set guideline values set for As, Cd and Ni. The high level of caution used in developing the generic guidelines adds a problem to their applicability, since they currently propose that several non-polluted sites, especially in urban areas, need remediation. In fact, the Stockholm City Development Administration (2006) states that the generic guidelines are as a rule not applicable in an urban area like Stockholm because of the generally increased metal contents compared to background levels. Instead, site-specific values are used for evaluating risks of soil contamination at all potentially polluted sites.

It is generally agreed that at most sites it is not realistic to take expensive and difficult remedial actions to ensure that soil metal contents are below the

background level. However, the present generic guideline values have been the only guidelines available and have had a much larger impact than was originally intended. This is not typical for Sweden. Nathanail & Earl (2001) report similar problems with using guideline values in the U.K. They speak of 'magic numbers' and refer to the loss of context and correct interpretation that occur when a table of guideline values is extracted from its explanatory text. The Swedish guideline values have been used as absolute values and as remediation goals, and have also been used for materials that they were not intended for, such as waste and sediments. There is also in reality a far greater number of land use areas than the three listed in the generic guidelines, which also should allow for more varied guidelines (Elert, 2002). However, a long-term perspective must always be applied, to ensure future use of the site. Because of the many difficulties with using the current generic guideline values, it is common practice to perform a site-specific investigation, which allows for a greater variation of soil metal contents both in depth and within a specific area. The Swedish EPA encourages the use of site-specific values since they provide better knowledge of the site in question (Y. Österlund, pers. comm. 2006). Although the cost for risk assessment is greater if site-specific values are to be calculated, savings may be made in transport and remediation if the assessment proposes a guideline value better adapted to site-specific conditions.

An effect of the low guideline values is the large masses of soil that have to be removed. Although it would be most desirable to re-use polluted soil and remediate polluted areas, a common solution to polluted soil is to extract it and put it on landfill. It is a cheap, fast and simple method compared to remediation, and the soil is at best used as cover material after some soil washing. The dumping on landfills is due both to difficulties with soil washing to an acceptable level and to the fact that there is no market for washed soil (Nahlin & Strid, 2003).

Because of the many difficulties experienced with the generic guideline values, and because the use of site-specific values has become more of a rule than an exception, a new tool for calculating guideline values is under development. The new model is intended to assist and improve the calculations of guideline values by automatically documenting the procedure and by making the decision process more transparent and available for review and discussion. In addition, the tool enables a better understanding of the effects that different parameters may have on the spread of contaminants and the exposure routes that may be most important (Naturvårdsverket, 2005). The new criteria are currently under evaluation and will be officially introduced shortly.

## **Materials and methods**

### **Description of study area and sampling sites**

Uppsala, the city of the current study, is Sweden's fourth largest city with a population of approximately 136,500. It is mainly an academic city with around

37% of its population enrolled or employed at its two universities (Uppsala City Council, 2004). It was founded in the 13<sup>th</sup> Century and developed into a religious and academic centre by being the home of the first Nordic university, which was founded by the archbishop in 1477. Uppsala has a short history of industrial activity, beginning in the later part of the 19<sup>th</sup> century with the establishment of several brickworks and milling industries. The post-glacial clay present in large parts of the city favoured the establishment of brickworks, which resulted in excavation of large areas of what is now the centre of Uppsala, and subsequent addition of foreign soil and waste material to fill the quarries (R. Agius, pers. comm. 2005). Metalworks were the most important industry in the beginning of the 1900s, followed by textile, food and chemical industries. During the second half of the same century most industries moved from the area and the city once again became more of an academic centre (Engström, 2001). More detailed information on the history and geology of Uppsala is given in Paper I.

### *Natural and anthropogenic sources of metals in Uppsala*

Uppsala County sits mainly on granitic bedrock with low metal content. Leptite rock containing Zn, Cu and small amounts of Cd is present in the central area, while scatters of greenstone containing high background values of Cr, Ni and Co are found throughout the county (Möller, 1993). According to Ek (1992), the soils of Uppsala County contain naturally elevated contents of As, Cd, Cu, Co, Cr, Mo, Ni, U and low contents of Hg, Pb and Se. The concentrations of V, W and Zn are in the same range as for the rest of the country. However, Ekelund, Nilsson & Ressar (1993) found in their study that W occurred at slightly elevated contents in the granite bedrock of Uppsala, resulting in elevated soil contents in the vicinity of exposed bedrock.

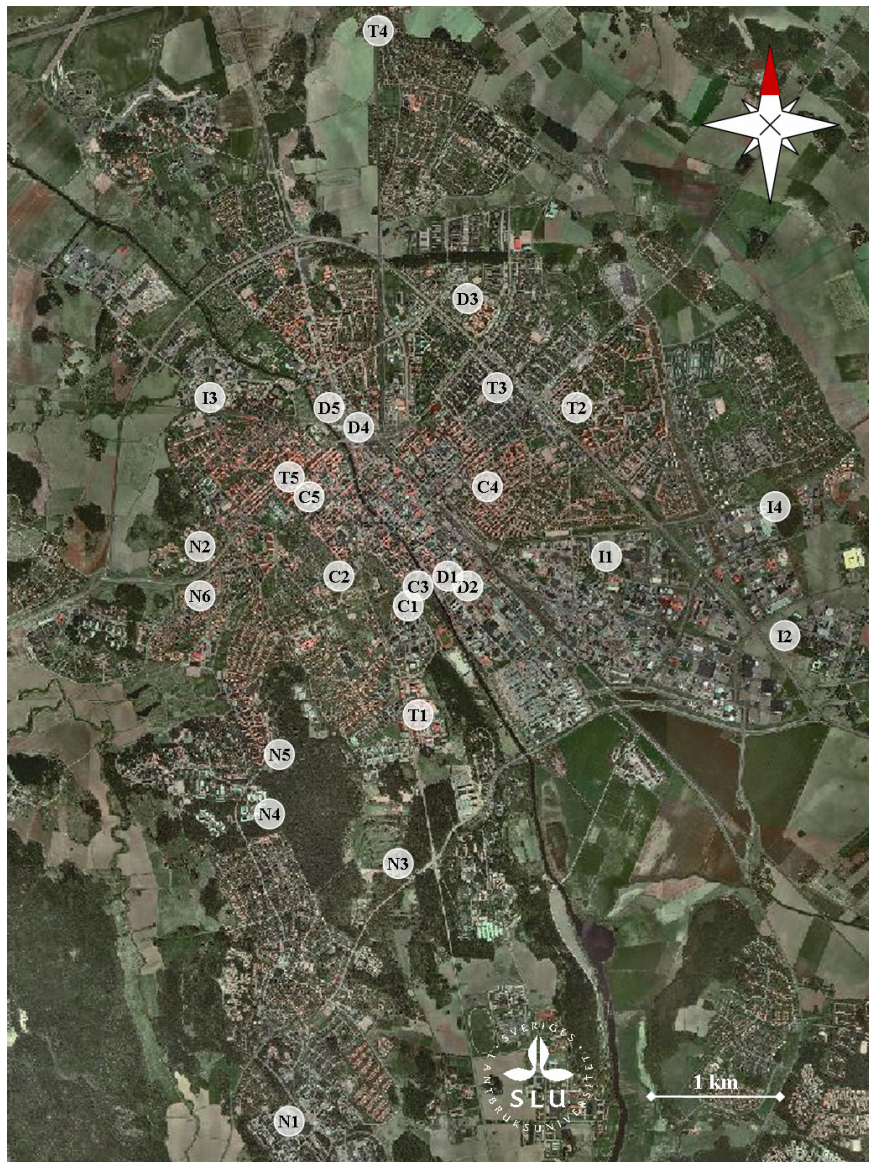
The main anthropogenic point pollution sources of metals located in Uppsala are the sewage treatment plant, the heat and energy plants, car washes and the airforce base. The heat and energy plants are the main sources of Hg, Pb, Cr, Cu, Ni, Zn and As. Important diffuse sources include traffic and long-range atmospheric deposition of metals (Stock, 1996). Other than the heat and energy plants, a major source of Hg to the soils in Uppsala has been the crematorium, which up until 2000 released approximately 8.5 kg of mainly metallic Hg into the air annually. The release of Hg has today decreased to 0.5 kg annually (R. Örnstam, pers. comm. 2003).

### *Sampled playgrounds*

There are approximately 190 day-care centres in urban Uppsala (2005). Figure 4 presents the location of the 25 playgrounds selected for this study. Nineteen of the sampled playgrounds were attached to day-care centres, while six were located in public parks. The playgrounds were located in five different land use areas:

*Discontinued industrial areas.* These playgrounds were selected after review of a report released by Uppsala City Council, investigating discontinued polluting





C1 Engelska Parken

C2 Slottsbaneret

C3 Stadsträdgården

C4 St. Göransplan

C5 Vasaparken

D1 Gudruns förskola

D2 Gunnars förskola

D3 Lötens förskola

D4 Svartbäckens Mont.

D5 Sörgården

T1 Glunten

T2 Kastanjelunden

T3 Kvarngårdesskolan

T4 Storgården

T5 Vindhemsparken

I1 Boländernas förskola

I2 Kastanjen

I3 Klockarparken

I4 Kristallen

N1 Berwalds förskola

N2 Eriksskolan

N3 Rosendal, Liten Lär

N4 Täljstensskolan

N5 Gläntan

N6 Voksenåsen

Figure 4. Location of sampled playgrounds in urban Uppsala.

industries (Lönnerberg, 2001). Day-care centres that were located on the same plot or nearby former polluting industries were selected to represent this land use category and were given the abbreviation D. The previous activities on these sites included metal works, dry cleaners and chemical industry.

*City centre.* Few of the day-care centres located in the city centre of Uppsala have their own playgrounds, but instead use the playground facilities of public parks. Soil from the playground areas of the parks Vasaparken, Engelska Parken, Stadsträdgården and St Göransplan were sampled to represent the city centre and were given the abbreviation C. One playground attached to a day-care centre was also included in the city centre category.

*Industrial land.* Since Uppsala is mainly an academic city rather than an industrial one, the industrial areas in the city are limited and naturally do not hold many day-care centres or playgrounds. Only four playgrounds were found within this category and were selected for sampling. Day-care centres with accompanying playgrounds were found in two of the main industrial areas, Boländerna and Fyrislund, while one selected site was located on the same plot as the Pfizer AB pharmaceutical factory, on the outskirts of the city. A fourth playground was situated in a park bordering an industrial area with several mechanical workshops (Börjetull). The playgrounds located in industrial areas were given the abbreviation I.

*Roadsides.* The selection of sampling sites in this category was based on information from a study on traffic intensities in Uppsala (Nayeri, 2002). Two such day-care centres were adjacent to the most intensely trafficked road in Uppsala, the E4 (28 000 vehicles per day). The other three playgrounds were adjacent to roads with traffic intensities of 14 000, 13 500 and 9 000 vehicles per day. One of these was located in a public park. The playgrounds in this category were given the abbreviation T for traffic.

*Natural land.* This category included playgrounds located in areas with little human impact on the ground cover and not near any point sources, such as in the periphery of forests. Six playgrounds were sampled in this category and were selected through visits to all playgrounds that were located in representative areas. The playgrounds located in these areas were given the abbreviation N.

Since the purpose of the study was to investigate children's exposure to any potential soil metals, the sampling points at each playground were selected on-site by finding spots where the grass had been eroded and the soil was exposed. This was commonly in the vicinity of designated playing equipment; by swings and at the end of slides. No spatial pattern design for sampling was thereby used and no samples were collected from sandboxes. In Uppsala, sandbox sand is replaced every other year (B. Mäkinen, pers. comm. 2004) and is therefore not likely to have elevated metal contents or represent urban soil input. The soil surrounding the play equipment in playgrounds is not commonly replaced, although this might occur when a new playground is being built. The year of construction for each playground was found through various sources: the City Planning Office, the

Recreation and Nature Office of Uppsala City Council, through contacts with the day-care centres and through former employees of Uppsala City Council.

A brief description of the aim of the studies included in this thesis and the methods used for preparation and analysis are presented in Table 4. More detailed information is contained in subsequent sections as well as in the Materials and Methods sections in the Papers I-IV. Table 4 summarizes the different depths, fractions and digestive methods used and the elements analyzed.

Table 4. *Basic description of the different papers presented in the study. Soil from playgrounds within urban Uppsala were used in all experiments*

Paper	Aim: To investigate...	Sampling depths (cm)	Particle size fraction	Digestion method	Elements analysed
I	origin of urban soil metals – natural vs. anthropogenic inputs	0-5 5-10 10-20	<2 mm	<i>Aqua regia</i>	Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, W, Zn
II	factors influencing geographic metal distribution in urban soil	0-5 0-20	<2 mm	<i>Aqua regia</i>	Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, W, Zn
III	metal distribution in particle size fractions relevant to children's soil ingestion	0-10	<50 µm 50-100 µm <4 mm	<i>Aqua regia</i>	Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, W, Zn
IV	bioaccessibility of metals in different particle size fractions	0-10	<50 µm <4 mm	<i>In vitro</i> digestion model	As, Cd, Cr, Ni, Pb

## Soil sampling and sample preparation

Three sampling points were selected at each site and composite samples consisting of five subsamples within 1 m<sup>2</sup> were sampled at each point. A stainless steel auger was used to a depth of 20 cm and the sample core was divided into depths of 0-5, 5-10 and 10-20 cm. This resulted in three depths from three sampling points, in total nine samples from each of the twenty-five playgrounds. The same soil samples were used in all experiments included in this thesis. The soil samples were stored at 4 °C and adequate amounts were extracted from the original soil samples for each of the subsequent experiments. In the study presented in Paper I, all three depths were considered separately with regard to metal distribution, while the results from all three depths (0-20 cm) were averaged for evaluating the origin of the investigated elements. In the study presented in Paper II, only the top 0-5 cm layer was investigated with regard to geographical distribution of metal contents. However, the combined data for the 0-20 cm depth were used for comparison with Swedish guideline values.

The two top layers of 0-5 and 5-10 cm from the three sampling points of each site were combined to give one sample from each playground for the particle size fractionation carried out in the study presented in Paper III. The soil samples were mixed because there was insufficient soil left from the original samples to only fractionate the top 0-5 cm samples. It was considered more appropriate to use the same samples to enable comparison than to re-sample the sites after two years' time.

The soil samples used for the studies presented in Papers I and II were ground and sieved to pass through a 2 mm mesh, while the soil samples were fractionated into particle sizes <4 mm, 50-100  $\mu\text{m}$  and <50  $\mu\text{m}$ , used for the study presented in Paper III. In the study presented in Paper IV, the <4 mm and <50  $\mu\text{m}$  fractions were used. The soils were fractionated by wet-sieving without the use of dispersing agents. This method may result in aggregates of finer particles being included in the larger fractions, but it was used in order to resemble field conditions as much as possible. A more detailed description of the fractionation procedure is found in Paper III.

## Soil analysis

### *General characteristics*

Texture and pH were measured only on the <2 mm soil fraction used for Papers I and II, while dry matter, organic matter content and carbonate content were measured for all experiments. Texture was investigated by using the pipette method (ISO, 2001a). Dry matter was determined by drying the samples at 105 °C overnight. The same samples were then put in a muffle furnace and ignited at 500 °C in order to get an estimate of the organic matter content. The weight loss (loss on ignition) was adjusted for adsorbed and chemically bound water by subtracting a correction constant (Ekström, 1926). The samples were then put back in the muffle furnace at 900 °C in order to get an estimate of the carbonate content. Presence of carbonates was also investigated by addition of 1 ml HCl to each dried sample and detection of any sizzling sound. Soil pH was determined in H<sub>2</sub>O and CaCl<sub>2</sub> (1:5) according to ISO 10390 (ISO, 2002a).

The cation exchange capacity (CEC) was not determined on the sampled soils. In soils with low metal contents, cation exchange is unlikely to limit the solubility of metals, and the low solubility in unpolluted soils is rather explained by specific adsorption mechanisms or precipitation (McBride, 1994). However, a study on five of the soils used here determined CEC at between 25 and 29 mmol kg<sup>-1</sup> in four of the soils and at 16 mmol kg<sup>-1</sup> in one of the soils (Johansson, 2003).

### *Metal analysis*

The results presented in Papers I, II and III were obtained by *aqua regia* (HCl:HNO<sub>3</sub>, 3:1) digestion for total metal contents (ISO, 2002b). *Aqua regia* is a strong acid solution which dissolves all metal phases except those bound to silicate phases. The extract is therefore more correctly termed the pseudo-total content

(Alloway, 1990). The analysis of the bioaccessible metal content (Paper IV) was carried out as an *in vitro* experiment simulating the gastrointestinal tract.

Papers I and II: Soil samples from each of the three depths from the three sampling points at each playground were digested with *aqua regia*, in total 225 samples. Two blank samples and two reference samples were included in the digestion.

Paper III: Duplicates of each of the particle size fractions of <50 µm, 50-100 µm and <4 mm from each of the twenty-five playgrounds were digested with *aqua regia*, giving a total number of 75 samples. Two blanks and two reference samples were included in each digestive run, in total six of each.

Paper IV: The method used for the *in vitro* experiment was developed by Oomen *et al.* (2003) and carried out in cooperation with Agnes Oomen and the Laboratory for Food and Residue Analysis (ARO) at the Dutch National Institute for Health and the Environment (RIVM) in Bilthoven in May 2005. Solutions representing saliva, gastric juice, intestinal juice and bile were sequentially added to the soil samples. The solutions were rotated at body temperature for time periods representing the transit times in the gastrointestinal system: 5 min in the saliva solution; 2 hours in the gastric solution; and 2 hours in the intestinal solution. Figure 5 shows the solutions used for the experiment.



Figure 5. Solutions used in the *in vitro* digestion. From left to right: Saliva, stomach juice, intestinal juice (duodenum) and bile.

The solution was sampled after the intestinal phase, representing the metal fraction available for uptake. Three scenarios were investigated using the *in vitro* method with different soil particle size fractions and soil masses: deliberate pica (excessive) ingestion (<4 mm, 2 g soil), deliberate soil ingestion (<4 mm, 0.6 g soil) and involuntary ingestion (<50 µm, 0.6 g soil). Duplicate samples were used and the procedure was repeated once for each scenario. Duplicate blanks and duplicates of two certified reference soils (Montana 2710 and 2711) as well as two in-house reference materials were included in each digestive run. All runs imitated

fasting conditions to simulate a worst-case scenario. A fed state scenario was also run but the pH effect from the added food was too large to ensure accuracy of the results. They were therefore not used.

### *ICP analysis*

All samples were analyzed for metals by ICP-MS and/or ICP-AES. For the results presented in Papers I, II and III the analyses were carried out at the Environmental Laboratory at SLU in Umeå where the samples were analyzed for Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, W and Zn. In the bioaccessibility experiment presented in Paper IV, the digestates were analyzed for As, Cd, Cr, Ni, Pb and Zn at the Laboratory for Environmental Monitoring (LVM) at RIVM in Bilthoven, Holland.

### **Statistical analysis**

The metal data presented in Papers I, II and III were not normally distributed and non-parametric statistical methods were therefore used throughout. Correlation analysis was carried out using Spearman's Rank Correlation, which presents the measure of the degree of linear relationship between variables, like the Pearson product moment correlation, but uses ranked data. The Mann-Whitney U-test was used for evaluating differences in metal contents between the top and the bottom soil layers (Paper I). In order to identify the total metal distribution in the sampled playgrounds, ranked multiple metal accumulation (rMMA) was used. The method of multiple metal accumulation (MMA) was used by Mielke *et al.* (2005) in order to compare the effect of the sum of metal accumulation in different districts in New Orleans, USA. The method presented in Paper II was used with ranked data in order to standardize the values and to compare the metal load of the different playgrounds.

Reimann & Filzmoser (1999) evaluated common statistical methods and their suitability for use on data without a normal distribution. They found cluster analysis as one of the more suitable multivariate methods. Cluster analysis of observations is used to classify similar observations, while cluster analysis of variables is used to classify similar variables into groups when the groups are initially unknown. Cluster analysis of variables was used to investigate the metal contents with regard to anthropogenic and natural origin. Cluster analysis of observations was used to group the playgrounds with regard to Cd, Cu, Hg, Pb and Zn load. The cluster analysis was performed using ranked data to standardize the values.

The data from the present study were also compared to data from a similar study carried out in Göteborg, Sweden (Rundquist & Johansson, 2000). It was assumed that elements found at significantly higher contents in Uppsala would indicate a geological rather than anthropogenic urban origin (comparison of medians, maximums and 10<sup>th</sup> and 90<sup>th</sup> percentiles).

In order to determine the proportions of metals present in each of the soil particle size fractions (PSF) investigated in Paper III, the metal content of each



fraction was calculated as a percentage of the metal content in the total soil fraction (<4 mm) using equation (1):

$$X (\%) = \frac{\text{PSF (\%)} \text{ of total sample} \times \text{metal content in PSF (mg kg}^{-1}\text{)}}{\text{metal content in total sample (mg kg}^{-1}\text{)}} \times 100 \quad (1)$$

Enrichment ratios were also calculated for the metal contents in each size fraction for the two soils with the highest and lowest sand content, in order to investigate the importance of texture for metal and As distribution in the different soil particle size fractions.

The investigation of the bioaccessible soil metal fraction of the total metal content is presented in Paper IV. The bioaccessibility (BA) was calculated as a percentage of the total metal content measured by *aqua regia* in the study presented in Paper III using equation (2).

$$\text{BA (\%)} = \frac{\text{metal content (}\mu\text{g g}^{-1}\text{) determined after intestinal phase}}{\text{metal content (}\mu\text{g g}^{-1}\text{) determined after aqua regia digestion}} \times 100 \quad (2)$$

The mean bioaccessibility (%) was calculated for each sampling site from the duplicate samples and runs. In order to compare the different size fractions and volumes, the bioaccessible contents expressed as  $\mu\text{g}$  were used. The bioaccessibility of each element from all sites (%) and the bioaccessible metal content of the different scenarios ( $\mu\text{g}$ ) were presented in box plots. Box plots present the shape, dispersion, and centre of a data set. The box represents values between the first and third quartiles, the line drawn through the box represents the median of the data and the lines extending from the box indicate the lowest and highest values in the data set. Outliers are represented by asterisks. For correlation analysis of the metal contents and soil parameters, the Pearson correlation was used.

In the Discussion section of this thesis, the results from Paper I are presented in an individual value plot together with the guideline values for comparison and to illustrate the variation between sites.

Minitab<sup>TM</sup> Statistical Software releases 13.31 and 14 for Windows® were used for the statistical analysis.

## Quality control

### *Sampling*

In order to ensure that representative soil samples were collected, each sample was composed of five sub-samples collected within one square metre, with one sample from each corner of the square, and one sample core from the middle. The five sub-samples were thoroughly mixed prior to soil sample extraction for analysis. Three composite samples were collected from each playground. For the studies

presented in Papers I and II, the three composite samples were analyzed individually, while the three samples were mixed giving one soil sample from each playground for the analyses presented in Papers III and IV.

### *Digestion*

The same analysis results were used for the studies presented in Papers I and II. One in-house reference sample and one reference sample from the Turin team of the URBSOIL project were used to assess bias. Two blank samples were included in the digestive run to assess contamination. Duplicate samples were not included for financial reasons, but each playground was instead represented by three samples.

In the *aqua regia* digestion presented in Paper III, the three soil samples from each playground were mixed, as stated above. Duplicate samples were digested to assess precision. In total, six reagent blanks were included to assess contamination and five in-house reference samples were included to assess bias.

Duplicate samples were used through all analytical runs in the *in vitro* digestion presented in Paper IV and the procedure was repeated for all trials. Duplicate blank samples and reference soils were included in each digestive run. Two of the reference soils were certified materials (Montana 2710 and 2711) while two were in-house reference materials (Oker 11 from Germany and Flanders from Belgium).

The blank values were subtracted from the data prior to further statistical treatment. High Zn contents were detected in the blank samples of the *in vitro* digestion. The Zn data were therefore not used.

### *Analysis*

The Environmental Laboratory at SLU has developed a computer programme (QLab) based on the principles of GUM (1995) and EURACHEM/CITAC (1999) to ensure quality. The programme calculates a 95% confidence interval from the uncertainty of measurement corrected for sources of errors from drift, calibration and bias. For the data presented in Papers I and II, the confidence interval was below 10% for all elements except Hg, which was found at 19%. For the data presented in Paper III, the confidence interval for all elements except Hg was less than 10%, while for Hg and W it was 22 and 14%, respectively.

The RVA laboratory at the RIVM is accredited according to ISO 17025 (ISO, 2001b) and a routine method was applied for analysis of the samples in the current study. For quality control aspects, the method is validated for the limit of detection, reproducibility, repeatability, recovery and trueness. The measurement uncertainties were 9% for As, Cd, Cr and Zn, 10.8% for Pb and 12.7% for Ni.



## Results and Discussion

This section presents the most important findings from each of the experiments carried out and a discussion on conclusive findings. A more general discussion on the significance of the results with regard to on-going risk assessment is made in a subsequent section.

### Uppsala urban soil

As discussed above, there are several soil characteristics that separate urban soil from naturally developed soils. The results from the current studies are presented in Table 5 and showed that Uppsala is not an exception.

Table 5. *Organic matter content (%), pH, texture and particle size distribution (%) in the different soil depths analysed*

Depth	0-5 cm			5-10 cm			10-20 cm		
	min	mean	max	min	mean	max	min	mean	max
pH H <sub>2</sub> O	4.7	7.1	8.1	4.6	7.2	8.1	4.8	7.3	8.4
LOI (%)	1.4	6.8	12.7	1.4	5.1	8.7	1.0	4.1	8.0
Depth	0-10 cm			10-20 cm					
	min	mean	max	min	mean	max	min	mean	max
Texture analysis (%)									
Clay (<2 µm)	7.7	22.1	35.4	8.3	26.7	44.8			
Silt (2 µm-20 µm)	11.1	23.7	41.0	13.9	28.0	45.4			
Fine sand (20 µm-200 µm)	13.7	29.6	50.1	9.6	25.8	45.7			
Coarse sand (200 µm-2 mm)	6.0	16.7	31.8	1.4	13.9	35.7			
Depth	0-10 cm								
	min	mean	max	min	mean	max	min	mean	max
Size distribution (%)									
<50 µm	7	23	42						
50-100 µm	5	10	16						
100 µm-4 mm	47	63	73						
>4 mm	0	5	13						

The relatively low content of fine particles in the sampled soil is contradictory to the large presence of glacial and postglacial clay in the area. The north-eastern part of Uppsala city is dominated by postglacial clay (Figure 1 in Paper I), with clay contents up to 60%. The esker that runs through the city is made up of glaciofluvial deposits overlain with clay, while the western part rests on glacial clay with clay contents of 45-80% (Gretener, 1994). The soils in the present study displayed average clay contents of 22% and a dominance of particles sized >50 µm. The finer particles were also more abundant in the bottom layer.

The relatively low presence of fine particles in the sampled soils indicates that foreign material has been added or mixed with the original soil, which is a common practice in urban areas. In fact, large parts of the central area of the city

were excavated in the 19<sup>th</sup> century for brick and pottery making, thereafter the quarries were filled with foreign material, most likely waste (R. Agius, pers. comm. 2005). Considering the location of the sampled sites in playgrounds, it is also likely that sandbox sand has been added to the soil by children playing nearby, increasing its content of larger particles, especially in the top layer. A contributing factor for the slight difference in particle size distribution between the top and the bottom layer is the lack of vegetation cover, which enables splashing raindrops to break up aggregates and wash finer particles downwards in the profile (Craul, 1985).

### Metals in Uppsala urban playground soil

Although Uppsala is Sweden's fourth largest city, it is relatively small, with a population of 136,500. Despite its main history of academic and religious importance, the short time period (~100 years) of significant industrial activity has left its marks on Uppsala's soil. In order to put the metal contents of Uppsala's playgrounds in relation to soil metal contents in other cities, the results from the current study (Table 6) can be compared to those of other cities (Table 1). Such a comparison shows that Uppsala does not have exceptionally high or low contents of any metal.

#### *Natural and anthropogenic origin of metals in Uppsala playgrounds (Paper I)*

In the study presented in Paper I, an attempt was made to distinguish between metals of natural and anthropogenic origin. Results from a study in Göteborg,

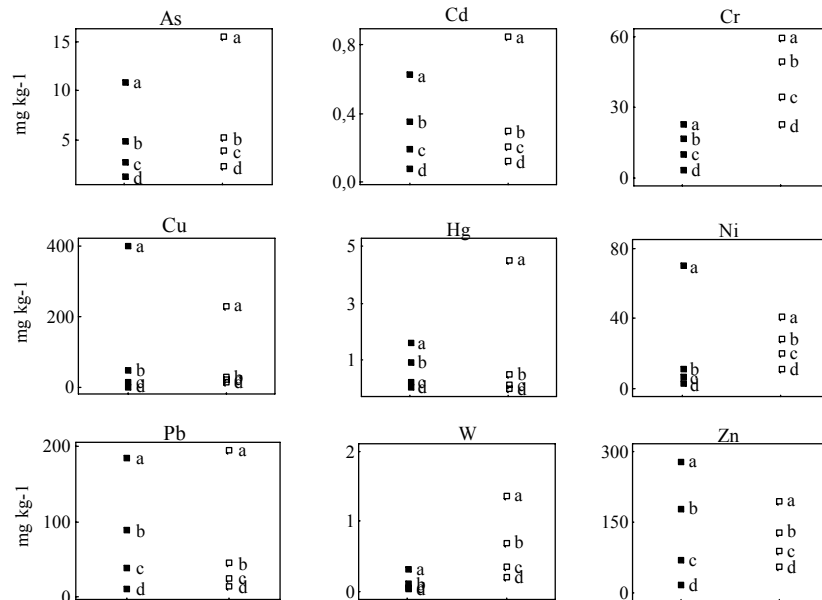


Figure 6. Comparison between maximum (a), 90th percentile (b), median (c) and 10th percentile (d) of metal contents in Göteborg (■) and Uppsala (□). 0-20 cm.

Sweden's second largest city were chosen for comparison. The Göteborg samples were collected and analyzed in a similar way compared to the methods used in the Uppsala study (Rundquist & Johansson, 2000). It was assumed that metals present at significantly higher contents in Uppsala compared to Göteborg (a larger and more industrialized city) would indicate a natural origin of those elements. Figure 6 shows a comparison of nine elements in Uppsala and Göteborg.

All elements except Hg and Pb had higher median contents in Uppsala than in Göteborg. Median contents of W were 700% higher in Uppsala, while Cr and Ni were found at 400% higher and As, Cu and Zn at 150% higher contents. Mercury and Pb were enriched in the Göteborg soil by 150%. Considering the large differences in Cr, Ni and W between the cities as well as findings by other authors on elevated contents of these metals in the Uppsala area (Ek, 1992; Möller, 1993; Ekelund, Nilsson & Ressar, 1993) it suggests that they are mainly derived from natural rather than anthropogenic sources. The similar median contents of As, Cu, Hg, Pb and Zn in the two cities suggest that these metals either mainly originate from anthropogenic sources, common for the two soil environments, or that the background contents are similar for the two cities. The Uppsala and Göteborg data are presented in Table 6 together with urban background values and metal contents of agricultural soil both nationally and in the Uppsala area.

Table 6. Median urban soil metal contents ( $\text{mg kg}^{-1}$ , Al & Fe %) in Uppsala playgrounds and Göteborg together with background values and mean metal content in agricultural soils nationally and in Uppsala

	Urban soil			Urban background values		Agricultural soil		
	Uppsala playgrounds	Göteborg <sup>1</sup>		Uppsala <sup>2</sup>	Sweden <sup>3</sup>	Uppsala <sup>4</sup>	Sweden <sup>4</sup>	
Depth (cm)	0-5	5-10	10-20	0-20	0-20	0-20	0-20	0-20
Al	1.84	2.25	2.47					
As	3.46	3.91	3.86	2.6	8	3	4.4	4.0
Cd	0.21	0.21	0.22	0.19		0.23	0.27	0.23
Cr	31.6	37.7	43.3	10	35	20	40	20.5
Cu	25.4	25.6	26.0	18	24	12	29	14.6
Fe	2.49	2.76	3.03					
Hg	0.14	0.15	0.13	0.21		n.d.	0.04	0.04
Mn	494	526	573				518	422
Ni	18.5	21.1	23.2	6	21	14		
Pb	25.5	24.6	26.4	38	22	11	21	17.1
W	0.35	0.35	0.35	0.05				
Zn	84.0	90.4	98.6	69	85	41	95	59

<sup>1</sup> Rundquist & Johansson, 2000

<sup>2</sup> Andersson, unpublished

<sup>3</sup> Naturvårdsverket, 1997a

<sup>4</sup> Eriksson, Andersson & Andersson, 1997

A study on trace elements in Swedish agricultural soils carried out by Eriksson, Andersson & Andersson (1997) concluded that contents of Cd, Hg, Pb and Zn have been largely affected by anthropogenic additions. The soil contents have increased by 33, 46, 14 and 10%, respectively for the four elements during the past

century. In the study, the authors found that the contents of the remaining trace elements (As, B, Cr, Cu, Mn, Se) were largely affected by the parent material. Chromium was found at elevated contents in the Uppsala region due to natural sources, supporting the assumption on the origin of Cr stated above. The urban background values also showed a higher Cr content in Uppsala than in Sweden in general. However, the urban background values determined for Uppsala as well as the agricultural soil contents show elevated contents of most elements compared to the national contents.

The background values include diffuse metal addition, which should be higher in larger cities. Although Uppsala is not a large city, it is the fourth largest of the 22 cities sampled for the study of background values, which could explain its elevated metal contents compared to the national values. According to Eriksson, Andersson & Andersson (1997), elevated metal contents in agricultural soils in Uppsala are most likely due to the high clay content of soils in the region, favouring metal binding. The large difference in soil characteristics between urban and agricultural soils also makes comparison difficult. Moreover, while agricultural soils commonly contain significant contents of organic matter, which effectively retains metals, the urban soils investigated had very low organic matter contents. However, Table 6 shows that contents of all elements except As in the playground soils of Uppsala corresponded well with the background values determined for urban Uppsala.

In order to try to determine common main origin of the remaining elements of the Uppsala study, a cluster analysis was carried out. The dendrogram is shown in Figure 7.

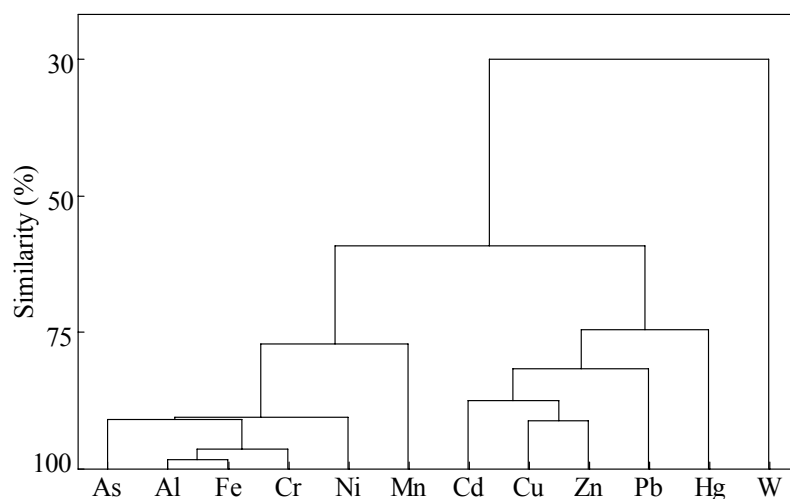


Figure 7. Cluster analysis of metals, 0-20 cm depth ( $n=75$ ) showing two separate clusters with similarities above 75%. The left cluster holds elements mainly of natural origin, while the right cluster shows elements of mainly anthropogenic origin.

The cluster analysis on the Uppsala data divided the metals into two main groups with a similarity of around 75%. The metals suggested as being of mainly natural origin from the comparison with the Göteborg data were clustered together, with Al, Fe and Mn. The separation of W into its own cluster is likely due to its differing chemical properties. All elements presumably of natural origin except Mn were found at a greater similarity (90%) than the elements of the other cluster, presumed to be of anthropogenic origin. This suggests that there are several sources of these elements and what clusters them together is the lack of similarity with the elements of the other cluster, rather than a similarity between the metals within the cluster.

According to Baize & Sterckeman (2001), there is a linear relationship between the Fe content of a soil and its contents of Cu, Cr, Ni, Pb and Zn, which can be used to determine natural origins of these elements. A strong significant correlation was found between Fe and Cr and between Fe and Ni, while no correlation was found for Fe and Cu, Pb or Zn, which further supports the division of these elements into anthropogenic and natural origins presented above. Moreover, findings by De Miguel *et al.* (1997), Senesi *et al.* (1999) and Tijhuis, Brattli & Sæther (2002) on the origin of urban metals in Madrid, Mieres and Oslo respectively, support the division of the investigated metals into the two clusters identified in the present study.

#### *What determines the metal distribution in urban playground soil? (Paper II)*

The original hypothesis for the study presented in Paper II was that the land use in which the sampled playgrounds are located would determine the level of soil metal input. However, the results showed that there was no correlation between the land use categories and the metal amounts found in the soil. Instead, the metal content was found to be more determined by the soil's clay content and the year of construction of the playground. While enriched clay content increases the soil's adsorption capacity, the general immobility of metals once in the soil enables an accumulation over time, resulting in higher metal contents in older soils. Moreover, the older soils were present on-site during the relatively short period of significant industrial activity in Uppsala, while fresh soil has been added to the more recent playgrounds built during the second half of the 1900s.

The results of the current study deviate from other authors' findings on relationships between land use and soil metal content (Linde, Bengtsson & Öborn, 2001; Li, Poon & Liu, 2001). It should be noted that Uppsala is not an industrial city with large internal pollution sources, but instead receives its greatest metal input from long distance atmospheric deposition, which is most likely deposited evenly over the city. Age of land and soil clay content may therefore be relatively more important factors for metal distribution in soils of cities without major internal pollution sources.

The relationships between the ranked multiple metal accumulation (rMMA) of each playground and its clay content and pH, as well as the year of construction

are displayed in Figure 8. Four of the five playgrounds located in the city centre were found to have high rMMA values. The city centre playgrounds were expected to have enriched metal contents due to higher traffic intensities and the more central location of industrial areas in the past. However, two of the playgrounds located on natural land, at some distance from any metal sources, were found to have the third and fourth highest rMMAs. Likewise, several of the playgrounds located in land use areas with expected high metal inputs were found to have low rMMAs (traffic, discontinued and present industrial land).

Figure 8 shows a general decrease in clay content with decreasing rMMA value, which suggests that the clay content is a more important factor for metal and As content than surrounding land use. Strong correlations were found between the clay content and contents of As, Al, Cu, Fe, Ni, Pb and Zn. Tungsten was found to correlate to the general parameters in the opposite way to the remaining elements and was also found at low contents where the remaining elements were elevated. This further indicates a stronger association between metal content and soil conditions on-site than with input from surrounding pollution sources in Uppsala.

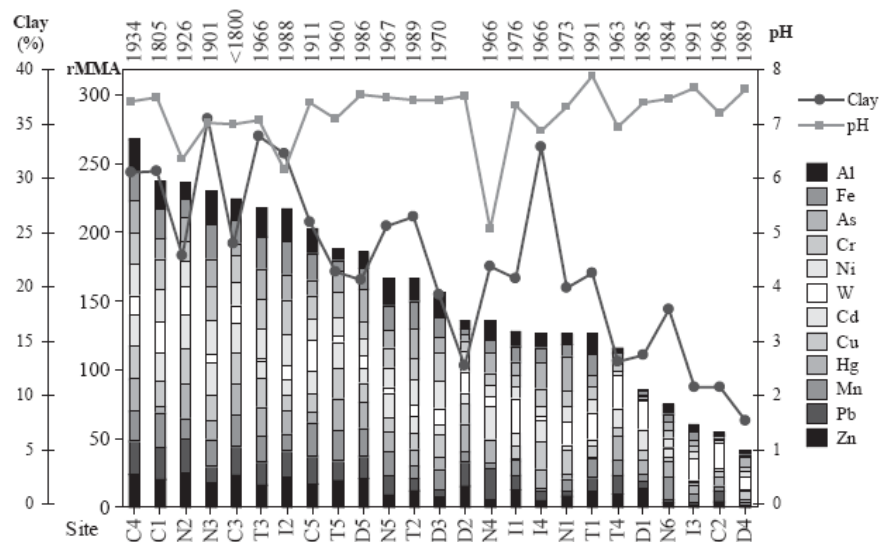


Figure 8. Bar chart of ranked multiple metal accumulation (rMMA) (0-5 cm) for each playground together with pH, clay content (%) and year of construction (C=city centre, I=industrial area, T=roadsides, D=discontinued industrial land, N=natural land).

Another important factor is likely to be the age of the playground, since the playgrounds with high rMMA values were in general also the oldest. Since metals are rather immobile once they reach the soil system, any relocation is likely to be physical rather than chemical. Metals disseminated on the soil surface in the past are therefore still present in the soil today. It could explain why the playgrounds located on natural land, expected to have low metal contents, were found to have high rMMA values. Those playgrounds have not been built up, like the playgrounds constructed on old industrial sites, and the children play on soils that have not been imported and renewed.

The four playgrounds located in public parks had high rMMAs. Those areas have been kept as green areas as the city expanded around them. This further explains why several of the playgrounds located on past and present industrial land as well as near trafficked roads do not have the expected high metal contents. It is common practice to import soil for the upper horizon to a site for new constructions. By the time most of the sampled playgrounds with low rMMA values were built, the industrial days of Uppsala were past by about one century.

A cluster analysis was performed in order to evaluate the distribution of Cd, Cu, Hg, Pb and Zn (previously concluded to be of anthropogenic origin) among the sampled playgrounds (Figure 9). The analysis divided the sites into two main clusters, where the sites in cluster A had low contents of these five metals. These sites were also found to have low rMMA values, with the exception of sites T2 and D3. The high rMMA values for these two sites were due to high contents of Fe, As and Cr, Ni, respectively. The sites in cluster B had elevated contents of the metals of anthropogenic origin. All sites but T4 had high rMMA values, and the division of T4 into cluster B was likely due to its high contents of anthropogenic metals in comparison with its contents of natural elements. The sites with elevated anthropogenic metal contents in cluster B also had elevated contents of the natural elements, which explain the similarity in distributions between the cluster analysis and the rMMA. It indicates that the metal content of the sampled sites was not mainly determined by point-pollution sources, which would be apparent from a metal distribution by land use, but was more dependent on the soil characteristics on-site as well as addition from diffuse pollution sources.

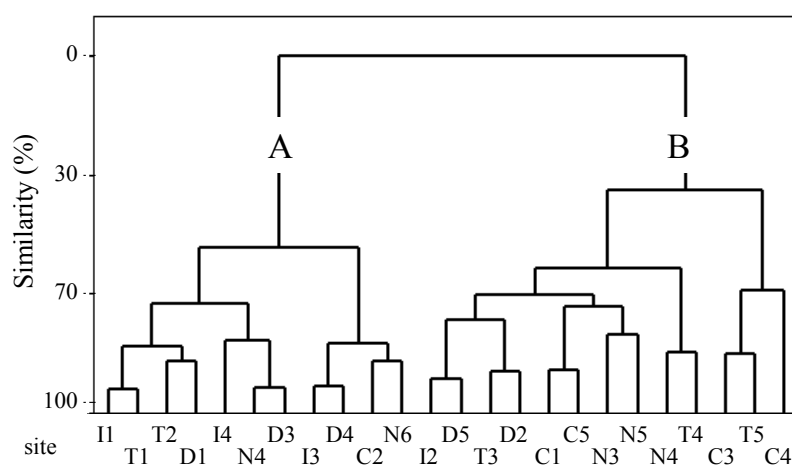


Figure 9. Dendrogram of cluster analysis of observations; Cd, Cu, Hg, Pb and Zn, showing A) sites less affected by anthropogenic metals and B) sites with elevated contents of anthropogenic metals.

## Soil metals and children's soil ingestion

While most playgrounds in Uppsala had metal contents below the generic guideline values, there were a few that exceeded the Swedish guideline values for As, Cd, Cu, Hg, Ni and Pb. This finding was surprising, in particular since these playgrounds were mainly located in seemingly unaffected areas; in forested areas classified as natural land use. Further studies were carried out to assess the metal content with regard to soil particle sizes of relevance to children's soil ingestion, as well as the bioaccessibility of the soil metals detected.

### *Differences in metal contents between soil particle size fractions (Paper III)*

In the study presented in Paper III, the difference in metal contents between different particle size fractions of relevance to children's soil ingestion was investigated. The <50 µm fraction represents soil that may be involuntarily ingested, since particles in this fraction adhere easily to hands. The <4 mm fraction was chosen to represent soil that may be ingested deliberately. A third size fraction of 50-100 µm was included to represent soil particles that are easily transported by suspension to locations away from the original source. All fractions were measured after dissolution in *aqua regia*, which is comparable to the method recommended for using the guideline values (Lax, unpublished). The results are presented in Table 7 together with enrichment ratios between the different size fractions.

Table 7. Median metal contents (mg kg<sup>-1</sup>) in each of the investigated soil particle size fractions together with the median ratios between the different size fractions (0-10 cm depth, n=25)

	mg kg <sup>-1</sup>				median ratio		
	<2 mm	<4 mm	50-100 µm	<50 µm	<2mm: <4 mm	<50 µm: <4 mm	<50 µm: <2 mm
Al	20100	25214	23499	37250	0.8	1.5	1.9
As	3.83	3.26	3.22	5.47	1.2	1.7	1.4
Cd	0.21	0.20	0.22	0.30	1.1	1.5	1.4
Cr	34.6	40.2	33.8	64.0	0.9	1.6	1.8
Cu	24.8	25.4	28.3	43.1	1.0	1.7	1.7
Fe	26960	29900	27454	43550	0.9	1.5	1.6
Hg	0.14	0.51	0.52	0.66	0.3	1.3	4.7
Mn	508	713	960	1445	0.7	2.0	2.8
Ni	20.1	21.5	20.3	36.1	0.9	1.7	1.8
Pb	23.7	25.9	25.6	38.4	0.9	1.5	1.6
W	0.35	0.27	0.50	0.32	1.3	1.2	0.9
Zn	88.2	83.5	75.5	147	1.0	1.7	2.1

The study found that there was little or no difference in metal contents between the 50-100 µm and the <4 mm fractions as well as the <2 mm fraction measured in previous experiments. This suggests that analysis of the <2 mm fraction used for risk assessment purposes accurately predicts the metal content in soil ingested



deliberately. However, the <50  $\mu\text{m}$  fraction had on average 150% higher metal contents compared to the larger size fractions. The enrichment in the finest fraction is likely attributable to the affinity of metals to bind to small particles because of the relatively larger surface area and the data demonstrate the difference in metal content obtained from analyzing different soil particle fractions.

The study also found differences in metal content of the finest size fraction related to texture of the total soil sample. While the metal contents in the two larger size fractions displayed an expected increase in metal content with decreased sand content of the total sample, the metal content of the smallest size fraction showed the opposite relationship; samples with a high sand content displayed elevated metal contents in the smallest size fraction compared to samples with low sand content, corresponding to high clay content. Enrichment ratios between the different size fractions were calculated for the two soils with the highest and lowest sand contents (58% and 13%, respectively) and are displayed in Table 8.

Table 8. *Metal enrichment ratios for different soil particle size fractions in two soils with high and low sand content (58% and 13%, respectively)*

	High sand content (58%)			Low sand content (13%)		
	<2 mm : <4 mm	<50 $\mu\text{m}$ : <4 mm	<50 $\mu\text{m}$ : <2 mm	<2 mm : <4 mm	<50 $\mu\text{m}$ : <4 mm	50 $\mu\text{m}$ : <2 mm
Al	0.6	1.7	2.8	0.8	1.0	1.3
As	0.3	2.8	3.1	1.1	1.0	0.9
Cd	0.3	2.7	3.9	1.3	1.0	0.8
Cr	0.3	2.2	2.9	0.9	1.0	1.2
Cu	0.3	2.5	3.8	0.9	1.0	1.1
Fe	0.8	1.7	2.3	0.4	1.1	1.2
Hg	0.0	3.3	-	0.4	0.9	2.3
Mn	0.3	2.3	4.0	0.6	1.4	1.8
Ni	0.3	2.4	3.1	0.9	1.0	1.1
Pb	0.3	2.7	3.7	1.1	0.9	0.9
W	1.1	1.2	0.9	1.5	1.1	0.7
Zn	0.3	2.5	3.1	1.0	1.1	1.0

The enrichment ratios showed that while there was little or no difference in metal contents between the smallest and largest particle size fractions in the soil with a low sand content, the high sand content soil had on average 250% higher metal content in the <50  $\mu\text{m}$  fraction than in the <4 mm fraction, and on average 300% higher metal contents than in the <2 mm fraction (Table 8). This is probably due to the preference of metal ions to sorb to small-sized particles, and in a sandy soil the scarcity of attractive binding sites results in a concentration of metal ions on the smallest particles. The results support findings by Sheppard & Evenden (1994), who demonstrated that the highest metal enrichment in soil adhering to skin was associated with sandy soils, since the bulk of the sorbed contaminant is on the fine particles that adhere readily to skin but make up only a small fraction

of the total soil mass. The findings that the low sand content soil showed insignificant differences in metal contents between the particle size fractions suggest that in soils with low metal load and a large proportion of fine particles, the effect of particle size is diminished since enough of the most attractive binding sites are available.

The results of the study have implications for risk assessment with regard to children's soil intake, since a soil analysis on the recommended size range of <2 mm will generate a total metal content quite different from the metal content in the smallest-sized particles of the same soil. Stanek *et al.* (1998) found that children more often put sand and stones in their mouths than soil and dirt. While parents are likely to hinder children from swallowing stones and large amounts of sand, children may well swallow the smaller particles attached to the ingested sand and stones, which may hold the highest metal content.

#### *Effects of soil mass and particle size on metal bioaccessibility (Paper IV)*

As has been stated above, the potential health risks for children from soil ingestion depend on the bioaccessibility of the ingested metals in the human body. The soil particle size fractions investigated in Paper III representing deliberate and involuntary soil ingestion were in the study presented in Paper IV investigated with regard to bioaccessibility using an *in vitro* digestion model. Differences between particle size fractions and between ingested soil masses were studied. The results from the *in vitro* digestion were compared with the total contents obtained in the study presented in Paper III, giving a percentage bioaccessibility of the different elements.

Figure 10 presents the results from the *in vitro* analyses of three different intake scenarios for As, Cd, Cr, Ni and Pb. The bioaccessibility as a percentage of the amount obtained from the *aqua regia* digestion is presented on the y-axis, while the letters on the x-axis represent three different intake scenarios: A = deliberate intake of 2 g soil (pica behaviour) of the particle size <4 mm, B = deliberate intake of a smaller amount of soil (0.6 g) sized <4 mm, and C = involuntary intake (0.6 g) of small particles (<50 µm).

The results show that the bioaccessible fraction was generally quite low for Cr, Ni and Pb, while Cd and As showed higher bioaccessibility. The difference between the elements is probably due to differences in sorption behaviour. As stated above, metals derived from anthropogenic sources are commonly more bioaccessible than those derived from natural sources. The results support this assumption on bioaccessibility with regard to origin for Cd, Cr and Ni. Since metals of mainly natural origin have been on-site for a longer period of time than those of anthropogenic origin, the metals of natural origin are more likely to be less soluble than the more recent inputs from anthropogenic sources because of rate limiting processes. The rate of diffusion into pore spaces and particles decreases with increasing ionic diameter: Pb>Cd>Ni>As>Cr (Sparks, 2003), which also supports the results of low bioaccessibility of Ni and Cr and higher

bioaccessibility of Cd. However, it is contradictory to the findings of high As bioaccessibility and low Pb bioaccessibility.

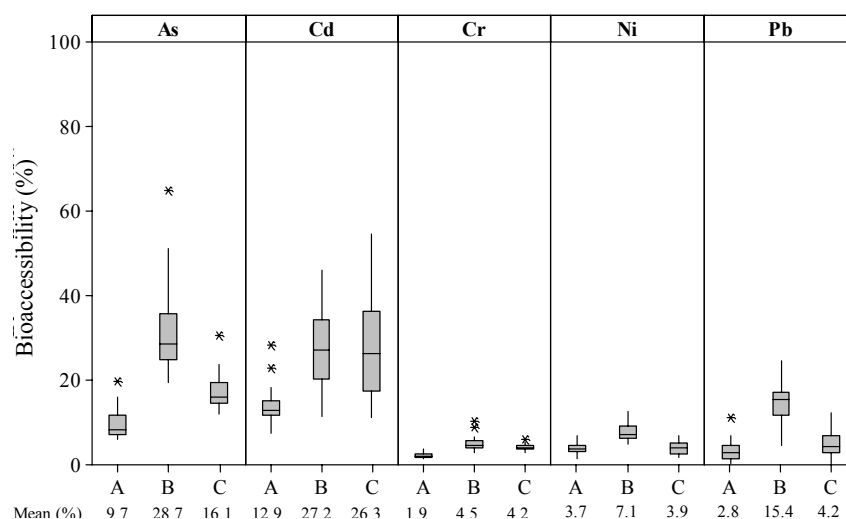


Figure 10. Boxplot of As, Cd, Cr, Ni and Pb bioaccessibility (%) from the three intake scenarios: A= Deliberate ingestion, pica behaviour (<4 mm, 2 g), B= Deliberate ingestion, non-pica (<4 mm, 0.6 g), C= Involuntary ingestion (<50 µm, 0.6 g). (n=25).

The relatively high bioaccessibility of As compared to Ni and Cr, also of natural origin in the studied soils, can therefore not be explained by higher solubility related to origin or a slower rate of diffusion into pore spaces and particles. However, the results support previous findings by other authors: Davis, Ruby & Bergstrom (1992) found the bioaccessibility of Pb and As in the intestinal compartment to be 0.18% and 12% respectively, while Ellickson *et al.* (2001) found 65.9% As and 10.7% Pb to be bioaccessible in the same compartment. The higher bioaccessibility of As is therefore more likely due to its differing chemical properties. Arsenic present in oxygen-rich soils is commonly found as As(V), which is present as an anion in the natural pH range of soils (pH 4-8) (Ruby *et al.*, 1999). It can then be assumed that the As of the soils investigated here was primarily in anionic form in the neutral intestinal environment, more readily bioaccessible than the cations. The decreased mobility of cations with increasing pH and the converse behaviour of anions could thereby explain the high bioaccessibility of As in the neutral intestinal environment compared to the other elements of natural origin.

The bioaccessible fraction of the total Pb content was similar to that of Cr and Ni. A correlation analysis of the playground soils showed that only Pb demonstrated a strong correlation to variations in gastrointestinal pH. Ruby *et al.* (1996) found that Pb, but not As, was largely removed from solution by re-adsorption and precipitation in the intestinal compartment with higher pH because of the stronger pH dependence of Pb. Yang *et al.* (2003) also found that Pb

bioaccessibility was strongly influenced by gastrointestinal pH, while the bioaccessibility of As was relatively unaffected. Regarding the re-adsorption to soil constituents in the intestinal phase, the low bioaccessibility results for Pb in the present study imply that the re-adsorption and precipitation reactions were more pronounced for Pb than for Cd and As.

#### Bioaccessibility of the different intake scenarios

The bioaccessibility expressed as a percentage of total content is affected by soil mass and total content. In order to compare the different soil intake scenarios, the bioaccessibility values expressed as  $\mu\text{g}$  were used instead (Figure 11). Chromium was excluded, since most sites had contents below the detection limit. More detailed data from each playground and each intake scenario is found in Table 3 of Paper IV.

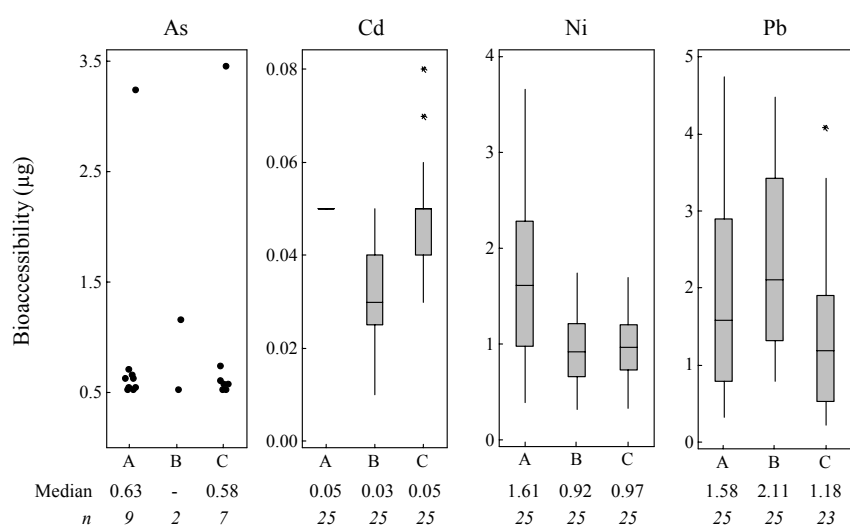


Figure 11. Bioaccessible contents of As, Cd, Ni and Pb ( $\mu\text{g}$ ) for the different intake scenarios: A= Deliberate ingestion, pica behaviour (<4 mm, 2 g), B= Deliberate ingestion, non-pica (<4 mm, 0.6 g), C= Involuntary ingestion (<50  $\mu\text{m}$ , 0.6 g).

Since small particles have larger adsorption capacity, the bioaccessible amount was expected to be larger for the <50  $\mu\text{m}$  fraction than for the <4 mm fraction, when the same soil mass was used. This was true for the few sites that had detectable As contents. It was also true for around half the sites for bioaccessible Cd and Ni. However, several sites had similar bioaccessible contents ( $\mu\text{g}$ ) for both size fractions. The soils used in the current study have low metal loads, and also a significant proportion of clay particles (on average 22%). It can then be assumed that the preferred sorption sites of the soils were not saturated due to the low metal load. The separation of particles into the fractions analyzed would therefore not influence the Cd and Ni distributions significantly, since both fractions contain the smallest sized particles. In contrast to As, Cd and Ni, all but five sites had higher bioaccessible Pb contents in the larger size fraction of <4 mm than in the smaller size fraction of <50  $\mu\text{m}$ . The bioaccessible Pb content also differed from As, Cd

and Ni when comparing the different soil mass scenarios. The expected result of higher bioaccessible content with larger amount of ingested soil held true for As, Cd and Ni. For Pb, it was instead the smaller soil mass of the larger soil particle size fraction (scenario B) that had the highest bioaccessible content at most sites.

Since Pb has the strongest pH dependence of the elements investigated, it is necessary to analyze the relationship between the gastrointestinal pH values and the bioaccessibility of Pb in order to understand its behaviour. It is likely that the strong pH dependence of Pb is the reason for its divergent bioaccessibility results. Figure 12 presents the stomach and intestinal pH values measured after two hours of mixing of the different soil fractions with the stomach juice and the subsequent two hours of mixing with the intestinal juice. The peaks observed for sites N5 and T1 were due to enriched  $\text{CaCO}_3$  contents compared to the remaining sites.

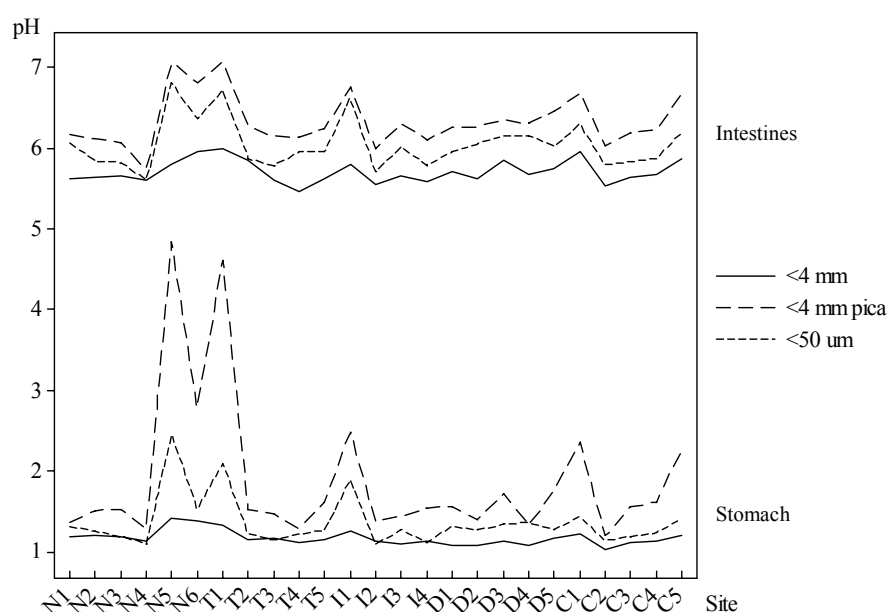


Figure 12. Measured pH in stomach and intestinal compartments after digestion.

The different scenarios displayed significant differences in gastrointestinal pH. The <4 mm pica scenario had the greatest variation in pH and also the highest pH values. While a smaller variation was observed for the involuntary <50  $\mu\text{m}$  scenario, the deliberate non-pica scenario of <4 mm showed almost no variation between sites and also the lowest pH values. The differences in pH are due to interactions between the gastrointestinal juices and the soil constituents when soil reaches the stomach and intestinal compartments. It can be assumed that since both a smaller particle size and a larger soil mass increases the potential exchange capacity of the soil, the pH is raised through exchange of surface sorbants with hydrogen ions. As pH increases, metals become less mobile and less bioaccessible. As elements differ in pH dependence, differences in pH affect the bioaccessibility of metals to different degrees.

In correlation analyses of the gastrointestinal pH values and the bioaccessible metal contents, Pb only showed a strong correlation to pH in the involuntary ingestion and pica scenarios. For the <4 mm non-pica scenario, Pb was equally weakly correlated to the gastrointestinal pH as the remaining elements, most likely due to the lack of variation in gastrointestinal pH for that scenario. The bioaccessible Pb content showed a stronger correlation with the total Pb content in the <4 mm non-pica scenario ( $r=0.729$ ,  $p<0.01$ ) than in the pica scenario ( $p=0.537$ ,  $p<0.01$ ). This suggests that the bioaccessible content in the <4 mm non-pica scenario was related to the total content, while gastrointestinal pH largely determined the bioaccessible Pb content in the pica scenario. It can be concluded that while the bioaccessibility of Pb is strongly dependent on the gastrointestinal pH, the total content determines the variation in Pb bioaccessibility between sites in the absence of pH variation. The ingested mass of soil did not seem to determine the Pb bioaccessibility.

All but five sites displayed higher bioaccessible Pb contents in the <4 mm fraction than in the <50  $\mu\text{m}$  fraction. As has been stated above, the pH was higher in both the stomach and intestinal compartments for the smaller size fraction. This implies that the bioaccessibility of Pb was also more dependent on pH than on particle size. The five sites that had higher bioaccessible Pb content in the <50  $\mu\text{m}$  fraction than in the <4 mm fraction were also those with the lowest clay contents (around 10%). As suggested above, the preference for Pb sorption to fine particles diminishes the effect of particle size range in soils with low metal loads, since most metal ions are bound to these small particles, which were present in both scenarios. However, when the number of fine particles was limited, an effect of particle size on Pb bioaccessibility was observed.

## Guideline Values and Risk Assessment

### Uppsala playgrounds and guideline values

While most playgrounds in Uppsala had metal contents below the guideline values, there were a few sites that exceeded the Swedish guideline values (GV) for As, Cd, Cu, Hg, Ni and Pb. Figure 13 shows the individual metal contents of the <2 mm fraction at each sampling site, measured after dissolution in *aqua regia*, together with the generic guideline values.

Analysis carried out in accordance with the Swedish recommendation for risk assessment showed that three playgrounds within Uppsala exceeded the guideline values for Cd, Cu, Hg, Pb, Ni and As. The playground with elevated contents of Cd, Cu, Hg and Pb is situated on the grounds of an old school built in 1905 and was categorized into the natural land use group. Only soil from the sampling points nearest to the school building exceeded the guideline value. It is likely that the soil at the two other sampling points has been altered and imported soil has been added during renewal of parts of the playground, resulting in lower soil metal contents. Elevated Pb content at the sampling site closest to the building may also

originate from Pb based paint used in the past. Another probable source of metals to the playground is a crematorium located nearby, known to release the above metals, particularly Hg.

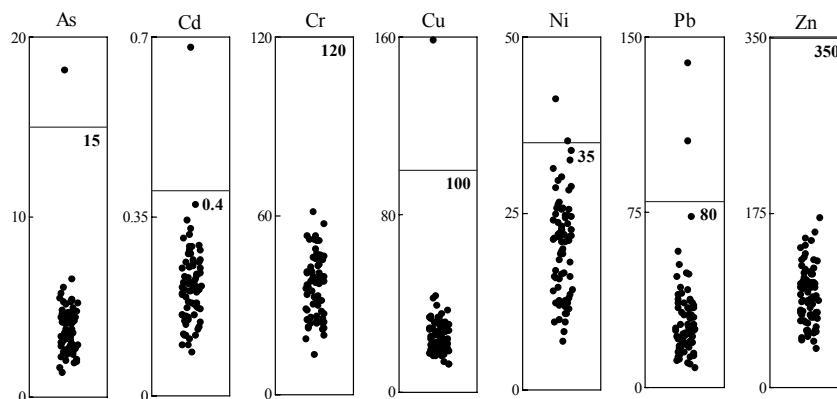


Figure 13. Individual value plots of As, Cd, Cr, Cu, Ni, Pb and Zn contents (mg kg<sup>-1</sup>) in the <2 mm fraction for each playground. Guideline values are presented in bold letters and with black lines (—),  $n=75$ .

The playground having soil contents of Ni exceeding the guideline value was also located at an old school in the natural land use category. This site also had elevated contents of Al, Fe and Cr and had the highest clay content of all sampling sites, supporting the above conclusion that soil characteristics is a more important factor for soil metal content than surrounding land use. The site with As contents exceeding the guideline value is also classified as a natural land use playground. Apart from As, elevated contents of Cu, Cr and W were detected at this playground. Since all elevated elements except W are common components of wood preservatives, frequently used in the past for outdoor wood constructions, this is a likely source.

The present guideline values are set with regard to intended land use. Areas where children reside, such as playgrounds, have the highest protection value. Although the guidelines are not strict values, but rather indications of soil metal contents that should not be exceeded, they are often wrongly used as action limits. If the total contents of the three playgrounds described above were carelessly used for risk assessment, the results would suggest a need to remediate the three playgrounds. The finding that playgrounds located in seemingly undisturbed forested areas in the outskirts of a rather small urban area have metal contents that exceed the guideline values supports what has already been suggested; that the present guideline values are set with unrealistic precaution. However, the recommended procedure for analyzing soil metals for risk assessment does not consider differences in metal contents between particle size fractions or between total and bioaccessible content. Depending on soil type and investigated element, these differences may be significant, and disregarding these differences may result in an over- or underestimation of potential risks from soil intake.

## Implications of using different measurement techniques for risk assessment

In the experiments carried out for this thesis, metal contents in soil were measured from different aspects. Table 9 presents the metal contents from three different experiments: 1) Median total content ( $\text{mg kg}^{-1}$ ) in the  $<2$  mm fraction; 2) median total contents ( $\text{mg kg}^{-1}$ ) in the  $<50$   $\mu\text{m}$ , 50-100  $\mu\text{m}$  and  $<4$  mm fractions and; 3) bioaccessible contents (%) in the  $<50$   $\mu\text{m}$  and  $<4$  mm fractions, from both normal and pica soil intake. The data in Table 9 show significant differences in metal contents between the different experiments.

Table 9. Median metal contents of the investigated soils from the aqua regia ( $\text{mg kg}^{-1}$ ) and in vitro (%) digestions of each particle size fraction used

Particle size Depth (cm)	Aqua regia digestion						In vitro digestion		
	2 mm			$<50$ $\mu\text{m}$	50-100 $\mu\text{m}$	$<4$ mm	$<50$ $\mu\text{m}$ 0.6 g	$<4$ mm 0.6 g	$<4$ mm 2 g
	0-5	5-10	10-20	0-10	0-10	0-10	0-10	0-10	0-10
Al	18400	22500	24700	37250	23600	25300	-	-	-
As	3.46	3.91	3.86	5.47	3.31	3.31	17	31	10
Cd	0.214	0.212	0.218	0.30	0.22	0.21	28	27	14
Cr	31.6	37.7	43.3	64.0	34.3	40.2	4	5	2
Cu	25.4	25.6	26.0	43.1	28.6	25.8	-	-	-
Fe	24900	27600	30300	43550	27600	29900	-	-	-
Hg	0.139	0.146	0.130	0.66	0.52	0.52	-	-	-
Mn	494	526	573	1445	963	714	-	-	-
Ni	18.5	21.1	23.2	36.1	20.3	21.5	4	8	4
Pb	25.5	24.6	26.4	38.4	25.7	26.0	5	9	3
W	0.346	0.350	0.345	0.32	0.50	0.27	-	-	-
Zn	84.0	90.4	98.6	147	84.7	89.2	-	-	-

### Soil particle size

The particle size chosen for analysis for the application of the guideline values,  $<2$  mm, is set from a practical point of view: It is, and has long been, a common particle size for soil analysis, but it is not necessarily the most relevant particle size fraction for soil analysis with regard to children's soil ingestion. The results from the study in Paper III showed that the metal intake from the  $<2$  mm particle size fraction, which was investigated for comparison with the guideline values corresponded well to an assumed particle size of  $<4$  mm for deliberate ingestion. However, it is unlikely that children sieve soil down to 2 mm in size prior to ingestion. Studies have instead shown that children mainly ingest soil of a much smaller particle size due to involuntary soil ingestion through their hand-to-mouth behaviour. Since metals and other pollutants are commonly concentrated on the smallest particles, these may have a higher metal content per soil mass than particles of a larger soil fraction. It is therefore more valid to investigate metal contents of a smaller particle size with regard to children's soil ingestion,



especially if a worst-case scenario is to be evaluated in risk assessments. The results from Paper III showed that it is especially important to consider differences in metal content between particle sizes in coarse-grained soils, where the finer fraction probably holds a considerably higher soil metal content than what is obtained from analysis of the total fraction.

### *Bioaccessibility*

In the risk assessment guidelines that are currently used in Sweden, the metal contents in soil are assumed to be 100% bioaccessible, *i.e.* equal to the total content. As can be seen in Table 9, the bioaccessible metal fractions were below 100% in the investigated soils. Moreover, the bioaccessibility differed between soil particle sizes, as well as ingested soil mass. However, while the bioaccessibility of As, Cd and Ni at many sites corresponded to the findings of Paper III regarding higher metal content in smaller particles compared to a larger soil particle size fraction, the relationship did not apply for Pb. Likewise, the expected result of increased bioaccessibility with increased soil mass held true for most, but not all, sites for As, Cd and Ni, and only for a few sites for Pb. The finding that the expected relationship was not applicable to all sites shows the difficulties with predicting bioaccessibility from results on total metal contents. In the human body, both soil characteristics and factors in the gastrointestinal environment affect the bioaccessibility of soil metals. The age of the child, whether it has eaten or not as well as the soil's clay and organic matter content, the ingested soil mass and particle size fraction are some of the factors that affect the bioaccessibility as well as the gastrointestinal pH, which in turn had a large effect on especially Pb bioaccessibility in the experiments in Paper IV. Moreover, whether the metal is of natural or anthropogenic origin and its dependence on pH affect its sorption and desorption behaviour which also affects bioaccessibility.

The results presented in Paper IV also showed that because of the relatively low metal load of the soils investigated, the clay content was an important factor for metal bioaccessibility in the different size fractions. At sites where the clay content was high enough to provide sufficient sorption sites, the effect of particle size was diminished since both fractions investigated included the finer sized particles. In more contaminated soils, the clay content may have a different effect on metal bioaccessibility.

## **Concluding remarks**

The work carried out within the context of this thesis provides evidence of the necessity of thorough soil investigations in order to correctly assess risks from soil contamination with regard to children's soil ingestion. It is of course better to be safe than sorry after remediation efforts have been carried out, but generalizations and assumptions of unrealistic conditions may result in gross overestimations of risks from soil intake, with corresponding costs for society. One example is the Uppsala playground with elevated Hg, Pb and Cd contents. According to the

guidelines, the soil metal contents were such that remedial action should be taken to ensure safe soil metal levels, while the bioaccessibility results showed that the metal contents did not pose any particular health risks to the children playing at the site. Generalisations may also result in underestimations of risks, as has been shown by the metal analysis of the different soil particle size fractions, where the fine particles that are often ingested involuntarily had significantly higher metal contents than the original soil. Increasing costs in the initial stages of risk assessment by going beyond soil analysis of the bulk soil's total metal content, by including bioaccessibility tests and a more exposure-specific perspective might lower the cost of actual remediation. Of course, exposure routes other than direct soil intake also have to be considered in risk assessment, but it is likely that a more realistic starting point would result in more site-specific and effective remedial efforts, regardless of exposure route.

Including more thorough soil analyses in risk assessment would also provide better knowledge on the behaviour of metals once ingested, since knowledge on metal behaviour in soil seems to be inadequate for accurate health risk assessment. Moreover, it seems difficult to set a generic bioaccessibility value for a specific metal, because of its varied degree of interaction with soil and gastrointestinal solution constituents. More studies on metal bioaccessibility in different types of soils and various metal contents are necessary to attain greater understanding of the risks of soil metals. Moreover, the complex chemistry of Pb with regard to bioaccessibility, as well as its severe negative health effects on children even at low blood levels, warrant further studies on polluted as well as non-polluted soils.

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