



## **Distribution of Biogenic and Non-biogenic Trace Metals in Roadside Soils**

*A study of Uppsala City, Sweden*

**Master of Science Thesis**  
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## ABSTRACT

This study determined and evaluated soil properties and distribution of biogenic (copper, iron, manganese and zinc) and non-biogenic (arsenic, cadmium, chromium, nickel, lead and wolfram) trace metals in the road side topsoil (0-10 cm) and subsoil (10-20 cm) at six sites in Uppsala City. The hypothesis of the study was that depending on the, location traffic intensity, history and industrial activities soil contents of the metals vary regardless of similar bedrock.

Four composite samples 20 m apart were taken 10 m from the roadside. Soil texture was determined by the pipette method, total C on Leco CNS-200 equipment, chemicals properties (cation exchange capacity (CEC) in BaCl<sub>2</sub> solution at pH 8.1, pH in deionised H<sub>2</sub>O and in calcium chloride solution and metals by digestion in aqua regia and measuring on ICP-MS equipment.

The soils were characterized mainly as sandy clay loams and the pH was nearly neutral. The CEC ranged between 10.6 and 37.9 c mol kg<sup>-1</sup>, with a mean of 20.0 c mol kg<sup>-1</sup>. Percentage base saturation was below 100.

The biogenic trace metals were evenly distributed in both the topsoil and subsoil, whereas the pattern for non-biogenic metals was not consistent. The results of biogenic metals were lower than the limits set by the Swedish Environmental Code, whereas some of the non-biogenic metals were close to the limits. The distribution of non-biogenic metals may suggest anthropogenic source of metals.

Metal accumulation, especially Pb, Cd, and Ni did not conform to trends of traffic intensity; rather it tended to follow the age of the road. Thus, although the E4 highway (relatively young road) with traffic density of 25000-40000 per d, Pb accumulation was not as high as Pb determined on the roadsides of Kungsgatan, the oldest street in central Uppsala with traffic intensity of 15000-20000 per day. Surprisingly the soil were enriched with W. Some of the metal contents could in the long term enhance health and environmental concerns, especially at school and children's day centres located close to the roadsides, where the risk of repeated exposure is apparent. More investigations are justified to verify these risks.

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## 1. INTRODUCTION

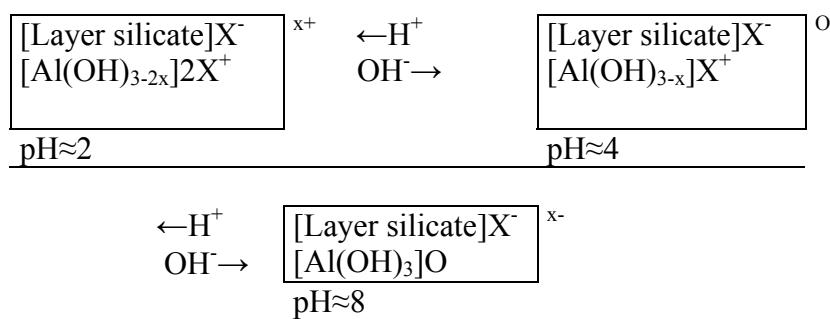
### 1.1. Soil physical properties

Physical properties are the most important characteristics that can let us understand the history, behaviour and future of the soil. Soil properties such as texture, structure, drainage, porosity, groundwater level and depth of the soil profile, interact to control water and nutrient supplies, gas exchange, microbial activities and root exploration (Brady, 1996). The major components of physical properties include clay, organic matter, silt and sand contents. They generally cluster together as aggregates, but can be separated from one other by chemical and mechanical means. The particles have diverse structures and composition, and generally differ in both size and shape. The particle size distribution of a soil indicates the proportion of the various sizes of particles it contains. The proportions are represented by the relative numbers of particles within stated size classes or by relative weights of such classes. The most common methods of particle-size analysis are sieving and sedimentation (Brady, 1996).

### 1.2. Soil chemical properties

#### 1.2.1. Anion and cation exchange properties of soils

With the term “exchange properties of soils” it is implied the ability of soil components to carry charges to which anions and cations can be adsorbed or the sites from which anions and cations can be exchanged as summarized as follows (Coleman & Thomas, 1967):



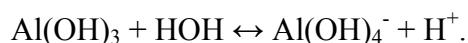
Long ago, Mattson (1931) had observed that the anions  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were held in quantities only by soils whose contents of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  oxides were large. At low pH, when the hydroxyl ion ( $\text{OH}^-$ ) concentration is low and the amount of  $\text{SO}_4^{2-}$  or  $\text{Cl}^-$  retained is relatively higher than at high pH when the concentration of hydroxyl is high (Mattson & Wiklander, 1937). The anions  $\text{HPO}_4^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{F}^-$  behave similarly.

### **1.2.2. Definition of soil cation exchange capacity**

Cation exchange capacity (CEC) represents the total sum of exchangeable cations that a soil can adsorb or is defined as a measure of negative sites that can absorb cations. The common cations that constitute CEC are the basic cations, calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), potassium ( $\text{K}^+$ ) and sodium ( $\text{Na}^+$ ) and the acidic cations, hydrogen ( $\text{H}^+$ ) and aluminium ( $\text{Al}^{3+}$ ) as well as  $\text{NH}_4^+$ . The CEC is expressed in meq ( $100\text{g}^{-1}$  dry soil or c mole  $\text{kg}^{-1}$  dry soil).

### **1.2.3. Sources of CEC**

The CEC of soils is highly dependent upon soil texture and organic matter content. In general, the larger clay and organic matter contents in the soil, the higher the CEC. The effective CEC (CEC determined using solutions adjusted to soil pH) is due to the permanent charges derived from the isomorphous substitutions that occur in different types of clay. There are also what known as pH-dependent charges (charges that develop as pH increases), which occur as a result of the dissociation of the hydroxyl or carboxyl on the organic matter fraction of the soil or as result of the dissociation of the hydroxyl edges on the clay minerals. Another source of the pH-dependent charges in strongly acid soils (pH below 5.5) are the adsorbed aluminium-hydroxyl polymers that are adsorbed on the negative exchange sites. As the pH rises, these polymers precipitate and the exchange sites become free for other cations. Iron oxides have a similar effect as the aluminium hydroxyl polymers, but the effect can be seen at higher pH. For example, at pH >7.5,  $\text{Al(OH)}_3$  hydrolyses, producing  $\text{Al(OH)}_4^-$  and  $\text{H}^+$ , thus:



The  $\text{Al(OH)}_4^-$  can adsorb cations. Further more, anions such as  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  adsorbed on the soil particles cause CEC (Brady, Coleman & Thomas, 1967). Another example of pH- dependent CEC are carboxyls (-COOH) and -OH in phenols (see example in table below).

**Table 1.** pKa of carboxylic groups of different organic acids (Otabbong, 1983)

Name of acid	Formula	pKa <sub>1</sub>	pKa <sub>2</sub>	pKa <sub>3</sub>
Acetic	$\text{H}_3\text{CCOOH}$	4.7		
Oxalic	$\text{HOOCCOOH}$	1.2	4.2	
Succinic	$\text{HOOC(CH}_2)_2\text{COOH}$	4.2	5.5	
Citric	$\text{HOOCCH}_2$	3.1		
	$\text{HOCCOOH}$		4.8	
	$\text{H}_2\text{CCOOH}$			6.4

#### **1.2.4. Base saturation**

The relative proportion of the different cations adsorbed by clays is determined by two factors. First, the cations are not held equally tight by the soil colloids. When they are present in equivalent amounts, the order of strength of adsorption is  $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+$ . Second, the relative concentrations of the cations in the solution help determine the degree of adsorption (Mattsson & Wiklander, 1937). The proportion of CEC (T) occupied by base-forming cations ( $S = \sum \text{Ca, Mg, K, Na}$ ), termed percentage base saturation (V%).

$$V = (S/T) \times 100.$$

The V, S and T were proposed by Hissink (1925)

This property, i.e. V, is usually directly related to soil acidity (pH). As V increases, pH also increases or vice versa. When base saturation is below 100% it indicates that part of CEC is occupied by  $\text{H}^+$ , arising from hydrolysis of  $\text{Al}^{3+}$  and ionizing of the acidic groups as follows:

- 1)  $\text{Al}^{3+} + 3\text{HOH} \leftrightarrow \text{Al}(\text{OH})_3 + 3\text{H}^+$ ;
- 2)  $\text{RCOOH} \leftrightarrow \text{RCOO}^- + \text{H}^+$
- 3)  $\text{ROH} \leftrightarrow \text{RO}^- + \text{H}^+$ ;

Where R is an organic radical or Al- and Fe-hydroxyl.

## **2. URBAN SOILS AND GENERAL CHARACTERISTICS**

Urban areas contain a very wide variety of open spaces including gardens, playing fields, waste lands, parks, spoil heaps, railway, roads and canal embankments and islands of natural land. The soil found in these areas is a complex medium, differing from rural soil with regard to its varying composition and development stages as well as form and degree of anthropogenic inputs. Typically urban soils are exposed to more pressure by human activities than rural soils.

The urban soil materials originate from several different locations; some are non-soil materials (Bullock and Gregory, 1991; Linde et al., 2001). The term “soil”, in an urban area, includes a wide spectrum of composition and stages of development, ranging from areas that appear to lack any soil cover such as roads, pavements and buildings, to well developed soils with a natural profiles, such as the types found in city forest and gardens. Most city soils contain more coarse-grained material than rural soil. This includes building waste and other waste material. Urban soils have often a different vertical variability than rural soils, resulting from excavation and backfilling, as well as an increased horizontal variability due to the different land uses (Effland & Pouyat, 1997). Building waste is the most common waste material found in urban soils, but there are also other quite important sources of waste material like industries, road construction wastes and plants, power stations, oil spills, organic and chemical waste spills, transport system, scrapyards and waste

disposal sites. Other than the solid phase, waste materials may also be found in the gaseous and liquid phases, derived from different processes of decomposition.

## ***2.1. Urban soil properties***

Several attempts have been made to define urban soil. Urban soil is material that has been manipulated, disturbed or transported by human activities in the urban environment and is used as a medium for plant growth. In this kind of environment, sometimes the soils are too toxic to support plants growth. Several properties differentiated urban soil from the other ones, below is an attempt by Hollis (1991) to summarize these:

- *Soil temperature and moisture regimes*: higher temperature and rainfall, lower wind speed, relative humidity and radiation;
- *Composition*: altered by addition of man-made materials, either as physical or chemical components.
- *Physical properties*: more compact topsoils and/or subsoils, less aeration and downward percolation of surface water;
- *Variation of properties*: vertical and spatial, greater and less predictable because of human activities.

## ***2.2. Physical characteristics***

Different land uses require different soil properties in the urban environment.

The topsoil in urban areas is usually referred to as the dark-coloured soil layer, which is commonly derived from the top 30 cm of a natural soil and then placed with minimal compaction as a surface layer. The subsoil is the layer underneath, originates from a greater depth and is likely to have been compacted when the surface was applied. Urban soils are usually more compact than the common ones; this is also due to treading and soil packing by vehicles and heavy machinery. Some physical properties related to different uses are showed in the following table.

**Table 2.** Soil physical properties of relevance to various uses (Mullins, 1991):

<i>Application</i>	<i>Requirements</i>
Playing field	A, B and C
Footpath	B and D
Gardens	C
Restored land for amenity use	C and D
Effluent disposal areas	A and D

Explanation to the requirement

<i>Requirements</i>	<i>Relevant physical properties</i>
A. Drainage	Local hydrology, saturated hydraulic conductivity, soil structure;
B. Load-bearing capacity	Penetrometer resistance, bulk density, compactability, water content, drainage;
C. Plant growth	Drainage status, air capacity, available water capacity, bulk density, structure and/or penetration resistance;
D. Freedom from erosion and runoff	Infiltration, drainage, structural stability, (type of vegetation cover)

### **2.3. Biological and chemical characteristics**

Soil organisms are important in developing and maintaining the soil structure and are responsible for incorporation of organic matter and its turn over, and cycling of nutrients. In urban environment these processes are usually disturbed by human activities. It is common to find a decreases in population and diversity of organism species, that can determine a badly affects in certain processes, like interruption in nutrient cycling and modification of organisms activities. As a result, urban soil contains less organic matter than the corresponding rural soils. (Harris, 1999; Craul, 1985). The inclusions of non-soil materials, degradable and non-degradable, affect pH, biological activities and redox conditions. The urban climate is characterized by higher temperature and rainfall and lower wind speed and relative humidity that have effects on soil temperature and moisture regimes. (Craul, 1985).

### **2.4. Pollutants: anthropogenic origin**

Chemicals:

- Agricultural chemicals;
- Fuel;
- Medical chemicals;

- Industrial chemicals;
- Paints.

Solids:

- Building materials;
- Residuals from burning;
- Electrical garbage.

Traffic:

- Vehicles;
- Aircraft.

Power system:

- Electricity;
- Fossil combustion for generating energy.

Wastewater:

- From household
- From industries including hospitals, schools, offices, etc.

## ***2.5. Pollutants of geochemical and geophysical origin***

When igneous rocks are formed isomorphous substitution result in metal ions being incorporated into the crystal lattice of primary minerals. Soil minerals act as reservoirs and release them slowly (Deng et al., 1998). Sedimentary rocks comprise approximately 75% of the rocks outcropping on the earth's surface and are therefore important as soil parent materials. The metals concentration in this kind of rock depends on the mineralogy and adsorptive properties of the sedimentary materials as well as the matrix and metal concentration in the water in which the mineral was deposited. A significant concentration of heavy metals there is also in coal due to similar conditions in the early stage of coal formation. Sandstones, since they consist mainly of quartz grains with little adsorbing ability, have low concentration of heavy metals. (Alloway, 1990). Metals with smaller coordination numbers fit into the crystal pattern of secondary minerals, while those having larger coordination numbers are enriched in clay by adsorption.

## ***2.6. Main metal pollutants***

The most common metals of concern for human being and the environment are arsenic, lead, cadmium, cobalt, copper, mercury, nickel, selenium, vanadium, chromium and zinc. They occur naturally in soils, some being essential to biological life others have no documented biological function but have been used by human for centuries. More details are presented in chapter 4.

## **2.7. Background level and guideline values**

The definition of a trace metal's background level can be synonymous to the concentration of the trace metal of natural origin (Wepl & Brümmer, 2003). Natural levels of metals in soil can sometimes exceed the values set up by authorities for contamination of soils (Lax, 2002). The Swedish Environmental Protection Agency has defined background levels as the natural pollutant level in addition to the normal load of added natural and anthropogenic pollutants (Petsonk & Sjölund, 1997). It should be pointed out that the anthropogenic pollutant addition is diffuse, and separates the background level to metal concentrations found in point polluted sites. Local parameters have to be used such as parent material, land use, soil horizon and type of area. (Welp & Brümmer, 2001). High concentrations of metals in soil do not always indicate a health risk or a negative impact on the environment. Many metals appear in non-soluble minerals or oxidation states with low toxicity.

Regional rural background levels are the most useful set of data to be used in urban soil investigations. (Petsonk & Sjölund, 1997)

## **2.8. The Swedish legislation on Environment**

In 1874, laws on protection of human health were established in Sweden. The first law specifically protecting the environment came in 1969 and in 1999, all environmental laws were collected in one Act. The EU-directive of IPPC (Integrated Polluting Prevention Contract) has been implemented into Swedish environmental law. The aim of the directive is to prevent, limit and as far as possible eliminate pollution at its source – PPP (Polluters Pay Principle). This applies to air- soil and water pollution. The Swedish Environmental Protection Agency (Naturvårdsverket) has constructed a methodology for surveying contaminated sites to be used by all Swedish municipalities (Miljöbalken 1999).

Quality norms for the environment can be found in the Environmental Management Bill (Naturvårdsverket, 2001). These include norms for certain geographical areas as well as maximum/minimum tolerance level for humans, the environment and for biological life. Both types and contents of the contaminants in soils are considered when assessing potential risks to human health or to the environment. Two types of guideline values (GV) are compiled for the assessment: one for human health and another for the environment. The GV are based on the background values (BV), i.e. values obtained in soils under natural condition and have not been contaminated with anthropogenic substances.

In the following table the guidelines used in different countries are shown.

**Table 3.** Guidelines used in different countries (adopted from Chen, 1999)

Element	Germany	France	U.K.	U.S.A.	Australia	Canada	Netherlands	Japan	Taiwan	Sweden	Italy*
	mg kg <sup>-1</sup>										
As	20	20	10	5.6	20		55	15	20	15	20
Cd	3	2	3.5	2			12	1	4	0.4	2
Cu	100	100	140	45	60		190	125	150	100	120
Cr	100	150	600	212	50	120	380		200	120	150
Hg	2	1	1				10		2	1	1
Ni	50	50	35	31	60	32	210			35	120
Pb	100	100	550	68			580		100	80	100
Zn	300	300	280	50	200		720		300	350	150

\* The Italian guidelines were compiled in D.M. 471/99

### 3. FACTORS INFLUENCING METAL RETENTION IN SOILS

#### 3.1. Metals sorption and desorption

Metals are retained to the particulate phase of soils with three different mechanisms (Peijnenburg et al., 1997):

- a) Precipitation: formation of precipitates when the solubility product for a reaction between a metal ion and ligand has been exceeded;
- b) Ion exchange: where charged cations are exchanged for another at a constant-charged surface.
- c) Adsorption: resulting from the surface chemistry of soil materials, is highly pH-dependent.

Desorption (release) of metals occurs when the metal is released from the soil into the solution. This is an important process for determining metal bioavailability in the environment. Desorption reactions are usually slower than sorption reactions. This could be due to the transformation that the sorbate undergoes from one state to another which requires large activation energies. This kind of reaction can occur through changes in pH, chelation with an organic compound and reduction reactions.

#### 3.2. Factors influencing metal sorption by soil properties

The major factors controlling trace metal adsorption in temperate soil are: organic matter, pH and ionic strength the mineral fraction becomes important when soils have low organic content or very high metal oxides content (Lee et al., 1990). Metals are usually co-precipitated with secondary minerals in which isomorphous substitution has occurred (Alloway, 1990), with the three main forms being, adsorption on the surface of particle (Sposito, 1989).

### ***3.2.1. Colloid***

The charged surface of clay and humus attract metals ions, play a large part in soil processes and they have a great impact on the water content of the soil. The relation between soil properties and metals content is close since the metals are positively correlated to soil content of clay, Al and Fe and negatively correlated to sand content. Clays are negatively charged. Sand contains very few negative sites that can adsorb metals; those differences explain the diverging correlation.

### ***3.2.2. Organic matter***

Organic matter has a high affinity for heavy metals due to the presence of ligands that can form chelates with metals ions in soil. High-molecular weight organic ligands form insoluble stable chelates (organo-metal complexes) while low-molar weight organic ligands form with metals soluble organo-metal complexes that prevent metals from being adsorbed or precipitated. The soluble organo-metal complexes are also known as chelates. The pH-dependent hydroxyl sites are the most important for metal adsorption onto organic matter. (Alloway, 1990)

### ***3.2.3. Cation exchange capacity***

Heavy metals exist as cations in the soil solution or anions (for example As). The cations are adsorbed on soil particles surfaces; their adsorption depends on the density of negative charges on the adsorbing surface. Cation exchange is reversible, stoichiometric and its diffusion is controlled. Changes in pH affect trace metals solubility both directly and indirectly. One direct effect is the adsorption edge, where sorption increases rapidly over a relatively narrow pH-range.

### ***3.2.4. Selectivity of adsorbents for different metals***

Metals are adsorbed by different mechanisms. The selectivity can be largely explained by the Lewis hard-soft acid-base principle, which states that hard acids prefer to react or complex with hard bases, and soft acids prefer soft bases. “Hard” indicates a high electron negativity, low polarization and small ionic radius. (Alloway, 1990). The extent of specific adsorption and desorption depend on pH, temperature, surface coverage, physical-chemical properties of the adsorbent and length of contact period between adsorbate and adsorbent (Atassanova, 1999).

### ***3.2.5. External factors***

*Pressure and temperature:* the difference between pressure in the field and laboratory is usually not too large, and any alteration that may occur due to pressure changes will probably be minor compared to other factors. The temperature has shown large effects on metal sorption. Increased temperature determines a shift in

sorption edge to a lower pH, an increased reaction rate, an increase in total amount of ions sorbed by the surface and the initial reaction is more rapid.

*Time:* metal reactions occur both as fast and slow reactions. Fast reactions are attributed to high affinity sites, while slow reactions have been attributed to diffusion into crystal defects or dead-end pores, surface precipitation and a change in the type of complex. (Glover et al., 2002). For example, adsorption reactions are fast and only minutes, while absorption reactions are slow and can reach equilibrium for months or years.

### ***3.3. Metals in urban soils***

In the urban environment soils are receiving a higher load of metals from the surroundings than the corresponding rural soil (Thornton, 1991). The presence of metals in urban soils is of great concern since more people are subjected directly to soils in the urban environment, where the soils have been subjected to many different kinds of pollution over a long period. As more metal-containing residues are deposited on the soil surface, concentration can reach levels that are harmful to humans upon repeated exposure (Brinkmann, 1994). In addition to metal loading in urban areas, salt used on roads can sometime result in increased metal mobility, especially Cd and Zn, and subsequent leaching (Hollis, 1991). The main diffuse emission sources of metals are traffic, including road materials and vehicles, and buildings, including paints.

## **4. UPPSALA CITY**

Education, research, health care, and a private sector as well as a public service sector dominate Uppsala. The city's area has more than doubled its size during the last 35 years. The present area is shown in table 4 (Uppsala kommun, 2000).

### ***4.1. Geography***

Uppsala City is situated in Uppsala County, in the Uppland Province of Sweden. The city stretches out over a large part of the Uppland province and is the fourth largest in Sweden ([www.uppsala.se](http://www.uppsala.se)). It is situated in the Mälardalen valley, which holds about one-third of Sweden's population and also encompasses the Greater Stockholm area and Arlanda Airport.

**Table 4.** A summary of Uppsala County (Uppsala kommun, 2000).

Location	59°8'N, 17°6'E
Altitude	51 m above sea level
Population	188 500
Uppsala County	2 523 km <sup>2</sup>
<i>Forest</i>	60%
<i>Agriculture</i>	25%
Uppsala City	100 km <sup>2</sup>
City parks and green areas	840 ha

#### **4.2. Climatic conditions of Uppsala City**

The data presented below cover precipitation, temperature, wind speed, solar radiation as well as relative humidity are for the 1961 to 2001 period. The measurements were carried out by the Department of Earth Sciences at Uppsala University. The data presented here represent yearly mean values.(Personal communication, Bergström, H., Department of Earth Sciences, Uppsala University, 2002). The data from 1994-2001 on global radiation and relative humidity presented in this section were published by SLB-analys (2002).

##### *Precipitation*

Mean precipitation 1961-2001⇒ 547,95 mm

##### *Temperature*

Mean average temperature 1961-2001⇒ 5,93 °C

Minimum of the mean minimum temperature 1961-2001⇒ -29,8 °C

Maximum of the mean maximum temperature 1961-2001⇒ 34,3 °C

##### *Wind speed*

Mean value ⇒ 3,96 m s<sup>-1</sup>

##### *Global radiation*

Mean value ⇒ 122,58 W m<sup>-2</sup>

##### *Relative Humidity*

Mean value ⇒ 77%

#### **4.3. Demography**

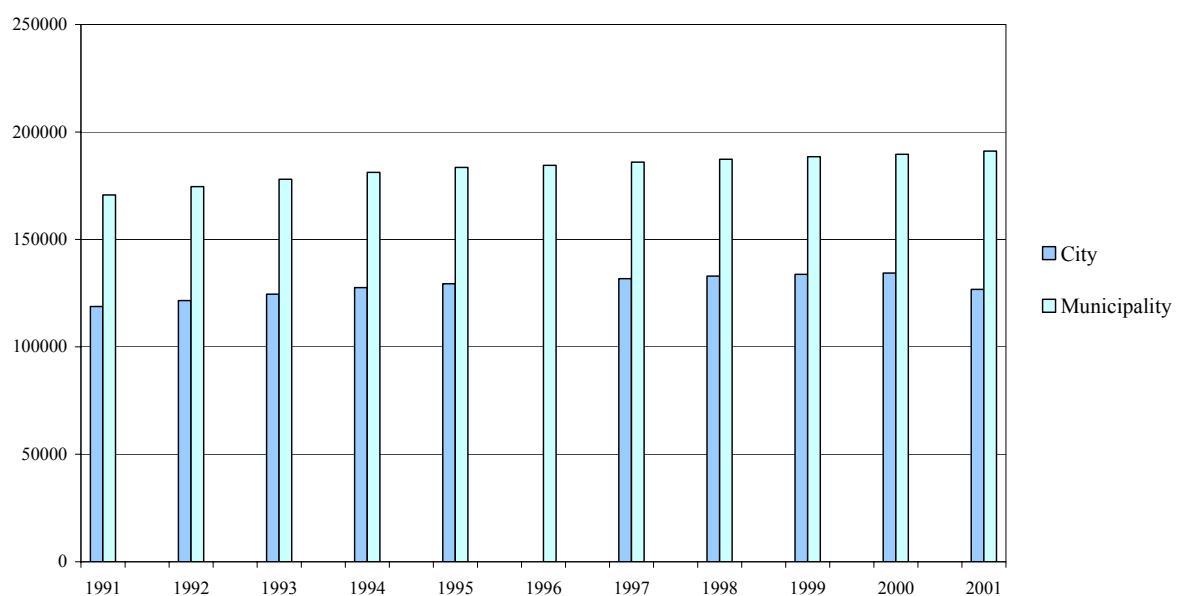
The population of Uppsala country counts 300495 habitants ( Uppsala Kommun, 2003). The density is 43 habitants per km<sup>2</sup>. The major part of the population lives in the urban part of the Uppsala Kommun. There are 110780 employees, the majority of them working in service (include health, education and administration sectors),

industries and other sectors, and just 2.3% is employed in agriculture. The rate of unemployment is 2.3%.

The working population is relatively low compare to the total, thing that is easy to explain since Uppsala counts a really big student community (online data bases, Assembly of European Regions)

The graph below shows the distribution of the population in the city and in the surrounding municipality of Uppsala from 1991 to 2001.

**Graph 1.** Population, city/municipality



#### 4.4. Uppsala urban soils

The bedrock in Uppsala County (Uppsala Kommun), shown in table 5, consist primarily of granite (plutonic igneous rock having visibly crystalline texture; generally composed of feldspar and mica and quartz), with leptite rock (fine-grained geissose to granulose metamorphic rocks of sedimentary origin mainly composed of feldspar and quartz with subordinate mafic minerals) in the neighborhood of Uppsala City and small fraction of green stones (metamorphic rock, where the green color comes from chlorite and epidote) scattered all over the county (Möller, 1993).

**Table 5.** Uppsala bedrock

Bedrock	Heavy metal content
Granite	Low, except for U
Leptite	Zn, Cu and small amounts of Cd
Greenstone	High background values of Cr, Ni, Co

#### **4.4.1. Soil types**

The landscape surrounding Uppsala is mainly formed by the most recent ice age. The region is undulating with outcrops and till on higher parts and fine-particle sediments in depressions. Clusters of De Geer moraines, some of them boulder-rich (boulder: water-weathered stone, glacial formation) are common and pronounced eskers (postglacial gravel in river valley) run largely in a south-north direction through the country. Wave-washed sediments and glacial-fluvial deposits are usually a few meters thick and are found at the bottom of slope in exposed upland areas. The glacial clay is varved, reddish-brown and often calcareous. (SGU, 2002). According to the FAO soil classification, most of the soils in Uppsala County are classified as *Cambisols* (soils having a cambic B horizon or an umbric A horizon which is more than 25 cm thick), predominated by *Dystric* (*Cambisols* having a base saturation of less than 50 percent (by NH<sub>4</sub>OAc) at least in some part of the B horizon) sub groups (Eriksson & Wiberg, 1988). The soil of Uppsala County is generally rich in U, As, Mn, Cu, Co, Cr, Ni and Cd, and has low contents of Hg, Pb and Se, compared to the Swedish reference values.

#### **4.4.2. The Uppsala Esker (*Uppsalaåsen*)**

A large part of the esker is covered by glacial and postglacial clays that are not visible in the surface, especially in north of Uppsala. Several large gravel pits have existed in the esker and the municipal water supply plants of Uppsala are located here. (Möller, 1993). Most of the till (moraine) in the area can be classified as sandy. The thickness of the till is seldom more than a few meters, but thicker till also occurs. The predominant glacial fine-grained sediment within the mapped area is glacial varved clay. The varves mainly consist of pure clay except for the bottom varves where strata of sand, fine sand and silt occur. The clay content in the upper parts varies between 60 and 70 %. (Möller, 1993). The CaCO<sub>3</sub> content is about 10-30% in the greatest part of the clay. Postglacial clay is common in the area and the clay content of the sediment varies between 40-60%. (Möller, 1993).

### **4.5. Sources of trace metals in urban soils of Uppsala**

Below are examined and listed the sources of pollution and trace metals in Uppsala, analysis of waste management first and sources of pollution.

#### **4.5.1. Waste management**

During the past ten years, waste management in Uppsala has been improved by introducing household waste sorting, constructing recycling stations and biogas for energy. This is due to increased demand by society to reduce waste pressure on the environment and as well as increased awareness of positive values of waste materials. The basic guidelines are:

- ◆ Reuse

- ◆ Recycling of waste material
- ◆ Recycling for energy production
- ◆ Incineration
- ◆ Disposal into landfills

Of 44 000 tons wastes collected from Uppsala households in 2000, 5500 tons was biodegradable. That was an increase of 20% from 1999. Recycling and collection of other fractions of waste, such as electrical and hazardous have also increased. (Uppsala kommun, 1999). In Uppsala, and in Sweden as a whole, there is what is known as “producers responsibility”. This means that each producer is responsible for recycling the containers sold with his products. Containers are divided into plastic-, glass-, paper- and metal containers, which are left by the consumer at different recycling stations. Newspapers are also recycled. (Uppsala kommun, 1999). The municipality is responsible for the collection of combustible, organic, electrical, large and solid waste as well as hazardous wastes. The municipality provides containers to households for sorting combustible and biodegradable wastes (Uppsala kommun, 1999).

#### ***4.5.2. Organic waste***

There are two plants for organic wastes processing in Uppsala. At one of the plants, biodegradable wastes from households are mixed with waste generated from gardens etc, and turned into compost. The other plant receives wastes from slaughtering, fertiliser and food plants. The wastes from slaughtering, food and household wastewater plants are used to produce biogas and bio fertiliser. At present, 30-40 buses in Uppsala City run on biogas produced from wastes. (Uppsala kommun, 1999).

#### ***4.5.3. Combustible wastes***

This type of waste is burnt and transformed into steam that is used to produce heat and electricity for a few households. The ashes that remain are transported to a damping place and the polluted smoke is cleaned. (Uppsala kommun, 1999).

#### ***4.5.4. Wastes from electrical appliances***

This fraction includes all waste with batteries or cables. The waste is collected and hazardous parts are destroyed. The metals are recycled. (Uppsala kommun, 1999).

#### ***4.5.5. Large and solid waste***

This fraction includes all wastes that do not fit in the regular household waste containers, such as freezers, refrigerators, radio and tv sets, furniture etc. That type of waste is sorted at special recycling stations. At those stations, about 80-90% of the wastes delivered is processed for re-use. (Uppsala kommun, 1999).

## **4.6. Main sources of pollution**

### **4.6.1. Kungsängsverket – Sewage Treatment Plant**

Heavy metals are released to the environment via wastewater and sludge from the sewage treatment plant. The plant is the largest known anthropogenic source of pollution in Uppsala. Table 6 shows heavy metal contents in sludge between 1990 and 1992. Since then, the metal content has decreased and new limit levels have been introduced. (Stock, 1997).

Table 6. Discharge of heavy metals from Kungsängsverket, 1990-1992 (Dressie & Wallsten, 1994)

Element	Heavy metal content in sludge (kg)		
	<b>1990</b>	<b>1991</b>	<b>1992</b>
Hg	11	12	16
Pb	290	190	130
Cd	11	9	8
Cu	6000	6100	8000
Cr	80	100	120
Ni	90	60	50
Zn	5200	4300	3600

### **4.6.2. Uppsala Energi – Heat- and Energy Plant**

Uppsala Energi (UEAB, Uppsala electricity waterfall company) combusts one tenth of Sweden's household wastes. The discharge of gases in smoke and condensed water has reduced considerably in recent years. Since 1980 the discharge of different metals have decreased by 10-200 times. This is due to a more effective cleaning of the smoke and a better sorting of the waste from the households (Stock, 1997).

Discharge from Uppsala Energi is mainly deposited in districts outside Uppsala, just as the Metals deposited on to soil in Uppsala City originates mainly from sources outside the city. Solid waste originating from the cleaning procedure of smoke gases, mentioned earlier is disposed of at the city's main disposal area at Hovgården (Stock, 1997).

### **4.6.3. Waste water from vehicle washing**

There are 25 large car-washing plants at filling stations in Uppsala City. By 2005, these must have a system for re-cycling of at least 80% of the wastewater produced. Six car plants have a closed system for wastewater treatment at present. (Stock, 1997).

#### 4.6.4. Air force

The air force generates polluted discharges. Polluted water is transported to the treatment plant as well as to the river Fyrisån via surface runoff. The wastewater has been analysed for metal content and the results showed that only Cd exceeded the limit level. (Stock, 1997)

Table 7. Discharge ( $\text{kg year}^{-1}$ ) of heavy metals to water from different sources in 1992 (Wallsten & Dressie, 1994).

Source	Co	Cd	Hg	Zn	Cu	Pb	Ni
STP	37	2	4.5	600	400	17	103
UEAB	0.23	0.09	0.5	8.9	0.09	0.36	0.88
DP	-	0.022	0.01	4.61	3.14	0.15	2
Runoff	-	28	-	4400	1450	250	

Sources:

UEAB: Uppsala Energy

STP: sewage treatment plant

DP: disposal plant

Table 8. Discharge ( $\text{kg year}^{-1}$ ) of heavy metals to air from different sources (Wallsten & Dressie, 1994).

Source	Co	Cd	Hg	Zn	Pb	Ni	Cr	As	Mn
Crematory			7						
UEAB	16	5	66	135	90	70	61		6
Traffic					7011				
Longway transport		35	18	11450	3000	360	150	114	

#### 4.7. Traffic

Traffic intensity has increased by 4% since 2000 (Översiktsplan, 2001).

Table 9. Main choices of transport (%) during the week (Översiktsplan, 2001).

	Weekdays	Saturday	Sunday
Car	38	53	60
Bus	14	10	6
Train	2	1	0
Bicycle	29	18	16
Taxi	0	1	1
Walk	17	17	17

Table 10. Main choices of transport (%) for different purposes (Översiktsplan, 2001)

	Car	Bus	Bicycle	Walk
To work	45	15	27	9
Work-related	65	6	16	9
School	11	22	44	21
Food supply	39	6	19	35
Other supplies	38	19	21	21
Other	41	10	28	19

#### **4.8. Old industries**

Uppsala is a dynamic industrial and commercial municipality where knowledge, ideas and entrepreneurship are at the centre. At Uppsala University, extensive research is carried out in a number of fields for industry and commerce and entrepreneurship. Research activity at the Swedish University of Agricultural Sciences (Sveriges Lantbruksuniversitet) is also important and of interest also for industry and commerce and entrepreneurship outside the agricultural sector. In 1866 the railway reached Uppsala, which contributed to the establishment of many industries here. In 1890 there were 23 factories. This increased rapidly to 93 in 1910. Eighty people worked within industry in 1867, but the number increased sharply at the beginning of the 20th century to around 3,000 in 1920. At that time Larssons shoe factory (Hästen), Nymans workshops and Uppsala-Ekeby were the biggest industries with around 200 employees each. Production was local – there was no export industry to speak of at that time.

#### **4.9. Main sources and concentration of some metals in Uppsala**

##### **4.9.1. Lead**

The heavy metal Pb is the most common toxic element and the most abundant contaminant of our environment and our body. It is the worst and most widespread pollutant, though luckily not the most toxic; Cd and Hg are worse. Since it was discovered, four or five thousand years ago, as a by-product of silver smelting, it has been used progressively throughout history. In the twentieth century, Pb has been widely used in paint, some containing a high percentage of Pb. This has been a problem especially with children, who are more sensitive to Pb than adults because of their better absorption and smaller bodies. In the 1920s, tetraethyl Pb was added to gasoline as antiknock additive. This has probably been the most widespread and pervasive source of environmental contamination from Pb to date. Other common uses for Pb are as seals for tin cans, in pewter, in ceramics and pottery glazes, in insecticides, and more. In recent years, however, there has been an attempt to decrease this environmental contamination. Cars are now using unleaded gasoline. This does not, of course, eliminate the problems of carbon monoxide and burned hydrocarbons, but it will help to decrease Pb exposure in the future. In 1971, Congress passed the Lead Paint Act, limiting the use of Pb in paints. This will also

help, but not for many years to come, since many older homes still contain leaded paints. As they deteriorate, Pb gets into the soil and does not degrade. In 1979, a law was passed decreasing the use of Pb in food storage cans, though it is still present in some solders. Bone analysis of very old skeletons indicates that modern humans have nearly 500-1,000 times more Pb in our bones than did our ancient ancestors. Our total body content of Pb nowadays is estimated at 125-200 mg. We can handle nearly 1-2 mg daily with normal functioning, but the margin of safety is narrow. Luckily, most people's daily exposure is less than that, about 300-400 mg. Lead is a neurotoxin and commonly generates abnormal brain and nerve function. It passes into the brain and can also contaminate the in-uterus fetus and breast milk. Most Pb, though, is stored in the bones. With Pb intoxication, "lead lines" are visible in the bones on X-rays. Some is also stored in the liver and soft tissues. Infants have very little Pb, but our body concentrations usually increase with age. Fortunately, Pb is not very well absorbed, usually less than 5 percent, though children absorb it at a higher rate. Many minerals, such as calcium and iron, interfere with further Pb absorption. When Pb gets into the blood, it does not stay long, either going into the bones and other tissues or being eliminated. Most ingested Pb is expelled via the feces; the kidneys, through perspiration, will usually clear that which is absorbed or inhaled. Evaluating Pb exposure and measuring Pb levels in humans is not easy. Hair analysis is the simplest and best test for evaluating chronic Pb poisoning, which has become much more common with long-term exposure. Hair-test screening for Pb is fairly reliable and can be done on both adults and children. Lead exposure and body lead levels are higher in North America than anywhere else in the world. In the United States alone, it is estimated that approximately 1.3 million tons of Pb are used yearly in batteries, solder, pottery, pigments, gasoline, paint, and many other useful substances. Somewhere between 400,000 and 600,000 tons per year go into our atmosphere, onto our earth, into our food, and into our body and tissues. So there is a lot of Pb around.

The following are some of the common contaminants and contaminated:

- Leaded gasoline: tetraethyl Pb was previously added to all gasoline; it. After combustion, this Pb goes directly into the atmosphere as air pollution, and it also settles onto the soil and its living vegetation. Heavily travelled roadways show higher concentration of Pb in the air, soil, and nearby vegetation.
- Paint: some still contain Pb and the amount of Pb in paints must be reduced.
- Food: Pb is contained in many foods, especially in those grown near industrial areas or busy cities or roadways. Liver and lung meats are usually higher in Pb content.
- Water: may be contaminated with Pb. Lead solder in pipes or Pb plumbing in older homes and drinking fountains, can leach into the water especially soft water.
- Cans: solder in tin cans, usually used to hold the seam together, contains Pb. The leaded plugs in evaporated milk may cause contamination of the milk.
- Cosmetics: pigments and other substances used for makeup and other cosmetics contain Pb.
- Cigarettes: Pb is occasionally a contaminant in cigarettes. Lead arsenate may be used as an insecticide in tobacco growing.

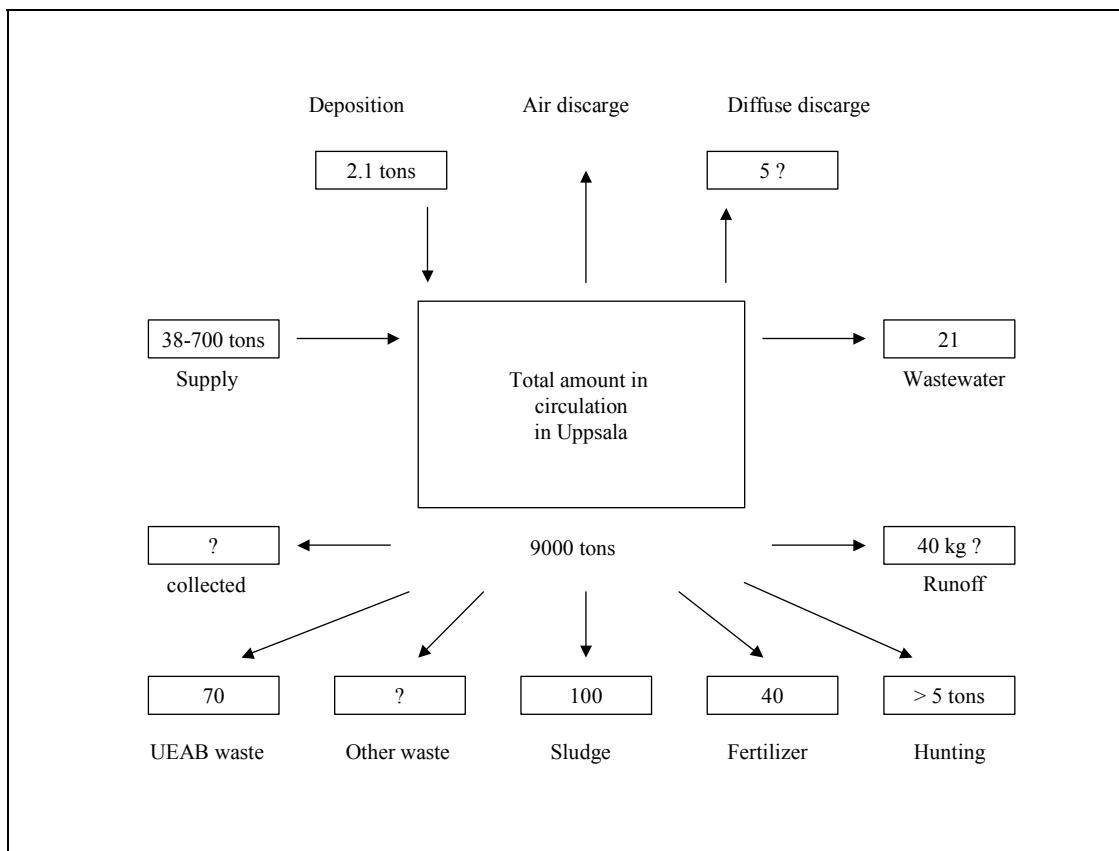
- Pesticides: they contain some Pb, mainly as the lead-arsenate base.
- Sewage sludge.

An estimated nearly 20 percent of men and 10 percent of women have problems with Pb toxicity, though it is not clear what levels of chronic Pb toxicity, which is most common, will produce symptoms. Lead in the body subtly interferes with optimum function and general health, and other toxicity factors may affect this. Lead accumulation may also cause shifts in important body minerals, such as zinc, calcium, and manganese. Early signs of Pb toxicity may be overlooked, as they are fairly vague: headache, fatigue, muscle pains, anorexia, constipation, vomiting, pallor, anemia. These can be followed by agitation, irritability, restlessness, memory loss, poor coordination and vertigo, and depression. Acute lead toxicity symptoms include abdominal pain similar to colic, nausea and vomiting, anemia, muscle weakness, and encephalopathy. Lead encephalopathy is a brain syndrome that can arise also from advanced chronic toxicity. It is characterized by poor balance, confusion, vertigo, hallucinations, and speech and hearing problems. A low level of Pb intoxication may affect brain function and activity more subtly, influencing intelligence, attention span, language, and memory. Insomnia and nightmares may be experienced. Hyperactivity and even retardation and senility may also result. Moderate levels of Pb may reduce immune and kidney function and increase risk of infection, and may be another factor in increasing blood pressure. There is some suggestion that lead intoxication may correlate with cancer rates. Further research is needed in this area. With heavy lead intoxication, death may result.

**Table 11.** Main sources of Pb in Uppsala (Stock, 1997).

Industries and activities (discharge in 1995)	Products (amounts in 1995)
Sewage Treatment Plant (21 kg)	Glass
UEAB (6 kg)	Lead bullets
Disposal Site	Batteries
Printing works	Paint (reduced due to new legislation in 1996)
Traffic (reduced since 1995 due to introduction of unleaded fuel)	PVC-products (42 tons/year) Cables (1400 tons in ground, 7 tons added/year)
Waste material	Canned foodstuffs (500 kg imported/year)
Shooting grounds	Electronic waste (105 tons?)
Longway deposition	

**Figure 1.** Pb flow in Uppsala 1995 (kg/year) (Stock, 1997).



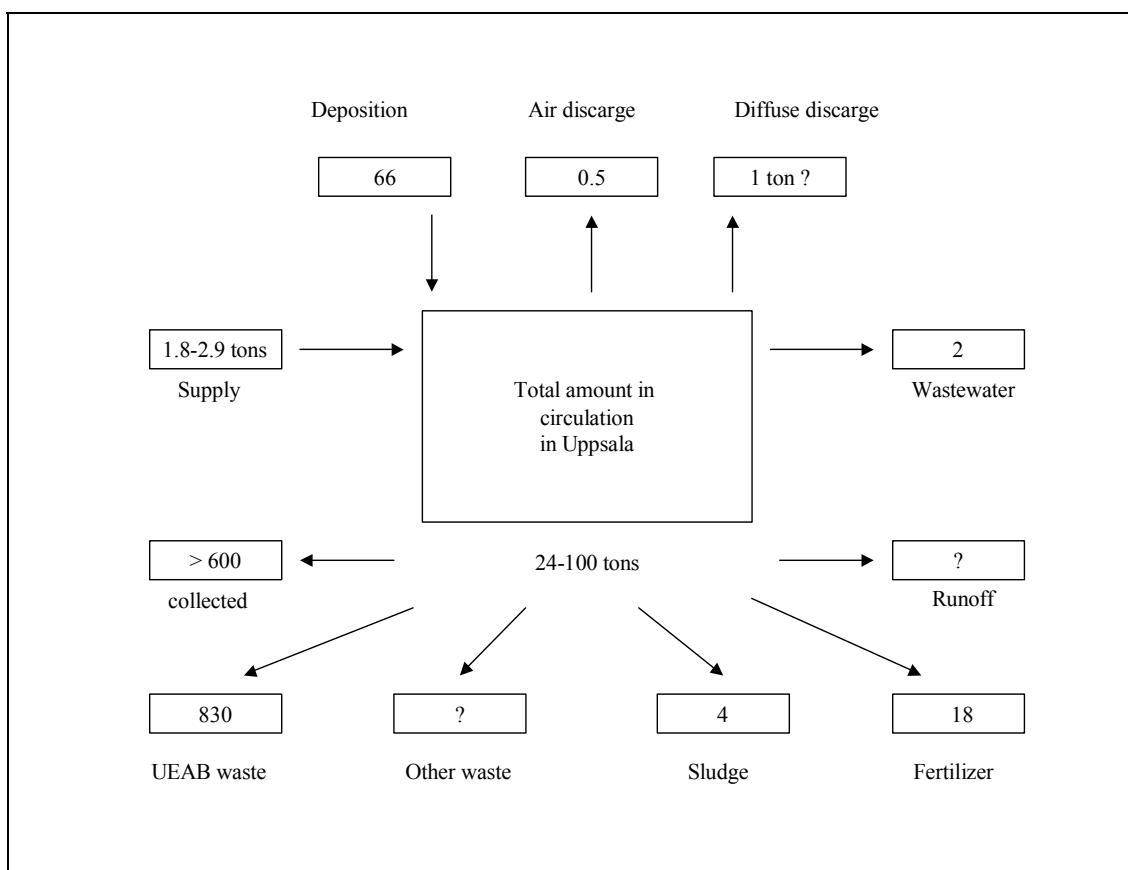
#### 4.9.2. Cadmium

Cadmium is a soft, bluish-white metal and is easily cut with a knife. It is similar in many respects to zinc. Cadmium and its compounds are highly toxic. Greenockite ( $\text{CdS}$ ), the only Cd mineral of importance, is nearly always associated with sphalerite ( $\text{ZnS}$ ). Consequently, Cd is produced mainly as a byproduct from mining, smelting, and refining sulfide ores of zinc, and to a lesser degree, lead and copper. Small amounts of Cd, about 10% of consumption, are produced from secondary sources, mainly from dust generated by recycling of iron and steel scrap. Cadmium has become a more prevalent cause for concern in recent years. It is an underground mineral that did not enter our air, food and water in significant amounts until it was mined as part of zinc deposit. Now there is widespread environmental contamination with Cd. The zinc-cadmium ratio is really important, as Cd toxicity and storage are greatly increased with zinc deficiency, and good level of zinc protect against tissue damage by Cd. We get most of it from soil byway of our food, small part from water, cigarette smoke plus industrial burning of metals. It is not very well absorbed and is stored primarily in the liver and kidneys. Cadmium is involved in generating, or at least contributing to, high blood pressure. Cadmium concentrated in the kidney can generate tissue damage and hypertension, appears to depress some immune function, generate prostate enlargement, it affects also bones, can cause cancer.

**Table 12.** Main sources of Cd in Uppsala (Stock, 1997).

Industries and activities (release in 1995)	Products	Amounts in 1995
Sewage Treatment Plant (2 kg)	Diffuse leakage	1 ton
UEAB (0.5 kg)	Batteries	2.3 tons brought into
Disposal Site	Paint	2-20 tons
	Tyres	
	Electronic waste	2 tons
	Construction waste	200 kg

**Figure 2.** Cd flow in Uppsala 1995 (kg/year) (Stock, 1997).



#### 4.9.3. Copper

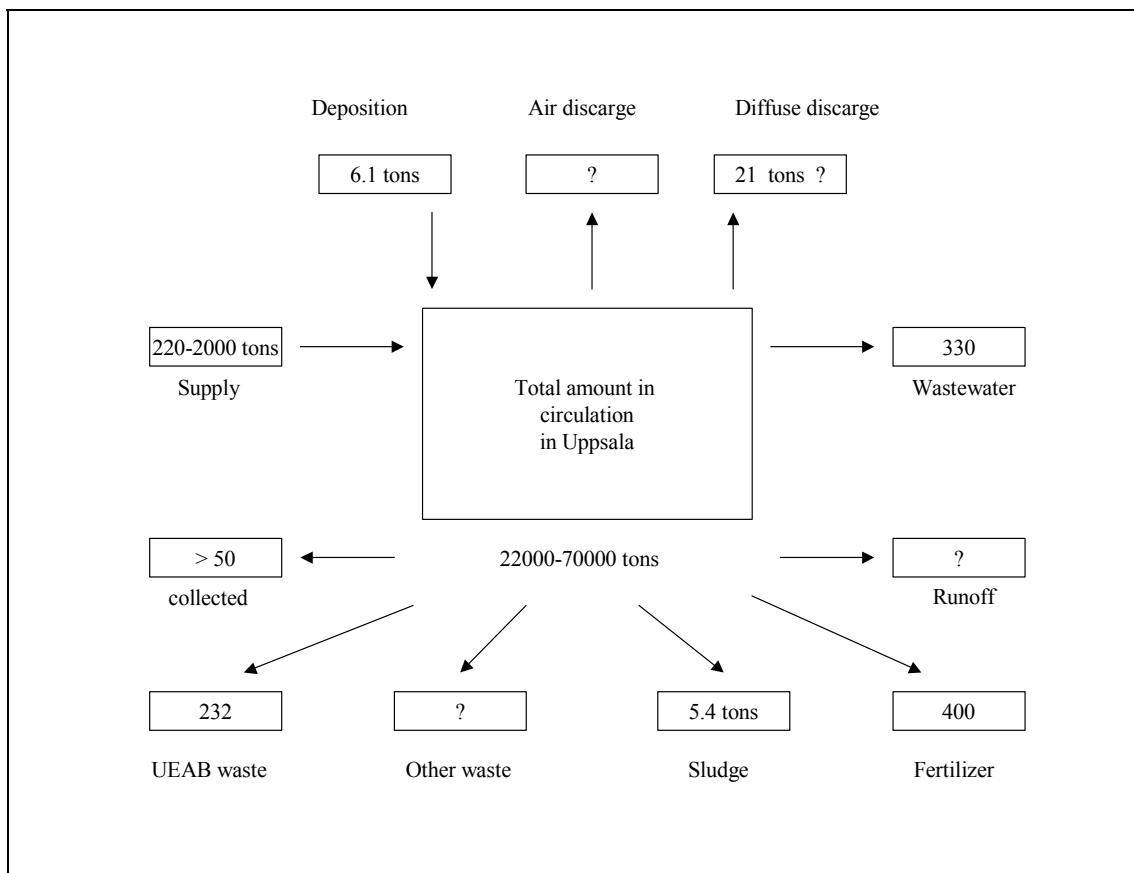
Copper is reddish with a bright metallic lustre. It is malleable, ductile, and a good conductor of heat and electricity (second only to silver in electrical conductivity). It is a very common substance that occurs naturally in the environment and spreads through the environment through natural phenomena. Humans widely use Cu. For instance it is applied in the industries and in agriculture. The production of Cu has

lifted over the last decades and due to this Cu quantities in the environment have expanded. Copper can be found in many kinds of food, in drinking water and in air. Because of that we absorb eminent quantities of Cu each day by eating, drinking and breathing. The absorption of Cu is necessary, because Cu is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of Cu, too much Cu can still cause eminent health problems. Most Cu compounds will settle and be bound to either water sediment or soil particles. Soluble Cu compounds form the largest threat to human health. Usually water-soluble Cu compounds occur in the environment after release through application in agriculture. Long-term exposure to Cu can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhoea. Intentionally high uptakes of Cu may cause liver and kidney damage and even death. Whether Cu is carcinogenic has not been determined yet. Industrial exposure to Cu fumes, dusts, or mists may result in metal fume fever with atrophic changes in nasal mucous membranes. Chronic Cu poisoning results in Wilson's disease, characterized by a hepatic cirrhosis, brain damage, demyelization, renal disease, and Cu deposition in the cornea. Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. A few examples of human activities that contribute to Cu release have already been named. Other examples are mining, metal production, wood production and phosphate fertilizer production. On copper-rich soils only a limited number of plants has a chance of survival. When Cu ends up in soil it strongly attaches to organic matter and minerals. As a result it does not travel very far after release and it hardly ever enters groundwater. In surface water Cu can travel great distances, either suspended on sludge particles or as free ions. Copper can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms. The decomposition of organic matter may seriously slow down because of this.

**Table 13.** Main sources of Cu in Uppsala (Stock, 1997).

Industries and activities (discharge in 1995)	Products (amount in 1995)
Sewage Treatment Plant (330 kg)	Breakage systems in cars (1-2 tons/year)
UEAB	Paints
Atmospheric deposition (6.1 tons)	Impregnated products Roof runoff Corrosion of water pipes Construction waste (620 tons) Electronic waste (95 tons)

**Figure 3.** Cu flow in Uppsala 1995 (kg/year) (Stock, 1997).



#### 4.9.4. Chromium

Chromium is steel-gray, lustrous, hard, metallic, and takes a high polish. Its compounds are toxic. It is found as chromite ore.

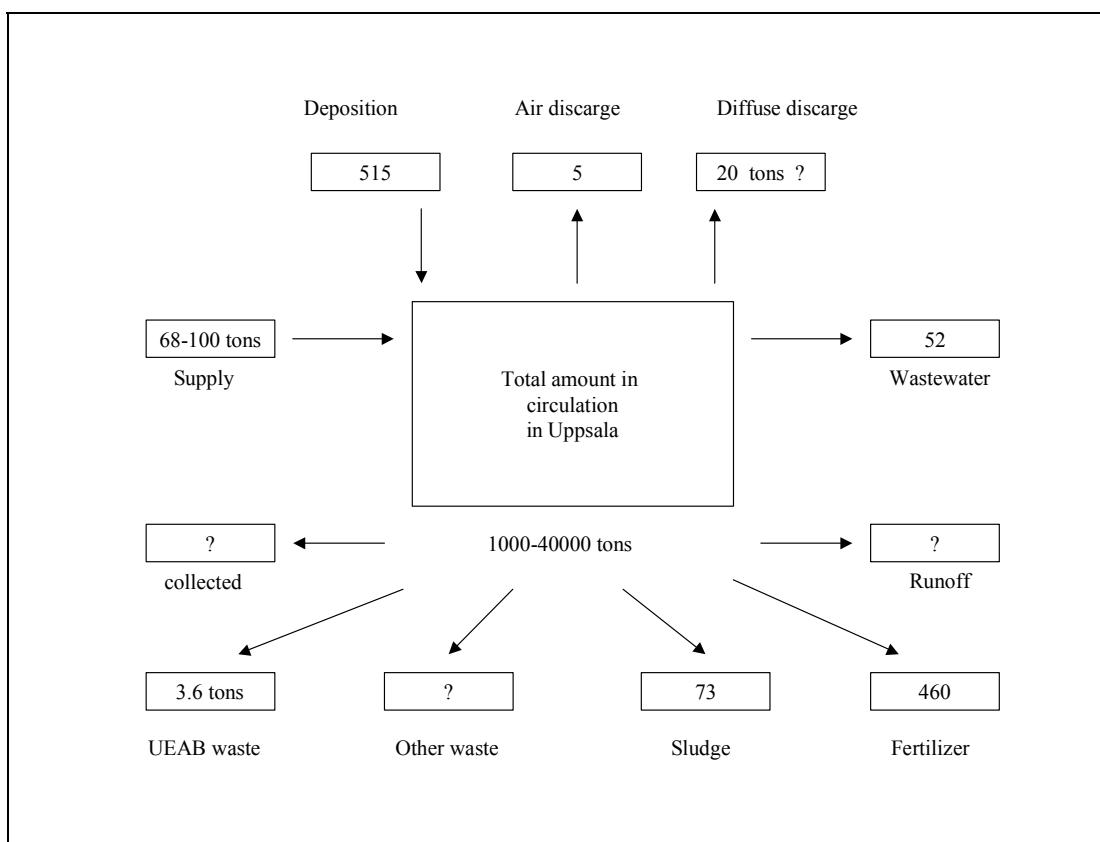
People can be exposed to Cr through breathing, eating or drinking and through skin contact with Cr or Cr compounds. Chromium (III) is an essential nutrient for human and shortages may cause heart conditions, disruptions of metabolisms and diabetes, but the uptake of too much Cr (III) can cause health effects as well. Chromium (VI) is a danger for human health as well as skin rashes, upset stomachs and ulcers, respiratory problems, weakened immune system, kidney and liver damage, alteration of genetic material, lung cancer, death. The main human activities that increase the concentrations of Cr (III) are steel, leather and textile manufacturing. The main human activities that increase Cr (VI) concentrations are chemical, leather and textile manufacturing, electro painting and other Cr (VI) applications in the industry. These applications will mainly increase concentrations of Cr in water. Through coal combustion Cr will also end up in air and through waste disposal Cr will end up in soils.

Chromium in soils strongly attaches to soil particles and as a result it will not move in solution towards groundwater. In water Cr will absorb on sediment and become immobile. Only a small part of the Cr that ends up in water will eventually dissolve. Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of Cr in the soil rises, this can still lead to higher concentrations in crops. Acidification of soil can also influence Cr uptake by crops. Plants usually absorb only Cr (III). This may be the essential kind of Cr, but when concentrations exceed a certain value, negative effects can still occur.

**Table 14.** Main sources of Cr in Uppsala (Stock, 1997).

Industries and activities	Discharge in 1995 (kg)	Products (amount in 1995)
Sewage Treatment Plant	52	Breakage systems in cars
Swerock (cement producer)	5	Paints and plastics
UEAB	5.8 + 3.6 tons	Impregnated products
Disposal site	515	Cement
Car washes		Electronic waste (800 kg?)

**Figure 4.** Cr flow in Uppsala 1995 (kg/year) (Stock, 1997).



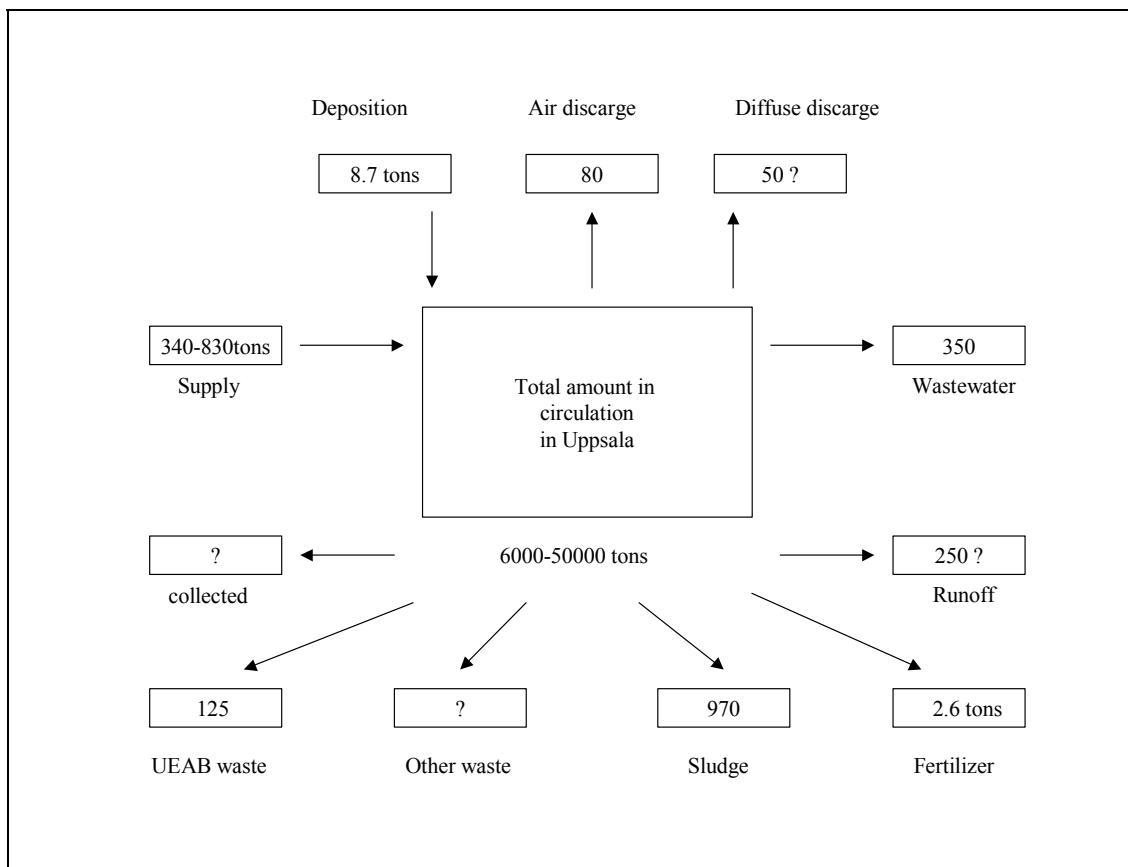
#### **4.9.5. Zinc**

Zinc is a very common substance that occurs naturally. Many foodstuffs contain certain concentrations of Zn. Drinking water also contains certain amounts of Zn, which may be higher when it is stored in metal tanks. Industrial sources or toxic waste sites may cause the Zn amounts in drinking water to reach levels that can cause health problems. Zinc is a trace element that is essential for human health. When people absorb too little Zn they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc-shortages can even cause birth defects. Too much Zn can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of Zn can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. Extensive exposure to Zn chloride can cause respiratory disorders. Zinc occurs naturally in air, water and soil, but Zn concentrations are rising unnaturally, due to addition of Zn through human activities. Most Zn is added during industrial activities, such as mining, coal and waste combustion and steel processing. The world's Zn production is still rising. This basically means that more and more Zn ends up in the environment. Water is polluted with Zn, due to the presence of large quantities of Zn in the wastewater of industrial plants. This wastewater is not purified satisfactory. One of the consequences is that rivers are depositing zinc-polluted sludge on their banks. Zinc may also increase the acidity of waters. Large quantities of Zn can be found in soils. When the soils of farmland are polluted with Zn, animals will absorb concentrations that are damaging to their health. Water-soluble Zn that is located in soils can contaminate groundwater. Zinc cannot only be a threat to cattle, but also to plant species. Plants often have a Zn uptake that their systems cannot handle, due to the accumulation of Zn in soils. Finally, Zn can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms. The breakdown of organic matter may seriously slow down because of this.

**Table 15.** Main sources of Zn in Uppsala (Stock, 1997).

Industries and activities	Discharge in 1995 (kg)	Products (amount in 1995)
Sewage Treatment Plant	347	Anticorrosive
UEAB	35	Batteries
Wood burning	45	Plastics and paints
Atmospheric deposition	8.7 tons	Diffuse leakage (50 tons) Buildings and roofs Electronic waste (90 kg)

**Figure 5.** Zn flow in Uppsala 1995 (Stock, 1997).



#### 4.9.6. Nickel

Nickel is silvery white metal that takes on a high polish. It is of the iron group, and is hard, malleable, and ductile. It occurs combined with sulphur in millerite, with arsenic in the mineral niccolite, and with arsenic and sulphur in Ni glance. Nickel is a compound that occurs in the environment only at very low levels. Humans use Ni for many different applications. The most common application of Ni is the use as an ingredient of steel and other metal products. It can be found in common metal products such as jewellery. Foodstuffs naturally contain small amounts of Ni. Nickel uptake will boost when people eat large quantities of vegetables from polluted soils. Plants are known to accumulate Ni and as a result the Ni uptake from vegetables will be eminent. Smokers have a higher Ni uptake through their lungs. Finally, Ni can be found in detergents. Humans may be exposed to Ni by breathing air, drinking water, eating food or smoking cigarettes. Skin contact with nickel-contaminated soil or water may also result in Ni exposure. In small quantities Ni is essential, but when the uptake is too high it can be a danger to human health. An uptake of too large quantities of Ni has the following consequences:

- Higher chances of development of lung cancer, nose cancer, larynx cancer and prostate cancer;

- Sickness and dizziness after exposure to Ni gas;
- Lung embolism;
- Respiratory failure;
- Birth defects;
- Asthma and chronic bronchitis;
- Allergic reactions such as skin rashes, mainly from jewellery;
- Heart disorders;

Nickel fumes are respiratory irritants and may cause pneumonitis. Exposure to Ni and its compounds may result in the development of a dermatitis known as “nickel itch” in sensitized individuals. The first symptom is usually itching, which occurs up to 7 days before skin eruption occurs. The primary skin eruption is erythematous, or follicular, which may be followed by skin ulceration. Nickel sensitivity, once acquired, appears to persist indefinitely.

Nickel is released into the air by power plants and trash incinerators. It will then settle to the ground or fall down after reactions with raindrops. It usually takes a long time for Ni to be removed from air. Nickel can also end up in surface water when it is a part of wastewater streams. The larger part of all Ni compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result. In acidic ground however, Ni is bound to become more mobile and it will often rinse out to the groundwater.

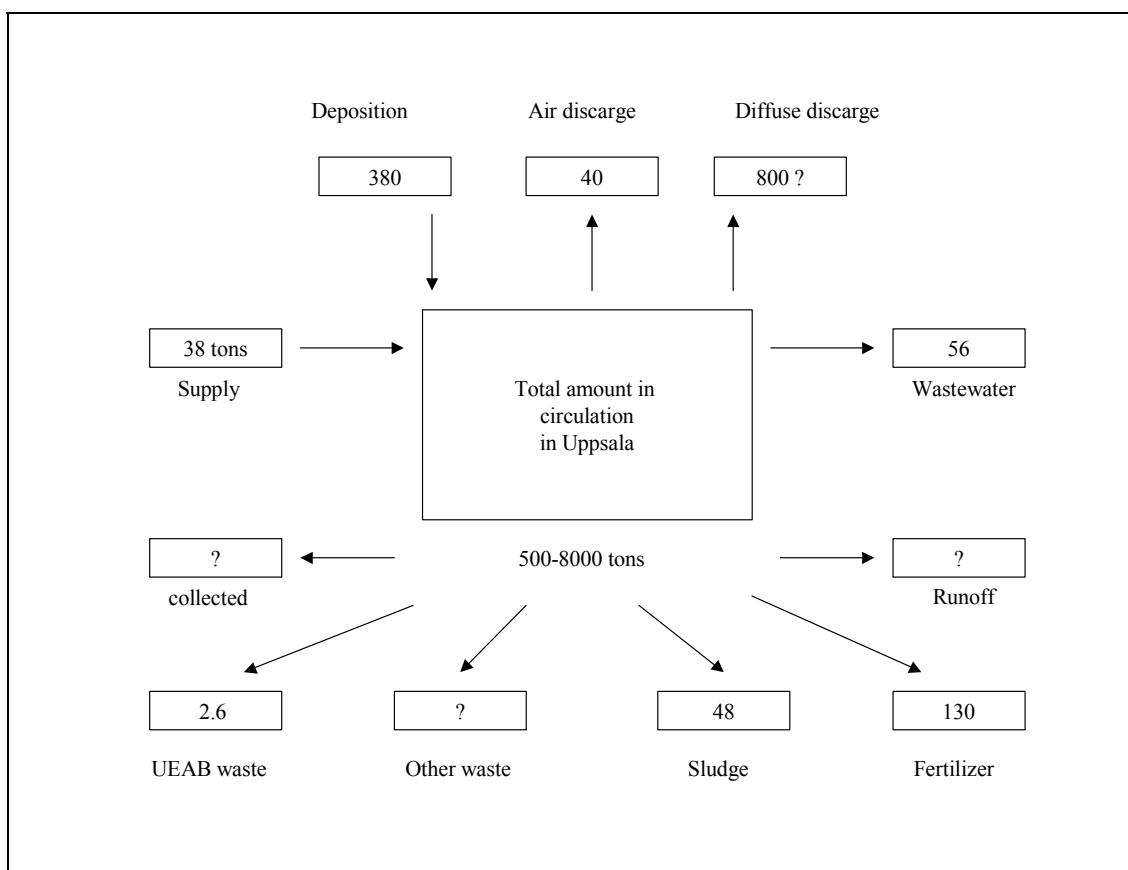
There is not much information available on the effects of Ni upon organisms other than humans.

Nickel is not known to accumulate in plants or animals. As a result Ni will not up the food chain.

**Table 16.** Main sources of Ni in Uppsala (Stock, 1997).

Industries and activities	Discharge in 1995 (kg)	Products (amounts in 1995)
Sewage Treatment Plant	56	Stainless steel
UEAB	56 kg + 2.6 tons waste	Coatings
Disposal site		Chemicals
Atmospheric deposition	380	Batteries Paints Electronic waste (5.4 tons)

**Figure 6.** Ni flow in Uppsala 1995 (kg) (Stock, 1997)



#### 4.9.7. Arsenic

Arsenic is a naturally occurring element widely distributed in the earth's crust. In the environment, As is combined with oxygen, chlorine, and sulfur to form inorganic As compounds. Arsenic in animals and plants combines with carbon and hydrogen to form organic As compounds. Inorganic As compounds are mainly used to preserve wood. Organic As compounds are used as pesticides, primarily on cotton plants. Arsenic has fairly low toxicity in comparison with some other metals, although with chronic exposure there is some concern about his effect on chromosomes and its carcinogenicity. In fact, it may even be essential in human in very small amounts. Organic As as arsenate and elemental As both found naturally in the earth and in foods do not readily produce toxicity. It accumulates in the body, particularly in the skin, hair and nails but also in internal organs. Arsenic can accumulate when kidney function is decrease. Luckily, absorption of As is usually really low. It is present in small amounts in soil, in the ocean (As in most seafood), and as contaminant in meats as well. Arsenic is also found in many fuel oils and coal, in weed killers and some insecticides. Possible effects of As toxicity include hair loss, dermatitis, diarrhea and other gastrointestinal symptoms, fatigue, headaches, confusion, muscle

pains, red and white blood cell problems, neurological symptoms and liver and kidney damage.

**Table 17.** Main sources of As in Uppsala (Stock, 1997).

Industries and activities	Discharge in 1995 (kg)	Products (amounts in 1995)
Heat- and energy Plant	1.6 kg + 2.8 tons waste	Impregnated wood
Metal works		Vermin control
Disposal Plant	0.16	Coatimngs
Atmospheric deposition	330	Plastics
Traffic		

## 5. OBJECTIVES AND HYPOTHESIS

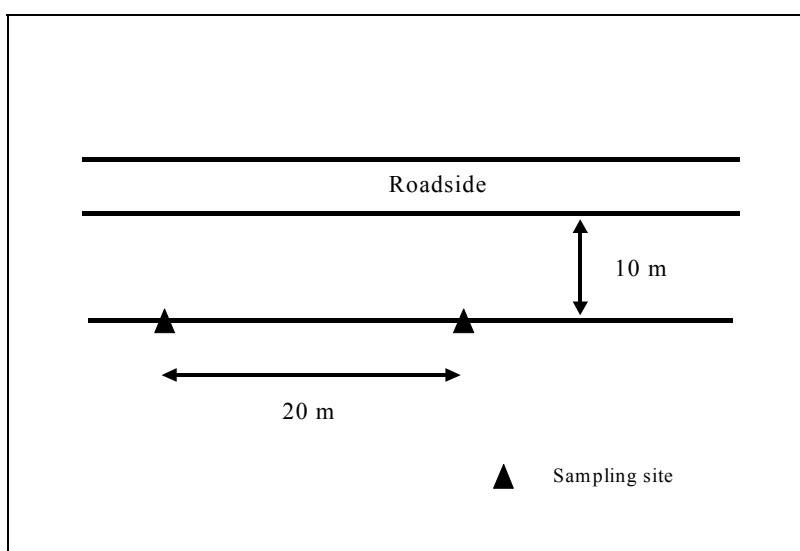
The objective of this study was to determine and evaluate contents of biogenic and non biogenic trace metals and some properties in roadside soils of Uppsala City. The working hypothesis was that depending on the traffic intensity, location, history and activities soil contents of the metals vary regardless of a similar bedrock.

## 6. MATERIALS AND METHODS

### 6.1. Soil sampling

Each sampling point lay 10 m from the roadside. The points lay 20 m from each other, giving a grid of 10 m \* 20 m (figure 7). One composite sample was taken at each site ( $200 \text{ m}^2$ ). Four such sites were sampled at each roadside, giving a total area of  $200 \text{ m}^2 * 4 = 800 \text{ m}^2$  along the roads.

**Figure 7.** Sampling method



**Table 19.** The roadsides sampled

sampling site code	Road's name	Traffic intensity/day (2001)	*Number of points sampled
DAG	Daghammarskjöldvägen	$\geq 10000 \leq 15000$	4
E4	European Highway	$\geq 25000 \leq 40000$	4
KUN	Kunsgatan	$\geq 15000 \leq 20000$	4
LUT	Luthagsesplanaden	$\geq 12000 \leq 17000$	4
EKE	Ekeby	$\geq 7000 \leq 10000$	4
KÅB	Kåbovägen	$\geq 4000 \leq 6000$	4

\*Number=5 sites per road where samples but only four were analysed to minimized the cost.

A Stainless steel auger was used and the samples were stored in plastic bags for transport to laboratory. About 1 kg was taken at each point from the horizons 0-10 cm and 10-20 cm layers.

### 6.1.1. Soil sample preparation

The samples were placed into open paper boxes and dried at 35°C for one week. Following drying the soils were crushed and passed through a  $\leq 2$  mm sieve for chemical and physical analyses.

**Uppsala map** (Uppsala turist & kongress, phosworks interactiv AB)



## ***6.2. Analysis of physical properties***

The determination of the soil texture was done by the pipette method.

The pipette method is widely used and it is a sedimentation procedure. It utilizes pipette sampling at controlled depths and times. It was simultaneously developed by Jennings et al. (1922), Krauss (1923) and Robinson (1922). This method depends on the fact that sedimentation eliminates from the depth ( $h$ ) in a time ( $t$ ) all particles having settling velocities greater than  $h/t$ , while retaining at that depth the original concentration of particles having settling velocities less than  $h/t$ .

Where modern equipment is not available, organic carbon is usually determined by Wakley and Black (1965) wet combustion method.

Today many laboratories have LECO2000 analyzer, which simultaneously analyzes C, N and S by dry combustion. Organic matter is then calculated by multiplying %C by the factor 1.724. Organic matter can also be approximated by determining loss on ignition at 450-500 °C.

Finely grained ( $\leq 0,004$  mm) duplicate samples were used to determine total C on Leco CNS-2000 furnace equipment (in this thesis only total C is represented).

Another duplicated sample was ignited to determine loss on ignition.

### ***6.2.1. Loss on ignition***

#### *Equipment*

- Crucible;
- Balance (0,001 resolution);
- Desiccator;
- Muffle furnace;

#### *Procedure*

The crucibles and samples of 1 g were weighed using the balance with 0,001 resolution. The 1 g samples and the crucibles were then weighed together to measure the combined mass.

The samples were put in the muffle furnace and ignited at 450-500 °C, for 3 h. Thereafter the crucibles were cooled in a desiccator (room temperature) for at least one h.

The crucibles with the ignited soil were then weighed again.

Loss on ignition was finally calculated.

### ***6.2.2. Soil texture: pipette methods***

#### *Equipment*

- Suction filtration;
- Pipette sampling;
- Brass plunger;
- Constant-temperature room;

- Shaker, horizontal reciprocating type;
- Sieve shaker, vertical and lateral movements;
- Sieves, set of 6, 3-inch diameter frame.

#### *Reagents*

- Hydrogen peroxide ( $H_2O_2$ ), 30%;
- Calgon solution: 50g of Calgon in water and dilute the solution to 1 l.

#### *Procedure*

##### *Sampling and pre-treatment.*

The samples were dried and crumbled and the “fine earth” was separated by hand sieving through 2 mm sieve. A subsample of approximately 10 g was placed in a tared 250 ml beaker dried overnight at 105°C and later on cooled in a desiccator. Thirty ml of water were added into the beaker and the content stirred by swirling. Cautiously a few ml of  $H_2O_2$  were added and the suspension was swirled. When the reaction subsided an additional amount of  $H_2O_2$  was added and the digestion completed by heating the beaker for 1 hour or more at 90°C. The treatment was repeated if visual inspection indicated that the reaction was not completed.

##### *Filtration*

By filtration apparatus the excess of liquid had been removed, water was added and the suspension mixed by a jet of water. The suspension was filtered again and mixing and filtering repeated several time. The soil was then dislodged from the filter and put in a beaker and dried in a oven at 105°C and cooled in a desiccator. The dry sample and beaker were weighed.

##### *Dispersion and wet-sieving*

An amount of 10 ml of Calgon solution was added and the contents brought into suspension by swirling the beaker. Samples of 10 ml of Calgon solution were transferred to a tared weighed bottles and dried overnight at 105°C, cooled in a desiccator and weighed. The suspension was then transferred though a funnel into a 250 ml shaker bottle and water was added to bring the volume to 180 ml. The bottles were shaken overnight in a horizontal reciprocating shaker and later on the suspension was let settle for a few minutes. The solution was transferred in a 1l graduated cylinder through a wide-mouth funnel where 47  $\mu$  sieve was placed. The mixing and decanting were repeated several times until most of the fine material had been transferred. Distilled water was then added to bring the volume of suspension to 1l; a rubber stopper was inserted and the cylinder transferred to the constant temperature room.

##### *Dry sieve analysis*

The screen and contents were put in a tared evaporating dish and dried in the oven. The screen was cooled and the coarse fraction transferred from this to the dishes,

which were put in an oven for two hours at 105°C. They were then cooled and a desiccator and dishes and sand were weighed to the nearest 0.01 g. The coarse fraction was transferred into the top screen and shaken for 3 minutes. The separates were transferred into tared evaporating dishes and weighed; the weight was then compared with the total weight of the coarse fraction previously determined.

#### *Sedimentation analysis with pipette sampling*

The temperature of the suspension was recorded when had become constant, and the plunger inserted and moved up and down to mix the contents thoroughly. Any sediment was dislodged, the plunger removed and the time was recorded immediately. The pipette was immersed for 10cm in the suspension when the proper time had arrived. At the chosen time the suction stopcock was opened and closed at the instant the liquid had filled the pipette. The suspension was reversed into a tared weighing bottle, which was heated in an oven at 150°C for 12hours and later on cooled in a desiccator. The bottle was then weighed.

#### *Calculations*

The weight of particles was calculated from the formula:  $wV/v$ , where “ $w$ ” was dry weight of the pipette sample, “ $v$ ” was volume of the pipette and “ $V$ ” was total volume of the suspension.

**Table 20.** Particles classification

<b>Particles classification</b>	<b>Dimension of the particles</b>
Clay	> 0.002 mm
Fine silt	0.002 mm < x < 0.006 mm
Coarse silt	0.006 mm < x < 0.02 mm
Fine sand	0.02 mm < x < 0.06 mm
Coarse sand	0.06 mm < x < 0.2 mm
Medium sand	0.2 mm < x < 0.6 mm
Very coarse sand	0.6 mm < x < 2 mm

### *6.3. Analysis of chemicals properties*

#### *6.3.1. Cation exchange capacity determination*

Different methods are used to determine CEC of soils. For example, a solution of ammonium acetate (1 M, pH 7) is used to extract soil exchangeable basic cations, followed by saturation of the soil with calcium acetate solution (1 M, pH 7), thereafter the excess Ca is removed with a solution ethanol (1:1 in water) and finally Ca adsorbed by soil is extracted with the ammonium acetate solution. In another method, a preliminary step involves extracting exchangeable bases and Al using 0.1 M BaCl<sub>2</sub> – triethanolamine solution (pH 8.2). The Ba adsorbed by the soil (representing soil CEC) is extracted with MgSO<sub>4</sub> solution. This procedure is preferred to the first one due to Ba's strong replacing power without being

preferentially adsorbed, and the fact that it does not cause the collapse of expanded phyllosilicates as does K<sup>+</sup> or NH<sub>4</sub><sup>+</sup>. The solution of BaCl<sub>2</sub>, triethanolamine and MgSO<sub>4</sub> were prepared by technical committee ISO/TC 190, Soil quality, Chemical methods and soil characteristics authorized by the International Organization of Standardization (ISO, 1995, International Organization of Standardization Case postal 5b CH-1211 Genève 20 Switzerland). The cation exchange capacity was determined using 0.1 M BaCl<sub>2</sub> – triethanolamine solution (pH 8.2).

#### *Equipment*

- Centrifuge tubes (100 ml);
- 100 ml battles;
- pipettes (25 ml and 40 ml)
- balance;
- filter paper;
- shaker;
- centrifuge;
- 5 g soil sample ( $\leq$  2mm).

#### *Reagents*

- Distilled water;
- BaCl<sub>2</sub> (0.1 mol/l), sol. A, dissolve 24,43 g of BaCl<sub>2</sub>. 2H<sub>2</sub>O in 900 ml of distilled water. Make to 1liter;
- HCl (2 mol/l), sol. B, 166 ml conc. ( $\rho$ = 1,19 g/ml) dilute to 1 l with distilled water;
- BaCl<sub>a</sub> (0,02 mol/l), sol. C, dilute 25 ml of sol. A to 1l with distilled water;
- MgSO<sub>4</sub> (0,02 mol/l), sol. D, 4,93 g MgSO<sub>4</sub>\*7H<sub>2</sub>O dissolve in 900 ml of distilled water and dilute to 1l. Preserve in refrigerator (0-4°C);
- Triethanolamine, sol E, 90 ml (HOCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N make to 1l with distilled water; adjust pH to 8.2 $\pm$ 0,02 by adding 140-150 ml sol B and dilute to 2l with distilled water;
- Extraction solution, sol. F, mix sol. A and sol. E at 1:1 ratio;
- Methanol (95%), sol. G, for removal of excess BaCl<sub>2</sub> in the extraction procedures.

#### *Extraction of exchangeable basic cations*

Samples of 5g were weighed into 50ml centrifuge tubes. Twenty-five ml of solution F (BaCl<sub>2</sub>) were added and the tubes shaken for one hour. The samples were then centrifuged at 2000 rpm for 15 min and the supernatant solution filtered through filter paper. The solution was collected in polyethylene battles. This procedure was repeated for 4 times, after the last one the polyethylene battles were filled to 100ml with solution F and kept in a refrigerator for analysis of Na, Ca, Mg on ICP (and NH<sub>4</sub> on colorimeter).

### *Removing excess of Ba<sup>2+</sup> from soils*

The soil therefore was saturated with BaCl<sub>2</sub>, the excess was removed using solution C first and then solution G.

Forty ml of solution C were added to the centrifuge tube to remove the excess of Ba<sup>2+</sup> in the soils. The tubes were shaken by hand until the soil cake was broken and then centrifuged at 2000 rpm and the solution was discarded.

Solution G was then added to further remove the excess of Ba<sup>2+</sup>, and after had been shaken with hand and then centrifuged at 2000 rpm, the solution was threw a way. The tubes with soil were then weighed.

### *Extraction and determination of Ba<sup>2+</sup> from soils*

Twenty-five of solution D were added to the tubes and then shaken over night. After this they were centrifuged at 2000 rpm for 10 min.

The solution was then collected into 100ml polyethylene battles. This procedure was repeated for 4 times, after the last one the battles were filled with solution D.

The Ba<sup>2+</sup> was then determined on ICP MS equipment, (Inductively coupled plasma-mass spectrometry), which is a fast, precise and accurate multi-element analytical technique for the determination of trace elements in a variety of liquid and solid sample materials.

#### **6.3.2. Determination of pH**

The pH was determined in deionised water and in calcium chloride solution

#### ***Equipment***

- Tubes;
- Pipettes (25 ml);
- Balance;
- pH meter;
- shaker.

#### ***Reagents***

- distilled water;
- calcium chloride solution (0.01 M);
- calibration buffer solution pH 7;
- calibration buffer solution pH 4.

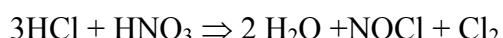
#### ***Procedure***

Samples of 5g were weighed into tubes, and 25 ml of calcium chloride was added. Another 5g was mixed with 25 ml of distilled water. The tubes were then shaken over night.

The pH meter was calibrated with buffer solutions, pH 4 and 7, before the soil suspension was measured.

#### *6.4. Trace metal analysis*

The amount of heavy metals (Cu, Mn, Zn, Cr, Ni, As, Pb, Cd, W) in the soil samples was determined by aqua regia digestion. This consists of treating the samples with a 3:1 mixture of hydrochloric and nitric acids. Nitric acid destroys organic matter and oxidizes sulphide material. It reacts with concentrated hydrochloric acid to generate aqua regia:



Aqua regia is an effective solvent for most base metal sulphates, sulphides, oxides and carbonates but only provides a “partial” digestion for most rock forming minerals, minerals of a refractory nature. The metal contents determined by the aqua regia method are approximate measure of total contents.

#### *Equipment*

- Digestion tubes;
- Pipettes;
- Digestion block;
- ICP-MS equipment.

#### *Reagents*

- 1 part of  $\text{HNO}_3$  (65% pro anal) mixed with 3 parts of HCl (37% pro anal) to obtain 1 l of solution, (250ml of  $\text{HNO}_3$  + 750ml of HCl);
- Distilled water.

#### *Procedures*

Three glass beads were placed into a 150 ml size digestion tube. The samples of 1,5 g air-dried soil of the  $\leq 2$  mm fraction were weighed and placed into the tube and 14 ml of aqua regia was added. After standing for 16 h the tubes were placed in a digestion block, and the temperature was gradually raised until foams appeared in the tube. Thereafter they were digested for 2 h. The formation of dark yellowish digestate indicates the presence of organic matter, which must be eliminated by adding more aqua regia. one ml of  $\text{HNO}_3$  was added and the digestion continued. The operation was repeated until a clear supernatant was obtained. Generally digestion is ready when about 5ml remains in the tube. Thereafter the tubes were cooled and 50ml of distilled water were added. The tubes were cooled then swirled and the solution diluted to the 100ml-mark, swirled again and suitable aliquots of solution was taken for analysis.

The metal concentration was determined on ICP-MS equipment.

The concentration of metals are expressed per unit soil dry matter (105 °C): mg kg<sup>-1</sup> or µg kg<sup>-1</sup> or %.

## 7. STATISTICAL ANALYSIS

The results were subjected to statistical analysis using the SAS package (SAS Institute, 1990). The student's t-test ( $P = 0.05$ ) was used to compare means.

Each grid (10\*20) was a replicate. Each road side consisting of 4 grids was a treatment.

## 8. RESULTS AND DISCUSSION

### 8.1. Soil Characteristics

#### 8.1.1. Physical characteristics

Mean pH values are presented in Table 21. The soil pH in water was nearly neutral at all places. At all road sides, pH increased with depth, with pH values determined in water being higher than the ones determined in CaCl<sub>2</sub>. The latter method eliminates the effects of small differences in electrolyte concentration that may be caused by upward salt movement in soils. The pH measured in H<sub>2</sub>O ranged between 6.6 and 7.8, with a mean of 7.3. The differences between the two measurements (water and CaCl<sub>2</sub>) were 0.3-0.4 units in the topsoil and 0.9-1.5 in the subsoil. In Table 21 data on organic matter, loss on ignition and carbonates are also presented. The organic matter contents ranged from 2.4 to 8.4%, with a mean value of 5.1%. Loss on ignition was higher than organic matter content. This was not surprising because part of the mineral C in carbonates is also lost during ignition at 500°C. The results on organic matter were corrected for carbonates.

**Table 21.** Soil pH, carbonate, organic matter and loss on ignition

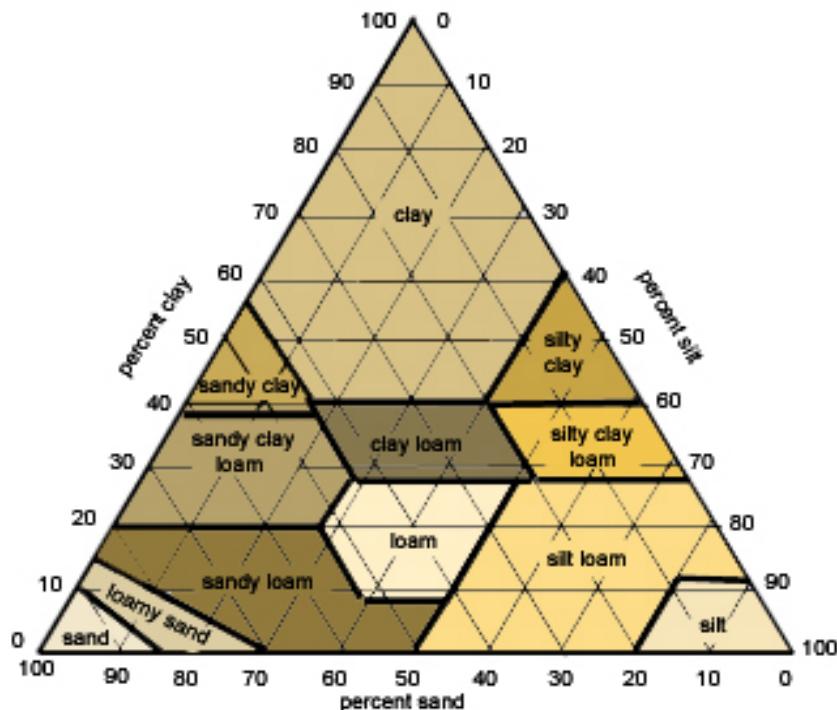
Sampling site	Depth cm	pH	pH	Difference	CaCO <sub>3</sub>	OM	Loi
		H <sub>2</sub> O	CaCl <sub>2</sub>			%	
<b>DAG</b>	0-10	6.9	6.5	0.4	1.53	8.4	9.7
	10-20	7.4	6.1	1.2	1.33	4.8	5.3
<b>EKE</b>	0-10	7.7	7.3	0.4	0.50	7.0	9.8
	10-20	7.8	6.3	1.5	0.48	3.3	5.4
<b>E4</b>	0-10	6.6	6.2	0.4	0.29	5.5	7.1
	10-20	6.6	5.7	0.9	0.67	4.7	5.9
<b>LUT</b>	0-10	7.5	7.1	0.4	0.80	5.4	7.6
	10-20	7.8	6.3	1.5	1.6	4.4	5.6
<b>KUN</b>	0-10	7.1	6.8	0.3	1.42	6.3	10.1
	10-20	7.4	6.2	1.3	1.74	3.4	7.4
<b>KÅB</b>	0-10	7.4	7.0	0.3	1.12	5.1	7.6
	10-20	7.5	6.1	1.3	0.61	2.4	5.1
<b>Mean</b>		7.3	6.5	0.8	1.0	5.1	7.2
<b>Median</b>		7.4	6.3	0.7	1.0	4.9	7.3
<b>Min</b>		6.6	5.7	0.3	0.3	2.4	5.1
<b>Max</b>		7.8	7.3	1.5	1.7	8.4	10.1
<b>Std (±)</b>		0.42	0.48	0.49	0.51	1.68	1.84

In Table 22 are presented soil contents of clay, silt and sand. According to the textural classes (Figure 8), the E4 soil was “silt loam” while the rest of soils were “sandy clay loams”. Distribution of the fractions was relatively even in both the topsoil and subsoil.

**Table 22.** Textural properties

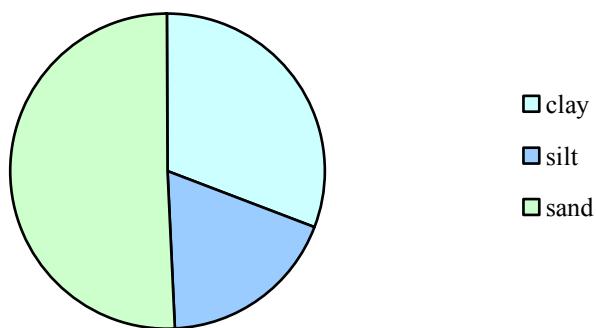
Sampling sites	Depth cm	Clay	Fine silt	Coarse silt	Fine sand	Coarse sand	Medium sand	Very coarse sand
		%	%	%	%	%	%	%
<b>DAG</b>	0-10	28	9	7	9	19	16	4
	10-20	30	10	7	10	17	15	7
<b>EKE</b>	0-10	25	8	7	9	14	16	14
	10-20	26	10	8	8	11	17	17
<b>E4</b>	0-10	24	5	5	14	45	1	1
	10-20	24	5	5	14	46	1	0
<b>LUT</b>	0-10	33	11	13	13	7	7	10
	10-20	34	12	14	13	5	7	9
<b>KUN</b>	0-10	30	8	8	13	12	11	11
	10-20	36	11	10	10	9	10	9
<b>KÅB</b>	0-10	30	12	6	5	15	19	7
	10-20	30	13	6	6	19	20	3
<b>Mean</b>		29	10	8	10	18	12	8
<b>Median</b>		30	10	7	10	15	13	8
<b>Min</b>		24	5	4	5	5	1	0
<b>Max</b>		36	13	14	14	46	20	17
<b>Std dev</b>		3.9	2.6	3.0	3.3	13.6	6.5	5.2

**Figure 8.** Soil textural triangle (Brady & Weil, 1996).



Compared to the results obtained in a similar research that have been done in Torino (Pezzuolo, 2004), where the means of the samples examined were 7% for clay, 39% for silt and 55% for sand, the results from the Uppsala studies discussed above were higher for clay and lower for silt and sand. The average of the amount of the different particles in the soils analysed is shown in Figure 9.

**Figure 9.** The proportions of clay, silt and sand in the soil of Uppsala.



### 8.1.2. Chemical characteristics

Analytical data on CEC and base saturation (V) are presented in Table 23. The CEC values ranged between 10.6 and 37.9 cmol kg<sup>-1</sup>, with a mean of 20.0 cmol kg<sup>-1</sup>. The topsoils usually showed higher values than in the subsoils, possibly due higher organic matter contents in the topsoil.

**Table 23.** Soil Cation exchange capacity (CEC) and base saturation (V)

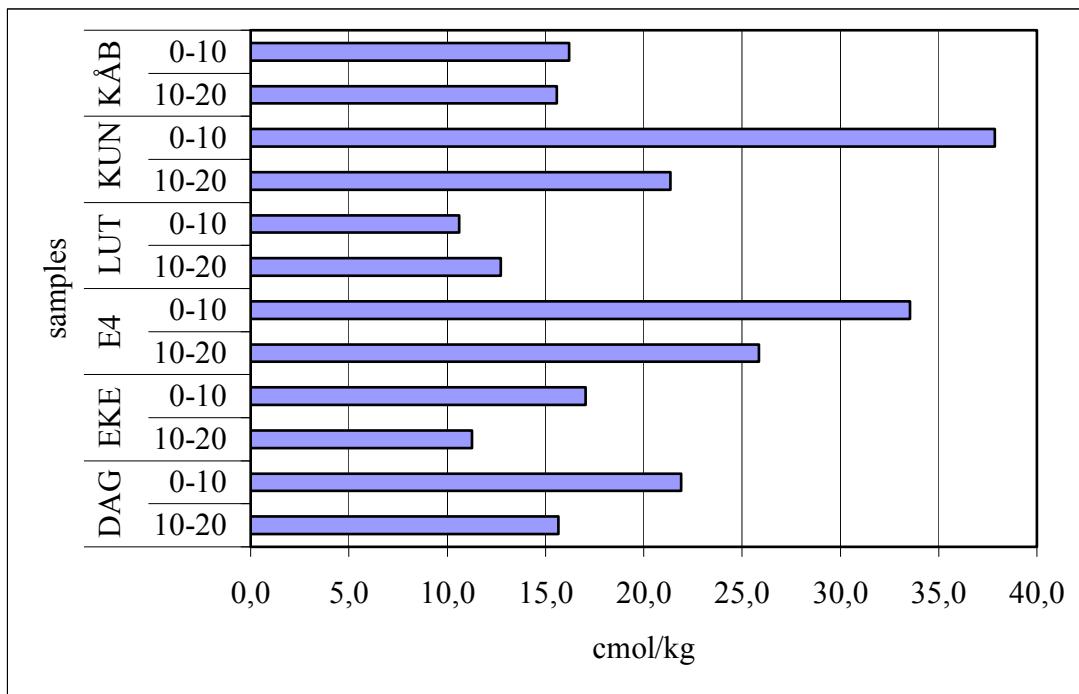
Sampling sites	Depth cm	CEC cmol/kg	V %
<b>DAG</b>	0-10	21.9	44.3
	10-20	15.7	50.9
<b>EKE</b>	0-10	17.0	59.6
	10-20	11.3	74.4
<b>E4</b>	0-10	33.5	27.8
	10-20	25.9	35.6
<b>LUT</b>	0-10	10.6	87.0
	10-20	12.7	75.4
<b>KUN</b>	0-10	37.9	28.2
	10-20	21.4	49.8
<b>KÅB</b>	0-10	16.2	46.5
	10-20	15.6	39.3
<b>Mean</b>		20.0	51.6
<b>Median</b>		16.6	48.2
<b>Min</b>		10.6	27.8
<b>Max</b>		37.9	87.0
<b>Std (±)</b>		8.64	19.08

Base saturation in soils ranged between 27.8 to 87%. This was rather surprising considering the nearly neutral pH of the soils. CEC was determined at pH 8.3. At that reaction pH-dependent negative sites are determined as well, explaining the high CEC giving low base saturation. This could have happened for negative charges in clay and organic matter (Coleman & Thomas, 1967). CEC due organic matter was calculated as follows:

$$(CEC/\% \text{organic matter}) * 100$$

In figure 10 is depicted CEC. Interestingly, the results sharply contrasted among soils, especially in the Kun and E4 samples whose CEC was 37.9 and 33.5 cmol kg<sup>-1</sup>, respectively. Quantities of organic matter seem to have not impacted on the size of calculated CEC. Apparently, the results reflect quality of the organic matter. The higher humified organic matter is the higher CEC. It seems that organic matter at Kun and E4 were more humified than in other soils.

**Figure 10.** Cation exchange capacity.



## 8.2. Distribution of metals

### 8.2.1. Distribution of biogenic metals

The term “bio” means “life” or “associated with life”. The term “biogenic” means “essential for maintaining the fundamental life processes”. Therefore, “biogenic trace metals” means the metals essential for maintaining the fundamental life processes. “Essential” means “basic” or “fundamental”. Those metals are Cu, Fe, Zn, Mn, Mo and Se. Chromium and nickel sometime play an important role in life processes. For example, if taken up in small amount in food, Cr is involved in the metabolism of insulin (Pickston et al., 1985). The “non-biogenic” metals are Pb, Cd, As, Hg, Co, etc.

The amounts of the metals in soil samples were, in most cases, lower than the limits imposed by the Environmental Code.

As evidenced in the Table 24 contents of the biogenic trace metals increased in the following order: Cu < Zn < Mn < Fe.

**Table 24.** Soil contents of Fe, Mn, Cu and Zn

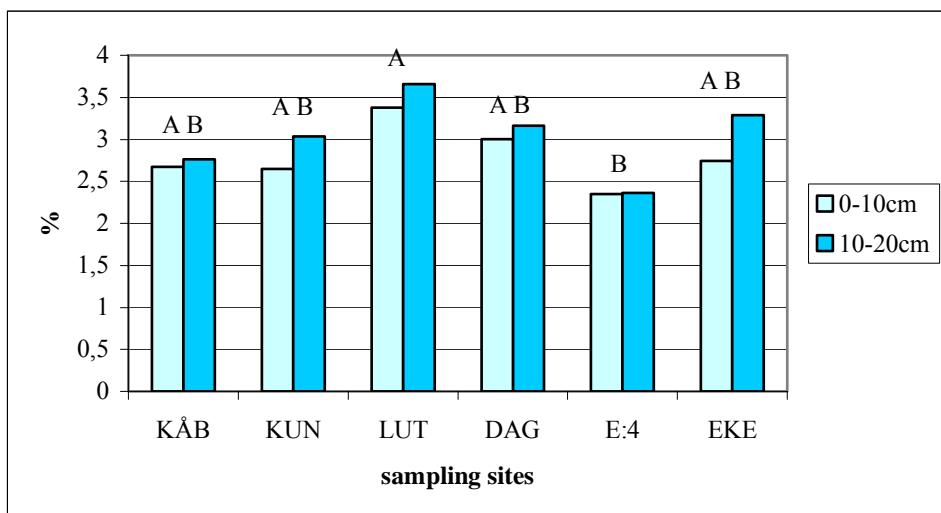
Sampling sites	Depth cm	Fe	Mn	Cu	Zn
		%	mg kg <sup>-1</sup>		
<b>DAG</b>	0-10	3.00	666	28.2	148
	10-20	3.16	704	35.1	150
<b>EKE</b>	0-10	2.74	580	24.8	123
	10-20	3.29	643	27.6	128
<b>E4</b>	0-10	2.35	387	21.3	111
	10-20	2.36	396	23.3	111
<b>LUT</b>	0-10	3.38	772	32.4	150
	10-20	3.66	745	27.0	139
<b>KUN</b>	0-10	2.65	504	37.1	151
	10-20	3.04	553	47.3	146
<b>KÅB</b>	0-10	2.67	672	21.3	117
	10-20	2.76	676	20.2	112
<b>Mean</b>		2.9	608	28.8	132
<b>Median</b>		2.9	654	27.3	134
<b>Min</b>		2.3	387	20.2	111
<b>Max</b>		3.7	772	47.3	151
<b>Std (±)</b>		±0.40	±127	±8.0	±16.8

These elements have a role in the enzymes reactions and they are involved in the production of chlorophyll. Deficiencies of these metals appeared as pale green condition of the plants. (Thompson & Troeh, 1978). When large quantities of those elements accumulate in the plants or in the soil they can also be toxic and harmful for human being.

### *Iron*

Iron plays an important role as a micronutrient for plant grow. Iron is extremely insoluble in certain compounds and its deficiencies in plant occurs mainly in alkaline soils. In well-drained soils it is oxidized and precipitated as ferric iron ( $Fe^{3+}$ ). It can be associated with humus or other soil components in which forms Fe becomes unavailable for plants. In waterlogged soils,  $Fe^{3+}$  is reduced to  $Fe^{2+}$ . Compounds of divalent Fe are soluble and available to plants. For example,  $FePO_4$  is insoluble, whereas  $Fe_3(PO_4)_2$  is soluble(Ponnampерuma, 1972). In this study, pH was nearly neutral and the soils were aerated, Fe could, hence, not have been in the available forms to plants. The amount of Fe ranged between 2.3% and 3.7%, with a mean of 2.9%. The amount of Fe was higher in the subsoil (Figure 11).

**Figure 11.** Percentage contents of Fe in the topsoil and in the subsoil.



Blocks whit a similar letter are not significantly different at 95% probability. Comparisons are made for each roadside.

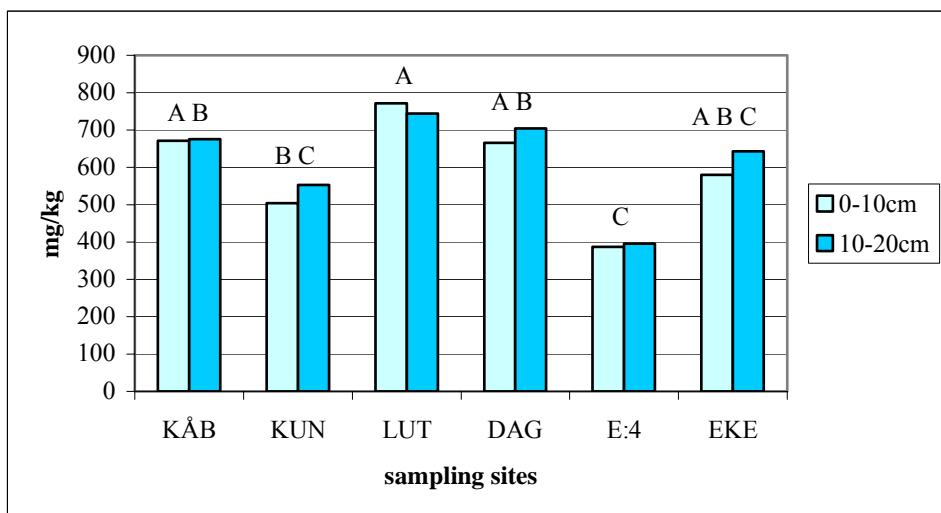
Antagonistic interaction between Fe and heavy metals has been observed in several crops (Kabata-Pendias & Pendias, 1991). Excess amounts of heavy metals, and of Mn, Ni and Co, has been reported to cause a reduction in adsorption and translocation of Fe. Manganese and Cu can serve as oxidizing agents. Indeed and as we will be seen later, Fe significantly correlated with Mn and Cu (Table 26).

#### *Manganese*

Manganese is involved in the production of chlorophyll and in the enzymic reactions. It is essential in small amount, even if toxic when it accumulates in large amount, it cannot be classified as contaminant.

Soil analytical data are presented in Table 24 and figure 12. In the experimental soils the contents ranged between  $387$  and  $771 \text{ mg kg}^{-1}$ , with a mean of  $608 \text{ mg kg}^{-1}$ . The determinations varied widely ( $\text{Std dev } \pm 126 \text{ mg kg}^{-1}$ ). This suggests different sources of Mn in the soils. At all sites, Mn was evenly distributed in both the topsoil and subsoil. The smallest contents were recorded in the E4 samples and largest in the LUT roadsides.

**Figure 12.** Concentrations of Mn in the topsoil and in the subsoil.



In the oxidized forms ( $Mn^{4+}$ ) Mn is not available to plants. In the reduced forms ( $Mn^{2+}$ ) Mn is available to plants (Ponnampерuma, 1972).

## Copper

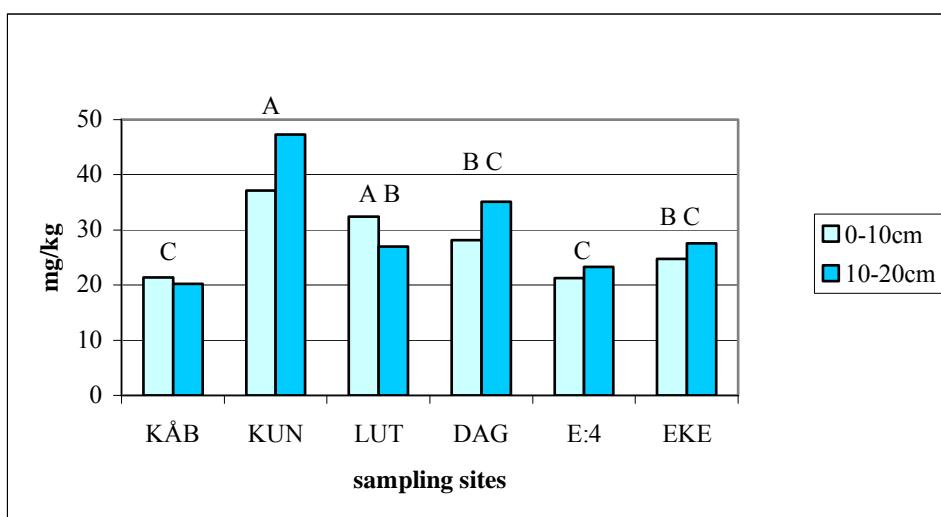
Copper is a stimulator of plant growth. This element in the soil occurs as ion, Cu<sup>++</sup> and it is held tightly by the cation exchange sites. Deficiencies of this element are common in organic (peat) soils and it is more soluble in acid than in alkaline conditions. (Thompson & Troeh, 1978). Chelation and complexion are the key reactions governing Cu behaviour in most soils. Many kind of organic substances form both soluble and insoluble complexes with Cu. Also soil minerals are capable of adsorbing Cu, this type of reaction depends on pH of the solution and is more important in the soils with large content of variable- charge minerals. (Thompson & Troeh, 1978). Contamination of soil by Cu compounds results from utilisation of Cu-containing material such as fertilizers, sprays, and agricultural or municipal wastes as well as from industrial emission.

Analytical data are presented in Table 24 and Figure 13.

Most of the samples showed a concentration at least half the permissible limits, i.e. they are below the 50 mg kg<sup>-1</sup> Swedish limit (Naturvårdsverket, 2001).

The concentration of Cu in the samples ranged between 20.2 mg kg<sup>-1</sup> and 47.3 mg kg<sup>-1</sup>, with a mean of 28.8 mg kg<sup>-1</sup>. The amounts were usually higher in the subsoil than in the topsoil, but in the samples from KÅB and LUT the concentrations decreased with depth. This is usually a common characteristic of Cu distribution in soil profiles and it reflects the bioaccumulation of the metal and also recent anthropogenic sources of the element (Kabata-Pendias & Pendias, 1991). Also in this case the higher amount of Cu in the subsoil can be explained by the presence of Leptite, which is a common component in the bedrock of Uppsala (Möller, 1993).

**Figure 13.** Concentrations of Cu in the topsoil and in the subsoil.



The results reported in this study coincide with those reported for the roadsides in Stockholm (Linde, Bengtsson & Öborn, 2000). In Uppsala, the roadsides of KUN were the most enriched with Cu. This is the main and oldest street in Uppsala and the

high Cu contents could be associated with water pipelines, which discharge Cu into soils. The Cu contents in KUN are nearly twofold greater than the contents determined in arable soils in Stockholm region ( $18.8 \text{ mg kg}^{-1}$ ). The mean content of Cu in the corresponding samples taken from the roadsides of Torino was  $60 \text{ mg kg}^{-1}$ , two times higher than the concentration in Uppsala samples. The Italian limit is  $100 \text{ mg kg}^{-1}$ , whereas the Swedish limit is  $50 \text{ mg kg}^{-1}$ .

In other urban areas Cu contents in soils ranged between 4 and  $128 \text{ mg kg}^{-1}$  for the samples from Adelaide, Australia, (Tiller, 1992), and around  $27 \text{ mg kg}^{-1}$  for the samples from Aberdeen, Scotland (Paterson *et al.*, 1996). In the latter case the concentration of copper was quite similar to the results of Uppsala's soils.

### Zinc

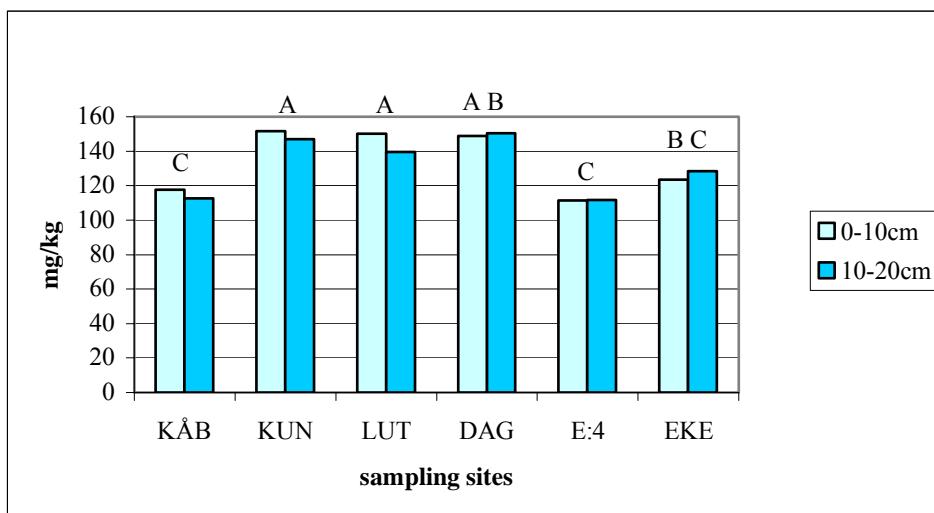
Zinc occurs in small but adequate amounts for plants. Zn deficiency usually takes place where the parent materials are poor in zinc (Thompson & Troeh, 1978). Zinc plays essential metabolic roles in the plant, as a component of a variety of enzymes, related to metabolism of carbohydrates, proteins, phosphate and auxins, RNA and ribosome formation (Lindsay, 1972; Price *et al.*, 1972; Shkolnik, 1974). This metal is usually strongly adsorbed on the cation exchange sites, and it becomes insoluble when the pH is higher than 6.0. It is possible to assume that in the soils analysed the Zn shows a pretty high insolubility since the pH was above 6.0.

Zinc in soil is mainly associated with Fe and Al oxides (Kabata-Pendias & Pendias, 1991). In this study, soil Zn contents significantly correlated with Fe, Mn, As, Cd, Cr Cu and Pb. Accumulation and contamination by Zn can be due to nonferric metal industry and from agricultural practice. In certain areas soil contamination with Zn has already brought it to an extremely high accumulation in the topsoil (Kabata-Pendias & Pendias, 1991).

The Swedish environmental code has set a limit of  $350 \text{ mg Zn kg}^{-1}$ . The results obtained in samples from Uppsala roadsides (Table 24, Figure 14) were nearly two times smaller than that limit. Therefore it is possible to assume that the concentration of zinc does not show potential risks. The mean was  $132.7 \text{ mg kg}^{-1}$  and the results ranged between  $111.5 \text{ mg kg}^{-1}$  and  $151.6 \text{ mg kg}^{-1}$ .

The differences of concentration, between the topsoil and the subsoil were not really marked, and the samples did not show high statistically differences.

**Figure 14.** Concentrations of Zinc in the topsoil and subsoil.



Compared to Stockholm ( $126 \text{ mg Zn kg}^{-1}$ ), the results reported here are quite similar, i.e. mean  $132 \text{ mg kg}^{-1}$ . Also in the soils analysed in Torino the mean concentration of Zn was around  $123 \text{ mg kg}^{-1}$  quite similar to the samples from Uppsala and Stockholm. It is possible to noticed that some of the samples of Uppsala were very close or higher than the limit settled by the Italian guidelines. Other investigations that were done in several cities around the world showed concentration of Zn not close to our results. For example, at Aberdeen in Scotland mean concentration was around  $50 \text{ mg kg}^{-1}$  (Paterson *et al.*, 1996), in Spain, Seville, it ranged between 46 and  $388 \text{ mg kg}^{-1}$  (Madrid *et al.*, 2002). By contrast, in Australia, Pit Pirie mean Zn concentration was high:  $1500 \text{ mg kg}^{-1}$  (Tiller, 1992). The major contributor to that high concentration can be bedrock and emission by burning (hence, deposition of Zn from the atmosphere). This can be explained with the atmospheric deposition, in fact Zn is profusely present in the atmosphere; in Europe the concentration of this metal in the air it is around  $1200 \text{ ng m}^{-3}$  (Bowen, 1979), a value higher than the ones relative to the other metals. In Uppsala, Zn is associated with Leptite rock, which is also rich in As. (Möller, 1993).

The traffic can be another source of deposition of this metal with the wear of the tyre, but the main sources of zinc in Uppsala are Sewage treatment plant, wood burning and different kind of waste like electronic waste, anticorrosive, plastic, batteries. These sources of Zn can explain why in the most of the cases the concentration was higher in the topsoil than in the subsoil (Otabbong *et al.*, 2002).

### **8.2.2. Distribution of non-biogenic metals**

Analytical data on non-essential metals are presented in Table 25.

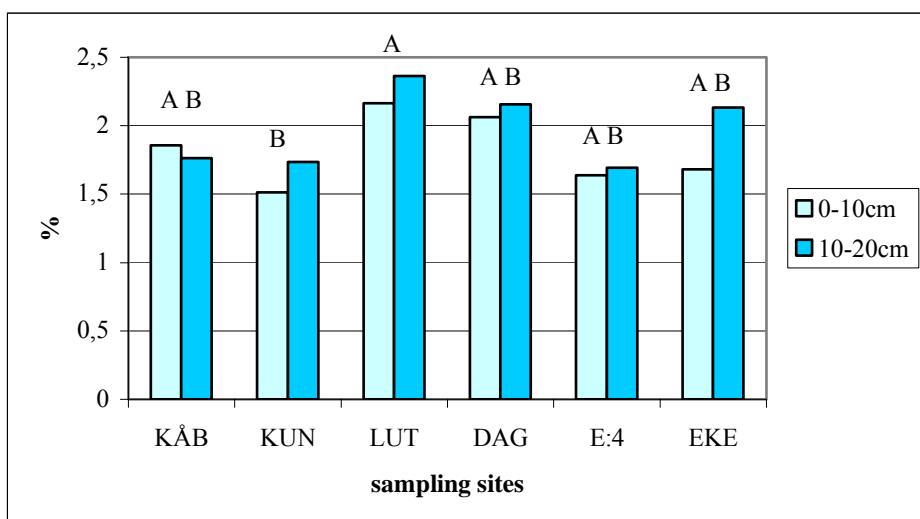
**Table 25.** Non-biogenic metals

Sampling sites	Depth cm	Al %	As mg kg <sup>-1</sup>	Cd µg kg <sup>-1</sup>	Cr mg kg <sup>-1</sup>	Ni mg kg <sup>-1</sup>	Pb mg kg <sup>-1</sup>	W µg kg <sup>-1</sup>
<b>DAG</b>	0-10	2.1	3.3	251.2	36.6	21.0	47.7	256
	10-20	2.2	3.2	217.8	38.6	22.0	39.8	194
<b>EKE</b>	0-10	1.7	3.1	204.7	29.8	18.5	32.4	163
	10-20	2.1	3.9	199.6	39.5	24.2	30.1	229
<b>E4:AN</b>	0-10	1.6	3.4	174.7	29.6	17.0	24.2	244
	10-20	1.7	3.4	178.1	29.3	16.7	23.4	246
<b>LUT</b>	0-10	2.2	4.2	239.6	41.3	25.9	35.3	226
	10-20	2.4	4.5	178.2	44.5	28.4	24.8	153
<b>KUN</b>	0-10	1.5	3.7	292.6	32.5	20.2	75.6	250
	10-20	1.7	4.4	239.2	38.9	24.8	77.6	166
<b>KÅB</b>	0-10	1.9	3.0	201.0	36.0	22.0	25.2	222
	10-20	1.8	3.0	124.8	33.7	21.2	22.6	184
<b>Mean</b>		1.9	3.6	208.5	35.9	21.8	38.2	211
<b>Median</b>		1.8	3.4	202.8	36.3	21.6	31.2	224
<b>Min</b>		1.5	3.0	124.8	29.3	16.7	22.6	153
<b>Max</b>		2.4	4.5	292.6	44.5	28.4	77.6	256
<b>Std (±)</b>		0.27	0.53	43.74	4.96	3.55	19.44	37.4

### *Aluminium*

The results on aluminium are presented in table 25 and figure 15. Aluminium is one of the main constituents of the earth's crust, (Kabata-Pendias & Pendias, 1991). In soil it occurs mainly as Al hydroxides and contributes greatly to various soil properties. Since the pH in the soils analysed was nearly neutral, it is probable that Al was not mobile. Soluble Al exists at pH below 5.5 (Colemand Thomas 1967). The amount of Al in the samples ranged between 1.5% and 2.4%, with a mean of 1.9%. The contents tended to increase with depth. As was the case for Fe, Cu and Mn, the contents of Al were largest in the LUT samples.

**Figure 15.** Percentage of Al in the topsoil and subsoil.

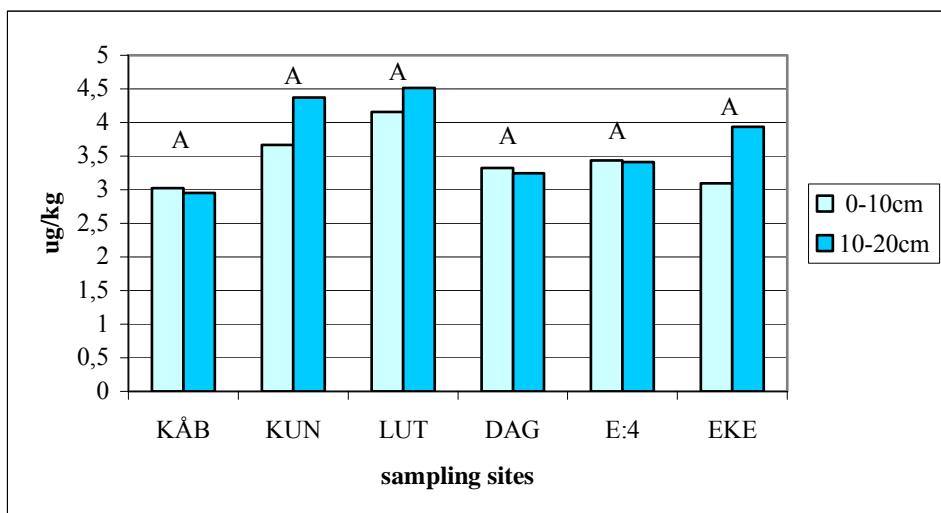


### Arsenic

Analytical data on As are presented in Table 25 and Figure 16. Arsenic is distributed rather uniformly in major types of rocks; it is highly associated with deposits of many metals and therefore is known as a good indicator in geochemical prospecting surveys (Kabata-Pendias & Pendias, 1991). This element shows a strong sorption by clays, hydroxides and organic matter; it has a high association with Fe. In this study, As was correlated with Al, Cr, Ni and Zn (Table 26).

Accumulation of As in soils can be related to industrial activities and the use of Asal sprays. Chilver and Peterson (1987) calculated that, at least 60% of the atmospheric global inputs of As is derived from natural sources. The behaviour of this element is dependent on the soils oxidation state, and it varies in its vertical distribution. Its toxicity depends on the concentration of its soluble form. In the samples analysed, the amount of As, ranged between  $3.0 \mu\text{g kg}^{-1}$  and  $4.5 \mu\text{g kg}^{-1}$ . The mean was  $3.6 \mu\text{g kg}^{-1}$ . The As amounts in the topsoil and in the subsoil were quite similar. According to the Swedish guidelines the results do not exceed the limit. In an investigation that was conducted in Stockholm roadside soil samples, park and wasteland soils, were compared with arable soils from Stockholm region (Linde et al., 2000). The mean concentration was  $6.1 \text{ mg kg}^{-1}$  and  $2.5 \text{ mg kg}^{-1}$  for the roadsides and arable land respectively. It is apparent that small differences existed between Uppsala and Stockholm roadside soils. Also the samples from arable soils had a mean of  $3.39 \text{ mg kg}^{-1}$ , higher than the mean of Uppsala samples. It can be common to find high amount of As in arable soil, since As compounds are used as pesticides. The Stockholm roadside soils were rather elevated compared to the corresponding soil of Uppsala. However, the Uppsala soils were nearly similar with arable soils of Stockholm.

**Figure 16.** Concentrations of As in the topsoil and subsoil.



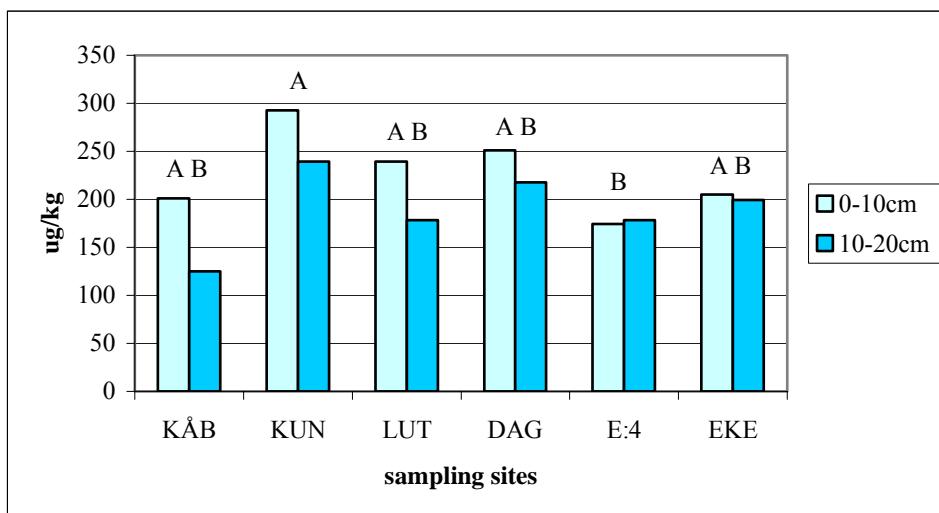
### Cadmium

The main factor determining Cd contents of soils is the chemical composition of the parent rock, therefore also in the samples analysed it is assumed that some Cd determined in the investigated soils comes from the bedrocks. Uppsala bedrock contains leptite that shows small amount of this element (Kabata-Pendias & Pendias, 1991). Cadmium in condition of high pH is not easily mobile, and its solubility is strongly related to pH. In acid soils, organic matter and sesquioxides may largely control Cd solubility, and that in alkaline soil; precipitation of Cd compounds is likely to account for Cd equilibrium (Tiller et al., 1979; Soon, 1981).

In this study, the results on Cd are presented in Table 25 and Figure 17. Most of the samples showed a moderate to low amount of Cd. The results ranged between  $124 \mu\text{g kg}^{-1}$  and  $292 \mu\text{g kg}^{-1}$ , with a mean of  $208 \mu\text{g kg}^{-1}$ . In the majority samples the amount of Cd was higher in the topsoil than in the subsoil.

Several elements are known to interact with Cd in regard to both plant uptake and in biochemical roles. For example Cd-Zn interactions are commonly observed (Tiller et al., 1979). In this study Cd showed a high correlation with Zn and Pb (Table 26). Contamination with Cd is believed to be a most serious health risk. Widespread anthropogenic inputs of Cd may explain why the higher Cd amounts in the topsoil than in the subsoil. According to the Swedish guidelines the results presented in this study do not exceed the limits. The mean of Stockholm roadsides was  $370 \mu\text{g kg}^{-1}$  for the samples from roadside and  $400 \mu\text{g kg}^{-1}$  for all sites. The results on Cd obtained in Uppsala City were relatively comparable to the results reported for arable soils in Stockholm (Linde et al., 2000).

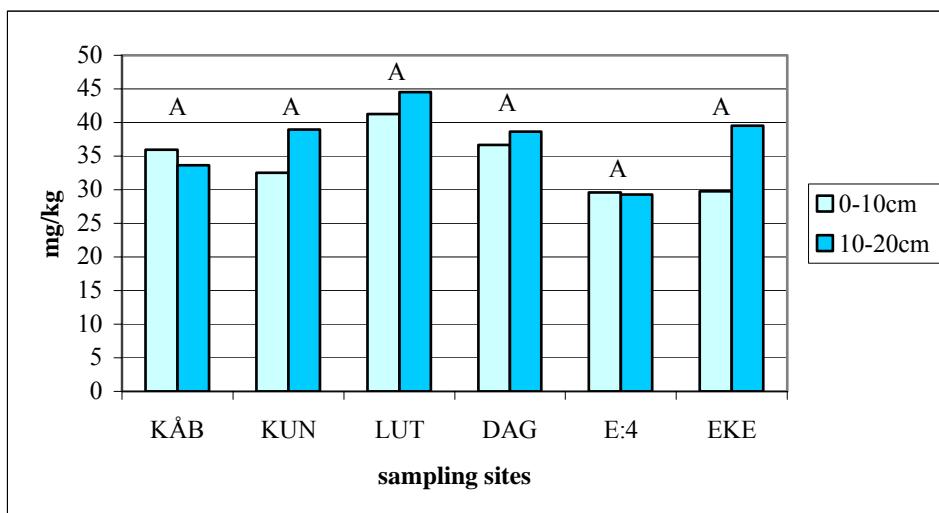
**Figure 17.** Concentrations of Cd in the topsoil and in the subsoil.



### *Chromium*

The terrestrial abundance of Cr indicates association mainly with ultramafic and mafic rocks, but it is also common in acid igneous and sedimentary rocks, even if in a smaller amount. Cr shows highly variable oxidation states (from +3 to +6) (Kabata-Pendias & Pendias, 1991). It has been shown that most of the soil Cr occurs as Cr<sup>3+</sup>, which is slightly mobile only in very acid conditions, otherwise its compounds are considered to be very stable in soils. On the other hand, Cr<sup>6+</sup> is very unstable in soils and is easily immobilized via reduction in both acid and alkaline soils. In oxidation states Cr is toxic to plants and animals. In this study, the amount of Cr in the soil sampled ranged between 29.3 mg kg<sup>-1</sup> and 44.3 mg kg<sup>-1</sup>, with a mean of 35.9 (Table 25). Otabbong (1989) reported interactions in plants between Cr and P and between Cr and Si. Cr was relatively evenly distributed in 0-10 and 10-20 cm layer. Contents of Cr were highest in the LUT samples. See also Figure 10. As the range of Cr contents is small, it is probable that anthropogenic input was negligible. Its source seems to be natural. Indeed, the bedrock of Uppsala's soils is characterized by the presence of Greenstone that contains high amount of Cr, Ni and Cu.

**Figure 18.** Concentrations of Cr in the topsoil and in the subsoil.



The Swedish environmental limit for Cr is  $120 \text{ mg kg}^{-1}$ . The results obtained in this study were more than threefold smaller than that limit. It is therefore, reasonable to conclude that the road soils were not contaminated with Cr. The results presented here were in the same magnitude as those determined in Stockholm. The mean in Uppsala was  $25 \text{ mg kg}^{-1}$ , while the corresponding value determined in Stockholm was  $29 \text{ mg kg}^{-1}$ .

Investigations similar to the ones presented in this thesis were carried out in Torino, Italy (Pezzuolo, 2004). The mean for Torino was almost three times higher. The Italian limit (D.M. 471/99) for chromium concentration is  $150 \text{ mg kg}^{-1}$ .

In other investigation done in several places showed concentration of Cr contents about  $23.9 \text{ mg kg}^{-1}$  in soils taken from parks in Aberdeen, Scotland (Paterson *et al.*, 1996) and between  $3\text{-}41 \text{ mg kg}^{-1}$  in soils taken in Adelaide, Australia.

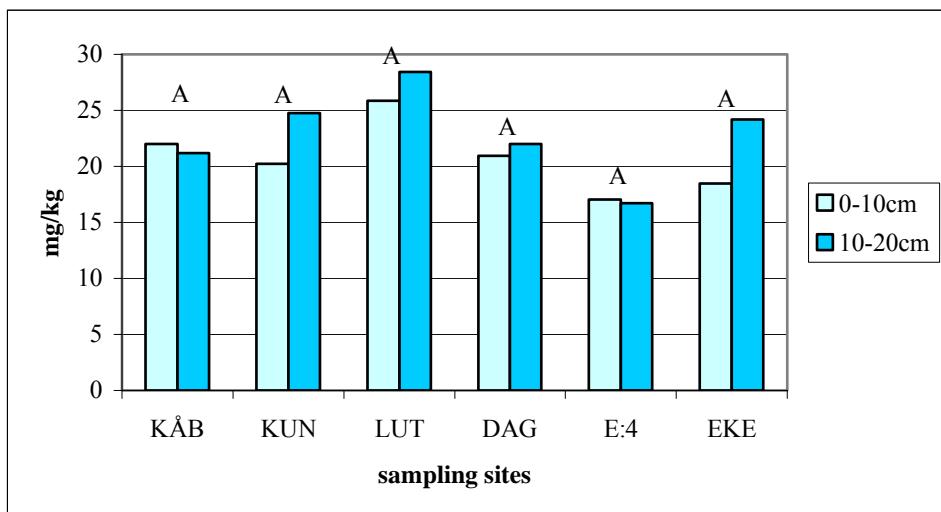
### Nickel

The results for Ni presented in Table 25 and depicted in Figure 19 Soil contents of Ni are of the same magnitude as those obtained for Cr. Two elements exhibit similar distribution the topsoil and subsoil. In the samples taken from Uppsala Kommun, Ni concentrations ranged between  $16.7$  and  $28.4 \text{ mg kg}^{-1}$ ; with a mean of  $21.8 \text{ mg kg}^{-1}$ . The source can be the bedrock in Uppsala which is characterised by the presence of the greenstone, containing Ni.

There is a general similarity between the distribution of Ni, Co, and Fe in the earth's crust (Kabata-Pendias & Pendias, 1991). Ni contents are highest in ultramafic rock, and its concentration decrease with increasing acidity of the rocks. In surface soil horizon, Ni appears to occur mainly in organically bound forms, and it shows a strong association with Mn and Fe, (Norrish, K., 1975). In this study, Ni was not correlated with LOI.

Nickel recently has become a serious pollutant that is released in the emission from metal processing operations and from the increasing combustion of coal oil, from application of sludges and certain phosphate fertilizer, from industrial activity (Kabata-Pendias & Pendias, 1991).

**Figure 19.** Concentrations of Nickel in the topsoil and subsoil.



The limit set by the Swedish guidelines is  $35 \text{ mg kg}^{-1}$ , therefore according to this value, Ni concentration determined does not exceed the limit and Ni does not pose environmental risks. However, the results show similarities with those determined in similar studies carried out in Stockholm. The mean obtained in Stockholm was  $11.4 \text{ mg kg}^{-1}$  almost half of the mean calculated for the samples of Uppsala.

In the arable soils around Stockholm, the amount of this metal was higher than in the city,  $15.3 \text{ mg/kg}$ , but still lower than Uppsala's soils.

Compared to the soils that were analysed in Torino (Italy), Ni concentration in the Swedish soils was low. The mean of the samples from Turin was  $138 \text{ mg kg}^{-1}$ , more than five times higher than the mean of the Swedish soils.

In Aberdeen, Scotland the average concentration was  $14.9 \text{ mg kg}^{-1}$ , (Paterson *et al.*, 1996); in Adelaide Australia, it ranged between  $2$  and  $31 \text{ mg kg}^{-1}$ .

It can be concluded that Uppsala soil were enriched with Ni even though contents did not exceed the guidelines values.

### *Lead*

The terrestrial abundance of Pb indicates a tendency for Pb to concentrate in the acid series of magmatic rocks and argillaceus sediments (Kabata-Pendias & Pendias, 1991). Pb occurs mainly as  $\text{Pb}^{2+}$ , although its oxidation state, (+4), is also known, and it forms several others minerals which are quite insoluble in natural waters.

The natural Pb content of soils is strongly related to the composition of the bedrock, Pb is reported to be the least mobile among the others heavy metals. In high soil pH, as is the cases in this study Pb might have been presented as a precipitate, hydroxide, phosphate, or carbonate and in association with organic complexes, which are rather

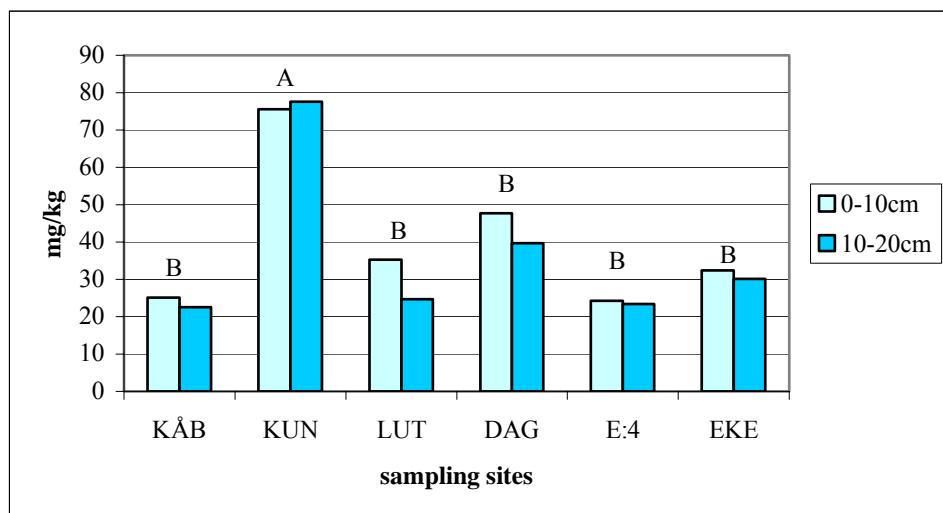
stable. Increasing acidity may increase Pb solubility. The characteristic localization of Pb near to the soil surface in most soil profiles is primarily related to the superficial accumulation of organic matter. Therefore organic matter should be considered as the important sink of Pb in polluted soils (Fleming et al., 1968).

The interference of Pb with others trace elements has been reported only for Zn and Cd (Kabata-Pendias & Pendias, 1991). Table 24. Pb correlated with Zn, Cu and Cd. The fate of anthropogenic Pb in soils has recently received much attention since Pb is hazardous to man and animals. The main Pb source, as it has been presented in previous sections, are emitted from smelters that produces Pb in mineral forms, while Pb in automobile exhausts is mainly in the form of halide salts. Exhaust Pb particles are unstable and readily convert into oxides, carbonates and sulfates.

Results on Pb contents in roadside soils in Uppsala were presented in Table 25 and are also depicted in Figure 20. The table shows wide variation: std  $\pm$  19.44, with a minimum of 23 and maximum of 78 and a mean of 38 mg kg<sup>-1</sup>. It is apparent from the figure that KUN samples were particularly enriched with Pb. KUN, which is the abbreviation of Kungsgatan (King Street) is one of the oldest streets in Uppsala and was subjected to anthropogenic emission of Pb for a long time. Nonetheless, the Pb results did not exceed the Swedish guidelines of 80 mg kg<sup>-1</sup>. The next in Pb contents is DAG (Daghammersjöld Street). This too was impacted upon by the military base and it is probable that ammunition remains contributed to Pb determined in the soils. The main source of Pb contamination is traffic, usually the highest concentration of this metal is found close to roads with high traffic intensity. This is due to the fact that Pb is too heavy for being transported by the air. In the case of analytical data presented, the highest concentration was found in the samples from Kungsgatan, as mentioned before and not in the samples taken from European Highway, the roads with the highest traffic intensity in Uppsala. This can be explained by the fact that Kungsgatan is the oldest road in Uppsala. The traffic in this part of the city has always been quite intense, compare to the other roads, and since the introduction of use of fuel without Pb came into force in 1995, until that time the Pb deposition from fuel was even higher.

The samples taken from European Highway, E4 showed the lower concentration of Pb, despite the fact that the road has the highest traffic intensity. This could be due to the fact that the road was recently constructed (less than 50 years).

**Figure 20.** Concentrations of Pb in the topsoil and subsoil.



Compared to the concentration of Pb in Stockholm soil the mean calculated in Uppsala was almost three times lower. Indeed the mean of the samples taken from roadside sites was 100 mg/kg, just one point slower than the mean calculated about all samples. Average contents of Pb in the arable soils around Stockholm 17.4 mg kg<sup>-1</sup>.

In Torino roadside soils, Pb mean content is 159 mg kg<sup>-1</sup>, whereas the limit settled by the guidelines is 100 mg kg<sup>-1</sup>.

Since this heavy metal is associated with cancer occurrence, several investigations on Pb were carried out. The results obtained in several places around the world, showed really different concentration of this metal in relation of the characteristic of the soil. The soils taken from park in Aberdeen, Scotland showed Pb concentration of around 94 mg kg<sup>-1</sup> (Paterson *et al.*, 1996); in Hong Kong soils Pb values were elevated, 400 mg kg<sup>-1</sup> (Li and Liu, 2001); in Hobart, Australia around 2200 mg Pb kg<sup>-1</sup> was determined (Tiller, 1992).

### Tungsten

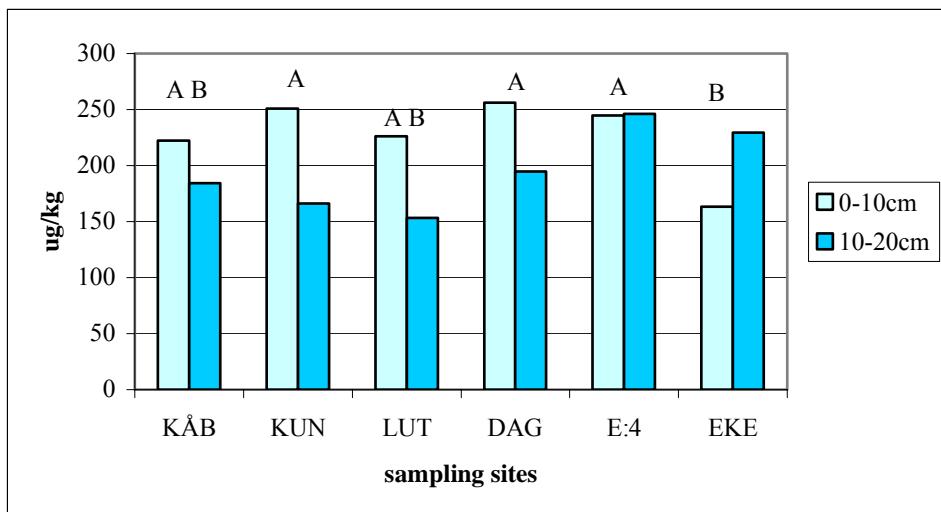
The distribution of W in the earth's crust shows that its concentration seems to increase with increasing acidity of magmatic rocks and with increasing clay content of sedimentary rocks. All W minerals are only slightly soluble and hence have low mobility (Kabata-Pendias & Pendias, 1991).

Industrially, tungsten does not constitute an important health hazard. Exposure is related chiefly to the dust arising from the crushing and milling of the two chief ores of tungsten, namely scheelite and wolframite. Large overdoses cause central nervous system disturbances, diarrhea, respiratory failure and death in experimental animals (Sax, Dangerous Properties of Industrial Materials, eighth edition, [www.espmetals.com](http://www.espmetals.com)).

The concentration of W was calculated in µg kg<sup>-1</sup> and ranged between 153.2 and 256.2 µg kg<sup>-1</sup>, with a mean of 211.5 µg kg<sup>-1</sup>. The concentration was usually higher in

the topsoil, a part from the samples from DAG and E4 as showed in the Figure 21. This dominance in the topsoil suggests anthropogenic origin (deposition the atmosphere).

**Figure 21.** Concentration of W in topsoil and subsoil.



**Table 26.** Relationship among various parameters (Pearson's r coefficients)

	CEC	V	pH CaCl <sub>2</sub>	pH H <sub>2</sub> O	Loi	Al	Fe	Mn	As	Cd	W	Cr	Cu	Ni	Pb
<b>V</b>	-0.756 •••														
<b>pH CaCl<sub>2</sub></b>	-0.265 ••	0.420 ••										●→P ≥ 0.01 ≤ 0.05			
<b>pH H<sub>2</sub>O</b>	-0.574 •••	0.627 •••	0.668 •••									●••→P ≥ 0.001 ≤ 0.005			
<b>Loi</b>	0.347 •	-0.035 •	0.353	-0.135								••••→P ≤ 0.0001		n = 48	
<b>Al</b>	-0.471 ••	0.547 •••	0.273	0.579 •••	-0.346 •										
<b>Fe</b>	-0.473 ••	0.658 •••	0.338 •	0.638 •••	-0.216 •••	0.886 •••									
<b>Mn</b>	-0.483 ••	0.520 ••	0.368 •	0.544 •••	-0.126 •••	0.781 •••	0.808 •••								
<b>As</b>	-0.191 ••	0.489 ••	0.246	0.457 ••	-0.089 •••	0.679 •••	0.832 •••	0.479 ••							
<b>Cd</b>	0.170	0.030	0.155	-0.100	0.253	0.040	0.204	0.077	0.273						
<b>W</b>	0.3343 •	-0.3181 •	-0.1689 ••	-0.4849 •••	0.1160 •	-0.3337 ••	-0.3976 ••	-0.3053 •	-0.4113 ••	0.2191 ••					
<b>Cr</b>	-0.364 •	0.526 •••	0.352 •	0.598 •••	-0.210 •••	0.839 •••	0.929 •••	0.725 •••	0.891 •••	0.159 •••	-0.439 ••				
<b>Cu</b>	0.007	0.143	0.006	0.050	0.077	0.180	0.386	0.271	0.418	0.481	-0.105	0.332	•		
<b>Ni</b>	-0.343 •	0.524 •••	0.378 ••	0.628 •••	-0.169 •••	0.778 •••	0.904 •••	0.687 •••	0.902 •••	0.151 •••	-0.483 •••	0.984 •••	0.292 •		
<b>Pb</b>	0.367 •	-0.216	-0.053	-0.135	0.196	-0.127	0.053	0.103	0.082	0.535 •••	0.074	-0.018	0.602 •••	-0.034	
<b>Zn</b>	-0.063	0.268	0.197	0.196	0.043	0.487	0.658	0.554	0.551	0.719 •••	-0.026 •••	0.561 •••	0.698 •••	0.515 •••	0.574 •••

Owing to the limited funds, soil texture, (clay, silt and sand) only one of the replicate was used for each depth and roadside. Therefore analytical data on texture was not included in the correlation calculation.

## **9. CONCLUDING REMARKS**

The pH was near neutral with small contents of carbonates and relatively low organic matter contents. The soils were different in terms of the sizes of CEC and base saturation, especially when CEC based on organic matter.

The metals usually correlated with each other, especially with Al and Fe, suggesting that some of them were in association with Al and Fe oxides.

Of the biogenic trace metals determined, the soils contained considerable amounts of Fe, Mn, Cu and Zn, evenly distributed in the soils (0-10 and 10-20 cm), and the contents were below the Swedish guideline limits.

Of the non-biogenic metals, Pb at KUN and Ni at LUT and KUN were close to the Swedish guideline limits and, hence can be of health concern in the future. Heavy metal loads do not follow traffic intensity. For example E4, the most trafficked road did contain as much metals as KUN, which was moderately trafficked. It seem that the rather high Pb content at KUN was due to long-term Pb, discharge in fuel. KUN is the oldest and main street in Uppsala, while E4 was constructed in 1960s.

Based on the data obtained fruits growing along Daghamskjöldsväg road might not be safe to eat. Moreover, there is a primary school and day center where the samples where collected that increases exposure of children to health risky. This too applies to Kungsgatan. Hence, health risks are warranted to be investigated in the future.

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