The Geochemistry of the Topsoil in Oslo, Norway.

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Abstract

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In co-operation with the Geological Survey of Norway, 395 samples of topsoil, 44 bedrock samples and 24 samples of sand from sandboxes at kindergartens taken in Oslo, the capital city of Norway, were analysed for a wide range of elements. To get a measure on the bio-availability of arsenic, a five stage sequential extraction procedure was accomplished on a subset of 98 topsoil samples and on all 24 samples of sand from sandboxes. These fractions (i.e. “Exchangeable”, “Carbonate”, “Reducible substrate”, “Organic” and “Residual”) were analysed for arsenic. Bulk concentrations in a representative subset of 10 bedrock samples were determined by XRF analysis.

For the concentrations of the elements As, B, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Ni, P, Pb and Zn in soil, geologic sources are important, but human activity has had a large effect on concentrations in topsoil, especially in the central districts. At least 81% of the samples contain more arsenic than the Norm value for polluted soil used by the Norwegian authorities. For chromium, zinc and lead, the percentages are 65, 74 and 25 respectively. In topsoil, up to 50% of the arsenic is extractable in the exchangeable, the carbonate and the reducible substrate fractions, but only 2% of the samples exceeded the Norm value after the three extraction stages. After four stages of extraction, 69% of the samples exceeded the Norm value.

At 24 kindergartens in the central districts of Oslo, concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn in topsoil samples are higher than in samples of sand from sandpits, but differences in arsenic are low. All topsoil samples and 63% of the sandbox samples exceed the arsenic Norm value for polluted soil used by the Norwegian authorities. Concentrations of at least one of the elements Cr, Cu, Ni, Pb and Zn exceed the Norm value in the topsoil. At two kindergartens all elements, except Cd, exceed the Norm value in the topsoil.

In the samples from the sandboxes, arsenic concentrations in the exchangeable, the carbonate and the reducible substrate fractions, lie at a higher level than in topsoil samples. Leakage of arsenic compounds from impregnated and painted wood have probably caused elevated concentrations of this element in the sand. At two kindergartens the cumulative arsenic content in samples from the sandboxes exceeds the Norm value of 2 mg/kg As for polluted soil already after two fractions (i.e. the “Exchangeable” and the “Carbonate” fraction). After three fractions, the arsenic content in sand at 5 kindergartens exceeds this value. After four fractions this number was still 5. Regarding soil, no kindergartens had a cumulative arsenic content after three stages of the extraction procedure. After four stages 16 kindergartens contained more arsenic than the Norwegian Norm value of 2 mg/kg As.

Bulk concentrations of metals, in the bedrock samples, are generally higher than the acid soluble concentrations. Differences are small for copper and zinc, somewhat higher for lead and nickel and considerably different for chromium. Acid soluble chromium concentrations in soil differ little when compared with acid soluble concentrations in bedrock, but are in general much lower than bulk concentrations in rock. Chromium is probably strongly incorporated in the mineral structure of rock samples and concentrated HNO_3 cannot solubilize all chromium molecules. For copper, lead and zinc, the acid soluble concentrations in soil are higher than the bulk concentrations in bedrock. The parent rock material cannot be the only source for these elements in soils and various anthropogenic sources dispersed by air or water probably have major influence.

The enrichment of nickel in topsoil near highways in Oslo might be due to the bitumen content of road dust. The enrichment of chromium and copper might be due to wear and tear of cars and engine parts. There is no enrichment of cadmium and zinc in topsoil near highways. Concentrations of zinc in topsoil in Oslo are generally high, most probably because of industry. The possible addition of zinc from traffic to the topsoil is not observed, in this study.

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Contents

1 Introduction

In recent years, research has made us increasingly aware of the importance of the quality of the soil on which we live. Research on soil quality in urban areas, investigation of contaminated land and groundwater pollution has been given high priority during the last decade. The result of this increasing interest in urban geochemistry is a large number of publications, geochemical atlases and surveys on this topic.

Also in Norway, investigation of the geochemistry of urban areas has been given higher priority. The city council of Trondheim, the third largest city and situated in the middle of Norway, started in 1993 investigation of the urban areas. The results of this investigation have been used in city planning, and further investigation of polluted areas in later years has resulted in a “cleaner” city. Also in Bergen, the second largest city and situated in the western part of Norway, investigation of urban soil has been started, and the results have been used in city planning.

In most studies in urban areas, soil samples have been analysed on the acid soluble concentrations of a large variety of elements. Speciation of the elements has not been carried out and little is known about the bio-availability of the elements in these soils to human beings. Also investigation of the parent rock material could be helpful on interpretation of the results of a geochemical survey.

1.1 Hypotheses

The principal objectives of the present work have been to test the following hypotheses:

I. The composition of topsoil in Oslo is largely affected by human activity

II. The metal content in topsoil and sand from sandboxes at kindergartens in Oslo constitutes a potential hazard for children playing on it.

III. Analysis of bedrock material in addition to analysis of topsoil makes it easier to explain distribution patterns for the elements in the soil.

IV. Traffic has considerable influence on the composition of nearby topsoil

1.2 Organisation of the thesis

The objective of this thesis is to give a broad overview of the inorganic geochemistry of the topsoil and bedrock in Oslo, the largest and capital city of Norway. Samples of topsoil are taken systematically, one per square km, to get an overview of the geochemical distribution of about 30 elements in the topsoil in an area of 500 km^2. Comparison of acid soluble metal concentrations in bedrock and soil samples, taken at the same location, has been used in finding sources for possible pollution and to see if concentrations might be due to the parent material. Total metal concentrations are determined in some bedrock samples. The results are used to see if this can give a better understanding of the geochemical patterns in topsoil, compared with a survey based on acid soluble concentrations in soil and bedrock samples only. Special emphasis has been paid on the soil quality at kindergartens in the central parts of the city. At these kindergartens, samples of sand from sandpits are taken in addition to topsoil samples. Playing equipment at kindergartens are often made of impregnated material. Leakage of arsenic from this material can lead to elevated concentrations in soil. Speciation of arsenic has been used to get an impression on the bio-availability of this element in soil and sandpit material.

The following can be divided into three parts.

- Part one consists of Chapters 2-7. Chapter 2 is a description of the area and intended to provide the necessary historical and geological background information. In Chapter 3, the different methods, both analytical and statistical are outlined briefly. Chapter 4 gives a description of health criteria and occurrence of the elements in soil and bedrock. The results from the investigations are discussed and summarised in Chapters 5 and 6 followed by the references in Chapter 7.
- In part two the research is presented in the form of four papers of which Paper 1 is published and the others are submitted to different journals. A geochemical survey of topsoil in Oslo is given in Paper 1. In this paper statistical methods are used to find sources behind the different elements in the soil. Only eight elements are presented in detail. This paper is published in Environmental Geochemistry and Health. A detailed description of the other elements has not been published before and is given in Appendix A. Paper 2 gives a further description of seven elements in topsoil. In this paper, special emphasis has been paid on soil and sand quality at kindergartens and the results of a five stage sequential extraction procedure for arsenic are presented. The paper is not published yet, but the manuscript is submitted to Water, Air and Soil Pollution. In Paper 3, the composition of the parent bedrock material is compared with the composition of topsoil. The manuscript is submitted to the Norwegian Journal of Geology. The influence of traffic on the composition of topsoil in the vicinity of highways is presented in Paper 4. The manuscript is submitted to Environmental Geology.
- The last part consist of three appendices. Appendix A is an extension of Paper 1 and consists of a detailed description of the unpublished elements. Appendix B consists of 6 conference abstracts. Appendix C is a Compact Disk containing 4 files with the results of the different analyses.

2 Area description

The city of Oslo is situated centrally in the Oslo-Graben, which consists of an approximately 250x50 km area of largely Permian igneous rocks and Cambro-Silurian sedimentary rocks in a rifted Precambrian terrain. The investigated area is about 500 km^2 (Figure 1) and can be divided into four parts. The south-eastern area is part of the Precambrian terrain. It is named the Østfold complex and formed during the early and middle Proterozoic era. It consists of granitic gneisses. The central part of the area contains sedimentary rocks from the Cambrian to the Silurian period. The northern part of the investigated area contains intrusive rocks of Permian age such as quartz syenite and monzodiorite. Finally the north-western part is of Carboniferous and Permian age and contains volcanic rocks such as basalt and rhomb-porphyry and sedimentary rocks such as shale, sandstone and conglomerate (Berthelsen and Sundvoll, 1996).

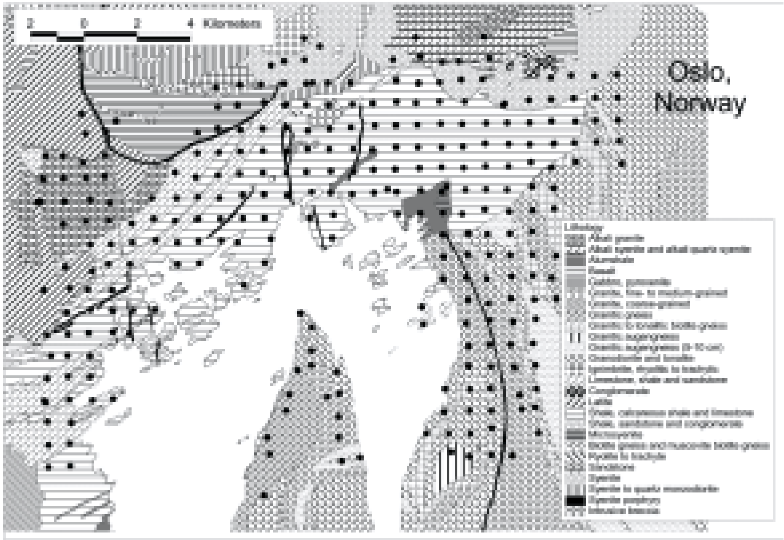

Figure 1. Geological map of Oslo including sample localities

2.1 Østfold complex - Precambrian

The Precambrian terrain in the southern and eastern parts of the area continues into Sweden and Finland. The geological history of the terrain is very complex. The rocks have been metamorphosed and deformed several times during mountain forming processes. The dominating rocks in this area are gneisses of different types, mostly granitic. The minerals that can be found in these rocks are quartz, feldspar and dark minerals such as amphiboles and biotite. Pegmatite bodies or veins up to a metre broad are common. These are coarse-grained formed by slow crystallisation from water-rich solutions (Dons, 1977).

2.2 Sedimentary rocks – Cambro-Silurian

Shale, calcareous shale, limestone and sandstone are the most common rock types in the central and south-western parts of the city. These rocks are from the Cambro-Silurian period. The terrain is low and the soil is usually thicker than in the Precambrian area. The Cambro-Silurian rocks are layered with a total thickness of about 1500 metres. In Norway the Cambro-Silurian stratigraphy is divided in 10 main stages and some of these are divided into smaller units. The Cambrian stages (1 and 2) contain mostly sandstones, conglomerate and alum shale. The Alum Shale Formation can be recognised over a large portion of Baltoscandia. It extends from the Middle Cambrian to lowest Ordovician period and ranges in thickness from about twenty to almost a hundred metres and has been the subject of detailed reviews by Andersson et al. (1985). It is composed largely of black, organic rich shales, together with discontinuous beds and concretions, some several cubic metres in size, of dark bituminous limestone (´Stinkstone'). The shales have a very low $CaCO_3$ content and are enriched in a variety of trace elements including uranium, vanadium, molybdenum and nickel (Bjørlykke, 1974, Andersson et al., 1985, Berry et al., 1986). On top of this one can find the Bjørkåsholmen Formation (stage 3aα), also called Ceratopyge Limestone. It contains pale grey, irregularly bedded limestones with thin intercalations of shale (Owen, et al., 1990). Unit 3b is called the Tøyen Formation with black and grey shales. The Huk Formation or Orthoceras Limestone (stage 3c) succeeds the shales of the Tøyen Formation. In Oslo these three Middle Cambrian and Early Ordovician stages are called the Røyken Group.

On top of this group one can find the Oslo Group from the Middle and Late Ordovician. It comprises several stages. Stage 4aα is the Elnes Formation, also called Cephalopod Shale. The main lithology is shale. The boundary with the underlying Huk Formation is sharp (Owen, et al., 1990). Stage 4aβ consists of limestone and is called the Vollen Formation or Ampyx Limestone. It comprises rhythmically alternating limestone horizons (beds and nodules) with interbedded calcareous shale (Owen, et al., 1990). The base of the Arnestad Formation or Lower Chasmops Shale (stage 4bα) is defined at the development of thick dark shales with subordinate limestone horizons. Shale horizons within the formation are commonly 30-40 cm thick with a maximum of about 70 cm. Nodular and bedded limestone horizons are almost invariably less than 10 cm. In Oslo, the shales are dark grey weathering to light grey (Owen, et al., 1990). The base of the next stage (4bβ), the Frognerkilen Formation marks an abrupt change from a shale dominated succession to rubbly limestones up to 10 cm thick passing upwards into nodular limestones (up to 10 cm) and shales (up to 35 cm) (Owen, et al., 1990). The Skjerholmen Formation or Upper Tretaspis Shale (stage 4cγ) comprises light grey, rusty weathering calcareous shale beds up to 50 cm thick but commonly less than 20 cm alternating with nodular silty limestones, calcareous siltstones and fine calcareous sandstone. The siltstones and sandstones are more common towards the top of the formation (Owen, et al., 1990). The main lithology of stage 5b is sandstone. It is called the Langøyene Formation or Calcareous Sandstone Formation. Beside sandstone it contains shale and thin layers of limestone (Naterstad, et al., 1990).

The Bærum Group lies on top of the Oslo Group. It originates from the earliest part of the Early Silurian period. The Solvik Formation (stage 6) contains shale with thin layers of siltstone and limestone. The amount of limestone increases towards the top of the formation. Stages 7a and b are called the Rytteråker Formation. These contain limestone, densely packed with small to coarse nodules. Stage 7c, the Vik Formation, is a stage with greyish-green and red shale, with thin layers of limestone, partly nodular. The top stage (8a-8b) of the Bærum group is the Skinnerbukta Formation. It is a stage of dark grey, silty shale, locally with thin calcareous zones (Naterstad, et al., 1990).

The Hole Group originates from the latest part of the Early Silurian period. The Malmøya Formation contains limestone as lenses and nodules alternating with shales (stage 8c) and massively bedded limestone (stage

8d). On top of these stages one can find the Steinsfjorden Formation (stage 9). It is a stage of greyish-green shale, irregularly alternating with marlstone, reddish dolomite-bearing shale, dolomite and limestone (Naterstad et al., 1990).

The last group of the Cambro-Silurian period is the Ringerike Group (stage 10). In Oslo it contains fine- to medium-grained sandstone with intraformational conglomerates, the Stubdal Formation, and, sandstone and siltstone, with carbonate nodules and intraformational conglomerates (Naterstad et al., 1990).

There are no sedimentary rocks between the Late Silurian Ringerike Group and the strata above the sub Permian peneplain, i.e. from the Devonian and Early Carboniferous periods. During this interval the Cambro-Silurian strata of the Oslo region were folded, most probably during a late phase of the Caledonian orogeny in Devonian time, and then peneplanation followed (Henningsmoen, 1978).

2.3 Sedimentary rocks – Carboniferous and Permian

Immediately above the peneplain, but below the Permian basal lava, in the north-western part of the area, one can find sedimentary rocks. This is the Asker Group, which originates from the Middle and Late Carboniferous period. It comprises three formations. The Kolsås Formation consists mainly of red, less commonly green, silty and sandy calcareous mudstones or shales. The formation is 10-16 m thick in Asker and Bærum west of Oslo. The Tanum Formation is up to 20 m thick and comprises mainly light coloured conglomerates and calcareous sandstones, with or without thin shale partings. The fragments in the conglomerates, mainly quartz and quartzite, are usually less than 10 cm in diameter, but some exceeding 20 cm have been found. The Skaugum Formation, about 15 m thick, is characterised by a predomination of grains of volcanic rocks. It consists of sandstones and conglomerates, generally with a reddish-brown calcareous matrix coloured by hematite (Henningsmoen, 1978).

2.4 Igneaous rocks - Permian

The northern part of the investigated area is from the Permian period. In this period volcanic activity was widespread in the Oslo area. The Permian strata rest on the peneplaned and more or less weathered surface of the sedimentary rocks of the Cambro-Silurian period. In the beginning of the Permian period, dark mafic lava was erupted from north-south oriented large shield volcanoes. Later in this period the lavas became more felsic and formed rhomb-porphyry layers. Much of this lava is eroded, but can still be found in cauldrons (Dons, 1977). The extensive magmatic activity resulted in a wide variety of igneous rocks. The oldest intrusive rocks are mainly gabbros, called Oslo essexite, which is found in small volcanic necks. It contains light feldspar and dark pyroxenes or hornblende. Their intrusion was followed by a period of extrusion of basalt and rhomb porphyry lavas, and intrusion of monzonitic rocks called kjesåsites/larvikites and nepheline syenites. The next period of magmatic activity started with extrusion of felsite porphyry and related rocks, and continued with intrusion of akerite, which is a quartz monzodiorite, Grefsen syenite, nordmarkite, which is a alkali syenite and a alkali granite called ekerite (Neumann, 1979). The border areas between the intusive rocks and Cambro-Silurian rocks has been influenced by contact metamorphism. In these areas one can find hornfels and marble. In former days, the mining of minerals such as magnetite, galena, chalcopyrite, sphalerite and pyrite was widespread in this area (Dons, 1977).

3 Methods

3.1 Sampling and pre-treatment of samples

Soil samples were collected during two periods. In phase one of the project, 297 samples were taken systematically one per square kilometre. The co-ordinates of one point were chosen at random and all other samples were taken at a distance of one kilometre in both east-west and north-south directions (Figure 1). In cases where no adequate material was present the nearest point with soil was chosen. Samples were taken by cutting a 20 x 10 cm section of surface soil with a spade. A knife was used to exclude the soil from depth below 2-3 cm. The weight per sample was about 0.5-1 kg. To be able to measure the difference in concentration between samples over short distances (about 50 m) duplicates were taken at thirteen locations. Samples were collected in paper bags. The sampling period was 30. June – 10. July 1998. Samples were transported to the Geological Survey of Norway (NGU). At the NGU the material was dried at about 35°C for four days. Samples were afterwards sieved through a 2 mm nylon screen and split in two equal parts. One part was analysed and the other was stored as reference material for later investigations.

During the summer of the following year, 98 topsoil samples were taken at selected areas. Nineteen of these samples were taken in the near vicinity of highway E18, between Sandvika and Bygdøy. Twenty-four samples were taken at kindergartens. At these kindergartens, samples of sand from sandboxes were taken in addition to topsoil samples. Topsoil samples were taken in the same way as in phase one. Sand samples were taken in the vicinity of playing equipment. At 44 sites, samples were taken of both topsoil and bedrock. Rock samples were taken using a hammer. The sampling period was 13. July – 17. July 1999. All soil and sandbox samples were dissolved in concentrated HNO_3 and analysed for Cr, Cu, Ni, Pb and Zn by AAS-flame and for As and Cd by AAS-graphite furnace. The bedrock samples were crushed in the laboratory and acid soluble concentrations of 28 elements were determined by ICP-AES and of arsenic and cadmium by graphite furnace at the NGU. Bulk concentrations of 23 elements were determined by XRF. One aim, at this phase of the project, was to look at the bio-availability of arsenic in topsoil and in sand from sandboxes. Therefore a sequential extraction procedure existing of five different extracting agents was accomplished. All extracts were analysed for arsenic by AAS-graphite furnace.

3.2 Laboratory analyses

3.2.1 ICP-AES

Inductively coupled plasma – atomic emission spectrometry (ICP-AES) measures the elements specific atomic spectra of the electromagnetic waves emitted by different atoms under excitation. The inductively coupled plasma is a type of flame that reaches a much higher temperature than that reached in ordinary combustion flame and its high temperature and stability eliminate many of the interferences and sources of error encountered with conventional flames. High purity argon gas is fed through the plasma gas inlet and ionized. The Ar^+ ions are immediately accelerated by a powerful radio frequency field. The accelerated ions transfer energy to the entire gas by collisions between atoms. Once the process is begun, the ions absorb enough energy from the electric field to maintain a temperature of 6 000 – 10 000 K in the plasma. A spectrometer measures the emission intensity of a given spectral line which is proportional to the concentration of the corresponding analyte (Harris, 1991).

Soil (297) and crushed bedrock (44) samples were analysed for 29 elements by ICP-AES, at the Geological Survey of Norway (NGU). The extraction procedure used was accomplished in accordance to Norwegian Standard - NS 4770 (NSF, 1994). 1.000 g of each sample was extracted in 20 ml 7 N HNO_3 in borosilicate bottles. Generated gas in samples, rich in organic matter and carbonate was released from the bottles before they were covered with a screw cap. Bottles were placed into an autoclave filled with water and heated on a hot-plate. Generated air was lead through the water by a plastic hose until the temperature had reached 96 °C. After this the temperature was raised to 120 °C and held at this temperature in 30 minutes. The pH of the water was measured to see if there had been leakage of fluid out of the bottles. Samples were stored over night and 24 hours after addition of acid samples were filtrated through a fluted filter and diluted with double distilled and ion exchanged water to 100 ml. The elements Ag, Al, B, Ba, Be, Ca, Ce, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sc, Si, Sr, Ti, V, Y, Zn and Zr were determined by ICP-

AES analysis. For all these elements the total uncertainty for the extraction and the analysis is estimated to ± 10 rel.%. Control samples were analysed (NGU, 1998).

3.2.2 AAS

In atomic absorption spectrophotometry (AAS), detection limits are lower than in ICP-AES. In AAS the sample is atomized in a flame or in a graphite furnace. The light absorbance of the atoms, in the flame or graphite furnace, from a light source is measured. This light source, made of a cathode, emits light with the characteristic frequency of the specific element. The absorption is proportional to the concentration of the analyte. An advantage of graphite furnace is that elements with lower atomizing temperatures which interfere with the analyte can be removed. Another advantage of a graphite furnace is the lower detection limit (Perkin-Elmer, 1984).

At the NGU, arsenic and cadmium were determined by the graphite furnace technique (GF-AAS). The sample treatment is the same as for the ICP-AES analysis. The uncertainty is ± 20 rel.% for arsenic and ± 10 rel.% for cadmium. Mercury was analysed by atom-absorption analysis, cold-vapour technique (CV-AAS). The sample treatment is the same as for the ICP-AES analysis, but the extract was diluted with a fluid containing 50 ml concentrated HNO_3 + 0.1 g $K_2Cr_2O_7$ to 1000 ml distilled water. The uncertainty for the analysis is estimated to ± 10 rel.% (NGU, 1998).

At the NTNU, soil (98) and sand (24) samples were extracted in concentrated HNO_3. About 2 g of each sample was extracted in 20 ml 65% HNO_3 in Erlenmeyer flasks. To prevent evaporation of the liquid a watchglass was placed on top of the flasks. Samples were heated at a temperature of 85°C for 20 hours. After this the mixture was filtered and diluted to 50 ml with distilled water. From this solution, 10 ml was taken and evaporated. The non-evaporable residue was dissolved in 10 ml 0.1 M HNO_3 and stored in polyethylene bottles before analysing. About 20 samples were extracted in one turn. In addition to this, 3 reagent blanks, containing all reagents but no soil, underwent the same procedure. In addition to this a five stage sequential extraction procedure was accomplished on these samples. The procedure is described in Chapter 3.2.4.

A GBC Avanta Σ was used for analysing the samples for cadmium (GF-AAS). The total acid soluble concentration of Cd was determined with a hollow cathode lamp. Calibrating of the instrument was done by one standard solution of about 6 ppb, which was made by diluting a 1000 ppm solution with 0.1 M HNO_3. The ashing temperature was 350 °C and the atomisation temperature was 1800 °C. Every sample was analysed three times. Samples were analysed until the relative standard deviation was less than 5%. Samples with concentrations outside the calibration range were diluted by the instrument. When the concentration was too high after dilution by the instrument, samples were diluted by hand. A sample check of the standard solution was performed on each seventh sample. These were used to control the quality of the analysis. The instrument was recalibrated if the concentration of the sample check was outside the range of 90-110% of the expected value.

A Perkin Elmer AAnalyst 600 was used for analysing the samples for arsenic (GF-AAS). This element was determined with an Electrodeless Discharge Lamp (EDL-2). Calibration of the instrument was done by one standard solution of about 175 ppb, which was made by diluting a 500 ppm solution with the respective reagents. The ashing temperature was 1400 °C and the atomisation temperature was 2300 °C. Every sample was analysed three times. Samples were analysed until the relative standard deviation was less than 5%. This was a problem in samples with very low concentrations (<10 µg/l in solution, <250 µg/l in soil), especially at stage 1 and 2 in the sequential extraction procedure. These samples were reanalysed a maximum of three times. Samples with concentrations outside the calibration range were diluted by the instrument. When the concentration was too high after dilution by the instrument, samples were diluted by hand. Arsenic is quite volatile, so to prevent loss of arsenic a 0.3% Pd, 0.1 M HNO_3 modifier was used. Recovery was measured on each seventh sample. These were used to control the quality of the analysis. The instrument was recalibrated after seven samples.

A GBC Avanta Σ was used for analysing the samples for Cr, Cu, Ni, Pb and Zn (AAS Flame). The elements were determined with hollow cathode lamps. Calibrating of the instrument was done by five standard solutions of about appropriate concentration, which were made by diluting a 1000 ppm solution 6.0 M HNO_3. The flame type used for the determination of Cr was N_2O-Acetylene. Air-Acetylene was used for the other elements. Each sample was analysed three times. Samples were analysed until the relative standard deviation was less than 5%. Samples with concentrations outside the calibration range were diluted by hand.

3.2.3 XRF

X-ray fluorescence spectrometry (XRF) is a standard method for determining the chemical composition of rocks. When a material is placed in a beam of x-rays, the x-rays are absorbed. The absorbing atoms of the material become excited and emit x-rays of characteristic wavelength. This characteristic wavelength makes it possible to identify the fluorescing elements. The intensity of the fluorescence is proportional to the concentration of the elements and makes it possible to produce a quantitative determination of the elements. Advantages of XRF analysis are numerous. Samples can be examined with little or no pre-treatment, the method is fast and non-destructive, it has high accuracy and precision and multi-element analyses are possible. A disadvantage is that the method is inconvenient for the lighter elements (Thornhill, 1999).

Ten rock samples were selected for XRF analysis. These samples are considered as representative for the range of bedrock compositions in the investigated area.

LOI was first determined by the weight loss of adsorbed water by heating 2-3 gram sample powder in a porcelain cup at 120°C overnight (M1). Subsequently, the weight loss was determined of the samples in the same porcelain cup by heating to 900°C in a furnace for 5 hours (M2). The reported LOI values are M2-M1.

The XRF analysis were made using a Philips PW1480 XRF. The rock samples were crushed and subsequently ground in a tungsten-carbide shatter-box to < 200 µm in diameter. Major elements were determined on glass beads, which were made by fusing 0.5000 gram ignited rock powder with 5.0000 gram $LiBO_2/LiB_4O_7$ (66/34). Trace elements were determined on pressed powder pellets. These were made of 8.0 gram sample powder mixed with 2 ml elvacite (1:5 =elvacite: acetone) as a binding agent and pressed under 25 tonne/cm^2 for 2 minutes.
The accuracy, the deviation of the ‘true’ value, as determined on international standards, is generally better than 3% for the major elements and 10% for the trace elements.

3.2.4 Sequential extraction

A five stage sequential extraction procedure was accomplished on 24 sand and 98 soil samples.

Fraction 1: “Exchangeable fraction”

At the first stage about 2 g of each sample was extracted in 20 ml 1 M $MgCl_2$, in which the pH was adjusted to 7.0 with HNO_3, in borosilicate centrifuge tubes. Samples were placed into a shaker filled with water at a temperature of 37 °C. The samples were shaken at 120 rpm.

After twenty hours the samples were centrifuged at 4500 rpm for twenty minutes. The supernatant liquid was removed and the remaining soil washed with distilled water and centrifuged for another 20 minutes at 4500 rpm. The supernatant liquid was removed and added to the first extract. Distilled water was used to get a total volume of 50 ml. The liquid was stored in polyethylene bottles before analysis.

Fraction 2: “Bound to carbonates”

At the second part of the sequential extraction procedure, 20 ml 1 M NaAc in which the pH was adjusted to 5.0 with HAc, was added to the remaining soil from the first step. Samples were shaken for 20 hours at 120 rpm at a temperature of 37 °C. After this, the samples were centrifuged and washed following the procedure used on the exchangeable fraction.

Fraction 3: “Bound to reducible substrates”

To the residue from the second stage a 20 ml 0.04 M $NH_2OH{\cdot}HCl$ in 25% HAc solution was added. Samples were shaken for 20 hours at 60 rpm at a temperature of 85 °C. After this, the samples were centrifuged and washed following the procedure used on the exchangeable fraction.

Fraction 4: “Bound to organic compounds”

At the fourth stage of the sequential extraction procedure, 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 adjusted to pH 2.0 with HNO_3 was added to the residue from the third stage. Samples were shaken at 60 rpm at a temperature of 85 °C. After 2 hours another aliquot of 3 ml 30% H_2O_2 was added to the samples. This mixture was shaken for another 3 hours. After cooling 5 ml 3.2 M NH_4Ac in 20% HNO_3 and 4 ml of distilled water was added. The samples were agitated continuously for 14 hours. The addition of NH_4Ac is to prevent adsorption of the extracted metals onto the oxidised sediment. After this, the samples were centrifuged and washed following the procedure used on the exchangeable fraction.

Fraction 5: “Residual fraction”

Finally, 20 ml concentrated HNO_3 was added to the residue from the fourth stage. Samples were shaken at 60 rpm at a temperature of 85°C for 20 hours. After this the mixture was filtered and diluted to 50 ml with distilled water.

The extractions were carried out in centrifuge tubes to prevent loss of solid material. From the extracts of the fourth and fifth stages, 10 ml was taken and evaporated. The non-evaporable residue was dissolved in 10 ml 0.1 M HNO_3.

3.3 Statistical methods

3.3.1 Factor analysis

The essential purpose of factor analysis is to describe, if possible, the covariance relationships among many variables in terms of a few underlying, but unobservable, random quantities called factors. Basically, the factor model is motivated by the following argument: Suppose all variables within a particular group are highly correlated among themselves, but have relatively small correlations with variables in a different group. Then it is conceivable that each group of variables represents a single underlying construct, or factor, that is responsible for the observed correlations (Johnson and Wichern, 1998). Different rotation methods can be used in factor analysis. In a varimax or orthogonal rotation, the axes of rotation are perpendicular to each other. The assumption behind this rotation method is that all factors are independent of each other. However, if one suspects that the factors are not totally independent of each other, one can use a rotation method in which the rotation is oblique or nonrigid of the coordinate system such that the rotated axes are no longer perpendicular to each other (Johnson and Wichern, 1998).

Because of the great variety of geological material in soil samples, with small differences in geochemical composition, it is anticipated that there will be more than one geological and several anthropological factors, not totally independent to each other. A factor analysis with an oblique rotation is therefore used on the analytical data from 297 soil samples taken in 1998 and on the topsoil and sand data from 24 kindergartens taken in 1999. A complete description of the factor analysis used on these data are presented in Papers 1 and 2.

Another factor analysis has been completed on the acid soluble concentrations in bedrock and soil samples taken in the near vicinity of each other. The purpose of this factor analysis was to see which of the elements in soil were derived from the parent material. In this case, the number of samples was low compared with the number of variables. The set of data might therefore not be suitable for factor analysis. However, the data is approximately multivariate normal and thus acceptable for factor analysis (George and Mallery, 1999). A description of the factor analysis is presented in Paper 3.

3.3.2 Boxplots

The boxplot is a useful presentation technique for comparison of different data subsets, because location, spread, skewness, tail length and outlying data points appear at a glance (Reimann et al. 1988). Boxplots are based on the median, quartiles, and extreme values. The box represents the interquartile range which contains the 50% of values. The whiskers are lines that extend from the box to the highest and lowest values, excluding outliers and extremes. A line across the box indicates the median. Outliers are cases with values between 1.5 and 3 box lengths from the upper or lower edge of the box. Extremes are cases with values more than 3 box lengths from the upper or lower edge of the box. Boxplots are used in Paper 2.

3.3.3 Scatterplots and bar charts

The scatterplot or xy-plot plots two numeric variables against each other. They are used to evaluate reproducibility between duplicates and to evaluate analyses of different laboratories in Papers 2 and 3. Bar charts are used in Paper 3 to evaluate concentrations of chromium, copper, nickel, lead and zinc in bedrock samples and topsoil samples taken in the near vicinity of each other.

4 Health criteria and occurrence of the elements in soil and bedrock

In the following, the health criteria, the occurrence and the properties of a range of elements in soil and bedrock are briefly described.

4.1 Health criteria

Dutch authorities use Target and Intervention Values for Contaminated Land to determine whether contaminated land poses a serious threat to public health (VROM, 1994). Also the Norwegian Pollution Control Authority uses Norm values on this matter (SFT, 1999). Target, Intervention and Norm values are shown in Table 1.

Table 1. Dutch Target and Intervention values and Norwegian Norm values for polluted soil (mg/kg).

	Target value	Intervention value	Norm value
As	29	55	2
Ba	200	625	
Cd	0.8	12	3
Co	20	240	
Cr	100	380	25
Cu	36	190	100
Hg	0.3	10	1
Mo	10	200	
Ni	35	210	50
Pb	85	530	60
Zn	140	720	100

Intervention values used by the Dutch government are based on a detailed study by the RIVM (National Institute for Public Health and Environmental Protection; reports 725201001 to 725201008) into the human toxicological effects of soil contaminants. These effects are quantified in terms of those concentrations in the soil which result in the so-called maximum permissible risk level for humans being exceeded. For non-carcinogenic substances, this corresponds to the TDI (tolerable daily intake). Eco-toxicological effects are quantified in terms of the concentration in the soil at which 50% of the species actually (or potentially) occurring may undergo adverse effects. The Intervention values finally adopted are based on the results of the RIVM study, which integrates the toxicological and eco-toxicological effects together. Target values indicate the soil quality levels ultimately aimed for (VROM, 1994). Norm values used by the Norwegian authorities lie generally between Target and Intervention values.

4.2 Arsenic

Some of the most important typical minerals in which arsenic is part of the structural formula are arsenopyrite (FeAsS), realgar (AsS), orpiment (As_2S_3), arsenolite (As_2O_3), nickeline (NiAs) and cobaltite (CoAsS). Possible host minerals, which can contain arsenic as trace element, are feldspars, magnetite, ilmenite, apatite, and in sulphides such as pyrite, galena and sphalerite. Natural concentrations in gabbro and basalt are 0.7 mg/kg, in granite and granodiorite 3 mg/kg, in shale and schist 13 mg/kg, in limestone 1.5 mg/kg, in sandstone 0.5 mg/kg and in coal 10 mg/kg. Toxicity is dependent on valence: As^{5+} compounds are less toxic than As^{3+} compounds. Arsenite (+3) is most likely to be found in anaerobic soils. Arsenate (+5), the oxidised state is stable in aerobic soils (Reimann & de Caritat, 1998).

4.3 Boron

Despite the fact that boron has a low atomic number, occurrences of the element in the earth crust are small. Elementary boron does not exist in nature. Boron is a trace element in minerals such as amphiboles, plagioclase, micas, tourmaline and biotite. Boron is used in glass, alloys, antiseptics and as flame retardant. Coal can contain boron (Wedepohl, 1969). Environmental pathways for boron are sea spray, coal combustion, sewage and fertilisers (Reimann & de Caritat, 1998).

4.4 Barium

Barium is a toxic element, but its toxicity depends on its ability to dissolve. The ion is easily absorbed from the lungs and from the digestive apparatus. Barium-sulphate does not absorb into the human body. Barium accumulates in the bone structure, and can lead to heart problems because it has effect on muscles in the heart region (Friberg, et. al., 1986). The Target value, used by the Dutch authorities is 200 mg/kg and the Intervention value is 625 mg/kg (VROM, 1994). Typical minerals in which Ba is part of structure formula are barite ($BaSO_4$) and witherite ($BaCO_3$). Possible host minerals which can contain Ba as trace element are micas, K-feldspar, apatite and calcite. In general natural sources are more important than anthropogenic ones, which include Cu smelting, automobile industry and steel works (Reimann & de Caritat, 1998). Barium is one of the less common elements which may be considerably concentrated in certain coal ashes. The amount of BaO in such ash may reach 1.000-10.000 ppm and over (Goldschmidt, 1954).

Bjørlykke (1974) showed barium concentrations up to 6-7% Ba in the Lower Ordovician shales of the Oslo Region. Relatively high barium concentrations are also found in some Ordovician limestones.

4.5 Beryllium

Beryllium is considered non-essential. It is toxic if inhaled and carcinogenic for several animal classes. Both the metal and its compounds are allergenic. Beryllium, although widely distributed, exists in relatively small quantities, comprising less than 10 ppm of the major rock types. The metal is likely to concentrate in the acid magmatic rocks (Kabata-Pendias et. al. 1992). Typical minerals that contain Be are beryl ($Be_3Al_2Si_6O_{18}$) and bertrandite ($Be_2SiO_4.H_2O$). Minerals that can contain traces of Be are plagioclases, micas, pyroxenes and clay minerals. Coal combustion, Cu rolling, non-ferrous metal smelting, Al smelting and rock dust are sources of beryllium. BeO ceramics are used for their high thermal conductivity and good electrical insulation properties (Reimann & Caritat, 1998).

4.6 Calcium

Calcium is a major nutrient and is essential for most organisms. It is non-toxic. One can find calcium in many minerals. The most important minerals are calcite ($CaCO_3$), gypsum ($CaSO_4.2H_2O$) and fluorite (CaF_2). Possible host minerals which can contain traces of Ca are carbonates, feldspars, pyroxenes and amphiboles. Calcium is very mobile under weathering. The element is used in lime, cement, fertilisers and in metallurgy as reducer, deoxidiser and desulphuriser. Generally geologic sources are more important than anthropogenic (Wedepohl, 1969, Reimann & Caritat, 1998).

4.7 Cadmium

Cadmium is closely related to zinc and will be found wherever zinc is found in nature. Cadmium will be emitted to air and water by mining, by metal smelting, especially from lead, copper and zinc smelters and by industries using cadmium in alkaline accumulators, alloys, paints and plastics. The burning of oil and waste will also contribute, as well as the use in agriculture of fertilisers, either as chemicals or as sludge from sewage plants (Friberg, et.al, 1974). Analysis of cadmium in mosses from the Oslo area shows that local sources contribute to cadmium pollution in this area (Steinnes, et al. 1993).

4.8 Cerium

Cerium is considered non-essential and has generally low toxicity. Toxicity of the Rare Earth Elements (REE) decreases as atomic number increases. Inhaled REE probably cause pneumoconiosis. REE taken up orally accumulate in the skeleton, teeth, lungs, liver and kidneys. Cerium is most abundant of all REE and can replace Ca in biological processes. Typical minerals containing cerium are monazite $((Ce,La,Nd,Th,Y)(PO_4SiO_4))$, bastnaesite $((Ce,La,Y)CO_3(F,OH)$, cerite $((Ce,La)_9(Mg,Fe)Si_7(O,OH,F)_{28})$, allanite $((Ca,Ce,La)_2FeAl_2Osi_3O_{11}(OH))$ and xenotime $((Y,Ce)PO_4)$. Minerals which can contain traces of Ce are feldspars, apatite, sphene, fluorite and zircon. Environmental pathways are poorly understood. Windblown dust and weathering of REE bearing minerals are probably most important (Reimann & Caritat, 1998).

4.9 Cobalt

Cobalt is essential to humans but toxic at doses of 25 mg/day or more. Cobalt is essential in vitamin B_{12} (Friberg, et. al., 1986). Possible host minerals are olivine, pyroxenes, amphiboles, micas, garnets, pyrite and sphalerite (Reimann & Caritat, 1998). Environmental pathways are Ni, Ag, Pb, Cu, Fe mining and processing, coal combustion, geological dust, weathering and fertilisers (Reimann & Caritat, 1998). The Norwegian authorities do not have a Norm value for Co. The Dutch Target value for soil is 20 mg/kg (VROM, 1994).

4.10 Chromium

The average content of chromium in the earth´s crust is 125 mg/kg (Friberg et. Al. 1986). Typical minerals that contain Cr are chromite ($FeCr_2O_4$) and crocoite ($PbCrO_4$). Important host minerals which can contain traces of Cr may be pyroxenes, amphiboles, micas, garnets and spinels. Some environmental pathways are geological dust, weathering, Cu smelting, combustion of natural gas, oil and coal, sewage sludge and waste incineration. Chromium is essential for some organisms. Cr^{3+} is considered relatively harmless, while Cr^{6+} is highly toxic. Some compounds are known to be carcinogenic (Reimann & Caritat, 1998). Cr^{6+} is more mobile than Cr^{3+}, but usually reduced to $Cr(3^+)$ within a few weeks. There is generally low uptake by most vegetables, expect spinach. Some trees, such as lichen and moss can accumulate Cr (Reimann & Caritat, 1998). The Norm value used by Norwegian authorities is 25 mg/kg (SFT, 1999). In the Netherlands the Target value is 100 mg/kg, and the Intervention value 380 mg/kg (VROM, 1994). The Norm value of Cr is very low. However, high chromium concentrations might not indicate a serious problem if it is not know whether the chromium is present as Cr^{3+} or Cr^{6+}.

In the Cambrian shales of the Oslo Region, chromium concentrations are about 140 ppm Cr. In the Ordovician sequence there is an increase in chromium contents up to the Middle Ordovician/Upper Ordovician boundary. In the Cambrian shales, chromium is probably largely present in illite substituting for Al^{3+}. Chromium may also be a trace element in chlorites. Very high concentrations of chromium, up to 1200 ppm, occur in some samples of the Tretaspis Shale (4c) and the Chasmops Limestone (4b). The average chromium content for the Lower Palaeozoic shales of the Oslo Region is 284 ppm Cr which is considerably higher than for the average shale (90 ppm) (Bjørlykke, 1974).

4.11 Copper

Most of the important copper minerals are sulphides and related compounds. In most of these compounds, the structure is controlled mainly by the packing of the sulphur or similar large ions, with the copper fitting into the interstices. In magmatic rocks many important deposits of copper ores are associated with gabbro and basalt. To a lesser extent, a number of copper deposits are directly associated with diorites, monzonites, andesites, granites and granodiorites. Copper ores, especially chalcopyrite, are sometimes associated with pyro-metasomatic deposits which grade continuously into hydrothermal veins and zones of impregnation. In the Oslo district the copper ores, are associated with syenites, but only on a small scale (Goldschmidt, 1954). In sediments copper precipitates mostly in black shales, in red bed facies and associated sandstones, but can be found occasionally in carbonate rocks (Fairbridge, 1972).

Copper concentrations are generally low in the grey shales of the Oslo Region. Average copper values for Cambrian shales are about 70 ppm. The average content of copper declines from about 50-60 ppm in the Middle Ordovician to about 20-30 ppm in the Silurian. In the limestones, the copper content is lower, mostly 15-30 ppm. The average copper content for Lower Palaeozoic limestones is 18 ppm. For the whole Lower Palaeozoic sequence the average is 33 ppm Cu. High copper concentrations (150-200 ppm Cu) are found in the Peltura beds (2d) in shale with a high sulphide content (8-10% S) (Bjørlykke, 1974).

4.12 Mercury

Mercury is a toxic metal and exists in both organic and inorganic material. Much of the mercury in the atmosphere has natural sources. Each year 30-150 thousand tons Hg gas releases from the crust and the oceans. Human activity releases about 20 thousand tons each year, from crude oil and coal combustion. 95% of mercury in the atmosphere is Hg°. Because of low solubility in water only a small amount of Hg is removed with rainfall. A nation-wide investigation of atmospheric deposition of mercury in Norway suggests that dry-deposition may be considerable especially in areas with low summer temperatures in which re-emission probably is less (Friberg, et.al., 1974, Steinnes, et.al, 1995). Possible host minerals for Hg are amphiboles, sphene, sphalerite and other sulphides (Reimann & Caritat, 1998). All commercial deposits of mercury ores are connected with hydrothermal solutions related to magmatic rocks. In hydrothermal deposits of sulphides of other metals, mercury, sometimes with antimony, seems to favour the middle, but mostly the lower part of the hydrothermal temperature range. Relatively high amounts of Hg, (10-100 mg/kg), have been observed in specimens from the pyrite-chalcopyrite deposits in Norway, (Goldschmidt, 1954).

4.13 Lanthanum

Lanthanum is considered non-essential. Toxicity is generally low. It is a trace element in minerals such as apatite, titanite and epidote (Kofstad, 1992). Y is also a trace elements in these minerals (Wedepohl, 1969). Typical minerals are monazite ($(\mathrm{(Ce,La,Nd,Th,Y)(PO_4SiO_4)})$), bastnaesite ($\mathrm{(Ce,La,Y)CO_3(F,OH)}$, cerite ($\mathrm{(Ce,La)_9(Mg,Fe)Si_7(O,OH,F)_{28}}$) and allanite ($\mathrm{(Ca,Ce,La)_2FeAl_2OSi_3O_{11}(OH)}$). All these minerals also contain Ce and some of these Y. Environmental pathways are geologic dust and mining and processing of alkaline rocks. Geologic sources are generally more important than anthropogenic ones.

4.14 Manganese

Manganese is essential for all organisms and is non-toxic. Just a few percent is absorbed by the human body. Iron deficiency causes higher uptake. The highest concentrations are found in the liver and kidneys. Concentrations in the brain are usually low, but with exposure over longer time, manganese can be accumulated. This can lead to an incurable disease much like Parkinsons disease. Many minerals contain manganese. Possible host minerals are among others garnets, olivine, pyroxenes, amphiboles, micas, calcite and dolomite (Friberg, et. al., 1986). Uses are widespread. It is used in steel, alloys, batteries, fertilisers, pigment, wood preservative, antiknock agent in gasoline (as a replacement for Pb in unleaded gasoline). Some environmental pathways are rock weathering, windblown dust, agriculture, traffic, mining and smelting (Reimann & Caritat, 1998).

Bjørlykke, (1974), showed that the Cambrian and Tremadocian black shales in the Oslo Region are characterized by very low manganese contents (0.01-0.03%). An increase in MnO content can be observed from the Lower Didymograptus Shale (3b) to the top of the Ogygiocaris Series (4aα 3-4) (0.06%). Upper Ordovician and Silurian shales have relatively constant contents of about 0.05-0.07% Mn. Limestones in the Oslo Region generally have higher contents of manganese than do the black shales. The highest manganese contents are found in the Middle Ordovician limestones and marly shales (average 0.19% MnO).

4.15 Molybdenum

The geochemical distribution of molybdenum in igneous rocks is characterised by a preference for late products of magmatic fractionation. We can find concentrations of molybdenum associated with granites, syenites and their pegmatites, nearly always as the mineral molybdenite (MoS_2). The occurrence of molybdenum, however, is not restricted solely to such residual magmas as granites, syenites or nepheline syenites. Small amounts of molybdenite are sometimes found in basic gabbroid magmas such as norites, where it is a minor constituent. The concentration of molybdenum in certain black shales is fairly pronounced but the distribution is very erratic (Goldschmidt, 1954). Other sources for molybdenum are oil and coal combustion, phosphate fertilisers, sewage sludge and phosphate detergents.

4.16 Sodium

Minerals containing sodium are albite ($NaAlSi_3O_8$), halite (NaCl), soda (Na_2CO_3) and major rock forming minerals such as plagioclases, micas, amphiboles and pyroxenes. Also sea spray contains Na. This has an effect on the sodium content of soil in areas near the coast (Wedepohl, 1969).

4.17 Nickel

The first systematic investigations on the occurrence of nickel in magmatic rocks were made by Vogt, (1923). He recognised the intimate geological association between one of the most common types of nickel ores, the magmatic pyrrhotite-pentlandite masses, and certain types of igneous rocks of the gabbro family, especially norites and peridotites. He also emphasised and demonstrated that nickel occurs not only in the sulphide ores of norites and peridotites, but that considerable amounts also enter into silicate minerals of these rocks. Further he showed that the nickel occurs in the ferromagnesian silicates of magmatic rocks, especially in the olivines and in minor amounts, also in pyroxenes. In general the amount of nickel decreases in the normal sequence of magmatic rocks starting from dunites and periodites, the early crystal differentiates from gabbroid or basaltic magmas, through the series gabbro-diorite-granodiorite or granite. The same holds for the series of volcanics from olivine basalts through basalts, andesites to dacites and liparites. As regards to the distribution of nickel in the various rock minerals, it is expected that the element will tend to concentrate in the earliest crystallizates of the ferromagnesian minerals (Goldschmidt, 1954). In soil nickel can accumulate in the B-horizon as mixed oxides or in humus or organic material (Adriano, 1986). Most of the nickel in soil is Ni^{2+}. Solubility increases with low pH. Nickel precipitates most often as nickel ferrite ($NiFe_2O_4$) (McGrath, 1995). Sewage can contain large amounts of nickel. Use of sewage as fertiliser may lead to accumulation of nickel in top soil. Transport of nickel down into the soil is small (McGrath, 1987).

Bjørlykke (1974) shows that nickel in the Oslo Region is present both in the silicate phase, mainly in chlorites, and in the sulphide phase. In the section through the Lower Palaeozoic sediments the distribution of nickel has two peaks. The one in the Upper Cambrian alum shale corresponds to the maximum sulphide content. Samples of alum shale with sulphur contents between 8-10% contain between 230-275 ppm Ni. The rest of the Cambrian and Lower Ordovician shales contain 50-70 ppm Ni. In the Middle Ordovician nickel values climb from 100-120 ppm in the Lower Ordovician to about 200 ppm in the Chasmops Series. The limestones have generally rather low nickel contents, around 50 ppm or below, but in the impure Middle Ordovician limestone with more than 10% CaO contain up to 150 ppm Ni. The Lower Silurian shales contain between 115 and 168 ppm Ni. Higher up in the Silurian succession one find values around 100 ppm.

4.18 Phosphorus

The bulk of phosphorus occurs from apatite($Ca_5(PO_4,CO_3)_3(F,OH,Cl)$). Other minerals containing phosphorus are xenotime (YPO_4), monazite ($(Ce,La,Nd,Th,Sm)(PO_4,SiO_4)$) and many other phosphates. One can find traces of phosphorus in minerals such as olivine, garnets, pyroxenes, amphiboles, micas and feldspars (Goldschmidt, 1954). Minerals containing phosphorus have low solubility in water. Availability for animals and plants is therefore low. Use of phosphorus is widespread. Fertilisers, detergents, insecticides, herbicides, fungicides, pyrotechnics and matches contain phosphorus. Phosphorus is also used in chemical industry (Wedepohl, 1969).

Bjørlykke, (1974) showed that limestones and marly shales in the Oslo Region have an average P_2O_5 content of 0.07%. In shales the P_2O_5 content is 0.10%. In the black shale facies (Middle Cambrian to Lower Ordovician) phosphorus contents are very low, generally 0.03-0.06% P_2O_5. The shales in the Middle Ordovician to Silurian beds average from 0.10-0.15% P_2O_5.

4.19 Lead

Lead is very toxic to animals and plants. Human uptake is through the lungs in which 30% is absorbed and through digestion in which 10% is absorbed. 90% of absorbed lead in the human body is accumulated in the bones. The halftime is about 20 years. The rest (10%) is stored in blood and tissue with a halftime of about 20 days. Inorganic lead has most often oxidation state 2^+. Salts of Pb^{2+} do not dissolve in water, except for lead-acetate, lead-chlorate and lead-chlorite. Organic lead, such as tetramethyl-lead and tetraethyl-lead has been used over a long time as antiknock agent in leaded gasoline (Friberg, et. al, 1986). With combustion of gasoline most tetraethyl-lead is broken down to halides and oxides, but some tetraethyl-lead escapes through the air with the exhaust (Merian, 1984). Typical minerals in which Pb is part of the structure formula are galena (PbS), anglesite ($PbSO_4$), cerussite ($PbCO_3$) and minium (Pb_3O_4). Possible host minerals which can contain traces of Pb are K-feldspar, plagioclase, micas, zircon and magnetite. Lead is generally strongly immobilised in the humic fraction of the soil, leading to strong Pb enrichment in the upper few cm of soil (Reimann & Caritat, 1998). Lead ores often contain zinc and small amounts of copper and iron. Uses of lead are widespread. It is used in batteries, as pigments, as stabiliser in plastics, in ammunition, in special alloys and as solder (Bjørtomt, et. al. 1992). Norm values in soil used by the Norwegian authorities are 60 mg/kg (SFT, 1999). In the Netherlands, the Target value is 85 mg/kg and the Intervention value is 530 mg/kg (VROM, 1994).

4.20 Strontium

Strontium is considered non-essential for most organisms. Strontium-90 is highly radiotoxic especially when it replaces calcium in organisms. Strontium is a trace element in calcium containing pyroxenes and amphiboles. Other host minerals are plagioclases, apatite, titanite, feldspars, micas, calcite and dolomite. Strontium is used in alloys, colour television tubes, pyrotechnic materials, ferrite magnets, and in zinc refining. Sources for strontium are weathering, geologic dust and sea spray. Nuclear tests and accidents are sources for radiogenic strontium (Reimann & Caritat, 1998, Wedepohl, 1969, Kofstad, 1992).

In Oslo, strontium contents are higher in limestones than in shales. The distribution of strontium in the Lower Palaeozoic limestones is stratigraphically controlled. The strontium content of the Lower Palaeozoic limestones increases from an average of about 265 ppm in the Middle Cambrian to 1021 ppm in the Upper Ordovician. Silurian limestones have intermediate values (498 ppm Lower Silurian, 678 ppm Upper Silurian). The weighted average of 581 ppm Sr for the Lower Palaeozoic limestones of the Oslo Region is somewhat higher than average values for limestones reported elsewhere (Bjørlykke, 1974).

4.21 Titanium

A few minerals are the carriers of titanium in practically all the various magmatic rocks: ilmenite ($FeTiO_3$), rutile (TiO_2), sphene ($CaTiSiO_5$), titaniferous magnetite and a few silicates which in certain special magmatic rocks contain titanium, for example, titaniferous amphiboles, biotites and andadrite. There are also some minerals which contain titanium together with an essential amount of an alkali metal found only in rocks rich in sodium. Ilmenite can be host mineral for a variety on ions. For ferrous iron small amounts of divalent magnesium, nickel, cobalt, zinc and manganese may be substituted. Vanadium may replace titanium. Ilmenite is the dominant titanium mineral in gabbros and basic nepheline rocks (Goldschmidt, 1954).

4.22 Yttrium

Yttrium is considered non-essential and has generally low toxicity, but seems to have a higher acute toxicity than REE. Typical minerals containing Y are monazite ($(\mathrm{(Ce,La,Nd,Th,Y)(PO_4SiO_4)})$), bastnaesite ($(\mathrm{Ce,La,Y})\mathrm{CO_3(F,OH)}$), euxinite ($(\mathrm{(Y,Ca,Ce,U,Th)Nb,Ta,Ti})_2\mathrm{O}_6$), xenotime ($(\mathrm{Y,Ce})\mathrm{PO_4}$) and yttrialite ($(\mathrm{(Y,Th)_2Si_2O_7})$). Possible host minerals are feldspars, apatite, pyroxenes and biotite. Geologic sources are thought to be more important than anthropogenic ones (Reimann & Caritat, 1998).

4.23 Zinc

Typical minerals containing zinc are sphalerite (ZnS, cubric), wurtzite (ZnS, hexagonal), smithonite ($ZnSO_4$) and zincite (ZnO). Traces of Zn can be found in pyroxenes, amphiboles, micas, garnets and magnetite. The main zinc ores mineral, sphalerite, generally contains many trace elements such as Cd, Se, Mn, Ag, Cu, Ga, Hg, In, Co, Ge, Sn, Ni, Sb, Bi and Pb (Reimann & Caritat, 1998). Zinc is an essential element for plants and animals and the toxicity is low. Deficiency is in fact more important. Zinc-chromate and zinc-arsenate are carcinogenic, but this causes mainly the chromate and arsenate part of these salts (Friberg, et.al., 1986). Zinc is used in galvanising, alloys, rubber industry, paint, glass, plastics, batteries and as wood preservative. Car tyres contain up to 5% zinc. The Norwegian Norm value for zinc in soil is 100 mg/kg (SFT, 1999), the Dutch Target value is 140 mg/kg and Intervention value is 720 mg/kg (VROM, 1994).

In the Oslo Region, high zinc values are found in lower Upper Cambrian limestones (250-300 ppm Zn). The zinc content in the Middle and Upper Cambrian shales, 86 ppm, is lower than in the Ordovician and Silurian calcareous shales, where average concentrations are between 100-120 ppm Zn (Bjørlykke, 1974).

4.24 Zirconium

Zirconium is considered non-essential for organisms and data on toxicity to humans are scarce. Host minerals which can contain traces of zirconium are pyroxenes, amphiboles, micas, garnets, ilmenite and rutile (Reimann & Caritat, 1998).

5 Discussion

5.1 The distribution of 32 elements in the topsoil of Oslo

Hypothesis I: “The composition of topsoil in Oslo is largely affected by human activity.”

To verify hypothesis I, a sampling campaign was performed during the summer of 1998. Approximately three hundred samples of surface soil (2-3 cm) were taken systematically, one per square kilometre. The investigated area covers about 500 km^2. The sample distribution is shown in Figure 2. Samples were dissolved in 7 N HNO_3 and analysed for 29 elements by ICP-AES, mercury by cold-vapour technique (CV-AAS) and arsenic and cadmium with a graphite furnace (GF-AAS).

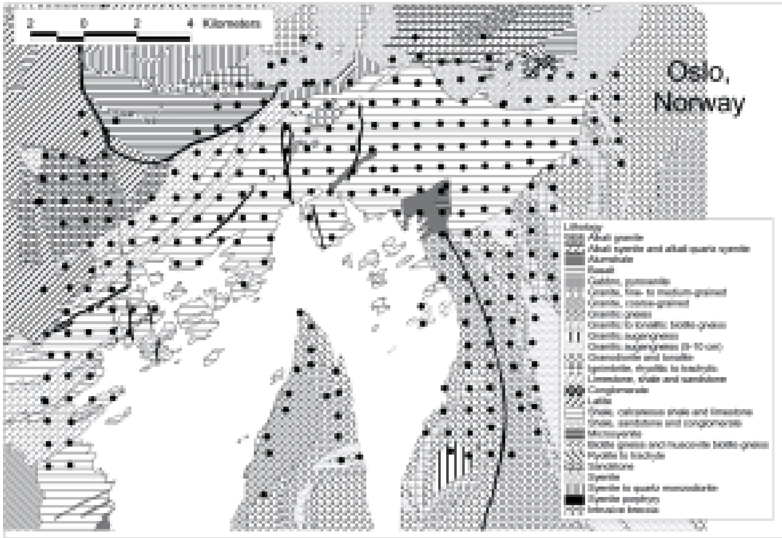

Figure 2: Distribution of samples in 17 districts of Oslo

A factor analysis has been completed to identify relationships among the elements. The first factor contains the elements Sc, Fe, Li, Co, Al, Cr, Be, K, Ni, V, Mg, Y, Ba, Zr, Mn and As (listed with decreasing factor loading).

These elements are typical for the minerals in the area and most of these elements have a near normal distribution. Sources for this factor are probably geological.

The second factor contains Cd, Hg, P, Zn, Cu, Ba and Pb. They have a log-normal distribution. Road traffic is probably one of the sources contributing to this factor. In Norway studded tyres are frequently used in the winter season which results in large amounts of road dust. Leaded petrol has been a major source for Pb, but is not in use any more. Wear and tear of tyres and brakes contribute also to this factor. Other sources contributing to this factor are probably industry, garbage incineration, crematoria and release of some of these elements from structural material by fire.

Factors 3, 4 and 6 with elements such as Ca, Na, La, Ti and Sr probably have geologic sources. They are associated with minerals like amphiboles, pyroxenes and feldspars and some of the elements are part of sea dust.

Factor 5 contains Mn, Cd, Zn, As and Pb. Manganese may be derived from many different sources such as rock weathering, windblown dust, agriculture and traffic. Since As and Mn are placed in both factor 1 and 5 they probably have both geologic and anthropogenic sources.

Concentrations of the elements in the second factor are much higher in the central parts of Oslo, than in the rest of Oslo. Figure 2 shows a map of 17 districts in the investigated area. Each district contains 15-20 sampling sites with geographical, infrastructural or municipal boundaries. A pollution index is created by dividing the median of the elements As, Cd, Cu, Hg, Pb and Zn, in each district by the median of the whole city. A graphical display of pollution indices is shown in Figure 3.

Especially the centre has large indices. The total index, which is the sum of the indices of the 6 elements, is 18. The median value of Hg in the centre is eight times higher than in the rest of the city, but also the other elements have a much higher level in the centre. Økern has also a high total index. This area lies near the centre and has large industrial activity.

Norm values for contaminated land used by the Norwegian authorities are 2 mg/kg As and 25 mg/kg Cr (SFT, 1999). Of 297 samples, 65% contain more than 25 mg/kg Cr and 81% more than 3 mg/kg As, which is the detection limit of the analysis. These samples will therefore be regarded as contaminated. Factor analysis places these elements in the geologic factor. The Norm value of zinc is 100 mg/kg, and 74% of the samples contain more than this. The Norm value of lead is 60 mg/kg, and 25% of the samples exceed this value. Road traffic is probably the major source for these elements.

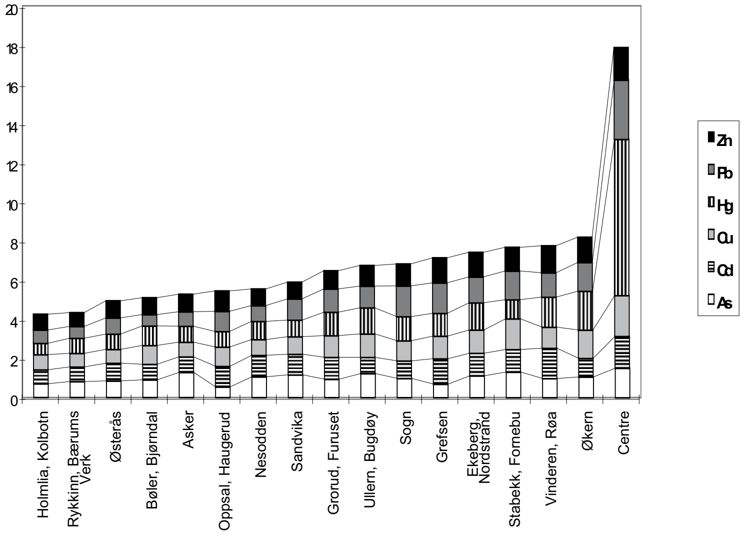

Figure 3. Indices of 6 elements in 17 districts of Oslo

The distribution of arsenic is regular through the whole area, but it has a slightly higher level in the centre of Oslo. Together with the results of the factor analysis, it may be concluded that the values of arsenic in the outermost areas are due to geological components, while in the centre the element probably has an anthropogenic origin.

In the summer of 1999, 98 samples of topsoil were taken near traffic arteries and on playgrounds at schools and kindergartens. A sequential five stage extraction was accomplished for all samples. These five fractions, (i.e. exchangeable, carbonate, reducible substrate, organic and residual) were analysed for arsenic.

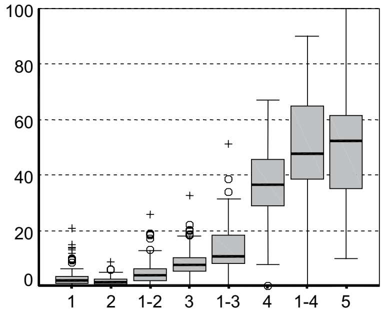

Figure 4. Boxplots of arsenic concentrations in 98 topsoil samples of each stage of the sequential extraction procedure presented as percentages of the total concentration. Boxplots 1-2, 1-3 and 1-4 are cumulative concentrations presented as percentages of the total concentration. Symbols: ° outliers, + extremes.

Up to 50% of the arsenic is extractable in the exchangeable, the carbonate and the reducible substrates fractions (Figure 4). In only two samples the cumulative concentrations in these three stages exceed the Norwegian Norm value of 2 mg/kg As. After four stages the number of samples exceeding the Norwegian Norm value is 68. Stomach acid is dissolved hydrochloric acid with a pH of 1.6 to 2.4 (Wallace et al., 1990). These conditions are quite comparable with the conditions in stage four of the extraction procedure and the cumulative concentrations of arsenic in the first four stages can therefore be a measure of the bio-availability of the element to human beings. The total concentration seems to have little effect on the concentrations in the first three extracted fractions. In samples with high total concentrations, most of the arsenic is found in the organic and residual fractions. At low total concentrations, the arsenic content in the organic fraction is generally higher than the arsenic content in the residual fraction. At intermediate and high total arsenic concentrations, concentrations in the residual fraction are generally higher than concentrations in the organic fraction.

Conclusions

1. In topsoil in Oslo, sources for the elements Ag, Al, Be, Ca, Ce, Co, Fe, K, La, Li, Mg, Na, Sc, Si, Sr, Ti, V, Y and Zr are mainly geologic.

2. For the elements As, B, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Ni, P, Pb and Zn, geologic sources are important but human activity has had a large effect on concentrations in topsoil, especially in the central districts.

3. At least 81% of the samples contain more arsenic than the Norm value for polluted soil used by the Norwegian authorities. Percentages for chromium, zinc and lead are 65, 74 and 25 respectively.

4. In topsoil, up to 50% of the arsenic is extractable in the exchangeable, the carbonate and the reducible substrate fractions, but only 2% of the samples exceeded the Norm value after the three extraction stages. After four stages 68% of the samples exceeded the Norm value.

The given hypothesis, that "The composition of topsoil in Oslo is largely effected by human activity" has not been rejected.

5.2 The composition of topsoil and sand from sandboxes at kindergartens in the central districts of Oslo

Hypothesis II: "The metal content in topsoil and sand from sandboxes at kindergartens in Oslo constitutes a potential hazard for children playing on it."

To verify hypothesis II, the acid soluble content of arsenic, cadmium, chromium, copper, nickel, lead and zinc in topsoil and sand from sandboxes from 24 kindergartens has been determined. In addition, a sequential extraction procedure has been accomplished to get a measure on the bio availability of arsenic.

5.2.1 The distribution of 7 elements in topsoil and in sand from sandpits

Samples of topsoil and of sand in sandpits were taken at 24 kindergartens in the central districts of Oslo. The samples were dissolved in concentrated HNO_3 and analysed for chromium, copper, nickel, lead and zinc by AAS-flame and for arsenic and cadmium with a graphite furnace (GF-AAS). These elements were chosen because of the potential hazardous effects they have on humans. The results of the analyses are presented in Figure 5. At kindergartens, the total acid soluble concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn in topsoil samples are higher than in samples of sand found in the sandboxes. The differences in arsenic concentrations between soil and sandbox samples are small. In all the soil samples the concentrations of arsenic exceed the Norm value for polluted soil used by the Norwegian authorities (SFT, 1999). In the sandbox samples, 63% of the samples exceed this value. For the other elements, none of the sandbox samples contains more than the Norm value. Regarding soil samples, at 13 of 24 kindergartens (54%), concentrations of at least one of the elements Cr, Cu, Ni, Pb and Zn, exceed the Norm value used by the Norwegian authorities. At two kindergartens all elements, except Cd, exceed the Norm value for polluted soil.

To describe the covariant relationships among the elements, a factor analysis has been completed on both soil and sand samples. For soil samples, the factor analysis extracted only one component explaining 83% of the total variance. This indicates that the major part of the total variance is explained by only one factor. Sources behind this factor might be natural, but since these elements are rare in geologic material in urban areas, and concentrations in the soil samples are relatively high, anthropogenic sources probably have a large effect on the concentrations of these elements.

For the sandpit samples, the factor analysis extracted two components. Factor 1 contains, listed in decreasing order of factor loadings, the elements Ni, Cu, Cd, Zn and Cr. Concentrations of these elements in samples from sandboxes are relatively low. Sources behind this factor are therefore probably natural, although anthropogenic sources might have some influence on the metal concentrations of these elements.

Factor 2 contains the elements Pb, As, Cr and Cu. The major part of the sandpit material are light minerals like quartz and feldspars in which these elements are minor constituents. Arsenic concentrations in these samples are relatively high. Beside natural sources, leakage of these elements from impregnated and painted wood is probably the main source for the elements in the second factor, since samples are taken in the near surroundings of this kind of material. Pressure treatment with CCA (Chromated Copper Arsenate) is often used for this purpose.

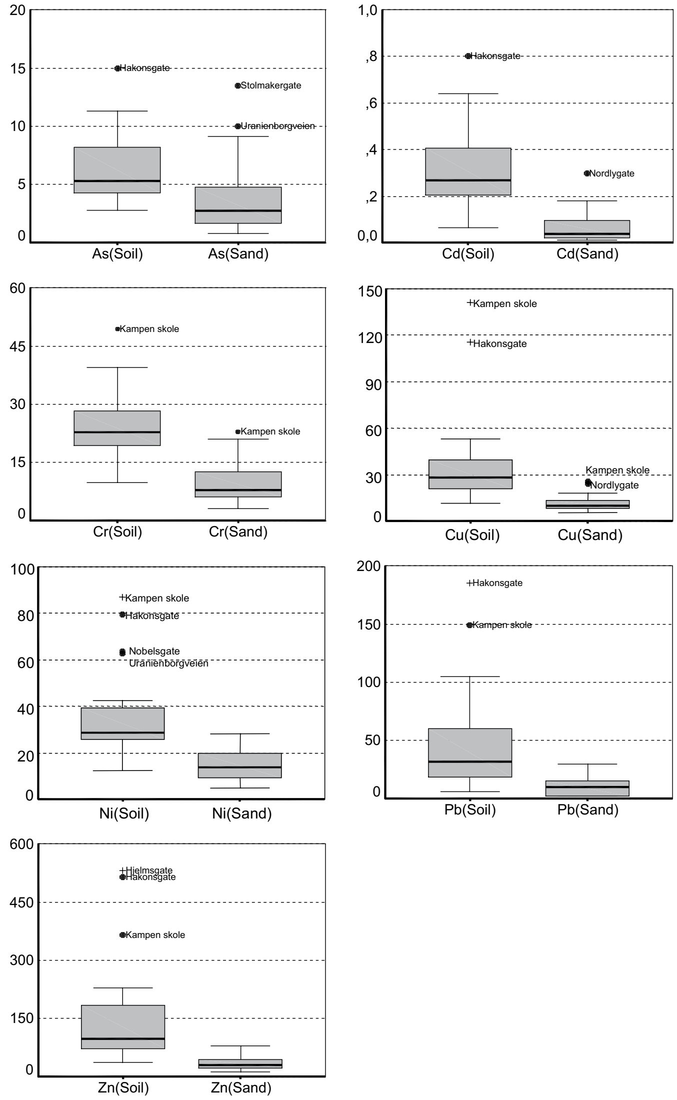

Figure 5. Boxplots of the total acid soluble concentrations (mg/kg) of selected elements in soil and sandpit samples of kindergartens in the central districts of Oslo. Symbols: • outliers, + extremes.

5.2.2 The speciation and bio-availability of arsenic in topsoil and sand

A sequential five stage extraction was accomplished for all sand and topsoil samples. These five fractions, (i.e. exchangeable, carbonate, reducible substrate, organic and residual) were analysed for arsenic.

At kindergartens, the exchangeable, the carbonate and the reducible substrate fractions, arsenic concentrations in the sandbox samples lie at a somewhat higher level than concentrations in soil samples (Figure 6). Leakage of arsenic compounds from impregnated and painted wood have probably caused elevated concentrations of this element in these fractions. In the organic fractions, only one kindergarten has a higher concentration in the sandbox sample than in the soil sample. In the residual fraction, only four kindergartens have arsenic concentrations that are higher in the sandbox sample than the concentration in the soil. Despite the fact that concentrations in sand are lower than in soil, 15 of 24 sandbox samples contain more arsenic than the Norm value for polluted soil.

At two kindergartens the cumulative arsenic content in sandbox samples exceed the Norm value of 2 mg/kg As for polluted soil already after two fractions (i.e. the exchangeable and the carbonate fraction). After three fractions, the arsenic content in sand at 5 kindergartens exceed this value. After four fractions this number was still 5.

Regarding soil, no kindergartens had a cumulative arsenic content exceeding the Norm value after three stages of the extraction procedure. After four stages 16 kindergartens contained more arsenic than the Norwegian Norm value of 2 mg/kg As.

Stomach acid is dissolved hydrochloric acid with a pH of 1.6 to 2.4 (Wallace et al., 1990). These conditions are quite comparable with the conditions in stage four of the extraction procedure and the cumulative concentrations of arsenic in the first four stages can therefore be a measure of the bio-availability of the element to human beings.

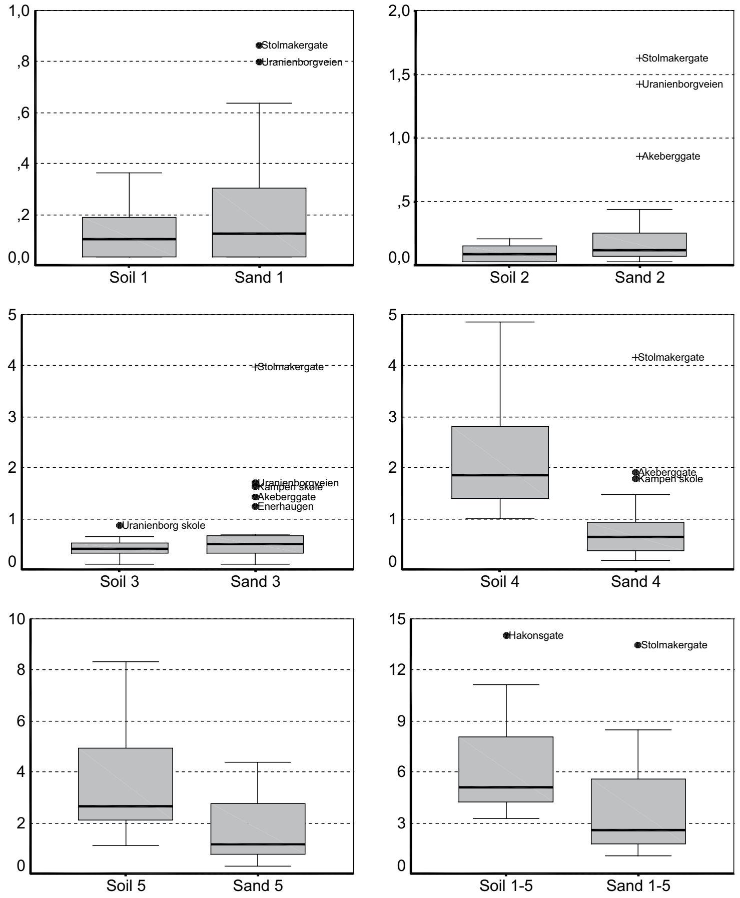

Figure 6. Boxplots of the arsenic concentrations (mg/kg) in 5 different fractions and the total concentration in samples of soil and sandboxes in kindergartens in the central districts of Oslo. 1 = exchangeable fraction, 2 = carbonate fraction, 3 = reducible substrate fraction, 4 = organic fraction, 5 = residual fraction and 1-5 = total concentration.

Conclusions

1. At kindergartens in the central districts of Oslo, concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn in topsoil samples are higher than in samples of sand from sandpits, but differences in arsenic are low.

2. At kindergartens, all topsoil samples and 63% of the sandbox samples exceed the Norm value for polluted soil used by the Norwegian authorities.

3. At 13 of 24 kindergartens, concentrations of at least one of the elements Cr, Cu, Ni, Pb and Zn exceed the Norm value in the topsoil. At two kindergartens all elements, except Cd, exceed the Norm value in topsoil.

4. In the sandbox samples at kindergartens, arsenic concentrations in the exchangeable, the carbonate and the reducible substrate fractions, lie at a higher level than in topsoil samples. Leakage of arsenic compounds from impregnated and painted wood have probably caused elevated concentrations of this element in the sand.

5. At two kindergartens the cumulative arsenic content in sandbox samples exceeds the Norm value of 2 mg/kg As for polluted soil already after two fractions (i.e. the exchangeable and the carbonate fraction). After three fractions, the arsenic content in sand at 5 kindergartens exceeds this value. After four fractions this number was still 5.

6. Regarding soil, no kindergartens had a cumulative arsenic content exceeding the Norwegian Norm value after three stages of the extraction procedure. After four stages 16 kindergartens contained more arsenic than the Norwegian Norm value of 2 mg/kg As.

7. Stomach acid is dissolved hydrochloric acid with a pH of 1.6 to 2.4 (Wallace et al., 1990). These conditions are quite comparable with the conditions in stage four of the extraction procedure and the cumulative concentrations of arsenic in the first four stages can therefore be a measure of the bio-availability of the element to human beings.

The given hypothesis, that “The metal content in topsoil and sand from sandboxes at kindergartens in Oslo constitutes a potential hazard for children playing on it” has not been rejected.

5.3 The influence of the parent bedrock composition on concentrations of heavy metals in topsoil in Oslo

Hypothesis III: “Analysis of bedrock material in addition to analysis of topsoil makes it easier to explain distribution patterns for the elements in the soil”

Most studies dealing with metals in soil systems do not consider the variation of metal concentrations in the parent bedrock material. Analysis of rock material taken in the vicinity of soil samples collected for analysis of trace metals might help to interpret the results. As expansion of a geochemical survey of topsoil in the city of Oslo in Norway (Paper 1) based only on soil samples, we wanted to investigate whether the content of trace metals in soil differs much from those of rock samples collected nearby.

To verify hypothesis III, rock and topsoil samples were taken at 44 locations in Oslo, Norway. Acid soluble concentrations of 30 elements in rock samples were measured using ICP/AAS and of seven elements in soil samples using AAS. These elements were chosen because of their potential hazard to human beings. Ten rock samples were analysed for the bulk concentration of 23 elements using XRF. These samples are considered as representative for the range of bedrock compositions in the investigated area.

At most sites, the bulk concentrations of metals, measured by XRF, in the bedrock samples, are generally higher than the acid soluble concentrations. Differences are small for copper and zinc, somewhat higher for lead and nickel and considerably different for chromium.

Acid soluble chromium concentrations in soil differ little when compared with acid soluble concentrations in bedrock, but are in general much lower than bulk concentrations in rock. Chromium is probably strongly incorporated in the mineral structure of rock samples and concentrated HNO_3 can not get all chromium molecules into solution.

For copper, lead and zinc, the acid soluble concentrations in soil are higher than the bulk concentrations in bedrock. The parent rock material cannot be the only source for these elements in soils and various anthropogenic sources dispersed by air or water probably have major influence.

The bulk concentrations in rock of arsenic and cadmium are not available. However, at many locations, acid soluble concentrations in soil are considerably higher than in rock samples. At these locations, human activities must have caused these elevated levels in soil.

Analysis of rock samples, both bulk and total acid soluble content, in addition to the sole analysis of soil samples gives a new dimension on interpreting the results of a survey on soil. Geological patterns influencing geographical variations in the material become more clear and this gives a better understanding of processes which might have lead to elevated levels of some of the elements in soil, especially in cases where the total acid soluble concentrations in soil are much higher than the bulk concentrations in rock.

Conclusions

1. Bulk concentrations of metals, in the bedrock samples, are generally higher than the acid soluble concentrations. Differences are small for copper and zinc, somewhat higher for lead and nickel and considerably different for chromium.

2. Acid soluble chromium concentrations in soil differ little when compared with acid soluble concentrations in bedrock, but are in general much lower than bulk concentrations in rock. Chromium is probably strongly incorporated in the mineral structure of rock samples and concentrated HNO_3 can not get all chromium molecules into solution.

3. For copper, lead and zinc, the acid soluble concentrations in soil are higher than the bulk concentrations in bedrock. The parent rock material cannot be the only source for these elements in soils and various anthropogenic sources dispersed by air or water probably have major influence. This supports the first conclusion which was based on statistical methods.

The given hypothesis that “Analysis of bedrock material in addition to analysis of topsoil makes it easier to explain distribution patterns for the elements in the soil” has not been rejected.

5.4 The influence of traffic on the heavy metal content in topsoil in Oslo

Hypothesis IV. “Traffic has considerable influence on the composition of nearby topsoil”

In an attempt to see if traffic has an influence on the heavy metal concentrations in topsoil, nineteen samples of topsoil were collected along Highway E-18 in Oslo. These samples show that the topsoil adjacent to Highway E-18 in Oslo is enriched in chromium, copper and nickel, when compared to samples of topsoil from the greater Oslo area. Samples along all larger highways in Oslo exhibit higher concentrations of these elements and arsenic compared with topsoil from the Oslo area. Other investigations on the heavy metal content of topsoil have shown enrichment of lead and zinc along highways. However, no enrichment of these elements is evident in this study. This result, and the fact that the enrichment and heavy metal profile of elements in topsoil is different near the various highways, show that applying the concept of enrichment factors to decipher the anthropogenic contribution of heavy metals in topsoil from road traffic is not straightforward. Many factors play a role in the processes concerning traffic and its possible pollution of the environment. Modern road construction, with import of soil from other geographical areas, often with different geology, can have an effect in a survey like this. Other sources of airborne heavy metals are industry and incineration plants. They may affect the heavy metal content in topsoil also near highways and obliterate the contribution from traffic.

The enrichment of nickel in topsoil near highways in Oslo might be due to the bitumen content of road dust. The enrichment of chromium and copper might be due to wear and tear of mechanical and engine parts on cars. There is no detectable enrichment of cadmium, lead and zinc in topsoil near Highway E-18 or other highways in Oslo. Concentrations of zinc in topsoil in Oslo are generally high compared to results from other cities in Norway, most probably due to airborne particulate matter from industry. The possible addition of zinc due to traffic is not observed, in the topsoil neither along Highway E-18 nor highways in the greater Oslo area.

Conclusions

1. The topsoil in the near vicinity of highway E18 in Oslo is enriched in chromium, copper and nickel relative to samples of topsoil in the Greater Oslo Area. The enrichment of nickel might be due to the bitumen content of road dust. The enrichment of chromium and copper might be due to wear and tear of cars and engine parts.

2. There is no enrichment of cadmium, lead and zinc in topsoil near highways. Concentrations of zinc in topsoil in Oslo are generally high, most probably because of industry. The possible addition of zinc from traffic to the topsoil is not notable. The lack off enrichment in lead is difficult to explain. Studies, both national and international, have shown high (in some cases very high) enrichment factors of this element. Also studies of residue deposits along highways in Oslo show that lead is a major constituent in this medium.

3. To get a better understanding of the variations in heavy metal concentrations in topsoil along different roads, more detailed and systematic investigations are necessary. The number of samples should be increased. Samples should be taken at various distances from the highway and different highways should be investigated separately. In such an investigation, one should carefully consider the area to which the soil data along highways is compared. In a large area with other major sources of pollution or in an area in which natural concentrations of specific elements are high, comparison of median values might not clearly show the elevation of heavy metals in an accurate way. In such a case comparison with a smaller area, parallel to the highway or comparison with deeper soil at sampling sites might be more appropriate.

The given hypothesis that “Traffic has considerable influence on the composition of nearby topsoil” can not be rejected at this stage, but further investigation is necessary.

Summary and conclusions

This study has mainly tried to address the following five issues:

A. What is the distribution of 32 elements in the topsoil of Oslo (Paper 1)

B. What is the distribution of 7 elements in sand from sandpits and in topsoil from playing grounds at 24 kindergartens in the central districts of Oslo (Paper 2)

C. What is the speciation of arsenic in topsoil and in sand from sandpits at kindergartens and are arsenic concentrations a potential danger for children playing on it (Paper 2)

D. What is the influence of the parent bedrock composition on concentrations of heavy metals in topsoil in Oslo (Paper 3)

E. What is the influence of traffic on the heavy metal content in topsoil in Oslo (Paper 4)

The principal objectives of the present work have been to test the following hypotheses:

I. The composition of topsoil in Oslo is largely affected by human activity

II. The metal content in topsoil and sand from sandboxes at kindergartens in Oslo constitutes a potential hazard for children playing on it.

III. Analysis of bedrock material in addition to analysis of topsoil makes it easier to explain distribution patterns for the elements in the soil.

IV. Traffic has considerable influence on the composition of nearby topsoil

None of the hypotheses could be rejected, although further research on hypothesis IV is necessary. The results of the present work can be summarised by the following conclusions.

Conclusions

1. In topsoil in Oslo, sources for the elements Ag, Al, Be, Ca, Ce, Co, Fe, K, La, Li, Mg, Na, Sc, Si, Sr, Ti, V, Y and Zr are mainly geologic.

2. For the elements As, B, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Ni, P, Pb and Zn, geologic sources are important but human activity has had a large effect on concentrations in topsoil, especially in the central districts.

3. At least 81% of the samples contain more arsenic than the Norm value for polluted soil used by the Norwegian authorities. Percentages for chromium, zinc and lead are 65, 74 and 25 respectively.

4. In topsoil, up to 50% of the arsenic is extractable in the exchangeable, the carbonate and the reducible substrate fractions, but only 2% of the samples exceeded the Norm value after the three extraction stages. After four stages 69% of the samples exceeded the Norm value.

5. At 24 kindergartens in the central districts of Oslo, concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn in topsoil samples are higher than in samples of sand from sandpits, but differences in arsenic are low.

6. At these kindergartens, all topsoil samples and 63% of the sandbox samples exceed the Norm value for polluted soil used by the Norwegian authorities.

7. At 13 of 24 kindergartens, concentrations of at least one of the elements Cr, Cu, Ni, Pb and Zn exceed the Norm value in the topsoil. At two kindergartens all elements, except Cd, exceed the Norm value in the topsoil.

8. In the sandbox samples at kindergartens, arsenic concentrations in the exchangeable, the carbonate and the reducible substrate fractions, lie at a higher level than in topsoil samples. Leakage of arsenic compounds from impregnated and painted wood have probably caused elevated concentrations of this element in the sand.

9. At two kindergartens the cumulative arsenic content in sandbox samples exceeds the Norm value of 2 mg/kg As for polluted soil already after two fractions (i.e. the exchangeable and the carbonate fraction). After three fractions, the arsenic content in sand at 5 kindergartens exceeds this value. After four fractions this number was still 5.

10. Regarding soil, no kindergartens had a cumulative arsenic content exceeding the Norwegian Norm value after three stages of the extraction procedure. After four stages 16 kindergartens contained more arsenic than the Norwegian Norm value of 2 mg/kg As.

11. Stomach acid is dissolved hydrochloric acid with a pH of 1.6 to 2.4 (Wallace et al., 1990). These conditions are quite comparable with the conditions in stage four of the extraction procedure and the cumulative concentrations of arsenic in the first four stages can therefore be a measure of the bio-availability of the element to human beings.

12. Bulk concentrations of metals, in the bedrock samples, are generally higher than the acid soluble concentrations. Differences are small for copper and zinc, somewhat higher for lead and nickel and considerably different for chromium.

13. Acid soluble chromium concentrations in soil differ little when compared with acid soluble concentrations in bedrock, but are in general much lower than bulk concentrations in rock. Chromium is probably strongly incorporated in the mineral structure of rock samples and concentrated HNO_3 cannot get all chromium molecules into solution.

14. For copper, lead and zinc, the acid soluble concentrations in soil are higher than the bulk concentrations in bedrock. The parent rock material cannot be the only source for these elements in soils and various anthropogenic sources dispersed by air or water probably have major influence. This supports the first conclusion which was based on statistical methods.

15. The topsoil in the near vicinity of highway E18 in Oslo is enriched in chromium, copper and nickel relative to samples of topsoil in the Greater Oslo Area. The enrichment of nickel might be due to the bitumen content of road dust. The enrichment of chromium and copper might be due to wear and tear of cars and engine parts.

16. There is no enrichment of cadmium, lead and zinc in topsoil near highways. Concentrations of zinc in topsoil in Oslo are generally high, most probably because of industry. The possible addition of zinc from traffic to the topsoil is not notable. The lack off enrichment in lead is difficult to explain. Studies, both national and international, have shown high (in some cases very high) enrichment factors of this element. Also studies of residue deposits along highways in Oslo show that lead is a major constituent in this medium.

17. To get a better understanding of the variations in heavy metal concentrations in topsoil along different roads, more detailed and systematic investigations are necessary. The number of samples should be increased. Samples should be taken at various distances from the highway and different highways should be investigated separately. In such an investigation, one should carefully consider the area to which the soil data along highways is compared. In a large area with other major sources of pollution or in an area in which natural concentrations of specific elements are high, comparison of median values might not clearly show the elevation of heavy metals in an accurate way. In such a case comparison with a smaller area, parallel to the highway or comparison with deeper soil at sampling sites might be more appropriate.

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Paper 1:

A Geochemical Survey of Topsoil in the City of Oslo, Norway.

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Paper 2:

The Geochemistry of Urban Topsoil in Oslo, Norway, with Emphasis on Kindergartens – A Sequential Analysis Procedure for Arsenic.

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THE GEOCHEMISTRY OF URBAN TOPSOIL IN OSLO, NORWAY, WITH EMPHASIS ON KINDERGARTENS –

A SEQUENTIAL ANALYSIS PROCEDURE FOR ARSENIC

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Abstract

Most studies dealing with metals in soil systems concern total metal concentration. However, availability of metals to organisms is not dependent on the total amount of a metal which is present in the soil, but rather how it is chemically bound within the soil. In the summer of 1999, 98 samples of topsoil were taken near traffic arteries and on playgrounds at schools and kindergartens in the centre of Oslo, the capital of Norway. At 24 kindergartens in the central districts, additional samples of sand from sandboxes were taken near playing facilities made of impregnated or painted wood. Beside the determination of the total acid soluble concentration of seven elements, a sequential five stage extraction was accomplished for all 122 samples. These five fractions, (i.e. exchangeable, carbonate, reducible substrate, organic and residual) were analysed for arsenic.

At the 24 kindergartens, the total acid soluble concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn in topsoil samples are higher than in samples of sand found in the sandboxes. The differences in arsenic concentrations between soil and sandbox samples are small. In all the soil samples the concentrations of arsenic exceed the Norm value for polluted soil used by the Norwegian authorities (SFT, 1999). In the sandbox samples, 63% of the samples exceed this value. For the other elements, none of the sandbox samples contains more than the Norm value. Regarding soil samples, at 13 of 24 kindergartens (54%), concentrations of at least one of the elements

Cr, Cu, Ni, Pb and Zn, exceed the Norm value used by the Norwegian authorities. At two kindergartens all elements, except Cd, exceed the Norm value for polluted soil.

In the exchangeable, the carbonate and the reducible substrate fractions, arsenic concentrations in the sandbox samples lie at a higher level than concentrations in soil samples taken at the same kindergarten. Leakage of arsenic compounds from impregnated and painted wood have probably caused elevated concentrations of this element. In the organic fractions, only one kindergarten has a higher concentration in the sandbox sample than in the soil sample. In the residual fraction, only four kindergartens have arsenic concentrations that are higher in the sandbox sample than the concentration in the soil. Despite the fact that concentrations in sand are lower than in soil, 15 of 24 sandbox samples contain more arsenic than the Norm value for polluted soil.

Regarding all 98 soil samples, up to 50% of the arsenic is extractable in the exchangeable, the carbonate and the reducible substrates fractions. In only two samples the cumulative concentrations in these three stages exceed the Norwegian Norm value of 2 mg/kg As. After four stages the number of samples exceeding the Norwegian Norm value is 68. Stomach acid is dissolved hydrochloric acid with a pH of 1.6 to 2.4 (Wallace et al., 1990). These conditions are quite comparable with the conditions in stage four of the extraction procedure and the cumulative concentrations of arsenic in the first four stages can therefore be a measure of the bio-availability of the element to human being. At low total concentrations the arsenic content in the organic fraction is generally higher than the arsenic content in the residual fraction. At intermediate and high total arsenic concentrations, concentrations in the residual fraction are generally higher than concentrations in the organic fraction.

Keywords

Geochemistry, sequential extraction, heavy metals, pollution, urban topsoil, kindergartens

1 Introduction

Most investigations of metal concentrations in soil systems measure total metal concentration. However, availability of metals to organisms is not dependent on the total amount of a metal which is present in the soil, but rather how it is chemically bound within the soil. One would like to measure concentrations in soil solutions over time but these are often below the detection limits of the analysis. To avoid this problem one can measure concentrations in the soil. However, instead of measuring the total concentration of the different elements, a sequential extraction of the soil may indicate more about the stability and mobility of the elements.

The city of Oslo is situated centrally in the Oslo Graben, which is a Permian rift basin consisting of volcanic and sedimentary rocks. To get a regional overview on the concentrations of about 35 elements in the topsoil of Oslo, approximately three hundred samples of surface soil (2-3 cm) were taken systematically, one per square kilometre, during the summer of 1998 (Tijhuis, et.al., 2002). During the summer of 1999, an additional 122 samples were taken near traffic arteries and on playgrounds at schools and kindergartens in the centre of the city. An additional issue at kindergartens is the use of arsenic impregnated wood in climbing frames and sandpits, so samples were taken both of the lawn and near playing equipment.

A five step sequential extraction, based on Tessier (1979) was applied to these samples. At stage one exchangeable ions will go in solution. The elements bound to carbonates are extracted in fraction two. The elements bound to Fe-Mn oxides are extracted at stage three. At stage four the metals bound to organic matter are extracted. And finally, the residual fraction is extracted at stage five.

2 Metals in the environment

2.1 Bio-availability of heavy metals

Pollution of soil, sediments and water by heavy metals is an important environmental problem. While most metals take part in metabolic processes and are therefore essential for organisms, they are toxic, or become toxic, if taken up in large amounts. High total concentrations of metals might not constitute a danger for some organisms.

The bioavailability of metals is dependent on the speciation, i.e. the partitioning among the various forms in which they might exist, of the metals in the soil. Metals might exist as (Campbell and Tessier, 1991):

1. Free ions in interstitial water
2. Ions bound to colloids
3. Precipitates such as insoluble carbonates, sulphates, phosphates and oxides
4. Ions adsorbed on particulate matter
5. Compounds incorporated in the lattice of primary and secondary minerals
6. Compounds organically bound to or in complexes with organic material

The first two categories are the most available for plants. The other forms are not available directly, but can be transferred, by different causes, into free ions. The rhizosphere receives organic matter from the plants. These organic compounds lead to biological activity. This can mobilise metal ions which are strongly absorbed to the soil by pollution, redox reactions and by formation of organic complexes.

Soil solutions provide great opportunity for variety in speciation, as they can contain organic ligands (fulvic acid), HCO_3^-, CO_3^{2-}, OH^- and other anions that are capable of forming soluble complexes with metal cations. The organic ligands in particular increase the carrying capacity of soil solutions for strongly complexing metals such as Cu^{2+}, increasing total metal solubility. HCO_3^-, CO_3^{2-}, OH^- and organic matter all increase in concentration as the soil pH is raised. At the same time, metal cation adsorption at mineral and organic surfaces is favoured at higher pH. Consequently, total metal solubility in soil solutions often displays a two-stage trend, decreasing up to pH 6 or 7, but increasing again at higher pH as soluble ligands bring the metals into solution. The speciation behaviour of an element in soils profoundly affects its bioavailability (McBride, 1994).

Uptake of metals through roots can take place both actively and passively. Passive uptake includes diffusion of ions from soil into the roots, following concentration gradients. With active uptake the ions are transported against the concentration gradient, so energy is needed. Uptake of lead occurs usually passively while uptake of copper and zinc can occur both actively and passively or by a combination of these. Ions which are taken up by the same mechanism often compete with each other. Absorption of zinc is restrained if copper or hydrogen ions are present but not in the presence of iron or manganese. After adsorption through the roots, ions are transported in plants. The mobility in plants depends on the metal. Manganese, zinc, cadmium, boron, molybdenum and selenium are metals with great mobility. Nickel, cobalt and copper are less mobile, while chromium, lead and mercury are almost immobile. Fungi can also accumulate relatively large amounts of metals in unpolluted areas. The swallowing of soil particles can lead to metal uptake in organisms living in soils. (Fergusson, 1990; McBride 1994)

2.2 Metals in soil

Fertile soils supply plants with all of the trace elements essential for growth. The most important of these are Fe, Mn, Zn, B, Cu, Mo, and Cl. These are called micronutrients. Small quantities are needed by plants, but deficiencies can occur in soils either because they contain extremely low concentrations of these elements or because the elements are present in insoluble forms. Many trace elements, including all of the micronutrients, can reach concentrations in soils that are toxic to plants and micro-organisms. Some of the most toxic are Hg, Pb, Cd, Cu, Ni and Co. The first three are particularly toxic to higher animals and the last three are more toxic to plants than animals and are called phytotoxic. Other elements with potential hazard effects on human beings are As, Be, Sb, Cr, Se, Ag, Tl and Zn. The specific elemental composition of soils reflects, to a degree modified over time by weathering, the chemical composition of the parent material from which the soil formed. Knowledge of a soil’s total elemental concentration is usually not very useful when it comes to understanding the processes and dynamics of element availability and cycling. If elemental concentrations are greatly in excess of those expected for a particular soil type, this may be a sign of pollution from human activity or accumulation from natural bio-geochemical processes (McBride 1994).

A measure more useful than total element concentration for most purposes is an estimation of availability of the element. This property can be related to mobility and uptake by plants or organisms and extractability by chemical treatments. The extractability of different elements depends on their properties, such as their tendency to:

- complex with organic matter
- chemisorb on minerals
- precipitate as insoluble sulphides, carbonates, phosphates or oxides
- co-precipitate in other minerals

Some elements can be partially extracted from soils with solvents such as water or salt solutions, whereas others may resist extraction even by chemically aggressive solutions such as concentrated acids or powerful chelating agents (McBride 1994).

2.3 Sequential extraction

Extraction schemas with a combination three to eight different extractions are described by Engler, Brannon and Rose (1977) and by Tessier, Campbell and Bisson (1979). Table 1 gives an overview over extraction methods and extraction agents which can be used.

In general the pH decreases through the procedure. The chemical reactions between the solid phases and the extraction agents are dependent on different parameters such as: concentration, pH, temperature, reaction-time and -intensity. The choice of method is dependent on what problems one wishes to solve. Because of the many parameters it is difficult to compare the results of different investigations.

One area of investigation in which sequential extraction is used is identification of the most important binding sites of trace metals. Examination of suspended material and marine sediments has shown that the residual fraction has the highest content of trace metals, while the carbonate fraction and the organic/sulphide fraction contain less than 30% of the metals. In the acid-reducible fraction the trace metals are bound to the oxy-hydrates at the surface of the particles The exchangeable metal fraction is larger in suspended matter than in sediments (Jenne, 1977).

Table 1: Extraction methods agents used in sequential extraction procedures.

Fraction	Extraction agent
Exchangeable cations	$CaCl_2$, $MgCl_2$, NH_4Oac
Carbonates	HAc, NaAc (pH=5)
Easily reducible substrates	$NH_2OH{\cdot}HCl$ (pH=2), $NH_2OH{\cdot}HCl/NH_4OAc$
Easily extractable organic compounds	$K_4P_2O_7$, NaOCl, $Na_4P_2O_7$
Moderate reducible oxides	$NH_2OH{\cdot}HCl/HOAc$
Oxidizable oxides and sulphides	H_2O_2, H_2O_2/NH_4Oac
Crystalline iron-oxides	HNO_3, $NH_2NH_2{\cdot}HCl$
Minerals (residual fraction)	HF, HF/HNO_3, $HF/HClO_4$, HNO_3/HCl

Another area in which sequential extraction is used is for estimating the bioavailability of contaminants. Factors which effect metal uptake in organisms are (Kersten and Förstner, 1989):

- The physiological and ecological properties of the organisms
- The chemical and physiological conditions of the water and the dissolved trace metals
- The chemical and physiological conditions of the trace metals in the soil

Many investigations have shown that care must be taken with interpretation of geochemical analyses as regards bioavailability of trace metals. One reason for this is that the mechanisms the organisms use for uptake of trace elements are not entirely known. Another reason is that uptake of trace elements in organisms takes place over a long period, while extraction in laboratories takes place relatively fast. Some extraction methods have shown positive results. Experiments of Häni and Gupta (1985) showed that metal concentrations in soil solutions have biological effects, irrespective of soil properties such as temperature and oxygen content, which can be measured by extraction with neutral salts. Swiss authorities have therefore suggested two maximum values for metals in soil (Gupta and Häni, 1985):

- HNO_3- soluble (total metal content)
- $NaNO_3$- soluble (bioavailable metal content)

A combination of chemical and biological tests can also be useful on investigation of bioavailability of trace metals. Diks and Allen (1983) found correlation in uptake of copper in the easily reducible fraction of their sequential extraction schema. The redox potential and pH conditions in the intestine of examined macro-benthonic species lead to the dissolution of manganese coatings and the associated trace metals. Luoma and Bryan (1978) showed that the Pb/Fe ratio in the 1 M HCl fraction represents the availability of Pb to mollusc species. Similar results are found on uptake of Cu, Zn and Pb in freshwater molluscs.

2.4 Arsenic

Arsenic is a ubiquitous element with metalloid properties. Its chemistry is complex and there are many different compounds of both organic and inorganic arsenic. In nature, it is widely distributed in a number of minerals, mainly as the arsenides of copper, nickel and iron, or as arsenic sulphide or oxide. Uncontaminated soils were found to contain arsenic levels between 0.2 and 40 mg/kg, while arsenic treated soils contained up to 550 mg/kg (Walsh & Keeney, 1975).

2.4.1 Arsenic in water

Arsenic can be mobilized in waters with pH values typically found in groundwaters (pH 6.5-8.5) and under both oxidising and reducing conditions. Arsenic can occur in the environment in several oxidation states (-3, 0, +3 and +5), but in natural waters is mostly found in inorganic forms as oxyanions or trivalent arsenite or as pentavalent arsenate (Smedley and Kinniburgh, 2002).

Most toxic trace metals occur in solution as cations which generally become increasingly insoluble as the pH increases. At the near neutral pH typical of most groundwaters, the solubility of most trace metal cations is severely limited by precipitation as, or coprecipitation with, an oxide, hydroxide, carbonate or phosphate mineral, or more likely by their strong adsorption to hydrous metal oxides, clay or organic matter. In contrast, most oxyanions including arsenate tend to become less strongly sorbed as the pH increases (Dzombak and Morel, 1990).

Under some conditions at least, these anions can persist in solution at relatively high concentrations even at near neutral pH values. Therefore the oxyanion forming elements such as Cr, As, U and Se can be common trace contaminants in groundwaters. Arsenic is among the most problematic in the environment because of its relative mobility over a wide range of redox conditions. Redox potential (Eh) and pH are the most important factors controlling As speciation. Under oxidising conditions $H_2AsO_4^-$ is dominant at low pH (less than about pH 6.9), whilst at higher pH, $HAsO_4^{2-}$ becomes dominant. Under reducing conditions at pH less than about 9.2, the uncharged arsenite species $H_3As_4^0$ will predominate. In the presence of extremely high concentrations of reduced S, dissolved As sulphide species can be significant (Smedley and Kinniburgh, 2002).

2.4.2 Arsenic in the atmosphere

Arsenic enters the atmosphere through inputs from wind erosion, volcanic emissions, low temperature volatilisation from soils, marine aerosols and pollution. It is returned to the earth's surface by wet and dry deposition. Baseline concentrations of As in rainfall and snow in rural areas are invariably low at typically less than 0.03 $\mu g\ l^{-1}$. Concentrations in areas affected by smelter operation, coal burning and volcanic emissions are generally higher. Unless significantly contaminated with industrial sources of As, atmospheric precipitation contributes little As to the soil and to surface and groundwater bodies (Smedley and Kinniburgh, 2002).

2.4.3 Arsenic in soils

Arsenic occurs in soils, mainly as arsenate, AsO_4^{3-}, under oxic conditions. The species is strongly, and sometimes irreversibly, sorbed onto clays, iron and manganese oxides/hydroxides and organic matter. The amount of sorption relates to the arsenic concentration, time and the iron and manganese content of the soil. In acidic soils the main forms of arsenic are aluminium and iron arsenates ($AlAsO_4$ and $FeAsO_4$). In alkaline and calcareous soils, the main form is $Ca_3(AsO_4)_2$. The mobility of arsenic in soils is increased under reducing conditions, such as found in a flooded soil, because of the increase in the proportion of arsenite (As(III)). Arsenite salts are estimated to be around 5 to 10 times more soluble than the corresponding arsenates. Unfortunately, As(III) is both the more available and more toxic form of the element. An increase in pH, e.g. by liming, also increases the mobility of the arsenic, presumably by bringing about a change from aluminium and iron arsenates to calcium arsenate. Bacteria are also important in the chemistry of soil arsenic, as methylation can occur, giving As(III) methyl derivatives. The mobility of arsenic is increased by the alkylation. Bacteria also accelerate the oxidation of arsenite to arsenate. (Fergusson, 1990)

The adsorption of arsenic to soils is highly associated with the clay, aluminium and iron content of the soil. The affinity is greater to iron than to aluminium. Leaching of arsenic from surface soils will be greater in soils where arsenic is less strongly sorbed such as sandy soils (Finnish Environment Institute, 1995).

Akins and Lewis (1976) also indicated that water soluble arsenic was inversely correlated to clay content. Dudas (1987) found that arsenic had about fourfold higher concentrations in clay than in silt fraction with only less than 1% arsenic in sand fraction in acid sulphate soils.

2.4.4 Arsenic in minerals

One important commercial compound is arsenic(III) oxide. This compound is recovered from copper smelters as a by-product of copper production. The arsenic in natural occurring metal arsenides and arsenic sulphides is volatised and oxidised during the ore roasting process and condenses as the trioxide in flues. Arsenic containing coal also produces chiefly arsenic(III) oxide, when it is combusted. Maximum arsenic concentrations found in various Finnish peat bogs are between 16 and 340 mg/kg dry peat (Minkkinen & Yliruokanen, 1978).

The most abundant As ore mineral is arsenopyrite, FeAsS. It is generally believed that arsenopyrite, together with the other dominant As-sulphide minerals realgar and orpiment, are only formed under high temperature conditions in the earth’s crust. However, authigenic arsenopyrite has been reported in sediments (Rittle et al., 1995) and orpiment has recently been reported to have been formed by microbial precipitation (Newman et al., 1998).

Although often present in ore deposits, arsenopyrite is much less abundant than As-rich pyrite, $Fe(S,As)_2$ which is probably the most important source of As in ore zones (Nordstrom, 2000). Though not a major component, arsenic is also often present in varying concentrations in other rock-forming minerals. As the chemistry of As follows closely that of S, the greatest concentrations of the element tend to occur in sulphide minerals, of which pyrite is the most abundant. Pyrite is not stable in aerobic systems and oxidises to Fe oxides with the release of large amounts of SO_4, acidity and associated trace constituents, including As. High As concentrations are also found in many oxide minerals and hydrous metal oxides, either as part of the mineral structure or as sorbed species. Arsenic concentrations in phosphate minerals are variable but can also reach high values. However, phosphate minerals are much less abundant than oxide minerals. Most common silicate and carbonate minerals contain little As (Smedley and Kinniburgh, 2002).

2.4.5 Arsenic in impregnated wood

Releases to the environment from production of impregnated wood can result in a considerable contamination of soil, especially in relation to old plants. The arsenic compound which has been used in impregnation fluid is primarily arsenic pentoxide (As_2O_5), which is easily dissolved in water (65.8 g/l). Another way of impregnating wood is by pressure treatment with chromated copper arsenate (CCA). An estimate on the accumulated amount of preserved wood in Norwegian buildings and installations has been made by the state pollution control (SFT, 1995). The estimate shows that the buildings retained an accumulated amount of 6,000 tonnes of arsenic in 1992. Buildings contain arsenic in joint filler, in glass and in plastic, which leads to an estimate of the total amount of arsenic of 6,750 tonnes in 1992. The annual growth is estimated at 560 tonnes (SFT, 1995).

2.4.6 Arsenic in organisms

The mobility and bioavailability of arsenic depend on both the chemical form of the substance speciation and several factors related to the physical and chemical properties of soil and water such as pH and redox conditions, presence of precipitating, complexing and sorbing agents, mineralogical composition of the soil and grain size. Also climatic, hydrogeological and geomorphological characteristics will influence the mobility and availability of arsenic. Ionic species in the form of oxides and hydroxides interact with organic components such as fulvic and humic acids to form metal-organic complexes which are retained significantly in the soil environment (Swedish National Chemicals Inspectorate, 1998).

Anion formation facilitates the movement of arsenic through soil. Arsenic leached in the pentavalent form is able to form anions such as $H_2AsO_4^-$. This negative charge will prevent interaction with the net negative surface charge of soil particles allowing further movement through the soil at pHs above the point of zero charge (ZPC) (Stumm and Morgan, 1981). The optimum adsorption of As(V) occurs at a pH of about 6 and occurs by the displacement of hydroxyl ions on clay particles (SFT, 1986).

Dissolved trivalent inorganic arsenic is readily absorbed from the gastrointestinal tract. Absorption is approximately 80 – 90 % of a single dose. Bettley and O´Shea (1975) gave 8.5 mg of arsenic as arsenic(III) oxide dissolved in potassium hydroxide, neutralised with hydrochloric acid and diluted with chloroform water, to seven patients in a skin ward. The total amount of arsenic recovered in the faeces over a 10-day period was, at most 3.5% of the total dose implying that by far the major part of the dose was absorbed. In an experiment on himself, Mappes (1977) took a single oral dose of 12 mg of finely powdered arsenic selenide (equal to 4.8 mg As). The urinary level did not increase, indicating that this compound, which is almost insoluble in water or in 0.1 M hydrochloric acid, was poorly absorbed from the gastrointestinal tract. Hair and nails are significant accumulator tissues for arsenic. The arsenic in blood serum, responds to the content of food, especially fish intake (Heydorn, et.al., 1974).

3 Methods

3.1 Sampling and sample preparation

Approximately 120 samples of surface soil were taken by cutting a 20 x 10 cm section of surface soil with a spade. A knife with a steel blade was used to exclude the soil from below 2-3 cm depth. Each sample weighed about 0.5-1 kg. The samples were gathered in paper bags and the material was dried at a temperature of about 35°C for four days. They were afterwards sieved through a 2 mm nylon screen.

3.2 Dissolution - Sequential extraction procedure

3.2.1 Exchangeable fraction

About 2 g of each sample was extracted in 20 ml 1 M $MgCl_2$, in which the pH was adjusted to 7.0 with HNO_3, in borosilicate centrifuge tubes. Samples were placed into a shaker filled with water at a temperature of 37 °C. The samples were shaken at 120 rpm.

After twenty hours the samples were centrifuged at 4500 rpm for twenty minutes. The supernatant liquid was removed and the remaining soil washed with distilled water and centrifuged for another 20 minutes at 4500 rpm. The supernatant liquid was removed and added to the first extract. Distilled water was used to get a total volume of 50 ml. The liquid was stored in polyethylene bottles before analysis.

3.2.2 Bound to carbonates

At the second part of the sequential extraction procedure, 20 ml 1 M NaAc in which the pH was adjusted to 5.0 with HAc, was added to the remaining soil from the first step. Samples were shaken for 20 hours at 120 rpm at a temperature of 37 °C. After this, the samples were centrifuged and washed following the procedure used on the exchangeable fraction.

3.2.3 Bound to reducible substrates

To the residue from the second stage a 20 ml 0.04 M $NH_2OH \cdot HCl$ in 25% HAc solution was added. Samples were shaken for 20 hours at 60 rpm at a temperature of 85 °C. After this, the samples were centrifuged and washed following the procedure used on the exchangeable fraction.

3.2.4 Bound to organic compounds

At the fourth stage of the sequential extraction procedure, 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 adjusted to pH 2.0 with HNO_3 was added to the residue from the third stage. Samples were shaken at 60 rpm at a temperature of 85 °C. After 2 hours another aliquot of 3 ml 30% H_2O_2 was added to the samples. This mixture was shaken for another 3 hours. After cooling 5 ml 3.2 M NH_4Ac in 20% HNO_3 and 4 ml of distilled water was added. The samples were agitated continuously for 14 hours. The addition of NH_4Ac is to prevent adsorption of the extracted metals onto the oxidised sediment. After this, the samples were centrifuged and washed following the procedure used on the exchangeable fraction.

3.2.5 Residual fraction

Finally, 20 ml concentrated HNO_3 was added to the residue from the fourth stage. Samples were shaken at 60 rpm at a temperature of 85°C for 20 hours. After this the mixture was filtered and diluted to 50 ml with distilled water.

The extractions were carried out in centrifuge tubes to prevent loss of solid material. From the extracts of the fourth and fifth stages, 10 ml was taken and evaporated. The non-evaporable residue was dissolved in 10 ml 0.1 M HNO_3.

3.3 Dissolution - Total concentration procedure.

In addition to the sequential extraction procedure, samples were extracted in concentrated HNO_3. About 2 g of each sample was extracted in 20 ml 65% HNO_3 in Erlenmeyer flasks. To prevent evaporation of the liquid a watchglass was placed on top of the flasks. Samples were heated at a temperature of 85°C for 20 hours. After this the mixture was filtered and diluted to 50 ml with distilled water. From this solution, 10 ml was taken and evaporated. The non-evaporable residue was dissolved in 10 ml 0.1 M HNO_3 and stored in polyethylene bottles before analysing.

About 20 samples were extracted in one turn. In addition to this, 3 reagent blanks, containing all reagents but no soil, underwent the same procedure.

3.4 Atomic Absorption Spectrometry

3.4.1 Graphite furnace (As)

A Perkin Elmer AAnalyst 600 was used for analysing the samples. Arsenic was determined with an Electrodeless Discharge Lamp (EDL-2). Calibration of the instrument was done by one standard solution of about 175 ppb, which was made by diluting a 500 ppm solution with the respective reagents. The ashing temperature was 1400 °C and the atomisation temperature was 2300 °C. Every sample was analysed three times. Samples were analysed until the relative standard deviation was less than 5%. This was a problem in samples with very low concentrations (<10 µg/l in solution, <250 µg/l in soil), especially the samples of stages 1 and 2. These samples were reanalysed a maximum of three times. Samples with concentrations outside the calibration range were diluted by the instrument. When the concentration was too high after dilution by the instrument, samples were diluted by hand. Arsenic is quite volatile, so to prevent loss of arsenic a 0.3% Pd, 0.1 M HNO_3 modifier was used. Recovery was measured on each seventh sample. These were used to control the quality of the analysis. The instrument was recalibrated after seven samples.

3.4.2 Graphite furnace (Cd)

A GBC Avanta Σ was used for analysing the samples. The total acid soluble concentration of Cd was determined with a hollow cathode lamp. Calibrating of the instrument was done by one standard solution of about 6 ppb, which was made by diluting a 1000 ppm solution with 0.1 M HNO_3. The ashing temperature was 350 °C and the atomisation temperature was 1800 °C. Every sample was analysed three times. Samples were analysed until the relative standard deviation was less than 5%. Samples with concentrations outside the calibration range were diluted by the instrument. When the concentration was too high after dilution by the instrument, samples were diluted by hand. A sample check of the standard solution was performed on each seventh sample. These were used to control the quality of the analysis. The instrument was recalibrated if the concentration of the sample check was outside the range of 90-110% of the expected value.

3.4.3 Flame

A GBC Avanta Σ was used for analysing the samples. The total acid soluble concentration of Cr, Cu, Ni, Pb and Zn were determined with hollow cathode lamps. Calibrating of the instrument was done by five standard solutions of about appropriate concentration, which were made by diluting a 1000 ppm solution 6.0 M HNO_3. The flame type used for the determination of Cr was N_2O-Acetylene. Air-Acetylene was used for the other elements. Each sample was analysed three times. Samples were analysed until the relative standard deviation was less than 5%. Samples with concentrations outside the calibration range were diluted by hand.

3.5 Reproducibility of laboratory work

3.5.1 Total acid soluble concentration

To get a measurement on the reproducibility of the laboratory work, duplicate samples were analysed. The total acid soluble concentration in 18 samples was determined twice. The total acid soluble concentration of As, Cd, Cr, Cu, Ni, Pb and Zn was determined in these samples. Scatterplots of the results are presented in Figure 1. Correlation coefficients for all elements were good ($r=0.96$ for Cd, $r=0.99$ for As and Ni, $r=1.00$ for Cr, Cu, Pb and Zn) with a significant level of 0.01.

In the sequential extraction procedure five samples were analysed twice. Scatterplots of the results are presented in Figure 2. Correlation coefficients of fractions 1 ($r=1.00$), 3 ($r=0.97$), 4 ($r=0.99$) and 5 ($r=1.00$) were good with a significance level of 0.01. The major part of the arsenic content of the soil is extracted in stages 3-5. The correlation coefficient of fraction 2 is

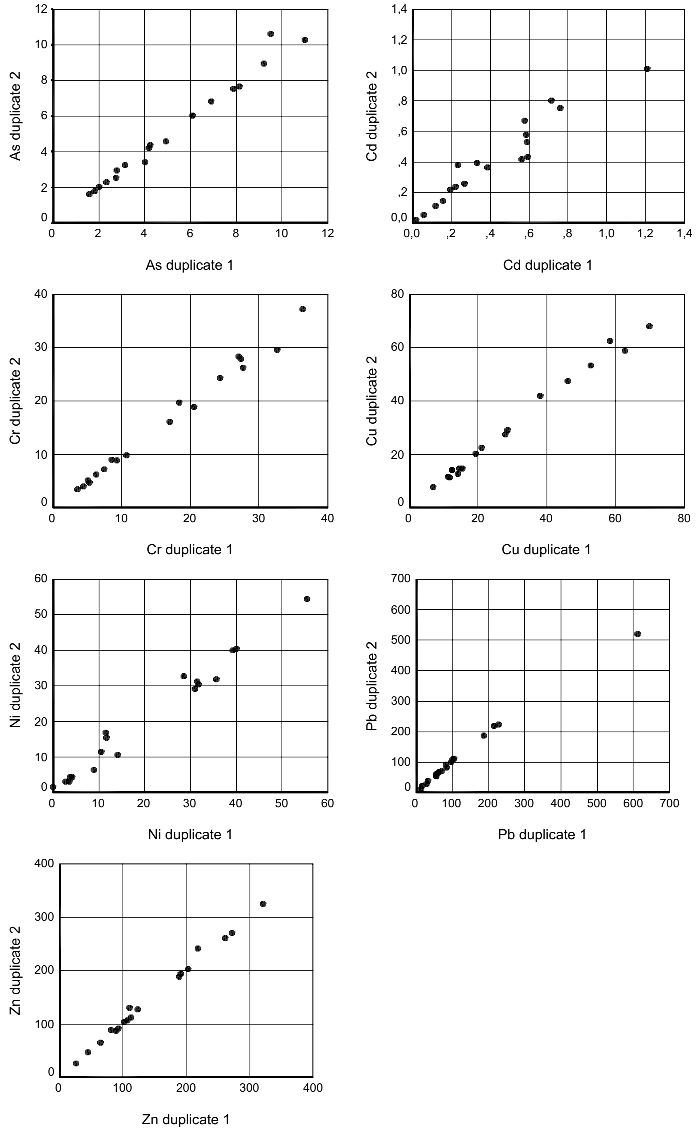

Figure 1: Scatterplots of duplicate samples of the total acid soluble concentration (n=18).

0.41. The concentrations in these samples in this fraction are near the detection limit of the analysis.

3.5.2 Sequential extraction

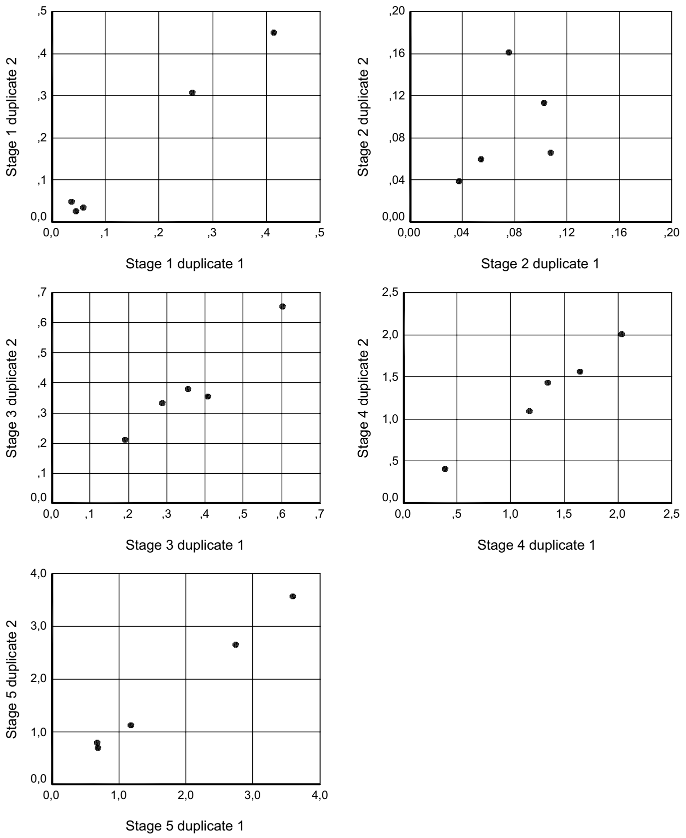

Figure 2: Scatterplots of duplicate samples of the sequential extraction procedure stages (n=5).

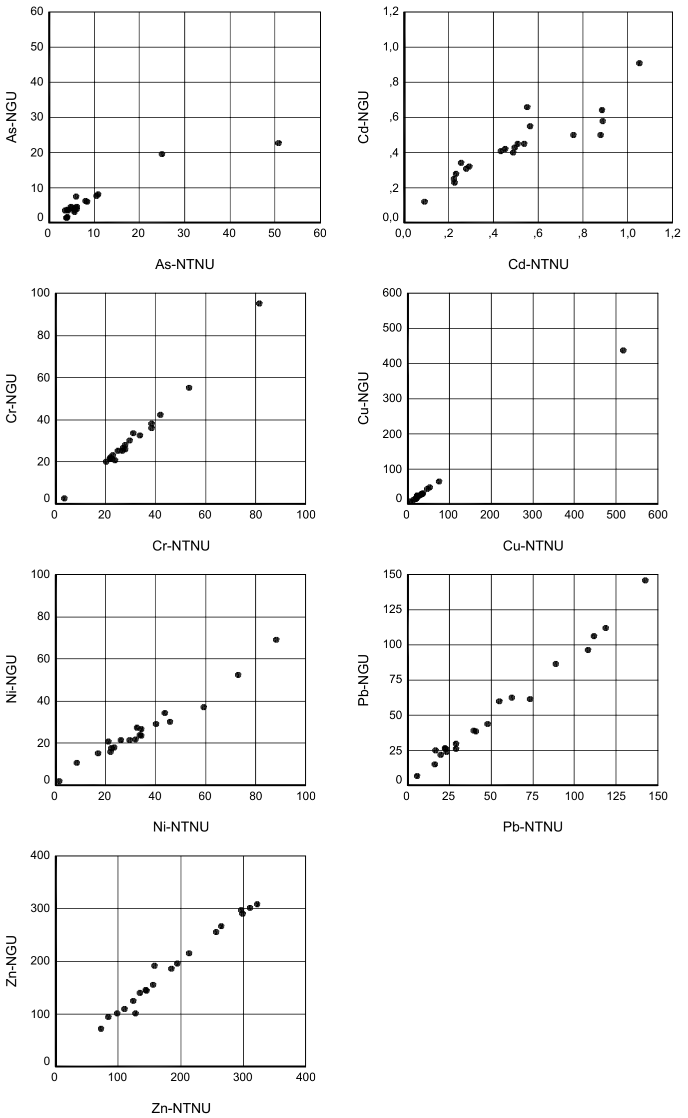

Figure 3: Scatterplots of the analysis by the laboratories of NGU and NTNU (n=20).

3.6 Reference material

To get a measurement on the precision of the analyses, 20 samples of topsoil from Oslo, taken in the summer of 1998 and analysed at the Geological Survey of Norway (NGU, 1998), were extracted and used as reference material. The total acid soluble concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn were determined in these samples. The results are presented in scatterplots (Figure 3). Table 2 shows the correlation coefficients for the different elements. All correlation coefficients are significant at the 0.01 level. Correlation coefficients of the elements determined with the graphite furnace are somewhat lower than those determined by the flame technique.

Table 2: Correlation coefficients of the analysis by the laboratories of NGU and NTNU.

Element	Correlation coefficient (n = 20)
Arsenic	0.93 (0.84 without 2 extreme values)
Cadmium	0.90
Chromium	0.99
Copper	1.00 (0.99 without extreme value)
Nickel	0.98
Lead	0.99
Zinc	0.99

4 Results and Discussion

4.1 Total acid soluble concentrations in soil and sandpit samples at 24 kindergartens.

Results of the total acid soluble concentrations of 7 elements in soil and sandpit samples of 24 kindergartens in the central districts of Oslo, some descriptive statistics and Norm values for contaminated soil used by the Norwegian authorities (SFT, 1999) are listed in Table 3. Figure 4 shows the distribution of these elements as boxplots. A factor analysis of total acid soluble concentration in soil and sandpit samples of kindergartens in the central districts of Oslo is presented in Table 4.

Correlation coefficients between soil and sandbox samples for each element are low. In general, total acid soluble concentrations of soil samples are higher than in samples of sandboxes. The differences in arsenic concentrations between soil and sandbox samples are small compared to the other elements. The arsenic concentrations in all soil samples exceed the Norm value for polluted soil used by the Norwegian authorities. Regarding arsenic in sandbox samples, the total acid soluble concentrations of 15 out of 24 samples (63%) exceed the Norm value. For the other elements, none of the sandbox samples contains more than the Norm value. At 13 of 24 kindergartens (54%), concentrations in soil samples of at least one of the elements Cr, Cu, Ni, Pb and Zn, exceed the Norm value used by the Norwegian authorities. The situation is worst in the kindergartens at Håkonsgate and Kampen skole at which all elements, except Cd, exceed the Norm value for polluted soil.

To describe the covariant relationships among the elements, a factor analysis has been completed on both soil and sand samples (Table 4). For soil samples, the factor analysis extracted only one component explaining 83% of the total variance. This indicates that the major part of the total variance is explained by only one factor. Sources behind this factor might be natural, but since these elements are rare in geologic material in urban areas, and concentrations in the soil samples are relatively high, anthropogenic sources probably have a large effect on the concentrations of these elements.

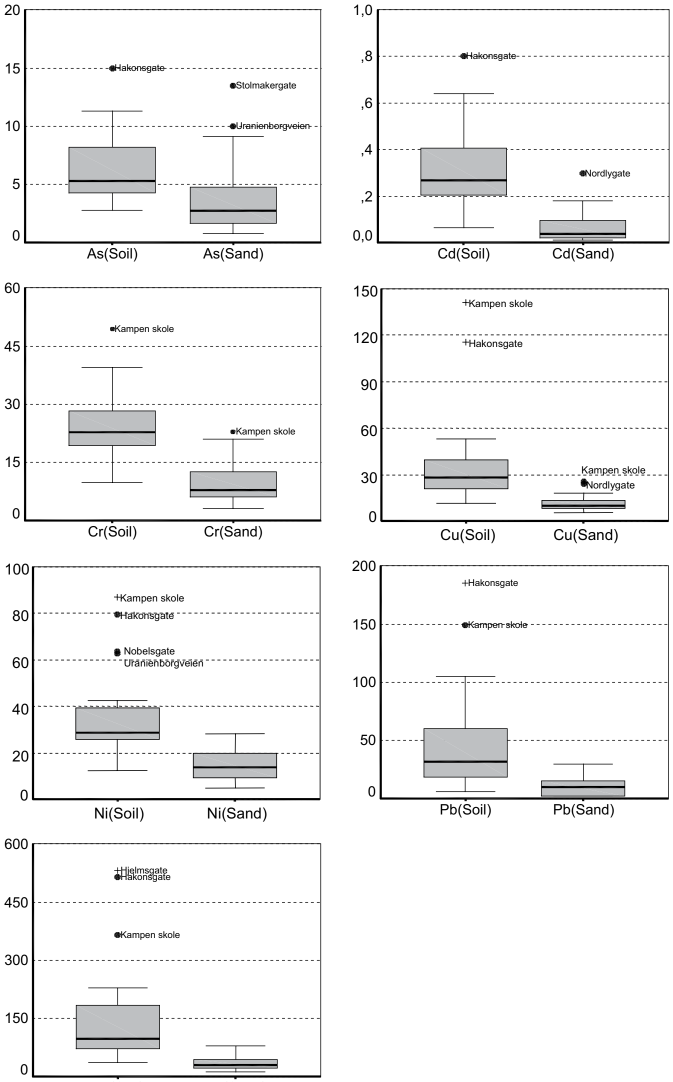

Figure 4. Boxplots of the total acid soluble concentrations (mg/kg) of selected elements in soil and sandpit samples of kindergartens in the central districts of Oslo.

Table 3: Total acid soluble concentrations (mg/kg), some descriptive statistics and Norwegian Norm values for polluted soil of selected elements in soil and sandpit samples of kindergartens in the central districts of Oslo.

Address	Arsenic		Cadmium		Chromium		Copper		Nickel		Lead		Zinc	
	soil	sand	soil	sand	soil	sand	soil	sand	soil	sand	soil	Sand	Soil	sand
Jordalgate	4.47	.791	.267	.020	18.2	4.33	26.7	9.77	26.3	10.9	25.0	<4.4	67.4	12.7
Åkeberggate	8.71	9.15	.468	.108	29.7	16.9	51.9	18.2	38.8	21.3	78.2	17.8	224	44.7
Håkonsgate	14.9	3.41	.802	.077	39.5	21.1	115	13.3	79.4	16.9	185	12.4	515	46.9
Kampen skole	10.2	7.81	.640	.083	49.4	22.9	141	25.7	87.1	28.3	149	23.1	366	42.9
Opplandgate	4.11	2.03	.252	.057	18.7	8.84	21.0	11.4	26.1	11.0	10.2	29.9	65.2	45.8
Enebakkveien	3.25	1.83	.134	.021	14.8	5.52	16.8	7.45	19.3	7.58	25.8	<4.4	75.4	19.3
Jens Bjelkesgt.	3.48	3.48	.213	.040	24.0	14.8	35.4	8.98	26.3	21.0	24.4	<4.4	88.4	31.1
Sørligate	6.00	7.92	.206	.115	20.9	6.30	28.2	15.0	25.4	14.2	39.4	11.7	83.1	64.6
Nordlygate	7.71	4.32	.491	.298	27.7	13.9	52.9	24.1	40.3	24.5	105	<4.4	230	79.7
Stolmakergate	4.80	13.5	.286	.013	20.1	5.99	21.2	6.75	28.1	4.83	6.01	21.7	152	20.4
Sofienberggate	4.62	3.79	.202	.037	29.0	9.92	20.6	7.77	42.4	17.0	15.0	16.3	96.9	27.0
Nedre gate	2.77	2.17	.134	.015	10.5	7.83	12.2	8.81	16.0	7.97	20.5	<4.4	47.5	22.1
Torgbakk gate	5.38	1.89	.217	.047	20.2	7.79	25.7	9.33	31.9	14.8	16.9	11.6	98.9	31.6
Sporveisgate	4.71	4.34	.273	.179	16.7	11.3	22.3	14.6	28.7	22.5	40.8	9.94	71.6	47.7
Uranienb. Sk.	5.45	1.20	.067	.032	9.87	6.86	11.4	12.0	12.3	11.8	20.1	8.97	38.2	34.1
Vestkant torvet	5.71	3.26	.417	.125	26.4	9.69	31.3	9.28	30.1	18.8	47.2	<4.4	105	40.4
Frogner	5.22	1.78	.396	.014	26.9	5.18	35.3	5.68	22.8	6.03	50.3	7.68	171	22.4
Prof. Dahlsgt.	3.57	2.22	.111	.030	26.8	5.31	17.7	11.4	30.2	11.5	17.3	11.0	71.9	20.0
Hjelmsgate	9.40	5.27	.494	.180	23.9	14.6	40.0	14.1	28.9	22.0	66.6	14.3	532	47.8
Uranienborgv.	11.2	9.98	.375	.053	34.9	8.09	44.0	13.0	62.8	13.5	88.8	13.7	193	35.5
Oscarsgate	5.63	1.60	.220	.020	21.3	9.07	28.1	7.44	28.5	7.70	53.5	18.9	162	25.6
Nobelsgate	11.3	1.57	.271	.024	36.3	7.51	38.9	7.84	63.5	14.5	38.5	<4.4	174	22.7
Gabelsgate	4.46	1.57	.277	.028	21.7	3.16	31.7	9.79	36.5	8.20	25.0	<4.4	84.7	22.5
Drammensv.	4.14	1.37	.141	.012	20.1	6.32	20.9	10.1	22.5	10.5	11.9	8.57	67.7	19.8
Minimum	2.77	.791	.067	.012	9.87	3.16	11.4	5.68	12.3	4.83	6.01	<4.4	38.2	12.7
Maximum	14.9	13.5	.802	.298	49.4	22.9	141	25.7	87.1	28.3	185	29.9	532	79.7
Median	5.30	2.74	.269	.039	22.8	7.96	28.2	10.0	28.8	13.9	32.1	10.5	97.9	31.4
Mean	6.30	4.01	.306	.068	24.5	9.72	37.1	11.7	35.6	14.5	48.4	10.6	158	34.5
Norm value	2		3		25		100		50		60		100	
No. exceeding	24	15			10		2		4		6		11	

For the sandpit samples, the factor analysis extracted two components. Factor 1 contains, listed in decreasing order of factor loadings, the elements Ni, Cu, Cd, Zn and Cr. Concentrations of these elements in samples from sandboxes are relatively low. Sources behind this factor are therefore probably natural, although anthropogenic sources might have some influence on the metal concentrations of these elements. Factor 2 contains the elements Pb, As, Cr and Cu. The major part of the sandpit material are light minerals like quartz and feldspars in which these elements are minor constituents. Arsenic concentrations in these samples are relatively high. Beside natural sources, leakage of these elements from impregnated and painted wood is probably the main source for the elements in the second factor, since samples are taken in the near surroundings of this kind of material. Pressure treatment with CCA (Chromated Copper Arsenate) is often used for this purpose.

Table 4. Factor analyses of total acid soluble concentration in topsoil and sandpit samples of kindergartens in the central districts of Oslo.

Soil				Sand			
Structure matrix		Factor		Structure matrix		Factor	
Element	Communality	1		Element	Communality	1	2
Lead	0.89	0.94		Nickel	0.82	0.91	0.19
Copper	0.88	0.94		Copper	0.81	0.89	0.34
Cadmium	0.86	0.93		Cadmium	0.83	0.89	0.03
Nickel	0.82	0.91		Zinc	0.79	0.89	0.23
Arsenic	0.82	0.91		Chromium	0.65	0.77	0.44
Chromium	0.79	0.89		Lead	0.81	0.13	0.89
Zinc	0.74	0.86		Arsenic	0.65	0.34	0.80
Variance explained (%)		82.8		Variance explained (%)		57.1	76.6

Extraction method: Principal Component Analysis.
Rotation method (sand): Oblique with Kaiser Normalisation

4.2 Sequential extraction of arsenic in soil and sandpit samples at 24 kindergartens.

The results of sequential extraction of arsenic in soil and sandpit samples of 24 kindergartens in the central districts of Oslo are listed in Table 5. Boxplots of the results of the sequential extraction are shown in Figure 5.

The recovery percentage (total sequential extraction/total acid soluble concentration) is rather good. For the soil samples the range of 23 out of 24 samples is 82-119% of the total acid soluble concentration. In the soil sample from Vestkanttorvet the recovery is 140%. In this sample the concentration in the residual fraction is of the same size as the total acid soluble concentration. The recovery range of 22 sandbox samples is 75-116%. At Jordalgate the recovery is 136%, but the low concentration in this sample, the lowest of all samples, can have caused this rather large difference. At Nordlygate the recovery is 140%. As for the soil sample at Vestkanttorvet, the arsenic concentration in the residual fraction of this sample is of the same size as the total acid soluble concentration. Inhomogeneity of the samples or random errors might have caused the differences in these samples.

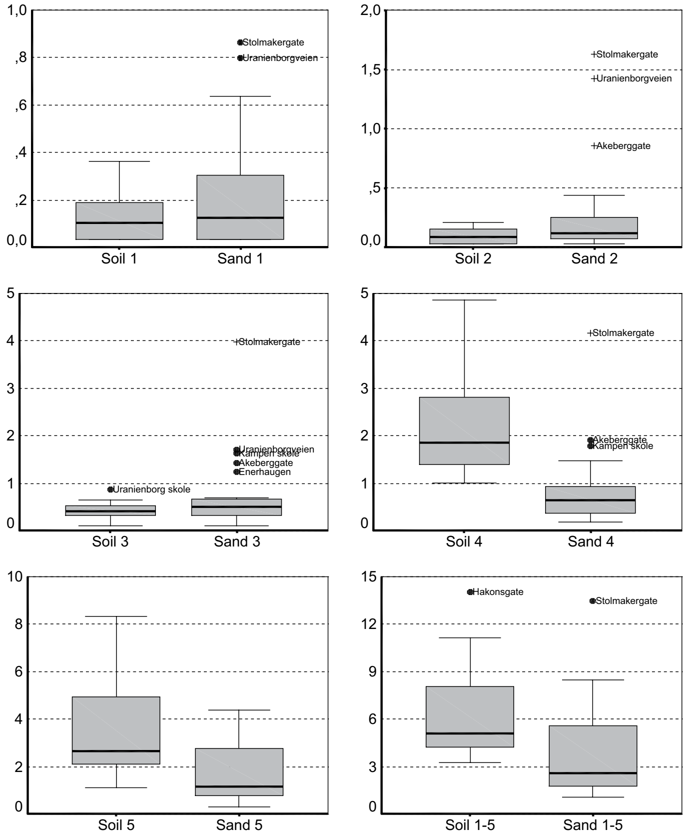

Figure 5. Boxplots of the arsenic concentrations (mg/kg) in 5 different fractions and the total concentration in samples of soil and sandboxes in kindergartens in the central districts of oslo.

In the exchangeable, the carbonate and the reducible substrate fractions, arsenic concentrations in the sandbox samples lie at a higher level than concentrations in soil samples taken at the same kindergarten. All sandbox samples are taken near playing equipment made of impregnated or painted wood. Leakage of arsenic compounds from this material has probably caused elevated concentrations of this element. In the organic fractions, only one kindergarten has a higher concentration in the sandbox sample than in the soil sample. Sandbox samples contain little organic material and

Table 5. Arsenic concentrations (mg/kg) in 5 fractions after sequential extraction, the total concentration in these 5 fractions and the total acid soluble concentration of soil and sandpit samples of 24 kindergartens in the central districts of Oslo.

	Exchange-able fraction		Bound to carbonates		Bound to reducible substrates		Bound to organic compounds		Residual fraction		Total sequential extraction		Total acid soluble conc.	
Address	soil	sand	soil	sand	soil	sand	soil	sand	soil	sand	soil	sand	soil	Sand
Jordalgate	.281	.283	<.060	.072	.374	.106	1.26	.315	2.78	.302	4.72	1.08	4.47	.791
Åkeberggate	<.068	.323	<.060	.855	.446	1.43	2.98	1.90	5.07	3.98	8.59	8.50	8.71	9.15
Håkonsgate	<.068	.332	.212	.122	.622	.632	4.86	.897	8.33	1.60	14.0	3.58	14.9	3.41
Kampen sk.	<.068	.138	.190	.383	.447	1.63	2.94	1.78	7.34	3.73	10.9	7.66	10.2	7.81
Opplandgate	.084	.098	<.060	<.060	.246	.560	1.02	.635	2.06	.869	3.40	2.21	4.11	2.03
Enebakkv.	.148	<.068	.077	.189	.297	.482	1.39	.461	1.68	.860	3.60	2.03	3.25	1.83
Jens Bjelkesg	<.068	<.068	<.060	.071	.312	.692	1.24	.841	2.14	1.76	3.79	3.38	3.48	3.48
Sørligate	.201	.638	.144	.441	.564	1.24	2.21	1.48	2.10	2.71	5.21	6.51	6.00	7.92
Nordlygate	.123	<.068	.162	.111	.594	.576	3.11	.954	3.23	4.37	7.21	6.05	7.71	4.32
Stolmakergt.	<.068	.863	.077	1.63	.281	3.97	1.49	4.15	2.30	2.85	4.15	13.5	4.80	13.5
Sofienberggt.	.121	<.068	.135	.149	.316	.513	1.84	.678	2.84	1.65	5.26	3.05	4.62	3.79
Nedre gate	<.068	<.068	.073	.123	.595	.498	1.40	.311	1.12	.878	3.25	1.81	2.77	2.17
Torgbakkgt.	.155	.148	.128	<.060	.326	.279	1.09	.372	3.16	.959	4.86	1.77	5.38	1.89
Sporveisgt.	.177	.211	.088	.083	.481	.420	1.87	.655	2.44	3.00	5.06	4.37	4.71	4.34
Uranienb. sk.	.306	.077	.184	.062	.877	.225	1.97	.183	1.78	.596	5.11	1.14	5.45	1.20
Vestkanttorv	<.068	.343	<.060	.317	.420	.331	1.62	.326	5.87	1.38	8.00	2.70	5.71	3.26
Frogner	.363	.092	.106	.185	.341	.437	2.00	.389	1.47	.665	4.28	1.77	5.22	1.78
Prof. Dahlsgt	.069	.179	<.060	<.060	.323	.501	1.29	.764	2.52	.968	4.23	2.45	3.57	2.22
Hjelmsgate	.348	.179	.186	.164	.110	.655	2.67	.881	4.83	3.23	8.14	5.11	9.40	5.27
Uranienb.v.	.296	.798	.133	1.42	.472	1.70	3.75	1.03	5.06	2.51	9.72	7.46	11.2	9.98
Oscarsgate	.092	<.068	<.060	.118	.413	.366	2.23	.400	3.22	.732	6.01	1.66	5.63	1.60
Nobelsgate	.069	.115	.167	.064	.659	.329	3.26	.507	6.99	.808	11.1	1.82	11.3	1.57
Gabelsgate	<.068	.106	.096	.117	.345	.323	1.40	.385	2.54	.687	4.42	1.62	4.46	1.57
Drammensv.	.117	<.068	<.060	.190	.404	.277	1.57	.311	2.37	.618	4.51	1.44	4.14	1.37
Minimum	<.068	<.068	<.060	<.060	.110	.106	1.02	.183	1.12	.302	3.25	1.08	2.77	.791
Maximum	.363	.863	.212	1.63	.877	3.97	4.86	4.15	8.33	4.37	14.0	13.5	14.9	13.5
Median	.152	.179	.134	.149	.408	.500	1.86	.645	2.66	1.17	5.09	2.57	5.30	2.74
Mean	.185	.290	.135	.327	.428	.758	2.10	.859	3.47	1.74	6.24	3.86	6.30	4.01

the main minerals in these samples are light minerals like quartz and feldspar. This may explain the lower concentrations in the sandbox samples in the organic fraction. In the residual fraction, only four kindergartens have arsenic concentrations that are higher in the sandbox sample than the concentration in the soil. This can also be explained by the fact that the main constituents of sandbox sand are quartz and feldspar in which the natural content of arsenic is low. Despite the fact that concentrations in sand are lower than in soil, 15 of 24 sandbox samples contain more arsenic than the Norm value for polluted soil used by the Norwegian authorities. At five kindergartens, cumulative concentrations of the first four stages exceed this Norm value. The conditions in the forth stage of the extraction procedure are quite comparable with the conditions in stomach acid (Wallace et al., 1990). The cumulative concentrations of arsenic in the first four stages can therefore be a measure of the bio-availability of the element to children.

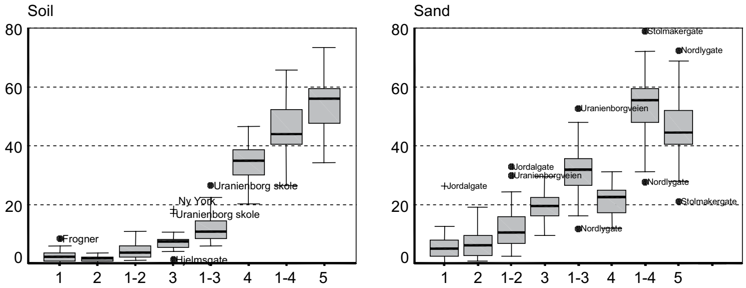

Figure 6. Boxplots of arsenic concentrations of each stage of the sequential extraction procedure presented as percentages of the total concentration. Boxplots 1-2, 1-3 and 1-4 are cumulative concentrations presented as percentages of the total concentration.

Figure 6 shows the boxplots of arsenic concentrations of each stage of the sequential extraction procedure presented as percentages of the total concentration. Cumulative concentrations are also plotted in this figure. In soil samples, arsenic concentrations in the first three stages lie in the range of 6-27% of the total concentration. The corresponding range of the sandbox samples is 12-53%. This indicates that the arsenic in sandbox samples, although generally lower in concentration, is less bound to the material than the arsenic in soil samples. Of the five sandbox samples containing most arsenic, 28-53% of the total concentration is extracted in the first 3 stages and 51-79% in the first 4 stages. For the five soil samples with the highest concentrations of arsenic the corresponding ranges are 6-9% and 33-48%.

Since the arsenic in sand from sandboxes, although generally lower in concentration, is less bound to the material than in the soil, it is more hazardous for children to play in sandboxes. The arsenic in the sand from the sandboxes is more easily released from this sand in the gastrointestinal tract, with its low pH, than the arsenic from the soil.

4.3 Sequential extraction of arsenic in all soil samples.

Boxplots of arsenic concentrations in all extraction stages and cumulative concentrations, calculated as percentages of the total concentration, are shown in Figure 7. Descriptive statistics are listed in Table 6.

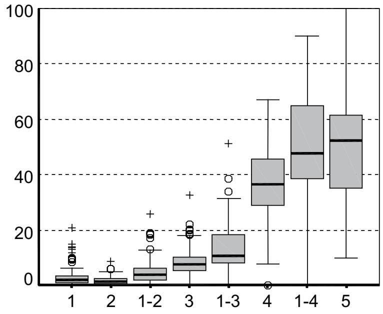

Figure 7. Boxplots of arsenic concentrations in 98 soil samples of each stage of the sequential extraction procedure presented as percentages of the total concentration. Boxplots 1-2, 1-3 and 1-4 are cumulative concentrations presented as percentages of the total concentration.

These figures show that 0-51% of the total arsenic is extractable in the exchangeable, the carbonate and the reducible substrates fractions. The 90-percentile of this range is 27%. This means that in 90% of the samples, the extractable arsenic in the first three fractions is 0-27% of the total arsenic in these samples. If the organic fraction is included, 0-90% of the arsenic is extractable in the first four fractions. In 90% of the samples, the extractable arsenic in the first four fractions is 0-27% of the total arsenic in these samples. For the majority of the samples (25-75 percentile) this range is 39-65%. The 25-75 percentile range for the residual fraction is 35-61%.

Of 98 samples only 2 samples exceed the Norwegian Norm value of 2 mg/kg As after the first three extraction stages. The total acid soluble concentration in these samples is about 10 mg/kg. After four stages the number of samples exceeding the Norwegian Norm value is 68.

Table 6: Percentiles of arsenic content in different fractions (in mg/kg and in % of the total concentration), cumulative content (in mg/kg and in % of the total concentration), total acid soluble concentration (in mg/kg) and recovery percentage (Total sequential extraction/Total acid soluble) in topsoil samples from Oslo, Norway.

	Exchangeable fraction		Bound to carbonates		1+2		Bound to reducible substrates		1-3	
	mg/kg	% of total	mg/kg	% of total	mg/kg	% of total	mg/kg	% of total	mg/kg	% of total
min.	<0.068	0	<0.060	0	0.041	0	0.110	0	0.277	0
5 %	<0.068	0	<0.060	0	0.076	1	0.216	3	0.348	4
10 %	<0.068	0	<0.060	0	0.084	1	0.262	3	0.381	5
25 %	<0.068	1	<0.060	1	0.107	2	0.304	5	0.468	8
50 %	0.116	2	0.082	2	0.218	4	0.367	8	0.600	11
75 %	0.203	4	0.125	2	0.318	6	0.504	10	0.809	18
90 %	0.316	9	0.185	4	0.439	11	0.676	17	1.03	27
95 %	0.355	12	0.205	5	0.521	14	0.882	18	1.40	30
max.	0.617	21	0.917	9	1.08	26	1.81	33	2.39	51

	Bound to organic compounds		1-4		Residual fraction		1-5	Total acid soluble	Recovery
	mg/kg	% of total	mg/kg	% of total	mg/kg	% of total	mg/kg	mg/kg	%
Min.	0.550	0	0.977	0	0.242	10	1.69	1.81	71
5 %	0.922	15	1.42	18	0.499	16	2.53	2.64	82
10 %	1.08	22	1.57	32	0.684	20	3.03	2.87	83
25 %	1.39	29	1.86	39	1.44	35	3.79	3.58	87
50 %	1.76	37	2.42	48	2.69	53	5.15	5.33	96
75 %	2.56	45	3.37	65	3.90	61	7.60	7.90	108
90 %	3.99	56	4.89	80	7.38	68	11.0	11.6	116
95 %	5.18	60	6.85	84	13.7	82	18.6	19.4	121
Max.	8.86	67	9.99	90	1050	100	1050	1120	220

The total concentration seems to have little effect on the concentrations in the first two extracted fractions. Concentrations below detection limit in the fractions are found in samples at all total concentration levels. Also concentrations in the reducible substrate fraction seem to be independent of the total concentration. Concentrations in the organic and residual fractions seem to be dependent of the total concentration. Concentrations in these fractions are generally higher in samples with high arsenic content. At low total concentrations the arsenic content in the organic fraction is generally higher than the arsenic content in the residual fraction. At intermediate and high total arsenic concentrations, concentrations in the residual fraction are generally higher than concentrations in the organic fraction.

5 Summary and Conclusions

5.1 Total acid soluble concentrations in soil and sandpit samples at 24 kindergartens.

With a few exceptions, total acid soluble concentrations of As, Cd, Cr, Cu. Ni. Pb and Zn in soil samples are higher than in samples of sandboxes. The differences in arsenic concentrations between soil and sandbox samples are small. In all soil samples the concentrations of arsenic exceed the Norm value for polluted soil. Regarding sandbox samples, the total acid soluble concentrations of 15 out of 24 samples (63%) exceed this value. For the other elements, none of the sandbox samples contains more than the Norm value. Regarding soil samples, at 13 of 24 kindergartens (54%), concentrations of at least one of the elements Cr, Cu, Ni, Pb and Zn, exceed the Norm value used by the Norwegian authorities. The situation is worst at two kindergartens at which all elements, except Cd, exceed the Norm value for polluted soil.

Since the investigated elements are rare in geologic material in urban areas, and concentrations in the soil samples are relatively high, anthropogenic sources probably have a large effect on the concentrations of these elements in the soil. For the sandpit samples, concentrations of all elements, except arsenic, are relatively low. Sources are therefore probably natural, although anthropogenic sources might have some influence on the metal concentrations of As, Cr, Cu and Pb. The major part of the sandpit material are light minerals like quartz and feldspars in which the investigated elements are minor constituents. Arsenic concentrations in these sandbox samples are relatively high. Leakage of arsenic from impregnated and painted wood is probably important.

5.2 Sequential extraction of arsenic in soil and sandpit samples at 24 kindergartens.

In the exchangeable, carbonate and reducible substrate fractions, arsenic concentrations in the sandbox samples lie at a higher level than concentrations in soil samples taken at the same kindergarten. Leakage of arsenic compounds from impregnated and painted wood have probably caused elevated concentrations of this element.

In the organic fractions, only one kindergarten has a higher concentration in the sandbox sample than in the soil sample. Sandbox samples contain little organic material and the main minerals in these samples are light minerals like quartz and feldspar. This may explain the lower concentrations in the sandbox samples in this fraction.

In the residual fraction, only four kindergartens arsenic concentrations are higher in the sandbox sample than the concentration in the soil. Also this can be explained by the fact that the main constituents of sandbox sand are quartz and feldspars in which the natural content of arsenic is low. Despite the fact that concentrations in sand are lower than in soil, 15 of 24 sandbox samples contain more arsenic than the Norm value for polluted soil.

In sandbox samples, the percentage of the total arsenic concentration, extracted in the first four stages is larger than in soil samples. This indicates that the arsenic in sandbox samples, although generally lower in concentration, is less bound to the material than the arsenic in soil samples. It is therefore more hazardous for children to play in sandboxes. The arsenic in the sand is more easily released in the gastrointestinal tract, with its low pH, than the arsenic from the soil.

5.3 Sequential extraction of arsenic in all soil samples.

Up to 50% of the arsenic is extractable in the exchangeable, carbonate and reducible substrates fractions. In only two samples the cumulative concentrations in these three stages exceed the Norwegian Norm value of 2 mg/kg As. After four stages the number of samples exceeding the Norwegian Norm value is 68. Stomach acid is dissolved hydrochloric acid with a pH of 1.6 to 2.4 (Wallace et al., 1990). These conditions are quite comparable with the conditions in stage four of the extraction procedure and the cumulative concentrations of arsenic in the first four stages can therefore be a measure of the bio-availability of the element to human being.

The total concentration seems to have little effect on the concentrations in the first three extracted fractions. In the organic and residual fractions, arsenic concentrations seem to be dependent on the total concentration. Concentrations in these fractions are generally higher in samples with high arsenic content.

At low total concentrations the arsenic content in the organic fraction is generally higher than the arsenic content in the residual fraction. At intermediate and high total arsenic concentrations, concentrations in the residual fraction are generally higher than concentrations in the organic fraction.

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Paper 3:

The Influence of Parent Bedrock Composition on Concentrations of Heavy Metals in Topsoil.

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THE INFLUENCE OF PARENT BEDROCK COMPOSITION ON CONCENTRATIONS OF HEAVY METALS IN TOPSOIL

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Abstract

Most studies dealing with metals in soil systems do not consider the variation of metal concentrations in the parent bedrock material. Analysis of rock material taken in the vicinity of soil samples collected for analysis of trace metals might help to interpret the results. As expansion of a geochemical survey of topsoil in the city of Oslo in Norway (Tijhuis, et al, 2002) based only on soil samples, we wanted to investigate whether the content of trace metals in soil differ much from those of rock samples collected nearby.

Rock and topsoil samples were taken at 44 locations in Oslo, Norway. Acid soluble concentrations of 30 elements in rock samples were measured using ICP/AAS and of seven elements in soil samples using AAS. Ten rock samples were analysed for the bulk concentration of 23 elements using XRF.

At most sites, the bulk concentrations of metals, measured by XRF, in the bedrock samples, are generally higher than the acid soluble concentrations. Differences are small for copper and zinc, somewhat higher for lead and nickel and considerably different for chromium.

Acid soluble chromium concentrations in soil differ little when compared with acid soluble concentrations in bedrock, but are in general much lower than bulk concentrations in rock. Chromium is probably strongly incorporated in the mineral structure of rock samples and concentrated HNO_3 can not get all chromium molecules into solution.

For copper, lead and zinc, the acid soluble concentrations in soil are higher than the bulk concentrations in bedrock. The parent rock material cannot be the only source for these elements in soils and various anthropogenic sources dispersed by air or water probably have major influence.

The bulk concentrations in rock of arsenic and cadmium are not available. However, at many locations, acid soluble concentrations in soil are considerably higher than in rock samples. At these locations, human activities probably have caused these elevated levels in soil.

Analysis of rock samples, both bulk and total acid soluble content, in addition to the sole analysis of soil samples gives a new dimension on interpreting the results of a survey on soil. Geological patterns influencing geographical variations in the material become more clear and this gives a better understanding of processes which might have lead to elevated levels of some of the elements in soil, especially in cases where the total acid soluble concentrations in soil are much higher than the bulk concentrations in rock.

Keywords

Geochemistry, heavy metals, pollution, urban soils, rock

1 Introduction

Over the last few years urban geochemistry, contaminated land and ground water pollution has been given high priority in the European Union. Research on these topics is given high priority. Also in Norway, there has been some research on the geochemistry of urban areas. In the city of Trondheim, situated in central Norway, samples of top soil have been analysed for about thirty elements. The results, presented in the form of geochemical maps are currently being used in city planning (Ottesen et al., 1995, Tijhuis, 1996). Recently, a similar investigation has been carried out in the city of Bergen, south-western Norway (Ottesen & Volden, 1999). A geochemical survey of topsoil in the city of Oslo is currently performed by Tijhuis et al. (2002).

In all these surveys, the metal content in topsoil is presented as the total acid soluble (TAS) concentration. However, little is known about actual concentrations in bedrock formations nearby the locations where soil samples were taken. As some bedrocks have a high metal content, the question arises to what extent the parent bedrock attributes to the metal budget of the soil. In an effort to put constraints on this contribution, the metal content of bedrock samples, bulk as well as TAS, and the TAS content of topsoil samples from the same locality have been determined. The potential of the results in discriminating ‘natural’ contribution from anthropogenic is evaluated.

2 Area description

Oslo, the capital city of Norway, is about a thousand years old. Over the last century the population has increased from a few thousand to 700,000. The city is situated in a geological province, with rocks of Permian age, called the Oslo graben. The graben forms the onland part of the Oslo rift in southeastern Norway, which is part of the Skagerrak-North Sea-Norwegian-Greenland Sea rift system, formed between 305 and 240 Ma (Sundvoll et al. 1990). Based on geological criteria (Berthelsen and Sundvoll, 1996), the populated area can be divided into four parts. The southeastern area is part of the neighbouring Precambrian terrain, the Østfold-Akerhus sector, which largely accreted between 1.75 and 1.55 Ga (Mansfeld and Andersen, 1999). It largely consists of granitic gneisses. The central part of the area is made up by sedimentary rocks from the Cambrian to the Silurian period. The northern part of the investigated area is made up by intrusive rocks of Permian age and comprises quartz syenites and monzodiorites. The north-western part is of Carboniferous and Permian age and comprises volcanic rocks such as basalt and rhomb-porphyry and sedimentary rocks like shale, sandstone and conglomerate (Berthelsen and Sundvoll, 1996).

3 Sampling and analytical methods

3.1 Sampling

Bedrock samples were taken at 44 locations in the northern and western parts of the city of Oslo. The samples comprise syenite and other intrusives, gneiss, hornfels, rhomb-porphyry and sedimentary rocks. At the same locations, samples of topsoil (2-3 cm) were collected. Rock samples were taken of bedrock using a hammer. Rock samples were crushed in the laboratory. Soil samples were taken by cutting a 20 x 10 cm section of surface soil with a spade. A knife was used to exclude the soil from depth below 2-3 cm. Soil samples were taken as close as possible to the rock samples. The weight per sample was about 0.5-1 kg. Samples were gathered in paper bags and the material was dried at a temperature of about 35 ºC for four days. Afterwards the samples were sieved through a 2 mm nylon screen.

3.2 Analysis of rock samples

3.2.1 Total acid soluble metal concentrations

The extraction procedure was performed in accordance with Norwegian Standard - NS 4770 (NSF, 1994). Exactly 1.000 g of ground rock sample was extracted in 20 ml 7 N HNO_3 in borosilicate bottles. Samples rich in carbonate released gas during digestion. This gas was released from the bottles before they were covered with a screw cap. Samples were placed into an autoclave filled with water and heated on a hot-plate. Generated air was lead through the water by a plastic hose until the temperature had reached 96 °C. Then the temperature was raised to 120 °C and kept constant for 30 minutes. The pH of the water was measured to check if leakage from the bottles had occurred. Samples were stored over night, and 24 hours after addition of acid, the samples were filtrated through a fluted filter and diluted with double distilled and ion exchanged water to 100 ml. The elements Cr, Cu, Ni, Pb and Zn were determined by ICP-AES analysis, using a Thermo Jarrell Ash ICP 61 at the Geological Survey of Norway

(NGU), Trondheim. For all these elements the total uncertainty for the extraction and the analysis is estimated to ± 10 rel.%.

Arsenic and cadmium were determined by graphite furnace AAS, using a Perkin Elmer SIMAA 6000 at the NGU. The uncertainty is ± 20 rel.% for arsenic and ± 10 rel.% for cadmium. Control samples were analysed (NGU, 2000).

3.2.2 Bulk composition

Ten rock samples were selected for XRF analysis. These samples are considered as representative for the range of bedrock compositions in the investigated area.

LOI was first determined by the weight loss of adsorbed water by heating 2-3 gram sample powder in a porcelain cup at 120°C overnight (M1). Subsequently, the weight loss was determined of the samples in the same porcelain cup by heating to 900°C in a furnace for 5 hours (M2). The reported LOI values are M2-M1.

The XRF analysis were made using a Philips PW1480 XRF at the department of Geology and Mineral Resources Engineering, NTNU, Trondheim. The rock samples were crushed and subsequently ground in a tungsten-carbide shatter-box to < 200 µm in diameter. Major elements were determined on glass beads, which were made by fusing 0.5000 gram ignited rock powder with 5.0000 gram $LiBO_2/LiB_4O_7$ (66/34). Trace elements were determined on pressed powder pellets. These were made of 8.0 gram sample powder mixed with 2 ml elvacite (1:5 =elvacite: acetone) as a binding agent and pressed under 25 tonne/cm^2 for 2 minutes.

The accuracy, the deviation of the ‘true’ value, as determined on international standards, is generally better than 3% for the major elements and 10% for the trace elements.

3.3 Analysis of soil samples

Soil samples were extracted in concentrated HNO_3 in batches of 20 samples. In addition three reagent blanks were included. About 2 g of each sample was extracted in 20 ml 65% HNO_3 in Erlenmeyer flasks. To prevent evaporation of the liquid a watchglass was placed on top of the flasks. Samples were heated at a temperature of 85°C for 20 hours. After this the mixture was filtered and diluted to 50 ml with distilled water. From this solution, 10 ml was taken and evaporated. The non-evaporable residue was dissolved in 10 ml 0.1 M HNO_3 and stored in polyethylene bottles before analysing.

3.3.1 Graphite furnace AAS

The total acid soluble concentration of arsenic was analysed with a Perkin Elmer AAnalyst 600, equipped with an Electrodeless Discharge Lamp (EDL-2), at the Department of Chemistry, NTNU, Trondheim. A standard solution of about 175 ppb was prepared from a 500 ppm stock solution with 0.1 M HNO_3. Calibration was performed by analysing this standard and two dilutions with ratio 1:2 and 1:4 prepared by the instrument. The ashing temperature was 1400 °C and the atomisation temperature was 2300 °C. Every sample was analysed three times. If the relative standard deviation was more than 5%, samples were re-analysed. Samples with concentrations outside the calibration range were diluted by the instrument. When the concentration was too high after dilution by the instrument, samples were diluted manually. To prevent loss of arsenic a 0.3% Pd, 0.1 M HNO_3 modifier was added. Recovery was measured on each seventh sample. These results were used to control the quality of the analysis. When the results of the recovery measurement were unacceptable, all analyses after the last calibration were rejected. The instrument was recalibrated after seven samples.

The total acid soluble concentrations of cadmium was determined with a GBC Avanta Σ, equipped with a hollow cathode lamp, at the Department of Geology and Mineral Resources Engineerig, NTNU, Trondheim. A standard solution of about 6 ppb was prepared from a 1000 ppm stock solution with 0.1 M HNO_3. Calibration was performed by analysing this standard and two dilutions with ratio 1:2 and 1:4 prepared by the instrument. The ashing temperature was 350 °C and the atomisation temperature was 1800 °C. Every sample was analysed three times. If the relative standard deviation was more than 5%, samples were re-analysed. Samples with concentrations outside the calibration range were diluted by the instrument. When the concentration was too high after dilution by the instrument, samples were diluted manually. A sample check of the standard solution was performed on each seventh sample. These were used tocontrol the quality of the analysis. The instrument was recalibrated if the concentration of the sample check was outside the range of 90-110% of the expected value.

3.3.2 Flame AAS

The total acid soluble concentrations of Cr, Cu, Ni, Pb and Zn were determined with the GBC Avanta Σ instrument using hollow cathode lamps. For all elements, calibration of the instrument was done by analysing five standard solutions of appropriate concentration, which were prepared from a 1000 ppm stock solution with 6.0 M HNO_3. An Air-Acetylene flame was used for all elements except for Cr in which case a N_2O-Acetylene flame was applied. Each sample was analysed three times. If the relative standard deviation was more than 5%, samples were re-analysed. Samples with concentrations outside the calibration range were diluted manually.

4 Results

The results of the soil and rock analyses are presented in Table 1.

Scatterplots of TAS concentrations in rock and soil samples are shown in Figure 1. Bar charts of Cr, Cu, Ni, Pb and Zn concentrations in rock and soil samples from the ten locations with bulk analyses of rock material are shown in Figure 2.

The Norwegian authorities use Norm values for polluted soil (SFT, 1999). Of all soil samples, 95% exceed these values for at least two of the elements. Of 44 soil samples, 42 exceed the Norm value of arsenic. The percentages for Pb, Zn, Ni and Cr are 71, 73, 23 and 45. Regarding Cu, none of the soil samples exceed the Norm value of 100 mg/kg.

Concentrations of As, Cd, Cu, Pb and Zn are, with a few exceptions, higher in soil than in rock samples. Correlation coefficients between soil and rock concentrations are rather low. Only Ni, Cr and Cu have correlation coefficients with a significance level better than 10% (Ni 1%).

Regarding chromium, bulk concentrations in rock are much higher than TAS concentrations in both soil and rock. The correlation coefficient between rock-TAS and rock-bulk is on the other hand very good, 0.96. Chromium is probably strongly incorporated in the mineral structure such that concentrated HNO_3 only partially can get the element in solution. TAS concentrations in soil show rather good correlation with bulk concentrations for the bedrock samples, 0.66. In fact, this correlation coefficient is the highest among correlation coefficients between rock and soil data of the other metals.

Lead concentrations in soil are much higher than concentrations in bedrock, both bulk and TAS. At some locations, differences are considerable. Bulk concentrations are somewhat higher than TAS concentrations in rock, but the correlation coefficient is rather good, 0.80. The correlation coefficient between TAS-soil and bulk rock is -0.35.

The correlation coefficient between TAS-rock and bulk-rock for copper is 0.99. TAS concentrations of copper in soil are higher than TAS-rock at 36 of 44 locations and at 8 of 10 location higher than bulk-rock. Correlation coefficients between rock and soil are low.

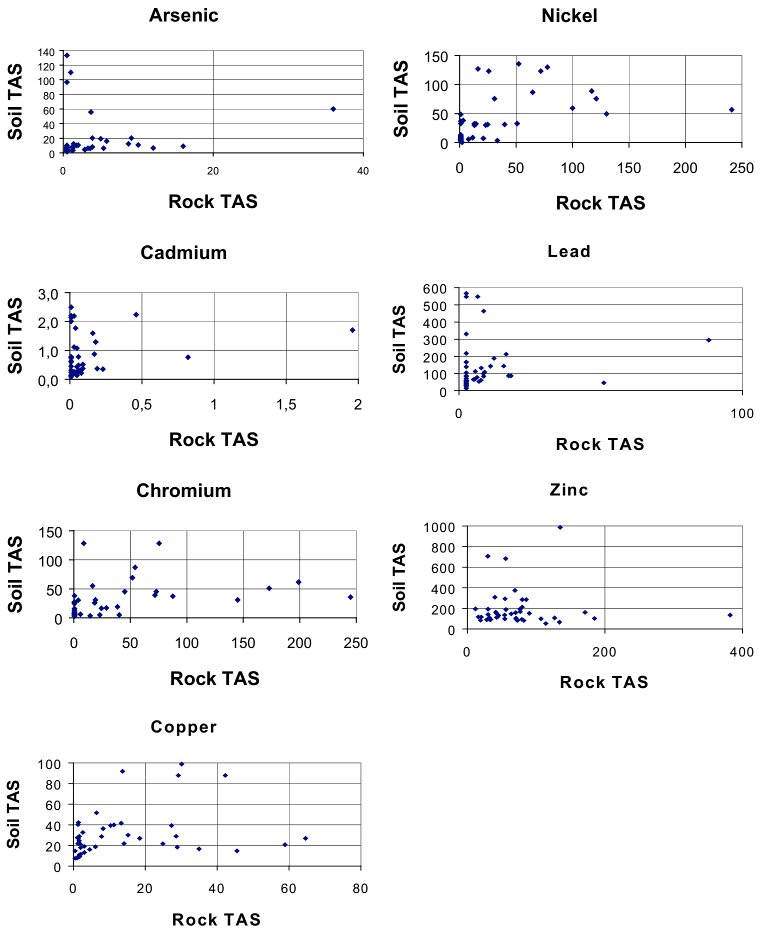

Figure 1: Scatterplots of TAS concentrations (mg/kg) in bedrock and soil samples from 44 sites in Oslo, Norway. Correlation coefficients: Arsenic 0.15, Cadmium 0.22, Chromium 0.38, Copper 0.29, Nickel 0.49, Lead 0.11 and Zinc 0.01.

Table 1: Total acid soluble concentrations (mg/kg) in bedrock and soil samples from 44 sites in Oslo, Norway and bulk concentrations in bedrock samples from 10 of these sites. < indicates detection limit.

	Arsenic		Cadmium		Chromium			Copper			Nickel			Lead			Zinc		
Site	a	b	a	B	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
1	<1	8.03	<.02	2.50	<1	8.19	52	1.28	40.2	<3	<2	8.09	<9	8.69	463	12	29.9	707	66
2	<1	3.32	<.02	2.00	5.74	6.06	172	8.33	36.3	5	7.9	5.77	9.00	15.8	143	24	30.3	141	40
3	<1	4.16	.05	.44	<1	7.96	80	1.08	7.80	<3	<2	8.16	<9	6.33	77.9	15	45.2	133	62
4	<1	2.66	.82	.76	<1	5.14	109	1.20	27.6	<3	<2	4.27	<9	8.97	108	20	185	103	229
5	1.3	3.45	.16	1.59	<1	3.26	43	1.40	8.87	<3	<2	7.74	<9	7.8	132	18	70.7	106	121
6	36	60.0	.04	.17	38.6	19.2	128	58.9	20.7	53	50.9	32.6	60	<5	30.8	5	34	92.4	66
7	10	10.7	<.02	.63	<1	7.35	27	<1	14.7	<3	<2	4.13	<9	<5	566	5	19.4	84.5	31
8	2.9	4.05	.06	.24	28.8	17.3	218	4.53	16.1	<3	13.1	29.8	112	<5	60.1	12	20.3	117	78
9	5.4	6.38	<.02	.23	51.8	69.3	152	30.1	99.0	31	77.7	130	91	<5	104	12	70.3	159	82
10	16	9.09	<.02	.08	199	61.7	683	35.0	16.6	28	241	56.5	232	<5	29.2	15	82.1	82.6	92
11	1.2	3.15	.03	2.19	<1	4.32		24.9	21.7		<2	2.99		<5	139		171	162	
12	<1	4.86	.08	.32	<1	7.09		1.72	9.05		<2	4.78		8.70	83.8		72.6	82.8	
13	<1	3.21	<.02	2.14	<1	5.02		1.64	10.6		<2	4.72		<5	166		28.1	90.2	
14	<1	1.81	.03	1.11	<1	4.24		2.04	11.5		2.1	.63		8.62	98.6		42.7	113	
15	1	110	.04	1.77	<1	10.6		1.40	21.9		<2	13.2		5.68	112		55.9	683	
16	<1	96.9	<.02	2.19	23	5.28		7.85	28.7		11.5	8.61		<5	167		41.4	163	
17	<1	133	.09	.37	14.3	3.47		45.5	14.7		21	7.39		7.77	61.2		114	53.2	
18	2.9	4.75	<.02	.76	40.1	4.98		11.3	40.0		33.4	3.34		<5	217		127	107	
19	<1	6.62	.06	.48	<1	27.4		1.96	21.1		<2	36.7		<5	13.3		54.1	136	
20	<1	7.81	<.02	.60	245	36.0		6.45	51.7		130	49.5		<5	58.8		54.9	293	
21	<1	10.1	.09	.51	145	31.1		1.68	28.9		39.9	31.4		18.3	86.6		30.1	193	
22	1.8	10.1	.09	.51	19.1	31.1		28.6	28.9		24.8	31.4		<5	86.6		76.5	193	
23	<1	3.13	.23	.35	<1	3.38		<1	7.49		<2	6.18		17.5	86.3		134	66.8	
24	<1	3.03	1.96	1.70	<1	5.58		1.52	22.6		<2	5.04		16.6	213		382	136	
25	<1	3.16	.46	2.24	<1	16.3		1.40	42.2		<2	9.21		88.1	295		135	987	
26	1.2	7.93	.02	.25	<1	38.0		6.13	18.6		<2	48.7		<5	48.9		32.1	111	
27	<1	4.06	.17	.87	<1	13.5		1.60	24.5		<2	10.8		5.57	67.4		69.2	375	
28	<1	2.51	.18	1.29	<1	5.11		1.28	21.8		<2	4.57		12.3	188		79.3	93.9	
29	<1	1.81	.06	.26	<1	8.97		2.04	17.9		<2	9.61		11.1	143		32.9	89.9	
30	<1	6.78	.19	.36	<1	27.3		1.36	26.8		<2	32.6		7.05	53.4		77	169	
31	1.3	6.88	.08	.21	<1	24.3		3.08	13.2		<2	12.3		5.12	65.5		44.3	120	
32	3.9	20.2	.05	.14	8.66	128		64.6	26.9		25.8	123		<5	52.8		107	98.7	
33	9.1	20.2	<.02	.14	75.5	128		18.5	26.9		71.8	123		<5	52.8		70.9	98.7	
34	5	19.3	<.02	.12	16.6	55.3		2.68	32.6		16.2	127		<5	84.0		16.2	118	
35	3.3	6.27	<.02	.31	18.4	26.0		10.4	39.3		14.5	32.2		<5	42.0		42.3	152	
36	<1	6.27	.06	.31	<1	26.0		27.3	39.3		12.9	32.2		<5	42.0		90.1	152	
37	3.7	55.7	<.02	.45	3.81	30.6		3.00	19.0		3.04	38.1		<5	21.9		11.8	196	
38	3.6	6.07	.04	.23	24.4	16.5		14.1	21.8		23.1	30.1		<5	35.9		56.1	189	
39	12	6.65	.03	.26	87.6	37.4		15.2	30.0		64.6	86.7		51.1	45.8		54.7	99.1	
40	2	10.5	.05	1.07	173	51.2		13.3	41.6		117	88.7		<5	71.2		79.8	213	
41	8.7	12.3	<.02	.77	73.0	45.1		42.3	88.0		121	75.7		6.58	548		85.5	285	
42	1.4	12.3	.06	.77	45.0	45.1		29.2	88.0		30.8	75.7		<5	548		79.7	285	
43	5.8	15.9	<.02	.74	54.2	87.2		13.7	91.9		52.4	136		<5	330		40.2	309	
44	3.9	7.98	.08	.33	71.8	39.2		28.9	18.3		100	59.4		<5	31.9		63.7	147	

a: Rock-TAS b: Soil-TAS c: Rock-Bulk

Table 1: continued.

	Arsenic		Cadmium		Chromium			Copper			Nickel			Lead			Zinc		
	a	b	a	b	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
Min	<1	1.81	<.02	.08	<1	3.26	27	<1	7.49	<3	<2	.63	<9	<5	13.3	5	11.8	53.2	31
Max	36	133	1.96	2.50	245	128	683	64.6	99.0	53	241	136	232	88.1	566	24	382	987	229
Mean	3.5	16.9	.13	.79	33.5	28.1	166	13.2	30.3	13	30.1	37.5	52	8.58	138	14	73.6	193	87
Med.	1.2	6.72	.05	.50	4.78	18.3	119	5.33	23.6	<3	9.70	30.0	7	<5	85.2	14	59.9	136	72
Norm		2		3		25			100			50			60			100	

a: Rock-TAS b: Soil-TAS c: Rock-Bulk

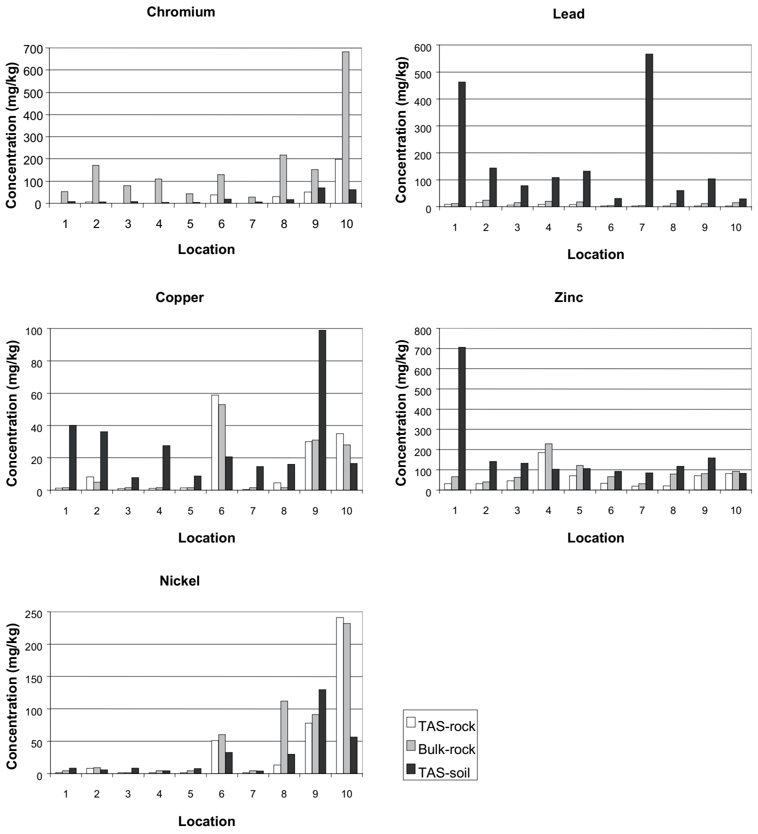

Figure 2: TAS and bulk concentrations in rock samples and TAS concentrations in soil samples at ten locations in Oslo, Norway

Regarding nickel, there is good correlation between TAS-rock and bulk-rock, 0.92. Correlation between TAS-soil and bulk-rock is rather good, 0.57. At only four of six locations TAS concentrations in soil are higher than bulk concentrations in bedrock.

At seven of ten locations, zinc concentrations in soil are higher than both TAS-rock and bulk-rock. At 37 of 44 locations, TAS-soil concentrations are higher than TAS-rock concentrations. There is good correlation (r=0.95) between TAS-rock and bulk-rock. The correlation coefficient between TAS.soil and bulk-rock is -0.15.

5 Statistical methods

5.1 Factor analysis

To describe the covariant relationships among TAS concentrations in bedrock and soil, a factor analysis has been completed. Concentrations below detection limit were set as half this limit. The data set, in which the number of samples (n=44) is relatively low in relation to the number of variables (14), might not be suitable for factor analysis. However, the Barlett test of sphericity implicates that the data distribution is approximately multivariate normal and thus acceptable for factor analysis (George and Mallery, 1999).

The results of the factor analysis are shown in Table 2. The communality, which is the portion of the variance of the variables contributed to the factors, is good for most variables. Only As in rock and Pb in both soil and rock have moderate communalities. About 75% of the variance in the data set is explained by the five factors.

Factor 1 shows that Cu, Ni and Cr in soil correlate with each other. Also Cu and Ni in rock and Pb in soil are placed in this factor but with relatively low loadings. This factor shows that the Ni and Cu content in soil, in some way reflects the composition of the parent material and that these elements most likely have geological origin.

The relation between elements in soil and rock is shown even better in factors 3 and 5. In factor 3 there is a clear relation between Cr and Ni in rock and soil samples. Factor 5 shows that also As in soil is dependent on the concentration in rock.

Factor 4 contains Zn and Cd in rock. These elements have a comparable ionic radius and Cd can therefore substitute for Zn in Zn-rich minerals like sphalerite .

Factor 2 contains Zn, Cd, Pb and Cu in soil with no influence of the geologic parent material. Geological sources are therefore negligible for this factor. Only Pb in rock is part of this factor. However, the communality of Pb in rock is low and conclusions on lead must therefore be taken with care. Concentrations of Zn, Cd, Pb and Cu in soil are higher than in rock. The difference in Pb is very large. Human activity is probably the major source behind this factor.

Table 2: Factor analysis of total acid soluble data of bedrock and soil samples in Oslo (n=44)

Structure matrix		Factor				
Element	Communality	1	2	3	4	5
Cu soil	0.81	**0.83**	**0.34**	0.09	-0.03	0,03
Ni soil	0.84	**0.81**	-0.22	**0.34**	-0.13	0,04
Cr soil	0.76	**0.74**	-0.28	**0.35**	-0.07	0,06
Zn soil	0.76	0.08	**0.86**	0.04	-0.06	-0,06
Cd soil	0.71	-0.22	**0.75**	-0.28	0.13	0,03
Pb rock	0.53	-0.19	**0.60**	0.22	0.24	-0,15
Pb soil	0.63	**0.44**	**0.59**	-0.29	0.04	0,01
Cr rock	0.83	0.18	0.01	**0.89**	-0.10	-0,01
Ni rock	0.86	**0.31**	-0.06	**0.85**	-0.03	0,19
Zn rock	0.94	-0.01	0.07	-0.04	**0.97**	0,00
Cd rock	0.91	-0.12	0.10	-0.10	**0.93**	-0,13
As soil	0.70	-0.21	0.15	-0.17	-0.19	**0,76**
Cu rock	0.81	**0.44**	-0.24	0.22	0.09	**0,71**
As rock	0.58	0.12	-0.18	**0.40**	-0.04	**0,60**
Variance explained (%)		29.3	45.7	58.2	67.7	76.1

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

5.2 Correlation coefficients

Correlation coefficients between the elements in soil and rock samples with significance levels are presented in tables 3 and 4.

In soil samples there is good correlation between Cd, Pb, Zn and Cu. Copper has also good correlation coefficients with Cr and Ni, but these elements have a negative correlation coefficient (-0.43) with Cd. The significance level of this negative correlation is 1%. Arsenic doesn't correlate significantly with the other elements.

Also in rock samples there is good correlation between Cr, Ni and Cu, but in rock samples also As correlates with these elements. As in soil samples, there is good correlation between Zn and Cd in rock, but correlation between these elements and Pb is low in rock samples, and there is no correlation with Cu.

Table 3. Correlation between 7 elements in soil samples and significance levels (n=44)

Soil	Cd	Pb	Zn	Cu	Cr	Ni	As
Cd	1.00	0.40	0.52		-0.43		
Pb	0.40	1.00	0.37*	0.49	-0.43		
Zn	0.52	0.37*	1.00	0.30**			
Cu		0.49	0.30**	1.00	0.42	0.59	
Cr	-0.43			0.42	1.00	0.90	
Ni	-0.43			0.59	0.90	1.00	
As							1.00

Significance level = 0.01
* Significance level = 0.05
**Significance level = 0.10

Table 4. Correlation between 7 elements in rock samples and significance levels (n=44)

Rock	Cr	Ni	As	Cu	Zn	Cd	Pb
Cr	1.00	0.87	0.26*				
Ni	0.87	1.00	0.44	0.46			
As	0.26*	0.44	1.00	0.55			
Cu		0.46	0.55	1.00			
Zn					1.00	0.86	
Cd					0.86	1.00	0.26*
Pb						0.26*	1.00

Significance level = 0.01
* Significance level = 0.10

6 Discussion

Correlation coefficients between the total acid soluble concentrations in rock samples, presented in Table 4, show that there is good correlation between Cr, Ni and As, between Ni, As and Cu, between Zn and Cd and to a lesser extent between Cd and Pb. These geological relations can also be seen in the factor analysis. Factors 1, 3 and 5 show the relations between Cr, Ni, As and Cu in rock, while factor 4 shows the geological relation between Zn and Cd. Factors 1, 3 and 5 also show that the Cr, Ni, Cu and As content in soil related to concentrations in rock. For these elements it is clear that part of the metal content in soil originates from the geological material.

For the elements Cd, Pb and Zn, there is not such a clear geological connection between the content in soil and rock. These elements in soil are placed in factor 2 together with Cu in soil. This factor probably has sources which are not geologic. The correlation coefficients between these elements in soil, presented in Table 3 are rather good. Industry, road traffic and combustion of waste might explain the relations between these elements in soil. Chromium and nickel in soil are not part of this factor and the presence of these elements in soil is therefore mainly the result of geological influence.

The factor analysis, doesn't give a good picture of Pb. This might be explained by the low communality of Pb-soil and Pb-rock. Lead concentrations in soil are higher than concentrations in rock at almost all locations. In some cases differences are considerable. Since concentrations in the parent material are low compared with concentrations in soil, the elevated levels of Pb in soil probably are caused by human activity.

Arsenic

The total acid soluble concentrations of arsenic in soil correlate poorly with TAS concentrations in rock (0.11). Also correlation coefficients with the other elements in soil are low (Table 3). In the factor analysis arsenic in soil has negative factor loadings in the 'geological' factors 1, 3 and 4 and a loading of 0.15 in the 'human' factor 2. At 95% of the sampling sites, TAS concentrations in soil are higher in soil than in rock. Ratios between soil and rock are in some cases more than 100. Despite this fact, the factor analysis shows that part of the arsenic content in the soil samples originates from the arsenic in minerals. However, at some locations, TAS concentrations in soil and bedrock samples differ much and this might be explained by anthropogenic input.

Cadmium

At 42 of 44 locations, TAS concentrations of cadmium in soil samples are higher than in bedrock samples. Differences between concentrations in soil and rock samples are at some locations very high. The correlation coefficient is poor, 0.22. Locations 1 and 2, where the difference between concentrations in soil and rock are largest, are in the north-eastern part of the city. Most of the industrial sites of Oslo are located in this area. Industrial activity probably has caused the elevated levels of cadmium in this area. Locations 3, 4 and 5 are located in the northern part of the city. Syenites of Permian age are dominating in this area. In this part of the city, cadmium concentrations in soil are generally higher than in other districts of Oslo (Tijhuis et al., 2002). Part of the cadmium concentrations in soil may be derived from the rocks in the area, but human influence can not be excluded.

Chromium

At all locations, TAS concentrations in soil and bedrock samples are lower than bulk concentrations in bedrock samples. At many locations, the chromium content in soil reflects largely the chromium content in bedrock and the element has therefore most likely geological origin with low or negligible contribution of anthropogenic sources. The correlation coefficient between TAS-rock and bulk-rock analysis is good, but bulk concentrations are much higher than TAS concentrations. Chromium is probably strongly incorporated in the mineral structure such that concentrated HNO_3 only partially can get the elements in solution. Concentrations in soil samples show rather good correlation with concentrations in bedrock.

Copper

Difference in TAS and bulk concentration of rock samples are small. The correlation coefficient is 0,99. At eight of ten locations acid soluble concentrations in soil samples are higher than TAS and bulk concentrations in rock. In soil, correlation coefficients (Table 3) between copper and lead, zinc, chromium and nickel are relatively high. In rock (Table 4), there is relatively good correlation between copper, nickel and arsenic. The factor analysis (Table 2) shows that Cu in both rock and soil is placed in factor 1. This factor show that part of the copper in soil originates from the parent material. Copper in soil is also placed in factor 2 which has little influence of the geologic material. It seems that the copper content in soil samples has two different sources. A geological source and an anthropogenic source which lead to elevated concentrations in soil compared to the concentrations found in bedrock.

Nickel

Bulk and TAS values of samples show minor differences. Their mutual correlation coefficient is 0.92. Location 8 is an exception with a bulk rock concentration over eight times the TAS-rock value. Correlation coefficients between nickel in soil and in rock are somewhat low, but still rather good. Differences in concentrations between soil and rock samples are rather small. The factor analysis places Ni in both rock and soil in factors 1 and 3. These factors have geologic origin. Correlation coefficients, between Ni and Cr, an element with mainly geologic origin, are good in both soil (0.90) and rock (0.87). Correlation coefficients between Ni and the other elements in soil are small in both rock and soil. Anthropogenic sources are probably small in the area and nickel concentrations in soil are therefore mainly the result of weathering of parent rock material.

Lead

The total acid soluble concentrations of lead in rock samples show little difference with bulk concentrations in these rock samples. The correlation coefficient is 0,80. TAS concentrations of lead in soil are higher than both TAS and bulk concentrations in the rock samples. At some locations, the difference are considerable. Because of these differences, anthropogenic sources probably have a large effect on the concentrations of lead in the soil at these locations. In the soil samples, lead correlates rather well with cadmium, zinc and copper. Also the factor analysis of bedrock and soil data places these four elements in soil in the same factor (Table 2).

Zinc

At seven of the ten locations TAS concentrations of zinc in soil are higher than TAS and bulk concentrations in rock samples. The zinc content in soil samples is therefore not only the result of weathering of the parent material at these locations. There is good correlation between bulk concentration and TAS concentration in the rock samples, with the bulk concentrations somewhat higher than TAS concentrations.

7 Conclusions

Analysis of rock samples, both bulk and TAS, in addition to analysis of soil samples brings in a new dimension on interpreting the results of a survey on soil. Geological patterns in the material become more clear and this gives a better understanding of processes which might have lead to elevated levels of some of the elements in soil, especially in cases where TAS concentrations in soil are much higher than bulk concentrations in rock. The results of this survey confirm the conclusions made in earlier work (Tijhuis, et al., 2002).

In general, bulk concentrations of bedrock samples, lie at a higher level than TAS concentrations. Differences are small in copper and zinc, somewhat higher in lead and nickel and considerable in chromium.

The TAS-soil values of chromium differ little with TAS-rock values, but are much lower than bulk-rock values.

The chromium and nickel content in topsoil in Oslo originates mainly from the parent rock material. This rock material is also a major source for the arsenic and copper content in topsoil but human influence has caused elevated levels of these elements. For cadmium, lead and zinc, human activity has had major impact on concentrations in soil .

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Paper 4:

The Heavy Metal Content in Topsoil Along a Major Highway in Oslo, Norway.

Submitted to Water, Air and Soil Pollution.

THE HEAVY METAL CONTENT IN TOPSOIL ALONG A MAJOR HIGHWAY IN OSLO, NORWAY

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Abstract

In an attempt to see if traffic has an influence on the heavy metal concentrations in topsoil, nineteen samples of topsoil were collected along Highway E-18 in Oslo. These samples show that the topsoil adjacent to Highway E-18 in Oslo is enriched in chromium, copper and nickel, when compared to samples of topsoil from the greater Oslo area. Samples along all larger highways in Oslo exhibit higher concentrations of these elements and arsenic compared with topsoil from the Oslo area. Other investigations on the heavy metal content of topsoil have shown enrichment of lead and zinc along highways. However, no enrichment of these elements is evident in this study. This result, and the fact that the enrichment and heavy metal profile of elements in topsoil is different near the various highways, show that applying the concept of enrichment factors to decipher the anthropogenic contribution of heavy metals in topsoil from road traffic is not straightforward. Many factors play a role in the processes concerning traffic and its possible pollution of the environment. Modern road construction, with import of soil from other geographical areas, often with different geology, can have an effect in a survey like this. Other sources of airborne heavy metals are industry and incineration plants. They may affect the heavy metal content in topsoil also near highways and obliterate the contribution from traffic.

The enrichment of nickel in topsoil near highways in Oslo might be due to the bitumen content of road dust. The enrichment of chromium and copper might be due to wear and tear of mechanical and engine parts on cars. There is no detectable enrichment of cadmium, lead and zinc in topsoil near Highway E-18 or other highways in Oslo. Concentrations of zinc in topsoil in Oslo are generally high compared to results from other cities in Norway, most probably due to airborne particulate matter from industry. The possible addition of zinc due to traffic is not observed, in the topsoil neither along Highway E-18 nor highways in the greater Oslo area.

More detailed and systematic investigations are necessary to get a better understanding of the variations in heavy metal concentrations in topsoil along different roads. The number of samples should be increased and different highways should be investigated separately. In such an investigation, one should carefully consider which data the topsoil samples along the highways is compared to. In a large area with many other major sources of airborne heavy metals or in an area where the natural concentrations of specific elements are high, comparison of median values might not clearly show the enrichment of heavy metals due to anthropogenic perturbation in an accurate way. In such a case, comparison with a smaller area, presumably unpolluted, parallel to the highway or with deeper soil samples shielded from airborne contamination at each sampling site might be more appropriate.

Keywords

Heavy metals, highways, Highway E-18, contamination, urban areas, Norway, Oslo.

1 Introduction

To decipher which anthropogenic factors contribute to the heavy metal concentration of soils in urban areas beyond the natural composition is complicated. This is especially the case when one attempts to evaluate the contribution from traffic along a major highway, as is the aim of this study. Combustion of gasoline as well as the wear and tear of tyres, with or without studs, brake linings, engine parts and road surfaces (bitumen and aggregates) are sources of pollutants.

In an effort to understand more of the problems arising from traffic in Oslo, samples of topsoil were collected near a stretch of Highway E-18 between Sandvika and Bygdøy in Southwest Oslo (Figure 1). It is emphasized that this investigation should be considered as a preliminary study as the conclusions are based on relatively few samples.

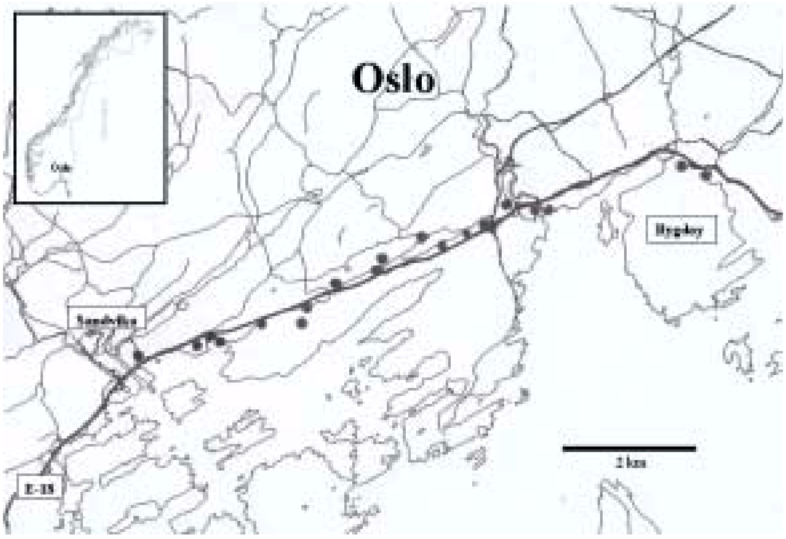

Figure 1: Sampling sites along a 10 km section of Highway E-18.

Along the highway Ljubljana to Zagreb in Slovenia, the average enrichment factor of lead in soils was found to be 17, and the highest lead accumulation was localised in the top soil layer and within 10 m from the roadside (Zupancic, 1999). Williams and others (1998) showed that the average scalp hair and pubic hair lead levels in traffic police were significantly higher than in non occupationally-exposed general population. In Spain, lead levels in leaves of citrus decrease rapidly with increasing distance from the roads (Caselles, 1998). In Brisbane, Australia, vehicular emissions were the major source of lead in the roadside soil (Al-Chalabi and Hawker, 2000). At sites located in relatively enclosed areas of higher atmospheric stability, both lead and bromide contents decreased markedly with increasing distance from the roadway. In Honolulu, Hawaii, calcium, copper, lead and zinc exhibited anthropogenic enhancement, with lead and zinc having the greatest enrichment in road sediment by locations nearest the road. Copper displayed a narrower band of contamination than either lead or zinc (Sutherland and Tolosa, 2001). In Oahu, Hawaii, median lead concentrations from a weak (cold) HCl digestion and a hot HNO_3 digestion were 3 and 7 mg/kg, respectively, for the background soil, and 256 and 303 mg/kg, respectively, for the sediments deposited along roads in an urban non-industrialized basin (Sutherland and others 2003). Kelly and Thornton (1996) showed that the highest concentrations of lead in the London Borough of Richmond-upon-Thames, a residential suburb with little history of industrial activity, tend to occur close to major road junctions on roads with high traffic densities.

Laden and others (2000) used the elemental composition of size-fractionated particles to identify several distinct source-related fractions of fine particles and examined the association of these fractions with daily mortality in six eastern U.S. cities. They identified a silicon factor classified as soil and crustal material, a lead factor classified as motor vehicle exhaust, a selenium factor representing coal combustion, and up to two additional factors. They found that a 10 $\mu g/m^3$ increase in $PM_{2.5}$ (i.e. particulate matter with diameter less than 2.5 μm) from mobile sources accounted for a 3.4% increase in daily mortality (95% confidence interval), and the equivalent increase in fine particles from coal combustion sources accounted for a 1.1% increase. $PM_{2.5}$ crustal particles were not associated with daily mortality.

In Norway estimates show that 300 – 400 000 tons of particles are formed by wear and tear of the top pavement each year due to the extensive use of studded tyres during the winter season (Myran and Hedalen, 1994). The top layer of asphalt roads may consist of about 90% rock, 5% filler (stone dust) and 5% bitumen (Hedalen and Myran, 1994). Bitumen is a complex mixture of a great number of organic compounds. A small amount of these are organic toxins as PAH and organic chlorides. Also nickel and vanadium exist in relative high quantities in bitumen, in the ranges 15-100 mg/kg and 50-600 mg/kg, respectively (Bækken, 1993).

The specific wear from studded tyres varies with the kind and quality of the road surfaces as well as traffical and climatic variables. On common Norwegian road surfaces, this specific wear is 20-50 g/km pr. car (Lyngren and others, 1984).

A survey on health effects of traffic pollution in the central parts of Oslo, (NILU, 1991) indicated that:

- Air pollution from vehicular traffic does have adverse effects on human health
- 40 % of the population showed a relationship between the increased severity of at least one health symptom and air pollution
- The current hourly ambient air guidelines of 200 $\mu g/m^3$ do not seem to protect the population from health effects.

In the winter season 1993/1994, the Norwegian Institute for Air Research investigated the air quality at four sites next to trafficked roads in Oslo (Torp, 1994). The mean concentrations of PM_{10} (i.e. particulate matter with size less than 10 μm) and $PM_{2.5}$ were below the Norwegian air quality criteria of 40 $\mu g/m^3$ and 30 $\mu g/m^3$ during a mean year, but 26 day concentrations exceeded the PM_{10} quality criteria of 70 $\mu g/m^3$ at one site. Concentrations were generally lower than in the winter of 1992/1993, in which there were more days without snow on the road pavement. The current criteria for PM_{10} in air are lower than in 1994. Mean air criteria are now 50 $\mu g/m^3$ per day or 40 $\mu g/m^3$ per year (Miljøverndepartementet, 2002).

Pedersen (1990) carried out an analysis of elements in dry residual deposits along a highway in Oslo. The heavy metal content in these deposits was high. Especially the concentrations of lead (780 mg/kg), zinc (800 mg/kg) and copper (150 mg/kg) were high.

In the city of Bergen, in south-western Norway, the topsoil beside roads contained more Cr, Cu, Hg, Pb and Zn than the topsoil in the rest of the city (Ottesen and Volden, 1999). Similar results were shown in Trondheim, in central Norway (Tijhuis, 1996). Here, concentrations of cadmium, mercury, phosphorus, lead and zinc were higher near the main traffic ores than in the rest of the city. A geochemical survey of topsoil in the city of Oslo has been carried out by Tijhuis and others (2002). The sampling design of that survey was not directed specifically towards traffic pollution.

2 Methods

2.1 Sampling design and methods

Nineteen samples of topsoil were collected along 10 km of Highway E-18 between Sandvika and Bygdøy on the southwest of Oslo (Figure 1). The highway runs parallel to the strike of the bedrocks in the area which are Palaeozoic limestones and shales (Berthelsen and Sundvoll, 1996; Naterstad, 1990). Samples were taken within 5-100 m of the roadside with 100-2000 m spacing. Sampling was performed the same way as the sampling in the geological survey of topsoil in Oslo presented by Tijhuis and others (2002). At each site one sample was collected by cutting a 20 x 10 cm section of surface soil with a spade. A knife was used to exclude the soil from depth below 2-3 cm. Vegetation in the form of grass and debris was removed manually. The weight per sample was about 0.5-1 kg. Samples were gathered in paper bags and the material was dried at a temperature of about 35 °C for four days. Afterwards the samples were sieved through a 2 mm nylon screen.

2.2 Dissolution

Soil samples were extracted in concentrated HNO_3 (14N). In addition three reagent blanks were included. Two grams (± 2.5%) of each sample was extracted in 20.0 ml 14 N HNO_3 in Erlenmeyer flasks. A watchglass was placed on top of the flasks to prevent evaporation of the liquid. Samples were heated at a temperature of 85°C for 20 hours, then filtered (filter paper brand 604 H) and diluted to 50 ml with distilled water. The concentrations of Cr, Cu, Ni, Pb and Zn in the soil were determined from this solution. An aliquot of 10.0 ml of this solution was removed and evaporated for determination of As and Cd. The non-evaporable residue was dissolved in 10 ml 0.1 N HNO_3. All solutions were stored in polyethylene bottles before being analysed.

2.3 Determination

The concentrations of arsenic (As) and cadmium (Cd) were determined by graphite furnace AAS (GF-AAS). The concentrations of chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) were determined by flame AAS. Every sample was analysed three times. If the relative standard deviation was more than 5%, samples were re-analysed. Samples with concentrations outside the calibration range were diluted manually (flame-AAS) or automatically by the instrument (GF-AAS). When the concentration was too high after dilution by the instrument, samples were diluted manually. To prevent loss of arsenic, 0.3 wt % Pd 0.1 N HNO_3 was added as modifier. Recovery was measured on each seventh sample (GF-AAS). These results were used to in the quality control. When the results of the recovery measurement were unacceptable, all analyses after the last calibration were rejected. The instrument was recalibrated after seven samples (GF-AAS). Analysis of a standard solution (on about each tenth sample) were used to control the quality of the analyses by flame AAS. If the concentration of the standard solution was outside the range of 90-110% of the expected value, the instrument was recalibrated, and the analyses of the samples after the last control check were rejected.

2.3.1 Graphite furnace AAS

The total acid soluble concentration of As was analysed with a Perkin Elmer AAnalyst 600, equipped with an Electrodeless Discharge Lamp (EDL-2), at the Department of Chemistry, NTNU, Trondheim. A standard solution of about 175 µg/L was prepared from a 500 mg/L stock solution with 0.1 N HNO_3. Calibration was performed by analysing this standard and two dilutions with ratios 1:2 and 1:4 prepared by the instrument. The ashing temperature was 1400 °C and the atomisation temperature 2300 °C.

The total acid soluble concentrations of Cd was determined with a GBC Avanta Σ, equipped with a hollow cathode lamp. A standard solution of about 6 ℓg/L was prepared from a 1000 mg/L stock solution with 0.1 N HNO_3. Calibration was performed by analysing this standard and two dilutions with ratios 1:2 and 1:4 prepared by the instrument. The ashing temperature was 350 °C and the atomisation temperature was 1800 °C.

2.3.2 Flame AAS

The total acid soluble concentrations of Cr, Cu, Ni, Pb and Zn were determined with the GBC Avanta Σ instrument using hollow cathode lamps. For all elements, calibration of the instrument was done by analysing five standard solutions of appropriate concentration, which were prepared from a 1000 mg/L stock solution with 6.0 N HNO_3. An Air-

Acetylene flame was used for all elements except for Cr in which case a N_2O-Acetylene flame was applied.

3 Results

Statistical results of the concentrations of the seven elements As, Cd, Cr, Cu, Ni, Pb and Zn in the collected topsoil samples along a 10 km section of Highway E-18 are compared to statistical parameters of samples from the greater Oslo area (Table 1).

Table 1: Descriptive statistics of the concentrations of the elements, As, Cd, Cr, Cu, Ni, Pb and Zn in samples of topsoil along a 10 km section of Highway E-18 in Oslo, "Highway E-18"-data (n=19) and in the greater Oslo area, "Greater Oslo Area"-data (n=348). The enrichment factors for each element X is calculated as:

$$E_X \text{ “Highway E-18”} = \frac{Median\ [X]\ \text{"}Highway\ \ E-18\text{"}-data}{Median\ [X]\ \text{"}Greater\ \ Oslo\ \ Area\text{"}-data}$$

	As	Cd	Cr	Cu	Ni	Pb	Zn
"Highway E-18"-data							
Minimum (mg/kg)	2.33	0.06	12.8	10.4	17.6	<4.40	36.6
Maximum (mg/kg)	9.10	0.59	44.0	69.0	65.2	187	323
Mean (mg/kg)	5.00	0.27	27.9	32.4	35.7	52.0	135
Median (mg/kg)	4.19	0.26	27.7	25.5	33.8	33.0	101
"Greater Oslo Area"-data							
Minimum (mg/kg)	1.50	0.07	2.85	4.76	<0.95	<4.40	22.90
Maximum (mg/kg)	1120	5.21	224	437	232	1000	1150
Mean (mg/kg)	9.21	0.47	30.5	31.4	29.4	65.1	167
Median (mg/kg)	4.62	0.35	26.5	22.9	24.2	38.5	132
Enrichment factor (E_X) "Highway E-18"	0.91	0.75	1.04	1.11	1.40	0.86	0.77

Highway E-18 is the main traffic artery on the south-west of Oslo city's centre and the data-set (n=19) along both sides of this highway is referred to as the "Highway E-18" data-set. The "Greater Oslo Area" data-set (n=348) consists of samples of topsoil from parks, lawns, wooded areas etc. within the city of Oslo which were collected and analysed following the same procedures as the "Highway E-18" data-set of this study. The results of the "Greater Oslo Area" study are presented and discussed in Tijhuis and others (2002). Enrichment factors are calculated by dividing the median concentration of each element in the "Highway E-18" data-set by the median concentrations of the respective elements in the "Greater Oslo Area" data-set.

Among the analysed elements, only nickel, copper and chromium have an enrichment factor greater than 1.00. Lead and zinc seem to be depleted in topsoil along the Highway E-18, i.e. the enrichment factor for both of these elements is less than 1.00.

The total data-set of Oslo presented by Tijhuis and others (2002) contains also samples taken near other highways. Table 2 shows descriptive statistics of all samples next to major highways in Oslo and their enrichment factors when compared to the median concentration of each element in the Greater Oslo Area" data-set.

Table 2: Descriptive statistics of the concentrations of the elements, As, Cd, Cr, Cu, Ni, Pb and Zn in samples of topsoil along highways in Oslo, "Highways Oslo"-data (n=47) and in the greater Oslo area, "Greater Oslo Area"-data (n=348). The enrichment factors for each element X is calculated as:

$$E_X \text{ “Highways Oslo”} = \frac{Median\ [X]\ \text{"}Highways\ \ Oslo\text{"}-data}{Median\ [X]\ \text{"}Greater\ \ Oslo\ \ Area\text{"}-data}$$

	As	Cd	Cr	Cu	Ni	Pb	Zn
"Highways Oslo"-data							
Minimum (mg/kg)	1.50	0.06	9.30	10.4	9.60	<4.40	36.6
Maximum (mg/kg)	34.1	0.74	89.2	69.0	86.5	205	323
Mean (mg/kg)	5.32	0.31	31.1	31.0	32.6	51.3	138
Median (mg/kg)	5.23	0.27	30.0	26.0	29.9	38.1	119
"Greater Oslo Area"-data							
Minimum (mg/kg)	1.50	0.07	2.85	4.76	<0.95	<4.40	22.90
Maximum (mg/kg)	1120	5.21	224	437	232	1000	1150
Mean (mg/kg)	9.22	0.47	30.5	31.4	29.4	65.1	167
Median (mg/kg)	4.62	0.35	26.5	22.9	24.2	38.5	132
Enrichment factor (E_X) "Highways Oslo"	1.13	0.77	1.13	1.14	1.24	0.99	0.90

The concentration of nickel in topsoil samples from the "Highways Oslo" data-set is higher than in the topsoil from the "Greater Oslo Area", but the enrichment factor is lower than along Highway E-18. Enrichment factors of chromium and copper are somewhat higher than those calculated from the “Highway E-18”-data. The enrichment factor of arsenic is 1.13. The enrichment factors of lead and zinc in the “Highways Oslo”-data are somewhat higher than in the “Highway E-18”-data, but also in this data-set are these elements depleted, i.e. enrichment are negative relative to the median concentration of the samples of the “Greater Oslo Area”.

4 Discussion

The data show that the nickel, chromium and copper content in topsoil near Highway E-18 is generally higher than in the rest of the city (Table 1). The high enrichment factor of nickel along Highway E-18 might be caused by the bitumen content in road dust, since bitumen contain 15-100 mg/kg nickel (Bækken, 1993). Of the other elements only copper and chromium are enriched in samples from Highway E-18, but the enrichment is only 4% for chromium and 11% for copper. This could be related to the fact that this road section of Highway E-18 is relatively new, as road construction was completed in 1975. This relatively short time may not have been enough to allow an easily detectable enrichment of heavy metals in topsoil near the Highway E-18. The accumulation of heavy metals is probably relatively small due to this small time factor. When other highways in the Oslo area are related to samples of the greater Oslo area (Table 2), the elements arsenic, copper and chromium exhibit a higher enrichment factor in topsoil samples compared with the results from Highway E-18.

4.1 Lead and zinc

The median concentrations of lead and zinc in topsoil near highways in Oslo are lower in the “Greater Oslo” area, compared with results obtained in the cities Trondheim and Bergen (Table 3). In Trondheim and Bergen, the enrichment factors of lead are 2.1 and 1.6 and of zinc, 1.4 and 1.3, respectively (Tijhuis, 1996; Ottesen and Volden, 1999). The median value of zinc concentrations in topsoil in Oslo is high (132 mg/kg) compared with those in Trondheim (94 mg/kg) and Bergen (85 mg/kg). Airborne zinc from industry, might contribute to this generally higher level of zinc in Oslo. The contribution of zinc from road traffic might obliterate due to the relatively high level of zinc in soils elsewhere in Oslo. Median concentrations of lead and zinc in overbank sediments in Norway are 20 mg/kg Pb and 44 mg/kg Zn (Reimann, de Caritat, 1998). Bølviken and Steinnes (1987) showed that B horizons in Norway contain 13 mg/kg Pb and 25 mg/kg Zn. These values are much lower than the median values in the topsoil samples from the greater Oslo area and in topsoil next to the highways. This might show that the topsoil in the greater Oslo area and topsoil next to the highways are contaminated at about the same level and that the use of soils from the “Greater Oslo Area” as background is invidious. In this case comparison with deeper soil at each sampling site might be more appropriate.

4.2 Nickel

Bitumen is a major source for nickel (Bækken, 1993). This might explain the enrichment of this element in topsoil when considering data from samples of topsoil near highways in Oslo. However, in the cities of Trondheim and Bergen, such an enrichment of nickel in topsoil near highways was not observed. In Trondheim, this might be explained by the fact that the nickel content in the parent geological material, which is mainly Palaeozoic greenschist's (Wolff, 1979), is high. The median concentration of Ni in topsoil in Trondheim is 46 mg/kg (Tijhuis, 1996), while in Oslo it is 24 mg/kg (Table 3).

Table 3: Median concentrations (mg/kg) of the elements As, Cd, Cr, Cu, Ni, Pb and Zn in topsoil in Oslo, Trondheim and Bergen and calculated enrichment factors (see Table 1 for definition) of these elements along highways.

	Oslo		Trondheim		Bergen	
	Median	Enrichment	Median	Enrichment	Median	enrichment
As	4,6	1,13	2,8	1,1	2,8	1,0
Cd	0,4	0,77	0,2	1,2	0,2	1,0
Cr	27	1,13	71	0,9	18	1,1
Cu	23	1,14	35	1,0	29	1,1
Ni	24	1,24	46	0,9	13	1,0
Pb	39	0,99	32	2,1	38	1,6
Zn	132	0,90	94	1,4	85	1,3

In Trondheim, the nickel content in road dust might be negligible compared with the natural background. In Oslo, however, the natural nickel content is low compared with the nickel content in road dust, which leads to measurable enrichment in topsoil near highways.

4.3 Chromium and copper

A comparable enrichment of chromium and copper which is observed in topsoil along highways in Oslo, is also seen in samples along highways in the city of Bergen (Ottesen and Volden, 1999). However, in Trondheim (Tijhuis, 1996), there is no detectable enrichment of these elements in topsoil along the main roads. The median values of these elements (Table

3) in the respective cities can give an explanation of these results. The median values of chromium (71 mg/kg) and copper (35 mg/kg) in Trondheim are much higher than in Bergen (18 mg/kg and 29 mg/kg) and Oslo (27 mg/kg and 23 mg/kg). The additional contribution of these elements from traffic might therefore be negligible in Trondheim but notable in Oslo and Bergen. Copper and chromium are used in the car industry in different processes. Tyres contain copper, and chromium is part of several engine parts. Wear and tear of these parts has probably lead to enrichment in the topsoil along the highways. Analysis of road dust in Trondheim showed that the copper and chromium content is considerable (Brattli and Ottesen, 1996). The PM_{10} fraction in road dust contained 84 mg/kg chromium and 973 mg/kg copper.

4.4 Arsenic

The median concentration of arsenic in topsoil in Oslo dependends on the area in which the samples are taken. The arsenic content is much higher in the western and central districts than in other parts of the city. High concentrations in the centre may be due to combustion of coal in households, and the lithology of the central and western parts of Oslo contains shale and limestone in which natural concentrations of arsenic have been shown to be high (Tijhuis and others, 2002). The samples near highways in Oslo referred to in this survey are taken in the central districts. It is therefore difficult to decide if the enrichment of arsenic in soil near highways in an urban area such as this is caused by traffic. It is possible that the measured enrichment of arsenic near highways is caused by the generally higher level of the element in soil in these districts.

5 Conclusions

The topsoil in the vicinity of Highway E-18 in Oslo is enriched in chromium (1.04), copper (1.11) and nickel (1.40) relative to samples of topsoil in the greater Oslo area. The enrichment of nickel might be due to the bitumen content of road dust. The enrichment of chromium and copper might be due to wear and tear of cars and engine parts.

When topsoil samples along other highways in Oslo are compared with those of the greater Oslo area, the median concentration of arsenic is higher. The enrichment of arsenic near highways might be explained by the fact that these highways are placed in districts with generally higher levels of the element, due to higher population density and more air pollution from coal fired heating systems up until the last two decades. It is therefore not certain that traffic has an additional effect on arsenic concentrations in topsoil.

There is no detectable enrichment of cadmium, lead and zinc in samples of topsoil near highways in the greater Oslo are. The concentrations of zinc in topsoil in Oslo are generally high, most probably due to air pollution from industry. The possible additional contribution of zinc from traffic to the topsoil is not notable in our data. The lack off enrichment in lead is difficult to explain. Studies, both national and international, have shown high (in some cases very high) enrichment factors of this element. Also studies of residue deposits along highways in Oslo show that lead is a major constituent in this medium.

Many factors play a role in the processes concerning traffic and its possible contribution of heavy metals to the surrounding environment. The current practise in road construction, with import of soil from other areas, with different geology and geomorphology, can affect the sensibility of topsoil as a medium monitoring environmental pollution and the results of a survey like this.

To get a better understanding of how the heavy metal concentrations in topsoil along different roads vary, more detailed and systematic investigations are necessary. It might be an advantage to investigate how the concentration of heavy metals vary as a function of distance from the road by sampling several transepts perpendicular to the road. The number of samples should be increased. Samples should be taken at various distances from the highway and different highways should be investigated separately. In such an investigation, one should carefully consider to which reference data-set, the soil data along highways is compared when calculating enrichment factors. In a large area with other major sources of pollution or in an area in which natural concentrations of specific elements are high, comparison of median values might not clearly show the contribution of heavy metals due to road traffic. In such a case comparison with a smaller area, far away from the highway, but with similar geology and climate, or comparison with deeper soil at each sampling site might be more appropriate.

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Appendix A:

The Distribution of 15 Elements in Topsoil in the City of Oslo, Norway.

Unpublished

The Distribution of 15 Elements in Topsoil in Oslo, Norway.

The geochemical distribution in topsoil of the elements As, Cd, Cr, Cu, Hg, Ni, Pb and Zn is presented in detail in Paper 1. However, the results of the other elements are not published before and will therefore be presented in this chapter. The elements Ag, Al, Fe, K, Li, Mg, Sc, Si and V, which most probably have geological origin are not presented in detail, but descriptive statistics are shown in tables 1,3,4,5,6,7 and 8.

1 Boron

Despite the fact that boron has a low atomic number, occurrences of the element in the earth crust are small. Elementary boron does not exist in nature. Boron is a trace element in minerals such as amphiboles, plagioclase, micas and biotite. Also tourmaline ($(Na,Ca)(Mg,Fe^{2+},Fe^{3+},Al,Li)Al_6(BO_3)_3Si_6O_{18}OH_4$) contains boron. Boron is used in glass, alloys, antiseptics and as flame retardant. Coal can contain boron (Wedepohl, 1969). Environmental pathways for boron are sea spray, coal combustion, sewage and fertilisers (Reimann & de Caritat, 1998).

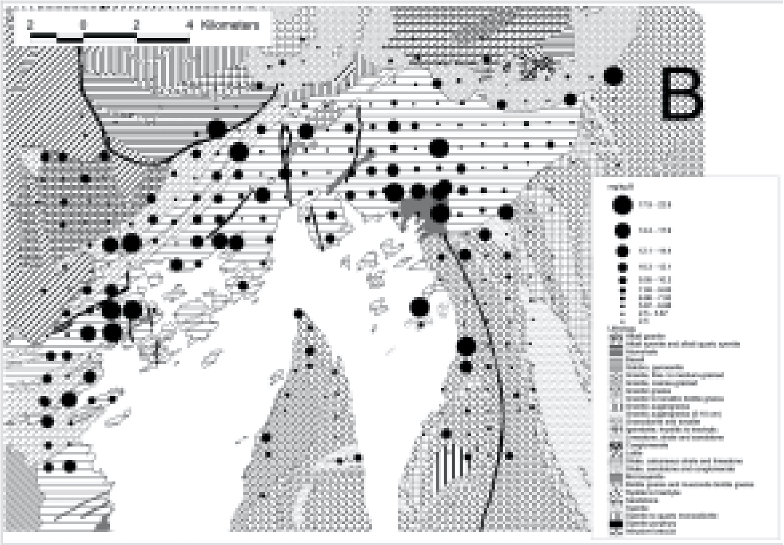

Figure 1. Acid soluble boron in top soil of Oslo

Table 1. Geochemical analysis of Ag, Al and B (mg/kg) in surface soil of Oslo

	Silver				Aluminium				Boron			
	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean
Centre	<1	3.20	<1	<1	7350	22000	16700	16400	7.27	22.4	11.1	12.8
Ullern, Bygdøy	<1	1.21	<1	<1	10400	25100	17900	17400	<5	13.6	7.34	7.15
Vinderen, Røa	<1	<1	<1	<1	5630	28200	17000	17700	<5	15.1	5.69	6.20
Sogn	<1	<1	<1	<1	8110	29400	15700	16900	<5	12.8	6.11	6.01
Grefsen	<1	<1	<1	<1	9140	20700	13400	14400	<5	19.6	6.09	6.60
Økern	<1	<1	<1	<1	9060	23600	19700	18600	<5	11.1	7.75	7.24
Grorud, Furuset	<1	2.12	<1	<1	2620	31400	21350	18700	<5	18.7	5.64	6.36
Oppsal, Haugerud	<1	<1	<1	<1	2080	28400	18050	16800	<5	15.7	5.27	5.42
Ekeberg, Nordstrand	<1	1.06	<1	<1	10200	26800	15700	16200	<5	18.3	6.37	7.59
Bøler, Bjørndal	<1	<1	<1	<1	5180	29400	21600	18400	<5	8.58	5.75	5.19
Holmlia, Kolbotn	<1	<1	<1	<1	8460	19000	13050	13300	<5	12.1	<5	5.53
Nesodden	<1	<1	<1	<1	11500	27500	19700	19700	<5	11.3	7.63	7.12
Stabekk, Fornebu	<1	<1	<1	<1	8610	23900	17150	16800	<5	16.9	10.1	10.2
Asker	<1	1.69	<1	<1	11500	43200	20300	21400	<5	22.9	10.5	10.8
Sandvika	<1	1.21	<1	<1	8160	37600	16400	18600	<5	19.8	7.11	8.28
Rykkinn, Bærums Verk	<1	<1	<1	<1	8630	29200	15350	16000	<5	11.8	5.68	5.92
Østerås	<1	<1	<1	<1	5030	27400	16750	17200	<5	18.6	7.21	8.18
Oslo	<1	3.20	<1	<1	2080	43200	17200	17500	<5	22.9	6.98	7.56

In the Oslo area (Table 1 and Figure 1), concentrations of boron lie between <5 and 22.9 mg/kg and are highest in the central and western parts of the city. Pearson correlation with most other elements is low but significant. Correlation coefficients higher than 0.4 are between boron and Al, Cr, Fe, K, Li, Ni and Sc. These elements have mainly natural sources. Sources for boron are therefore probably mainly geological. In the central parts of the city, anthropogenic sources such as coal combustion in former days, are probably important.

2 Barium

Barium is a toxic element, but its toxicity depends on its ability to dissolve. The ion is easily absorbed form the lungs and from the digestive apparatus. Barium-sulphate does not absorb into the human body. Barium accumulates in the bone structure, and can lead to heart problems because it has effect on muscles in the heart region (Friberg, et. al., 1986). The Target value, used by the Dutch authorities is 200 mg/kg and the Intervention value is 625 mg/kg (VROM, 1994). Typical minerals in which Ba is part of structure formula are barite ($BaSO_4$) and witherite ($BaCO_3$). Possible host minerals which can contain Ba as trace element are micas, K-feldspar, apatite and calcite. In general natural sources are more important than anthropogenic ones, which include Cu smelting, automobile industry and steel works (Reimann & de Caritat, 1998). Barium is one of the less common elements which may be considerably concentrated in certain coal ashes. The amount of BaO in such ash may reach 1.000-10.000 ppm and over (Goldschmidt, 1954).

Descriptive statistics of barium in surface soil in the investigated area are shown in Table 2. A geochemical map is shown in Figure 2. 37 samples of 297 (21%) contain more barium than the Dutch Target value, but only one sample exceeds the Intervention value. The highest values of barium are located in the central, the northern and the north-eastern parts of the city. Sources of barium in these parts are probably anthropogenic, such as combustion of coal. In the factor analysis Ba is in the same factor as Cd, Hg, Cu, P, Zn and Pb, but has also a relatively high loading on the first factor, which is geologic.

Table 2. Geochemical analysis of Ba, Be and Ca (mg/kg) in surface soil of Oslo

	Barium				Beryllium				Calcium			
	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean
Centre	53.9	1350	222	281	2.70	9.50	5.94	6.24	4790	32000	7560	9670
Ullern, Bygdøy	65.8	242	99.9	132	3.38	10.4	5.56	5.98	3680	20300	7360	8620
Vinderen, Røa	34.6	336	142	146	1.01	8.83	5.66	5.56	2490	10200	6790	6720
Sogn	43.2	292	135	150	2.44	7.87	5.68	5.44	1330	8400	5670	5280
Grefsen	71.2	271	105	118	2.60	5.95	4.67	4.56	2940	9010	5960	5980
Økern	81.2	273	156	154	3.50	7.09	5.97	5.69	3390	8590	6190	5840
Grorud, Furuset	41.5	221	146	138	0.617	8.57	5.56	5.61	1710	13400	5350	5690
Oppsal, Haugerud	53.1	289	125	125	0.681	9.88	5.24	4.99	2610	25900	5400	7210
Ekeberg, Nordstrand	47.1	345	124	129	2.82	8.86	5.02	5.37	1340	24100	6070	8330
Bøler, Bjørndal	32.2	205	143	128	2.39	10.9	5.05	5.49	2570	11100	4730	5140
Holmlia, Kolbotn	52.2	137	88.4	90.9	2.60	6.20	4.24	4.46	2240	14000	5280	6040
Nesodden	95.4	258	148	163	4.03	7.77	6.41	6.36	1840	14000	4010	4530
Stabekk, Fornebu	31.1	250	112	132	3.25	8.70	5.35	5.36	6180	16600	10000	10200
Asker	50.7	170	96.2	106	4.24	10.3	6.11	6.39	3400	37900	7660	9780
Sandvika	33.3	257	99.1	105	3.23	10.3	5.81	5.81	4470	21000	8290	10400
Rykkinn, Bærums Verk	43.5	103	85.7	78.8	2.11	7.18	5.16	4.97	2810	19600	5800	7100
Østerås	23.0	238	92.8	106	1.78	8.40	5.49	5.06	1710	9950	7570	6940
Oslo	23.0	1350	115	131	0.617	10.9	5.54	5.52	1330	37900	6280	7380

Figure 2. Acid soluble barium in top soil of Oslo

3 Beryllium

Beryllium is considered non-essential. It is toxic if inhaled and carcinogenic for several animal classes. Both the metal and its compounds are allergenic. Beryllium, although widely distributed, exists in relatively small quantities, comprising less than 10 ppm of the major rock types. The metal is likely to concentrate in the acid magmatic rocks (Kabata-Pendias et. al. 1992). Typical minerals that contain Be are beryl ($Be_3Al_2Si_6O_{18}$) and bertrandite ($Be_2SiO_4.H_2O$). Minerals that can contain traces of Be are plagioclases, micas, pyroxenes and clay minerals. Coal combustion, Cu rolling, non-ferrous metal smelting, Al smelting and rock dust are sources of beryllium. BeO ceramics are used for their high thermal conductivity and good electrical insulation properties (Reimann & Caritat, 1998).

Some descriptive statistics of the beryllium content in top soil in Oslo are shown in Table 2. A geochemical map is shown in Figure 3. Concentrations of beryllium in the analysed samples of topsoil of Oslo are generally low and lie between 0.617 and 10.9 mg/kg. Beryllium has high and significant correlation values with Al, Co, Cr, Fe, K, Li, Mg, Sc, V and

Y. The factor analysis places beryllium together with most of these elements in the first factor. Anthropogenic sources beside coal combustion are probably few. Natural sources are dominating for beryllium in Oslo.

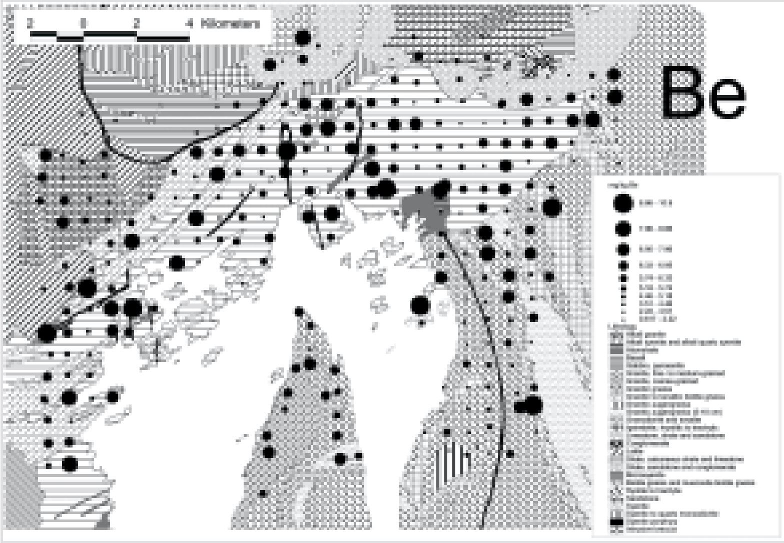

Figure 3. Acid soluble beryllium in top soil of Oslo

4 Calcium

Calcium is a major nutrient and is essential for most organisms. It is non-toxic. One can find calcium in many minerals. The most important minerals are calcite ($CaCO_3$), gypsum ($CaSO_4.2H_2O$) and fluorite (CaF_2). Possible host minerals which can contain traces of Ca are carbonates, feldspars, pyroxenes and amphiboles. Calcium is very mobile under weathering. The element is used in lime, cement, fertilisers and in metallurgy as reducer, deoxidiser and desulphuriser. Generally geologic sources are more important than anthropogenic ones (Wedepohl, 1969, Reimann & Caritat, 1998).

In topsoil in the Oslo area (Table 2 and Figure 4), calcium correlates with strontium. Strontium is a trace element in many calcium containing minerals. Correlation of calcium with other elements is very low. Sources of calcium in Oslo are probably mainly natural.

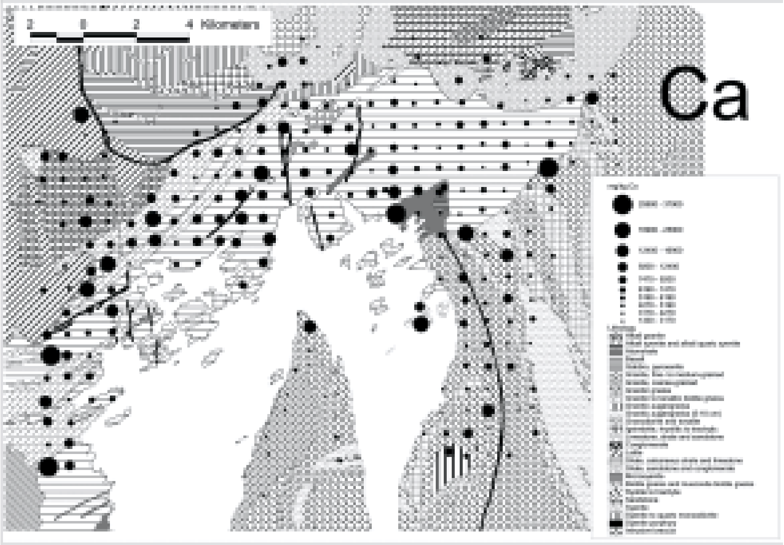

Figure 4. Acid soluble calcium in top soil of Oslo

5 Cerium

Cerium is considered non-essential and has generally low toxicity. Toxicity of the Rare Earth Elements (REE) decreases as atomic number increases. Inhaled Ree probably cause pneumoconiosis. REE taken up orally accumulate in the skeleton, teeth, lungs, liver and kidneys. Cerium is most abundant of all REE and can replace Ca in biological processes. Typical minerals containing cerium are monazite ($(Ce,La,Nd,Th,Y)(PO_4SiO_4)$), bastnaesite ($(Ce,La,Y)CO_3(F,OH)$, xenotime ($(Y,Ce)PO_4$), allanite ($(Ca,Ce,La)_2FeAl_2Osi_3O_{11}(OH)$) and cerite ($(Ce,La)_9(Mg,Fe)Si_7(O,OH,F)_{28}$). Minerals which can contain traces of Ce are feldspars, apatite, sphene, fluorite and zircon. Environmental pathways are poorly understood. Windblown dust and weathering of REE bearing minerals are probably most important (Reimann & Caritat, 1998).

Some descriptive statistics of cerium and a geochemical map are shown in Table 3 and Figure 5. The distribution of cerium in topsoil in Oslo is very much the same as that of La and Y. The factor analysis places these three elements in the same factor.

Table 3. Geochemical analysis of Ce, Co and Fe (mg/kg) in surface soil of Oslo

	Cerium				Cobalt				Iron			
	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean
Centre	38.5	93.8	67.8	67.1	4.59	19.4	10.0	10.6	10100	39700	25000	25300
Ullern, Bygdøy	39.8	97.5	63.6	65.8	6.90	16.1	12.2	11.3	14500	38100	23200	23000
Vinderen, Røa	33.0	150	71.8	76.4	2.23	22.2	9.48	9.87	5420	41500	20500	21600
Sogn	39.2	105	78.5	77.0	3.06	17.4	9.40	9.43	7030	31600	21300	20500
Grefsen	51.6	260	73.1	84.6	4.48	10.5	8.58	7.88	12000	23800	17100	17300
Økern	36.7	86.5	64.2	64.7	6.39	13.6	10.9	10.1	14300	30100	24200	23400
Grorud, Furuset	<10	87.8	60.1	56.1	1.80	14.8	10.8	9.67	2200	32600	27400	23200
Oppsal, Haugerud	10.5	88.6	58.6	56.8	1.43	18.5	9.91	9.49	2800	37700	19450	19800
Ekeberg, Nordstrand	44.6	72.6	53.5	56.1	5.04	14.5	9.83	9.94	11800	31300	18500	20900
Bøler, Bjørndal	35.6	92.3	66.4	63.2	3.55	19.2	11.0	10.4	7870	37200	26200	23200
Holmlia, Kolbotn	39.8	92.4	64.5	64.5	2.61	12.4	7.63	7.78	11900	25200	17950	18400
Nesodden	54.3	108	80.6	80.8	7.38	13.6	9.70	10.0	18200	32300	25300	24600
Stabekk, Fornebu	43.7	81.3	67.7	65.0	7.88	16.0	10.6	10.9	12900	30100	21150	22000
Asker	47.0	140	68.8	69.9	6.63	26.4	10.2	12.2	16000	50200	23500	25900
Sandvika	43.5	125	59.0	67.1	5.01	29.5	10.8	12.1	12600	37600	21550	22400
Rykkinn, Bærums Verk	46.1	111	69.5	68.1	<1	12.2	8.68	8.02	6330	23700	17900	17700
Østerås	27.3	93.9	65.9	62.9	1.56	16.0	8.42	8.74	7400	34600	19550	20300
Oslo	<10	260	65.9	67.4	<1	29.5	9.74	9.98	2200	50200	21100	21900

These elements have natural associations within pegmatites, monazite veins, carbonatites and phosphorites. Biotite, feldspars, pyroxenes and apatite are possible host minerals for these elements. Sources for cerium in the topsoil of Oslo are probably geological.

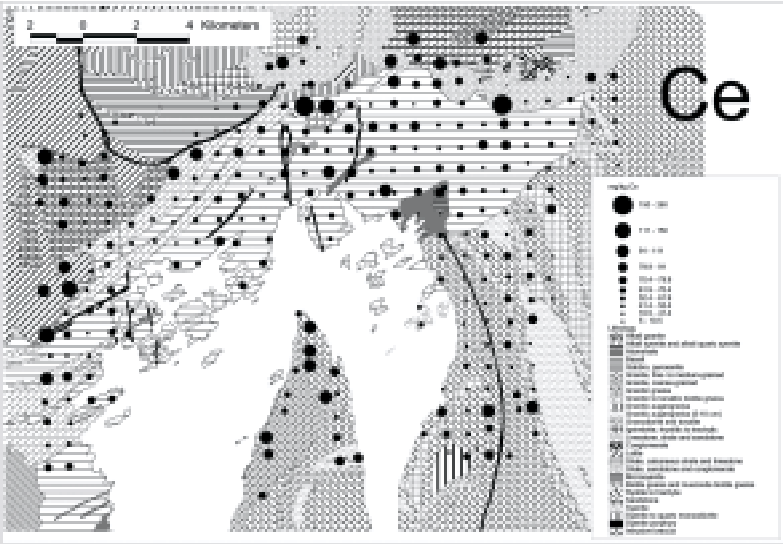

Figure 5. Acid soluble cerium in top soil of Oslo

6 Cobalt

Cobalt is essential to humans but toxic at doses of 25 mg/day or more. Cobalt is essential in vitamin B_{12} (Friberg, et. al., 1986). Possible host minerals are olivine, pyroxenes, amphiboles, micas, garnets, pyrite and sphalerite (Reimann & Caritat, 1998). Environmental pathways are Ni, Ag, Pb, Cu, Fe mining and processing, coal combustion, geological dust, weathering and fertilisers (Reimann & Caritat, 1998). The Norwegian authorities do not have a Norm value for Co. The Dutch Target value for soil is 20 mg/kg (VROM, 1994).

Descriptive statistics and the distribution of cobalt in Oslo are shown in Table 3 and Figure 6. Only 7 samples of soil in the Oslo area exceed the Target value. The factor analysis associates cobalt with Sc, Fe, Li, Al, Cr, Be, K, Ni, V, Mg and As. This indicates that cobalt in the investigated area has a natural source. The highest values of Co are situated in the western and northern parts of the city, in which limestones, shales and sandstones are the dominating minerals. Cobalt in the Oslo area is not an environmental problem.

Figure 6. Acid soluble cobalt in top soil of Oslo

7 Lanthanum

Lanthanum is considered non-essential. Toxicity is generally low. It is a trace element in minerals such as apatite, titanite and epidote (Kofstad, 1992). Y is also a trace elements in these minerals (Wedepohl, 1969). Typical minerals are monazite ($(Ce,La,Nd,Th,Y)(PO_4SiO_4)$), bastnaesite ($(Ce,La,Y)CO_3(F,OH)$, cerite ($(Ce,La)_9(Mg,Fe)Si_7(O,OH,F)_{28}$) and allanite ($(Ca,Ce,La)_2FeAl_2OSi_3O_{11}(OH)$). All these minerals also contain Ce and some of these Y. Environmental pathways are geologic dust and mining and processing of alkaline rocks. Geologic sources are generally more important than anthropogenic ones.

Table 4 shows some descriptive statistics of lanthanum. Figure 7 shows a geochemical map.

Table 4. Geochemical analysis of K, La and Li (mg/kg) in surface soil of Oslo

	Potassium				Lanthanum				Lithium			
	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean
Centre	1970	6130	4140	4160	16.9	44.5	31.3	30.8	8.82	33.3	18.7	18.6
Ullern, Bygdøy	1640	4770	2970	3220	16.3	43.4	28.2	28.5	11.8	30.0	17.3	18.6
Vinderen, Røa	762	6290	2610	2830	14.7	52.2	32.6	32.2	4.66	27.5	18.6	17.3
Sogn	795	6080	2890	3070	18.6	57.0	37.2	36.5	4.01	41.2	15.7	17.6
Grefsen	998	4610	2500	2580	24.8	104	32.8	37.2	7.30	18.9	13.1	13.4
Økern	1940	5470	4100	3980	17.2	38.9	29.0	29.7	9.82	26.2	20.1	18.7
Grorud, Furuset	695	5780	4115	3790	2.87	37.8	27.4	24.9	<1	25.0	18.1	16.8
Oppsal, Haugerud	951	6460	3210	3180	2.39	40.2	25.6	24.3	<1	25.8	15.9	15.9
Ekeberg, Nordstrand	978	6520	2560	3050	17.3	32.8	24.1	23.9	9.76	26.9	16.1	16.0
Bøler, Bjørndal	956	6040	4210	3550	15.5	40.9	30.9	28.3	2.55	38.2	21.0	19.0
Holmlia, Kolbotn	829	4380	2660	2830	18.6	43.6	29.8	28.8	1.79	23.0	14.0	14.2
Nesodden	2200	4780	3220	3370	21.6	68.3	33.2	37.2	15.6	30.9	21.2	21.3
Stabekk, Fornebu	1680	6780	3290	3510	19.2	37.8	28.4	28.2	9.60	27.0	19.1	18.0
Asker	2380	6960	3450	3670	18.0	56.3	29.2	29.5	13.5	52.0	22.4	24.4
Sandvika	658	5910	2725	3050	13.4	59.2	23.6	28.1	8.19	38.4	16.6	18.4
Rykkinn, Bærums Verk	1170	3640	2260	2260	18.7	55.2	29.3	30.1	1.35	36.1	13.8	14.4
Østerås	638	5140	3025	3270	11.5	41.4	27.3	28.1	3.89	30.0	16.1	17.2
Oslo	638	6960	3130	3260	2.39	104	29.2	29.7	<1	52.0	17.3	17.9

The factor analysis places La together with Ce and Y in the third factor. Concentrations are highest in the northern, the eastern and southern parts of the area. It is anticipated that lanthanum in the Oslo area will have geological origin.

Figure 7. Acid soluble lanthanum in top soil of Oslo

8 Manganese

Manganese is essential for all organisms and is non-toxic. Just a few percent is absorbed by the human body. Iron deficiency causes higher uptake. The highest concentrations are found in the liver and kidneys. Concentrations in the brain are usually low, but with exposure over longer time, manganese can be accumulated. This can lead to an incurable disease much like Parkinsons disease. Many minerals contain manganese. Possible host minerals are among others garnets, olivine, pyroxenes, amphiboles, micas, calcite and dolomite (Friberg, et. al., 1986). Uses are widespread. It is used in steel, alloys, batteries, fertilisers, pigment, wood preservative, antiknock agent in gasoline (as a replacement for Pb in unleaded gasoline). Some environmental pathways are rock weathering, windblown dust, agriculture, traffic, mining and smelting (Reimann & Caritat, 1998).

Table 5. Geochemical analysis of Mg, Mn and Mo (mg/kg) in surface soil of Oslo

	Magnesium				Manganese				Molybdenum			
	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean
Centre	4110	9360	5580	6040	157	621	412	410	<1	45.2	2.42	6.26
Ullern, Bygdøy	4190	10400	6890	6790	270	917	438	471	<1	10.4	1.41	1.95
Vinderen, Røa	1770	13900	6150	5930	99.3	1420	522	645	<1	4.74	2.14	2.43
Sogn	791	20500	5380	6020	207	730	443	449	<1	2.45	1.34	1.34
Grefsen	2210	6960	5070	4810	242	2230	442	541	<1	5.50	1.46	1.57
Økern	3480	7810	6150	5810	287	585	445	429	<1	1.70	1.32	1.21
Grorud, Furuset	698	7670	6245	5530	85.0	720	472	445	<1	2.20	1.25	1.21
Oppsal, Haugerud	793	8890	5695	5350	153	706	420	437	<1	3.83	1.05	1.28
Ekeberg, Nordstrand	2280	10100	5800	5750	251	778	422	454	<1	29.5	1.34	2.97
Bøler, Bjørndal	1760	9060	6210	5630	166	968	477	529	<1	2.88	1.12	1.07
Holmlia, Kolbotn	981	6870	5260	4860	71.4	543	347	343	<1	3.72	1.37	1.43
Nesodden	4610	7320	5560	5730	215	1710	513	640	<1	7.12	1.71	2.03
Stabekk, Fornebu	3940	11600	6710	7060	277	685	412	419	<1	3.54	1.21	1.26
Asker	4230	22500	6750	8230	240	1300	496	563	<1	2.94	<1	<1
Sandvika	2730	24700	6755	8220	190	1050	437	515	<1	4.41	1.35	1.46
Rykkinn, Bærums Verk	751	9870	5315	5240	243	785	371	428	<1	6.81	<1	<1
Østerås	815	10200	6190	5940	181	1000	466	463	<1	3.77	1.43	1.43
Oslo	698	24700	6040	6140	71.4	2230	438	486	<1	45.2	1.31	1.79

Some descriptive statistics of manganese in Oslo are shown in Table 5 and a geochemical map in Figure 8. As can be seen manganese in topsoil has low correlation with other elements. Manganese has a correlation coefficient of about 0.4 with Al, Be, Ce, Co, Fe, La and Li. The factor analysis manganese has its highest loading in the last factor but have also relative high loadings in the first and third factor which probably have geologic origin. Other elements in the last factor with relative high loadings are As, Cd, Pb and Zn elements which probably have anthropogenic sources. Concentrations are lowest in the central parts of the city. Concentrations are highest in areas with gneisses, syenite, granodiorite and tonalite. Sources of manganese in Oslo are probably both geologic and anthropogenic.

Figure 8. Acid soluble manganese in top soil of Oslo

9 Molybdenum

The geochemical distribution of molybdenum in igneous rocks is characterised by a preference for late products of magmatic fractionation. We can find concentrations of molybdenum associated with granites, syenites and their pegmatites, nearly always as the mineral molybdenite (MoS_2). The occurrence of molybdenum, however, is not restricted solely to such residual magmas as granites, syenites or nepheline syenites. Small amounts of molybdenite are sometimes found in basic gabbroid magmas such as norites, where it is a minor constituent. The concentration of molybdenum in certain black shales is fairly pronounced but the distribution is very erratic (Goldschmidt, 1954). Other sources for molybdenum are oil and coal combustion, phosphate fertilisers, sewage sludge and phosphate detergents.

In Oslo, (Table 5 and Figure 9) levels of molybdenum are highest in the northern and south-eastern areas in which the dominating rock types are syenite and granitic gneisses. In these areas molybdenum probably has natural sources. In the centre of Oslo, elevated levels of molybdenum in some samples may be coursed by human activity. The Norwegian authorities do not have a Norm value for molybdenum. Four samples exceed the Dutch Target value of 10 mg/kg.

Figure 9. Acid soluble molybdenum in top soil of Oslo

10 Sodium

Minerals containing sodium are albite ($NaAlSi_3O_8$), halite ($NaCl$), soda (Na_2CO_3) and major rock forming minerals such as plagioclases, micas, amphiboles and pyroxenes. Also sea spray contains Na. This has an effect on the sodium content of soil in areas near the coast (Wedepohl, 1969).

Some descriptive statistics of the sodium content in surface soil in Oslo and a geochemical map are shown i Table 6 and Figure 10. The factor analysis places sodium together with Ti, Zr, V, Mg and Ca. Although human activity such as road salting, can have an effect on the sodium content in surface soil in Oslo, geogenic sources are most probably dominating in this area.

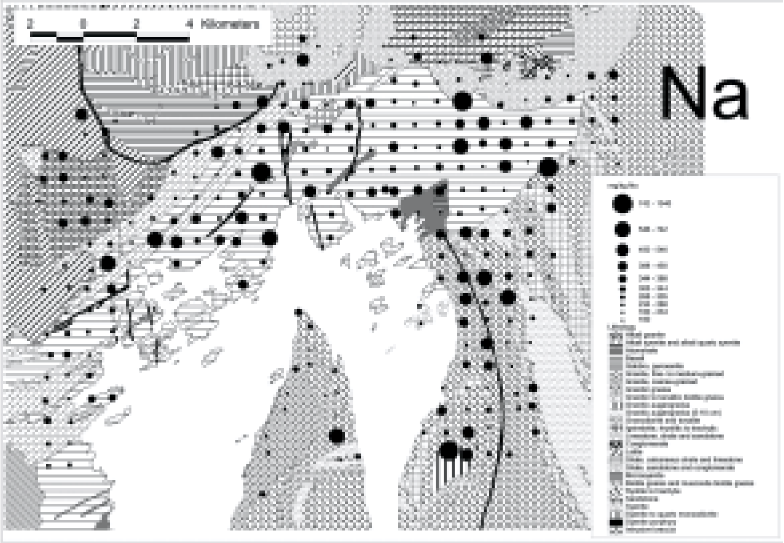

Figure 10. Acid soluble sodium in top soil of Oslo

11 Phosphorus

The bulk of phosphorus occurs from apatite($Ca_5(PO_4,CO_3)_3(F,OH,Cl)$). Other minerals containing phosphorus are monazite ($(Ce,La,Nd,Th,Sm)(PO_4,SiO_4)$), xenotime ($YPO_4$) and many other phosphates. One can find traces of phosphorus in minerals such as olivine, garnets, pyroxenes, amphiboles, micas and feldspars (Goldschmidt, 1954). Minerals containing phosphorus have low solubility in water. Availability for animals and plants is therefore low. Use of phosphorus is widespread.

Table 6. Geochemical analysis of Na, P and Sc (mg/kg) in surface soil of Oslo

	Sodium				Phosphorus				Scandium			
	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean
Centre	255	432	356	349	538	6180	1610	1900	2.06	8.00	4.75	4.85
Ullern, Bygdøy	220	924	310	356	651	1640	1060	1100	2.80	6.94	5.08	4.89
Vinderen, Røa	<200	532	281	308	339	2570	1080	1170	1.21	8.05	4.21	4.43
Sogn	234	392	288	289	579	1610	974	1070	1.61	7.98	4.41	4.35
Grefsen	229	838	298	363	508	2410	1010	1070	2.38	4.37	3.66	3.51
Økern	218	583	299	350	548	1730	996	1040	2.51	5.79	4.52	4.56
Grorud, Furuset	<200	424	319	313	546	2210	909	1050	0.482	6.49	4.41	4.08
Oppsal, Haugerud	218	742	305	334	684	1900	900	1010	0.683	7.45	3.80	4.07
Ekeberg, Nordstrand	209	546	342	370	449	1500	938	1010	2.15	7.05	3.86	4.14
Bøler, Bjørndal	202	640	281	298	343	1250	872	862	1.96	7.01	4.70	4.28
Holmlia, Kolbotn	216	1040	316	358	567	1630	835	945	1.59	5.37	3.62	3.60
Nesodden	204	577	276	289	445	1270	763	869	3.90	7.28	4.67	5.14
Stabekk, Fornebu	263	673	364	376	610	1900	1085	1130	3.30	7.10	5.35	5.01
Asker	211	382	281	287	290	3460	843	1020	3.21	13.5	5.38	5.84
Sandvika	208	650	303	349	537	1840	1135	1140	2.40	11.2	4.71	5.16
Rykkinn, Bærums Verk	218	474	319	322	597	1710	1125	1110	1.15	6.78	3.66	3.71
Østerås	<200	512	303	309	294	2040	1060	1050	1.12	6.87	4.22	4.30
Oslo	<200	1040	306	328	290	6180	994	1080	0.482	13.5	4.40	4.52

Fertilisers, detergents, insecticides, herbicides, fungicides, pyrotechnics and matches contain phosphorus. Phosphorus is also used in chemical industry (Wedepohl, 1969).

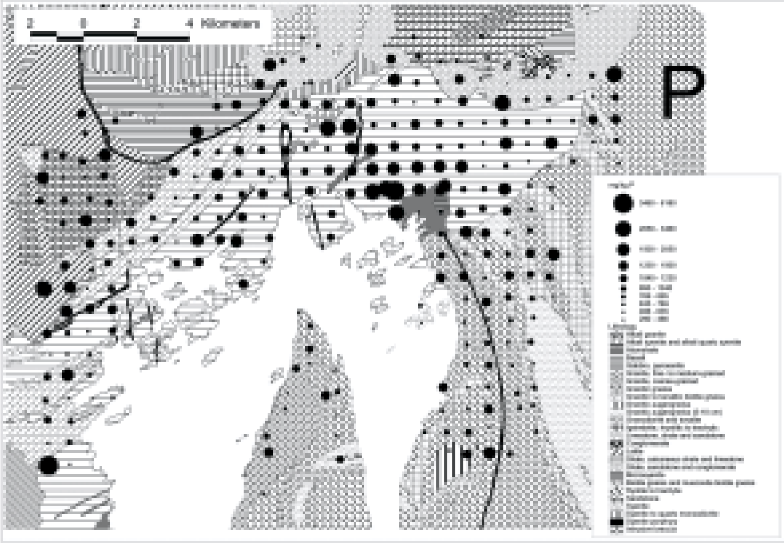

Figure 11. Acid soluble phosphorus in top soil of Oslo

The distribution of phosphorus in surface soil in Oslo is shown in Figure 11 and Table 6. Phosphorus correlates with Ba, Cd, Cu, Hg, Pb and Zn. Also the factor analysis places these elements in the same factor. In Oslo, phosphorus might have some natural background, but human activity is probably the main source for this element.

12 Strontium

Strontium is considered non-essential for most organisms. Strontium-90 is highly radiotoxic especially when it replaces calcium in organisms. Strontium is a trace element in calcium containing pyroxenes and amphiboles. Other host minerals are plagioclases, apatite, titanite, feldspars, micas, calcite and dolomite. Strontium is used in alloys, colour television tubes, pyrotechnic materials, ferrite magnets, and in zinc refining. Sources for strontium are weathering, geologic dust and sea spray.

Nuclear tests and accidents are sources for radiogenic strontium (Reimann & Caritat, 1998, Wedepohl, 1969, Kofstad, 1992).

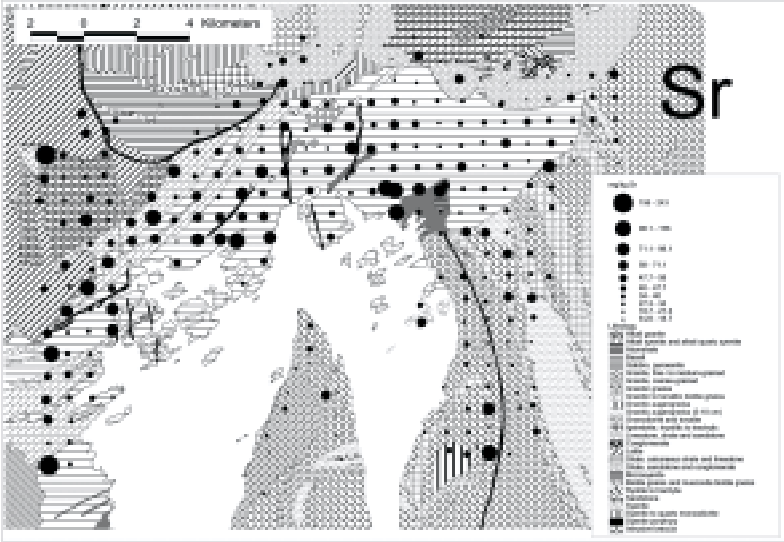

Figure 12. Acid soluble strontium in top soil of Oslo

In Oslo (Table 7 and Figure 12), strontium has only high and significant correlation with calcium. Also the factor analysis places these two elements in the same factor. Because of this, and the fact that strontium can replace calcium in calcium containing minerals, it can be concluded that sources of strontium in Oslo are mainly geologic. Strontium levels are moderate, but highest in central and western parts of the city.

13 Titanium

A few minerals are the carriers of titanium in practically all the various magmatic rocks: ilmenite ($FeTiO_3$), rutile (TiO_2), sphene ($CaTiSiO_5$) titaniferous magnetite and a few silicates which in certain special magmatic rocks contain titanium, for example, titaniferous amphiboles, biotites and andadrite. There are also some minerals which contain titanium together with an essential amount of an alkali metal found only in rocks rich in sodium. Ilmenite can be host mineral for a variety on ions.

Table 7. Geochemical analysis of Si, Sr and Ti (mg/kg) in surface soil of Oslo

	Silicon				Strontium				Titanium			
	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean
Centre	<100	167	126	114	29.8	131	54.5	63.8	212	974	541	596
Ullern, Bygdøy	<100	232	118	113	23.3	81.5	44.1	48.5	435	3480	785	1070
Vinderen, Røa	<100	388	126	130	20.9	70.6	42.8	43.8	415	1550	747	832
Sogn	<100	383	119	141	9.24	68.4	37.8	39.0	273	926	693	671
Grefsen	<100	338	119	127	18.6	63.2	36.6	36.7	346	1750	736	897
Økern	<100	149	<100	<100	23.7	62.1	36.1	40.3	408	1350	677	811
Grorud, Furuset	<100	465	<100	<100	11.9	58.6	40.7	37.8	199	1150	811	798
Oppsal, Haugerud	<100	441	121	146	12.0	83.5	39.1	37.8	240	2480	755	842
Ekeberg, Nordstrand	<100	218	135	129	9.23	70.6	39.1	40.3	191	1550	789	873
Bøler, Bjørndal	<100	203	108	106	10.6	71.0	36.1	35.2	468	2310	799	854
Holmlia, Kolbotn	<100	368	117	115	9.88	104	32.8	37.8	164	1830	763	849
Nesodden	<100	204	117	110	11.2	67.7	24.7	26.9	455	1500	737	815
Stabekk, Fornebu	<100	199	104	111	26.3	136	56.9	61.6	446	3040	946	1180
Asker	<100	224	110	104	21.9	156	45.3	53.7	45.9	1000	629	616
Sandvika	<100	221	118	114	22.3	121	56.8	59.8	287	6340	852	1380
Rykkinn, Bærums Verk	<100	366	104	110	29.1	243	42.7	55.8	713	2600	1090	1140
Østerås	<100	225	108	107	11.6	80.5	45.3	43.3	450	1910	843	956
Oslo	<100	465	113	116	9.23	243	41.2	45.2	45.9	6340	777	887

For ferrous iron small amounts of divalent magnesium, nickel, cobalt, zinc and manganese may be substituted. Vanadium may replace titanium. Ilmenite is the dominant titanium mineral in gabbros and basic nepheline rocks (Goldschmidt, 1954).

Some descriptive statistics of titanium are shown in Table 7 and a geochemical map is shown in Figure 13. The factor analysis places titanium together with Na, Zr, V, Ca and Mg. These elements are often associated in the minerals like pyroxenes, amphiboles, micas, garnets, ilmenite and rutile. Geogenic sources are therefore probably dominating for the titanium content in surface soil in Oslo.

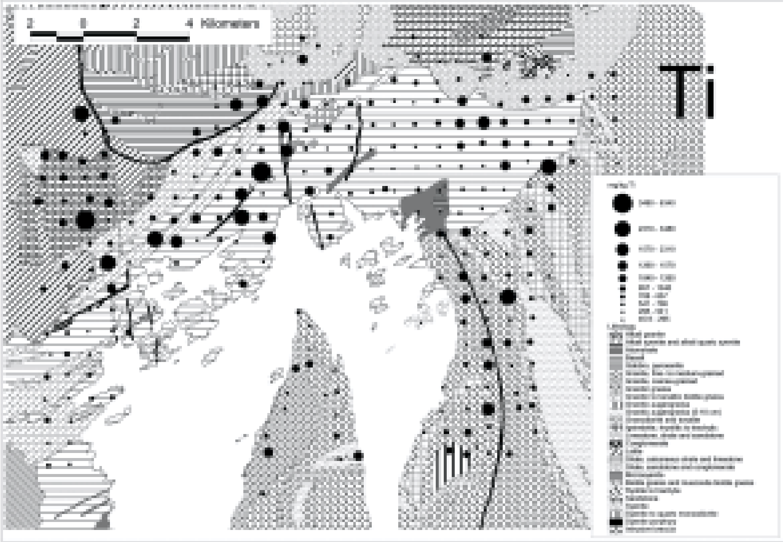

Figure 13. Acid soluble titanium in top soil of Oslo

14 Yttrium

Yttrium is considered non-essential and has generally low toxicity, but seems to have a higher acute toxicity than REE. Typical minerals containing Y are monazite ($(\text{Ce,La,Nd,Th,Y})(\text{PO}_4\text{SiO}_4)$), bastnaesite ($(\text{Ce,La,Y})\text{CO}_3(\text{F,OH})$, xenotime ($(\text{Y,Ce})\text{PO}_4$), euxinite ($(\text{Y,Ca,Ce,U,Th})\text{Nb,Ta,Ti})_2\text{O}_6$) and yttrialite ($(\text{Y,Th})_2\text{Si}_2\text{O}_7$). Possible host minerals are feldspars, apatite, pyroxenes and biotite. Geologic sources are thought to be more important than anthropogenic ones (Reimann & Caritat, 1998).

Some descriptive statistics of yttrium and a geochemical map are shown in Table 8 and Figure 14. The distribution of yttrium in topsoil in Oslo is very much the same as for Ce and La. The factor analysis places these three elements in the same factor. Since these elements can be found together in several minerals, both in typical and host minerals, sources of yttrium are probably mainly geologic.

Figure 14. Acid soluble yttrium in top soil of Oslo

15 Zirconium

Zirconium is considered non-essential for organisms and data on toxicity to humans are scarce. Host minerals which can contain traces of zirconium are pyroxenes, amphiboles, micas, garnets, ilmenite and rutile (Reimann & de Caritat, 1998).

Table 8. Geochemical analysis of V, Y and Zr (mg/kg) in surface soil of Oslo

	Vanadium				Yttrium				Zirconium			
	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean	Min.	Max.	Med.	Mean
Centre	21.9	101	62.0	61.5	7.65	17.3	12.5	12.6	6.58	21.0	8.45	9.90
Ullern, Bygdøy	29.5	82.6	55.5	54.0	7.71	18.3	11.8	11.6	5.02	21.1	9.40	10.4
Vinderen, Røa	12.3	82.1	50.9	49.2	5.51	19.3	11.9	12.1	3.31	25.4	6.81	8.30
Sogn	22.1	69.5	47.3	47.4	7.74	16.9	14.4	12.8	1.42	16.1	7.15	8.04
Grefsen	25.0	54.6	44.5	41.7	7.81	25.2	11.4	12.0	1.90	14.6	6.60	7.12
Økern	27.9	69.1	54.4	52.5	8.15	15.6	12.6	11.8	6.03	25.4	8.02	9.96
Grorud, Furuset	13.7	65.2	54.6	48.2	1.41	15.7	10.8	10.2	1.29	16.8	8.57	8.61
Oppsal, Haugerud	13.5	76.0	49.3	47.7	1.44	18.5	9.35	10.1	1.03	28.1	5.96	7.64
Ekeberg, Nordstrand	31.5	71.2	51.9	48.7	5.23	14.8	10.7	10.1	2.79	10.9	7.25	7.18
Bøler, Bjørndal	18.0	74.6	57.2	49.6	6.82	19.2	11.9	11.3	1.51	29.4	7.26	9.39
Holmlia, Kolbotn	17.9	60.8	42.1	42.2	5.32	14.2	11.0	10.7	1.08	50.9	6.77	9.24
Nesodden	44.0	78.3	59.4	62.2	7.40	27.3	14.7	15.2	5.01	12.7	6.63	7.84
Stabekk, Fornebu	41.5	74.6	54.5	56.4	8.81	16.6	12.1	12.1	4.80	21.0	11.0	11.7
Asker	33.7	89.7	55.3	56.4	4.61	19.7	12.3	12.2	3.89	22.3	8.02	9.27
Sandvika	25.4	113	58.7	58.6	7.82	15.5	11.1	11.7	2.01	22.2	9.50	10.4
Rykkinn, Bærums Verk	24.6	64.4	45.2	46.5	2.95	23.7	10.6	10.8	5.31	12.9	8.56	8.14
Østerås	18.5	67.4	50.4	47.0	3.67	18.0	11.6	11.5	2.94	16.8	9.24	9.30
Oslo	12.3	113	51.9	51.3	1.41	27.3	11.5	11.7	1.03	50.9	7.96	8.99

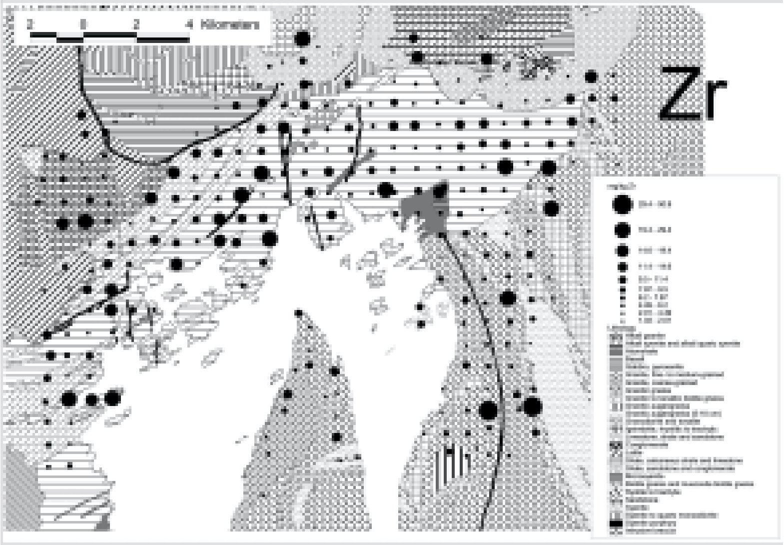

Figure 15. Acid soluble zirconium in top soil of Oslo

Descriptive statistics and a geochemical map of zirconium are shown in Table 8 and Figure 15. In Oslo, zirconium correlates with Ti, Na, V, Ca, and Mg. These elements are often associated in the same minerals. Zirconium in surface soil of Oslo has therefore most probably geogenic sources.

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Appendix B:

Conference abstracts

Urban Geochemistry - Oslo

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Urban geochemistry, investigation of contaminated land and ground water pollution is of current interest and highly prioritised in the EU. The relevance of risk for several key issues has been evaluated in the EU and Norway. At a scale of 0 (almost no risk) to 3 (high risk), the average relevance for contaminated land is 2,50 and for groundwater pollution 2,75. No other issue has such high values.

The city of Oslo is situated centrally in the Oslo-graben, which is a Permian rifting basin consisting of different kinds of volcanic and sedimentary rocks. The investigated area covers about 500 km^2. Approximately 300 samples of surface soil (2-3 cm) were taken systematically, one per square kilometre. Samples were dissolved in 7 N HNO_3 and analysed for 29 elements with ICP-AES, mercury with cold-vapour technique and arsenic and cadmium with a graphite furnace.

A factor analysis has been accomplished. The first factor contains elements like Sc, Al, Fe, Mg, Ni, Cr and As. These elements are typical for the minerals in the area and have a normal distribution. Sources for this factor are probably geological. The second factor contains Cd, Hg, P, Zn, Cu, Ba and Pb. They have a log-normal distribution and probably have anthropogenic sources. Factor 3, 4 and 5 with elements like Ca, Na, La and Sr probably have geologic sources. Factor 6 contains only Mn. Manganese may be derived from many different sources like rock weathering, windblown dust, agriculture and traffic. Mn has therefore probably both a geologic and anthropogenic origin.

Values of the elements in the second factor are much higher in the central parts of Oslo, than in the rest of Oslo. The median value of Hg in the centre is 0,48 mg/kg, which is eight times higher than that in the rest of the city. Also, the other elements have much higher levels. The industrial district north-east of the centre has also high values. The distribution of As is regular through the whole city but has a slightly higher level in the centre. More than 80% of the samples contain more As and 61% more Cr than the

Norm value for contaminated land used by the Norwegian authorities, and will therefore be regarded as polluted. Factor analysis places these elements in the geologic factor. 40% of the samples contain more Zn and 35% more Pb than the Norm value. Road traffic is probably the major source.

The Urban Geochemistry of Oslo

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Keywords: urban geochemistry, inorganic pollution, surface soil

Abstract

The city of Oslo is situated centrally in the Oslo-graben, which is a Permian rifting basin consisting of different kinds of volcanic and sedimentary rocks. In the summer of 1998, approximately 300 samples of surface soil (2-3 cm) were taken systematically, one per square kilometre. The investigated area covers about 500 km^2. Samples were dissolved in 7 N HNO_3 and analysed for 29 elements with ICP-AES, mercury with AAS-cold-vapour technique and arsenic and cadmium with a graphite furnace. A factor analysis has been compleated. The first factor contains the elements Sc, Fe, Li, Co, Al, Cr, Be, K, Ni, V, Mg, As, Ba, Y, Zr and Mn. These elements are typical for the minerals in the area and most of these elements have a normal distribution. Sources for this factor are probably geological. The second factor contains Cd, Hg, P, Zn, Cu, Ba and Pb. They have a log-normal distribution and probably have anthropogenic sources. Values of these elements are generally much higher in the central parts of Oslo, than in the rest of Oslo. Factor 3, 4 and 5 with elements like Ca, Na, La, Ti and Sr probably have geologic sources. Factor 6 contains Mn, As and Cd. Since As and Mn are placed in both factor 1 and 6 they probably have both a geologic and anthropogenic sources.

1 Introduction

Urban geochemistry, investigation of contaminated land and ground water pollution are of current interest in the European Union. Research in these areas is highly prioritised. The relevance of risk for several key issues has been evaluated in the EU and Norway. At a scale of 0 (almost no risk) to 3 (high risk), the average relevance for contaminated land is 2,50 and for groundwater pollution 2,75. No other issue has such high values.

In Norway, research on urban areas has been low. In the city of Trondheim, in the middle of Norway samples of top soil are taken and analysed for about 30 elements. Geochemical maps are published and the results of this investigation are used in city planning and other areas (Ottesen et al., 1995). Recently the city of Bergen in south-western Norway has started the same kind of investigation (Ottesen & Volden, 1999). Oslo is the capital city of Norway with a population of about 700.000. The city is about 1000 years old, but the population has been low until the last 50-100 years. Most industry is located in the north-eastern part of the city. In former days, small scale mining of sulphide minerals was widespread in the northern part of the city.

2 Locations and Material

The city of Oslo is situated centrally in the Oslo-graben, which consists of an approximately 250x50 km area of Permian volcanic rocks and Cambro-Silurian sedimentary rocks in a rifted Precambrian terrain. The investigated area is about 500 km^2 and can be divided into four parts. The south-eastern area is part of the Precambrian terrain. It is named the Østfold complex and originates from the early and middle Proterozoic area. It consists of granitic gneisses. The central part of the area contains sedimentary rocks from the Cambrian to the Silurian period. The northern part of the investigated area contains intrusive rocks of Permian age for example quartz syenite and monzodiorite. Finally the north-eastern part is of Carboniferous and Permian age and contains volcanic rocks such as basalt and rhomb-porphyry and sedimentary rocks such as shale, sandstone and conglomerate. (Berthelsen and Sundvoll, 1996).

The Precambrian terrain in the southern and eastern parts of the area continues through to Sweden and Finland. The geological history of the terrain is very complex. The rocks have been metamorphosed and deformed several times during mountain forming processes. The dominant rocks in this area are gneisses of different types, mostly granitic. The minerals that can be found are quartz, feldspar and dark minerals such as amphiboles and biotite. Pegmatite bodies or veins up to a metre broad are usual. (Dons, 1977).

Shale, calcareous shale, limestone and sandstone are the most common rock types in the central and south-western parts of the city. These rocks are from the Cambro-Silurian period. The terrain is low and the soil is usually thicker than in the Precambrian area. The Cambro-Silurian rocks are layered with a total thickness of about 1500 metres. (Dons, 1977).

There are no sedimentary rocks from the Devonian and Early Carboniferous periods. During this interval the Cambro-Silurian strata of the Oslo region were folded, most probably during a late phase of the Caledonian orogeny in Devonian time, and peneplanation followed. Immediately above the peneplain but below the Permian basal lava, in the north of the area, one can find sedimentary rocks from the Middle and Late Carboniferous period. It comprises silty and sandy calcareous mudstones, shales, sandstones and conglomerates. (Henningsmoen, 1978).

The northern part of the investigated area is from the Permian period. In this period volcanic activity was widespread in the Oslo area. The Permian strata rest on the peneplaned and more or less weathered surface of the sedimentary rocks of the Cambro-Silurian period. In the beginning of the Permian period, dark mafic lava was floating over the area from north-south oriented large shield volcanoes. Later in this period the lava became more felsic and formed rhomb-porphyric layers. Much of this lava is eroded through time, but can still be found in cauldrons. Igneous rocks in this area are types of gabbro called Oslo-essexite, which contain light feldspar and dark pyroxenes or hornblende. Other types of igneous rocks are granite and syenite. The border areas between eruptive rocks and Cambro-Silurian rocks has been influenced by contact metamorphism. In these areas one can find hornfels and marble. In former days, the mining of minerals like magnetite, galena, chalcopyrite, sphalerite and pyrite was widespread in this area. (Dons, 1977).

Approximately three hundred samples of surface soil were taken. To achieve an even coverage of the area, samples were taken systematically one per square kilometre. Samples of about 0,5-1 kg were taken by cutting a 20 x 10 cm section of surface soil with a spade. A knife was used to exclude the soil from depth below 2-3 cm. Analysis was carried out by the Geological Survey of Norway (NGU).

The material was dried at a temperature of about 35°C for four days and sieved through a 2 mm nylon screen. Samples were extracted in 7 N HNO_3 in a autoclave in accordance to Norwegian Standard - NS 4770. The elements Ag, Al, B, Ba, Be, Ca, Ce, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sc, Si, Sr, Ti, V, Y, Zn and Zr were determined in this solution by ICP-AES analysis. Mercury was analysed by atom-absorption analysis, cold-vapour technique AA/HMS. Arsenic and cadmium were determined by the graphite furnace technique. (NGU, 1998)

Table 1. Descriptive parameters of thirty-two elements in surface soil from Oslo.

Element	Min. (mg/kg)	Max. (mg/kg)	Median (mg/kg)	Mean (mg/kg)	Number < det. Limit	Skewness	Kurtosis	Norm value (mg/kg)	Number > norm value
Ag	<1	3.20	<1	<1	289				
Al	2080	43200	17200	17468		0.443	0.850		
As	<3	69.6	4.50	5.48	61	6.490	62.635	2*	236**
B	<5	22.9	6.98	7.56	76	0.968	0.983		
Ba	23.0	1350	115	131		8.141	104.229		
Be	0.617	10.9	5.54	5.52		0.145	0.222		
Ca	1330	37900	6280	7375		3.213	15.113		
Cd	0.06	3.10	0.34	0.41		3.831	24.513	1	11
Ce	<1	260	65.9	67.4	1	2.871	23.698		
Co	<1	29.5	9.74	9.98	1	1.153	4.134		
Cr	2.85	224	28.5	32.5		4.604	30.168	25	181
Cu	4.76	437	23.5	31.7		6.787	57.018	100	9
Fe	2200	50200	21100	21852		0.420	1.300		
Hg	<0.010	2.30	0.06	0.13	14	5.514	36.550	1	4
K	638	6960	3130	3258		0.257	-0.426		
La	2.39	104	29.2	29.7		1.845	11.128		
Li	<1	52.0	17.3	17.9	2	0.748	2.289		
Mg	698	24700	6040	6145		2.470	12.931		
Mn	71.4	2230	438	486		2.811	13.219		
Mo	<1	45.2	1.31	1.79	94	9.804	114.111		
Na	<200	1040	306	328	4	2.342	10.084		
Ni	2.23	232	24.1	28.4		4.688	30.822	60	15
P	290	6180	994	1082		3.981	32.196		
Pb	<5	1000	33.9	55.6	5	7.342	64.325	50	103
Sc	0.482	13.5	4.40	4.52		1.221	5.134		
Si	<100	465	113	116	103	1.808	5.438		
Sr	9.23	243	41.2	45.2		2.912	16.825		
Ti	45.9	6340	777	887		4.367	33.727		
V	12.3	113	51.9	51.3		0.175	1.057		
Y	1.41	27.3	11.5	11.7		0.618	2.293		
Zn	22.9	1150	130	160		3.695	22.821	150	119
Zr	1.03	50.9	7.96	8.99		2.894	15.946		

* The detection limit of the analysis is 3 mg/kg. ** Number > 3 mg/kg

3 Results

Table 1 shows a statistical summary of the thirty-two elements in surface soil from the investigated area.

Table 2: Factor analysis of chemical data of surface soil in Oslo

Rotated Factor Matrix		Factor					
Element	Communality	1	2	3	4	5	6
Sc	0,936	**0,939**	0,009	0,166	0,040	0,157	0,008
Fe	0,898	**0,917**	0,105	0,173	0,104	-0,073	-0,011
Li	0,888	**0,905**	-0,029	0,229	-0,109	0,062	-0,011
Co	0,906	**0,875**	0,032	0,019	0,296	0,111	0,198
Al	0,827	**0,867**	0,012	0,272	-0,006	-0,036	-0,022
Cr	0,876	**0,814**	-0,020	-0,122	-0,193	0,320	0,242
Be	0,762	**0,793**	0,107	0,304	0,106	-0,134	-0,012
K	0,842	**0,791**	0,093	0,183	0,015	-0,054	-0,414
Ni	0,828	**0,790**	-0,020	-0,119	-0,193	0,316	0,227
V	0,851	**0,784**	0,153	0,179	**0,419**	-0,056	0,024
Mg	0,875	**0,775**	-0,079	-0,044	**0,314**	**0,346**	0,221
As	0,235	**0,327**	0,139	-0,039	0,100	-0,004	**0,312**
Cd	0,759	-0,119	**0,775**	0,109	-0,028	0,084	**0,352**
Hg	0,599	0,054	**0,730**	-0,045	-0,125	0,116	-0,182
P	0,614	0,071	**0,716**	0,196	0,062	0,224	0,061
Zn	0,609	0,077	**0,711**	0,116	0,091	-0,010	0,275
Cu	0,509	0,079	**0,616**	0,067	0,042	0,269	-0,212
Ba	0,624	**0,379**	**0,567**	0,169	-0,060	-0,260	-0,245
Pb	0,396	-0,164	**0,479**	-0,299	0,067	-0,124	0,173
La	0,914	0,139	0,104	**0,939**	-0,020	-0,024	0,020
Ce	0,933	0,115	0,118	**0,938**	0,040	0,034	0,153
Y	0,813	**0,513**	0,078	**0,703**	0,130	0,121	-0,130
Ti	0,832	-0,038	-0,100	-0,030	**0,882**	0,124	0,165
Na	0,670	0,032	0,158	-0,009	**0,784**	0,170	-0,013
Zr	0,619	**0,352**	-0,104	0,151	**0,630**	0,140	-0,212
Ca	0,797	0,078	0,226	-0,058	**0,376**	**0,771**	-0,003
Sr	0,720	0,234	0,302	0,189	0,238	**0,689**	-0,082
Mn	0,743	**0,346**	0,126	**0,439**	-0,064	-0,100	**0,634**
Variance explained (%)		31,2	43,3	54,3	63,3	69,7	74,6

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalisation.

A factor analysis has been compleated. Values below the detection limit were replaced by half this limit. Arsenic has many values below the detection limit. 61 samples contain less than 3 mg/kg. Nevertheless As is included in the factor analysis because of its toxicity. A factor analysis without As did not produce results which varied greatly for the other elements. Table 2 shows the results of the factor analysis.

One can find the elements of the first factor in minerals like amphiboles, pyroxenes, micas, chlorites and feldspars. These minerals are probably the sources for this factor. Arsenic is part of this factor but has a very low communality. This low communality is probably because of many samples with values below detection limit. Most of the elements in this factor have a normal distribution, which also points in the direction of a geologic origin.

The compounds of the second factor have probably an anthropogenic origin. The elements have a log-normal distribution which also points in the direction of anthropogenic sources. Concentrations in soil in the central and industrial parts of the area are generally higher than in the rest of the city. Barium is part of this factor, but has also a moderate loading in the first factor. In the Oslo area Ba probably has both natural and anthropogenic sources.

The elements in factor three are all members of group IIIb of the periodic system of elements and have biotite, feldspars, pyroxenes and apatite as possible host minerals. The distribution of these elements is almost normal. Also factor four and five are probably of geologic origin.

The last factor contains Mn, and has also relatively high loadings on As and Cd. The elements of this factor probably have an anthropogenic origin. However, Mn has relatively high loadings in the geological factors 1 and 3. As this element has many environmental pathways for example rock weathering, windblown dust, agriculture and traffic, it is probable that the Mn is of both geologic and anthropogenic origin. The last 2 factors explain only about 5 % each of the total variance in the data, so conclusions about their origin must therefore be taken with care.

The Norwegian Pollution Control Authority uses Norm values for Contaminated Land to determine whether contaminated land poses a serious threat to public health. (SFT, 1995). Norm values and the number of samples which exceed these values are shown in Table 1. The detection limit of As is 3 mg/kg. The Norm value of the Norwegian authorities is 2 mg/kg. The number of samples exceeding the Norm value is probably much higher than 236, and will therefore be regarded as polluted. About 61% contain more Cr than the Norm value. Factor analysis places these elements in the geologic factor, with low and negative loading on the anthropogenic factor. It is questionable if these samples are polluted or if the elements are bound strongly into the crystal structure of the minerals and thus represent no danger. 40% of the samples contain more Zn and 35% more Pb than the Norm value. Road traffic is a major source for these elements.

4 Discussion

In Oslo, human activity has lead to high concentrations of the elements Cd, Cu, Hg, P, Pb and Zn in the surface soil. As, Ba and Mn have geological sources, but human activity has also affected the content of these elements in the soil. Geological sources dominate the other elements.

Levels of Hg are moderate throughout the whole area, but in the central districts median concentrations are 8 times higher than in the rest of the city. Also the values of Cd, Cu, P, Pb and Zn are much higher in the central parts of Oslo and in the industrial district north-east of the centre.

The distribution of As is regular through the whole city but has a slightly higher level in the centre. More than 80% of the samples contain more than 2 mg/kg As and 61% more than 25 mg/kg Cr. These are Norm values for contaminated land used by the Norwegian authorities and all samples will therefore be regarded as polluted. Factor analysis places the elements in the geologic factor, most probably that which is incorporated in the mineral structure. Bio-availability of the elements is probably low, and it is by now not certain if they represent a danger for the environment.

The Norm value of zinc is 150 mg/kg. 40% of the samples have a higher level than the Norm value. Regarding lead, 35% of the samples contain more than the Norm value of 150 mg/kg Pb. Road traffic is probably the major source for these elements.

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The Arsenic Content of Urban Topsoil in Oslo, Norway – A Sequential Analysis Procedure

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Abstract

The city of Oslo is situated centrally in the Oslo-graben, which is a Permian rifting basin consisting of different kinds of volcanic and sedimentary rocks. In the summer of 1998, approximately three hundred samples of surface soil (2-3 cm) were taken systematically, one per square kilometre. The investigated area covers about 500 km^2. Samples were dissolved in 7 N HNO_3 and analysed for 29 elements with ICP-AES, mercury with cold-vapour technique (CV-AAS) and arsenic and cadmium with a graphite furnace (GF-AAS). The elements Ba, Cd, Cu, Hg, P, Pb and Zn have anthropogenic sources. One of the sources is probably road traffic. In Norway studded tyres are frequently used in the winter season which results in large amounts of road dust. Leaded petrol has been a major source for Pb but is not in use any more. Wear and tear of tyres and brakes also contributes to this factor. Other sources contributing to these elements are probably industry, garbage incineration, crematoria and release of some of these elements from structural material by fire. The elements As and Mn probably have both geologic and anthropogenic sources.

Most studies dealing with metals in soil systems concern total metal concentration. However, availability of metals to organisms is not dependent on the total amount of a metal which is present in the soil but rather how it is actually stored within the soil. One would like to measure concentrations in soil solutions over time but these are often below the detection limits of the analysis. To avoid this problem one can measure concentrations in the soil. However, instead of measuring the total

concentration of the different elements, a sequential extraction of the soil can tell us more about the stability and mobility of the elements.

In the summer of 1999 additional samples were taken near traffic ores and on playgrounds at schools and kindergartens in the centre of the city. An additional problem at kindergartens is the use of arsenic impregnated wood in climbing frames and sandpits. Therefore samples were taken both of the lawn and near playing equipment.

A sequential extraction, which consists of five fractions was accomplished for these samples. At stage one the samples were dissolved in 1 M $MgCl_2$ at 37°C for 20 hours. At this stage the exchangeable ions will go in solution. The elements bound to carbonates are extracted in fraction two. The residue soil of stage one was leached with NaAc adjusted to pH 5.0 with HAc at 37°C for 20 hours. The elements bound to Fe-Mn oxides are extracted at stage three. Here the residue of stage two was added 0.04 M $NH_2OH{\bullet}HCl$ in 25% HAc at 85°C. The residue of stage three was added a 3 ml of 0.02 M HNO_3 and 8 ml of 30% H_2O_2 adjusted to pH 2.0 with HNO_3 at 85°C for 6 hours. After cooling 5 ml 3.2 M NH_4Ac in 20% HNO_3 was added and diluted to 20 ml and agitated continuously for 14 hours. The addition of NH_4Ac is to prevent adsorption of the extracted metals onto the oxidized sediment. At this stage the metals bound to organic matter are extracted. Finally the residue of stage four was added concentrated HNO_3 at 85°C for 20 hours. The extractions were conducted in centrifuge tubes to minimize losses of solid material. The analysis of the extractions is still in progress and the results will be presented at the conference.

The Inorganic Composition of Topsoil in the City of Oslo, Norway

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Abstract:

The city of Oslo is situated centrally in the Oslo-graben, which is a Permian rifting basin consisting of different kinds of volcanic and sedimentary rocks. In the summer of 1998, approximately three hundred samples of surface soil (2-3 cm) were taken systematically, one per square kilometre. The investigated area covers about 500 km^2. Samples were dissolved in 7 N HNO_3 and analysed for 29 elements with ICP-AES, mercury with cold-vapour technique (CVAAS) and arsenic and cadmium with a graphite furnace (GFAAS).

To describe the covariant relationships among the elements, a factor analysis has been completed. The first factor contains the elements Sc, Fe, Li, Co, Al, Cr, Be, K, Ni, V, Mg, Y, Ba, Zr, Mn and As. These elements are typical for the minerals in the area and most of these elements have a near normal distribution. Sources for this factor are probably geological. The second factor contains Cd, Hg, P, Zn, Cu, Ba and Pb. They have a log-normal distribution and probably have anthropogenic sources. Factors 3, 4 and 5 with elements such as Ca, Na, La, Ti and Sr probably have geologic sources. Factor 6 contains Mn, As and Cd. Manganese may be derived from many different sources such as rock weathering, windblown dust, agriculture and traffic. Since As and Mn are placed in both factor 1 and 6 they probably have both geologic and anthropogenic sources.

Values of the elements in the second factor are much higher in the central parts of Oslo, than in the rest of Oslo. The median value of Hg in the centre is 0.48 mg/kg, which is eight times higher than that in the rest of the city. Also, the other elements have much higher levels in the centre. The industrial district north-east of the centre also has high values. The

distribution of arsenic is regular throughout the whole city, but has a slightly higher level in the centre. Norm values for contaminated land used by the Norwegian authorities are 2 mg/kg As and 25 mg/kg Cr. Of 297 samples, 61% contain more than 25 mg/kg Cr and 79% more than 3 mg/kg As, which is the detection limit of the analysis. These samples will therefore be regarded as polluted. Factor analysis places these elements in the geologic factor. The Norm value of zinc is 150 mg/kg. 40% of the samples contain more Zn. 35% of the samples contain more lead than the Norm value of 150 mg/kg. Road traffic is probably the major source for these elements.

1 Introduction

The topics urban geochemistry, investigation of contaminated land and ground water pollution are currently of great interest in the European Union. Research in these areas is given high priority. The relevance of risk for several key issues has been evaluated in the EU and Norway. At a scale of 0 (almost no risk) to 3 (high risk), the average relevance for contaminated land is 2.50 and for groundwater pollution 2.75. No other issue has such high values (Follestad, 1997).

In Norway, there has been little research on the geochemistry of urban areas. In the city of Trondheim, situated in the middle of Norway samples of top soil have been taken, analysed for about thirty elements and the results presented in the form of geochemical maps. The results of this investigation are currently being used in city planning and other areas (Ottesen et al., 1995, Tijhuis, 1996). Recently the same kind of investigation has been carried out in the city of Bergen in south-western Norway (Ottesen & Volden, 1999). Oslo is the capital city of Norway with a population of about 700,000. The city is about a thousand years old, but the population has been much smaller until the last 50-100 years. Most of the industry is located in the north-eastern part of the city. In former days, small scale mining of sulphide minerals was widespread in the northern part of the city.

2 Area description

The city of Oslo is situated centrally in the Oslo-graben, which consists of an approximately 250x50 km area of Permian volcanic rocks and Cambro-Silurian sedimentary rocks in a rifted Precambrian terrain. The investigated area is about 500 km^2 and can be divided into four parts. The south-eastern area is part of the Precambrian terrain. It is named the Østfold complex and originates from the early and middle Proterozoic area. It consists of granitic gneisses. The central part of the area contains sedimentary rocks from the Cambrian to the Silurian period. The northern part of the investigated area contains intrusive rocks of Permian age such as quartz syenite and monzodiorite. Finally the north-western part is of Carboniferous and Permian age and contains volcanic rocks such as basalt and rhomb-porphyry and sedimentary rocks such as shale, sandstone and conglomerate (Berthelsen and Sundvoll, 1996).

3 Methods

3.1 Sampling and sample preparation

Approximately three hundred samples of surface soil were taken. To achieve an even coverage of the area, samples were taken systematically one per square kilometre. The co-ordinates of one point were chosen at random and all other samples were taken at a distance of one kilometre in both east-west and north-south directions. In cases where no adequate material was present the nearest point with soil was chosen. Samples were taken by cutting a 20 x 10 cm section of surface soil with a spade. A knife was used to exclude the soil from depth below 2-3 cm. The weight per sample was about 0.5-1 kg. The material was dried at a temperature of about 35°C for four days. Samples were afterwards sieved through a 2 mm nylon screen.

3.2 Analysis

The extraction procedure used was accomplished in accordance to Norwegian Standard - NS 4770 (NSF, 1994). 1.000 g of each sample was extracted in 20 ml 7 N HNO_3 in borosilicate bottles. Generated gas in samples, rich in organic matter and carbonate was released from the bottles before they were covered with a screw cap. Bottles were placed into an autoclave filled with water and heated on a hot-plate. Generated air was lead through the water by a plastic hose until the temperature had reached 96 °C. After this the temperature was raised to 120 °C and held at this temperature in 30 minutes. The pH of the water was measured to see if there had been leakage of fluid out of the bottles. Samples were stored over night and 24 hours after addition of acid samples were filtrated through a fluted filter and diluted with double distilled and ion exchanged water to 100 ml. For analysis of mercury the extract was diluted with a fluid containing 50 ml concentrated HNO_3 + 0.1 g $K_2Cr_2O_7$ to 1000 ml distilled water. The elements Ag, Al, B, Ba, Be, Ca, Ce, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sc, Si, Sr, Ti, V, Y, Zn and Zr were determined by ICP-AES analysis. For all these elements the total uncertainty for the extraction and the analysis is estimated to ± 10 rel.%. Mercury was analysed by atom-absorption analysis, cold-vapour technique (CVAAS). The uncertainty for the analysis is estimated to ± 10 rel.%. Arsenic and cadmium were determined by the graphite furnace technique (GFAAS). The uncertainty is ± 20 rel.% for arsenic and ± 10 rel.% for cadmium. Control samples were analysed (NGU, 1998).

4 Results and discussion

The results of the chemical analysis of the surface soil samples are presented in Table 1.

To describe the covariant relationships among the elements, a factor analysis has been completed. Table 2 shows the results of the factor analysis. The elements with many values below the detection limit have been omitted. These elements are Ag, B, Mo and Si. For elements with only a few values below the detection limit, these values are replaced by half this limit. Arsenic has many values below the detection limit and 61 samples contain less than 3 mg/kg As. The communality of arsenic, which is the portion of the variance of this element contributed by the factors, is rather low. Nevertheless arsenic is included in the factor analysis because of its toxicity. A factor analysis without arsenic did not produce results which varied greatly for the other elements.

Table 1. Descriptive parameters (mg/kg) of thirty-two elements in surface soil from Oslo.

	Minimum	Maximum	Median	Mean
Ag	<1	3.20	<1	<1
Al	2080	43200	17200	17468
As	<3	69.6	4.50	5.48
B	<5	22.9	6.98	7.56
Ba	23.0	1350	115	131
Be	0.617	10.9	5.54	5.52
Ca	1330	37900	6280	7375
Cd	0.06	3.10	0.34	0.41
Ce	<1	260	65.9	67.4
Co	<1	29.5	9.74	9.98
Cr	2.85	224	28.5	32.5
Cu	4.76	437	23.5	31.7
Fe	2200	50200	21100	21852
Hg	<0.010	2.30	0.06	0.13
K	638	6960	3130	3258
La	2.39	104	29.2	29.7
Li	<1	52.0	17.3	17.9
Mg	698	24700	6040	6145
Mn	71.4	2230	438	486
Mo	<1	45.2	1.31	1.79
Na	<200	1040	306	328
Ni	2.23	232	24.1	28.4
P	290	6180	994	1082
Pb	<5	1000	33.9	55.6
Sc	0.482	13.5	4.40	4.52
Si	<100	465	113	116
Sr	9.23	243	41.2	45.2
Ti	45.9	6340	777	887
V	12.3	113	51.9	51.3
Y	1.41	27.3	11.5	11.7
Zn	22.9	1150	130	160
Zr	1.03	50.9	7.96	8.99

Factor 1 contains the elements Sc, Fe, Li, Co, Al, Cr, Mg, Ni, V, Be, K, Y and Mn (listed with decreasing communality) and has moderate loadings on As, Zr, Ba and Sr. Minerals such as amphiboles containing e.g. Al, Fe, Mg, Ni, Li, Co and Cr, pyroxenes containing e.g. Mg, Fe, Mn, Li and Al, micas containing e.g. Fe, Mg, Al, K and Li, chlorites containing e.g. Al, Mg, Ni, Mn, Li and Fe and feldspars containing e.g. Al, Na and K could be contributing to this factor. Arsenic is part of this factor but has rather low communality. This low communality is probably because the 61 samples with values below the detection limit have been set to 1.5 mg/kg. Most of the elements in this factor have a normal distribution.

The second factor contains the elements Cd, P, Zn, Hg, Cu, Ba, Pb and has moderate loadings on Sr. These elements are not very usual in geologic materials and probably have an anthropogenic origin. Road traffic is in this context of great importance. In Norway studded tyres are frequently used in the winter season and their wear on the road surface creares large amounts of road dust. Pedersen (1990) shows that road dust contain increased levels of Cd, Cr, Cu, Pb and Zn. Leaded petrol has been a major source for Pb but is not in use any more. Wear and tear of tyres contribute Zn and Cd. Wearable parts on brakes e.g. disc pads contain Cu and Zn. Other source contributing to this factor may be industry, garbage incineration, crematoria and release of some of these elements from structural material by fire. Barium is part of this factor, but has also a moderate loading in the first factor, and has consequently probably both natural and anthropogenic origin. Elements in the second factor have a log-normal distribution.

Factor 3 contains the elements Ti, Na, Zr, V, Ca, Mg, Co and has moderate loadings on Sr, Y, Fe and Be. These elements are usual in minerals like pyroxenes containing e.g. Mg, Fe, Ti, Ca and Na, amphiboles containing e.g. Mg, Ca, Na and Co, micas containing e.g. Fe and Mg, garnets containing e.g. Mg, Fe and Ca, ilmenite containing e.g. Fe and Ti and rutile (Reimann & de Caritat, 1998).

Factor 4 contains the elements La, Ce, Y, Mn, Be, Al, Li, Fe and has moderate loadings on Sc, V and K. The first three are all members of group IIIb of the periodic system of elements and have natural associations with pegmatites, monazite veins, carbonatites and phosphorites. Biotite, feldspars, pyroxenes and apatite are possible host minerals. Geologic sources for these elements are often more important than anthropogenic ones (Reimann & de Caritat, 1998). This factor is therefore most likely geological.

The fifth factor contains Mn, and has also relatively high loadings on Cd, Zn, As and Pb. The elements of this factor probably have an anthropogenic origin. However, Mn has relatively high loadings in the geological factors 1 and 3. As this element has many environmental pathways such as rock weathering, windblown dust, agriculture and traffic, it is probable that the Mn is of both geologic and anthropogenic origin.

Table 2: Factor analysis of chemical data of surface soil in Oslo

Element		Factor					
	Comm	1	2	3	4	5	6
Sc	0.936	**0.95**			**0.40**		
Fe	0.898	**0.91**		0.23	**0.40**		
Li	0.888	**0.91**			**0.44**		
Co	0.906	**0.91**		**0.42**	0.24		
Al	0.827	**0.87**			**0.48**		
Cr	0.876	**0.85**					-0.26
Mg	0.875	**0.83**		**0.43**			**-0.33**
Ni	0.828	**0.83**					-0.25
V	0.851	**0.80**	0.21	**0.53**	**0.39**		
Be	0.762	**0.79**		0.22	**0.50**		
K	0.842	**0.74**			**0.38**		
As	0.235	**0.36**				0.26	
Cd	0.759		**0.79**			**0.37**	
P	0.614		**0.74**		0.26		-0.24
Zn	0.609		**0.73**			0.26	
Hg	0.599		**0.72**				
Cu	0.509		**0.62**				-0.30
Ba	0.624	**0.35**	**0.57**		0.30		
Pb	0.396		**0.46**			0.23	
Ti	0.832			**0.87**			-0.20
Na	0.670			**0.80**			-0.25
Zr	0.619	**0.36**		**0.68**	0.24		
La	0.914				**0.95**		
Ce	0.933				**0.95**		
Y	0.813	**0.55**		0.23	**0.81**		
Mn	0.743	**0.43**			**0.52**	**0.53**	
Ca	0.797		0.26	**0.44**			**-0.81**
Sr	0.720	**0.32**	**0.35**	**0.33**	0.27		**-0.70**
Var. (%)		35.3	47.9	57.8	65.8	70.5	74.6

Extraction Method: Principal Component Analysis
Rotation Method: Oblimin with Kaiser Normalisation

The last factor is also probably of geologic origin. It contains both Ca, Sr, and Mg, all members of group IIa. These elements are associated in minerals and are part of sea dust. Sr can replace Ca in minerals (Reimann & de Caritat, 1998). The last two factors explain only about 5% each of the total variance in the data, so conclusions about their origin must be taken with care.

5 Conclusions

In Oslo, human activity has lead to high concentrations of the elements Cd, Cu, Hg, P, Pb and Zn in the surface soil. As, B, Ba and Mn have geological sources, but human activity has also affected the content of these elements in the soil. Geological sources dominate the other elements.

Levels of Hg are moderate throughout the whole area, but in the central districts median concentrations are 8 times higher than in the rest of the city. Also the values of Cd, Cu, P, Pb and Zn are much higher in the central parts of Oslo and in the industrial district north-east of the centre.

The distribution of arsenic is regular through the whole city but has a slightly higher level in the centre. Norm values for contaminated land used by the Norwegian authorities are 2 mg/kg As and 25 mg/kg Cr. 61% of the samples contain more than 25 mg/kg Cr and 79% more than 3 mg/kg As, which is the detection limit of the analysis. All these samples will therefore be regarded as polluted. These Norm values are rather low especially since it is not known if the chromium is present as Cr^{3+} or as Cr^{6+}. Factor analysis places the elements in the geologic factor, most probably that which is incorporated in the mineral structure. Bio-availability is probably low, and it is at present uncertain that these elements represent a danger for the environment. A study of the bio-availability of arsenic in soil, especially at schoolyards, playgrounds and kindergartens is desirable and is planned in the near future.

The Norm value of zinc is 150 mg/kg. 40% of the samples have a higher level than the Norm value. Regarding lead, 35% of the samples contain more than the Norm value of 150 mg/kg. Road traffic, industry and incineration are probably the major sources for these elements.

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The Inorganic Composition of the Topsoil in the City of Oslo, Norway

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Urban geochemistry, investigation of contaminated land and ground water pollution is of current interest and highly prioritised in the EU. The relevance of risk for several key issues has been evaluated in the EU and Norway. At a scale of 0 (almost no risk) to 3 (high risk), the average relevance for contaminated land is 2,50 and for groundwater pollution 2,75. No other issue has such high values.

The city of Oslo is situated centrally in the Oslo-graben, which is a Permian rifting basin consisting of different kinds of volcanic and sedimentary rocks. The investigated area covers about 500 km^2. Approximately 300 samples of surface soil (2-3 cm) were taken systematically, one per square kilometre. Samples were dissolved in 7 N HNO_3 and analysed for 29 elements with ICP-AES, mercury with cold-vapour technique and arsenic and cadmium with a graphite furnace.

A factor analysis has been accomplished. The first factor contains elements like Sc, Al, Fe, Mg, Ni, Cr and As. These elements are typical for the minerals in the area and have a normal distribution. Sources for this factor are probably geological. The second factor contains Cd, Hg, P, Zn, Cu, Ba and Pb. They have a log-normal distribution and probably have anthropogenic sources. Factor 3, 4 and 5 with elements like Ca, Na, La and Sr probably have geologic sources. Factor 6 contains only Mn. Manganese may be derived from many different sources like rock weathering, windblown dust, agriculture and traffic. Mn has therefore probably both a geologic and anthropogenic origin.

Values of the elements in the second factor are much higher in the central parts of Oslo, than in the rest of Oslo. The median value of Hg in the centre is 0,48 mg/kg, which is eight times higher than that in the rest of the city. Also, the other elements have much higher levels. The industrial district north-east of the centre has also high values. The distribution of As is regular through the whole city but has a slightly higher level in the centre.

More than 80% of the samples contain more As and 61% more Cr than the Norm value for contaminated land used by the Norwegian authorities, and will therefore be regarded as polluted. Factor analysis places these elements in the geologic factor. 40% of the samples contain more Zn and 35% more Pb than the Norm value. Road traffic is probably the major source.

Levels of Trace Elements and a Sequential Extraction of Arsenic in Topsoil and Sand from Sandboxes at Playgrounds in Oslo, Norway.

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Introduction

Many studies dealing with metals in soil systems concern focus on metal concentration. However, availability of metals to organisms is not dependent on the total amount of metal present in the soil, but rather how it is actually stored within the soil. To assess the content of trace elements and their biological availability, samples of topsoil and sand from sandboxes were taken at twenty-four playgrounds in the central districts of Oslo. The total acid soluble concentration of seven elements was determined. In addition, aliquots from a sequential extraction was analyzed for arsenic.

Methods

Samples of topsoil were taken by cutting a 20x10 cm section of surface soil with a spade. A knife was used to exclude the soil from depth below 2-3 cm. Samples of sand from sandboxes were taken in the near vicinity of playing equipment, made of impregnated wood. The total acid (conc. HNO_3) soluble concentration of As, Cd, Cr, Cu, Ni, Pb and Zn was determined. In addition a sequential extraction procedure, based on Tessier et al. (1979), which yields an I) “exchangeable”, II) “carbonate”, III) “reducible substrate”, IV) “organic” and V) “residual” fraction, was performed for arsenic.

Results and discussion

Total acid soluble concentrations of all the analyzed elements are higher in topsoil samples than in sand from sandboxes (Table 1). However, the differences in concentrations of arsenic between topsoil and sandbox samples are small. At about half the playgrounds, concentrations of at least one of the elements Cr, Cu, Ni, Pb and Zn exceed the “Norm”-value (SFT, 1995) in the soil samples. At two playgrounds, all elements, except Cd, exceed the “Norm"-value. In all topsoil samples the concentrations of arsenic exceed the “Norm”-value for polluted soil used by the Norwegian authorities. At 15 of 24 playgrounds, concentrations of arsenic in sand from sandboxes exceed this value. None of the sandbox samples contain more than the “Norm”-value for the other elements.

Arsenic concentrations are higher in the sandbox samples than in the samples of topsoil from the same playground in the exchangeable, the carbonate and the reducible substrate fractions (Table 2). Leakage of arsenic compounds from impregnated wood has probably caused elevated concentrations of this element in the sandbox sand. Only one playground has a higher concentration in sand from the sandbox in the organic fraction. Four playgrounds have concentrations of arsenic that are higher in the sandbox sand than in the topsoil in the residual fraction.

The cumulative arsenic content in sandbox samples exceeds the “Norm”-value of 2 mg/kg As for polluted soil already after two fractions (i.e. the exchangeable and the carbonate fraction) at two playgrounds. After three stages, the cumulative arsenic content in sand from sandboxes at five playgrounds exceeds this value. None of the topsoil samples had a cumulative arsenic content exceeding this after three stages of the sequential extraction procedure. The “Norm”-value of cumulative arsenic content after four stages was exceeded in five playgrounds with respect to sand from sandboxes and in sixteen regarding the topsoil.

Stomach acid is dissolved hydrochloric acid with a pH of 1.6 to 2.4 (Wallace et al., 1990, p. 921). These conditions are quite comparable with the conditions in stage four of the extraction procedure and the cumulative concentrations of arsenic in the first four stages can therefore be a measure of the bio-availability of the element to human beings.

Despite the fact that the concentrations of arsenic in sandbox sand generally are lower than in topsoil, the sequential analysis show that the arsenic is more easily released from the material, and the bio-availability of the element is consequently higher in the sand from sandboxes than in the topsoil.

Table 1. Descriptive statistics of total acid soluble concentrations (mg/kg), and Norwegian "Norm"-values (SFT, 1995) for polluted soil in topsoil and sandbox samples from playgrounds (n=24) in Oslo.

	Arsenic		Cadmium		Chromium		Copper		Nickel		Lead		Zinc	
	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand
Minimum	2.77	.791	.067	.012	9.87	3.16	11.4	5.68	12.3	4.83	6.01	<4.4	38.2	12.7
Maximum	14.9	13.5	.802	.298	49.4	22.9	141	25.7	87.1	28.3	185	29.9	532	79.7
Mean	6.30	4.01	.306	.068	24.5	9.72	37.1	11.7	35.6	14.5	48.4	10.6	158	34.5
Median	5.30	2.74	.269	.039	22.8	7.96	28.2	10.0	28.8	13.9	32.1	10.5	97.9	31.4
"Norm"-value	2		1		25		100		60		50		150	
No. Samples > "Norm"-value	24	15			10		2		4		8		10	

Table 2. Descriptive statistics of arsenic concentrations (mg/kg) in five fractions in topsoil and sandboxes samples, the total concentration in these five fractions and the total acid soluble concentration at playgrounds (n=24) in Oslo.

	Exchange-able fraction		Bound to carbonates		Bound to reducible substrates		Bound to organic compounds		Residual fraction		Total sequential extraction		Total acid soluble conc.	
	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand
Minimum	<.068	<.068	<.060	<.060	.110	.106	1.02	.183	1.12	.302	3.25	1.08	2.77	.791
Maximum	.363	.863	.212	1.63	.877	3.97	4.86	4.15	8.33	4.37	14.0	13.5	14.9	13.5
Mean	.185	.290	.135	.327	.428	.758	2.10	.859	3.47	1.74	6.24	3.86	6.30	4.01
Median	.152	.179	.134	.149	.408	.500	1.86	.645	2.66	1.17	5.09	2.57	5.30	2.74

Conclusions

Concentrations of all analyzed elements in topsoil samples are higher than in samples of sand from sandboxes, but differences in arsenic are small. All topsoil samples and about two-third of the sandbox samples exceed the "Norm"-value for polluted soil for arsenic. Concentrations of at least one of the elements Cr, Cu, Ni, Pb and Zn exceed the "Norm"-value in the topsoil at about half the playgrounds, and at two playgrounds all elements, except Cd, exceed this value. Arsenic concentrations in sand from sandboxes lie at a higher level than in topsoil in the "exchangeable", the "carbonate" and the "reducible substrate" fractions. The bio-availability of this element is consequently higher in sand than in topsoil.

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Appendix C:

Geochemical data

Microsoft Excel files:

- Bedrock XRF.xls:
  Bulk concentrations of 10 bedrock samples.
- Sequential Extraction.xls:
  Results of the Sequential Extraction Procedure on 99 soil and 24 sandpit samples.
- Soil and Bedrock.xls:
  Total Acid Soluble concentrations of bedrock and soil samples taken at 44 locations.
- TAS Soil and Sandpits.xls:
  Total Acid Soluble concentrations of 396 soil and 24 sandpit samples.