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Trace elements in top- and subsoil on selected crop and dairy farms in Finland in 2004

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Abstract

This study was part of a three-year (2004-2007) project entitled "Assessment and reduction of heavy metal inputs into Finnish agro-ecosystems" that was funded by the Ministry of Agriculture and Forestry in Finland. The aims of the project were to clarify: 1) *aqua regia* extractable trace elements in Finnish cultivated soils with the international standard method at a national level; 2) *aqua regia* and AAAc-EDTA extractable trace elements in the top- and subsoil of Finnish arable land on selected crop and dairy farms; and 3) field mass balances of trace elements on the same selected crop and dairy farms at the farm level.

The main aim of this investigation was to study trace element contents in the Finnish arable land on crop and dairy farms. Five farms were selected from typical crop farming area in southwestern Finland and five from typical dairy farming area in Ostrobothnia. Topsoil and subsoil samples were collected from 23 fields on the crop farms and from 21 fields on the dairy farms at the time of harvest in 2004. Trace element contents studied were arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), vanadium (V) and zinc (Zn). Total contents of these elements were determined from the top- and subsoil samples with *aqua regia* extraction (ISO 11466), except Hg which was determined by pyrolysis. In addition, the topsoil samples were analysed for the particle size distribution, bulk density, pH(H_2O), electrical conductivity, organic carbon, humus, total contents of aluminium and iron, AAAc extractable nutrients and AAAc-EDTA extractable trace elements.

The crop farms were located on clay soils and the dairy farms on finesand soils. The *aqua regia* extractable trace elements in the top- and subsoil of the clay soils at the crop farms were two to three times those of the finesand soils at the dairy farms. Most of the elements were significantly correlated with the clay content. When the AAAc-EDTA extractable trace elements were compared with the respective *aqua regia* extractable ones, solubility (%) of all the elements studied was higher in the finesand soils on the dairy farms than in the clay soils on the crop farms.

Quantitatively more Cd, Pb and Hg enriched in the clay soils on the crop farms in southwestern Finland than in the finesand soils on the dairy farms in Ostrobothnia. However, dairy farming seemed to enrich the topsoil with more Cr, Cu, Se, V and Zn than crop farming, on average. Instead, the crop farming seemed to result in depletion of some trace elements, like Cu. Trace elements of the most concern as to their enrichment and/or solubility in the topsoil seem to be Cd, Hg and Pb in both farm types. In addition, Cu, Se, Zn and V seemed to be the elements that have to be followed up on the dairy farms. Trace element sources could not be identified in this study.

It was concluded that when top- and subsoil is sampled at the same site and time, contents of *aqua regia* extractable trace elements in subsoil can be considered as natural geologic background contents for a site, local or region depending on the coverage of sampling. Furthermore, estimates on the trace element quantities enriched in the topsoil can be a good tool to assess, compare, monitor and manage impacts of different land uses and production sectors on the quality of cultivated soils.

Index words: plough layer, topsoil, subsoil, enrichment, Finland, arable land, crop farm, dairy farm, arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, vanadium, zinc

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Muokkauskerroksen ja jankon hivenalkuainepitoisuudet suomalaisilla kasvin- ja maidontuotantotiloilla vuonna 2004

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Tiivistelmä

Tutkimuksen tavoitteena oli selvittää peltomaiden muokkauskerroksen ja jankon raskasmetallipitoisuuksia sekä tuotantosuunnan vaikutusta pitoisuuksiin. Tutkimukseen valittiin viisi maatilaa tyypilliseltä kasvintuotantoalueelta lounaisesta Suomesta ja viisi maatilaa tyypilliseltä maidontuotantoalueelta Pohjois-Pohjanmaalta. Maanäytteet kerättiin muokkauskerroksesta ja jankosta 23:lta kasvinviljelytilojen ja 21:ltä maidontuotantotilojen peltolohkolta sadonkorjuun aikaan vuonna 2004.

Tutkittavat alkuaineet olivat arseeni (As), kadmium (Cd), kromi (Cr), kupari (Cu), lyijy (Pb), elohopea (Hg), nikkeli (Ni), seleeni (Se), vanadiini (V) ja sinkki (Zn). Elohopean kokonaispitoisuus määritettiin pyrolyyttisesti ja kaikkien muiden alkuaineiden kokonaispitoisuudet kuningasvesiuutosta (*aqua regia*) kansainvälisen standardimenetelmän ISO 11466:n mukaan. Muokkauskerroksen näytteistä määritettiin lisäksi hiukkaskokojakauma, tilavuuspaino, pH(H_2O), johtoluku, orgaanisen hiilen ja humuksen pitoisuus sekä alumiinin ja raudan kokonaispitoisuudet. Samoin näistä näytteistä tutkittiin happamaan (pH 4,65) ammoniumasetaattiin uuttuvat liukoiset ravinteet ja happamaan (pH 4,65) ammoniumasetaatti-EDTA:han uuttuvat liukoiset hivenalkuaineet.

Kasvinviljelytilat sijaitsivat savimailla ja maidontuotantotilat karkeilla kivennäismailla. Maalajieroista johtuen hivenalkuaineiden kokonaispitoisuudet olivat kasvinviljelytiloilla sekä muokkauskerroksessa että jankossa kaksin- tai kolminkertaisia verrattuna maidontuotantotilojen vastaaviin pitoisuuksiin. Mitä savisempaa peltomaa oli, sitä korkeampia olivat myös useimpien hivenalkuaineiden pitoisuudet. Kun alkuaineiden liukoisia osuuksia verrattiin kokonaispitoisuuksiin, kaikkien alkuaineiden liukoisuusprosentti oli suurempi maidontuotantotilojen karkeilla kivennäismailla kuin kasvintuotantotilojen savimailla.

Peltojen muokkauskerrokseen kertyi määrällisesti enemmän kadmiumia, lyijyä ja elohopeaa kasvinviljelytiloilla lounaisessa Suomessa kuin maidontuotantotiloilla Pohjois-Pohjanmaalla. Kuitenkin maidontuotanto näytti kerryttävän peltoon enemmän kromia, kuparia, seleeniä, vanadiinia ja sinkkiä kuin kasvintuotanto. Kasvintuotanto näytti johtavan jopa joidenkin alkuaineiden vähenemiseen muokkauskerroksessa. Tällainen alkuaine oli muun muassa kupari. Kun huomioidaan alkuaineen kertyminen ja liukoisuus, peltomaiden likaantumisen kannalta uhkaavimmat alkuaineet näyttävät olevan sekä kasvin- että maidontuotantotiloilla kadmium, lyijy ja elohopea. Lisäksi maidontuotantotiloilla tulisi tarkkailla kuparin, seleenin, sinkin ja vanadiinin mahdollista kertymistä. Hivenalkuaineiden lähteitä ei tässä tutkimuksessa voitu selvittää.

Kun maanäytteet otetaan peltomaan muokkauskerroksesta ja jankosta samasta paikasta ja samaan aikaan, jankon kokonaispitoisuutta voidaan suurella todennäköisyydellä pitää luonnollisena taustapitoisuutena näytepisteelle, -paikalle tai -alueelle näytteenoton kattavuuden mukaan. Vastaavasti taas alkuaineen kertymisen tai vähenemisen määrää muokkauskerroksessa voidaan pitää maan saastumisen tai köyhtymisen mittarina. Näytteiden ottaminen samaan aikaan peltomaiden muokkauskerroksesta ja jankosta näyttäisi olevan hyvä keino muun muassa maankäytön ja tuotantosuunnan vaikutusten selvittämiseen, vertailuun, seurantaan ja hallintaan.

Tutkimus oli osa vuosina 2004–2007 toteutettua, Maa- ja metsätalous-ministeriön rahoittamaa yhteistutkimushanketta ”Raskasmetallikuormitusten selvittäminen ja vähentäminen Suomen maatalousekosysteemeissä”. Hankkeen tavoitteena oli selvittää viljelymaiden raskasmetallipitoisuuksia valtakunnallisesti käyttäen kuningasvesiuuttoa. Toiseksi tutkittiin kasvinviljely- ja maidontuotantotilojen viljelymaan raskasmetallipitoisuuksia kuningasvesiuutteesta ja happan (pH 4,65) ammoniumasetaatti-EDTA -uutteesta siten, että näytteet otettiin muokkauskerroksesta ja jankosta. Lisäksi hankkeessa analysoitiin raskasmetallien tilakohtaisia peltotaseita kasvinviljely- ja maidontuotantotiloilla.

Avainsanat: muokkauskerros, jankko, rikastuminen, saastuminen, köyhtyminen, maaperä, viljelymaa, kasvintuotanto, maidontuotanto, maatilat, arseeni, kadmium, kromi, kupari, lyijy, elohopea, nikkeli, seleeni, vanadiini, sinkki

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Foreword

This study was part of a three-year (2004-2007) project entitled "Assessment and reduction of heavy metal inputs into Finnish agro-ecosystems" (acronym RAKAS, Project number 310925) that was jointly funded by the Ministry of Agriculture and Forestry in Finland (MMM) and participating organisations. The project was coordinated by MTT Agrifood Research Finland, Plant Production Research (Ritva Mäkelä-Kurtto). Also other scientific staff (Annukka Laitonen) from the same department participated in the project. Other participating organisations were MTT Laboratories (Merja Eurola), Geological Survey of Finland (Timo Tarvainen, Tarja Hatakka), Evira Finnish Food Safety Authority (Arja Vuorinen, Kimmo Suominen, Riitta Rankanen), Viljavuuspalvelu Ltd (Soil Analysis Service) (Pirkko Laakso) and Suomen Rehu Ltd (Juha Salopelto). The project was monitored by a steering committee consisting of Senior Officer Pirjo Salminen (MMM), Senior Officer Elina Nikkola (MMM), Dr. Liisa Rajakoski (Ministry of Trade and Industry in Finland), Senior Officer Titta Pasanen (Evira Finnish Food Safety Authority), Dr. Matti Verta (Finnish Environment Institute) and Dr. Kari Kiltilä (Suomen Rehu Ltd). The aims of the project were to study the:

1) 'total' content of trace elements in Finnish cultivated soils with the international standard method at a national level,

2) 'total' content of trace elements in top- and subsoil of Finnish arable land at crop and dairy farms, and the effects of the production sector on possible enrichment or depletion of the trace elements

3) field mass balances of trace elements at a farm level in crop and dairy farms.

The main aims of this study were to analyze 'total' contents of trace elements in the top- and subsoil of Finnish arable land on crop and dairy farms, and to evaluate effects of the production sector on the possible enrichment or depletion of the trace elements in soil. Soil sampling on the farms and sample pre-treatment in the laboratory was conducted by the MTT Agrifood Research Finland. The samples were analyzed for total trace element contents in the Laboratory of the Geological Survey of Finland and for soluble trace element fractions and other soil characteristics in Viljavuuspalvelu (Soil Analysis Service).

LIST OF ABBREVIATIONS

Al	Aluminium
As	Arsenic
Cd	Cadmium
Ca	Calcium
Cr	Chromium
Cu	Copper
Fe	Iron
Hg	Mercury
K	Potassium
Mg	Magnesium
Ni	Nickel
P	Phosphorus
Pb	Lead
S	Sulphur
Se	Selenium
V	Vanadium
Zn	Zinc
AR	*Aqua regia*
AAAc	Acid (pH 4.65) ammonium acetate
AAAc-EDTA	Acid (pH 4.65) ammonium acetate -EDTA
Bulk dens.	Bulk density
EDTA	Na_2-ethylenediaminetetracetic acid
El. cond.	Electrical conductivity
dm	Dry matter
fm	Fresh matter
Max	Maximum
Med	Median
Min	Minimum
n	Number
r	Correlation coefficient
Org. C	Organic carbon
OM	Organic matter
Topsoil	Plough layer

Contents

1 Introduction

Soil must be considered as a finite, non-renewable resource since its regeneration through weathering of underlying rock requires a long time. Soil is defined (CEC 2006) as the top layer of the Earth´s crust and is formed by mineral particles, organic matter, water, air and living organisms. Soil is an extremely complex, variable and living medium. Soil, the interface between the earth, the air and the water, is a non-renewable resource performing many functions vital to life, such as food and other biomass production, storage, filtration and transformation of many substances including water, carbon and nitrogen. Soil has a role as a habitat and gene pool, serves as a platform for human activities, landscape and heritage and acts as a provider of raw materials. These functions are worthy of protection because of their socio-economic and environmental importance. Soil degradation is accelerating with resulting negative effects on human health, natural ecosystems and climate change, as well as on our economy.

One of the main issues is diffuse soil contamination by heavy metals. Soils naturally contain heavy metals at detectable levels. Heavy metals may function as micro-nutrients essential to plant and/or animal growth, while high concentrations can be a threat to the food chain. The elements of the most concern are mercury, lead, cadmium and arsenic that are especially toxic to humans and animals, and copper, nickel and cobalt, which are more of a concern because of phyto-toxicity. Concentrations of heavy metals in soil cover a very wide range. In many cases, the higher values indicate contamination from human activities, although large values can occur because of natural geological or soil-formation conditions.

Cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), nickel (Ni), chromium (Cr), mercury (Hg) and vanadium (V) are chemically metals and classified as heavy metals because their specific weight is >5 kg l^{-1}. Arsenic (As) and selenium (Se), in contrast, are metalloids. Cadmium, lead and mercury are not known to be essential to living organisms or biological functions. Instead, these heavy metals can be toxic even at relatively low concentrations. However, the other trace elements mentioned are needed by organism in small concentrations although they are harmful at high concentrations (United States Public Health Service 1993). All these elements are listed as dangerous in the Dangerous Substances Directive (1976/464/EEC). Cadmium, lead, mercury and nickel are listed as priority substances in the Water Framework Directive (2000/60/EC).

Arable lands are often situated in river valleys and are usually clayey soils that differ from each other. Characteristic to all these is the abundance of the clay fraction (<0.002 mm). The soils vary in composition depending on the chemical composition of the soil parent material, on climate, on topography and on biological activity. Finland is geographically located in a cool, humid climatic zone where the amount of rainwater coming on the ground surface is greater than the evaporation. Thus, the solutions that are dissolved from the upper layers of the soil migrate downwards. The climate favours the development of podzol but the formation is a slow process and may take centuries. In arable lands, podzolization is impossible because of soil cultivation. As a whole, the subsoil samples represent geology while the topsoil samples taken from plough layer represent the influences of human activities like emissions from traffic, industry or agriculture.

Whether a concentration of an element is regarded as high or low depends on the choice of the reference material. Concentration in the topsoil can be evaluated on the basis of the prevailing composition of the subsoil. Data on the subsoil trace elements helps to one to understand the natural variation of the trace element contents in the soil compartment on a regional scale (van der Veer 2006). Distribution of most elements in soil shows a pattern related to geology and/or mineralization (de Vos et al. 2006). The ratio topsoil/subsoil at the same site and time is called an enrichment factor and can be used to determine the trace element tendencies. A correlation coefficient (Pearson´s correlation) between the top- and subsoil shows how systematic an increasing or decreasing tendency is from subsoil to topsoil: a high coefficient means that enrichment (ratio >1) or depletion (ratio <1) in topsoil occurs in large areas but a low coefficient indicates that enrichment or depletion is more erratic or applies only to certain regions or sites (De Vos et al. 2006). Enrichment of trace elements may differ between mineral and organic soils, which is mainly due to a different density and not necessary so much to a different input to these soils (Van der Veer 2006). Density effect implies that the same input of the element leads to a much stronger enrichment in soils with a low density compared to soils with a higher density.

Influences of bedrock geology and farming type on the trace element contents can be clarified roughly by comparing the distribution of the trace element contents between the top- and subsoil. Higher element contents in the topsoil may indicate trace element enrichment and the lower contents were considered to indicate depletion, respectively. The reasons for elevated trace element contents in the topsoil may be natural and/or anthropogenic. One of the biggest natural sources is volcanic dust while the main anthropogenic sources into the arable land are feed and fertilizer preparations and atmospheric depositions originating from the emissions of the industry, traffic and waste incineration. Plant uptake, leaching and erosion are the main reasons for depletion.

The highest element contents that could dissolve from the soil in the extremely acidic conditions can be estimated by extracting the soil sample with *aqua regia* (ISO 11466). At 90°C, the a*qua regia* solution (a mixture of hydrochloric acid and nitric acid, 3:1) dissolves crystal precipitate minerals, sulphide minerals and the most salts like apatite and titanite, a part of micas (biotite), talc and clay minerals. However, it does not dissolve non-weathered feldspars, amphipoles or pyroxenes. Thus, the *aqua regia* extraction did not show the real total contents of the elements, but it is generally used in the environmental trace element studies for analyzing the soil for so called “total contents”. Conversely, they cannot be regarded as the “bio-available” fraction, as the extraction procedure is too vigorous to represent any biological process. Instead, an acid (pH 4.65) ammonium acetate Na_2-ethylenediamientetracetic acid solution (AAAc-EDTA) according to Lakanen and Erviö (1971) is a much weaker extraction solution than the *aqua regia* and is used to indicate plant availability and leaching ability of the trace elements in the cultivated soils in Finland.

The main aims of this study were to analyze top- and subsoil samples collected from Finnish crop and dairy farms for trace elements and on the basis of analytical results, evaluate effects of the production sector on the enrichment of trace elements in the topsoil. In addition, topsoil was analyzed for soil type, general soil characteristics, fertility and AAAc-EDTA extractable (soluble) trace elements for interpreting the agricultural and environmental importance of the trace elements.

2 Material and methods

2.1 Farms and sampling sites

Influences of the production sector on the trace element contents of arable land were studied on five crop farms (Numbers 1-5) in southwestern Finland (Appendix 1: Fig. 1 and 2) where crop farming has been a typical production sector and on five dairy farms (Numbers 6-10) in Ostrobothnia (Appendix 1: Fig. 1 and 2) where dairy farming has been a typical production sector. In 2004, top- and subsoil samples were collected from 23 fields of the crop farms and from 21 fields of the dairy farms. The number of fields studied per farm was approximately four, but varied from three to six.

The 10 farms studied practiced typical Finnish crop or dairy farming. Trace element inputs and outputs and field mass balances of these farms were reported at a farm level by Mäkelä-Kurtto et al. (2007b). Exact geographical information or detailed descriptions of the target farms or sampling sites could not be published here due to privacy protection. According to the Commission Directive on private ownership (Directive 2003/4/EC), the farms, farmers, sampling sites and other personal or individual data must be protected and will be published in a form that the identity of the farmers or farms cannot be recognized. The project had an agreement with the farmers to keep all the information and data collected from the farm or farmers anonymous.

2.2 Soil sampling and pre-treatment

Soil sampling on the crop farms in southwestern Finland was carried out between 27.9.- 1.10.2004 and on the dairy farms in Ostrobothnia between 4.- 6.10.2004. Top- and subsoil samples were collected from 23 fields on the crop farms and from 21 fields on the dairy farms. Totally, 44 fields were sampled for top- and subsoil. The number of fields studied per farm was supposed to be five but was determined to be four and varying from three to six. A sampling site was on the same field that was sampled for the crop plant, as well. A distance of the sampling site from the railway or highway/ motorway was at least 400 m, from the road 100 m and from the electric or telephone cables 50 m.

The soil sampling and pre-treatment was carried out by the MTT that has an accredited testing laboratory (T096) and the quality system follows the requirements of the standard SFS-EN ISO/IEC 17025:2005. The sampling system was principally the same as that used for arable land in the national soil testing (Agricultural Research Centre of Finland 1986) and in the national soil monitoring programme (Sippola & Tares 1978, Erviö et al. 1990, Mäkelä-Kurtto & Sippola 2002).

Samples from the topsoil (plough layer) and subsoil were taken on each site on the same day as four sub-samples from the four corners of the 10 x 10 m sampling area. At first, the plough layer was opened carefully down to the subsoil with a spade and the depth of the plough layer was measured. After removing all plant material from the surface of the soil, a slight slice from the whole depth of the topsoil was taken with a spade for a sub-sample. The volume of the slice was about one litre. After carefully removing all the topsoil material on the subsoil, a sub-sample from the subsoil was taken with an auger (a diameter 22 mm) or a spade down to a depth of about 20 cm. The volume of subsoil sub-sample was about 0.15 litres. The four subsoil sub-samples were collected in a colourless plastic vessel, mixed there and then removed to the soil boxes (600-700 ml) made of cardboard. The four topsoil sub-samples were collected into a colourless plastic vessel of five litres. The geographical coordinates (X, Y, Z) were taken with a GPS receiver (Trimble Geo XT or Trimble ProXR) in the middle of the sampling site. A layout of each site with its surroundings was drawn in a field book.

In the laboratory, fresh top- and subsoil samples were crushed and homogenized. Fresh top- and subsoil samples were air-dried at 35°C in an oven with air circulation and homogenized. Air-dried soils were ground, avoiding disintegration of primary particles by pressing the soil with a rotating wooden disc through a 2-mm sieve of hardened steel. The sieved soils were homogenized again and stored at room temperature in cardboard boxes for analyses. Dried and sieved soil samples were sent to the Geological Survey of Finland (GTK) laboratory to analyze for *aqua regia* extractable trace elements and to the Viljavuuspalvelu for soil testing and to analysis of AAAc-EDTA extractable trace elements. In addition, unground and unsieved soil samples were sent to the Viljavuuspalvelu to determine particle size distribution.

2.3 Soil analysis methods

Soil analyses were carried out in three different laboratories. The GTK Laboratory analyzed soils for the *aqua regia* extractable trace elements. The MTT Laboratory analyzed soils for total aluminium and iron. Due to the insufficient detection limit for subsoil Se in the GTK Laboratory, the MTT Laboratory conducted Se measurements from the *aqua regia* extracts prepared by the GTK laboratory. All the other analyses were made in the Viljavuuspalvelu (Soil Analysis Service).

Soil types and general soil characteristics. The topsoil samples were analyzed for soil types, general soil characteristics, AAAc extractable nutrients and AAAc-EDTA extractable trace elements by the Viljavuuspalvelu, which is an accredited testing laboratory (T096). Particle size distribution of the air-dried, but unsieved, soil samples was determined by sieving and for finer fractions by the pipette method (Elonen 1971) based on the sedimentation. Soil classification was made according to Aaltonen et al. (1949). In addition, soil type determination was also made by senses from the air-dried and sieved soils. Organic carbon (C) content was determined with the Dumas method (Modified standard method ISO 13878:1998) assuming that the sample contained only organic carbon. The instrument was the Elementar Vario MAX CNS elemental analyzer. The humus content was obtained by multiplying the organic C content by 1.73 (Agricultural Research Centre 1986). The volume weight of the soils studied here was determined by weighing a 25 ml sample of air-dried soil passed through a 2-mm sieve (Agricultural Research Centre 1986, Viljavuuspalvelu 2000). The dry matter content was determined at 105°C for 4 h. The pH and electrical conductivity were measured from a soil-water suspension (1:2.5) (Agricultural Research Centre 1986, Viljavuuspalvelu 2000).

AAAc extractable (soluble) macro nutrients: For the air-dried samples (25 ml), 0.5 M ammonium acetate + 0.5 M acetic acid (pH 4.65, AAAc) (1:10, 1h) (Vuorinen & Mäkitie 1955) was used to extract soluble macro-elements P, Ca, K, Mg and S (Agricultural Research Centre 1986, Viljavuuspalvelu 2000). Concentrations of Ca, K, Mg and S were measured by inductively coupled plasma optic emission spectrometer (ICP-OES) and P by autoanalyzer using ammonium-molybdate complexation. Instruments were Thermo Jarrel Ash, ICAP 61 E and Lachat Instruments Quick Chem 8000, respectively. Analytical results are presented in a unit of mg l^{-1} of air-dried soil, if not mentioned otherwise.

AAAc-EDTA extractable (soluble) trace elements. For the air-dried samples (25 ml), 0.5 M ammonium acetate + 0.5 M acetic acid + 0.02 M Na_2E-DTA (pH 4.65, AAAc-EDTA) (1:10, 1h) (Lakanen & Erviö 1971) was used to extract soluble As, Cd, Cr, Cu, Ni, Pb, Se, V and Zn (Agricultural Research Centre 1986, Viljavuuspalvelu 2002). Concentrations of As, Cu, Ni and Zn were measured by inductively coupled plasma optic emission spectrometer (ICP-OES) and Cd, Cr, Pb and V with graphite furnace atomic absorption spectrometer (GFAAS) and Se with hydride flow injection atomic absortion spectrometer (FIAAS). Instruments used were the Thermo Jarrel Ash, IRIS advantage High Resolution ICP Optical Emission Spectrometer with a CID detector, Perkin Elmer SIMAA 6000 Simultaneous Multi-element AA Spectrometer, AS 72 Autosampler and for Se the Perkin Elmer Analyst 100. Analytical results are presented in a unit of mg l^{-1} of air-dried soil, if not otherwise mentioned.

The Finnish soil testing involves determinations of pH(H_2O), AAAc extractable P, Ca, K, Mg, S and AAAc-EDTA extractable Cu and Zn and also some other parameters (Agricultural Research Centre 1986). Analytical results obtained are interpreted to seven fertility classes taking into account the soil type and humus content (Viljavuuspalvelu 2000). Fertility status is indicated by fertility classes that include: 1 = Poor: 2 = Rather poor; 3 = Fair; 4 = Satisfactory; 5 = Good; 6 = Very good; and 7 = Possibly excessive. The target status is class 4 = Satisfactory.

***Aqua regia* extractable ("total") trace elements.** In this study 'total' content refers to *aqua regia* extractable concentration, which shows the highest trace element concentration that can be released from natural sources in acidic conditions over the long term. *Aqua regia* extractions of the top- and subsoil samples were carried out by the GTK Laboratory, which is an accredited testing laboratory (T025). The method was based on the international standard (ISO 11466) and was modified by Niskavaara (1995). From the *aqua regia* extracts, Cd, Cr, Cu, Pb and Se were measured by ICP-MS (inductively coupled plasma mass spectrometry, Perkin Elmer Sciex Elan 5000). Arsenic contents were measured by GF-AAS (atomic absorption spectrometry, atomized using the graphite furnace technique, Perkin Elmer SIMAA-6000). Vanadium and Zn were measured by ICP-AES (inductively coupled plasma atomic emission spectrometry, Thermo Jarrel Ash IRIS Advantage). Mercury contents were determined with the Hg analyzer (AMA 254) using the pyrolysis technique. Analytical results are presented in a unit of mg kg^{-1} of air-dried soil, if not otherwise mentioned.

Detection limits (DL) for trace elements in the top- and subsoil samples analyzed in the GTK's laboratory. Elements were extracted by *aqua regia* (ISO 11466) except for Hg, which was analyzed pyrolytically.

Element	DL, mg kg^{-1}
As	0.1
Cd	0.02
Cr	1
Cu	0.5
Hg	0.01 for topsoil 0.005 for subsoil
Ni	2
Pb	0.1
Se	0.2 for topsoil
V	1
Zn	3

Selenium contents of the subsoil samples were measured from the *aqua regia* extracts prepared by the GTK Laboratory by hydride generation atomic absorption spectrometry (Hg-AAS, Varian SpectraAA 300 Plus) at the MTT Laboratories.

Total aluminium and iron. The air-dried soil sample (0.5 g) was digested in a mixture of 12 M HCl (2.5 ml) and 7 M HNO_3 (10 ml). Digestion was made with a microwave system and closed vessels. Concentrations of Al and Fe were measured by Thermo Jarrel Ash, IRIS advantage High Resolution ICP Optical Emission Spectrometer with a CID detector. Analytical results are presented in a unit of mg kg^{-1} of air-dried soil.

2.4 Statistical analysis

For the statistical processing, SPSS software was used. A mean value was not computed of over 50% of element contents or concentrations were below the detection limit. Values below the analytical detection limit (DL) were replaced by the value DL/2.

The correlations were counted using Pearson's correlation. Correlation coefficients were calculated with Pearson´s product-moment linear correlation method. The following notation was for the correlation coefficients (r):

Very strong correlation: >0.8;
Strong correlation: between 0.6 and 0.8;
Good correlation: between 0.4-0.6, and
Weak correlation: between 0.3 and 0.4.

3 Results and discussion

3.1 General soil characteristics and fertility

The soils for each farming types were clearly differentiated in the particle size distribution (Table 1 and 2, Fig. 1). On the crop farms, the mean clay (<0.002 mm) content was 45% and in the dairy farms 10%, while the mean finesand (0.02-0.2 mm) content were 15% and 60%, respectively. Also, according to Kurki (1972), the clay soil was the dominant soil type both in the top- and subsoil in southwestern Finland and the finesand soil in Ostrobothnia (Appendix 1: Fig. 1 and 2). The clay soils in southwestern Finland contained much more Al and Fe than the finesand soils in Ostrobothnia (Table 3 and 4). On the crop farms, the soil humus content (Fig. 2) and electrical conductivity were slightly lower than those in the dairy farms, on average (Table 3 and 4).

Analytical results obtained from the AAAc extraction indicated that the two production sectors differed in nutrient concentrations, as well (Table 3 and 4). In the crop farming, the P concentrations were lower, but the K, Ca and Mg concentrations were higher than the respective figures in dairy farming, on average. However, in both farming systems (Appendix 2: Table 1 and 2), the soil fertility status of P and Mg was at Class 4 = Satisfactory. On the crop farms, the K and Ca status was mostly Satisfactory and Ca Good, but the S status was Fair, thus below the target class. On the contrary, the K and Ca status was below the target level on the dairy farms, on average. The biggest difference in the soil fertility between the farm types occurred in the Ca status which was classified to Good (Class 5) on the crop farms and to Fair (Class 3) on the dairy farms. Median pH status was Very Good (Class 6) on the crops farms and Good (Class 5) on the dairy farms.

Table 1. Mean particle size distributions (%) of 23 fields (plough layer) on the five crop farms (1-5) in southwestern Finland in 2004.

Crop farms Particle size distribution, %									
Fraction	**Clay**	**Silt**		**Finesand**		**Sand**		**Gravel**	
Particle size, mm	<0.002	0.002 - 0.006	0.006 - 0.02	0.02 - 0.06	0.06 - 0.2	0.2 - 0.6	0.6 - 2.0	2.0 - 6.0	6.0 - 20.0
		Fine	**Coarse**	**Fine**	**Coarse**	**Fine**	**Coarse**	**Fine**	**Coarse**
Symbol	S	HHs	KHs	HHt	KHt	HHk	KHk	HSr	KSr
Farm									
1	46	20	19	9	4	2	2	0	0
2	51	20	14	9	3	2	1	0	0
3	23	10	7	7	13	17	12	8	2
4	36	29	21	6	5	3	1	0	0
5	56	9	7	11	13	2	2	0	0
Mean	**45**	**17**	**13**	**9**	**7**	**4**	**3**	**1**	**0**

Table 2. Mean particle size distributions (%) of 21 fields (plough layer) on the five dairy farms (6-10) in Ostrobothnia in 2004.

Dairy farms Particle size distribution, %									
Fraction	**Clay**	**Silt**		**Finesand**		**Sand**		**Gravel**	
Particle size, mm	<0.002	0.002 - 0.006	0.006 - 0.02	0.02 - 0.06	0.06 - 0.2	0.2 - 0.6	0.6 - 2.0	2.0 - 6.0	6.0 - 20.0
		Fine	**Coarse**	**Fine**	**Coarse**	**Fine**	**Coarse**	**Fine**	**Coarse**
Symbol	S	HHs	KHs	HHt	KHt	HHk	KHk	HSr	KSr
Farm									
6	14	20	29	21	10	4	3	0	0
7	5	8	21	29	35	2	1	0	0
8	24	22	19	14	11	6	4	1	0
9	5	3	6	21	61	4	1	0	0
10	2	0	3	15	77	3	1	0	0
Mean	10	11	16	19	38	4	2	0	0

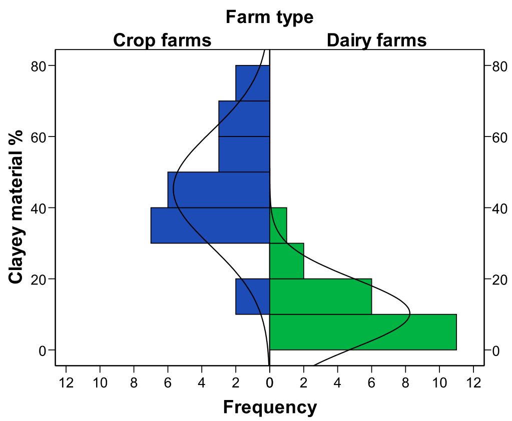

Figure 1. Clay (particle size <0.002 mm) contents (%) of topsoil of 23 fields on five crop farms in southwestern Finland and of 21 fields on five dairy farms in Ostrobothnia in 2004.

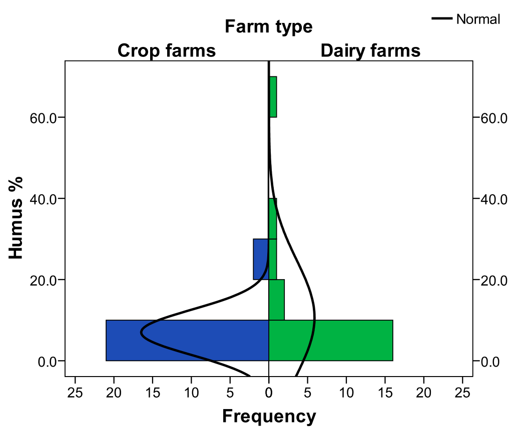

Figure 2. Humus contents (%) of topsoil of 23 fields on five crop farms in southwestern Finland and of 21 fields on five dairy farms in Ostrobothnia in 2004.

Table 3. Statistical indicators on general soil characteristics, AAAc extractable macronutrients and Al and Fe contents in the topsoil (plough layer) of 23 fields on five crop farms in southwestern Finland in 2004.

Crop farms	Minimum	Median	Mean	Maximum
Org. C (%)	1.9	3.0	4.1	14
Humus (%)	3.2	5.1	7	24
Bulk density (kg/l)	0.64	0.93	0.91	1.1
Clay (%)	13	41	45	76
pH (H_2O)	5.9	6.7	6.7	7.2
El. cond., (10^{-4} S cm^{-1})	0.60	1.1	1.2	2.3
AAAc-P (mg/l)	5.3	9.8	15	49
AAAc-K (mg/l)	126	205	206	262
AAAc-Ca (mg/l)	1470	2910	2781	4890
AAAc-Mg (mg/l)	100	305	409	1070
AAAc-S (mg/l)	10	13	13	20
Al (mg/kg)	1347	2781	3128	6843
Fe (mg/kg)	4889	8314	8152	12510
Al + Fe (mg/kg)	6236	11526	11280	16528

Table 4. Statistical indicators of general soil characteristics, AAAc extractable macronutrients and Al and Fe contents in the topsoil (plough layer) of 21 fields on five dairy farms in Ostrobothnia in 2004.

Dairy farms	Minimum	Median	Mean	Maximum
Org. C (%)	0.94	2.6	6.2	35
Humus (%)	1.6	4.5	11	60
Bulk density (kg/l)	0.40	1.00	0.95	1.2
Clay (%)	0.00	7.0	10	34
pH (H_2O)	5.8	6.4	6.5	7.6
El. cond. (10^{-4} S cm^{-1})	0.80	1.4	1.4	2.2
AAAc-P (mg/l)	3.8	16	17	41
AAAc-K (mg/l)	29	105	101	206
AAAc-Ca (mg/l)	631	1340	1599	2710
AAAc-Mg (mg/l)	102	177	253	684
AAAc-S (mg/l)	9.0	14	15	30
Al (mg/kg)	296	1845	2043	6238
Fe (mg/kg)	1085	5088	4505	11500
Al + Fe (mg/kg)	1841	7481	6548	16140

3.2 AAAc-EDTA extractable trace elements

There were differences in the concentrations of the AAAc-EDTA extractable trace elements in the topsoil between the farming systems (Table 5 and 6). Cultivated soil on the crop farms in southwestern Finland contained more AAAc-

EDTA extractable Cd and Pb than the soil on the dairy farms in Ostrobothnia mainly due to differences in the soil type. Also, Mäkelä-Kurtto et al. (2002) reported a decreasing concentration trend for these elements in Finnish cultivated soils in 1998 from the south to the north, partly resulting from the higher Cd and Pb emissions and depositions in the south.

Instead, the soil on the crop farms had less AAAc-EDTA extractable As and Se than the soil on the dairy farms, on average. The mean AAAc-EDTA extractable Cu concentration and the fertility status of Cu in the topsoil were at the same level on the crop and dairy farms. The AAAc-EDTA extractable Zn was mostly lower on the crop farms than in the dairy farms. Hence, the soil fertility status of Zn on the crop farms was Rather poor (Class 2) but Satisfactory (Class 4) on the dairy farms. All the Cr concentrations measured from the AAAc-EDTA extracts were under the detection limit. No clear differences were found in the AAAc-EDTA extractable V between the farming types.

When the AAAc-EDTA extractable trace elements were compared with the respective *aqua regia* extractable ones, solubility (%) of all the elements studied was higher in the finesand soils on the dairy farms than in the clay soils on the crop farms (Table 7 and 8). Obviously, the clay soils rich in small soil particles and with high Fe and Al contents (Table 3 and 4) bound trace elements more effectively than the finesand soils. *Aqua regia* extraction even dissolves some mica and clay minerals and releases metals from the crystal lattice. Solubility of the trace elements in the soil also depends on other soil characteristics, like pH (Fig. 3), as described by Mäkelä-Kurtto (1994) and humus content, too. In the present study, there was a small difference in the pH and humus content between the farm types or between the soil types (Table 3 and 4).

The most soluble trace element was Cd. Nearly half of the Cd extracted in *aqua regia* was soluble in the AAAc-EDTA solution (Table 7 and 8), on average. In some cases, nearly 100% of cadmium was extracted in the AAAc-EDTA solution. Copper and Pb were also quite soluble. About one fourth of *aqua regia* extractable Cu and one fifth of Pb occurred in the soluble form. About 10% or less of As, Ni, Se and Zn was soluble in the AAAc-EDTA. In this extraction solution, Cr was nearly insoluble. These findings were in line with the earlier observations made by Mäkelä-Kurtto et al. (1992 and 2006, Table 9). Trace element contents of the crop plants grown on the fields studied here were reported by Mäkelä-Kurtto et al. (2007b) to determine plant availability of the trace elements in the soil. Soil-to-plant uptake factors of As, Cd, Cu, Ni, Pb, V and Zn for wheat grains, potato tubers and timothy grass were reported by Mäkelä-Kurtto et al. (2006).

Table 5. Statistical indicators of AAAc-EDTA extractable trace element concentrations (mg l^{-1} of air dried soil) of topsoil (plough layer) in 23 fields of five crop farms in southwestern Finland in 2004. For statistical calculations, the values under the detection limit have been divided by 2.

Crop farms	Minimum	Median	Mean	Maximum
As	<0.5	<0.5		0.60
Cd	<0.05	0.090	0.088	0.180
Cr	<1	<1		<1
Cu	1.4	4.6	4.5	8.7
Pb	1.4	2.9	2.9	5.3
Ni	<1	1.1	1.1	2.2
Se	<0.01	0.01	0.01	0.014
V	<5.0	<5.0		18
Zn	0.7	1.3	1.5	8.5

Table 6. Statistical indicators of AAAc-EDTA extractable trace element concentrations (mg l^{-1} of air dried soil) of topsoil (plough layer) in 21 fields of five dairy farms in Ostrobothnia in 2004. For statistical calculations, the values under the detection limit have been divided by 2.

Dairy farms	Minimum	Median	Mean	Maximum
As	<0.5	<0.5		0.9
Cd	<0.05	<0.05		0.090
Cr	<1	<1		<1
Cu	1.2	4.3	4.1	11
Pb	<1.0	1.3	1.2	2.2
Ni	<1.0	<1.0		1.8
Se	<0.01	<0.01		0.01
V	<5	<5		14
Zn	1.9	3.3	3.5	5.2

Table 7. Percentages (%) of the concentrations (mg kg^{-1} of air-dried soil) of AAAc-EDTA extractable trace elements from the contents (mg kg^{-1} of air-dried soil) of *aqua regia* extractable elements in the topsoil of 23 fields on five crop farms in southwestern Finland in 2004.

Crop farms	Minimum %	Median %	Mean %	Maximum %
As	2.2	4.3		8.2
Cd	15	45	44	122
Cr	0.0	0.0		0.0
Cu	2.8	17	17	29
Pb	11	16	16	26
Ni	1.4	3.3	4.2	15
Se	0.6	5.0	4.2	13
V	2.4	3.7		23
Zn	0.6	1.1	1.7	8.9

Table 8. Percentages (%) of the concentrations (mg kg^{-1} of air-dried soil) of AAAc-EDTA extractable trace elements from the contents (mg kg^{-1} of air-dried soil) of *aqua regia* extractable elements in the topsoil of 21 fields on five dairy farms in Ostrobothnia in 2004.

Dairy farms	Minimum %	Median %	Mean %	Maximum %
As	2.3	11		25
Cd	24	48		108
Cr	0.0	0.0		0.1
Cu	18	36	37	66
Pb	9.1	18	23	66
Ni	2.5	9.1		19
Se	0.7	5.0		32
V	4.3	17		35
Zn	2.9	10	12	32

Table 9. Percentages (%) of AAAc-EDTA extractable trace elements from *aqua regia* extractable elements in the topsoil of 15 fields in the Tampere region in 2005 (Mäkelä-Kurtto et al. 2006).

Fields in the Tampere region	Minimum %	Median %	Mean %	Maximum %
As	0.1	1.0	1.2	3.1
Cd	30	38	39	47
Cr	0.2	0.3	0.3	0.4
Cu	7.4	16	17	33
Pb	12	16	16	23
Ni	1.8	3.4	3.7	5.7
V	0.6	1.5	1.7	2.8
Zn	0.9	1.7	2.0	4.5

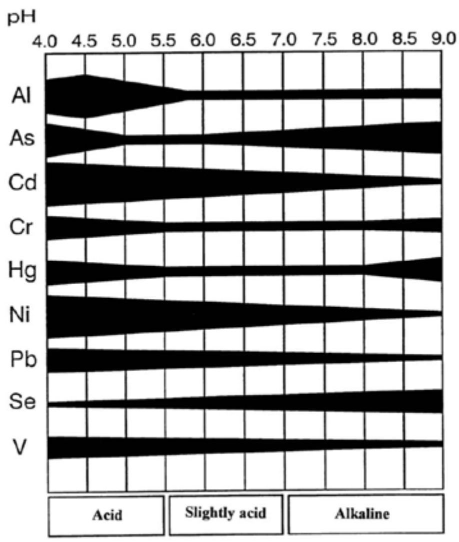

Figure 3. Solubility of some trace elements in soil at different pH levels (Mäkelä-Kurtto 1994).

3.3 *Aqua regia* extractable trace elements

Aqua regia extractable trace elements in the top- and subsoil of the fields on the five crop and five dairy farms are presented as statistical indicators in Appendix 3 (Table 1 and 2) and as frequencies in Appendix 4 (Figs. 1-20). Clearly, higher contents of all the elements occurred in the both soil horizons in the clay soils on the crop farms than in the finesand soils on the dairy farms (Table 10). Trace element contents in the clay soils were from two to three times the respective contents in the finesand soils, on average. Thus, the difference in the trace element contents between the farm types seemed to be due more to the difference in the geology of the regions than to the difference in the land use or farming. All the crop farms were located in the clay region in southwestern Finland and dairy farms in the finesand region in Ostrobothnia.

Table 10. Means of *aqua regia* extractable (ISO 11466) trace element contents (mg kg^{-1}) in the top- and subsoil of 23 fields on five crop farms in southwestern Finland and of 21 fields on five dairy farms in Ostrobothnia in 2004.

	Crop farms		**Dairy farms**	
	Topsoil	**Subsoil**	**Topsoil**	**Subsoil**
As	5.9	7.2	3.1	3.1
Cd	0.227	0.116	0.112	0.061
Cr	68	85	25	24
Cu	32	37	14	11
Pb	20	18	6.7	5.3
Hg	0.047	0.028	0.033	0.017
Ni	33	39	11	11
Se	- *	0.25	-*	0.13
V	90	90	43	32
Zn	114	106	42	33

* Over 50% of the values were below the detection limit, 0.2 mg kg^{-1} and the mean value was not computed.

The clay soils on the crop farms studied contained clearly more trace elements than the cultivated soils in Finland in 1998 (Table 11) (Mäkelä-Kurtto et al. 2007a) or in Sweden in the 1990s (Table 12) (Eriksson et al. 1997), on average. The elements also occurred in high contents in the subsoil on the crop farms. However, trace element means in the finesand soils on the dairy farms were closer to the respective national figures that were based on the whole natural variation of the Finnish soil types. Also, studies carried out in the Tampere region (Mäkelä-Kurtto et al. 2006, Table 13), Mikkeli region (Mäntylahti & Laakso 2002, Table 14), Porvoo area (Tarvainen et al. 2003, Table 15) and around the Helsinki metropolitan area (Tarvainen et al. 2006, Table 15) showed that trace element contents vary by the soil types, soil horizons and geological regions. The medians of *aqua regia* elements in the topsoil on crop farms were at the same level as the corresponding concentrations in Porvoo region and areas around the Helsinki metropolitan area in southern Finland (Table 15). The median concentrations of studied elements in the topsoil of the dairy farms were at the same level as those in the all of Finland.

Trace element contents in the topsoil increased in the following order: on the crop farms Hg<Cd<As<Pb<Cu=Ni<Cr<V<Zn; on the dairy farms Hg<Cd<As<Pb<Ni=Cu<Cr<Zn=V; and in soil monitoring material in 1998 Hg<Cd<Se<As<Pb<Cu=Ni<Cr<V=Zn (Mäkelä-Kurtto et al. 2007a), on average. Thus, there were not big differences in the relative abundance of trace elements between the various soil materials.

Table 11. Statistical indicators of *aqua regia* extractable (ISO 11466) trace elements (mg kg^{-1} dm) in Finnish cultivated fields (n = 338) sampled in the national soil monitoring programme in 1998 (Mäkelä-Kurtto et al. 2007a).

Finnish arable land in 1998 (Topsoil)	**Mean**	**Range**
As	4.13	0.32 - 17.9*
Cd	0.183	0.016 - 0.748
Cr	29.4	1.6 - 93.2
Cu	21.2	2.7 - 91.6
Hg	0.047	0.008 - 0.143**
Ni	13.8	1.2 - 46.4
Pb	9.7	2.1 - 57.9
Se	0.29	0.03 - 1.40***
V	39.7	2.7 - 273
Zn	54.5	5.7 - 264

* One case 166 mg kg^{-1} dm; ** One case 0.949 mg kg^{-1} dm; *** Three cases >1.4 mg kg^{-1} dm (2.3, 3.9 and 5.4)

Table 12. Mean trace elements in top- and subsoil of 1720 Swedish fields (Eriksson et al. 1997) and Swedish reference values for trace elements in urban soils (Xin 2005).

Swedish arable land	**Topsoil mg kg^{-1} dm**	**Subsoil mg kg^{-1} dm**	**Swedish limit mg kg^{-1} dm**
As	4.0	4.1	15
Cd	0.22	0.14	0.4
Cr	19.4	23.8	120*
Cr (VI)	-	-	5
Cu	14.2	14.9	100
Pb	16.7	13.5	80
Hg	0.042	0.017	35
Ni	11.8	16.5	35
V	35	39	120
Zn	56	53	350

* valid, if Cr (VI) is not present.

Table 13. Means of *aqua regia* extractable trace elements (mg kg^{-1} dm) in top- and subsoil of 15 fields in the Tampere region in 2005 (Mäkelä-Kurtto et al. 2006).

Arable land Tampere region	Mean	
	Topsoil	Subsoil
As	4.06	3.72
Cd	0.21	0.12
Cr	48.1	55.9
Cu	22.7	24.0
Pb	12.5	11.3
Ni	20.6	23.7
Se	0.20	0.16
V	64.4	66.1
Zn	107	91.5

Table 14. Means and ranges of *aqua regia* extractable (ISO 11466) trace element contents (mg kg^{-1}) in mineral (n = 274) and organic soils (n = 38) of arable land in the Mikkeli region in 2000 (Mäntylahti & Laakso 2002).

Mikkeli region 2000	Mineral topsoil		Organic topsoil	
	Mean	Range	Mean	Range
As	3.47	0.85-29.4	2.63	0.45-20.2
Cd	0.103	0.045-0.426	0.148	0.033-0.305
Cr	19.2	6.6-45.6	8.4	3.9-19.9
Cu	14.7	4.9-33.0	8.8	4.0-51.9
Pb	8.7	3.1-18.4	6.4	2.5-42
Hg	0.073	0.046-0.291	0.107	0.046-0.184
Ni	6.7	3.6-18.3	3.8	1.6-10.7
Zn	40.4	9.9-95.0	15.2	5.4-40.5

Table 15. Medians (mg kg^{-1}) of *aqua regia* extractable trace elements in arable topsoil (grain size <2 mm) in the Porvoo area, around the Helsinki metropolitan area and all of Finland (Tarvainen et al. 2003, Tarvainen et al. 2006, Tarvainen & Kuusisto 1999).

Elements in topsoil	Porvoo area 2002	Around the Helsinki metropolitan area 2004-2005	Finland 1996-1997
As	7.4	6.6	2.4
Cd	0.19	0.16	0.14
Cr	60.6	60.7	31.4
Cu	31.2	32.6	15.9
Hg	0.04	-	-
Ni	27.3	30.2	13.4
Pb	18.6	18.4	10.0
Se	<0.2	<1.0	-
V	71.8	81.9	36.2
Zn	96.8	108	37.1
n	47	49	42

Trace element contents of the soil horizons by farm types can be seen as frequencies in Appendix 5 (Figs. 1-20). In general, Cd, Pb, Hg and Zn contents were higher in the topsoil than in the subsoil on both farms, on average (Table 10). However, the topsoil had less As, Cr, Cu and Ni than the subsoil in crop farming. Based on large national soil material, Eriksson et al. (1997) made similar findings in Sweden (Table 12). In addition, the topsoil contained more Cr, Cu and V than the subsoil on the dairy farms. The V contents on the crop farms and As and Ni contents on the dairy farms were at the same level in the two soil layers, on average. In general, the selenium concentrations were higher in soils on crop farms than those on dairy farms.

To evaluate soil quality, the trace element means (Table 10) were compared to the respective natural background contents measured from fine-grained till in Finland and to the threshold values (GD 2007/214, Table 16). Mean Pb contents of top- and subsoil exceeded the natural background content (5 mg kg^{-1}) for Pb in both farming systems. In addition, the means of Cd and Zn in the topsoil on the crop farms were higher than the respective natural reference values. The main anthropogenic sources of these metals have been traffic for Pb, fertilization for Cd, and industry for Zn, respectively.

The mean As content and some Cr, Ni and V contents measured in the clayey top- and subsoil on the crop farms exceeded the respective threshold values (GD 2007/214, Table 16). On the dairy farms, some cases of As and V contents measured in the finesandy topsoil were higher than the respective threshold values. A maximum V content in the topsoil on the dairy farms exceeded even the low guide value for V (GD 2007/214, Table 16). However, the relative high concentrations of As, Cr, Ni and V were also found in subsoil samples, and the bioavailable content of the above mentioned trace elements were low. When the Finnish soil material of the monitoring program (Table 11) were compared with the Finnish natural background contents (GD 2007/214), exceeding levels in the Finnish cultivated soils (topsoil) occurred in the case of Cd, Hg, Pb, V and Zn, as well (Mäkelä-Kurtto et al. 2007a).

Table 16. Background value, threshold value, higher guidelines for industrial areas and similar land use, and lower guidelines for other land uses of trace element contents (mg kg^{-1}) for the evaluation of soil contamination and remediation needs (GD 2007/214).

Element	Background value	Threshold value	Lower guideline	Higher guideline
As	1 (0.1-25)	5	50 (e)	100 (e)
Cd	0.03 (0.01-0.15)	1	10 (e)	20 (e)
Cr	31 (6-170)	100	200 (e)	300 (e)
Cu	22 (5-110)	100	150 (e)	200 (e)
Hg	0.005 (<0.005-0.05)	0.5	2 (e)	5 (e)
Ni	17 (3-100)	50	100 (e)	150 (e)
Pb	5 (0.1-5)	60	200 (h)	750 (e)
Se	-	-	-	-
V	38 (10-115)	100	150 (e)	250 (e)
Zn	31 (8-110)	200	250 (e)	400 (e)

(e) = based on ecological criteria; (h) = based on health criteria

The Swedish limit values for trace elements in urban soils (Xin 2005) and Canadian limit values for arable land (CCME 2003) are presented in Table 12 and 17, respectively. In Sweden, the limit value for Cr is 120 mg kg^{-1} dm, if Cr (VI) is not present, and for Cr (VI) 5 mg kg^{-1} dm. Mäntylahti and Laakso (2002) proposed limit values for trace element for “Clean mineral and organic soil” of Finnish arable land (Table 17). It seems that the values are too low particularly for the clay soils because even the trace element contents in the subsoil of the clay areas contain more trace elements than is accepted in the “Clean Soil” contents.

Table 17. Canadian limit values for arable land (CCME 2003) and Finnish limit values for “Clean Soil” proposed by Mäntylahti and Laakso (2002).

	Canadian limit values mg kg^{-1} dm	Finnish “Clean Soil” values mg kg^{-1}	
Element	All arable soils	Mineral soils	Organic soils
As	12	10	10
Cd	1.4	0.3	0.3
Cr	64	70	70
Cu	63	35	35
Pb	70	20	20
Hg	6.6	0.10	0.15
Ni	50	35	25
Se	1	-	-
V	130	-	-
Zn	200	100	100

3.4 Trace element interactions in soil

In the crop farms, the clay interacted with concentrations of arsenic, chromium, copper, nickel, lead, vanadium and zinc in the topsoil (Table 18) and subsoil, except arsenic (Table 19). Cadmium and mercury had a statistically significant negative correlation between pH in topsoil and a positive correlation between humus. The more humus was in the topsoil, the higher was the selenium concentration. In the subsoil, the correlation between humus and cadmium and mercury could be clearly seen but there were no statistically significant correlations between pH and the abovementioned elements. The element concentrations in the soil in this study do not seem to have any influence on the electric conductivities of the soils. Also, there were no statistically significant correlations between the depth of the plough layer and the studied element concentrations.

Table 18. Significant correlations (Pearson's correlation) of *aqua regia* (ISO 11466) extractable (ISO 11466) trace elements in the topsoil to clay and organic carbon (C)/humus content and pH(H_2O) in the topsoil of 23 fields on the five crop farms in southwestern Finland in 2004.

Crop farms Elements in topsoil	Topsoil		
	Clay content	pH(H_2O)	Org. C/Humus
As	.642**	-	-
Cd	-	-.643**	.846**
Cr	.920**	-	-
Cu	.872**	-	-
Hg	-	-.546**	.707**
Ni	.895**	-	-
Pb	.874**	-	-
Se	-	-	.754**
V	.816**	-	-
Zn	.528**	-	-

Table 19. Significant correlations (Pearson's correlation) of *aqua regia* (ISO 11466) extractable trace elements in the subsoil to clay and organic carbon (C)/humus content in the topsoil of 23 fields on the five crop farms in southwestern Finland in 2004.

Crop farms Elements in subsoil	Topsoil	
	Clay content	Org. C/Humus
As	-	-
Cd	-	.780**
Cr	.824**	-
Cu	.769**	-
Hg	-	.563**
Ni	.797**	-
Pb	.773**	-
Se	-	-
V	.752**	-
Zn	.538**	-

In the dairy farms, the clay content in the topsoil influenced the concentrations of all the elements studied (Table 20). Humus correlated positively statistically significant with arsenic, cadmium, copper, mercury and selenium. There did not seem to be any significant correlation between the elements studied and pH and electrical conductivity in the topsoil. In the subsoil, the amount of clay correlated positively with all other elements but not with mercury (Table 21). There seemed to be a weak correlation between pH and cadmium and mercury in the subsoil. The concentrations of the elements studied in the subsoil did not influence the electrical conductivity values. Arsenic, cadmium and mercury concentrations in the subsoil were dependent on the amount of organic carbon.

Table 20. Significant correlations (Pearson's correlation) of *aqua regia* (ISO 11466) extractable trace elements in the topsoil to clay and organic carbon (C)/ humus content in the topsoil of 21 fields on the five dairy farms in Ostrobothnia in 2004.

Dairy farms Elements in topsoil	**Topsoil**	
	Clay content	**Org. C/Humus**
As	.646**	.584**
Cd	.813**	.616**
Cr	.936**	
Cu	.792**	.555**
Hg	.718**	.840**
Ni	.905**	
Pb	.841**	
Se	.648**	.658**
V	.934**	
Zn	.756**	

Table 21. Significant correlations (Pearson's correlation) of *aqua regia* (ISO 11466) extractable trace elements in the subsoil to clay and organic carbon (C)/ humus content and pH(H_2O) in the topsoil of 21 fields on the five dairy farms in Ostrobothnia in 2004.

Dairy farms Elements in subsoil	**Topsoil**		
	Clay content	**pH(H_2O)**	**Org. C/Humus**
As	.658**	-	.763**
Cd	.678**	-.449*, .041 sig.	.603**
Cr	.832**	-	-
Cu	.797**	-	-
Hg	-	-.511*, .018 sig.	.862**
Ni	.847**	-	-
Pb	.842**	-	-
Se	-	-	-
V	.824**	-	-
Zn	.803**	-	

3.4.1 Arsenic

Crop farms: Arsenic in the topsoil on the crop farms was significantly positive correlated with copper, chromium, lead, nickel and vanadium (Appendix 6: Table 1). In the subsoil, As correlated significantly only with lead (Appendix 6: Table 2). Arsenic in the plough layer had a significant positive correlation with As, Cr, Cu, Ni, Pb, V and Zn contents in the subsoil (Appendix 6: Table 3). Arsenic concentrations were 16.3% higher in the subsoil than in the topsoil, on average (Appendix 3: Table 1, Appendix 4: Fig. 1). In the crop farms, arsenic origin seems to be more geologic than anthropogenic.

Dairy farms: Arsenic in the topsoil on the dairy farms was statistically significantly correlated with cadmium and vanadium (Appendix 6: Table 4). In the subsoil, As correlated significantly with selenium, copper and mercury (Appendix 6: Table 5). The arsenic concentrations in the plough layer had significant positive correlations with arsenic, copper, vanadium and selenium concentrations in the subsoil (Appendix 6: Table 6). On the dairy farms, there was only slightly more arsenic in topsoil than in subsoil, on average and hence, the concentrations were almost equal (Appendix 3: Table 2, Appendix 4: Fig. 2).

3.4.2 Cadmium

Crop farms: Cadmium had significant positive correlations with mercury and selenium in the topsoil and in the subsoil on the crop farms (Appendix 6: Table 1 and 2). Also, cadmium concentrations in the top- and subsoil had a significantly positive correlation (Appendix 6, Table 3). Cadmium seems to enrich in the topsoil rather than in the subsoil (Appendix 4: Fig. 3). Means of the Cd concentrations in the topsoil were almost twice those in the subsoil (Appendix 3: Table 1).

Dairy farms: In the topsoil, cadmium had a statistically significant positive correlation with all the studied elements (Appendix 6: Table 4). In the subsoil, Cd correlated only with mercury and selenium (Appendix 6: Table 5). Topsoil concentrations of cadmium correlated positively with all other elements in subsoil except for arsenic, mercury, zinc and selenium. (Appendix 6: Table 6). Cadmium was enriched in the topsoil rather than in the subsoil (Appendix 4: Fig. 4). Also, in the dairy farms, the Cd concentrations in the topsoil were twice that in the subsoil (Appendix 3: Table 2).

3.4.3 Chromium

Crop farms: Chromium did not correlate with cadmium, mercury or selenium, but with other metals Cr had a significant positive correlation both in the top- and subsoil on the crop farms (Appendix 6: Table 1 and 2). Chromium had a significant positive correlation with arsenic in the topsoil. Chromium concentration in the topsoil correlated positively with other elements except for arsenic, cadmium, selenium and mercury in subsoil (Appendix 6: Table 3). Chromium concentrations were usually 17% higher in the subsoil (Appendix 4: Fig. 5) than in the topsoil, on average (Appendix 3: Table 1).

Dairy farms: In the dairy farms, the chromium the topsoil correlated positively statistically significant with all the other elements except arsenic and selenium (Appendix 6: Table 4). In the subsoil, Cr correlated positively with copper, lead, nickel, vanadium and zinc (Appendix 6: Table 5). Between the top- and subsoil concentrations, chromium correlated positively with all other elements but not with arsenic, cadmium, selenium and mercury (Appendix 6: Table 6). There was slightly more chromium in the subsoil than in the topsoil, on average (Appendix 4: Fig. 6 and Appendix 3: Table 2). Obviously, the origin of chromium is mainly geologic.

3.4.4 Copper

Crop farms: On the crop farms, copper had a significantly positive correlation in topsoil as well as in subsoil with other elements except cadmium, mercury and selenium (Appendix 6: Table 1 and 2). Only in the topsoil copper had positive correlation with arsenic. Copper concentrations in the topsoil correlated positively with subsoil Cr, Cu, Ni, Pb, V and Zn (Appendix 6: Table 3). Copper was geologic origin and hence, more copper usually occurred in the subsoil than in the topsoil (Appendix 4: Fig. 7). Copper concentrations in the topsoil were about 13% lower than those in the subsoil (Appendix 3: Table 1).

Dairy farms: Topsoil copper had a statistically significant positive correlation with all the studied elements except arsenic in the topsoil (Appendix 6: Table 4). Respectively, the subsoil Cu was correlated with arsenic, chromium, lead, nickel, selenium, vanadium and zinc in the subsoil (Appendix 6: Table 5). Topsoil Cu had a positive correlation with subsoil Cd, Cr, Cu, Pb, Ni, V and Zn (Appendix 6: Table 6). On the dairy farms, copper was clearly enriched in the topsoil (Appendix 6: Fig. 8 and Appendix 3: Table 2). There was about 23% more copper in the topsoil than in the subsoil, on average (Appendix 3: Table 2). Copper was not at all enriched in the topsoil of the Porvoo area (Tarvainen et al. 2003).

3.4.5 Lead

Crop farms: Lead had significant positive correlations with all studied elements except cadmium, selenium and mercury both in the top- and subsoil on the crop farms (Appendix 6: Table 1 and 2). Lead had a significant positive correlation with zinc only in the subsoil. Topsoil Pb correlated positively with subsoil As, Cr, Cu, Ni, Pb and V (Appendix 6: Table 3). Lead was distributed rather evenly in relation to the soil depth (Appendix 4: Fig. 9), because Pb contents in the topsoil were equal to those in the subsoil, on average (Appendix 3: Table 1).

Dairy farms: On the dairy farms, Pb concentrations in the topsoil had statistically significant positive correlations with all other studied elements except arsenic and selenium (Appendix 6: Table 4). In the subsoil, lead was correlating significantly with copper, chromium, nickel, vanadium and zinc (Appendix 6: Table 5). Excluding subsoil arsenic, cadmium, mercury and selenium, topsoil lead had a significant positive correlation with all other subsoil trace elements (Appendix 6: Table 6). In the dairy farms, lead was enriched in the topsoil (Appendix 4: Fig. 10). The topsoil Pb was about 31% higher than the subsoil Pb, on average (Appendix 3: Table 2).

3.4.6 Mercury

Crop farms: Mercury correlated significantly with cadmium and selenium both in the top- and subsoil (Appendix 6: Table 1 and 2). The same positive correlation was shown also between mercury in the topsoil and cadmium and selenium in the subsoil (Appendix 6: Table 3). Mercury was strongly enriched in the topsoil. Most probably, Hg originated from human activities (Appendix 4: Fig 11).

Dairy farms: In the topsoil, mercury correlated positively statistically significant with all the other elements except arsenic, nickel and zinc (Appendix 6: Table 4). In the subsoil, Hg correlated only with arsenic, selenium and cadmium (Appendix 6: Table 5). Topsoil Hg correlated positively with the subsoil cadmium, copper, selenium and vanadium (Appendix 6: Table 6). Also, on the dairy farms, Hg was strongly enriched in the topsoil (Appendix 4: Fig. 12). The topsoil Hg was about 65% higher than the subsoil Hg, on average (Appendix 3: Table 2).

On both farm types, the mean topsoil Hg was more than twice the subsoil Hg, on average.

3.4.7 Nickel

Crop farms: In the topsoil, nickel had significant positive correlations with arsenic, copper, chromium, lead, vanadium and zinc (Appendix 6: Table 1). In the subsoil, the correlations were the same as in the topsoil, excluding arsenic (Appendix 6: Table 2). Nickel in topsoil correlated positively with other elements except As, Cd, Se and Hg in the subsoil (Appendix 6: Table 3). Nickel is usually of geologic origin and hence the concentrations in the subsoil were 13% higher than those in the topsoil, on average (Appendix 4: Fig 13 and Appendix 3: Table 1).

Dairy farms: Nickel had a statistically significant positive correlation with all studied elements except arsenic and mercury in the topsoil (Appendix 6: Table 4). In the subsoil, nickel correlated positively with copper, chromium, lead, vanadium and zinc (Appendix 6: Table 5). There was a positive correlation between topsoil nickel and subsoil copper, chromium, lead, nickel, vanadium and zinc (Appendix 6: Table 6). The concentrations of nickel in the topsoil were slightly smaller than the concentrations in the subsoil, on average (Appendix 4: Fig. 14 and Appendix 3: Table 2).

3.4.8 Selenium

Crop farms: Selenium concentrations in the topsoil were mostly under the detection limit of 0.2 mg/kg. Hence, the correlations are unreliable. However, there seems to be a negative correlation between selenium and zinc (Appendix 7: Fig. 1) in the topsoil and also between topsoil selenium and subsoil zinc (Appendix 6: Table 1, 2 and 3). Selenium had a positive correlation with cadmium and mercury in topsoil and in subsoils. Selenium is distributed quite evenly in relation to soil depth (Appendix 4: Fig. 15). Some extreme values occurred in the topsoil samples.

Dairy farms: Also, on the dairy farms selenium concentrations in the topsoil were mostly under the detection limit of 0.2 mg kg^{-1}. Thus, the correlations are not reliable. However, Se might have a positive correlation with cadmium, copper, mercury and nickel in the topsoil and with arsenic, cadmium, copper and mercury in subsoil. Topsoil Se correlated positively with subsoil Cd and Cu. (Appendix 6: Tables 4-6). Se concentrations in topsoil are a bit higher than those in subsoil (Appendix 4: Fig. 16).

3.4.9 Vanadium

Crop farms: Vanadium was correlating positively with As, Cu, Cr, Pb, Ni and Zn in the topsoil, but in the subsoil the correlation with arsenic was missing. The same correlations could also be found between the top- and subsoil (Appendix 6: Table 1, 2 and 3). Vanadium was distributed quite evenly in relation to the soil depth (Appendix 4: Fig. 17). Vanadium concentrations had a strong positive correlation with each other in the top- and subsoil (Appendix 7: Table 3).

Dairy farms: In the topsoil, vanadium had a statistically significant positive correlation with all other elements but selenium (Appendix 6: Table 4). In the subsoil, V correlated with copper, chromium, lead, nickel and zinc (Appendix

6: Table 5). Vanadium in the topsoil correlated positively with all the elements in the subsoil except arsenic and mercury (Appendix 6: Table 6). There was to some extent more vanadium in the topsoil than in the subsoil, on average (Appendix 4: Fig. 18 and Appendix 3: Table 2). Vanadium concentrations had a positive correlation with each other in the top- and subsoil (Appendix 7: Fig. 4).

3.4.10 Zinc

Crop farms: Zinc concentrations had significant positive correlations with Cu, Cr, Ni and V in the topsoil (Appendix 6: Table 1). As mentioned above, there seemed to be a negative correlation between zinc and selenium in the topsoil but also between selenium in the topsoil and zinc in the subsoil (Appendix 6: Table 3). In the subsoil, zinc had the same correlations as in the topsoil, but also with lead (Appendix 6: Table 2). Zinc was, like lead and vanadium, evenly distributed in relation to the soil depth (Appendix 4: Fig. 19).

Dairy farms: Zinc in the topsoil had a statistically significant positive correlation with all other elements but not with arsenic, mercury and selenium (Appendix 6: Table 4). In the subsoil, it correlated positively with chromium, copper, nickel, lead and vanadium (Appendix 6: Table 5). The topsoil Zn correlated positively with the subsoil Cu, Cr, Ni, Pb, V and Zn (Appendix 6: Table 6). Zinc was enriched in the topsoil rather than subsoil. The topsoil zinc was 23% higher than subsoil Zn, on average (Appendix 3: Table 2). No Zn enrichment occurred in the topsoil in the dairy farms (Appendix 4: Fig. 20 and Table 22).

3.5 Trace element enrichment in topsoil

For the estimations of the trace element enrichment, the depth of the plough layer of the sampling sites was measured in the field. The depth on the crop farms was 21.6 cm, on average, varying between 18 and 27 cm and on the dairy farms 24.3 cm, on average, varying between 18 and 30 cm. On both farms, the subsoil layer sampled was about 20 cm. The enrichment/depletion estimations were based on the trace element contents determined from *aqua regia* extraction (ISO 11466) in the top- and subsoil. Trace element quantities in the top- and subsoil were calculated per one hectare. Based on the depth of the topsoil, the mean volume of soil on one hectare on the crop farms was 2.160 million liters (approximately 2.160 million kg) and on the dairy farms 2.430 million liters (approximately 2.430 million kg). The contents and amounts in the topsoil were compared to those in equal volumes of the subsoil.

Mean trace element enrichment or depletion factors (= a ratio of *aqua regia* extractable trace element in topsoil to *aqua regia* extractable trace element in subsoil) are presented for the crop farms and dairy farms by elements in Appendix 8. On the crop farms, a mean enrichment factor (top-/subsoil ratio) for As was 0.82 (Appendix 8: Table 1). This means 18% depletion (3 kg per ha) of As in the topsoil. According to a very strong correlation (r = 0.815) the tendency was quite systematic. On the dairy farms, there was no difference in the As contents between the soil horizons. Also, in other studies (Table 22), almost no enrichment is reported for As.

Cadmium contents in the topsoil on both farm types were nearly twice as high as that in the subsoil (Appendix 8: Table 2) showing considerable enrichment of Cd into the plough layer. The enrichment factor and amount enriched in the topsoil were 1.96 and 0.239 kg ha^{-1} on the crop farms and 1.84 and 0.124 kg ha^{-1} on the dairy farms, respectively. The amount of cadmium enriched in the clay soils in southwestern Finland was nearly two times that enriched in the fine-sand soils in Ostrobothnia. In both farming types, the main reasons might have been Cd inputs from P-fertilizers and atmospheric depositions of Cd that has been higher in the south than in the north. Cadmium enrichment in the topsoil was also documented in other parts of Finland, in other land uses and in other countries (Table 22).

The mean enrichment factor for Cr on the crop farms was 0.80 meaning that the Cr content in the topsoil was 80% of that in the subsoil (Appendix 8: Table 3). This indicates depletion of Cr (37 kg per ha) from the topsoil. The tendency was systematic which was indicated by the very strong correlation (r = 0.914) between the top- and subsoil. On the dairy farms, the difference in the Cr contents between the soil layers was very small showing only some enrichment (3 kg per ha).

Copper was depleted by 11 kg per ha in the topsoil on the crop farms but enriched by 7 kg per ha on the dairy farms, according to the enrichment factors 0.86 and 1.27, respectively (Appendix 8: Table 4). Correlation for the tendencies was very strong (r = 0.931). Mass balance estimations of the same farms studied here will give more information on the possible differences in the Cu inputs and Cu outputs between the farm types (Mäkelä-Kurtto et al. 2007b, Tarvainen et al. 2007). In spite of Cu depletion observed here on the crop farms, the fertility status of Cu was at the target level (Class 4 = Satisfactory) on both farm types (Appendix 8, Table 4). Although the crop farms had higher contents of *aqua regia* extractable Cu, there were no differences in the AAAc-EDTA extractable concentrations between the farm types.

Lead was an element that showed clear enrichment in the topsoil on both farm types (Appendix 8: Table 5). Enrichment (4 kg per ha) in the crop farming was greater than in the dairy farming (3 kg per ha), although the relative enrichment factor was smaller (1.11) on the crop farms than on the dairy farms (1.26). The tendencies seemed to be systematic (r = 0.919). The most important source of Pb has been the leaded gasoline used in automobiles in 1900´s. Since 1994, when unleaded gasoline became available for all motor vehicles, lead emissions from traffic into the atmosphere virtually ceased (Mäkelä 1996).

One of the elements enriched relatively more in the topsoil was mercury in both farming types, but particularly in the dairy farming (Appendix 8: Table 6). The amount of Hg enriched on the crop farms was 0.042 kg and 0.039 kg per ha on the dairy farms. Nickel contents in the two soil layers compared were systematically (r = 0.919) at the same level on the dairy farms, while Ni depletion (13 kg per ha) occurred on the crop farms (Appendix 8: Table 7). Selenium was enriched 0.065 kg per ha in the topsoil of the crop farms and 0.121 kg on the dairy farms (Appendix 8, Table 8). In the case of V, no difference was observed between the top- and subsoil on the crop farms, but enrichment (26 kg per ha) was found on the dairy farms (Appendix 8: Table 9).

Zinc was enriched in the topsoil on both farm types, but more on the dairy farms (22 kg per ha) than on the crop farms (17 kg per ha) (Appendix 8, Table 10). Tendencies seemed to be systematic due to the very strong correlation (r = 0.933). The topsoil of the crop farms clearly contained more *aqua regia* extractable Zn, nearly three times that in the topsoil on the dairy farms. However, it contained less AAAc-EDTA extractable (soluble) Zn and its fertility status of Zn was remarkably lower (Class 2 = Rather poor) than the topsoil on the dairy farms (Class 4 = Satisfactory) (Appendix 8: Table 10).

Based on the enrichment factors estimated in the present study, enrichment of trace elements in the topsoil was clearly more pronounced on the dairy farms than on the crop farms, on average (Table 22). On the dairy farms, Cd, Cr, Cu, Pb, Hg, Se, V and Zn were enriched, and no trace element was depleted. On the crop farms, Cd, Pb, Hg, Se and Zn were enriched as well, while As, Cr, Cu and Ni were depleted. When the amounts enriched in the topsoil per ha were compared between the farm types, more Cd, Pb and Hg was enriched in the clay soils in southwestern Finland than in the finesand soils in Ostrobothnia. Enrichments of Cd, Pb, Hg and Zn were 0.239, 4, 0.042 and 17 kg per ha on the crop farms and on the dairy farms 0.124, 3, 0.039 and 22 kg per ha, respectively (Appendix 8). On the crop farms As, Cr, Cu and Ni were depleted by 3, 37, 11, 13 kg per ha, respectively, and in the dairy farms, Cr, Cu, Se and V were enriched by 3, 7, 0.121 and 26 kg per ha, respectively (Appendix 8).

In this study, the sources of the trace elements could not be explained, but it was assumed that the sources of Cd, Pb, Hg and Zn have been atmospheric depositions. Due to high population and traffic densities in the south, the atmospheric depositions of these elements have been higher in the south than in the north. In addition, part of Cd and Zn enrichment has originated from fertilization and

Hg from Hg containing pesticides. In the dairy farms, an additional source for Cr, Cu and V might have been side products of the steel industry used for soil improving and for Se and Zn the feed additives used for animal nutrition.

In the Netherlands, agricultural, industrial and traffic activities are very intensely compared internationally due to the high population density and also high farm animal density. Hence, there is a severe threat of diffuse soil contamination. Recently, large studies have been conducted on the enrichment of the trace elements in the Dutch soil by Spijker (2005) and van der Veer (2006).

Spijker (2005) showed that As, Cd, Cu, Pb and Zn were enriched in the topsoil and enrichment of all these elements was related to anthropogenic activities. The studies of van der Veer (2006) were based on 358 locations in the Netherlands. According to his research results, by comparing the prevailing concentrations in the subsoil, the topsoil layer showed substantial (by factor 2 or more) enrichment for Cd, Cu, Hg, Pb and Zn. By comparing enrichment of the trace elements in various land uses and human activities between the regions van der Veer (2006) found that copper appeared mainly related to agricultural inputs through application of fertilizers, (pig) manure and historical use of Cu containing pesticides. The enrichment pattern of Pb and Hg suggested largely atmospheric inputs (source: energy and waste incineration plants, as well as road traffic for Pb). In the southern part, Cd and Zn enrichment were related to the atmospheric inputs from mining and zinc smelting and in the northern part, to the agricultural inputs.

In the present study, more Cd, Pb and Hg was enriched in the clay soils on the crop farms in southwestern Finland than in the finesand soils on the dairy farms in Ostrobothnia. Dairy farming seemed to enrich Cr, Cu, Se, V and Zn in the topsoil more than crop farming, on average. Instead, the crop farming resulted in depletion of some trace elements, like Cu. Trace elements of most concern as with regards to their enrichment and solubility in the topsoil seem to be Cd, Hg and Pb in both farm types (Table 23). In addition, Cu, Se, Zn and V seem to be the elements that have to be followed on the dairy farms. The elements of the least threat seemed to be Ni and As on the both farm types. When sampled at the same site and time, analysis of the top- and the subsoil for the trace elements might be a good tool to monitor the element enrichment (contamination) and depletion tendencies in the cultivated soils.

Table 22. Mean enrichment factors of arable land in southwestern Finland (crop farms), Ostrobothnia (dairy farms), the Tampere region (Mäkelä-Kurtto et al. 2006) and Sweden (Eriksson et al. 1997) and of natural/forest land in the Porvoo region (Tarvainen et al. 2003).

	Crop farms	Dairy farms	Tampere region	Porvoo region	Sweden national
As	0.82	1.00	1.09	0.90	0.98
Cd	1.96	1.84	1.75	1.70	1.61
Cr	0.80	1.04	0.86	0.82	0.82
Cu	0.86	1.27	0.95	0.78	0.96
Pb	1.11	1.26	1.11	1.00	1.23
Hg	1.68	1.94	-	3.80	2.52
Ni	0.85	1.00	0.87	0.70	0.72
Se	1.12[1]	1.38[1]	1.25	-	-
V	1.00	1.34	0.97	0.80	0.90
Zn	1.08	1.27	1.17	0.79	1.05
Mean	1.13	1.33	1.11	1.25	1.20
Mean*	**1.07**	**1.27**	**1.11**	**0.94**	**1.03**

* Hg excluded, [1] See Appendix 8: Table 8.

Table 23. Relative importance of trace elements for evaluating agricultural and environmental influences based on a sum of enrichment (%) and solubility (%) in clay soils on the five crop farms in southwestern Finland and in finesand soils on the five dairy farms in Ostrobothnia in 2004.

	Importance						
Farm type	**<100**	**100-120**	**120-140**	**140-160**	**160-180**	**180-200**	**>200**
Crop farms	As, Cr, Ni	Cu, V, Zn, Se	Pb		Hg		Cd
Dairy farms		As, Cr, Ni	Zn	Cu, Pb, Se, V		Hg	Cd

4 Conclusions

When sampled at the same site and at the same time, analysis of the top- and the subsoil for *aqua regia* extractable trace elements might be a good tool to:

1) get information on the natural variation of the geologic background concentrations (baselines) of the trace elements by sites, locals or regions;
2) evaluate impacts of land use, farming type, atmospheric depositions on trace element accumulation in topsoil;
3) determine tendencies of the trace element enrichment (contamination)/depletion in the topsoil;

4) have indicators on the impacts of human activities on the trace elements in the topsoil;
5) determine connections to other indicators, like soil P, production sectors, farming systems, use of organic and/or inorganic fertilizer preparations, farm animal manure, pesticides, nearby metal industry, motor way, etc.;
6) monitor the trace element tendencies in the topsoil and;
7) recognize and manage health and ecological risks of trace elements in agro-ecosystems.

Further studies are needed to get reliable information on the geologic distribution of the trace elements in various soil layers and to explain the sources of the trace elements enriched in the topsoil in various production sectors, farming systems, land use and various regions.

The natural baseline determines the average concentrations of most studied elements. Baselines are higher in the clayey soils of selected crop farms in south-western Finland. All the dairy farms were located in Ostrobothnia where the geologic baselines for metals are low. Based on the enrichment factors estimated in this study, enrichment of trace elements in topsoil was more pronounced on the dairy farms than on crop farms. On dairy farms, Cd, Cu, Pb, Hg, Se, V and Zn were enriched. On the crop farms, Cd, Pb, Hg, Se and Zn were enriched and As, Cr, Cu and Ni depleted.

Natural geochemical baseline concentrations of several trace elements are higher in Finland compared to the southern edge of the Baltic Sea (Reimann et al.2003 and Salminen et al. 2005). Natural concentrations of trace elements such as arsenic, chromium, nickel, vanadium and zinc often exceed the threshold values (GD 2007/214) designated for contaminated soils. Thus, the bio-available part of the trace elements should be also investigated while studying agricultural soils. Trace elements of the most concern regarding enrichment and solubility in the topsoil are Cd, Pb and Hg in both farm types.

5 Summary

This study was part of a three-year (2004-2007) project entitled "Assessment and reduction of heavy metal inputs into Finnish agro-ecosystems" that was funded by the Ministry of Agriculture and Forestry in Finland. The aims of the project were to clarify: 1) *aqua regia* extractable trace elements in Finnish cultivated soils with the international standard method at a national level; 2) *aqua regia* and AAAc-EDTA extractable trace elements in the top- and subsoil of Finnish arable land on selected crop and dairy farms; and 3) field mass balances of trace elements on the selected crop and dairy farms at the farm level.

The main aim of this investigation was to study trace element contents in Finnish arable land on crop and dairy farms. Five farms were selected from typical crop farming area in southwestern Finland and five from typical dairy farming area in Ostrobothnia. Topsoil and subsoil samples were collected from 23 fields on the crop farms and from 21 fields on the dairy farms at the time of harvest in 2004. Trace element contents studied were arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), vanadium (V) and zinc (Zn). Total contents of these elements were determined from the top- and subsoil samples with *aqua regia* extraction (ISO 11466), except Hg which was determined by pyrolysis. In addition, the topsoil samples were analyzed for particle size distribution, bulk density, pH(H_2O), electrical conductivity, organic carbon, humus, total contents of aluminium and iron, AAAc extractable nutrients and AAAc-EDTA extractable trace elements.

The crop farms located on the clay soils and the dairy farms were found on the finesand soils. Mean percentages of the clay and finesand fractions in the topsoil were 45% and 15% on the crop farms and 10% and 60% on the dairy farms, respectively. Thus, there was a great difference in the soil type between the farm types. The clay soils had clearly higher Al and Fe contents, to some extent higher concentrations of AAAc extractable Ca, K and Mg, but lower AAAc extractable concentration of P than the finesand soils.

As to fertility, the most remarkable difference between the farm types was in the Ca status which was classified as Good (Class 5) on the crop farms and Fair (Class 3) on the dairy farms. Instead, the fertility status of Zn on the crop farms was Rather poor (Class 2), but on the dairy farms Satisfactory (Class 4). A slight difference was also found in the pH status which was Very Good (Class 6) on the crop farms and Good (Class 5) on the dairy farms. Humus content was to some extent higher on the dairy farms than on crop farms.

Topsoil on the crop farms contained more AAAc-EDTA extractable Cd and Pb, but less As, Se and Zn than the dairy farms, on average. No clear differences occurred in the AAAc-EDTA extractable Cu, Ni and V between farm types.

All the Cr concentrations measured from AAAc-EDTA extracts were under the detection limit. When the AAAc-EDTA extractable trace elements were compared with the respective *aqua regia* extractable ones, solubility (%) of all the elements studied was higher in the finesand soils on the dairy farms than in the clay soils on the crop farms. The most soluble trace element was Cd and about half of the Cd was soluble in the AAAc-EDTA solution. Approximately one fourth of the *aqua regia* extractable Cu and one fifth of the *aqua regia* extractable Pb occurred in a soluble form. About 10% or less of As, Ni, Se and Zn was soluble in the AAAc-EDTA. Cr was nearly insoluble on both farm types.

The *aqua regia* extractable trace elements in the top- and subsoil of the clay soils on the crop farms were from two to three times those of the finesand soils on the dairy farms. Most of the elements were significantly correlated with the clay content. Cadmium and Hg correlated positively with the humus content and negatively with the soil pH. Selenium had a positive correlation to the humus content. Trace element interactions in the top- and subsoil and between these soil horizons were presented as Pearson´s correlation. When the contents were compared to the natural background contents, also called natural baselines, measured from fine-grained till in Finland, mean Pb contents of top- and subsoil in both farming systems and means of Cd and Zn in the topsoil on the crop farms exceeded the national background contents. The mean of As and some of Cr, Ni and V contents in the clayey top- and subsoil on the crop farms were higher than the current respective Finnish threshold values. A maximum V content in the topsoil on the dairy farms even exceeded the national lower guideline for V.

In the present study, more Cd, Pb and Hg was enriched in the clay soils on the crop farms in southwestern Finland than in the finesand soils on the dairy farms in Ostrobothnia. Dairy farming seemed to enrich more Cr, Cu, Se, V and Zn in the topsoil than crop farming, on average. In contrast, crop farming seemed to result in a depletion of some trace elements, like Cu. Trace elements of most concern regarding to their enrichment and solubility in the topsoil seem to be Cd, Hg and Pb in both farm types. In addition, Cu, Se, Zn and V seem to be the elements that have to be followed up on the dairy farms. The elements of the least threat seemed to be Ni and As on both farm types.

When sampled at the same site and time, analysis of the top- and the subsoil for *aqua regia* extractable trace elements might be a good tool to

1) get information on the natural variation of the geologic background concentrations of the trace elements by sites, locals or regions;
2) evaluate impacts of land use, farming type, atmospheric depositions on trace element accumulation in topsoil;
3) determine tendencies of the trace element enrichment (contamination)/depletion in the topsoil;

4) have indicators on the impacts of human activities on the trace elements in the topsoil;
5) determine connections to other indicators, like soil P, production sectors, farming systems, use of organic and/or inorganic fertilizer preparations, farm animal manure, pesticides, nearby metal industry, motor way, etc.;
6) monitor the trace element tendencies in the topsoil and;
7) recognize and manage health and ecological risks of trace elements in the agro-ecosystems.

Further studies are needed to get reliable information on the geologic distribution of trace elements in various soil layers and to explain the sources of the trace elements enriched in the topsoil in various production sectors, farming systems, land use and in various regions.

6 Acknowledgements

The authors first wish to thank the Ministry of Agriculture and Forestry in Finland for funding this study. The authors would also like to thank the 10 farmers and their families in southwestern Finland and Ostrobothnia for their kind cooperation and participation in the project. The farmer's great interest in and positive attitude towards the project made it possible to conduct and fulfil studies at the farm level according to the initial plans. The authors are very grateful to the field staff of MTT, Field Supervisor Unto Nikunen, Field Supervisor Pekka Kivistö and Field Supervisor Ari Seppänen for their assistance in the soil and plant sampling and to the laboratory staff of the MTT, Laboratory Supervisor Leila Lindstedt, Laboratory Supervisor Päivi Allén for analysing topsoil samples for total aluminium and iron and for measuring subsoil selenium from *aqua regia* extracts in the project. The authros wish to thank Virpi Karttunen for checking the chapter on *aqua regia* analytical method and the personnel of the chemical laboratory of the GTK for carrying out the *aqua regia* extraction and measurements of the elements. Sampling and analysis were the fundamental basis for the quality of analytical results. Best thanks are given to Mrs. Carrie Turunen in Canada, who was responsible for the linguistic checking of the English language of the manuscript. Special thanks are directed to Professor Martti Esala, MTT for his expertise and advice regarding the soil science.

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8 Appendixes

Appendix 1

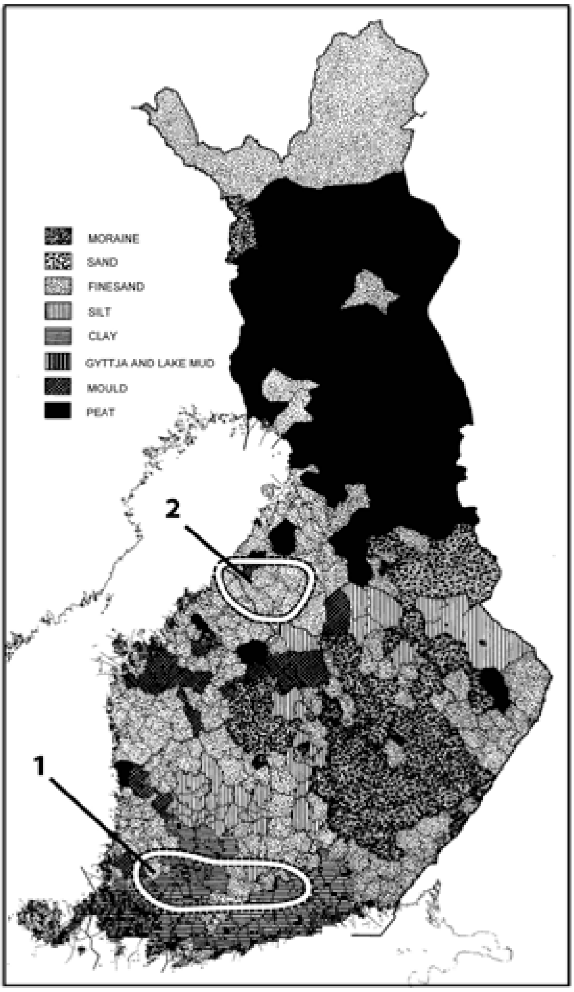

Figure 1. Dominant soil types in topsoil (plough layer) of arable land in Finland after Kurki (1972). A circle (1) in southwestern Finland indicates the region where the crop farms are located and a circle (2) in Ostrobothnia indi-cates the region where the dairy farms are located.

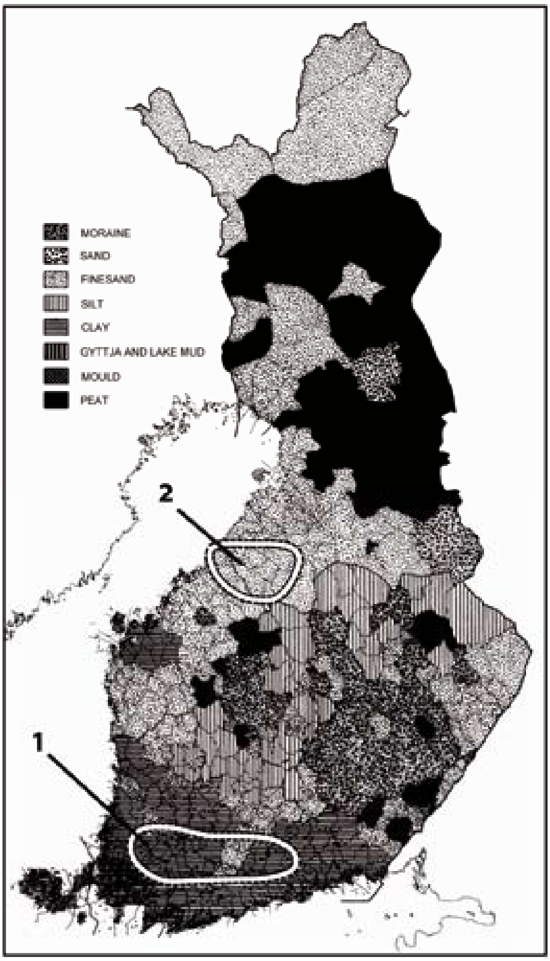

Figure 2. Dominant soil types in subsoil of arable land in Finland after Kurki (1972). A circle (1) in southwestern Finland indicates the region where the crop farms are located and a circle (2) in Ostrobothnia indicates the region where the dairy farms are located.

Appendix 2

Table 1. Means and (ranges) of fertility status of 23 fields (topsoil) on the five crop farms (Nr. 1-5) in southwestern Finland in 2004. Interpretation and classification of soil testing results were made according to Viljavuuspalvelu (2000).

Crop farm		**Fertility class***							
Nr.	**n**	**pH**	**P**	**K**	**Ca**	**Mg**	**S**	**Cu**	**Zn**
1	4	6.5	5.0	3.5	4.8	4.5	3.8	3.8	2.0
		(6 - 7)	(4 - 7)	(3 - 4)	(4 - 5)	(4 - 6)	(3 - 5)	(3 - 4)	(1 - 3)
2	6	5.8	4.3	3.7	4.8	4.7	3.7	4.8	1.7
		(4 - 7)	(3 - 6)	(3 - 4)	(3 - 6)	(4 - 6)	(3 - 5)	(4 - 5)	(1 - 2)
3	3	5.7	5.3	4.0	4.0	3.3	3.7	3.7	3.7
		(5 - 6)	(4 - 6)	(3 - 5)	(3 - 5)	(3 - 4)	(3 - 5)	(3 - 4)	(2 - 5)
4	4	5.3	3.5	3.5	3.5	4.0	3.3	3.3	1.3
		(5 - 6)	(3 - 5)	(3 - 4)	(2 - 4)	(4 - 4)	(3 - 4)	(3 - 4)	(1 - 2)
5	6	5.7	3.8	4.0	5.0	5.3	3.8	4.2	1.8
		(5 - 6)	(3 - 5)	(4 - 4)	(5 - 5)	(4 - 6)	(3 - 4)	(2 - 5)	(1 - 3)
Median		**6**	**4**	**4**	**5**	**4**	**3**	**4**	**2**
Mean		**5.8**	**4.3**	**3.7**	**4.5**	**4.5**	**3.7**	**4.0**	**2.0**
Minimum		**4**	**3**	**3**	**2**	**3**	**3**	**2**	**1**
Maximum		**7**	**7**	**5**	**6**	**6**	**5**	**5**	**5**

*Fertility classes: 1 = Poor; 2 = Rather poor; 3 = Fair; 4 = Satisfactory (Target class); 5 = Good; 6 = Very good; 7 = Possibly excessive

Table 2. Means and (ranges) of fertility status of 21 fields (topsoil) on the five dairy farms (Nr. 6-10) in Ostrobothnia in 2004. Interpretation and classification of soil testing results were made according to Viljavuuspalvelu (2000).

Dairy farm		**Fertility class***							
Nr.	**n**	**pH**	**P**	**K**	**Ca**	**Mg**	**S**	**Cu**	**Zn**
6	5	5.6	3.8	3.4	3.8	4.2	4.4	4.2	3.8
		(5 - 6)	(2 - 5)	(3 - 4)	(3 - 4)	(3 - 6)	(4 - 5)	(3 - 5)	(3 - 4)
7	3	5.0	3.3	4.0	3.0	4.3	4.3	2.7	4.0
		(5 - 5)	(3 - 4)	(3 - 5)	(3 - 3)	(4 - 5)	(4 - 5)	(2 - 3)	(4 - 4)
8	5	5.0	4.2	2.6	3.8	5.4	4.4	4.2	4.0
		(4 - 6)	(3 - 6)	(2 - 3)	(2 - 5)	(4 - 6)	(3 - 5)	(4 - 5)	(4 - 4)
9	3	4.7	4.3	3.0	2.7	4.0	4.7	3.7	3.7
		(4 - 6)	(3 - 5)	(2 - 4)	(2 - 3)	(3 - 5)	(4 - 5)	(3 - 5)	(3 - 4)
10	5	6.4	5.6	2.6	3.4	3.2	3.7	4.4	3.8
		(6 - 7)	(4 - 6)	(1 - 4)	(2 - 6)	(2 - 4)	(3 - 4)	(3 - 6)	(3 - 4)
Median		**5**	**4**	**3**	**3**	**4**	**4**	**4**	**4**
Mean		**5.4**	**4.3**	**3.1**	**3.4**	**4.2**	**4.2**	**4.0**	**3.9**
Minimum		**4**	**2**	**1**	**2**	**2**	**3**	**2**	**3**
Maximum		**7**	**6**	**5**	**6**	**6**	**5**	**6**	**4**

*Fertility classes: 1 = Poor; 2 = Rather poor; 3 = Fair; 4 = Satisfactory (Trarget class); 5 = Good; 6 = Very good; 7 = Possibly excessive

Appendix 3

Table 1. Statistical indicators on *aqua regia* extractable (ISO 11466) trace elements (mg kg^{-1}) in the top- and subsoil of 23 fields on the five crop farms in southwestern Finland in 2004. The mean value was not computed if over 50% of element contents were below the detection limit.

Crop farms	Minimum	Median	Mean	Maximum
Topsoil				
As	3.1	6.0	5.9	11.5
Cd	0.150	0.200	0.227	0.580
Cr	22	67	68	106
Cu	13	29	32	60
Pb	11	20	20	31
Hg*	<0.01	0.044	0.047	0.139
Ni	10	33	33	54
Se	<0.2	<0.2	- **	0.86
V	31	94	90	167
Zn	46	124	114	165
Subsoil				
As	2.5	7.1	7.2	11.1
Cd	0.040	0.100	0.116	0.320
Cr	29	89	85	136
Cu	14	34	37	70
Pb	10	18	18	29
Hg*	0.008	0.025	0.028	0.071
Ni	15	36	39	61
Se	0.12	0.22	0.25	0.63
V	38	93	90	134
Zn	43	113	106	150

* Pyrolytic determination, ** Over 50% from the values was below the detection limit

Table 2. Statistical indicators on *aqua regia* extractable (ISO 11466) trace elements (mg kg^{-1}) in the top- and subsoil of 21 fields on the five dairy farms in Ostrobothnia in 2004. The mean value was not computed if over 50% of element contents were below the detection limit.

Dairy farms	Minimum	Median	Mean	Maximum
Topsoil				
As	1.0	2.6	3.1	11
Cd	0.020	0.100	0.112	0.240
Cr	9	22	25	59
Cu	3.5	13	14	38
Pb	2.4	6.8	6.7	14
Hg*	0.011	0.025	0.033	0.079
Ni	3.7	8.7	11	21
Se	<0.2	<0.2	- **	0.88
V	11	40	43	135
Zn	16	35	42	72
Subsoil				
As	1.1	2.5	3.1	14
Cd	0.020	0.050	0.061	0.220
Cr	7.5	20	24	49
Cu	2.9	11	11	24
Pb	2.3	5.2	5.3	11
Hg*	0.006	0.009	0.017	0.090
Ni	3.1	9.0	11	24
Se	0.02	0.08	0.13	0.56
V	9.1	32	32	62
Zn	7.8	24	33	66

* Pyrolytic determination, ** Over 50% from the values was below the detection limit

Appendix 4

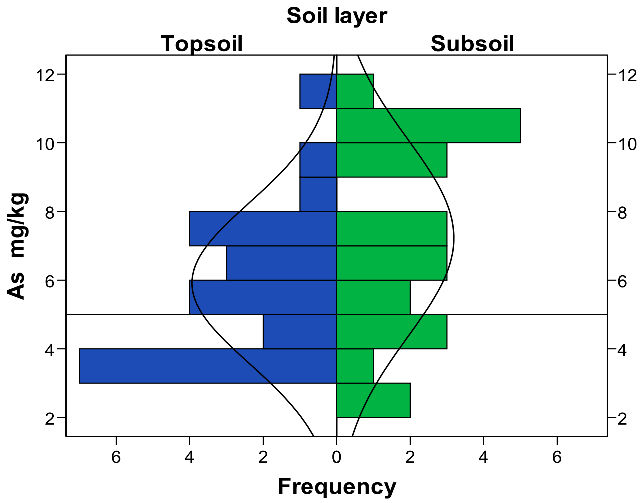

Figure 1. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) arsenic (As) contents (mg kg^{-1}) in the top- and subsoil sampled from 23 fields on the five crop farms in southwestern Finland in 2004. Threshold value, 5 mg kg^{-1}, is presented with solid line.

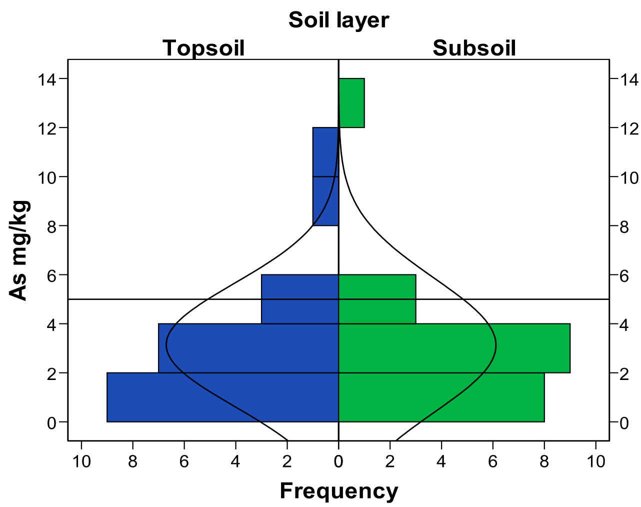

Figure 2. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) arsenic (As) contents (mg kg^{-1}) in the top- and subsoil sampled from 21 fields on the five dairy farms in Ostrobothnia in 2004. Threshold value, 5 mg kg^{-1}, is presented with solid line.

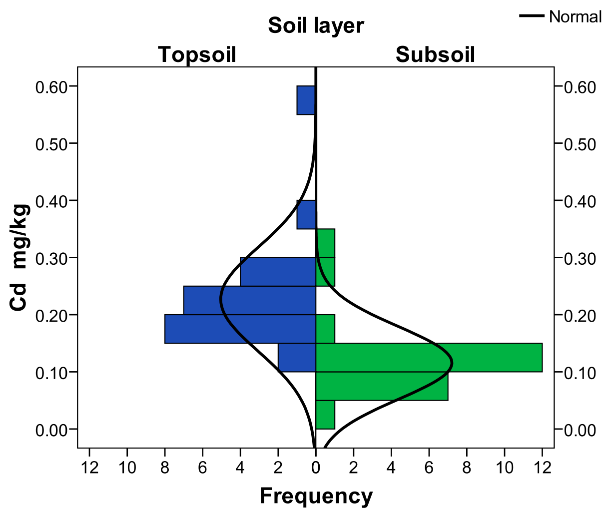

Figure 3. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) cadmium (Cd) contents (mg kg^{-1}) in the top- and subsoil sampled from 23 fields on the five crop farms in southwestern Finland in 2004.

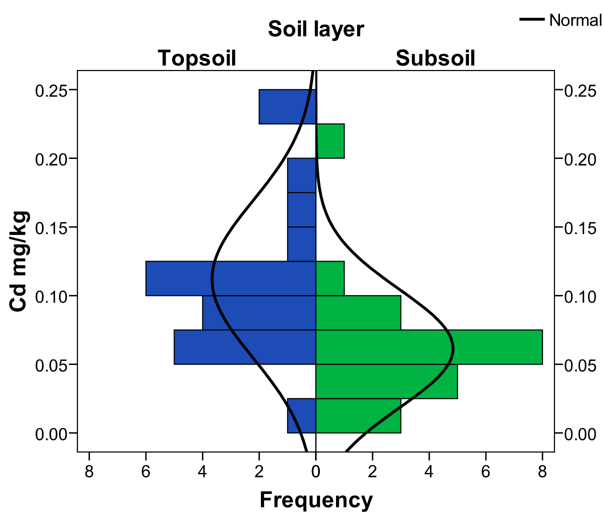

Figure 4. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) cadmium (Cd) contents (mg kg^{-1}) in the top- and subsoil sampled from 21 fields on the five dairy farms in Ostrobothnia in 2004.

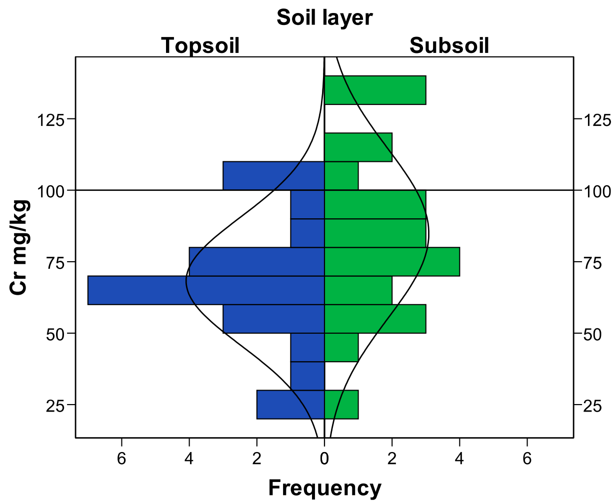

Figure 5. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) chromium (Cr) contents (mg kg^{-1}) in the top- and subsoil sampled from 23 fields on the five crop farms in southwestern Finland in 2004. Threshold value, 100 mg kg^{-1}, is presented with solid line.

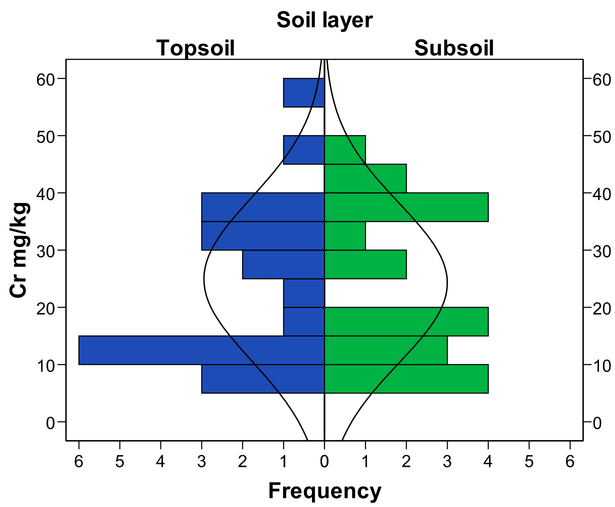

Figure 6. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) chromium (Cr) contents (mg kg^{-1}) in the top- and subsoil sampled from 21 fields on the five dairy farms in Ostrobothnia in 2004.

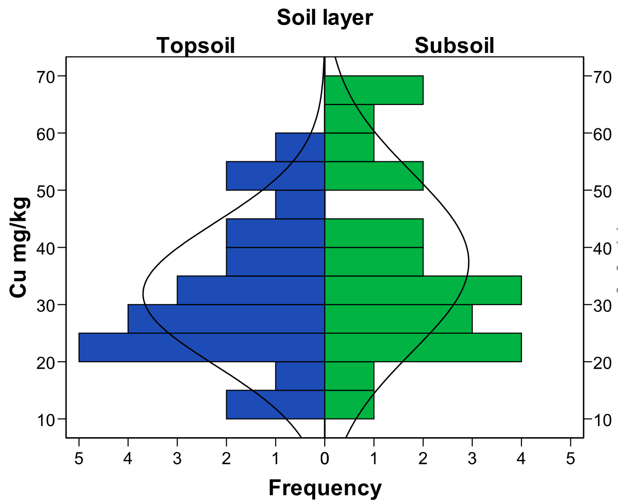

Figure 7. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) copper (Cu) contents (mg kg^{-1}) in the top- and subsoil sampled from 23 fields on the five crop farms in southwestern Finland in 2004.

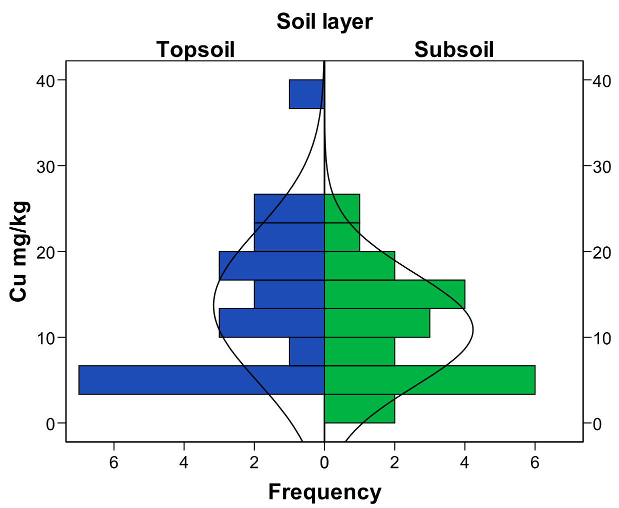

Figure 8. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) copper (Cu) contents (mg kg^{-1}) in the top- and subsoil sampled from 21 fields on the five dairy farms in Ostrobothnia in 2004.

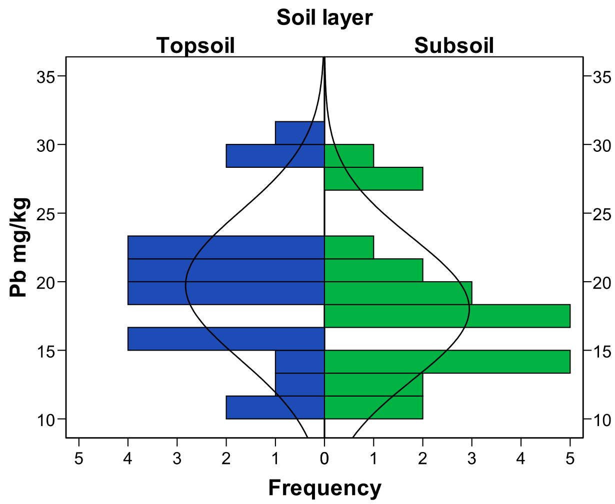

Figure 9. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) lead (Pb) contents (mg kg^{-1}) in the top- and subsoil sampled from 23 fields on the five crop farms in southwestern Finland in 2004.

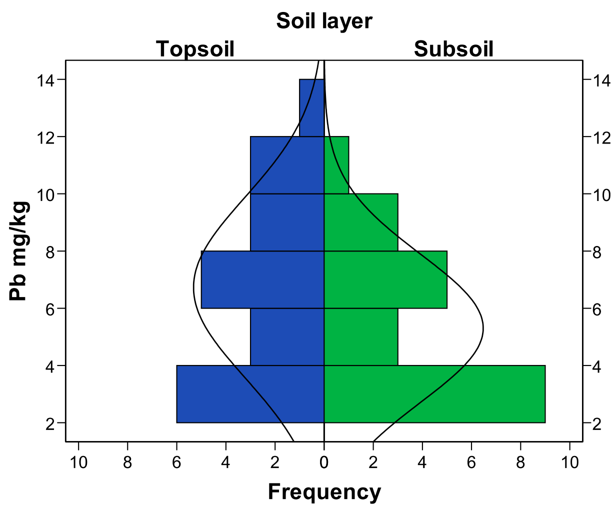

Figure 10. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) lead (Pb) contents (mg kg^{-1}) in the top- and subsoil sampled from 21 fields on the five dairy farms in Ostrobothnia in 2004.

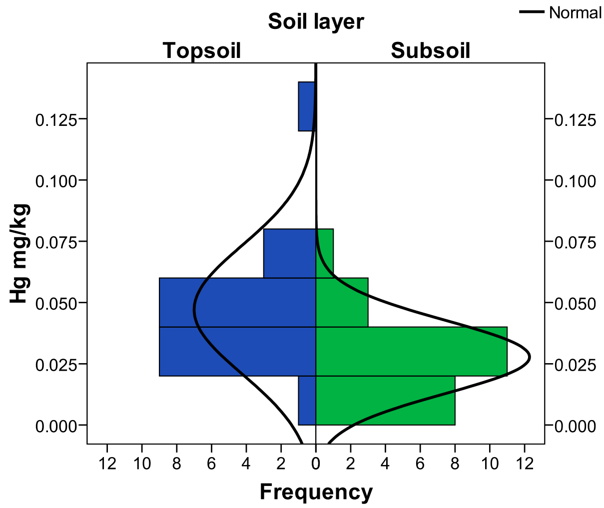

Figure 11. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) mercury (Hg) contents (mg kg^{-1}) in the top- and subsoil sampled from 23 fields on the five crop farms in southwestern Finland in 2004.

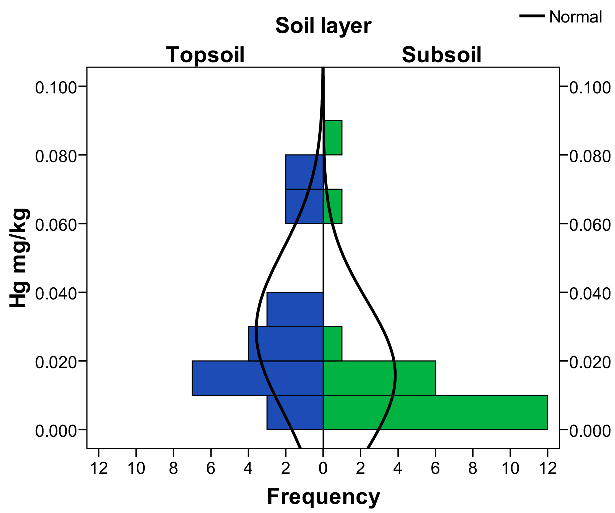

Figure 12. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) mercury (Hg) contents (mg kg^{-1}) in the top- and subsoil sampled from 21 fields on the five dairy farms in Ostrobothnia in 2004.

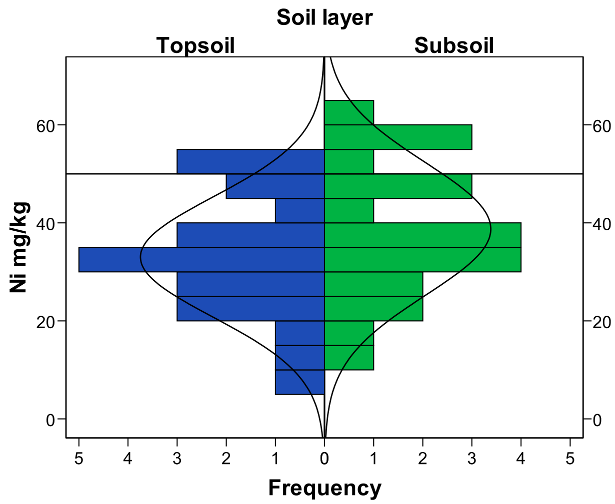

Figure 13. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) nickel (Ni) contents (mg kg^{-1}) in the top- and subsoil sampled from 23 fields on the five crop farms in southwestern Finland in 2004. Threshold value, 50 mg kg^{-1}, is presented with solid line.

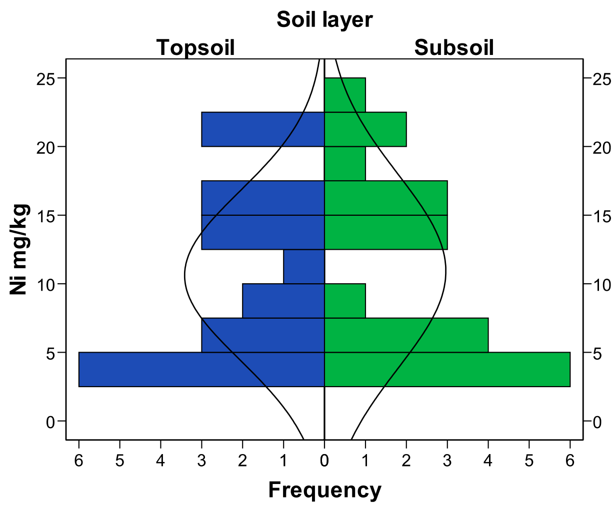

Figure 14. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) nickel (Ni) contents (mg kg^{-1}) in the top- and subsoil sampled from 21 fields on the five dairy farms in Ostrobothnia in 2004

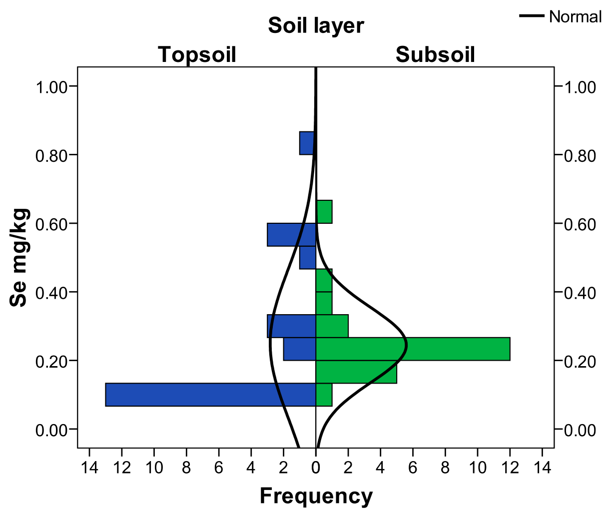

Figure 15. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) selenium (Se) contents (mg kg^{-1}) in the top- and subsoil sampled from 21 fields on the five crop farms in southwestern Finland in 2004.

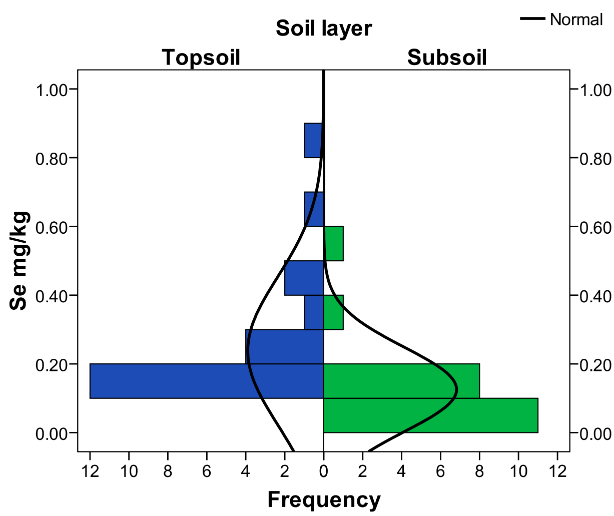

Figure 16. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) selenium (Se) contents (mg kg^{-1}) in the top- and subsoil sampled from 21 fields on the five dairy farms in Ostrobothnia in 2004.

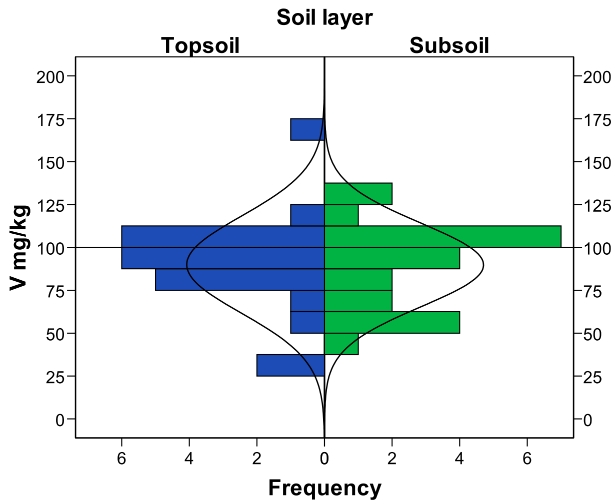

Figure 17. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) vanadium (V) contents (mg kg^{-1}) in the top- and subsoil sampled from 23 fields on the five crop farms in southwestern Finland in 2004. Threshold value, 100 mg kg^{-1}, is presented with solid line.

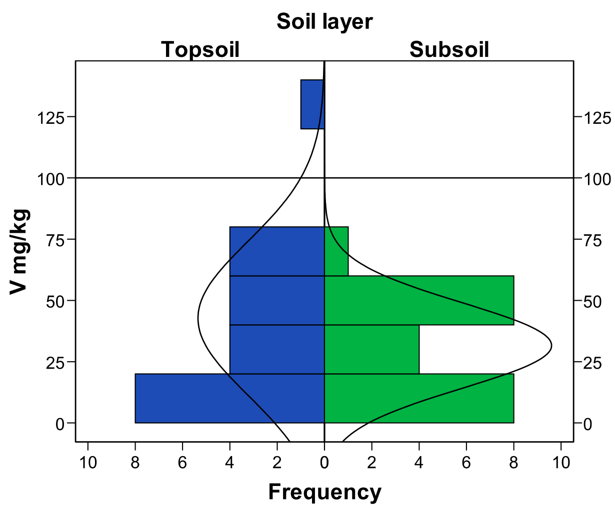

Figure 18. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) vanadium (V) contents (mg kg^{-1}) in the top- and subsoil sampled from 21 fields on the five dairy farms in Ostrobothnia in 2004. Threshold value, 100 mg kg^{-1}, is presented with solid line.

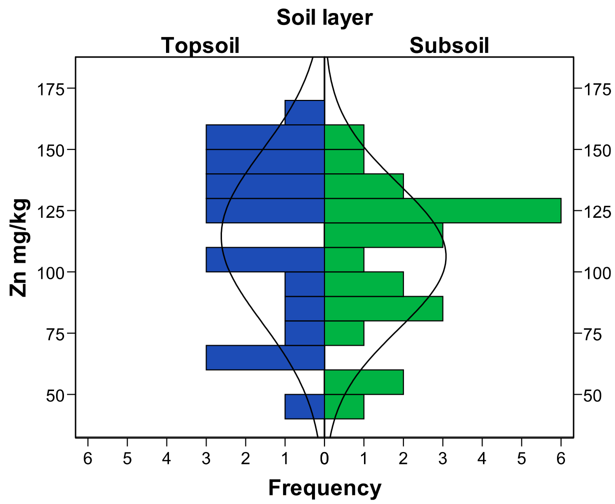

Figure 19. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) zinc (Zn) contents (mg kg^{-1}) in the top- and subsoil sampled from 23 fields on the five crop farms in southwestern Finland in 2004.

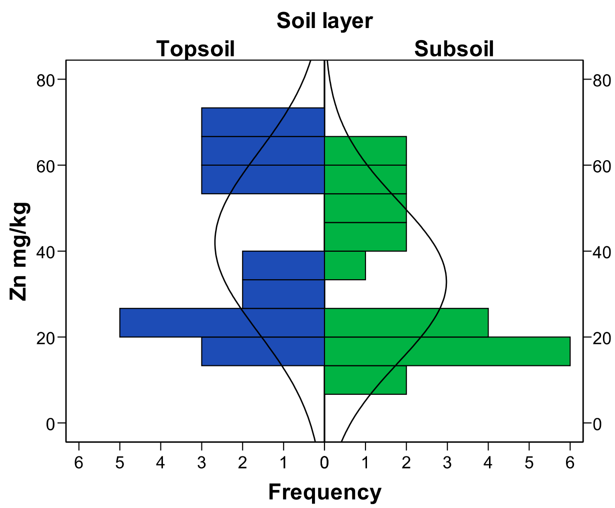

Figure 20. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) zinc (Zn) contents (mg kg^{-1}) in the top- and subsoil sampled from 21 fields on the five dairy farms in Ostrobothnia in 2004.

APPENDIX 5

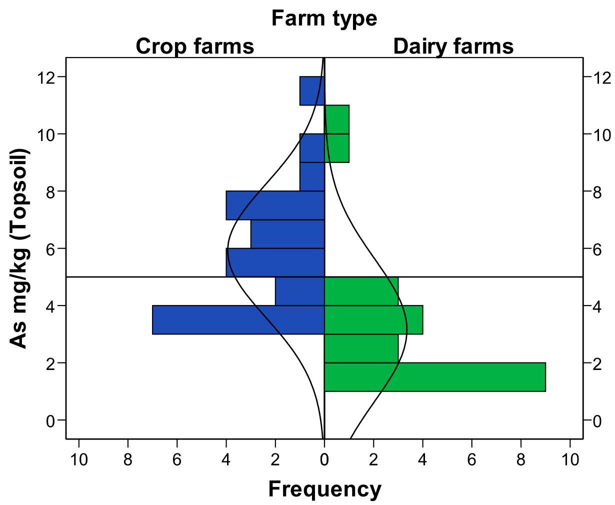

Figure 1. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) arsenic (As) contents (mg kg^{-1}) in the topsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004.

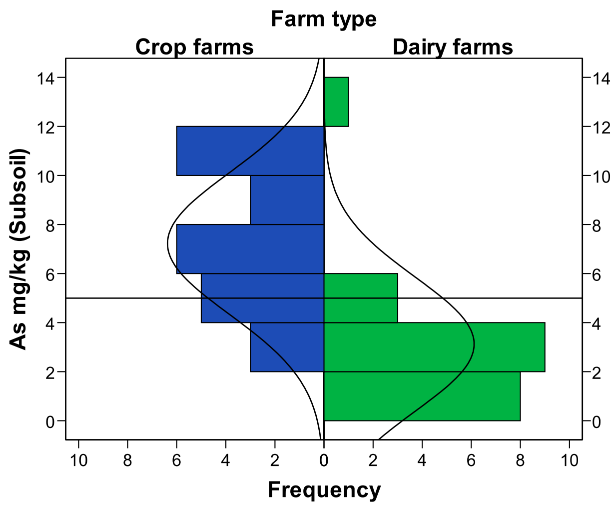

Figure 2. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) arsenic (As) contents (mg kg^{-1}) in the subsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004. Threshold value, 5 mg kg^{-1}, is presented with solid line.

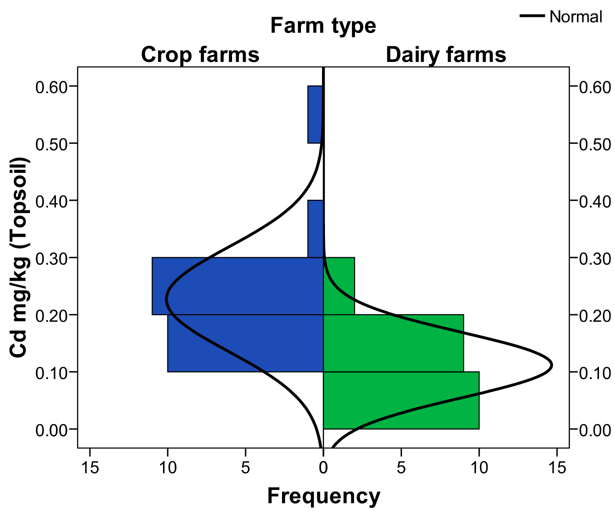

Figure 3. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) cadmium (Cd) contents (mg kg^{-1}) in the topsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004.

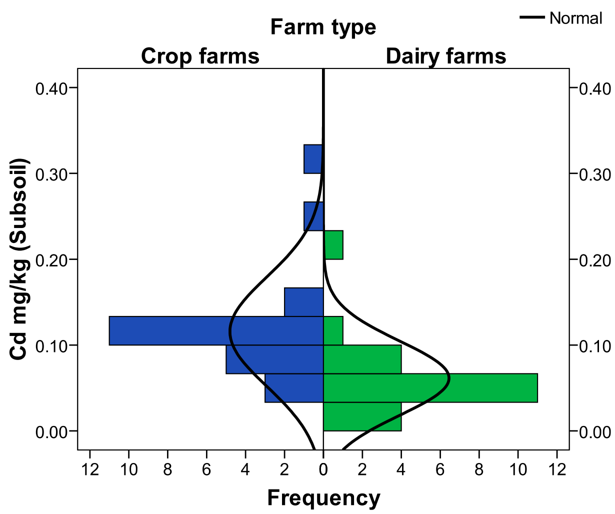

Figure 4. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) cadmium (Cd) contents (mg kg^{-1}) in the subsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004.

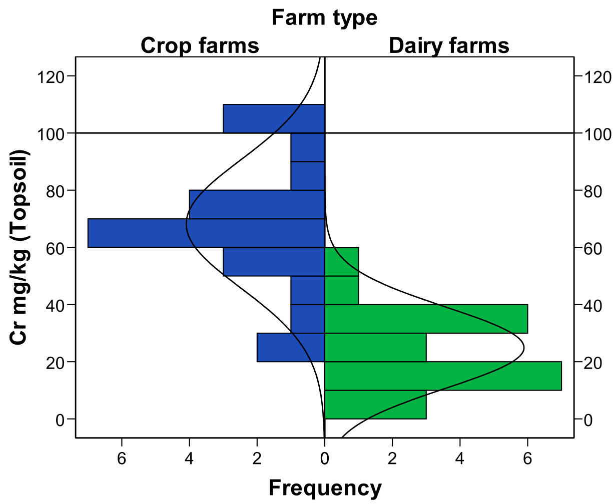

Figure 5. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) chromium (Cr) contents (mg kg^{-1}) in the topsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004. Threshold value, 100 mg kg^{-1}, is presented with solid line.

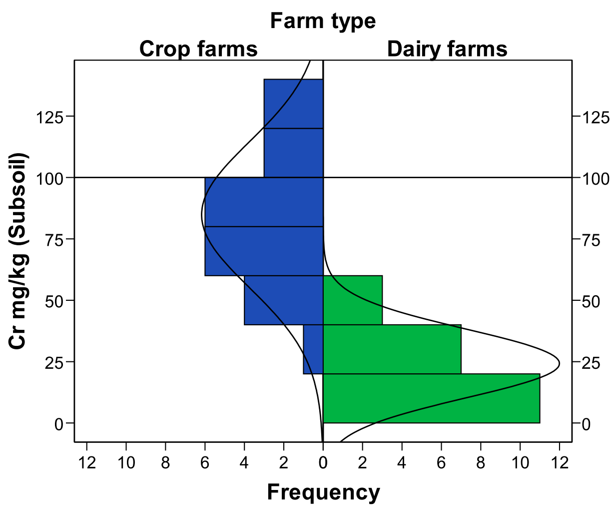

Figure 6. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) chromium (Cr) contents (mg kg^{-1}) in the subsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004. Threshold value, 100 mg kg^{-1}, is presented with solid line.

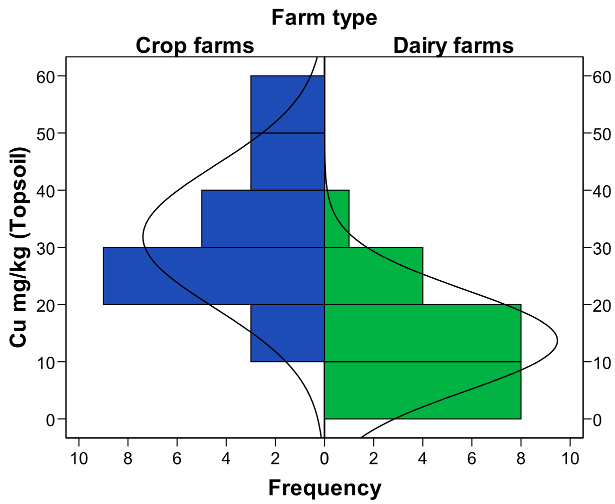

Figure 7. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) copper (Cu) contents (mg kg^{-1}) in the topsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004.

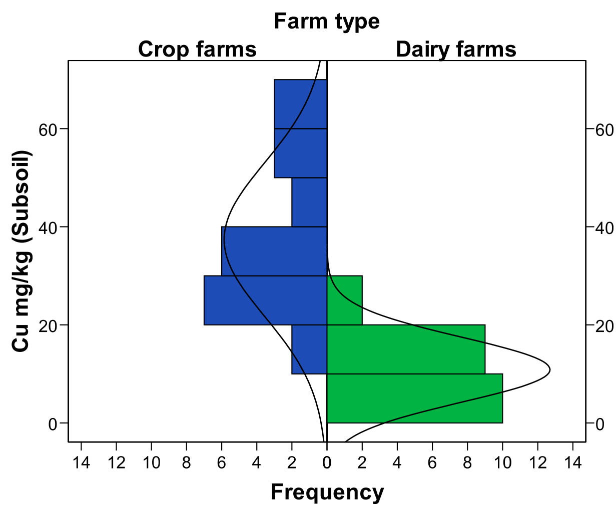

Figure 8. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) copper (Cu) contents (mg kg^{-1}) in the subsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004.

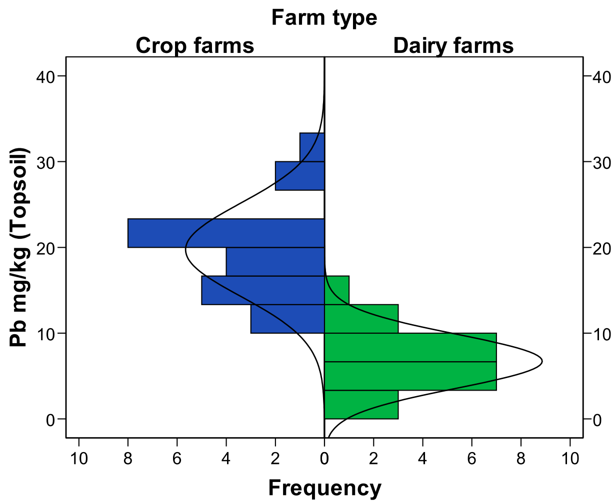

Figure 9. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) lead (Pb) contents (mg kg^{-1}) in the topsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004.

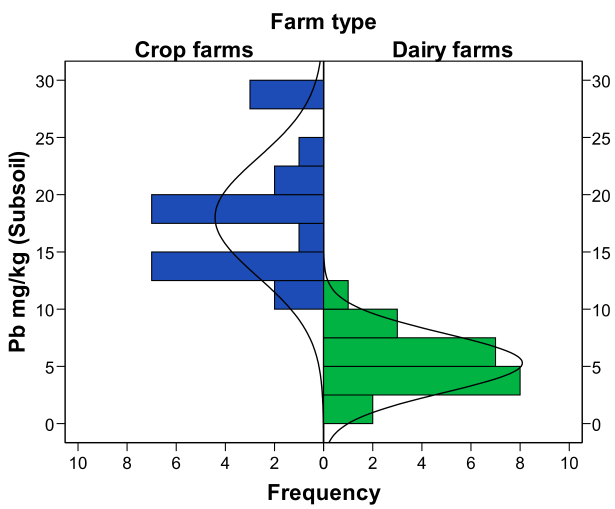

Figure 10. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) lead (Pb) contents (mg kg^{-1}) in the subsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004.

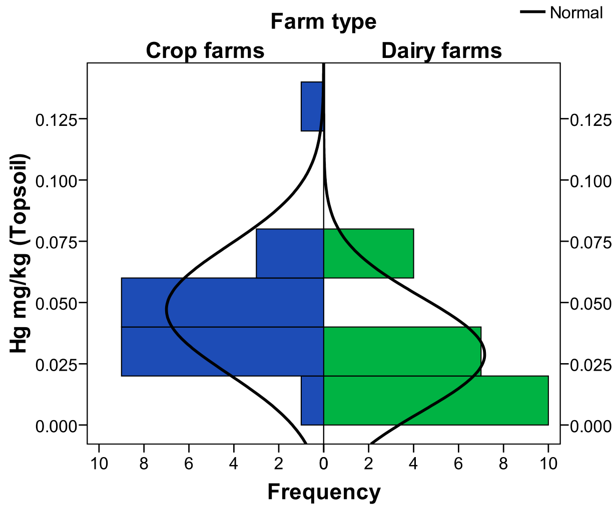

Figure 11. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) mercury (Hg) contents (mg kg^{-1}) in the topsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004

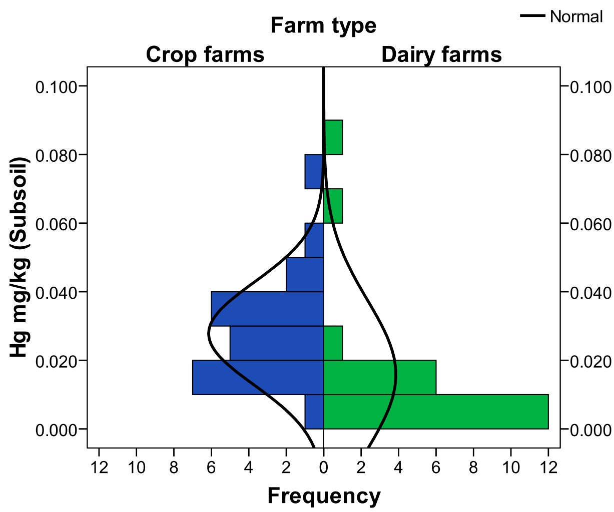

Figure 12. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) mercury (Hg) contents (mg kg^{-1}) in the subsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004.

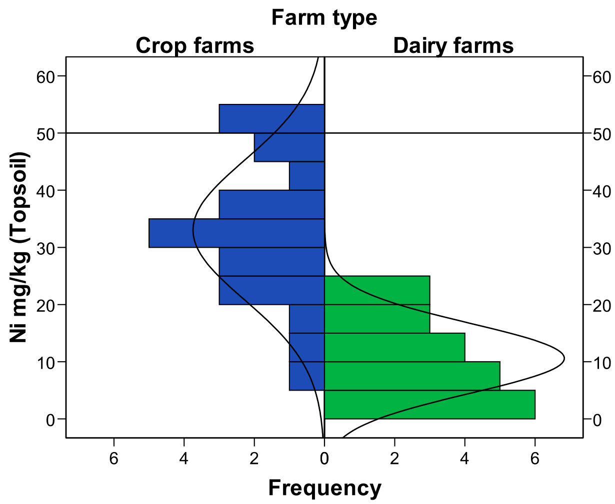

Figure 13. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) nickel (Ni) contents (mg kg^{-1}) in the topsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004. Threshold value, 50 mg kg^{-1}, is presented with solid line.

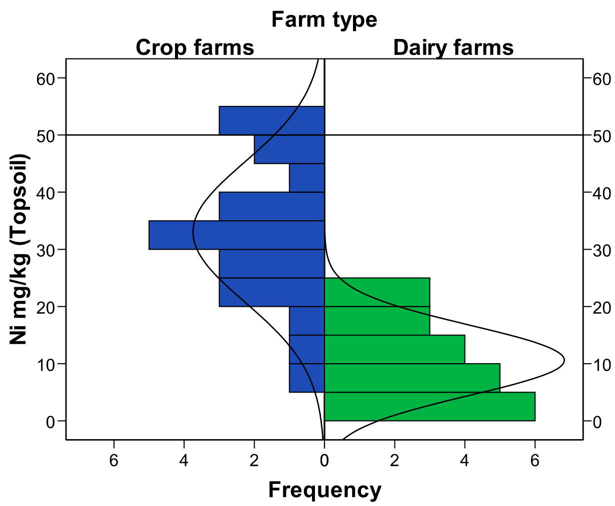

Figure 14. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) nickel (Ni) contents (mg kg^{-1}) in the subsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004. Threshold value, 50 mg kg^{-1}, is presented with solid line.

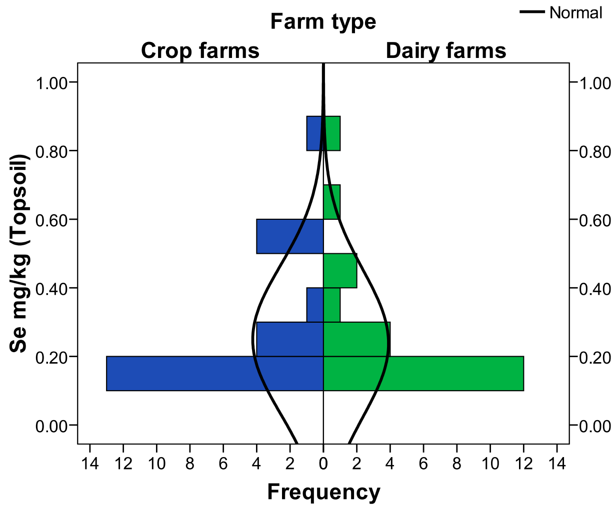

Figure 15. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) selenium (Se) contents (mg kg^{-1}) in the topsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004.

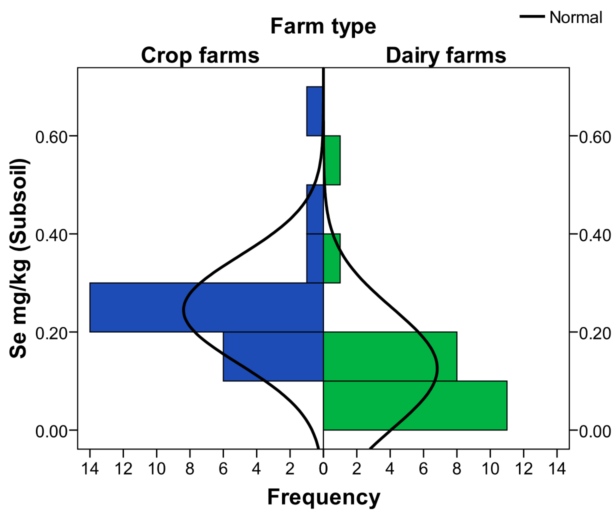

Figure 16. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) selenium (Se) contents (mg kg^{-1}) in the subsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004.

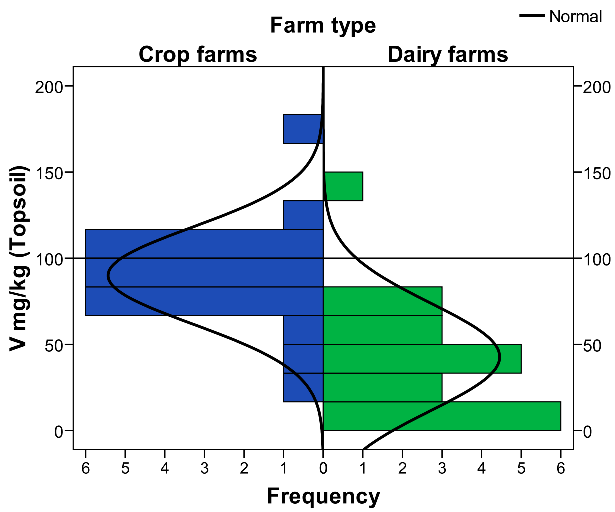

Figure 17. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) vanadium (V) contents (mg kg^{-1}) in the topsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004. Threshold value, 100 mg kg^{-1}, is presented with solid line.

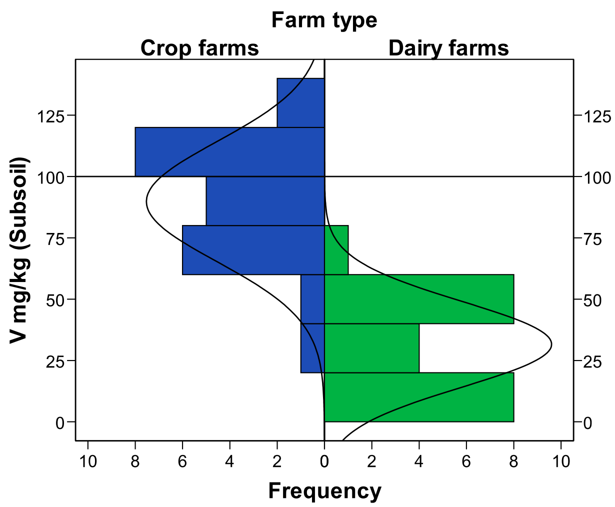

Figure 18. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) vanadium (V) contents (mg kg^{-1}) in the subsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004. Threshold value, 100 mg kg^{-1}, is presented with solid line.

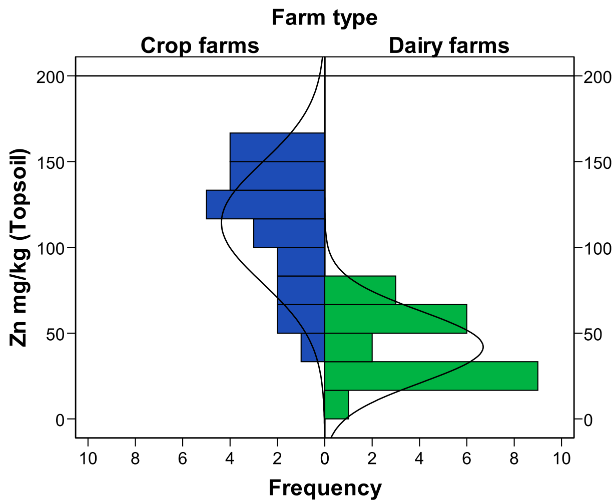

Figure 19. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) zinc (Zn) contents (mg kg^{-1}) in the topsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004. Threshold value, 200 mg kg^{-1}, is presented with solid line.

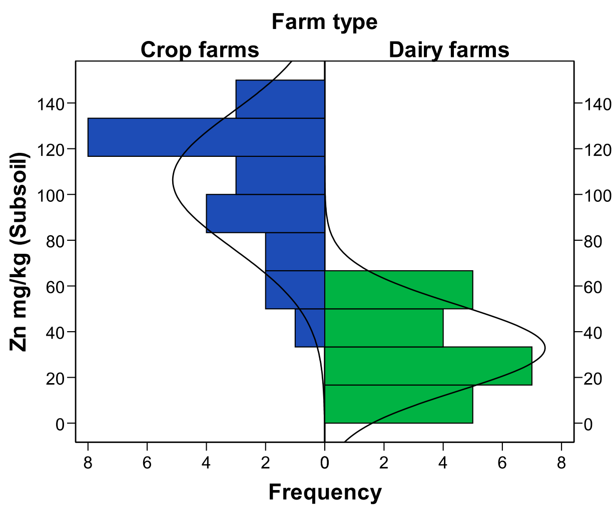

Figure 20. Frequency (as number of samples) of *aqua regia* extractable (ISO 11466) zinc (Zn) contents (mg kg^{-1}) in the subsoil sampled from 23 fields on the five crop farms in southwestern Finland and from 21 fields on the five dairy farms in Ostrobothnia in 2004.

APPENDIX 6

Table 1. Significant (**) correlations (Pearson's correlation) between *aqua regia* extractable (ISO 11466) trace elements in the topsoil of 23 fields on the five crop farms in southwestern Finland in 2004.

Crop farms	Topsoil								
	As	Cd	Cr	Cu	Pb	Hg	Ni	Se	V
Topsoil									
As									
Cd	-								
Cr	.611	-							
Cu	.678	-	.856						
Pb	.804	-	.802	.872					
Hg	-	.783	-	-	-				
Ni	.596	-	.968	.902	.791	-			
Se	-	.545	-	-	-	.530	-		
V	.651	-	.866	.738	.785	-	.796	-	
Zn	-	-	.717	.556	-	-	.760	-.596	.609

Table 2. Significant (**) correlations (Pearson's correlation) between *aqua regia* extractable (ISO 11466) trace elements in the subsoil of 23 fields on the five crop farms in southwestern Finland in 2004.

Crop farms	Subsoil								
	As	Cd	Cr	Cu	Pb	Hg	Ni	Se	V
Subsoil									
As									
Cd	-								
Cr	-	-							
Cu	-	-	.841						
Pb	.653	-	.722	.864					
Hg	-	.644	-	-	-				
Ni	-	-	.935	.944	.829	-			
Se	-	.859	-	-	-	.592	-		
V	-	-	.940	.865	.758	-	.941	-	
Zn	-	-	.845	.714	.564	-	.824	-	.903

Table 3. Significant (**) correlations (Pearson's correlation) of *aqua regia* extractable (ISO 11466) trace elements between the top- and subsoil of 23 fields on the five crop farms in southwestern Finland in 2004.

Crop farms	Topsoil									
	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	V	Zn
Subsoil										
As	.815	-	-	-	-	-	.554	-	-	-
Cd	-	.793	-	-	.526	-	-	-	-	-
Cr	.551	-	.914	.812	-	.919	.688	-	.795	.770
Cu	.713	-	.773	.931	-	.825	.801	-	.745	.579
Hg	-	-	-	-	-	-	-	-	-	-
Ni	.668	-	.857	.895	-	.919	.773	-	.765	.723
Pb	.826	-	.687	.818	-	.706	.919	-	.695	-
Se	-	.804	-	-	.674	-	-	-	-	-
V	.651	-	.851	.788	-	.873	.710	-	.841	.821
Zn	.538	-	.706	.613	-	.750	-	-.607	.643	.933

Table 4. Significant (**) correlations (Pearson's correlation) between *aqua regia* extractable (ISO 11466) trace elements in the topsoil of 21 fields on the five dairy farms in Ostrobothnia in 2004.

Dairy farms	Topsoil								
	As	Cd	Cr	Cu	Pb	Hg	Ni	Se	V
Topsoil									
As									
Cd	.578								
Cr	-	.729							
Cu	-	.865	.777						
Pb	-	.718	.932	.774					
Hg	-	.851	.575	.771	.689				
Ni	-	.768	.959	.825	.867	-			
Se	-	.862	-	.792	-	.841	.566		
V	.551	.699	.852	.688	.771	.656	.761	-	
Zn	-	.568	.892	.622	.792	-	.906	-	.682

Table 5. Significant (**) correlations (Pearson's correlation) between *aqua regia* extractable (ISO 11466) trace elements in the subsoil of 21 fields on the five dairy farms in Ostrobothnia in 2004.

Dairy farms	Subsoil								
	As	Cd	Cr	Cu	Pb	Hg	Ni	Se	V
Subsoil									
As									
Cd	-								
Cr	-	-							
Cu	.648	-	.856						
Pb	-	-	.975	.818					
Hg	.732	.709	-	-	-				
Ni	-	-	.993	.863	.978	-			
Se	.881	.678	-	.554	-	.894	-		
V	-	-	.954	.918	.909	-	.932	-	
Zn	-	-	.934	.741	.931	-	.940	-	.849

Table 6. Significant (**) correlations (Pearson's correlation) of *aqua regia* extractable (ISO 11466) trace elements between the top- and subsoil of 21 fields on the five dairy farms in Ostrobothnia in 2004.

Dairy farms	Topsoil									
	As	Cd	Cu	Cr	Pb	Hg	Ni	Se	V	Zn
Subsoil										
As	.832	-	-	-	-	-	-	-	-	-
Cd	-	.676	.551		-	.553	-	.570	.606	.568
Cr	-	.679	.713	.930	.878		.950	-	.692	.921
Cu	.819	.733	.724	.793	.730	.565	.866	.550	.737	.818
Pb	-	.624	.697	.908	.849	-	.945	-	.645	.886
Hg	-	-	-	-	-	-	-	-	-	-
Ni	-	.688	.699	.919	.847	-	.952	-	.689	.903
Se	.618	-	.559	-	-	.705	-	-	.584	-
V	.618	.686	.764	.917	.889	.550	.925	-	.770	.910
Zn	-	-	.596	.881	.769	-	.906	-	.621	.931

APPENDIX 7

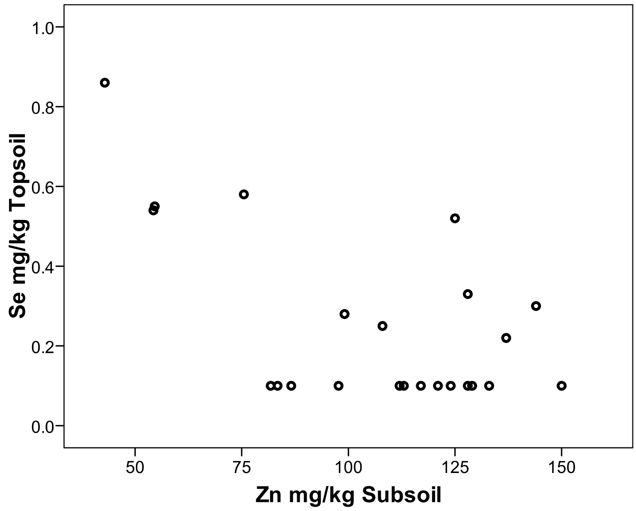

Figure 1. A scatter diagram of the relation of *aqua regia* extractable (ISO 11466) selenium (Se) in the topsoil and of *aqua regia* extractable (ISO 11466) zinc (Zn) in the subsoil of 23 fields on the five crop farms in southwestern Finland in 2004.

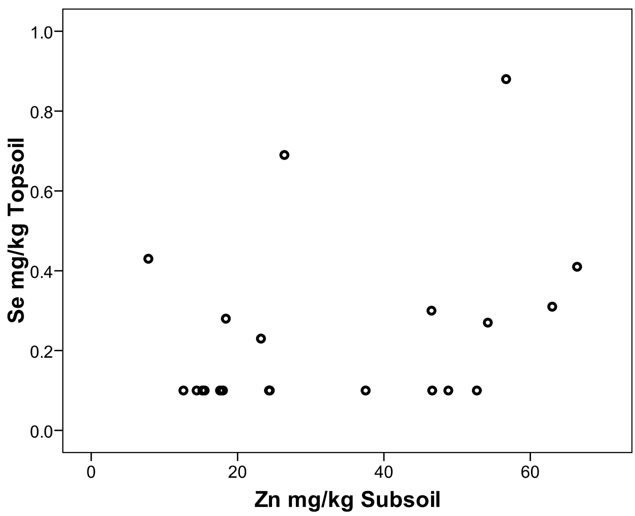

Figure 2. A scatter diagram of the relation of *aqua regia* extractable (ISO 11466) selenium (Se) in the topsoil and of *aqua regia* extractable (ISO 11466) zinc (Zn) in the subsoil of 21 fields on the five dairy farms in Ostrobothnia in 2004.

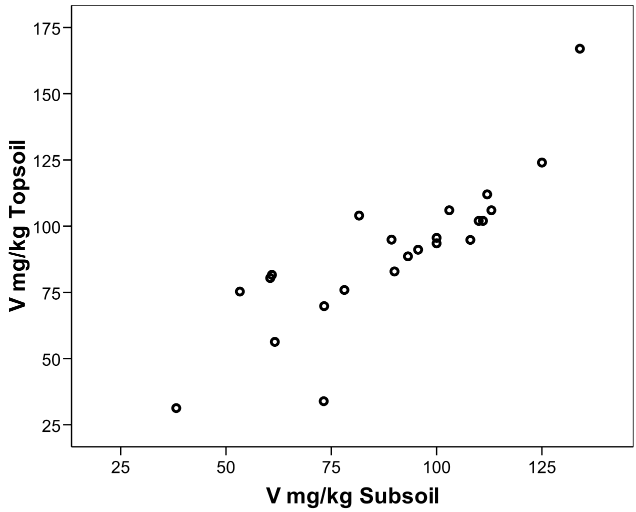

Figure 3. A scatter diagram of the relation of *aqua regia* extractable (ISO 11466) vanadium (V) in the top- and subsoil of 23 fields on the five crop farms in south-western Finland in 2004.

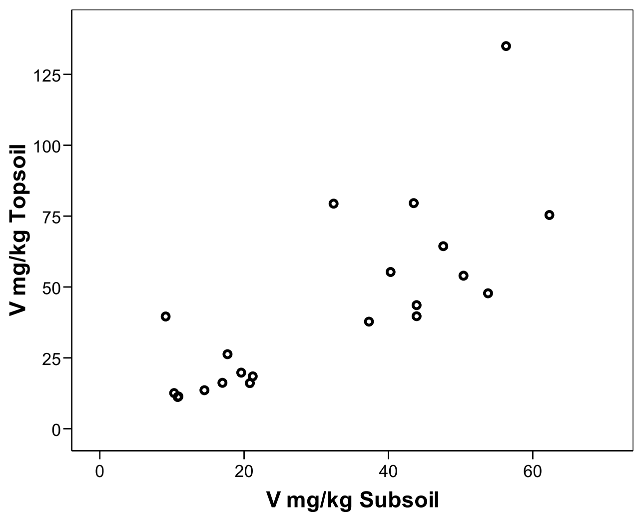

Figure 4. A scatter diagram of the relation of *aqua regia* extractable (ISO 11466) vanadium (V) in the top- and subsoil of 21 fields on the five dairy farms in Ostrobothnia in 2004.

APPENDIX 8

Table 1. Mean *aqua regia* extractable arsenic (As) in top- and subsoil as content and as amount per ha. Arsenic amount enriched in the topsoil, As enrichment factor and correlation coefficient (** = correlation is significant at the 0.01 level, 2-tailed). Mean AAAc-EDTA extractable As in topsoil as concentration and as percentage (%) from equivalent *aqua regia* extractable As. Sum of enrichment (%) and solubility (%) in clay soils (n = 23) on five crop farms in southwestern (SW) Finland and in finesand soils (n = 21) on five dairy farms in Ostrobothnia in 2004.

	As	
Year 2004	**Crop farms**	**Dairy farms**
Region	SW Finland	Ostrobothnia
Soil type	Clay	Finesand
Subsoil, cm	21.6-43.2	24.3-48.6
Aqua regia, mg kg^{-1}	7.2	3.1
Amount, kg ha^{-1}	16	7.5
Topsoil, cm	0-21.6	0-24.3
Aqua regia, mg kg^{-1}	5.9	3.1
Amount, kg ha^{-1}	13	7.5
Amount enriched, kg ha^{-1}	- 3	$\pm$ 0
Enrichment factor (Top-/Subsoil)	0.82	1.00
Correlation (Top-/Subsoil)	.815**	.832**
AAAc-EDTA, mg l^{-1}	0.53	0.90
AAAc-EDTA/*Aqua regia*, %	5.1	13
Enrichment, % + Solubility, %	87.1	113

Table 2. Mean *aqua regia* extractable cadmium (Cd) in top- and subsoil as content and as amount per ha. Cadmium amount enriched in the topsoil, Cd enrichment factor and correlation coefficient (** = correlation is significant at the 0.01 level, 2-tailed). Mean AAAc-EDTA extractable Cd in topsoil as concentration and as percentage (%) from equivalent *aqua regia* extractable Cd. Sum of enrichment (%) and solubility (%) in clay soils (n = 23) on five crop farms in southwestern (SW) Finland and in finesand soils (n = 21) on five dairy farms in Ostrobothnia in 2004.

	Cd	
Year 2004	**Crop farms**	**Dairy farms**
Region	SW Finland	Ostrobothnia
Soil type	Clay	Finesand
Subsoil, cm	21.6-43.2	24.3-48.6
Aqua regia, mg kg^{-1}	0.116	0.061
Amount, kg ha^{-1}	0.251	0.148
Topsoil, cm	0-21.6	0-24.3
Aqua regia, mg kg^{-1}	0.227	0.112
Amount, kg ha^{-1}	0.490	0.272
Amount enriched, kg ha^{-1}	0.239	0.124
Enrichment factor (Top-/Subsoil)	1.96	1.84
Correlation (Top-/Subsoil)	.793**	.676**
AAAc-EDTA, mg l^{-1}	0.093	0.069
AAAc-EDTA/*Aqua regia*, %	44	50
Enrichment, % + Solubility, %	240	234

Table 3. Mean *aqua regia* extractable chromium (Cr) in top- and subsoil as content and as amount per ha. Chromium amount enriched in the topsoil, Cr enrichment factor and correlation coefficient (** = correlation is significant at the 0.01 level, 2-tailed). Mean AAAc-EDTA extractable Cr in topsoil as concentration and as percentage (%) from equivalent *aqua regia* extractable Cr. Sum of enrichment (%) and solubility (%) in clay soils (n = 23) on five crop farms in southwestern (SW) Finland and in finesand soils (n = 21) on five dairy farms in Ostrobothnia in 2004.

	Cr	
Year 2004	**Crop farms**	**Dairy farms**
Region	SW Finland	Ostrobothnia
Soil type	Clay	Finesand
Subsoil, cm	21.6-43.2	24.3-48.6
Aqua regia, mg kg^{-1}	85	24
Amount, kg ha^{-1}	184	58
Topsoil, cm	0-21.6	0-24.3
Aqua regia, mg kg^{-1}	68	25
Amount, kg ha^{-1}	147	61
Amount enriched, kg ha^{-1}	- 37	3
Enrichment factor (Top-/Subsoil)	0.80	1.04
Correlation (Top-/Subsoil)	.914**	.930**
AAAc-EDTA, mg l^{-1}	<1	<1
AAAc-EDTA/*Aqua regia*, %	0.0	0.0
Enrichment, % + Solubility, %	80	104

Table 4. Mean *aqua regia* extractable copper (Cu) in top- and subsoil as content and as amount per ha. Copper amount enriched in the topsoil, Cu enrichment factor and correlation coefficient (** = correlation is significant at the 0.01 level, 2-tailed). Mean AAAc-EDTA extractable Cu in topsoil as concentration and as percentage (%) from equivalent *aqua regia* extractable Cu. Sum of enrichment (%) and solubility (%) in clay soils (n = 23) on five crop farms in southwestern (SW) Finland and in finesand soils (n = 21) on five dairy farms in Ostrobothnia in 2004.

	Cu	
Year 2004	**Crop farms**	**Dairy farms**
Region	SW Finland	Ostrobothnia
Soil type	Clay	Finesand
Subsoil, cm	21.6-43.2	24.3-48.6
Aqua regia, mg kg^{-1}	37	11
Amount, kg ha^{-1}	80	27
Topsoil, cm	0-21.6	0-24.3
Aqua regia, mg kg^{-1}	32	14
Amount, kg ha^{-1}	69	34
Amount enriched, kg ha^{-1}	- 11	7
Enrichment factor (Top-/Subsoil)	0.86	1.27
Correlation (Top-/Subsoil)	.931**	.724**
AAAc-EDTA, mg l^{-1}	4.5	4.1
Fertility class*	4	4
AAAc-EDTA/*Aqua regia*, %	17	37
Enrichment, % + Solubility, %	103	164

* Fertility classes: 1 = Poor; 2 = Rather poor; 3 = Fair; 4 = Satisfactory; 5 = Good; 6 = Very good; 7 = Possibly excessive (Viljavuuspalvleu 2000).

Table 5. Mean *aqua regia* extractable lead (Pb) in top- and subsoil as content and as amount per ha. Lead amount enriched in the topsoil, Pb enrichment factor and correlation coefficient (** = correlation is significant at the 0.01 level, 2-tailed). Mean AAAc-EDTA extractable Pb in topsoil as concentration and as percentage (%) from equivalent *aqua regia* extractable Pb. Sum of enrichment (%) and solubility (%) in clay soils (n = 23) on five crop farms in southwestern (SW) Finland and in finesand soils (n = 21) on five dairy farms in Ostrobothnia in 2004.

	Pb	
Year 2004	**Crop farms**	**Dairy farms**
Region	SW Finland	Ostrobothnia
Soil type	Clay	Finesand
Subsoil, cm	21.6-43.2	24.3-48.6
Aqua regia, mg kg^{-1}	18	5.3
Amount, kg ha^{-1}	39	13
Topsoil, cm	0-21.6	0.24.3
Aqua regia, mg kg^{-1}	20	6.7
Amount, kg ha^{-1}	43	16
Amount enriched, kg ha^{-1}	4	3
Enrichment factor (Top-/Subsoil)	1.11	1.26
Correlation (Top-/Subsoil)	.919**	.849**
AAAc-EDTA, mg l^{-1}	2.9	1.5
AAAc-EDTA/*Aqua regia*, %	16	23
Enrichment, % + Solubility, %	127	149

Table 6. Mean *aqua regia* extractable mercury (Hg) in top- and subsoil as content and as amount per ha. Mercury amount enriched in the topsoil, Hg enrichment factor and correlation coefficient in clay soils (n = 23) on five crop farms in southwestern (SW) Finland and in finesand soils (n = 21) on five dairy farms in Ostrobothnia in 2004 (* = Correlation is significant at the 0.05 level, 2-tailed).

	Hg	
Year 2004	**Crop farms**	**Dairy farms**
Region	SW Finland	Ostrobothnia
Soil type	Clay	Finesand
Subsoil,cm	21.6-43.2	24.3-48.6
Aqua regia, mg kg^{-1}	0.028	0.017
Amount, kg ha^{-1}	0.060	0.041
Topsoil, cm	0-21.6	0-24.3
Aqua regia, mg kg^{-1}	0.047	0.033
Amount, kg ha^{-1}	0.102	0.080
Amount enriched, kg ha^{-1}	0.042	0.039
Enrichment factor (Top-/Subsoil)	1.68	1.94
Correlation Top-/Subsoil	.382	.532*

Table 7. Mean *aqua regia* extractable nickel (Ni) in top- and subsoil as content and as amount per ha. Nickel amount enriched in the topsoil, Ni enrichment factor and correlation coefficient (** = correlation is significant at the 0.01 level, 2-tailed). Mean AAAc-EDTA extractable Ni in topsoil as concentration and as percentage (%) from equivalent *aqua regia* extractable Ni. Sum of enrichment (%) and solubility (%) in clay soils (n = 23) on five crop farms in southwestern (SW) Finland and in finesand soils (n = 21) on five dairy farms in Ostrobothnia in 2004.

	Ni	
Year 2004	**Crop farms**	**Dairy farms**
Region	SW Finland	Ostrobothnia
Soil type	Clay	Finesand
Subsoil, cm	21.6-43.2	24.3-48.6
Aqua regia, mg kg^{-1}	39	11
Amount, kg ha^{-1}	84	27
Topsoil, cm	0-21.6	0-24.3
Aqua regia, mg kg^{-1}	33	11
Amount, kg ha^{-1}	71	27
Amount enriched, kg ha^{-1}	- 13	$\pm$ 0
Enrichment factor (Top-/Subsoil)	0.85	1.00
Correlation (Top-/Subsoil)	.919**	.952**
AAAc-EDTA, mg l^{-1}	1.6	1.6
AAAc-EDTA/*Aqua regia*, %	4.2	9.3
Enrichment, % + Solubility, %	89.2	109.3

Table 8. Mean *aqua regia* extractable selenium (Se) in top- and subsoil as content and as amount per ha. Selenium amount enriched in the topsoil, Se enrichment factor and correlation coefficient (* = correlation is significant at the 0.05 level, 2-tailed). Mean AAAc-EDTA extractable Se in topsoil as concentration and as percentage (%) from equivalent *aqua regia* extractable Se. Sum of enrichment (%) and solubility (%) in clay soils (n = 23) on five crop farms in southwestern (SW) Finland and in finesand soils (n = 21) on five dairy farms in Ostrobothnia in 2004.

	Se	
Year 2004	**Crop farms**	**Dairy farms**
Region	SW Finland	Ostrobothnia
Soil type	Clay	Finesand
Subsoil, cm	21.6-43.2	24.3-48.6
Aqua regia, mg kg^{-1}	0.25	0.13
Amount, kg ha^{-1}	0.540	0.316
Topsoil, cm	0-21.6	0-24.3
Aqua regia, mg kg^{-1}	0.28[1]	0.18[2]
Amount, kg ha^{-1}	0.605	0.437
Amount enriched, kg ha^{-1}	0.065	0.121
Enrichment factor (Top-/Subsoil)	1.12	1.38
Correlation (Top-/Subsoil)	.477*	.513*
AAAc-EDTA, mg l^{-1}	>0.01	0.01
AAAc-EDTA/*Aqua regia*, %	4.2	6.7
Enrichment, % + Solubility, %	116.2	144.7

[1] >50% of the analytical results was below the detection limit for topsoil, 0.2 mg kg^{-1}. The value 0.28 mg kg^{-1} dm = the mean content of *aqua regia* extractable Se for clay soils (n=51) in 1998 (Mäkelä-Kurtto et al. 2007a);

[2] >50% of the analytical results was below the detection limit for topsoil, 0.2 mg kg^{-1}. The value 0.18 mg kg^{-1} dm = the mean content of *aqua regia* extractable Se for coarse mineral soils (n=219) in 1998 (Mäkelä-Kurtto et al. 2007a)

Table 9. Mean *aqua regia* extractable vanadium (V) in top- and subsoil as content and as amount per ha. Vanadium amount enriched in the topsoil, V enrichment factor and correlation coefficient (** = correlation is significant at the 0.01 level, 2-tailed). Mean AAAc-EDTA extractable V in topsoil as concentration and as percentage (%) from equivalent *aqua regia* extractable V. Sum of enrichment (%) and solubility (%) in clay soils (n = 23) on five crop farms in southwestern (SW) Finland and in finesand soils (n = 21) on five dairy farms in Ostrobothnia in 2004.

	V	
Year 2004	**Crop farms**	**Dairy farms**
Region	SW Finland	Ostrobothnia
Soil type	Clay	Finesand
Subsoil, cm	21.6-43.2	24.3-48.6
Aqua regia, mg kg^{-1}	90	32
Amount, kg ha^{-1}	194	78
Topsoil, cm	0-21.6	0-24.3
Aqua regia, mg kg^{-1}	90	43
Amount, kg ha^{-1}	194	104
Amount enriched, kg ha^{-1}	$\pm$ 0	26
Enrichment factor (Top-/Subsoil)	1.00	1.34
Correlation (Top-/Subsoil)	.841**	.770**
AAAc-EDTA, mg l^{-1}	12	10
AAAc-EDTA/*Aqua regia*, %	6.9	17
Enrichment, % + Solubility, %	106.9	151

Table 10. Mean *aqua regia* extractable arsenic (As) in top- and subsoil as content and as amount per ha. Arsenic amount enriched in the topsoil, As enrichment factor and correlation coefficient (** = correlation is significant at the 0.01 level, 2-tailed). Mean AAAc-EDTA extractable As in topsoil as concentration and as percentage (%) from equivalent *aqua regia* extractable As. Sum of enrichment (%) and solubility (%) in clay soils (n = 23) on five crop farms in southwestern Finland and in finesand soils (n = 21) on five dairy farms in Ostrobothnia in 2004.

	Zn	
Year 2004	**Crop farms**	**Dairy farms**
Region	S-W Finland	Ostrobothnia
Soil type	Clay	Finesand
Subsoil, cm	21.6-43.2	24.3-48.6
Aqua regia, mg kg^{-1}	106	33
Amount, kg ha^{-1}	229	80
Topsoil, cm	0-21.6	0-24.3
Aqua regia, mg kg^{-1}	114	42
Amount, kg ha^{-1}	246	102
Amount enriched, kg ha^{-1}	17	22
Enrichment factor (Top-/Subsoil)	1.08	1.27
Correlation (Top-/Subsoil)	.933**	.931**
AAAc-EDTA, mg l^{-1}	2.0	3.5
Fertility class*	2	4
AAAc-EDTA/*Aqua regia*, %	1.7	12
Enrichment, % + Solubility, %	109.7	139.0

* Fertility classes: 1 = Poor; 2 = Rather poor; 3 = Fair; 4 = Satisfactory; 5 = Good; 6 = Very good; 7 = Possibly excessive (Viljavuuspalvelu 2000).

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