Risk Assessment and Risk Management
Procedure for Arsenic in the Tampere Region

Arsenic and other elements in agro-ecosystems in Finland and particularly in the Pirkanmaa region

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ABSTRACT

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The current research belongs to the RAMAS-project, jointly funded by the EU LIFE ENVIRONMENT programme and participating organisations. A risk assessment and risk management procedure for arsenic will be produced for the Province of Pirkanmaa, Finland (www.gtk.fi/projects/ramas). The main aims of the present study were to: 1) investigate the contents of the arsenic and other potentially toxic elements in arable and forest soils and crops in the Pirkanmaa region, 2) assess the migration of arsenic in agricultural soils and crop, and 3) define and quantify arsenic sources in Finnish agro-ecosystems to clarify possible differences in soil arsenic contents in arable and forest lands and between different soil layers. Wheat grains (*Triticum aestivum* L.), potato tubers (*Solanum tuberosum* L.) and timothy grass (*Phleum pratense* L.) were selected as crop species to be studied because they are important in the human food chain in Europe and globally. Sampling of arable soils and crops were made by the MTT Agrifood Research Finland in 2005 and analysed in 2005-2006. Fifteen sites on the arable land of thirteen farms in the Pirkanmaa region were sampled. Five sites grew wheat, five potatoes and five timothy grass. The Geological Survey of Finland was responsible for collecting and analysing soil samples from forest land close to these farms. Soil samples were analysed for arsenic and 13 other elements (P, S, Al, Fe, Cd, Cu, Cr, Mn, Ni, Pb, V, Zn and Se) by digestion with *aqua regia* (ISO 11 466) and plant crops for the respective elements by wet digestion with concentrated HNO_3 (SFS 3 044). Soluble trace elements in soils were measured from AAAc-EDTA extraction.

The contents of arsenic and other elements in the arable soils and crops collected in the potentially high-arsenic areas in the Pirkanmaa region were of the same low level found in other regions in Finland. Arsenic contents were slightly higher in the plough layer than in the subsoil. Correlations of arsenic contents to other arable soil characteristics were weak, the strongest positive correlation being to the humus and clay content. Only about 1% of total arsenic was in a soluble form in the arable soil. Arsenic had one of the lowest soil-to-plant uptake factors among the elements studied. In contrast, the arsenic contents forest soils of the Pirkanmaa region were on a higher level than in the other areas in Finland. Arsenic had stronger correlations to the other elements in the deeper horizon than in the upper part. The deeper the mineral soil layer, the higher the arsenic content. However, the organic soil layer contained more arsenic than the next two mineral soil layers below. These two soil layers, which were comparable to the plough layer of the arable land, had a lower arsenic content than the plough layer. Instead, in the subsoil layer, the forest land contained more arsenic than the arable land. Based on the arsenic contents in various soils layers, a major source of arsenic in the arable and forest soil seems to be geogenic. Surface layers have received additional arsenic from anthropogenic sources. Anthropogenic sources of arsenic and material flows of Finnish agriculture were quantified. Arsenic mass balances of arable soils were presented at a national level and at a farm level. An arsenic accumulation in the soil was minor. Other projects showed that there is a small number of Finnish fields containing an elevated arsenic content (>10 mg kg^{-1}). Hence, recommendations for cultivation practices and for reducing human exposure to arsenic were elaborated.

Based on this study and the relatively large background data the farmers, their families and domestic animals living in the Pirkanmaa region seem to be exposed to arsenic by consuming home-grown food and feed crops or forest crops, by ingesting soil or by inhaling soil particles as dust to the same extent as people and animals elsewhere in Finland.

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Keywords (GeoRef, Thesaurus): arsenic, soils, arable lands, forest soils, topsoil, subsoil, geochemistry, wheat, timothy, potatoes, chemical composition, Pirkanmaa, Finland.

TIIVISTELMÄ

Mäkelä-Kurtto, R., Eurola, M., Justén, A., Backman, B., Luoma, S., Karttunen, V. & Ruskeeniemi, T., 2006. Arsenic and other elements in agro-ecosystems in Finland and particularly in the Pirkanmaa region. Geologian tutkimuskeskus, Erikoisjulkaisut, 119 sivua, 23 kuvaa ja 72 taulukkoa.

Tutkimus kuuluu RAMAS-projektiin, jota rahoittavat EU:n LIFE ENVIRONMENT –tutkimusohjelma ja hankkeeseen osallistuvat yhteistyökumppanit. Projektin tavoitteena on tuottaa menettelytapa arseeniriskinarviointiin ja –hallintaan Pirkanmaalle (www.gtk.fi/projects/ramas). Tutkimuksen tavoitteena oli selvittää arseenin ja eräiden muiden alkuaineiden pitoisuuksia pelto- ja metsämaissa sekä sadoissa sellaisilla Pirkanmaan alueilla, joista on todettu luontaisesti kohonneita arseenipitoisuuksia. Tavoitteena oli myös tutkia arseenin siirtymistä viljelymaasta satoihin ja selvittää suomalaisen agroekosysteemin arseenilähteitä selittämään mahdollisia arseenipitoisuuseroja pelto- ja metsämaissa sekä eri maakerroksissa. Tutkittaviksi valittiin elintarviketuotannon tärkeimpiä kasvisatoja: vehnä (*Triticum aestivum* L.), peruna (*Solanum tuberosum* L.) ja timotei (*Phleum pratense* L.). Maa- ja elintarviketalouden tutkimuskeskus (MTT) suoritti maa- ja satonäytteiden keruun pelloilta vuonna 2005 ja näytteiden analysoinnin vuosina 2005 ja 2006. Näytteitä kerättiin 15 pisteestä 13 pirkanmaalaiselta tilalta. Näytepisteistä otettiin myös satonäytteet, viisi kutakin kasvilajia. Geologian tutkimuskeskus (GTK) vastasi metsämaiden näytteenotosta ja analysoinnista. Metsämaanäytteet otettiin samoilta tiloilta ja samantyyppisiltä maalajeilta kuin peltomaanäytteet. Näytteistä analysoitiin arseenin lisäksi 13 muuta alkuainetta (P, S, Al, Fe, Cd, Cu, Cr, Mn, Ni, Pb, V, Zn and Se). Alkuaineiden pitoisuudet maasta määritettiin kuningasvesiuutosta, *aqua regia* (ISO 11 466), ja AAAc-EDTA –uutosta. Kasvinäytteiden pitoisuudet määritettiin typpihappohajotuksesta (SFS 3 044).

Arseenin ja muiden alkuaineiden pitoisuudet tutkituissa viljelymaissa ja -kasveissa olivat tutkituilla pirkanmaalaisilla tiloilla samaa alhaista tasoa kuin muualla Suomessa. Arseenipitoisuudet olivat hieman suurempia muokkauskerroksessa kuin jankossa. Viljelymaan arseenipitoisuudet korreloivat heikosti muihin maaperätekijöihin. Voimakkaimmat, positiiviset, korrelaatiot arseenilla oli maan humus- ja savespitoisuuteen. Viljelymaiden arseenista noin 1% oli liukoisessa muodossa. Verrattuna muihin tutkittuihin alkuaineisiin arseenin siirtyminen maasta kasveihin oli hyvin vähäistä. Sen sijaan metsämaissa pitoisuudet tutkituilla maatiloilla olivat keskimääräistä suurempia. Niissä arseenin korrelaatiot muihin alkuaineisiin olivat suurempia syvemmissä maakerroksissa kuin pintamaassa. Mineraalimaakerroksissa arseenipitoisuudet kasvoivat siirryttäessä syvempiin maakerroksiin. Kuitenkin orgaanisen kerroksen arseenipitoisuudet olivat jonkin verran suurempia kuin kahdessa alemmassa mineraalimaakerroksessa. Näissä, viljelymaan muokkauskerrosta vastaavissa kerroksissa arseenipitoisuudet olivat pienempiä, kun taas jankkoa vastaavassa kerroksessa pitoisuudet olivat suurempia kuin viljelymaissa. Maakerrosten arseenipitoisuuksien perusteella pelto- ja metsämaan arseeni näyttää olevan pääasiassa geologista alkuperää. Pintamaakerroksiin on lisäksi tullut arseenia ihmisen toiminnoista, kuten laskeumista ja lannoitevalmisteista. Maatalouden arseenilähteet ja materiaalivirrat selvitettiin. Arseenin massataseet peltomaissa esitettiin sekä kansallisella tasolla että maatilatasolla. Arseenin kerääntyminen maaperään oli vähäistä. Muiden tutkimusten perusteella Suomesta löytyy muutamia peltoja, joissa on kohonneita arseenipitoisuuksia (>10 mg kg^{-1}). Tästä syystä laadittiin suosituksia viljelytoimenpiteistä ja tavoista vähentää ihmisten arseenialtistusta.

Tämän tutkimuksen ja käytetyn laajahkon taustamateriaalin perusteella viljelijäperheen jäsenet, tuotanto- ja kotieläimet Pirkanmaan alueella eivät altistu arseenille kotovaraisten elintarvikkeiden ja rehujen sekä metsäsatojen, ilmasta pölynä tulevien maahiukkasten kautta tai syömällä maata sen enempää kuin muuallakaan Suomessa.

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Asiasanat (Geosanasto, GTK): arseeni, maaperä, viljelymaat, metsämaat, pintamaa, pohjamaa, geokemia, vehnä, timotei, perunat, kemiallinen koostumus, Pirkanmaa, Suomi.

PREFACE

RAMAS (LIFE04 ENV/FI/000300) is a three-year project which is jointly funded by the LIFE ENVIRONMENT –programme, by the beneficiary, the Geological Survey of Finland (GTK), and by the following partners: the Helsinki University of Technology (TKK), the Pirkanmaa Regional Environment Center (PIR), the Finnish Environment Institute (SYKE), the Agrifood Research Finland (MTT), Esko Rossi Oy (ER) and Kemira Kemwater (Kemira).

The acronym RAMAS arises from the project title "Risk Assessment and Risk Management Procedure for Arsenic in the Tampere Region". The project targets the whole Province of Pirkanmaa (also called the Tampere Region), which comprises 33 municipalities, and has 455 000 inhabitants within its area. Finland's third largest city, Tampere, is the economic and cultural center of the region.

The project works to identify the various sources of arsenic in the target area, to produce a health and environmental risk assessment for the region, and to present recommendations for the prevention/remediation and water and soil treatment methods. This project is the first in Finland to create an overall, large-scale risk management strategy for a region that has both natural and anthropogenic contaminant sources.

The project's work is divided into logically proceeding tasks, which have responsible Task Leaders who coordinate the work within their tasks:

1. Natural arsenic sources (GTK), Birgitta Backman
2. Anthropogenic arsenic sources (PIR), Kati Vaajasaari until 30.4.2006; Ämer Bilaletdin since 1.5.2006
3. Risk assessment (SYKE), Eija Schultz
4. Risk Management (SYKE), Jaana Sorvari
5. Dissemination of results (TKK), Kirsti Loukola-Ruskeeniemi
6. Project management (GTK), Timo Ruskeeniemi

The project produces a number of Technical Reports, which are published as a special series by the GTK. Each report will be an independent presentation of a topic of concern. More comprehensive conclusions will be drawn in the RAMAS-project Final Report, which will summarise the project's results. Most of the reports will be published in English with a Finnish summary.

A cumulative list of the reports published so far will be given on the back cover of each report. All documents can be also downloaded from the project's home page: www.gtk.fi/projects/ramas.

LIST OF ABBREVIATIONS

Al	Aluminium
As	Arsenic
B	Boron
Cd	Cadmium
Ca	Calcium
Co	Cobolt
Cr	Chromium
Cu	Copper
Fe	Iron
Hg	Mercury
K	Potassium
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
N	Nitrogen
Ni	Nickel
P	Phosphorus
Pb	Lead
S	Sulphur
Se	Selenium
V	Vanadium
Zn	Zinc

AR	*Aqua regia*
AAAc	Acid (pH 4.65 MTT; pH 4.8 GTK) ammonium acetate
AAAc-EDTA	Acid (pH 4.65 MTT; pH 4.8 GTK) ammonium acetate –EDTA
Bulk dens.	Bulk density
EDTA	Na_2-ethylenediaminetetracetic acid
El. cond.	Electrical conductivity
dw	Dry weight
fw	Fresh weight
n	number
Org. C	Organic carbon
OM	Organic matter

CONTENTS

1. INTRODUCTION

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 negative effects on human health, natural ecosystems and climate change, as well as on our economy. In 2006, the European Commission (EC) gave a final communication "Towards a Thematic Strategy for Soil Protection" (CEC 2006). Its purpose was to build on the political commitment to soil protection in the coming years.

Globally, about 95% of the protein and most of the calories the human population obtained are from traditional land-based agriculture of crops and livestock (Botkin & Keller 1995). Agriculture and forestry is dependant on soil for supply of water and nutrients and for root fixation. The importance of soil protection for agriculture, forestry and all society is recognized nationally and internationally, as well. One of the main issues for soils is diffuse contamination. Soil contamination by heavy metals and other trace elements is a relevant problem. Soils naturally contain arsenic and other trace elements at detectable levels. Trace elements may function as micronutrients essential to plant and animal growth, while high concentrations can be a threat to the food chain. The elements of the most concern are mercury (Hg), lead (Pb), cadmium (Cd) and arsenic (As), which are especially toxic to humans and animals, and copper (Cu), nickel (Ni) and cobalt (Co), which are a concern because of phytotoxicity. Concentrations of trace elements in soil cover a very wide range. In many cases, the higher values indicate contamination from human activities, but large values can also occur because of natural geological or soil formation conditions.

The Geological Survey of Finland (Koljonen 1992) has detected particularly high arsenic concentrations in glacial till in the Pirkanmaa region due to the high arsenic concentration in the soil parent material. The natural occurrence of arsenic in the Pirkanmaa region has been described in detailed by Backman *et al.* (2006) and anthropogenic sources in the region by Parviainen *et al.* (2006). In many other areas in the EU, high concentrations of arsenic exist in soils (Salminen *et al.* 2005). Arsenic is considered a priority element within the strategy for health and the environment (JRC and EEA 2004). Arsenic is a metalloid with a rich chemistry that forms a variety of inorganic and organic compounds. Arsenic can occur in the oxidation states -3, 0, +3 and +5 whereas in the environment, oxides of the oxidation state +3 (arsenites) and +5 (arsenates) are the most common compounds, with the most stable form being As_2O_3 (arsenic trioxide) (EC 2000). In Finland, arable soils have been monitored since 1974. The monitored soil material sampled in 1998 has been analysed for arsenic (RAKAS-project 2004-2007). National and also regional arsenic data for arable soils are presented in this report.

In Ontario, Canada (Ministry of the Environment in Ontario 2001), food and drinking water together account for 99% of total daily intake of arsenic through ingestion. The breakdown is roughly 84% from food, 15% from drinking water, less than 1% from soil/dusts and a negligible amount from skin contact. The greatest, most common, source of exposure to organic arsenic is from food, particularly shellfish, meat, poultry, grain and dairy products. It is assumed (SCOOP 2004) that the minor part of the total arsenic intake via diet in Finland, and in Europe, too, is land-based, on average, while the major part is water-based, mainly from fish and other seafood.

However, it has been difficult to make accurate estimates of the total intake of arsenic, because for most of the land-based food groups the available arsenic data have been very limited. This data is especially scarce in Finland. A low arsenic level in cultivated soils is important for the production of low-As crops and food and feed stuffs.

The main aims of this study were to investigate and demonstrate arsenic levels in arable and forest soils in potential high risk areas in the Pirkanmaa region and also arsenic contents of land-based food and feed crops produced in this region. Wheat (*Triticum aestivum* L.), potato (*Solanum tuberosum* L.) and timothy grass (*Phleum pratense* L.) were selected as indicator plants because they are cultivated all over Europe and because wheat and potato are commonly consumed by people, while timothy is a common feed plant for domestic animals.

2. ARSENIC IN SOILS AND CROPS IN FINLAND AT A NATIONAL LEVEL

2.1 Main features of agriculture in Finland

Finland is the northernmost country with significant agricultural production and is located between latitudes 60 and 70 degrees north and longitudes 19 and 31 degrees east. About one-third of Finland´s total length lies north of the Arctic Circle. Finland borders on Sweden to the west, Norway to the north and Russia to the east. The Baltic and continental Europe is to the south. The surface area of Finland is 337 000 square kilometres and the land area is 305 000 sq. km, of which 77% is forest land and 9% agricultural land, which means about 2 million hectares of available arable land (Ministry of Agriculture and Forestry & Ministry of Foreign Affairs 1992).

In comparison to the similar latitudes in Eastern Europe, Asia and North America, the climate is relatively warm due to the Gulf Stream, which brings in warm water to the Atlantic coast of the Scandinavia Peninsula and the frequent warm winds from the southwest and west. Nevertheless, natural vegetation is essentially boreal coniferous forest with a zone of treeless tundra in the north and small areas of temperate mixed forests in the southwest.

Finnish agricultural production is limited by the short growing season, which is about 170 days in the southernmost part of the country and about 130 days in the northern parts of the country. The effective temperature sum during this period is usually between 800 and 1300 degrees Celsius. These two variables are clearly the minimum factors for plant growth which thus have a very strong influence on yields and increase risks in crop production. Another source of uncertainty is the occasional frosts that can cause considerable damage to crops. The moisture conditions are usually less constraining. Total rainfall during the growing season is normally sufficient. Precipitation is 650 mm per annum in the south and 400 mm in the north. It can be, however, quite unevenly distributed causing occasional drought in the early part of the growing season and heavy rains and floods during the harvest season.

Table 1. Weather conditions in Finland during the growing seasons (Finnish Meteorological Institute 2005).

Site	Effective temperature, °C			Precipitation, mm		
	2004	2003	1971-2000	2004	2003	1971-2000
Jokioinen	1 253	1 347	1 225	478	349	346
Kauhava	1 188	1 283	1 102	414	335	285
Joensuu	1 220	1 323	1 150	399	463	336
Oulu	1 146	1 245	1 079	460	227	241
Sodankylä	790	955	759	243	246	229

Due to a marginal agricultural area, Finland is divided into five plant cultivation zones (I-V) from south to north (Fig. 1). Maximum growing seasons in the first (I), second (II), third (III), and fourth (IV) zones are 110, 104, 97, 90 days respectively, and in the fifth (V) zone less still. These zones are essentially geographical indicators of ripening limits, beyond which a certain variety of cereal crops will not reach maturity during an average growing season. The zoning is based mainly on the known close dependence of crop development rates on temperature, but also incorporates information on precipitation, soil type, altitude, effects of lakes and the sea, etc. The zonation has been developed using long-term average climatic data. The zone system is widely used in Finnish agriculture and together with a comprehensive series of long-term field experiments with different cereal crops, forms the basis for practical extension work at the farm level (Pohjonen *et al.* 1998) Most of the Pirkanmaa region is situated in the third (III) plant cultivation zone, with only the most southern part is in the second (II) zone.

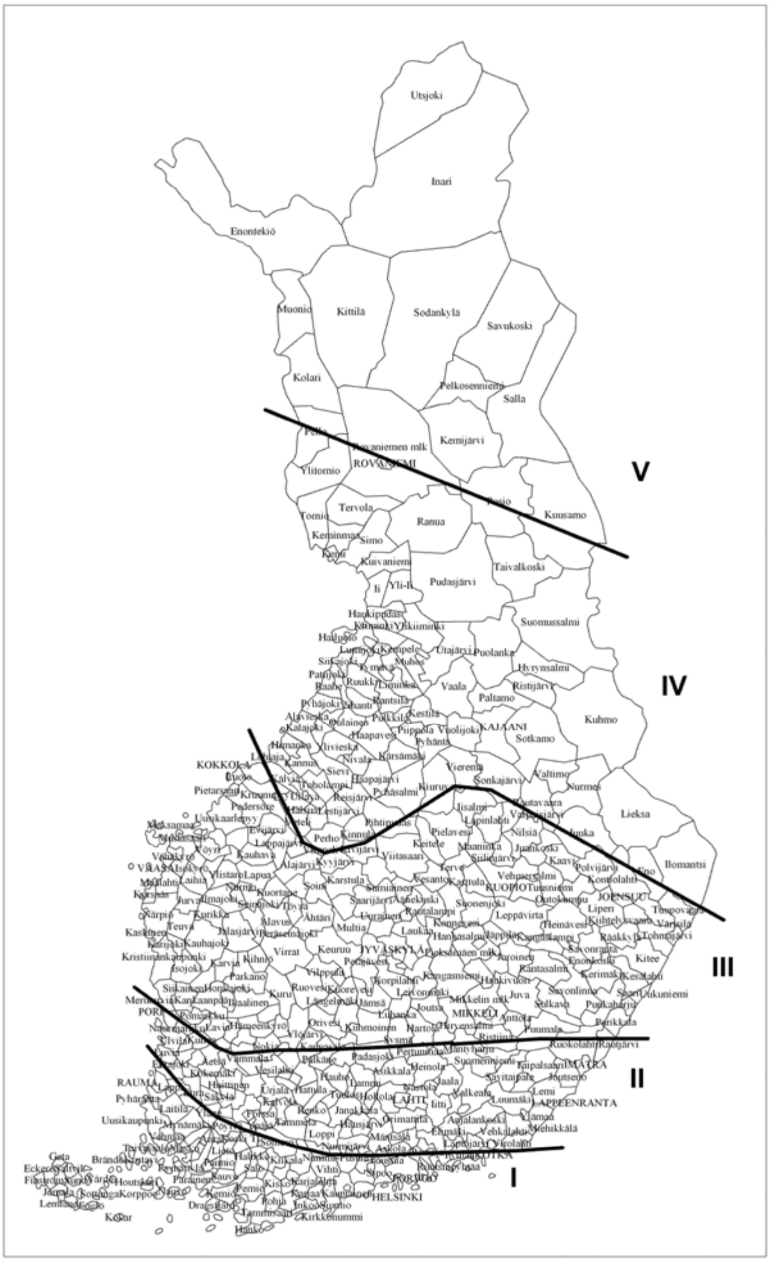


Figure 1. Plant cultivation zones (I-V) according to Suomela (1976) and municipalities in Finland. National Land Survey of Finland, Licence Nr 794/MYY/06.

Finnish agricultural production is mainly based on livestock. Milk is the most important product for Finnish agriculture. Only about 15% of arable land is used for crop production for human consumption, about 2/3 of which consists of bread grains and the rest mainly rapeseed, sugar beets and potatoes (Table 2). About a third of arable land is under grass cultivation and the greatest part of arable land is used for animal production when feed grains such as barley and oats are taken into account (Ministry of Agriculture and Forestry & Ministry of Foreign Affairs 1992). Annual crop yields are presented in Table 3 and national food consumption in various years in Table 4.

Table 2. The use of arable land in Finland (Tike, Information Centre of the Ministry of Agriculture and Forestry in Finland & the Finnish Field Drainage Center 2006).

Use of arable land	**1995**	**2003**	**2004**	**2005**
In thousands, ha	**1 000 ha**	**1 000 ha**	**1 000 ha**	**1000 ha**
Grassland	755	629	620	620
Cereals, total	978	1 196	1 221	1188
wheat	101	192	236	215
rye	21.0	31.0	31.0	14.0
barley	516	531	565	595
oats	329	426	372	346
mixed grain	11.0	16.0	17.0	16.0
other cereals	1.0	1.0	1.0	1.0
Oil plants	85.0	75.0	83.0	77.0
Sugar-beets	35.0	29.0	31.0	31.0
Potatoes	36.0	29.0	29.0	29.0
Other crops	29.0	34.0	39.0	49.0
Area in production	1 918	1 992	2 023	1993
Fallow	223	220	196	241
Cultivated area	2 141	2 212	2 219	2234
Drained area	1) 1 361	1 276	1 282	1290
	ha	ha	ha	ha
Mean arable land/farm	21.7	30.6	31.4	33.3

1) includes drained area that has been removed from cultivation

Table 3. Annual crop yields in Finland (Tike, Information Centre of the Ministry of Agriculture and Forestry in Finland 2005a).

	1995	**2001**	**2002**	**2003**	**2004**
Annual yield (exl. straw and tops), feed units per ha		**3 472**	**3 558**	**3 404**	**3 592**
kg per ha					
Wheat	3 770	3 420	3 270	3 550	3 470
Rye	2 770	2 210	2 400	2 390	2 320
Barley	3 420	3 290	3 330	3 210	3 240
Oats	3 330	3 090	3 350	3 050	3 080
Sugar beets	31 900	35 520	34 960	30 950	35 090
Oil plants	1 500	1 400	1 550	1 260	1 100
Peas	2 200	2 400	2 200	2 500	2 000
Potatoes	22 167	24 433	26 000	21 276	22 926
Total yield M kg					
All vegetables	234	232	238	233	234
tomatoes	31.0	34.0	36.0	36.0	35.0
cucumber (greenhouse)	24.0	31.0	31.0	31.0	31.0
cabbage	24.0	18.0	20.0	19.0	18.0
carrots	61.0	59.0	59.0	60.0	57.0
onions	17.0	17.0	20.0	17.0	24.0
Potted vegetables (M pcs)	30.0	53.0	56.0	55.0	59.0

Table 4. Food consumption in Finland (Tike, Information Centre of the Ministry of Agriculture and Forestry in Finland 2005b).

Consumption kg/ capita	**1995**	**2001**	**2002**	**2003**	**2004**
Grain	69.8	75.3	76.3	76.5	77.4
Potatoes	59.6	61.7	61.7	61.4	62.5
Meat total	60.3	64.8	65.5	67.7	69.3
beef and veal	18.8	17.8	17.9	18.4	19.0
pork	32.0	31.9	31.8	33.0	33.8
poultry meat	9.0	14.5	15.4	15.8	15.9
other meat	0.6	0.5	0.4	0.5	0.5
Liquid milk products	198.1	186.9	185.1	184.3	185.4
milk	145.6	137.1	136.2	136	136.5
sour milk products	37.1	37.0	36.3	35.9	36.3
cream	6.3	5.8	5.7	5.8	5.9
Butter	5.2	3.5	3.1	2.9	2.8
Cheese	15.3	17.8	17.6	18.0	18.4
Ice cream (litres)	14.1	13.3	13.5	13.7	13.2
Butter-vegetable oil mix	2.6	2.9	2.9	3.0	3.1
Margarine	8.3	7.9	7.6	7.3	7.5
Eggs	11.7	10.1	10.0	9.7	9.6
Sugar	35.4	32.3	32.9	32.1	29.9
Fruits and berries	75.9	91.1	86.2	87.3	86.9
Vegetables	61.7	63.1	64.5	64.1	66.5
Fish (gutted)	14.0	13.9	14.4	15.0	

2.2 General geology and properties of soils in Finland

In Finland, the contact between bedrock and the overburden is very sharp. A geologic discontinuity prevails between the crystalline bedrock, which is at least 1 000 million years old, and the young sediments, which are about 10 000 years old. The bedrock of Finland is part of the Fennoscandian Shield, which is composed almost completely of Precambrian bedrock. The most common bedrock types are the silicic like acid granite and gneiss rocks. Only about 3% of the bedrock is exposed. The overburden (soil cover) in Finland was formed during and immediately after the end of the last Weichselian glaciation quite recently about 12 000 years ago (Saarnisto & Saarinen 2001). The Quaternary deposits are composed of till, and glaciofluvial sediments like sand and gravel, and fine sediments like fine sand, silt and clay.

The physical and chemical features of different soil types are depending on the geological genesis processes and the geologic settings of which the material was eroded by the glacier. The glacial processes consist of abrasion, glacial transport and accumulation processes and an essential factor in all these processes was the amount of available water. The abrasion and glacial transport is very effective when a lot of water is present. The rule of thumb is that the smaller the grain size, the longer the glacial transport has been. The material in till is generally local and the sorting effect of water is low, therefore it reflects well the composition of the local bedrock. Till is a mixture of angular rock fragments and fine material in variable proportions. Due to the poor sorting and short transport distance, the geochemical features reflect the chemistry of the bedrock. The glacial transport distance of sand and gravel is often long in any cases more than 10 km, and sorting in flowing water is well developed. The grains are rounded and increasingly monomineral and of uniform size as the transport distance increases. The finest material is carried in suspension and finally deposited as silt and clay at the bottom of a basin. The transport is long and the dispersion of the material is wide. Accordingly, the fine sediments don't reflect the composition of the local bedrock, but much larger areas.

An additional issue explaining the variation in geochemical features is the difference in the relative age of the soil layers. The overburden may be composed of several successive till layers formed by the action of oscillating ice lobes. These lobes may have advanced from slightly different directions, bringing along minerogenic material from variable bedrock environments. Thus, the seemingly homogeneous till profile may contain distinct geochemical variations.

Clear age discordance is present between till and the clay formations. Till is formed below an advancing continental ice sheet, while the fine sediments have deposited slowly in a saline or fresh water basin (early stages of the Baltic Sea) formed in the margin of the melting and retreating ice sheet. The age difference between these soil layers may be between hundreds to thousands of years.

The grain size and weathering of soil particles have strong influences on a soil's geochemical properties. Since minerals tend to weather slowly in the cool Finnish climate, elements are released in smaller quantities in a form available to plants than under warmer conditions. The weathering process varies in different soil types. For example, the size of a clay grain is small and, therefore, the reaction area by unit of volume is high and many ions are capable of being dissolved. The clays of southern Finland contain calcium, potassium, and magnesium in abundance, while in the more coarse-grained glacial tills in central Finland and the peat soils of northern Finland, mineral elements occur in a soluble form to a lesser extent than in clays.

The soils are classified into three main groups: till soils (moraine), sorted mineral soils (gravel, sand, fine sand, silt and clay) and organic soil, including mull (organic matter, 20-40%), peat (organic matter, >40%); and gyttja (a mixture of sedimentary organic and mineral material; and little attention has been paid to pedogenic classification. The peatland area (peat layer >30 cm) in Finland is 7.2 million hectares (15% of land area). Soil types and thus their fertility vary considerably. The dominant soil types of the plough layer are clay in southern and southwestern Finland, till in the Central Lake districts, fine sand in parts of western and eastern Finland and peat in northern Finland (Kurki 1972).

Soil types of the cultivated fields vary considerably within Finland. About 35% of the Finnish cultivated soils can be classified as clays (clay content >30%), 32% silts, 18% as coarse mineral soils and 15% as organic soils (Puustinen *et al.* 1994). In the plough layer (about 0–25 cm), the dominant soil types are clay in southern and southwestern Finland, and till in the Central Lake districts; and peat in northern and eastern Finland (Kurki 1972). This pattern is largely inherited from the distribution of glaciogenic Quaternary deposits in Finland.

Soil testing of cultivated land begun in Finland more than 50 years ago (Uusitalo & Salo 2002) and national soil monitoring 30 years ago (Sippola & Tares 1978, Erviö *et al.* 1990, Mäkelä-Kurtto & Sippola 2002). The state of Finnish cultivated soils has been monitored for agricultural and environmental purposes. In Finnish soil testing and monitoring, macro-elements were determined by extracting air-dried samples with AAAc (Vuorinen & Mäkitie 1955) and micro-elements with AAAc-EDTA (Lakanen & Erviö 1971). Concentrations obtained by these methods indicate exchangeable or easily soluble fractions and thus, also reflect fractions available to plants and surface and ground waters.

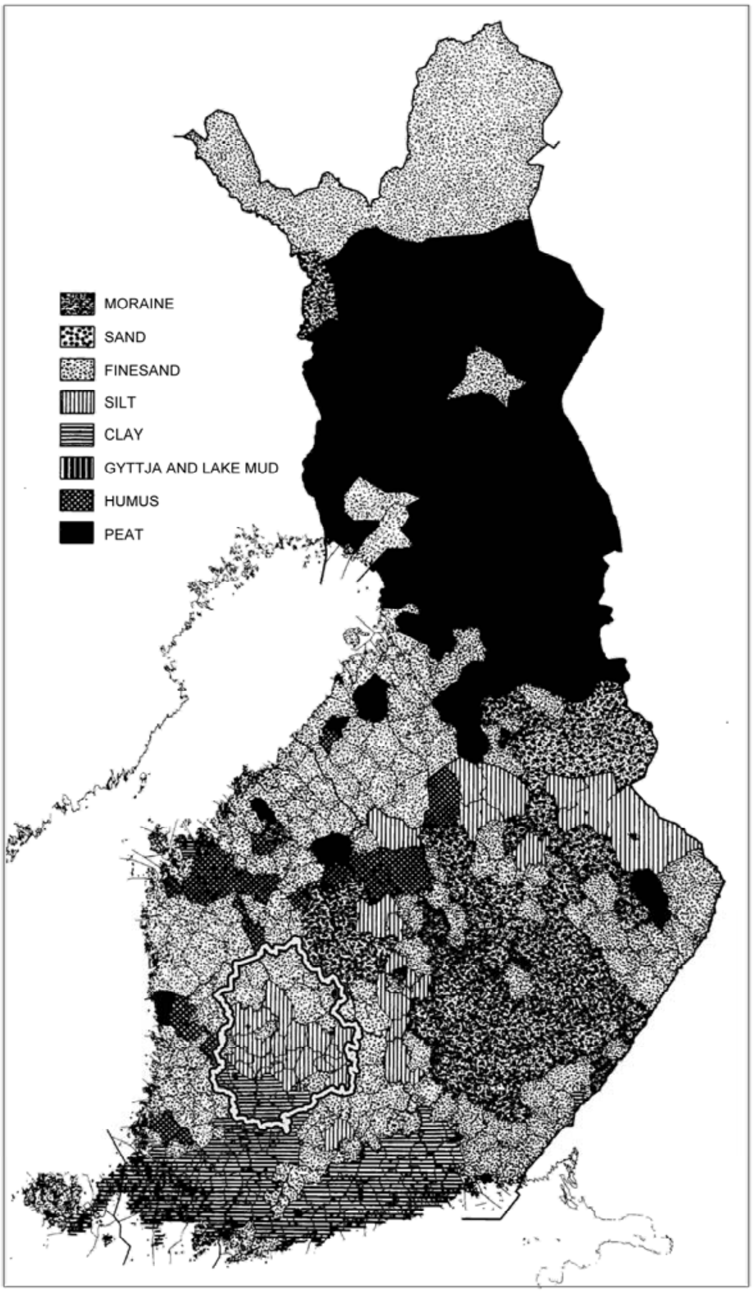


Figure 2. The Pirkanmaa region (white line) and dominant soil types in plough layer of arable land in Finland after Kurki (1972).

The status of Finnish arable soils (n = 720) in 1998 has been described by Mäkelä-Kurtto *et al.* (2002) and Mäkelä-Kurtto *et al.* (2006). Statistical indicators have been summarized in Table 5. In this study's soil material, 65% belonged to the coarse mineral soils, 15% to the clay soils (clay content <30%) and 20% to the organic soils (humus content >20%). The soil type distribution coincided well with the natural soil type distribution of Finnish cultivated soils (Kurki 1972, Puustinen *et al.* 1994). In addition, sampling sites representatively covered the whole cultivated area in Finland. In Finland, analytical results of soil testing are interpreted (Viljavuuspalvelu 2000) for agricultural purposes, fertilization and liming, and environmental purposes. Analytical results are grouped into seven fertility classes: poor, rather poor, fair, satisfactory, good, high, and possibly

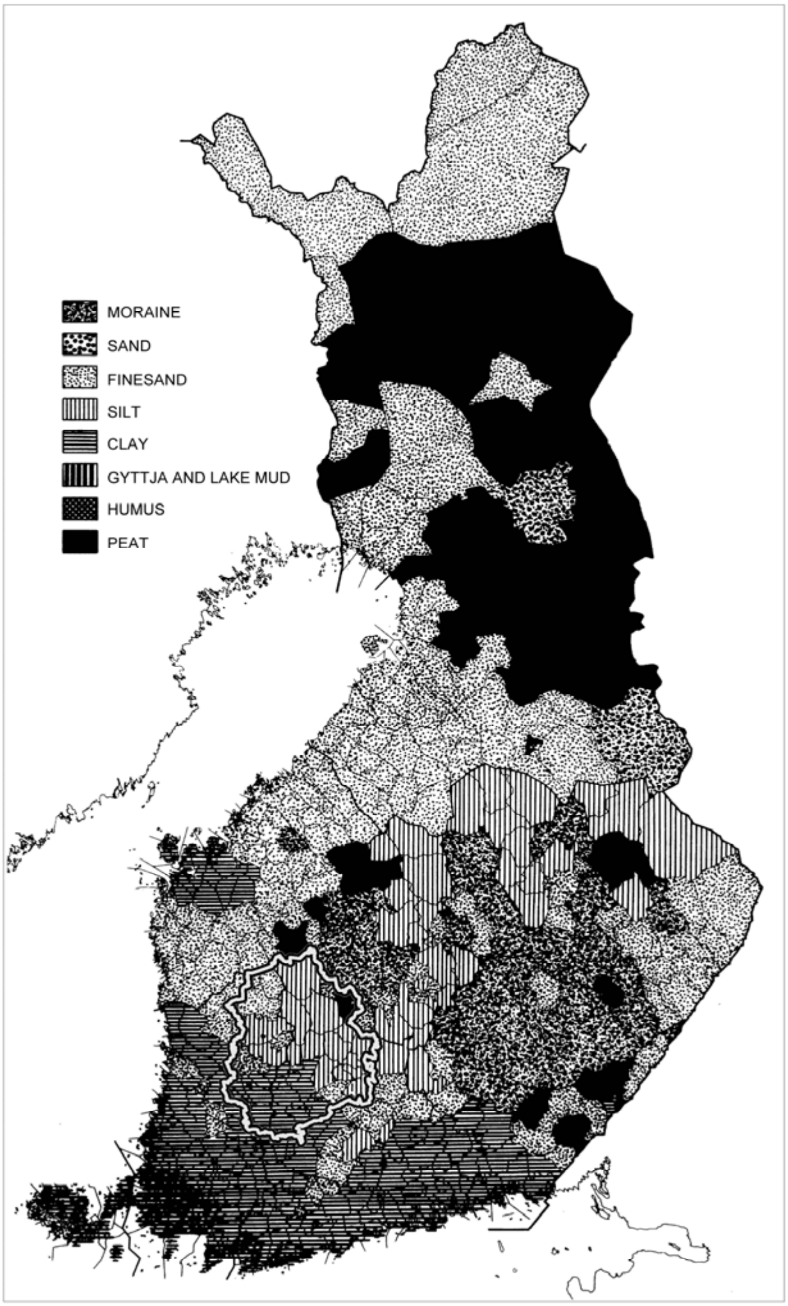


Figure 3. The Pirkanmaa region (white line) and dominant soil types in subsoil of arable land in Finland after Kurki (1972).

excessive. The current target class is satisfactory. Interpretation takes into account the soil type and humus content.

The humus content in arable soils was higher, on average, in the north than in the south due to the abundance of peat and other organic soils in northern Finland. A typical median for the humus content of the mineral soils was about 5%. A median and a mean of pH-values for the mineral soils were 5.9 and for organic soils 5.2, respectively. When comparing on a global scale, Finnish cultivated soils are quite acidic depending on the acid soil parent material. According to the national interpretation, nearly half of the pH values were under the target class (Table 6). About 30% of the values were at the target level. About one quarter of the pH values were above the target class.

Table 5. Statistical indicators of soil parameters of the plough layer in Finnish arable soils (n = 720) sampled in 1998 in a national monitoring study and analysed by Finnish soil testing methods (Mäkelä-Kurtto *et al.* 2006).

Soil parameter	Minimum	Median	Mean	Maximum
pH(H_2O)	3.89	5.76	5.76	7.72
Org. C, %	0.8	3.3	7.5	50.0
Humus, %	1.4	5.6	12.9	86.0
Volume weight, kg l^{-1}	0.24	1.02	0.95	1.42
El. cond., 10^{-4} S cm^{-1}	0.13	0.93	1.1	7.94
Ca, mg l^{-1}	116	1257	1441	10880
K, mg l^{-1}	14.0	92.0	111	605
Mg, mg l^{-1}	7.0	164	205	1072
P, mg l^{-1}	0.9	8.5	13.0	131.3
S, mg l^{-1}	6.0	18.0	24.0	678
Al, mg l^{-1}	24.0	435	490	2008
B, mg l^{-1}	0.07	0.52	0.59	2.16
Cd, mg l^{-1}	0.01	0.073	0.08	0.295
Co, mg l^{-1}	0.06	0.52	0.64	5.64
Cr, mg l^{-1}	0.01	0.28	0.36	4.32
Cu, mg l^{-1}	0.16	3.62	4.5	34.97
Fe, mg l^{-1}	114	520	741	6505
Mn, mg l^{-1}	1.0	44.0	58.0	1620
Mo, mg l^{-1}	0.001	0.038	0.056	0.978
Ni, mg l^{-1}	0.08	0.62	0.99	8.59
Pb, mg l^{-1}	0.37	1.92	2.15	15.57
Zn mg l^{-1}	0.35	2.95	4.28	40.87
Se, µg l^{-1}	2.9	9.5	10.4	69.3

Table 6. Classification of analytical results of Finnish arable soils (n = 720) sampled in 1998 in a national monitoring study (Mäkelä-Kurtto *et al.* 2006) according to interpretation of soil testing (Viljavuuspalvelu 2000). (Current target class: satisfactory; classes lower than target class: poor, rather poor and fair: classes higher than target class: good, high and possibly excessive) (Mäkelä-Kurtto *et al.* 2006).

Soil parameter	Interpretation of soil testing results			
	< Target class (%)	At target class (Satisfactory, %)	> Target class (%)	Possibly excessive (%)
pH (H_2O)	48.0	29.0	23.0	0.8
Ca	64.0	22.0	13.0	0.3
P	57.0	25.0	18.0	4.3
K	68.0	24.0	8.0	0.3
Mg	38.0	30.0	32.0	0.0
S	8.0	23.0	68.0	0.6
B	67.0	23.0	10.0	0,3
Cu	36.0	33.0	31.0	0.8
Mn	28.0	47.0	25.0	0.1
Mo	37.0	34.0	29.0	0.4
Zn	33.0	46.0	22.0	0.0
Mean	**44.0**	**31.0**	**25.0**	**0.7**

2.3 Arsenic in soils

2.3.1 Arsenic in arable soils at a national level

Results from the monitoring study of MTT (Unpublished data, RAKAS-project 2004-2007). A national soil monitoring study by MTT Agrifood Research Finland produced data on the contents of arsenic and other elements in soil material collected in 1998 (RAKAS-project 2004-2007, “Assessment and reduction of heavy metal inputs into Finnish agro-ecosystems, acronym RAKAS” funded by the Ministry of Agriculture and Forestry in Finland, Research Programme of Sustainable Use of Natural Resources, Project Nr 310 925). Statistical indicators for the contents of *aqua regia* extractable (ISO 11 466) arsenic in the plough layer of Finnish cultivated soils (n = 338) are presented in Table 7. Arsenic contents varied from 0.32 to 18 mg kg^{-1} dw. A mean of the whole study material was 4.13 and a median 2.76 mg kg^{-1} dw. More than 50% of the analytical results were between 1.8-4.6 mg kg^{-1} dw (Fig. 4) and more than 95% <10 mg kg^{-1} dw. However, one monitoring site in the plant cultivation zone II had an exceptionally high arsenic content, 166.1 mg kg^{-1} dw. This was a maximum and a real exception, because it was about 40 times bigger than the mean concentration of the whole country. It could not be determined, if the source of arsenic was anthropogenic or natural because the site was not sampled for the subsoil. As usual, clay soils had notably higher arsenic concentrations than the other soil types had (Table 7). The lowest concentrations occurred in coarse-grained mineral soils. Due to the clay soils, the biggest concentrations were found in plant cultivation zones I and II, where the mean arsenic contents were twice the means in zones III-V (Table 9). Low arsenic values occurred in cultivated soils in eastern and northern Finland (Fig. 4) similar to the vaues found for glacial till (Koljonen *et al.* 1992).

The Earth´s crust contains about 1.5 mg kg^{-1} arsenic on the average (Sparks 1995). The median and mean contents of Swedish agricultural soils between 1988-1995 were 4.0 and 3.2 mg kg^{-1} dw, respectively (Eriksson *et al.* 1997). Ninety percent of all Swedish soil samples (3 067) studied contained arsenic less than 6.8 mg kg^{-1} dw. In Sweden, there were also fields containing arsenic from 15 to 40 mg kg^{-1} dw and the maximum value was 78.9 mg kg^{-1} dw. Usually, arsenic concentrations in uncontaminated soils seldom exceed 10 mg/kg^{-1} (PennState 2001, Mahimairaja *et al.* 2005). In Canada, the environmental quality guideline for arsenic in agricultural soils is 12 mg kg^{-1} (Environment Canada 2002). In Finland, arsenic contents in about 1% of the cultivated soils studied exceeded Canadian guideline value. For Cd, Hg, Cr, Cu, Ni, Pb, V, Zn and Se, Canadian guideline values are 1.4, 6.6, 64, 63, 50, 70, 130, 200 and 1 mg kg^{-1}, respectively. According to Frank *et al.* (1976), a natural background level of 6.3 mg kg^{-1} for total arsenic was reported for agricultural soils in Ontario, Canada. The European Community has recommended that, in general, arsenic levels in soil not exceed 20 mg/kg (Léonard 1991). In Finland, a common background value for arsenic in soil is 2.6 (0.3-20); the soil is most probably polluted if it contains arsenic >50 mg kg^{-1}, and the soil may need remediation measures if it contains arsenic >100 mg kg^{-1} (Ministry of Environment 2006).

Table 7. Statistical indicators of *aqua regia* extractable (ISO 11 466) arsenic contents (mg kg^{-1} dw) by soil type groups in Finnish cultivated fields sampled in national soil monitoring in 1998. (Unpublished data, RAKAS-project 2004-2007).

As		**Percentiles**								
Soil type	**Min**	**5%**	**25%**	**50%**	**75%**	**95%**	**Max**	**Mean**	**Std**	**n**
Coarse mineral soils	0.32	0.72	1.56	2.40	3.58	6.92	166	3.61	11.2	219
Clay soils	1.98	2.35	5.74	7.79	9.12	12.2	17.9	7.51	3.16	51.0
Organic soils	0.69	0.99	1.93	2.53	3.60	9.05	16.9	3.30	2.66	68.0
All together	0.32	0.88	1.79	2.76	4.59	9.42	166*	4.13	9.28	388

* Maximum at a hot spot 166 mg kg^{-1} dw

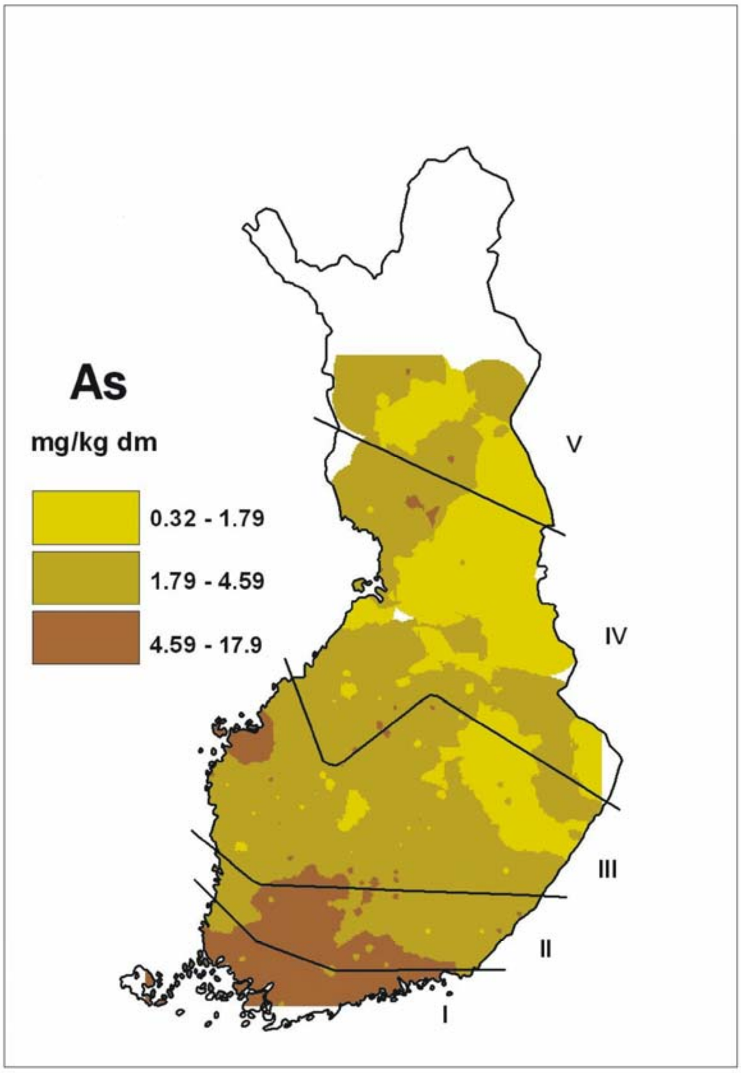


Figure 4. Spatial distribution of *aqua regia* extractable (ISO 11 466) arsenic contents in cultivated soils (n = 338) sampled in national soil monitoring in 1998 (Unpublished data, RAKAS-project 2004-2007).

Results from other Finnish projects. southwestern Finland (Unpublished data, RAKAS-project 2004-2007). Statistical indicators *of aqua regia* extractable arsenic in the cultivated soils of crop farms in southwestern Finland (Table 8) were at a higher level than the respective figures on a national level (Table 7). This was due to the abundance of clay soils in southwestern Finland which also affects other trace elements (Unpublised data, RAKAS-project 2004-2007). The plough layer contained more Cd, Pb, Hg and Se, obviously as a result of human activities, and less Cr, Cu and arsenic than the subsoil. Instead, there was only a minimal difference in the contents of Ni, V and Zn between the soil layers. According to Eriksson *et al.* (1997) arsenic contents in the plough layer were closely related to the arsenic content found in the subsoil in Swedish cultivated soils.

An acid (pH 4.65) ammonium acetate -EDTA (AAAc-EDTA) solution is routinely used in Finnish soil testing to measure an easily soluble fraction of trace elements (Viljavuuspalvelu 2000). Concentrations of AAAc-EDTA extractable arsenic in the plough layer of cultivated soils in crop farms in southwestern Finland were <0.5 mg l^{-1} of air dried soil, which was a sensitivity limit for arsenic measurements. However, the concentration might be 0.5 or 0.6 mg l^{-1} of air dried soil if the soil had received slag.

Table 8. Statistical indicators of *aqua regia* extractable (ISO 11 466) arsenic contents (mg kg^{-1}) in the plough layer and subsoil in fields (n = 23) of crop farms in south-western (S-W) Finland and in the plough layer and subsoil in fields (n = 21) of dairy farms in Ostrobothnia in 2004. (Unpublished data, RAKAS-project 2004-2007).

	Minimum	**Median**	**Mean**	**Maximum**
S-W Finland				
Plough layer	3.1	6.0	5.9	11.5
Susoil	2.5	7.1	7.2	11.1
Ostrobothnia				
Plough layer	1.0	2.6	3.1	10.7
Subsoil	1.1	2.5	3.1	13.5

Ostrobothnia (Unpublished data, RAKAS-project 2004-2007). Arsenic contents in the cultivated soils of dairy farms in the Ostrobothnia (Table 8) seem to be lower than the respective figures in southwestern Finland or even at the national level (Table 7). This was mainly due to the occurrence of coarser mineral soils in Ostrobothnia. Higher Cd, Cu, Zn and Se contents were observed in the plough layer than in the subsoil. One of the most important sources of Cu, Zn and Se might be the commercial feed preparations consumed by the domestic animals. Concentrations of AAAc-EDTA extractable arsenic in the plough layer of the dairy farms in the region were <0.5 mg l^{-1} of air dried soil and 0.9 mg l^{-1} of air dried organic soil.

Mikkeli region / South Savo Province (Viljavuuspalvelu / Soil Analysis Service in Finland 2002). Mäntylahti and Laakso (2002) studied arsenic contents in 274 mineral soil samples and in 38 organogenic soil samples taken from 23 farms in the Mikkeli region (South Savo Province) in 2000 by using the *aqua regia* extraction technique. A median arsenic concentration in mineral soils was 2.90 mg kg^{-1} and in organogenic soils 2.80 mg kg^{-1}, and a range from 1 to 35 mg kg^{-1} and from 1 to 28 mg kg^{-1}, respectively (Table 9). The arsenic content of 13 mineral soils in South Savo region exceeded 6.5 and the content in six organogenic soils was 7.1 mg kg^{-1}. Mäntylahti and Laakso (2002) proposed target values for “Clean Soil” (Table 9), including 10 mg kg^{-1} both in mineral soils and organogenic soils. Unpolluted soil usually contains arsenic values of <10 mg kg^{-1} (Mahimairaja *et al.* 2005).

Median arsenic contents in arable soils in South Savo were low, but maximum values were rather high compared to the soil materials collected from the regions of south-western Finland, Ostrobothnia or Pirkanmaa. South Savo Province is a region famous for organic farming that does not use commercial mineral fertilizers in plant production, but recycles various side-products or waste materials that may be rich in arsenic. However, the farms studied by Mäntylahti and Laakso (2002) represented conventional farming.

Table 9. Arsenic contents of cultivated soils in Finland (Unpublished data, RAKAS-project 2004-2007) and in the Mikkeli region / South Savo Province (Mäntylahti & Laakso 2002) and in Sweden (Eriksson *et al.* 1997). Canadian limit values for cultivated soils (Environment Canada 2002) and Finnish target values for “Clean Soil” of arable land (Mäntylahti and Laakso 2002).

	Finland 1998 Mean	**Mikkeli 2000 Median**	**Mikkeli 2000 Median**	**Sweden 1988-95 Mean**	**Canada 2002 Limit**	**Finland 2002 “Clean Soil”**	
Soil type	All soils	Miner. soils	Org. soils	All soils	All soils	Miner. soils	Org. soils
n	338	274	38	1720			
Unit	mg kg^{-1} dw	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1} dw	mg kg^{-1}	mg kg^{-1}
As	4.13	2.9	2.8	4.0	12	10	10

2.3.2 Arsenic in forest soils at a national level

The occurrence of arsenic in forest soil, which here means other areas other than arable soils and residential environments, was studied in considerably detail since the beginning of the 1980's when reliable analysis methods for arsenic were developed. In the past, geochemical soil studies were done mainly for mineral exploration. In these studies arsenic had an important role because it is a good indicator of gold. Later geochemical studies of arsenic developed a more independent role in environmental studies when the toxic character and mobility of arsenic became known.

The occurrence of arsenic in soils is based either on a geogenic or anthropogenic source. The arsenic content in Finnish bedrock is generally low with the median value of 6 544 bedrock samples being 0.9 mg kg^{-1} (Lahtinen *et al.* 2005). Regional variation in arsenic content is, however, large. Anthropogenic arsenic sources in Finland are limited both in number and extent (Parvianen *et al.* 2006). For anthropogenic arsenic, it is typical that the content of arsenic in soil decrease from top to bottom and for the occurrence of geogenic arsenic, the trend is reversed.

A nationwide geochemical soil study was conducted in Finland in the early 1980's (Koljonen *et al.* 1992). The material in this study was the fine fraction of till (<0.06 mm). The median value of arsenic analysed using the Neutron Activation method (NAA) was 2.6 mg kg^{-1} in 1054 samples and the range was 0.1 – 44 mg kg^{-1}. At the beginning of the 2000's, a wide geochemical survey of the eastern Barents region and nearly all of Finland was conducted and is included to this study. According to this study, the median value of arsenic in the subsoil of Finland was 1.61 mg kg^{-1} with a range of 0.12 – 20 mg kg^{-1}, n=163 (Salminen *et al.* 2004). In this survey, a grain size of <2mm and an *aqua regia* leaching were applied. The soil type used in this study was the dominant residual soil type in the selected catchment basin and it varied from glacial till, fluvial sand and gravel to clay. On a general scale, the most recent study in Europe shows that Fennoscandia is dominated by low arsenic level in soils (<2.48 mg kg^{-1}) (Salminen *et al.* 2005; de Vos & Tarvainen (eds.) 2006).

The other geochemical surveys of Finnish forest soils have been regional. Arsenic content, among other elements, has been studied in three soil types and at two different depths within nine municipalities in south Finland. The samples were collected mainly from forest areas and arable soil. The grain size in these studies was <2 mm and a*qua regia* and ammonia acetate leaching was applied for mineral soils and HNO_3 leaching for humus samples (Tarvainen *et al.* 2003, 2005 & 2006). The average arsenic content was highest in clay samples in all regions – the median values varied from 6.6 to 8.4 mg kg^{-1} - and also slightly higher in subsoil samples than in topsoil samples. In till and sand soils the median values were lower, varying from 1.7 to 3.3 mg kg^{-1} with the value for topsoil and subsoil being the same. Values were slightly higher in subsoil samples than in topsoil samples. The ammonium acetate leaching was done only for samples collected from the Porvoo region, on the southwest coast of Finland. Arsenic concentrations in these analyses were mainly less than the detection limit (<0.1 mg kg^{-1}). The arsenic content in humus samples was low all along the southern coastal area of the country and it varied from 0.95 to 4.6 mg kg^{-1} in samples taken from the Porvoo area, from 0.92 to 4.62 mg kg^{-1} in samples from the Hyvinkää – Sipoo area and from 0.82 to 3.27 mg kg^{-1} in samples from the Vihti - Kirkkonummi area.

2.4 Arsenic in agricultural products

Recent arsenic contamination of food and feed crops from natural and anthropogenic sources has been of great concern. Most of the studies have focused on the arsenic contents of fish and seafood, which are the major sources of arsenic in the human diet. Arsenic levels in contaminated areas have also been studied intensively.

Arsenic is well known for its toxicity, but there is also increasing evidence of the essentialness of arsenic by very low dietary intakes. The effects of arsenic depend on the chemical form and oxidation states of the element, with inorganic compounds usually being more toxic than most organic ones. Inorganic As (III) is more toxic than As (V). Most organisms convert inorganic arsenic by methylation to less toxic organoarsenic compounds like monomethylarsonicacid, dimethylarsinicacid, trimethylarsineoxide (micro-organisms, animals, humans), arsenobetaine, dimethylarsenoribosides or arsenolipids (aquatic organisms). Absorption is high from anionic and soluble arsenic species. In mammals arsenic accumulates to keratin-rich tissues like hair and nails. Besides general effects, chronic toxicity causes increased pigmentation and keratinisation of skin and increased risk for skin cancers. (WHO 1996, Mandal & Suzuki 2002, Súñer *et al.* 2002).

Most foods and feeds contain some arsenic, usually less than 1 mg kg^{-1} in dry matter with the exception of foods of marine origin (WHO 1996). In numerous studies, seafood has shown to present a major source of arsenic in the human diet (Varo & Koivistoinen 1980, Nriagu & Azcue 1990, Gundersson 1995, Sapurnar-Postružnik *et al.* 1996, Tao & Bolger 1998, Scoof *et al.* 1999, Leblanc *et al.* 2000, Ysart *et al.* 2000, Robberecht *et al.* 2002, Llobet *et al.* 2003). Variations in arsenic intakes reflect the variations in seafood consumption. Most of the organoarsenic compounds are easily taken up in gastrointestinal tract. However, these compounds are resistant and do not readily break down to toxic, active species and are rapidly excreted via the kidney (WHO 1989). However, arsenic speciation in terrestrial foods is not well characterized. The lack of information on concentrations of inorganic toxic forms of arsenic in foods is evident.

The EU has not set maximum limits for arsenic in foodstuffs. For drinking water, the maximum level is 0.01 mg l^{-1}. The World Health Organization maximum permissible limit for arsenic in drinking water is 0.05 mg l^{-1} with a recommendation of 0.01 mg l^{-1} (WHO 2001). WHO has also determined provisional tolerable weekly intake (PTWI) for inorganic arsenic at 15 µg kg^{-1} of body weight per week for adults. This means that the safe limit for a 60 kg person is about 128 µg per day (WHO 1989).

2.4.1 Plant crops

Cereals. The arsenic content of cereal grains and products is generally low, <0.05 mg kg^{-1} fw range <0.005-0.285 mg kg^{-1} fw (Varo *et al.* 1980, Wiersma *et al.* 1986, Petr *et al.* 1999, Schoof *et al.* 1999, Eriksson *et al.* 2000). In Finland, arsenic mean concentrations in cereal grains were <0.05 mg kg^{-1} fw (range 0.03-0.20 mg kg^{-1} fw) in the late 1970’s (Varo *et al.* 1980). In 1992-1993, Liukkonen-Lilja (1993) studied arsenic contents in some cereal products. Concentrations in wheat and rye flour were <0.02 mg kg^{-1} fw, and in wheat flakes <0.05 mg kg^{-1} fw. Higher arsenic contents were found only from rice and rice products, with a mean 0.24 mg kg^{-1} fw. In Sweden, a large survey of agricultural soils and crops has been performed. In 95% of winter wheat samples, the arsenic content was <0.03 mg kg^{-1} dw, with a maximum value of 0.08 mg kg^{-1} dw (Eriksson *et al.* 2000)

According to the Scientific Cooperation-report (SCOOP 2004), the mean arsenic content of cereal products was 0.005-0.007 mg kg^{-1} fw in the UK, 0.05 mg kg^{-1} fw in Germany and <0.0125 mg kg^{-1} fw in France. In the four-year Finnish project “Assessment and reduction of heavy metal inputs into Finnish agro-ecosystems” (RAKAS-project 2004-2007) arsenic was studied in dairy and crop farms. With the exception of rapeseed, the mean arsenic concentrations were usually <0.02 mg kg^{-1} dw, with a range of <0.02-0.063 mg kg^{-1} dw (Table 10). According to Schoof *et al.* (1999), inorganic arsenic accounted for about one-quarter of the total arsenic in grains.

Table 10. Arsenic concentrations in crops (Unpublished data, RAKAS-project 2004-2007).

Plant crop	n	Arsenic concentration, mg kg^{-1} dw	
		Mean	Range
Winter wheat	4	0.004	0.002-0.006
Spring wheat	5	0.008	0.003-0.016
Oats	6	0.024	0.004-0.063
Barley	15	0.010	0.005-0.022
Rye	3	0.003	0.002-0.004
Pea	1	0.019	
Rapeseed	4	0.040	0.022-0.087

Potatoes and root vegetables. Typical concentrations of arsenic in potatoes are below <0.01 mg kg^{-1} (Table 11). Helgesen and Larsen (1998) studied bioavailability of arsenic in carrots cultivated in soil of different arsenic levels. Arsenic concentrations were over 2 times higher in the skin than the core. In uncontaminated soil (total arsenic in soil 6.5 ± 0.3 mg kg^{-1} dw), total arsenic levels in carrots were <0.098 mg kg^{-1} dw. In contaminated soils, concentrations reached over 1 mg kg^{-1} dw. The availability of arsenic to carrots was 0.47 ± 0.06% (ratio of total arsenic in carrot to in the soil) and relative to extractable arsenic in soils 580 ± 150%. Arsenic was present in carrots as inorganic As(III) and As (V) species, but no methylated forms were detected. Helgesen and Larsen (1998) concluded that 20 mg kg^{-1} arsenic in soils was a safe criterion to prevent any unacceptable intake of inorganic arsenic via the consumption of carrots.

Muñoz *et al.* (2002) studied arsenic in vegetables in northern Chile, where high levels of arsenic have been detected from soil and water. Mean arsenic contents in potato, carrot and beetroot were 0.085, 0.118 and 0.188 mg kg^{-1} wet weight. Generally, over 90% of the arsenic was in inorganic form and concentrations were 2-5 times higher on the skin compared to the core. Arsenic concentrations tended to decrease from root to shoots and further to fruits. Carbonell-Barrachina *et al.* (1999) studied arsenic accumulation in turnip. The chemical form of the arsenic in the nutrient solution determined the availability of arsenic to turnip with concentrations being highest in the root skin. Organic arsenicals (methylarsonic acid, dimethylarsinic acid) showed higher accumulation into shoots than inorganic arsenicals. Similar results have also been detected in tomatoes (Burló *et al.* 1999).

Grass crops. There is a lack of data on arsenic contents of timothy grass in Finland or elsewhere. In the Finnish RAKAS-project (2004-2007, unpublished data), the arsenic content of 16 samples of silage and grasses were determined from five dairy farms (Table 12) and two timothy samples from crop farms. The range of arsenic concentrations was 0.011-0.107 mg kg^{-1} dw. Arsenic contents in unwashed fodder grass in the Netherlands were higher than in Swedish or Finnish studies, with a mean of 0.28 mg kg^{-1} dw and range from 0.07-1.11 mg kg^{-1} dw (Wiersma *et al.* 1986).

Table 11. Arsenic concentration in potatoes and some other tubers in various countries.

Vegetable	Arsenic concentration mg kg^{-1} fw	Country	Reference
Potatoes	<0.018	Belgium	Robberecht *et al.* 2002
Potatoes	0.01-0.12	Finland	Varo *et al.* 1980
Potatoes	<0.01	Finland	Liukkonen-Lilja 1993
Potatoes, peeled	0.0016	New Zealand	NZFSA 2005
Potatoes, with skin	0.002	New Zealand	NZFSA 2005
Potatoes, peeled	0.0023	Slovakia	Lindberg *et al.* 2006
Potatoes, with skin	0.033	Slovakia	Lindberg *et al.* 2006
Potatoes, peeled	0.03	U.S.	Kissel *et al.* 2003
Potatoes, with skin	0.05	U.S.	Kissel *et al.* 2003
Potatoes	0.013	The Netherlands	Wiersma *et al.* 1986
Potatoes	0.008	U.S.	Jelinek & Corneliussen 1977
Potatoes	0.0028	U.S.	Scoof *et al.* 1999
Potatoes	0.002	United Kingdom	Ysart *et al.* 2000
Potatoes	0.002	United Kingdom	Ysart *et al.* 2000
Carrot	0.06	Finland	Varo *et al.* 1980
Carrot	<0.01	Finland	Liukkonen-Lilja 1993
Carrot	<0.001	Greece	Stalikas *et al.* 1997
Carrot	0.001	New Zealand	NZFSA 2005
Carrot	0.022	The Netherlands	Wiersma *et al.* 1986
Carrot	0.0073	U.S.	Scoof *et al.* 1999

Table 12. Arsenic content, mg kg^{-1} dw, of silage and grasses in five dairy farms (Unpublished data, RAKAS-project 2004-2007).

Arsenic concentration mg kg^{-1} dw					
Farm number	**Silage**		**Mean**	**Pasture grass**	**Dry hay**
	2003 harvest	**2004 harvest**	**2003-2004**	**2004**	**2004**
1	0.085	0.045	0.065	0.050	
2	0.024	0.024	0.024	0.031	0.021
3	0.032	0.107	0.069	0.038	0.021
4	0.034	0.053	0.043	0.030	
5	0.075	0.021	0.048		

2.4.2 Animal crops

Milk. Arsenic content in milk is generally below 0.05 mg kg^{-1} fw in Finland (Varo *et al.* 1980, Liukkonen-Lilja 1993). In the RAKAS-project (2004-2007) milk samples (n = 20) were collected from five dairy farms. The mean arsenic content was 0.0012 mg kg^{-1} fw, ranging from 0.0009-0.0016 mg kg^{-1} fw. In the SCOOP (2004) report, the mean arsenic content of milk in EU member states was <0.005 mg kg^{-1} fw in Finland, 0.003 mg kg^{-1} fw in Gemany and 0.0004 mg kg^{-1} fw in the United Kingdom. Ireland reported a mean value of 0.020 mg kg^{-1} fw for skimmed milk powder.

Similar arsenic concentrations in milk have been reported worldwide: New Zealand <0.0005 mg kg^{-1} fw, Spain 0.0035-0.0113 mg l^{-1}, Turkey 0.00493 mg l^{-1}, USA 0.0018 mg kg^{-1} fw (NZFSA 2003, Cava-Montesinos *et al.* 2003, Ulman *et al.* 1998, Schoof *et al.* 1999). In Mexico, the Comarca Lagunera area is naturally rich in arsenic and as a result, the concentration in milk varied between

0.009-0.0274 mg kg^{-1} fw. The cow's milk biotransfer factors (BTF = concentration of arsenic in milk/mean daily animal arsenic intake) were 1 to 6 x 10^{-4} (Rosas *et al.* 1999).

Meat. Arsenic content in the muscle of farm animals is generally very low. Liver and kidney may contain higher amounts of arsenic depending of the arsenic content of feed (Table 13). Most of the arsenic in meat and poultry seem to be in a less toxic organic form (Schoof *et al.* 1999).

Table 13. Arsenic concentrations in meat and meat products in various countries.

Farm animal	n	Mean arsenic concentration mg kg^{-1}			Country	Reference
		Liver	Kidney	Muscle		
Cattle	177-181	<0.02	0.03	<0.02	Australia	Kramer *et al.* 1983
Cattle	2138	0.03	0.03		Canada	Salisbury *et al.* 1991
Swine	2062	0.26	0.17			
Poultry	1702	0.36	0.15			
Veal	210	0.03	0.05			
Lamb	155	0.04	0.03			
Pork	159-173	0.001	0.001	0.003	Croatia	Sapunar-Postružnik *et al.* 1996
Beef	145-173	0.006	0.001	0.012		
Poultry	79			0.005		
Cow	1-11	<0.02	<0.02	<0.02	Finland	Nuurtamo *et al.* 1980
Pig	1-6	<0.02	<0.02	<0.02		
Chicken	2			0.02		
Beef, mince	8			0.056	New Zealand	NZFSA 2005
Pork chop	8			0.045		
Chicken	8			0.01		
Swine	563	0.01*	-	-	Norway	Kluge-Berge *et al.* 1992
Cattle	571	0.01*	-	-		
Cattle	38	0.008	0.012	0.003	Poland	Zin 1995
Bovine, Pigs	1392	<0.05	<0.05	<0.05	Slovenia	Sinigoj-Gancnik & Doganoc 2000
Cattle, calves	312	0.0496	0.0663	0.0045	Spain, Asturias	Miranda *et al.* 2003
Cattle, calves	427-438	0.043	0.055	0.004	Spain, Galicia	Alonso *et al.* 2000
Cattle, cows	56	0.046	0.068	0.005		
Pork				0.0624	Spain, Huelva	Bordajandi *et al.* 2004
Beef	5			<0.030	Sweden	Jorhem *et al.* 1996
Pork	5			<0.030		
Cattle	33-68	<0.015	0.015	<0.015	Sweden	Jorhem *et al.*1991
Swine	338-625	0.023	0.019	0.024		
Cattle	118-192	0.013	0.048	0.004	The Netherlands	Vos *et al.* 1987
Beef				0.0515	U.S.	Scoof *et al.* 1999
Pork				0.0135		
Chicken				0.0864		
Carcase meat				0.003	United Kingdom	Ysart *et al.* 2000
Poultry				0.004		

* median

2.5 Arsenic sources in agriculture

The natural sources of arsenic in arable land are soil parent rock and volcanic eruptions. Major anthropogenic sources of arsenic in the cultivated soils are atmospheric depositions, fertilizer preparations (mineral fertilizers, liming agents, municipal and industrial sewage sludge, composts, ashes, slags, etc.), feed preparations and pesticides in the past. Arsenic in farm animal manure used on a farm is of the internal source of arsenic at that farm.

2.5.1 Fertilizer preparations

Mineral fertilizers. Continuous application of fertilizers that contain trace levels of arsenic may result in arsenic contamination of the soil, thereby reaching the food chain through plant uptake. Fertilizer preparations are known to be one major source of arsenic into cultivated soils. Arsenic finds its way into mineral fertilizers from parent rock materials, particularly from rock phosphate depending on its geologic characteristics, but also from equipment corrosion, catalysts and reagents, fillers, coaters, and conditioners. Contents of arsenic in phosphatic raw materials from different deposits varied as follows: from Syria 2.1-10.5, Algeria 8, Tunisia 5.7, Jordan 2.6-27.5, Republic of South Africa 8.7, Egypt 17.3, Russia, phosphate rock from Briansk 3.4 and Russia, Kola apatit 2 mg kg^{-1} (Kharikov & Smetana 2005). In the 1970´s and 1980´s, raw phosphates from North Africa were imported into Finland, as well. Commercial inorganic fertilizers may also contain high amounts of arsenic. In particular, P containing mineral fertilizers can be rich in arsenic and may have an arsenic value of 84 mg kg^{-1}, on average, or up to 155 mg kg^{-1} (U.S. Environmental Protection Agency and Center for Environmental Analysis 1999). The highest arsenic value found in the litterature for mineral ferilizer was 1 878 mg kg^{-1} measured from superphosphate used in India (SOS-arsenic.net 2006).

Polemio and Bufo (1984) determined that if NPK-fertilizers were applied in amounts varying from 100 to 800 kg per hectare, arsenic contribution from the fertilizers to the soil varied between 0.30 and 226 g ha^{-1} and if triple superphosphates were applied at the same rates, arsenic contribution varied between 64 and 257 g ha^{-1}. Arsenic inputs of these magnitudes at one application can be considered very high. In its Fertilizer Act, Washington State has adopted the Canadian standards for maximum acceptable heavy metal additions to soil (WSDA 2001). The standards limit the levels of nine metals (Cd, Co, Hg, Mo, Ni, Pb, Se and Zn) including arsenic. The standard limit for annual arsenic load is 333 g ha^{-1} which seems to be a huge amount from the Finnish perspective.

Currently, there is no limit value for arsenic in mineral fertilizers in Finland. However, the Finnish Food Safety Authority, Evira, has followed up on arsenic contents in fertilizers and monitoring results have been published in the half-year reports (Finnish Food Safety Authority 2003, 2004, 2005 and 2006). Mostly, arsenic contents have been <0.5 mg kg^{-1}. A limit value for arsenic in fertilizer preparations other than mineral fertilizers is 50 mg kg^{-1} (decision of the Ministry of Agriculture and Forestry 46/1994 on fertilizer preparations). In Finland, a new Fertilizer Act came into force on 1 July 2006 (MMM 539/2006). At the moment, regulations under the Fertilizer Act are under renewal. These regulations will probably have a limit value for arsenic for all the fertilizer preparations entering the Finnish market. In Finland, a phosphate rock mine was opened in the beginning of the 1980´s in Siilinjärvi. This mine produces phosphate rock of igneous origin. Finnish rock phosphate is known to contain very little arsenic. In 2001, domestic fertilizers manufactured by Kemira (2001) for the Finnish market had a quality certificate that guaranteed that mineral fertilizers contained arsenic <1 mg kg^{-1}, but today the guarantee is <5 mg kg^{-1} (Kemira GrowHow 2006).

The use of fertilizers has decreased markedly since the 1980´s and is now little more than 700 000 tons annually (Table 14). For instance, the use of P has been halved until today (Table 14). Implementation of the EU agro-environmental programme into the Finnish agriculture system in the 1990´s has continuously diminished the application of all N, P and K macronutrients as well as Ca (liming). The use of lime has decreased more drastically than the use of fertilizers (Table 14). Since 1994, the use of lime has decreased to nearly to one third. This means that today, on average, 240 kg of lime is applied annually per hectare.

Table 14. Annual use of mineral fertilizers and lime (as pure lime) during the fertilization period (1.7.-30.6.) in Finland (Tike, Information Centre of the Ministry of Agriculture and Forestry in Finland *et al.* 2005).

	1994	**2001**	**2002**	**2003**	**2004**
Total use of fertilizers (million kg)	861	770	753	743	721
Nutrients, kg ha^{-1}	153	114	115	114	108
Nitrogen (N) kg ha^{-1}	94.0	78.0	78.0	78.0	74.0
Phosphorus (P) kg ha^{-1}	19.0	10.0	10.0	10.0	9.0
Potassium (K) kg ha^{-1}	40.0	26.0	27.0	27.0	26.0
Total use of lime (as pure lime), (million kg)	1 217	1 105	1 197	555	478

In 1997, the quantity of imported inorganic fertilizers was over 105 166 tons, of which 71 180 tons was N-fertilizers (29 455 tons as N), 7 055 tons P-fertilizers (1 305 tons as P_2O_5), 444 tons K-fertilizers (70 tons as K_2O) and 26 487 tons other mineral fertilizers (National Board of Customs 1998 and 1999). In the same year, Finnish fertilizer exports totaled 41 951 tons, of which 40 080 tons was N-fertilizers (9 351 tons as N), 14 tons P-fertilizers (0.5 tons as P_2O_5), 231 tons K-fertilizers (41.7 tons as K_2O) and 1 626 tons other mineral fertilizers. The balance between import and export was as following: all fertilizers together +63 215 tons, N-fertilizers +31 100 tons (+20 104 tons as N), P-fertilizers +7 041 tons (+1 304.5 tons as P_2O_5) and K-fertilizers +213 tons (+28.3 tons as K_2O). The quality of the fertilizer preparations and fertilizer raw materials imported and for sale in Finland is controlled by the Finnish Food Safety Authority Evira.

According to statistics from the National Board of Customs, Finland's (2005) total import and total export of fertilizers manufactured (Table 15) were clearly higher in 2005 than those in 1997. The total balance between the imported and exported fertilizers was +63 215 tons in 1997 and -332 154 tons in 2005. The balances indicate that in 1997, more fertilizers came into Finland than was exported, but in 2005, much larger amounts of fertilizers were sold out to other countries than were bought into Finland. The total fertilizer import was about four times larger in 2005 than in 1997, but the total export was about 20 times greater than in 1997. The biggest change in imports occurred for K-fertilizers, which were imported into Finland about 700 times more in 2005 than in 1997. For exports, there seems to be an increasing trend especially for K fertilizers (Table 15). Fertilizers that may contain arsenic are mainly P-containing mineral fertilizers. Both in 1997 and 2005, they were exported very little. In 2005, 2 739 tons of P-fertilizers were imported, which is about one third of that in 1997 and less than 0.4% of all the fertilizers sold for agriculture in Finland in 2004. Thus, it seems to be very probable that P-fertilizers imported into Finland do not pose a great arsenic risk to the Finnish agro-ecosystems.

Table 15. Finnish imports and exports (the unit of quantity is metric tons) by fertilizer groups in 2005 and a change from 2004 (National Board of Customs, Finland 2005).

Fertilizer group	**January-December 2005**			
	Import		**Export**	
	Quantity	**Change**	**Quantity**	**Change**
Fertilizers, manufactured	450 641	+3.0	782 795	+15.0
- Mineral or chemical fertilizers, nitrogenous	94 734	+13.0	69 641	-47.0
- Mineral or chemical fertilizers, phosphatic	2 739	+7.0	18.0	+50.0
- Mineral or chemical fertilizers, potassic	304 375	-1.0	72 477	+99.0
Total balance = Import - Export			-332 154	

Based on the analytical results obtained in the RAKAS-project (2004-2007, unpublished data) commercial mineral fertilizers in the Finnish markets seem to contain less than 1 mg kg^{-1} of arsenic (Table 16). If about 721 million kg of mineral fertilizers is applied annually (Table 14) to 1 993 000 ha in production (Table 2), then 362 kg per ha per year of mineral fertilizers, on average are applied. This means that the arsenic contribution will be annually less than 0.362 g per ha and is internationally low. If the arsenic input from fertilizers is calculated on the basis of the current guaranteed value of <5 mg (Kemira GrowHow 2006), then the arsenic contribution is 1.810 g per ha. This is the mean maximum load from the mineral fertilizers for all the fields under cultivation.

Table 16. Arsenic content (mg kg^{-1}) of fertilizer preparations measured in the RAKAS-project (2004-2007, unpublished data) and nutrient (N, P, K or Zn) contents (%) of mineral fertilizers given by Kemira GrowHow (2004). (Se content 0.001% in each of mineral fertilizers).

Fertilizer preparation	**Trade mark**	**As (mg kg^{-1})**
NPK, 26/2/3	Kevätviljan Y1	<0.5
NPK, 23/3/5	Kevätviljan Y2	0.5
NPK, 20/3/8	Kevätviljan Y3	<1.0
NPK, 20/2/12	Kevätviljan Y4	<0.5
NPK, 20/2/12	Kevätviljan Y4	<0.5
NPK, 22/5/5	Kevätviljan Y5	0.6
NPK, 17/4/13	Kevätviljan Y6	<1.0
NPK, 13/7/13	Syysviljan Y1	0.7
NPK, 12/7/13	Syysviljan Y1	0.7
NPKZn, 18/3/5/0.1	Nurmen Y1	<0.5
NPKZn, 18/6/8/0.1	Nurmen Y2	<0.3
NKZn, 20/7/0.15	Nurmen NK1	<0.5
NKZn, 20/15/0.1	Nurmen NK2	<0.5
NK, 26/1	Suomensalpietari	<1.0
NK, 26/1	Suomensalpietari	<0.5
Blast-furnace slag	Koverhar	<1.0
Steel slag	Koverhar	2.0
Detection limit		0.5

The Finnish Food Safety Authority, Evira, controls the quality and use of all fertilizer preparations and also the quality of different waste products for use in agriculture. Such products are, for instance, biowaste composts, ashes and slags. According to the control authority's half-year reports (Finnish Food safety Authority Evira 2003, 2004, 2005 and 2006), arsenic contents in the compost and liming agents have been mostly <1 mg, in slags 1-2 mg, in mull products 1-4 mg, but in ashes often approximately 10 mg kg^{-1}. In 2005, the mean use of liming agents was 240 kg ha^{-1}. Based on this information, on average <0.24 g of arsenic was added via liming agents to one hectare per year. Fertilizer preparations other than commercial mineral fertilizers are particularly used in organic farming.

Municipal sewage sludge. In Finland, municipal wastewater treatment plants have generated sewage sludge annually about 1 000 000 tons of sewage sludge as fresh matter and 160 000 tons as dry matter annually (Ministry of Environment in Finland 1995, 2003). Probably, the amounts will remain the same in the upcomimg years. Since 2000, about 80% of municipal sewage sludge has been used as a growth medium in green building and as cover medium in landfills, 12% in agriculture after various treatments, 6% in landfills and 2% has been stored (Ministry of Environment in Finland 2003). By the year 2005, the target for sludge use was 90% and that has been reached. However, the use of sewage sludge as a cover medium in landfills will be reduced. Thus, additional routes for recycling of sewage sludge should be found out.

In the EU Member States, agricultural use of sewage sludge has been regulated by the Sewage Sludge Directive of EEC (278/1986), which it is now under revision. A Directive on the biological treatment of biodegradable waste is under preparation. The commission has announced in the communication “Towards a Thematic Strategy on Soil Protection” (CEC 2006) that the strategy will involve proposals for these two directives. In Finland, legislation on sewage sludge use in agriculture has been mainly based on the decision of the Council of State (282/1994). In this decision, no arsenic limit has been set for the sludge. When sewage sludge has been used as compost in agriculture, the requirements of the Ministry of Agriculture and Forestry (46/1994) have been met. When sewage sludge is so handled, it is classified to soil improver, and then a maximum arsenic content is 50 mg kg^{-1} fw. For a fertilized growth medium, the limit value is 10 mg l^{-1}. In 2005, the Ministry of Agriculture and Forestry supplemented requirements for the agricultural use of sewage sludge by publishing a guideline (Ministry of Agriculture and Forestry in Finland 2005). The Finnish sludge legislation deals with heavy metal limit values for sludge and soil, annual heavy metal loading and pre-treatment and hygienic requirements for sludge. Changes in the Finnish legislation for the use of fertilizer preparations, including sewage sludge preparations, are expected in the near future.

Use of municipal sewage sludge on the cultivated soil may have beneficial fertilizing, liming and humus increasing effects on the soil. However, sewage sludge may cause potential environmental and agricultural problems related to an excessive and/or unbalanced supply of nutrients, the introduction of pollutants, such as heavy metals and organic compounds, and the spreading of human, animal or plant pathogens (EC 2003). It has been determined that sewage sludge production in the EU is more than 8 million tons of dry matter. According to Sauerbeck (1986), sewage sludge has physical influences on soil texture, structure, pore volume, pore size distribution and soil colour, chemical influences on pH value, redox potential, carbon content, exchange capacity (cations and anions), colloidal and ionic precipitation and bonding reactions (like complexation), nutrient and pollutant content and biological influences on soil biological activity, microflora (bacteria, fungi and algae) and fauna (microfauna, mesofauna and macrofauna)

Due to the small population, low population density and low application rates of sludge in Finland, the importance of municipal sewage sludge as an arsenic source is small, but can be locally great, particularly if sludge is continuously applied into the same fields. The fields situated in the vicinity of the waste water treatment plant are at the highest risk to receive sewage sludge most often. The arsenic content of the municipal sewage sludge in a highly industrialized municipality was 35 mg/kg dw in the 1990´s (MTT, unpublished data), but of the sludge generated in the Helsinki waste water treatment plant was only 6 mg/kg dw in 2005 (Lundström 2006). In the future, use of sludge in agriculture may be enhanced especially in non-food production. A target of the EU is to double the use of renewable energy sources from the current 6% to 12% by 2010 (ProAgria Group 2006). One renewable energy source is the production of bioenergy plants on arable land, which would be a sustainable way to increase recycling of nutrients and organic matter in side-products generated by the municipalities and food or feed industry for bioenergy production, if the side-products have been proven to be safe to the agro-ecosystems.

2.5.2 Pesticides

In the past, inorganic arsenic compounds have been applied to arable soils as insecticides and herbicides. In Finland, calcium arsenate was used as an active ingredient from 1890-1964, lead arsenate from 1890-1959 and zinc arsenate from 1954-1955 (Markkula & Kurppa 1985). Total volumes of arsenic-bearing pesticides used in Finland are not available. In Finland, all arsenic bearing pesticides were prohibited in 1964 (Markkula 1990) in Finland. Volumes of pesticide sales as active ingredients and as products in Finland are presented in Table 17. Since 1995, the sales of fungicides and herbicides have increased, but those of insecticides and growth regulations have decreased in agriculture. Arsenic is produced commercially through the reduction of As_2O_3 with charcoal. In the 1960´s, 77% of commercial arsenic production was used for pesticides in the USA. and in the 1980´s arsenic pesticides were still largely in use. An estimated 22% of the world arsenic production is still used in agricultural chemicals (IPCS 2001).

Table 17. Volume of pesticide sales as active ingredients and as products in Finland (Plant Production Inspection Centre, 2005).

Active ingredient sales (tons)	**1995**	**2001**	**2002**	**2003**	**2004**
fungicides	114	192	225	222	237
agricultural insecticides	57.0	42.0	66.0	58.0	36.0
agricultural herbicides	791	1 120	1 278	1 339	1 175
growth regulations	73.0	69.0	52.0	47.0	42.0
Product sales (tons)					
fungicides	236	438	513	525	549
agricultural insecticides	160	108	181	158	107
agricultural herbicides	1 768	2 563	2 930	3 050	2 709
growth regulations	131	115	89.0	82.0	79.0

2.5.3 Feed preparations

Total annual amounts of feeds manufactured for the farms in Finland are presented in Table 18. In 2005, the amount was 1 298 million kg which was more than the total annual amount of mineral fertilizers and lime together (1 199 million kg) sold to the Finnish markets in 2004 (Table 14). About half of the feeds were used for cattle and about a fourth for pigs. Use of commercial feeds has increased while the use of mineral fertilizers and lime has decreased over the last few years.

The quality of feeds accepted for Finnish markets is regulated in detail by the Ministry of Agriculture and Forestry in Finland (MMM) with an act on feeds (MMM 396/1998). Maximum allowable contents of arsenic in different feed types were given in a decision on harmful substances in animal feeds (MMMp 163/1998). Maximum allowable contents of arsenic in feeds were changed in an ordinance (MMMa 80/2003). The valid maximum arsenic contents allowable in feeds are presented in Table 19. The highest maximum values, 15-40 mg kg^{-1}, are for feeds prepared from fish and other marine-originating materials. Also, for phosphates and other mineral containing feeds higher maximum values, 10-20 mg kg^{-1}, are allowed compared to other feed types, 2-6 mg kg^{-1}. In some marine feeds or feeds aimed for fish and fur animals, inorganic arsenic concentration is limited, as well. The concentration of inorganic arsenic for those feeds has to be <2 mg kg^{-1}. In Finland, the control authority is Evira (www.evira.fi/), which follows up on the quality of commercial feeding stuffs imported and geared towards Finnish markets. Evira regularly publishes its half-year control reports on the internet (www.evira.fi/). Exceeding of the arsenic limits seldom occurs, but if it occurs, marketing of the feed in question has to be stopped immediately.

Arsenic contents of feeding stuffs collected from dairy farms (n = 5) in RAKAS-project (2004-2007, unpublished data) are presented in Table 20. Contents seem to be clearly lower than the limit values. Also, these results indicate that mineral feeds have to some extent higher arsenic contents than the other feeds studied. However, feeds may be one source for the intake of arsenic by domestic animals and one arsenic source for soils via farm animal manure. The higher the arsenic content in the feeds, the greater the arsenic input into the soil through manure.

Table 18. Total amounts (million kg) of feeds manufactured annually for farms in Finland (Salopelto 2006).

Feeds for	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**
Cattle	444	493	458	458	524	616	640	642	655	645	661	697
Pig	252	279	270	270	263	254	246	246	268	288	285	304
Poultry	85	92	84	76	69	67	70	67	67	72	71	67
Broiler	110	121	138	145	169	185	178	211	228	235	235	230
Totally	**892**	**985**	**951**	**949**	**1024**	**1121**	**1133**	**1165**	**1218**	**1240**	**1252**	**1298**

Table 19. Maximum arsenic contents allowed in feed preparations at the Finnish markets (MMMa 80/2003).

Feed preparation	**Maximum allowable As content (1) mg/kg (ppm) in feed preparation (water content 12 %)**
Feed materials, except:	2.0
- green flour, alfalfa and clover flour and	4.0
dried sugar beet waste mass and	
molasses made of the mass	
- palm cake	4.0 (2)
- phosphates and lime containing marin	
lime containing marine algae	10.0
- calcium carbonate	15.0
- magnesium oxide	20.0
- feeds from preparation of fish and	
other marine fauna	15.0 (2)
- marine algae flour and	
feed materials prepared from marine algae	40.0 (2)
Complete feeds, except:	2.0
- complete feeds for fish and fur animals	6.0 (2)
Complementary feeds, except:	4.0
- mineral feeds	12.0

(1) Total content of As. (2) Maximum concentration of inorganic As has to be <2 ppm.

Table 20. Arsenic contents, mg kg^{-1} (88% dw) of various feed types (Unpublished data, RAKAS-project 2004-2007) analysed by Evira.

Feed type	**Trade mark**	**As**
Complementary feed for cattle	Huippu Krossi 23	<0.5
Complementary feed for cattle	Aseto-Melli	<0.5
Complementary feed for cattle	Tähti-145	<0.5
Complementary feed for cattle	Molassed rade seed meal	<0.5
Complementary feed for cattle	Rouhe-Tiiviste	<0.5
On average		**<0.5**
Complete feed for cattle	Maituri 10000	<0.5
Complete feed for cattle	Amino-Maituri	<0.5
On average		**<0.5**
Mineral feed for cattle	Mulli-Melli	0.75
Mineral feed for cattle	Kesä-Namino	3.1
Mineral feed for cattle	Onni-Kivennäinen	1.4
Mineral feed for cattle	Viher Hertta-Minera Muro	2.7
On average		**2.0**
Feed material for cattle	Sugar beet pulp, molassed	<0.5
Home mixture for cattle	Home mixture for cattle	<0.5

2.5.4 Farm animal manure

Over the past few years, the total amount of biodegradable waste in Finland has annually been about 34 million tons as fresh weight (fw) of which around 20 million tons is animal manure (Ministry of Environment 1995, 2003). This is about 20 times the amount of sewage sludge generated annually in the municipal waste water treatment plants in Finland. Numbers of animals in Finland are presented in Table 21. The numbers of cattle and sheep have had a decreasing trend, while the number of horses has increased. In 1997, the amount of manure generated in Finland was based on the numbers of farm animal species and is presented in Table 22. Finnish agricultural production is mainly based on livestock and milk is the most important product of Finnish agriculture. Therefore, a major part of animal manure, 18 million tons, was generated by cattle and consisted of about 85% of all the manure generated annually. Fresh animal manure contains about 20% dry matter. Thus, a total amount of animal manure as dry weight is about 4 million tons. Arsenic contents of dairy cattle were analysed in the RAKAS-project (2004-2007). According to the RAKAS-project (Unpublished data, 2004-2007), the arsenic content of cattle manure was about 0.8 mg per kg dw. Arsenic contents in slurry varied between <0.45 and 1.7 mg kg^{-1} dw (Table 24). Contents were roughly at the same level as those presented by Amlinger *et al.* (2004) (Table 25). The amount of arsenic in animal manure generated annually in Finland was 3 200 kg, more than three tons. The majority of arsenic origninates from the commercial feed preparations imported to the farms and the rest was part of the internal flow of arsenic occurring at the farms.

In America, the chickens have been fed organic arsenic compounds, like roxarsone, as an antibiotic to control infections and to increase weight gain (Bellows 2005). Roxarsone has been added to poultry feed at a rate of 22.7 to 45.4 g to ton. Little of the roxarsone is been retained in the meat, but most of it ends up unchanged in the manure excretes by the chickens. Each broiler excretes about 150 mg of roxarsone during the 42-day growth period that it has been administered. Litter collected following a single flock of birds can have contained from 1 to 70 mg of arsenic per kg of litter. Litter applications have resulted in elevated arsenic contents in soil.

Table 21. Livestock (in thousands) in Finland (Tike, Information Centre of the Ministry of Agriculture and Forestry *et al.* 2006).

Livestock	**1995**	**2003**	**2004**	**2005**
Horses	50.0	59.0	60.0	62.0
Cattle	1 148	1 000	969	959
of which dairy cows	399	334	324	319
Sheep	159	98.0	109	90.0
Pigs	1 400	1 375	1 365	1 401
of which sows	161	178	175	177
of which fattening pigs	451	444	441	460
Poultry	10 358	10 997	10 405	10 538
of which hens	4 179	3 016	3 069	3 128
broilers	4 276	6 050	5 573	5 472
turkeys	80.0	603	535	495
Reindeer	208	197	201	207

Table 22. Estimated quantities of animal manure recycled in agriculture in Finland in 1997 (Siika-aho 2000).

Animal manure	Tons x 10^6 fw, in 1997
Cattle manure	18.0
Pig manure	2.83
Sheep and goat manure	0.123
Horse manure	0.19
Poultry manure	0.223
Fur animal manure	0.096
Total	21.462

Table 23. Arsenic concentrations (mg kg^{-1} dw) in cattle manure from five dairy farms (Unpublished data, RAKAS-project 2004-2007).

Sample Nro.	Type*	As mg kg^{-1} dw
1	1	0.96
2	1	<0.45
3	1	0.73
4	1	0.49
5	1	1.7
6	1	1.3
7	1	<0.45
8	ns	
Mean		-
9	2	0.61
12	2	0.6
Mean		**0.61**
10	3	<0.45
11	4	1.2

* 1 = slurry; 2 = faeces and urine in peat; 3 = faeces; 4 = peat; ns = no sample

Table 24. Range of mean values found for different types of liquid and solid manure (Amlinger *et al.* 2004).

Manure type	As mg kg^{-1} dw
Cattle slurry	0.35-0.62
Cattle manure	0.67-1.77
Sheep & goat manure	0.99-2.65
Pig slurry	0.52-0.83
Pig manure	nd
Poultry manure/slurry	0.49-0.89

nd = no data

2.5.5 Atmospheric depositions

The major anthropogenic sources of arsenic are the burning of fossil fuels (mainly coal), smelting of metals (mainly Ni, Cu and Pb) and use of pesticides (Léonard 1991). Natural sources are continental and volcanic dust. Globally, arsenic emissions from the natural sources are only about a fourth of the anthropogenic ones (about 120 000 tons). In the atmosphere, arsenic is transported over long distances and then precipitated. In Finland, the main national anthropogenic source of arsenic emissions into the air is the burning of fossil fuels for energy production and for work machines (Table 25). About one-third of human-made emissions originate from industry, but agriculture is not a source of arsenic emissions. Domestic As-emissions have varied from year to year, and are clearly lower since the year 2000 than in the 1990´s (Table 26). The spatial distribution of arsenic emissions in Finland in 1994 is presented in Fig. 5. Atmospheric arsenic depositions are monitored by the Finnish Meteorological Institute at several of its research stations. At the research station in Kotinen, which is located nearby the Pirkanmaa region, arsenic depositions varied from 0.22 to 0.86 g ha^{-1} annually between 1997 and 2002 (Table 27). The arsenic deposition is about 1 g per hectare in southern Finland (Table 27) and about 0.5 g in the region of Ostrobothnia (Table 28). There seems to be a decreasing trend from the south to the north due to a diminishing trend in the human activities. In air, arsenic is present mainly in particulate form as arsenic trioxide, with background levels of 1-10 ng/m^3 in rural areas and 20 ng/m^3 in urban areas (NAS 1977).

Table 25. Domestic arsenic emissions (tons) by sectors into air in Finland in 2004 (Finnish Environment Institute 2006a).

Sector	**As**
Energy and work machines	2.7
Traffic, domestic	0.0
Industrial processes	1.0
Use of solvents and other chemicals	0.0
Agriculture	0.0
Waste	0.03
All together	3.8

Table 26. Domestic arsenic emissions in Finland from 1990-2004 (Finnish Environment Institute 2006b).

Year	**Annual arsenic emissions (tons)**
1990	33.2
1991	22.1
1992	16.0
1993	14.3
1994	9.3
1995	3.5
1996	7.2
1997	12.3
1998	12.4
1999*	-
2000	4.3
2001	5.3
2002**	3.7
2003	3.2
2004	3.8

Table 27. Annual arsenic deposition (µg/m^2) in three research stations (Utö, Virolahti and Kotinen) in a period from 1997-2002 as measured by the Finnish Meteorological Institute (1998-2003).

Research station	**Latitude**	**Longitude**	**Year**	**Precipitation (mm)**	**As (µg m^{-2})**
Utö	59° 47'	21° 23'	1997	430	149
Utö	59° 47'	21° 23'	1998	390	108
Utö	59° 47'	21° 23'	1999	329	137
Utö	59° 47'	21° 23'	2000	335	119
Utö	59° 47'	21° 23'	2001	363	82
Utö	59° 47'	21° 23'	2002	269	68
Virolahti	60° 32'	27° 41'	1997	438	143
Virolahti	60° 32'	27° 41'	1998	616	143
Virolahti	60° 32'	27° 41'	1999	326	109
Virolahti	60° 32'	27° 41'	2000	514	144
Virolahti	60° 32'	27° 41'	2001	582	94.0
Virolahti	60° 32'	27° 41'	2002	412	52.0
Kotinen	61° 14'	25° 04'	1997	526	63.0
Kotinen	61° 14'	25° 04'	1998	756	80.0
Kotinen	61° 14'	25° 04'	1999	528	86.0
Kotinen	61° 14'	25° 04'	2000	662	74.0
Kotinen	61° 14'	25° 04'	2001	662	62.0
Kotinen	61° 14'	25° 04'	2002	515	22.0
Mean, g/ha					**0.96**

Table 28. Annual arsenic deposition (µg/m^2) at two research stations (Hailuoto and Hietajärvi) from 1997-2002 as measured by the Finnish Meteorological Institute (1998-2003).

Researh station	**Latitude**	**Longitude**	**Year**	**Precipitation (mm)**	**As (µg m^{-2})**
Hailuoto	63° 10'	30° 43'	1997	268	35.0
Hailuoto	63° 10'	30° 43'	1998	459	39.0
Hailuoto	63° 10'	30° 43'	1999	335	47.0
Hailuoto	63° 10'	30° 43'	2000	418	59.0
Hailuoto	63° 10'	30° 43'	2001	364	40.0
Hailuoto	63° 10'	30° 43'	2002	311	13.0
Hietajärvi	65° 00'	24° 41'	1997	571	50.0
Hietajärvi	65° 00'	24° 41'	1998	727	64.0
Hietajärvi	65° 00'	24° 41'	1999	510	58.0
Hietajärvi	65° 00'	24° 41'	2000	640	61.0
Hietajärvi	65° 00'	24° 41'	2001	511	49.0
Hietajärvi	65° 00'	24° 41'	2002	476	11.0
Mean, g/ha					**0.44**

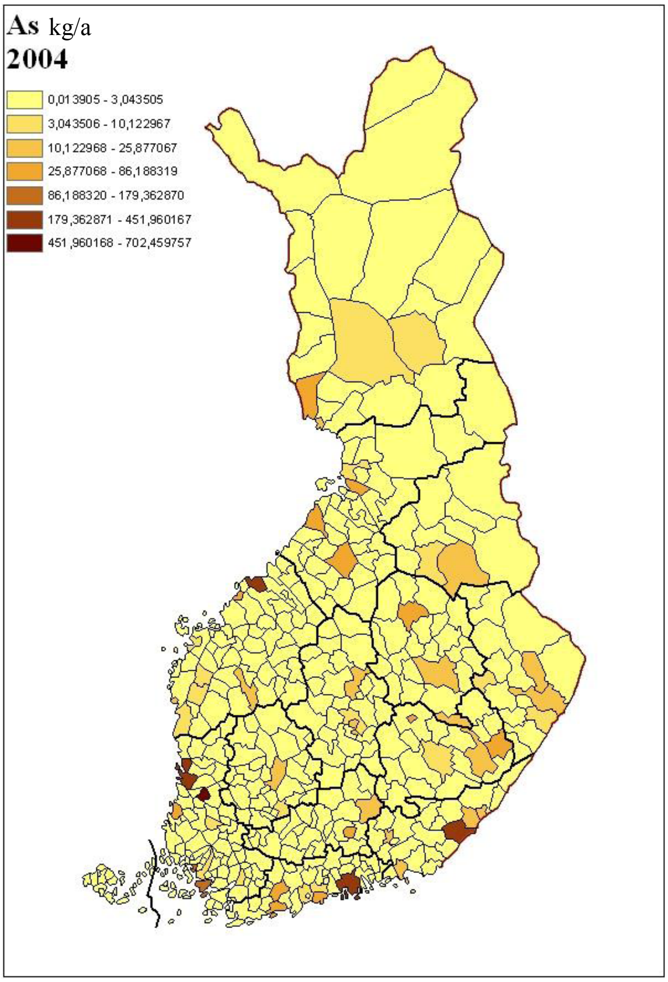


Figure 5. Spatial distribution of arsenic emissions in Finland in 2004 (Finnish Environment Institute 2004).

2.6. Arsenic mass balance in arable soil

Arsenic inputs into agricultural soils from various sources take place at a rather slow rate but over large areas. Hence, it may take decades to detect accumulation trends in soil by repeated sampling with statistical significance. A mass balance calculation is one tool to evaluate sustainability of arsenic fluxes in the soil. If arsenic inputs from different sources are balanced with the arsenic outputs, no change in the arsenic content of the soil will occur. If the inputs are higher than the outputs, the element will accumulate in the soil. If the inputs are smaller than the outputs, then the element content in the soil will decrease. Balanced approaches differ primarily with respect to spatial scale (field, farm, region and nation).

To calculate a national mean balance of arsenic in arable soils, total annual material flows in agriculture and their arsenic contents were clarified. Table 29 shows that more than 2.5 million tons of various materials as fresh matter were imported to the farms and annually applied directly or indirectly via manure to the whole cultivated area (1 993 000 ha) in Finland. Mineral fertilizers and liming materials together account for 1.2 million tons, which is to some extent less than the total annual use of feed preparations (1.3 million tons). Arsenic inputs to the soils can be from atmospheric deposition, the mineral fertilizers, lime, municipal sewage sludge and other waste-originated soil improvers and feed preparations via animal manure. About 20 million tons of farm animal manure is cycled inside farms. Routes for arsenic outputs from the soils are plant crops, leaching and erosion. A national mean arsenic balance in cultivated soil (Table 30) was calculated so that the total annual materials imported to the farms were assumed to be applied evenly to the whole cultivated area by taking into account the national mean values for arsenic uptake by the crops, leaching of arsenic into the surface and ground waters and loss of arsenic eroded via soil particles.

Table 29. Annual material flows in agriculture in Finland and their arsenic contents.

Material	Annual total use (million tons)	Mean use (kg ha^{-1})	Arsenic content (mg kg^{-1} dw)
Mineral fertilizers	0.721	362	0.5
Liming agents	0.478	240	< 1.0
Municipal sewage sludge, 15 % dw	1 fw/0.15 dw*	60 fw/9 dw	6.0
Feed preparations, 88 % dw	1.298 fw/1.142 dw	651 fw/573 dw	< 1.0
All together			
Farm animal manure, 20 % dw	21.5 fw/4.3 dw	10769 fw/2154 dw	0.8
(internal flow)			

* In this calculation, it is assumed that 12% of sludge was utilised in agriculture.

As a result of small crop yields in Finland (Table 3) and low arsenic contents in plants (Table 11 and 12) outputs of arsenic via plant crops were minor. In the national balance, a total output of arsenic in plant crops was evaluated to be about 0.05 g per ha annually (Table 30). The arsenic value for leaching was taken from a Swedish study (Andersson 1992), because no Finnish data was available. Measurements of arsenic eroded with soil particles from cultivated soils were not available for Finland. The mean slope (m/100 m) of arable land is 1.6%, on average, and only 10% of the fields have a mean slope more than 5% (Puustinen *et al.* 1994). An annual loss of total solids from Finnish fields may vary from 50 kg to 7 000 kg/ha depending on many factors such as soil type, slope of the fields, and precipitation, as reported by Uusi-Kämppä (1989). In the balance calculations, the annual loss of total solids from cultivated soil was assumed to be 500 kg ha^{-1}. The arsenic content of the eroded solids was assumed to be the same as the initial soil.

Table 30. Mean annual mass balance of arsenic in arable soil at a national level.

Mean national As balance	Annually
Inputs	**g ha^{-1}**
Atmospheric deposition	0.5-1.0
Mineral fertilizers	0.181
Liming agents	< 0.24
Feed prepartions	< 0.573
Municipal sewage sludge	0.054
All together	**<1.548 – 2.048**
Outputs	**g ha^{-1}**
Plant crops	0.05
Leaching	0.48
Erosion, 500 kg x 2.76 mg	1.38
All togerther	**1.91**
Accumulation	
Accumulation, g ha^{-1}	**from - 0.362 to +0.138**
Accumulation, % in a year	0.003

On a national level, atmospheric deposition seems to contribute arsenic to the soils more than mineral fertilizers, liming agents, sewage sludge and commercial feed preparations together, at least in southern Finland. It was very difficult to calculate the national arsenic input from the feed prepartions, because there were many types of feeds and the arsenic contents varied much depending on the feed type. For detailed calculations, exact amounts of various feed types used annually should have been needed. The biggest outflow of arsenic occurred via erosion. The fate of arsenic transported by the soil particles into the surface waters and the effects of arsenic on aquatic ecosystems should be studied in the future.

The annual net balance of arsenic at the national level varied from -0.362 to +0.138 g per ha and was near 0 (Table 30). This means that arsenic inputs to the cultivated soil and outputs from the soil are rather well balanced. In northern Finland, the balance was negative due to low atmospheric deposition and arsenic content in soil may decrease, while in southern Finland the balance was slightly positive, indicating that 0.138 g of arsenic will annually accumulate to the soil per ha. That is 0.003% of the current median arsenic amount in the plough layer (20 cm) in one ha, 5520 g. According to the Swedish balance calculations estimated by Andersson (1992) the annual increase in the soil arsenic content varied from 0.008 to 0.032%. If arsenic is assumed to be continuously accumulated in the Finnish soil by 0.003% in the future, it takes about 40 000 years before the current median arsenic (2.76 mg kg^{-1} dw) content (Table 7) in the soil will be doubled. Nationally, this rate of arsenic accumulation in the soil can be considered sustainable in the long term.

Farm animal manure used at the farm is considered to be an internal flow in the balance calculations. However, manure imported to the farm is classified as an input and manure exported from the farm is classified as an output. If all the cattle manure generated annually in Finland is thought to be applied evenly to the whole cultivated area, the mean arsenic input per ha is 1.723 g. If this is compared to the arsenic input from the feed preparations, <0.573 g, we can see that less than one third of the arsenic in manure originates from the commercial feed preparations and the rest, more than two thirds, comes from the air (by inhaling), soil (by ingesting) and home-grown feeds. The real situation is that the manure is not applied evenly to the whole cultivated area. Soils on animal farms or in their vicinity clearly receive more manure and also more arsenic via manure than the other soils.

In the RAKAS-project (2004-2007), field balances of arsenic for 2004 were calculated at the farm scale at five crop farms in south-western Finland and at five dairy farms in the Ostrobothnia. To clarify arsenic inputs, both production resources (fertilizer preparations, feed preparations, etc.) and products (plant and animal crops) were sampled at these farms and analysed for arsenic (Tables 21, 26, 10 and 12). Also data on the material flows at the farms were collected. Manure was taken into account only if it was received (imported) from another farm or if it was sent out (exported) to another farm. In addition to this, soil samples were collected from the fields and analysed for arsenic. Data on atmospheric deposition of arsenic in the regions were obtained from the Finnish Meteorological Institute (Tables 33 and 34). A leaching value of arsenic was obtained from Sweden (Andersson 1992) and was the same as in the national balance calculations. A value for arsenic removed from the soil via erosion was calculated in a way similar to the national balance calculations.

Balance calculations (Table 31) revealed that arsenic inputs and outputs were rather well balanced in the fields of all of 10 farms studied in the RAKAS-project (Unpublished data, 2004-2007). An arsenic net balance was negative at three crop farms, and at two dairy farms. A negative balance shows that arsenic content in these soils will diminish. Totally, the net balances at the farms ranged from -2.0 to +2.3 g ha^{-1} per annum (Table 31). The use of slag from the metal industry as a soil improver was the biggest source of arsenic in those farms that had used it. The next important inputs came from atmospheric deposition and lime. At the crop farms in the southwestern Finland, an arsenic load from the atmosphere was of the same magnitude as the total load from all fertilizer preparations, on average. At the dairy farms, an arsenic input from the fertilizer preparations was nearly twice that of the crop farms. An arsenic load from commercial feed preparations in different farms varied from 0.1 to 0.5 g ha^{-1} per annum and was about a tenth of the input from the fertilizer preparations and a half of that from the atmosphere, on average. A major part of the total outputs occurred via erosion and to a lesser extent via leaching. Exported manure in some dairy farms might be a moderate route for the arsenic output. Outputs in plant and animal crops were negligible, because arsenic contents were low and crop yields in Finland are low (Table 3). The net balances obtained here at a farm level were in good harmony with those on a national level. Arsenic inputs and outputs are rather well balanced in Finnish cultivated soils, which is an indicator of sustainable cultivation practices.

Table 31. Field mass balances of arsenic at five crop farms (1-5) in southwestern Finland and at five dairy farms (6-10) in Ostrobothnia in 2004. Average contents of *aqua regia* extractable arsenic in the soil plough layer at each farm. (* = farm received steel slag for soil improving in 2004) (Unpublished data, RAKAS-project 2004-2007).

Number of farm	**1***	**2**	**3**	**4**	**5***	**unit**
Inputs	**2.3**	**1.1**	**1.1**	**4.5**	**2.9**	(g/ha/a)
Fertilizer preparations	1.3	0.1	0.11	3.5	1.9	(g/ha/a)
Atmospheric deposition	1.0	1.0	1.0	1.0	1.0	(g/ha/a)
Outputs	**4.2**	**3.1**	**2.0**	**3.1**	**4.3**	(g/ha/a)
Leaching	0.48	0.48	0.48	0.48	0.48	(g/ha/a)
Plant crops	0.03	0.02	0.02	0.02	0.03	(g/ha/a)
Erosion	3.7	2.9	1.5	2.5	3.8	(g/ha/a)
Balance	**-1.2**	**-2.0**	**-1.0**	**1.5**	**-1.4**	(g/ha/a)
As in soil	7.4	5.2	3.1	5.1	7.6	(mg/kg ka)

Number of farm	**6***	**7**	**8**	**9**	**10**	**unit**
Inputs	**4.9**	**3.9**	**2.6**	**1.1**	**2.3**	(g/ha/a)
Fertilizer preparations	4.3	3.1	2.0	0.13	1.6	(g/ha/a)
Commercial feeds	0.1	0.41	0.15	0.54	0.2	(g/ha/a)
Atmospheric deposition	0.44	0.44	0.44	0.44	0.44	(g/ha/a)
Outputs	**3.0**	**2.3**	**3.6**	**1.3**	**1.3**	(g/ha/a)
Leaching	0.48	0.48	0.48	0.48	0.48	(g/ha/a)
Plant crops	0.00	0.00	0.00	0.00	0.00	(g/ha/a)
Erosion	2.5	1.1	2.3	0.84	0.67	(g/ha/a)
Animal crops	0.00	0.01	0.01	0.01	0.01	(g/ha/a)
Farm yard manure	0.0	0.08	0.89	0.0	0.15	(g/ha/a)
Balance	**1.9**	**2.3**	**-1.0**	**-0.2**	**1.0**	(g/ha/a)
As in soil	5.0	2.2	4.6	1.7	1.3	(mg/kg ka)

3. ARSENIC IN ARABLE AND FOREST SOILS AND CROPS AT THE FARMS STUDIED IN THE PIRKANMAA REGION

3.1 Aims of the study

The aim of this study was to investigate the contents of arsenic and other potentially toxic elements in arable soils and crops in the Pirkanmaa region in areas where the till and groundwaters are known to contain elevated amounts of arsenic. To assess the level of possible arsenic enrichment in soils and crops in the study area, an extensive literature review of potential arsenic sources in agriculture was conducted. Arsenic content in arable soils was compared to the forest soils in the vicinity with the same soil type to correlate the data obtained to the local geochemical environment.

The risk assessment for the Pirkanmaa region to be made later within the RAMAS-project will be based on selected test sites from which available information on arsenic and the related risk factors will be collected as completely as possible. The farms and their residents were identified as a potential source of information due to the wide-ranging activities carried out in agriculture. The group of test farms was selected and soils and crops were sampled in areas selected based on the arsenic concentrations in till. Clay soils were preferred because concentrations of arsenic tend to be higher in fine-grained soils than in coarse-grained soils. Sampling of soil and plant crops was done at the same sampling site and time to minimize the source of error.

In short, the aims of this study were to obtain answers to the following questions:

- Is arsenic enriched in fine sediments in areas where the concentrations are known to be high in bedrock, till or groundwater?
- Does arsenic migrate to agricultural soils from the surrounding high arsenic soils?
- Does the grain size of fine sediments – fine sand, silt, or clay – have an influence on the arsenic concentration in soil?
- Are the arsenic concentrations at the same level in arable soils and in forest soils, when the soil type is the same?
- Is the arsenic concentration different in the plough and subsoil layers in the arable land, or in the four different layers in the forest soil profiles?
- Does arsenic migrate from agricultural soils to the crops?
- What is the arsenic concentration level in crops?
- Is the mobility of arsenic different in arable soil from that in forest soil, and what is the role of fertilization?
- To what extent is a soluble form of arsenic present in soils?
- Are the arsenic concentrations at a high level in the Pirkanmaa region in comparison to the rest of Finland?

3.2 Study area and background data of the Pirkanmaa region

The study area of Pirkanmaa (also called the Tampere region) is located in southern Finland, about 160 km northwest of Helsinki, in the Häme province (Fig. 6). In 2006, this 14 700 km^2 area with 455 000 inhabitants consisted of 33 municipalities (Fig. 7). The industrial and commercial centre of the area is the city of Tampere (www.pirkanmaa.fi/english/). The topography of the Pirkanmaa region is relatively even in the south and more contoured in the northern parts. The low-lying and productive soil of southern Pirkanmaa is well-suited for agriculture. The amount of swamps and bedrock outcrops increases towards northern Pirkanmaa. Surface water bodies cover approximately 15% of the area of Pirkanmaa.

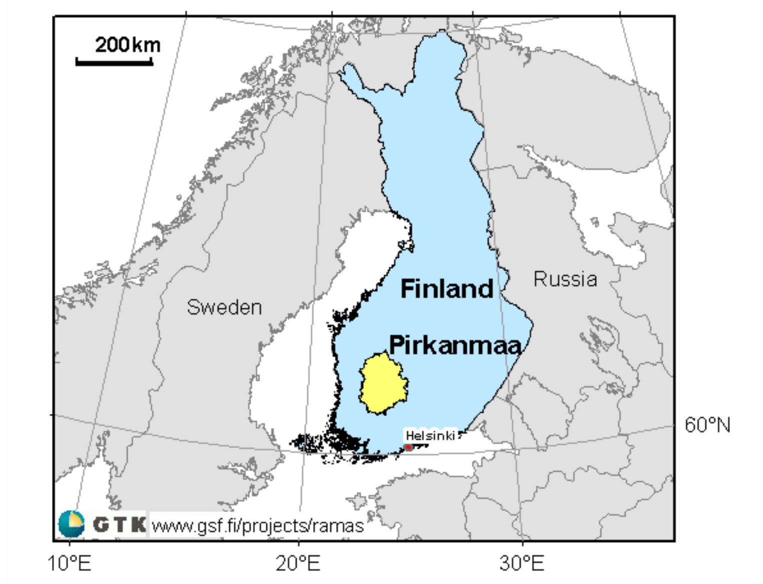


Figure 6. The study area of Pirkanmaa in southern Finland (Base map data © National Land Survey of Finland).

Figure 7. Municipalities of the Pirkanmaa region (Base map data © National Land Survey of Finland).

The bedrock of Pirkanmaa is predominantly composed of metasedimentary rocks, metavolcanic rocks and granitoids, which cut the former rock types (Kähkönen 1989, Korsman *et al.* 1997, Nironen 1997, Kilpeläinen 1998). The supracrustal rocks (sediments and volcanites), which formed on the Earth's surface, were subjected to deformation and metamorphosis after their formation.

The Pirkanmaa region can be divided in three geologically distinct units based on the dominant rock types encountered in the area and according to the air-borne geophysical electromagnetic measurement data. The main geological subdivisions in the study area are: the Central Finland Granitoid Complex (CFGC) in the north, the Tampere Belt (TB) in the centre, and the Pirkanmaa Belt (PB) in the south. For more details see Backman *et al.* (2006) and Fig. 8.

The CFGC mainly consists of tonalites, granites and granodiorites with minor proportions of supracrustal rocks and mafic plutonic rocks (Korsman *et al.* 1997). The TB is mainly composed of turbiditic metasedimentary rocks and felsic-intermediate arc-type metavolcanic rocks and plutonic intrusions that cut the supracrustal sequence (Ojakangas 1986, Kähkönen 1989, Kähkönen & Leveinen 1994). In the PB area, mafic and ultramafic plutons and granitoids cut the migmatitic metasedimentary rocks, sporadically containing graphite-bearing gneiss interlayers (Nironen *et al.* 2002).

Based on the data of 603 bedrock samples from the Pirkanmaa region, the median value of arsenic in the CFGC was 1.00 mg kg^{-1} (n=218), 2.22 mg kg^{-1} (n=128) in the TB, and 1.9 mg kg^{-1} (n=257) in the PB (Lahtinen *et al.* 2005, Backman *et al.* 2006). Thus, the arsenic content in the bedrock of the two southernmost subdivision (TB and PB) is elevated in comparison wit the northern part of Pirkanmaa and also compared to the whole country (med. 0.9 mg kg^{-1} (n=6 544; see chapter 2.2).

The overburden of the Pirkanmaa region was deposited during and immediately after the end of the last glaciation. The east-west striking Central Finland End Moraine, which cuts the Pirkanmaa region in the middle, was formed within one hundred years, between 11 000 – 10 900 years ago (Saarnisto & Saarinen 2001). This formation divides the Pirkanmaa region in two different units with characteristic Quaternary formations and topographic features. In the north, the relief is high and the overburden is predominantly composed of glacial till and the bedrock is relatively well exposed. In the southern part, the landscape is smooth and the fine-grained sediments, like clay and silt, are more common than in the north (Backman *et al.* 2006).

The most common soil type in the Pirkanmaa region – as in whole Finland – is till. About 38% of the ground in the area is covered by glacial till deposits as top soil. Till is more common in the northern Pirkanmaa than in southern Pirkanmaa. The average thickness of the till deposits is 3 – 4 metres. Fine-grained sediments – clays and silts deposits - found especially in the southern part of the region, cover about 14% of the whole Pirkanmaa area. Almost all of these areas are in agricultural use. About 79% of arable lands were in clay and only 4.4% in till in the Pirkanmaa region (Kurki 1972).

According to the nationwide geochemical survey (Koljonen *et al.* 1992), the median value of arsenic content in till fines in the Pirkanmaa region was 5.35 mg kg^{-1} (n=46), in the subdivision of CFGC 4.09 mg kg^{-1} (n=24), in the subdivision of TB 6.91 mg kg^{-1} (n=6), and in the subdivision of PB 14.2 mg kg^{-1} (n=16) (Fig. 9). The median value for the whole country was 2.57 mg kg^{-1} (n=1054). The values are a little bit higher in the PB and TB areas compared to the CFGC area or to rest of the country. In certain ore potential areas in the Pirkanmaa region, very high local arsenic content occurs particularly in the bottom layer of till. The maximum arsenic content in these sites was 9 280 mg kg^{-1} (Backman *et al.* 2006).

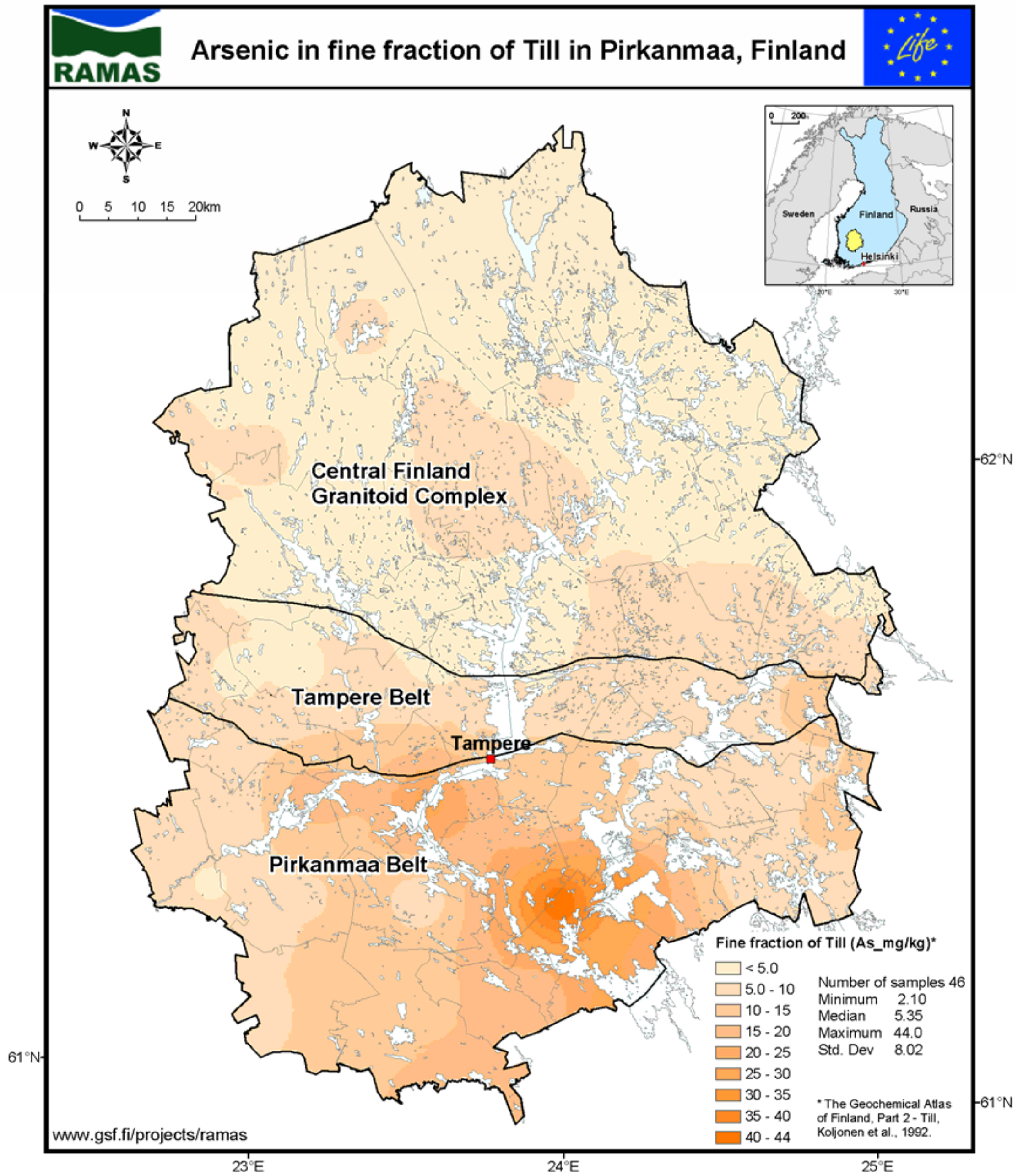


Figure 8. Arsenic concentrations in the fine fraction of till within the main geological subdivisions in Pirkanmaa region (based on data from Koljonen *et al.* 1992).

A Finnish soil monitoring study in 1998 included 35 fields in the Pirkanmaa region (Unpublished data, RAKAS-project 2004-2007). Contents of *aqua regia* extractable (ISO 11 466) arsenic in the plough layer of these fields are presented in Table 32. Contents varied from 2 to 17 mg kg^{-1} dw. The variation was nearly the same as the whole soil monitoring material (n = 338) in 1998 (Unpublished data, RAKAS-project 2004-2007) (Table 32). The median was 4.8 and mean 5.7 mg kg^{-1} dw. Arsenic contents between 7-11 mg kg^{-1} dw were found mostly in clay soils in the municipalities lying in the southwestern part of Pirkanmaa, in the Pirkanmaa Belt. Also at the national level, clay soils contained more arsenic than other soil types did. As well, one field on coarse mineral soil and one field in clay soil in the western part of the Pirkanmaa contained more than 7 mg kg^{-1} dw As. The maximum value was in organic soil in the northern part of the Pirkanmaa. Although high As contents have been detected in glacial till in the region (Koljonen *et al.* 1992), As levels observed in the cultivated soils were, in general, at the same level as the respective soil types in other parts of Finland.

Table 32. Contents of *aqua regia* extractable (ISO 11 466) arsenic by municipalities in cultivated fields (n = 35) sampled in the Pirkanmaa region in national soil monitoring in 1998 (Soil type groups: 1 = coarse mineral soil; 2 = clay soil; 3 = organic soil). (Unpublished data, RAKAS-project 2004-2007).

Municipality	**Plant cultivation zone**	**Soil type group**	**Arsenic mg kg^{-1} dw**
Hämeenkyrö	III	1	4.53
Ikaalinen	III	1	3.57
Kangasala	II	1	5.19
Kangasala	II	1	5.06
Kuru	III	1	3.72
Kuru	III	1	2.42
Luopioinen	II	1	3.67
Luopioinen	II	1	4.56
Längelmäki	III	1	8.32
Mouhijärvi	III	1	6.39
Mänttä	III	1	3.13
Orivesi	III	1	4.83
Orivesi	III	1	5.91
Orivesi	III	1	3.56
Parkano	III	1	3.04
Ruovesi	III	1	2.72
Suodenniemi	III	1	3.63
Tampere	III	1	2.42
Vammala	II	1	2.93
Vilppula	III	1	2.31
Virrat	III	1	2.24
Mean (n = 21)	**II-III**	**1**	**3.36**
Ikaalinen	III	2	6.60
Kylmäkoski	II	2	9.86
Lempäälä	II	2	10.9
Punkalaidun	II	2	8.72
Pälkäne	II	2	4.14
Sahalahti	III	2	7.13
Tampere	III	2	5.14
Toijala	II	2	8.06
Vammala	II	2	9.03
Vesilahti	II	2	8.11
Äetsä	III	2	7.88
Äetsä	II	2	9.21
Mean (n= 12)	**II-III**	**2**	**7.90**
Hämeenkyrö	III	3	2.51
Parkano	III	3	16.9
Mean ± Std	**II-III**	**1-2**	**5.66 ± 3.12**
Median			**4.83**
Minimum			**2.23**
Maximum			**16.9**

3.3 Study farms

Based on other studies performed during or prior to the RAMAS-project (2004-2007) it was possible to delineate the areas where the arsenic concentrations in groundwater and soil were known to be elevated (Koljonen *et al.* 1992; Unpublished data of RAKAS-project 2004-2007; Backman *et al.* 2006 etc.). The search for suitable test sites focused on these areas. The target was to cover the whole food chain and find farms that exploit local groundwaters and cultivate typical plants and/or have livestock. The selected 13 farms and their lifestyles are typical for the Tampere region and for Finland in general. This often means specialised production (livestock/agriculture), one or two main products and part-time farming (Fig. 9). A human health study will be carried out among the residents of these farms and some other households in 2006 and 2007.

Figure 9. A typical country scenery in the southern part of Pirkanmaa region (Photo M. Eklund).

There were both geological and agricultural criteria for the selection of the farms and sampling sites. The most essential demands were that

- the farm must locate in the vicinity of the potential arsenic risk areas
- the samples could be collected both from arable and forest land
- the farm had wheat, potato and/or timothy under cultivation in the 2005 growing season
- the farmer must be willing to participate in the project

Farms to be studied were selected from the areas where the arsenic content was known to be high (Backman *et al.* 2006). Therefore, the sampling was focussed on the Tampere Belt and the Pirkanmaa Belt. Most of the arsenic data available at the time of the site selection was from till formations. However, the national data material on arable soils collected by MTT contained a number of sampling sites in the Pirkanmaa region, as well (Unpublished data, RAKAS 2004-2007), which was a great help in the site selection process. In addition to soil data, also data on elevated arsenic concentration data in groundwater was available. The farms cultivating wheat, potato or timothy were sought and found in the farm register and field plot register of the Ministry of Agriculture and Forestry in Finland. The RAMAS-project made an agreement with the farmers willing to participate in the project.

Finally, the forest area in the vicinity of the arable land area was sampled. The sampling points were selected based on the Quaternary maps made by the GTK (Quaternary geological map data © Geological Survey of Finland). The samples were collected pair-wise from arable and forest area, so that the soil type was the same. The aim of this sampling procedure was that the soil samples taken from arable land and forestland could be comparable with each other. In most of the sampling sites, the soil type was the same in the field and forest. In three cases, the soil type was the same according to the Quaternary map and field observation, but after a grain size analysis in the laboratory the soil types turned out to be slightly different. Each soil sample from the forest area had one to three counter samples from arable soils.

Exact geographical information or detailed descriptions of the target farms or sampling sites could not be published here due to the privacy protection. This practice, which was adopted in Finland, is based on an agreement with the Ministry of Agriculture and Forestry on the confidential use of all the individual or personal data and information obtained from the farm register and the field plot register. Also, 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 in which the identity of the farmers or farms cannot be recognized. Therefore, the RAMAS-project was obligated to sign an agreement with the farmers to keep all the information and data collected from the farm or farmers anonymous.

The following chapters describe and discuss the outcome of the studies carried out at the study farms together with observations from the nearby forestlands.

3.4 Materials and methods

3.4.1 Sampling

The sampling criteria in this study were several, but the main criteria were, however, that the samples were collected pair-wise from arable and forest area, so that the soil type was the same.

First, the arsenic content should be high in the area. Therefore, the sampling was on a regional scale within the Tampere belt and Pirkanmaa belt where a high natural arsenic content had been found (Backman *et al.* 2006). At the time when sampling sites were to fix, there was arsenic content data available only from till settings. This data included the nationwide geochemical data (Koljonen *et al.* 1992) and several different ore exploration data from the GTK. This data gave no information about arsenic content in fine sediment settings. Most part of the arable land in the Tampere and Pirkanmaa Belt areas was in sites where the soil was composed of fine sediments. The proportion of fine sediments (fine sand, silt, clay) in arable land in the Pirkanmaa is 78.7% while the proportion of till is 4.4%, respectively (Kurki 1972).

The second criterion was that the farm should have wheat, potato or timothy under cultivation in 2005. The farms were selected from the farm and field plot registers of the Minstry of Agriculture and Forestry in Finland. Then, permission needed to be obtained from the farmer to participate in this study. Finally, a forest area in the vicinity of the arable land area with soil similar to the arable land area needed to be found. This work was based on the geological soil maps made by the GTK. Fieldwork was conducted to check the accuracy of the map determinations by a mapper from the GTK.

The result of this sampling was that the soil samples taken from the arable and forestry land in same area could be compared to each other. In most part of the sampling sites, the soil type was the same in both the field and forest sample pairs. In three sampling pairs the soil type was the same according to the map and field observation, but according to the grain size analysis in the laboratory, the soil types were determined to be different. In one area, there were two forest soil samples and three different arable soil sites and in two cases, there were two sampling sites for arable soils at the same farm and only one point of comparison in the forest area.

Agricultural soils and crops were sampled in high arsenic potential areas selected according to the geochemical map of arsenic concentrations in till. Sampling of soils and crops was done at the same sampling site and at the same time. Wheat and potato were selected as indicator crops for human health because they are commonly cultivated plant species consumed by the people across Europe. Timothy was selected as an indicator plant for animal farming and animal health, because timothy is largely cultivated in Europe and used as grass, forage or silage. The geographical coordinates of risk areas with high arsenic concentrations in till, pore or stream water were obtained from the GTK. The farms lying in the high-risk areas that cultivate wheat, potato and/or timothy grass were located using the Ministry of the Agriculture and Forestry farm register and field plot register. While many farmers were asked to participate in the study, thirteen finally agreed to become part of this investigation.

Plant crop samples. Plant samples studied here were collected from 15 sampling sites, five of which were situated in wheat fields (sites 5, 7, 8, 10 and 12) five in potato fields (sites 6, 9, 13, 14 and 15) and five in timothy fields (sites 1, 2, 3, 4 and 11). One timothy field (site 4) was sampled for red clover, as well. Sampling was done during between 26.07.-06.09.2005. Sampling time depended on the plant species. Each plant crop was collected at the time of its normal harvest. Thus, the samples of timothy grass from the second cut were taken in mid-summer and the samples of wheat grains and potato tubers later in the summer or in early autumn. A crop sample and its respective soil samples from the plough layer and subsoil were taken on the same day and each of them were collected as four subsamples from the four corners of the 10 x 10 m sampling area. To avoid contamination of crop samples with soil material, the sampling of each site always began by first taking the plant crop sample. A wheat subsample consisted of 150-200 spikes, a potato subsample of 10 tubers and a timothy and red clover subsample of 150-200 g of grass. Wheat spikes, timothy and red clover grass were cut with scissors. Timothy and red clover was cut at least five cm above the soil surface to avoid dead and dirty plant parts. The four subsamples were collected into separate paper bags and transported to the laboratory.

Soil samples from arable land. The soil sampling system was principlely 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 study (Sippola & Tares 1978, Erviö *et al.* 1990, Mäkelä-Kurtto & Sippola 2002). After removing all plant material from the surface of the soil the plough layer was opened with a spade and the depth of the layer was measured. A slight slice from the whole depth was taken at each corner of the sampling area with a spade. The volume of the subsample was about 1.25 litres. A subsample from the subsoil was taken with a spade down to a depth of about 20 cm and the volume of subsoil subsample was 0.75 litres. Each subsample from the soil was collected separately into a colourless plastic bag and transported into the laboratory. 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 fieldbook.

Soil samples from forest land. Forest soil sampling for this study was completed in the summer of 2005. The base line samples from forested areas were collected from areas with the same soil type that the arable soil samples were taken from. These samples were used as comparison material for arable soil samples. Sampling of the forest area podzol was from four different horizons: O=humus, from the organic layer, E=eluvial layer, B=illuvial layer and C=geogenic background from the non-weathered layer. Each about 1 kg sample was placed in a paper bag using a scoop from the wall of the pit excavated with a spade for this study (Figs. 10-11). The depth of the pits was about 70 – 80 cm. At each sample site, two or more photographs were taken after the sampling. The samples were stored in cool boxes and delivered to the laboratory. The number of forested area sampling sites was 11 and at every site four different horizons were sampled, bringing the total number of samples collected and analysed for this study to 44.

Figure 10. Soils sampling from the topsoil. Photo B. Backman.

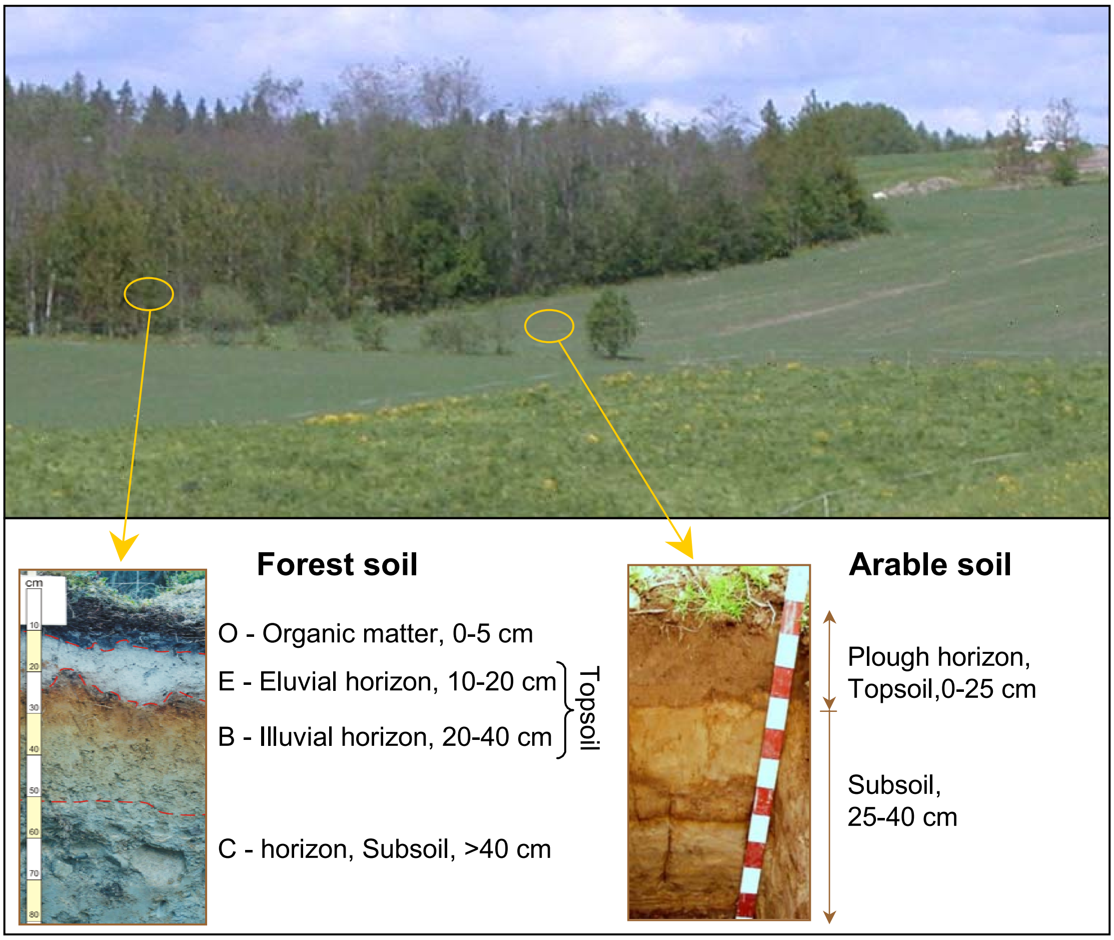


Figure 11. The sampling horizons in forest and arable soil profiles. Photos: M. Eklund, GTK and R. Uusitalo, MTT.

3.4.2 Pre-treatment of samples

Plant crop samples. Subsamples of fresh wheat spikes were dried first at room temperature in the laboratory for a couple of days and then in an oven at 60^{o}C with air circulation. Grains were separated from the chaff using a mini-thresher. Grain subsamples were homogenized. An equal amount (50 g) of each subsample was combined to form one wheat grain sample.

For the subsamples of fresh timothy grass, a botanical analysis was carried out in order to separate other plant species from the timothy. Then the grass subsamples were allowed to dry at room temperature for a couple of days and then in an oven at 60^{o}C with air circulation. An equal amount (50 g) of each subsample was combined to form one timothy grass sample. Similar pre-preparations were made for the red clover as well.

After sampling, potato tubers were stored as subsamples in a refrigerator (+4^{o}C) until pre-treatment. All 10 tubers of each subsample were thoroughly washed with tap water and dried with clean paper. After that, each potato was cleaved into four equal parts. A potato sample that was analysed with peels was composed of 40 quarters of the 40 tubers (10 tubers / subsample) with peels and a potato sample that was analysed without peels was composed of 40 quarters of the tubers after peeling. Next, the samples were dried in an oven at 60^{o}C with air circulation.

All the plant samples were ground in a hammer mill of pure carbon steel to pass a 2-mm sieve. The samples were stored in plastic bags at a room temperature until further analysis.

Soil samples from arable land. In the laboratory, fresh soil subsamples were mixed into one sample that was crushed, homogenized and air-dried at 35^{o}C in an oven with air circulation. 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 soil was homogenized again and stored at the room temperature in cardboard boxes for analyses.

Soil samples from forest land. The forest soil samples were dried in paper bags for about one week in a constant heat at 40°C. If the samples became cemented during the drying period, they were homogenized with light hammering. Then the samples were sieved with a plastic shaker (made of PVC plastic and nylon cloth) to the grain size fraction of <2 mm. For the soil sample used for grain size Sedigraph analysis, the sample was divided into two parts and only the other half of the sample was sieved as desribed. Most of the humus samples were also rehomogenized with a cutting mixer mill (Moulinex) before analysis, except for three samples (Sampling site numbers 1, 2, and 3). All analysis at the GTK's Geolaboratory were done using <2 mm fraction.

3.4.3 Soil and plant analyses

MTT Laboratories. To analyse soluble elements in soil samples, the methods employed were mainly the same as those used in the routine soil testing for cultivated soils in Finland (Agricultural Research Centre 1986, Viljavuuspalvelu 2000). The Finnish soil testing system involves an interpretation of the analytical results for agricultural and environmental purposes (Viljavuuspalvelu 2000). To analyse total concentrations of elements standard methods were used (see Table 33). The methods used for analysing soil samples and the instruments used for measurements are also presented in detail in Table 33. The methods used for analysing plant samples and the instruments used for measurements are presented in detail in Table 34.

To determine the dry matter content of soil or plant material, 5 g of a sample was placed into a quartz dish. The sample was dried at 105°C for 4 h. The dish was allowed to cool in a desiccator for 2 h. The dried residue in the dish was then weighed.

Table 33. Soil analysis methods and instruments used for measurements in this study at MTT Laboratories.

Chemical Parameter	**Analysis Method**	**Equipment, Model**
pH, El. cond.	pH and El. cond. were measured from soil-water suspension (1:2.5) (Agricultural Research Centre 1986, Viljavuuspalvelu 2002).	Beckman 40 pH Meter Radiometer CDM 83, conductivity meter
Volume weight	Volume weight was determined by weighing a 25 ml sample of air dried soil passed through a 2-mm sieve (Agricultural Research Centre 1986, Viljavuuspalvelu 2002).	Mettler PC 4400 Delta Range
Particle size distribution	Particle size distribution was determined by dry and wet sieving and for finer fractions by a pipette method according to Elonen (1971). Soil classification was made according to Aaltonen *et al* (1949).	Fritsch Vibratory Sieve Sheiker Analysette 3
Organic C, humus	Organic C content was determined with an automated dry combusting method (LECO Corporation 1999), assuming that the sample contained only organic carbon. Humus content was obtained by multiplying the organic C content by 1.73. (Agricultural Research Centre 1986)	Leco CN-2000 Carbon/Nitrogen Determinator
Ca, K, Mg, S, P	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 2002). Concentrations of Ca, K, Mg and S were measured by inductively coupled plasma optic emission spectrometer (ICP-OES), P by autoanalyzer using ammonium-molybdate complexation.	Thermo Jarrel Ash, IRIS Advantage High Resolution ICP Optical Emission Spectrometer with a CID detector Bran+Luebbe AutoAnalyzer 3
Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn, As	For the air-dried samples (25 ml), 0.5 M ammonium acetate + 0.5 M acetic acid + 0.02 M Na_2EDTA (pH 4.65, AAAc-EDTA) (1:10, 1h) (Lakanen & Erviö 1971) was used to extract soluble Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn (Agricultural Research Centre 1986, Viljavuuspalvelu 2002). Concentrations of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn were measured by inductively coupled plasma optic emission spectrometer (ICP-OES) and As with graphite furnace atomic absorption spectrometer (GFAAS).	Thermo Jarrel Ash, IRIS advantage High Resolution ICP Optical Emission Spectrometer with a CID detector Varian AA280 Zeeman, GTA 120 graphite tube atomizer, PSD 120 autosampler
Al, Cr, Cu, Fe, Mn, Ni, P, V, Zn, As, Cd, Pb, Se	For the air-dried samples (<1.0 g), *aqua regia* extraction (concentrated HCl and concentrated HNO_3 in a volume ratio 3:1) according to the international standard (ISO 11 644:1995) was used to determine total Al, Cr, Cu, Fe, Mn, Ni, P, V, Zn, As, Cd, Pb, Se. Concentrations of Al, Cr, Cu, Fe, Mn, Ni, P, V, Zn were measured by inductively coupled plasma optic emission spectrometer (ICP-OES) and As, Cd and Pb with graphite furnace atomic absorption spectrometer (GFAAS) and Se with hydride generation atomic absorption spectrometry (HGAAS).	Thermo Jarrel Ash, IRIS advantage High Resolution ICP Optical Emission Spectrometer with a CID detector Varian AA280 Zeeman, GTA 120 graphite tube atomizer, PSD 120 autosampler (As, Cd, Pb) Varian SpectrAA 300Plus, VGA-76 vapour generation accessory (Se)
S	An air-dried sample (<1.0 g) was heated (120 °C) in 7 M HNO_3 under pressure in a microwave oven according to standard SFS 3044:1980 in order to determine total S. A concentration of S was measured by inductively coupled plasma optic emission spectrometer (ICP-OES).	Mars 5 microwave oven, CEM Thermo Jarrel Ash, IRIS advantage High Resolution ICP Optical Emission Spectrometer with a CID detector

Table 34. Plant analysis methods and instruments used for measurements in this study at MTT Laboratories.

Chemical Parameter	**Analysis Method**	**Equipment, Model**
Cu, Mn, P, S, Zn, As, Cd, Ni, Pb, V	A wet digestion method, using concentrated nitric acid, was used to get P, S, Cu, Mn, Zn, As, Cd, Ni, Pb and V in solution (Luh Huang & Schulte 1985). A 0.5 g sample of plant was taken for digestion with 5 ml concentrated nitric acid. After standing overnight at 50°C the sample was gradually heated to 120°C until 2-3 ml acid remained. When cooled the sample was diluted to 50 ml and filtered. Concentrations of P, S, Cu, Mn and Zn were measured by inductively coupled plasma optic emission spectrometer (ICP-OES) and As, Cd, Ni, Pb, V by inductively coupled plasma mass spectrometer (ICP-MS).	Thermo Jarrel Ash, IRIS advantage High Resolution ICP Optical Emission Spectrometer with a CID detector Perkin Elmer PE-SCIEX ICP-MS system, ELAN 6000
Al, Fe, Cr	For the determination of Al, Fe and Cr, the plant sample (0.5 g) was digested in a mixture of 10 ml 7 M HCl-HNO_3 and 2.5 ml 12 M HCl in a closed vessels by a microwave system 37 min, 180^{o}C, maximum pressure in the vessel 25 Bar). The digestate was diluted into 50 ml. Concentrations of Al, Fe were measured by inductively coupled plasma optic emission spectrometer (ICP-OES) and Cr with graphite furnace atomic absorption spectrometer (GFAAS)	Mars 5 microwave oven, CEM Thermo Jarrel Ash, IRIS advantage High Resolution ICP Optical Emission Spectrometer with a CID detector Varian AA280 Zeeman, GTA 120 graphite tube atomizer, PSD 120 autosampler
Se	Wet digestion in a mixture of $HClO_4$-H_2SO_4-HNO_3 , reduction of Se(VI) to Se (IV) with HCl, chelation with APDC and extraxtion into MIBK. Concentrations of Se were measured with grafite furnace atomic absorption spectrometry (GFAAS)	Varian SpectrAA-400Z, GTA 96 graphite tube atomizer

Table 35. Detection limits (DL) of the RAMAS samples analysed at MTT Laboratories.

Element	**AR extraction ICP-OES or GFAAS DL mg kg^{-1}**	**HNO_3 or HCl-HNO_3 digestion ICP-OES/MS DL mg kg^{-1}**	**AAAc extraction ICP-OES DL mg l^{-1}**	**AAAc-EDTA extraction ICP-OES or GFAAS DL mg l^{-1}**	**HNO_3-H_2SO_4-$HClO_4$ digestion, extract into MIBK (Se from plants)**
Ca			60.0		
K			11.0		
Mg			7.0		
P	6.0	10.0	0.8 (P Autoanalyser)		
S**	7.0	17.0	6.0		
Al	17.0	1.0		6.0	
As	0.2 (GFAAS)	0.002 (ICP-MS)		0.04 (GFAAS)	
Cd*	0.04 (GFAAS)	0.001 (ICP-MS)		0.1	
Cr	0.2	0.003 (GFAAS)		0.1	
Cu*	2.0	1.0		0.3	
Fe	3.0	2.0		4.0	
Mn	0.2	0.1		0.1	
Ni	0.6	0.02 (ICP-MS)		0.2	
Pb*	1.3 (GFAAS)	0.02 (ICP-MS)		0.3	
Se***	0.06 (HGAAS)				0.010 (GFAAS)
V	3.0	0.004 (ICP-MS)		0.1	
Zn*	10.0	0.3		0.3	

* method accredited for soil analyses, AR extraction *** method accredited for plant analyses

** Total S in soils, method SFS 3044:1980

GTK Geolaboratory. Humus samples were extracted with concentrated nitric acid (HNO_3) according to EPA 3051 method and other mineral soil samples from different depths were extracted with *aqua regia* (method is based on standard ISO 11466). These extractions were used for the evaluation of the near total concentrations of cations in RAMAS soil samples. All forest soil samples were also extracted with AAAc-EDTA solution to evaluate the maximum cation concentrations available for plants.

0.3 g of weighted humus samples were extracted with 10 ml of concentrated HNO_3 in pressurized vials in microwave oven (CEM, Mars5) at 175°C. The samples were diluted into 50 ml after the cooling time and stored in acid washed plastic centrifuge tubes before the analyses.

2 g of weighted mineral soil samples were extracted with 12 ml of *aqua regia* (AR) solution (3 ml HNO_3 + 9 ml HCl) in glass tubes overnight. Next day the samples were tempered in heating unit at 90°C for one hour, cooled and diluted into 60 ml.

3 g of weighted forest soil samples were extracted with 30 ml of AAAc-EDTA solution (0.5 M CH_3COONH_4, 0.5 M CH_3COOH, 0.02 M Na_2EDTA, at pH 4.8) in plastic tubes and left for two hours on a plane shaker. Centrifugation and dilution 1:20 was done before analysis by ICP-AES technique.

The grain size distributions of forest soil samples were determined by Sedigraph analyses in GTK's Geolaboratory and humus contents were determined by spctrophotometric method or burning method, from the same samples. All cations were analysed by Thermo Jarrell Ash ICP-AES plasma emission spectrometer (TJA, Iris Advantage (Duo)) and HNO_3 extracted humus samples also by Perkin Elmer ICP-MS mass spectrometer (PE, ELAN 6000) technique at the Geolaboratory, GTK in Espoo. Arsenic was analysed by GFAAS graphite furnace atomic absorption spectrometer (PE, SIMAA6000) technique of the AR extracted solutions at the Geolaboratory, GTK in Kuopio. The detection limits of the multielemental analyses are presented in Table 36. Uncertainties (%) of the laboratory analyses are discussed later in section 3.4.4.Quality control.

Table 36. Detection limits (DL, mg kg^{-1}) of the RAMAS's forest soil samples analysed at the GTK Geolaboratory, Espoo.

Element	AAAc-EDTA extraction	AR extraction	HNO_3 extraction
Al	0.4	15.0	5.0
As	3.0	10.0 (0.1 GFAAS)	0.05
Ca	3.0	50.0	20.0
Cd	0.1	0.5	0.01
Cr	0.3	1.0	0.5
Cu	3.0	1.0	0.3
Fe	2.0	50.0	5.0
K	15.0	50.0	10.0
Mg	1.0	15.0	5.0
Mn	0.05	1.0	0.2
Ni	0.1	2.0	0.3
P	2.0	50.0	30.0
Pb	2.0	5.0	0.05
S	20.0	50.0	10.0
V	0.7	1.0	0.1
Zn	0.8	3.0	1.0

3.4.4 Quality control

MTT Laboratories and GTK's Geolaboratory are accredited testing laboratories (T024 and T025). The quality systems follow the requirements of the standard SFS-EN ISO/IEC 17025:2005. Uncertainties (%) have been evaluated for every accredited analyzing method. However, not all the methods used in this study were accredited. Detailed information on the quality of the analytical methods is described in ANNEX 1.

3.4.5 Data processing

Original arable soil and crop data were stored in Excel files in the MTT network prime where backups are driven regularly. For statistical and graphical processing, Excel 2002 SP3 software was used. If the numbers were below the detection limit, the original results were used in calculations.

All geochemical data produced at the GTK was stored in the Excel database. The statistical and graphical processing of the data was performed using SPPS 14 and Excel 2000 software. Corel Draw 12 software was used for the final editing of all graphs. The geological and geochemical data based on maps used in this study were prepared using ArcGIS 9.1 software. In this study, numbers below the analytical detection limit for a given element or compound have been processed statistically as the numerical value of the analytical detection limit.

3.5 Results and discussion

3.5.1 Arable soils

3.5.1.1 Soil types and general soil characteristics

Particle size distributions and soil types of the fields studied in the Pirkanmaa region are presented in ANNEX 2. Soil type of the plough layer of all the fields studied was classified into mineral soils: silty soils or clay soils with medium humus content (3-6%). The pH-level of the soils (Table 37) were mostly at a target level (fertility class: satisfactory) according to the national soil test interpretation (Viljavuuspalvelu 2000). When particle size distributions were compared between the soil layers by sites (ANNEX 2), it was found that the biggest difference came out in the clay fraction (particle size <0.002 mm). The mean difference was 4%, on average. Clay content in the subsoil was often higher than in the surface soil. Differences between the soil layers were also observed by Kurki (1972). The plough layer (Table 37) contained more humus and was more acidic than the subsoil underneath (Table 38). General soil characteristics of the plough layer of the arable soils studied in the Pirkanmaa region were typical for the mineral soils in plant cultivation zones II and III (Mäkelä-Kurtto *et al.* 2006). There were no marked differences in the soil types or general soil characteristics between wheat, potato and timothy fields.

Table 37. General soil characteristics of the plough layer in 15 fields studied in the Pirkanmaa region.

Parameter	**Unit**	**Minimum**	**Median**	**Mean**	**Maximum**
Bulk dens.	kg l^{-1}	0.94	0.99	1.02	1.21
Org. C, %	% dw	1.43	2.50	2.49	4.16
Humus, %	% dw	2.45	4.30	4.29	7.15
pH (H_2O)		5.73	6.30	6.38	7.33
El. cond.	10^{-4} S cm^{-1}	0.58	0.84	0.90	1.34
Clay content	%	5.0	24.6	24.9	50.8

Table 38. General soil characteristics of the subsoil in 15 fields studied in the Pirkanmaa region.

Parameter	**Unit**	**Minimum**	**Median**	**Mean**	**Maximum**
Bulk dens.	kg l^{-1}	0.99	1.08	1.11	1.34
Org. C, %	% dw	0.22	0.46	0.70	2.15
Humus, %	% dw	0.38	0.80	1.20	3.69
pH (H_2O)		5.79	6.44	6.34	7.07
El. cond.	10^{-4} S cm^{-1}	0.32	0.46	0.55	1.01
Clay content	%	1.8	34.1	29.0	54.9

3.5.1.2 Total concentrations of arsenic and other elements

Aqua regia extractable contents of Cd, Cr, Cu, Ni, Pb, V and Zn in the plough layer of the 15 fields studied in the Pirkanmaa region are presented in Table 39 and were normal for the respective soil types in the plant cultivation zones of II and III. Arsenic contents in cultivated soils in the Pirkanmaa region in 2005 were at the same level or even at a lower level than those observed in the cultivated soils in the Pirkanmaa region in 1998 (Table 32), south-western Finland in 2004 (Table 10), Ostrobothnia in 2004 (Table 12), the Mikkeli / South Savo region in 2000 (Table 14) or in other national soil material in 1998 (Tables 8 and 9). All the As concentrations measured from the fields in the Pirkanmaa region were lower than the target value for "Clean Soil" proposed by Finnish researchers (Mäntylahti & Laakso 2002) or the limits values for arable soils in Canada (2003).

There were some differences in the *aqua regia* extractable macro- and micro-element contents between the two soil layers studied. Contents of P and S were higher in the plough layer than in the subsoil, the former mainly due to fertilization and the latter due to fertilization and atmospheric deposition. Also more As, Cd, Pb and Zn occurred in the plough layer than in the layer beneath, obviously for anthropogenic reasons. Instead, Al, Fe, Cu, Cr, Ni and V were more abundant in the subsoil than in the plough layer partly because of the abundance of clay in the subsoil. Differences between the soil layers were not very big, especially in the case of arsenic. The arsenic inputs from the human activities to the cultivated soils may not have been very prominent. Also, the mass balance calculations (Tables 30 and 31) indicated that arsenic accumulation has obviously occurred, but currently arsenic inputs and outputs are rather well balanced.

In the RAMAS soil material, correlations between arsenic and other soil parameters in the plough layer were calculated (ANNEX 3, Table 1). Also, correlations of arsenic and other soil parameters were estimated to the respective factors in the subsoil (ANNEX 3, Table 2). In general, correlations were low. The highest correlations of the soil *aqua regia* extractable arsenic occurred in the humus content (0.64) and pH-level (0.39).

Table 39. Contents of *aqua regia* extractable (ISO 11 466) macro- and microelements in the plough layer of arable soils (n = 15) studied in the Pirkanmaa region.

Element	Unit	Minimum	Median	Mean	Maximum
P	g kg^{-1} dw	0.67	0.94	0.97	1.54
S	g kg^{-1} dw	0.16	0.27	0.26	0.33
Al	g kg^{-1} dw	15.1	22.0	23.8	34.5
Fe	g kg^{-1} dw	23.1	30.3	33.0	47.4
As	**mg kg^{-1} dw**	**2.90**	**3.90**	**4.06**	**6.80**
Cd	mg kg^{-1} dw	0.13	0.20	0.21	0.35
Cu	mg kg^{-1} dw	15.3	21.2	22.7	35.5
Cr	mg kg^{-1} dw	26.9	45.5	48.1	73.5
Mn	mg kg^{-1} dw	458	946	981	1432
Ni	mg kg^{-1} dw	9.21	19.7	20.6	34.4
Pb	mg kg^{-1} dw	8.43	12.0	12.5	17.2
V	mg kg^{-1} dw	47.9	60.3	64.4	94.5
Zn	mg kg^{-1} dw	71.5	103	107	152
Se	mg kg^{-1} dw	0.14	0.20	0.20	0.32

Table 40. Contents of *aqua regia* extractable (ISO 11 466) macro- and microelements in the subsoil layer of arable soils (n = 15) studied in the Pirkanmaa region.

Element	Unit	Minimum	Median	Mean	Maximum
P	g kg^{-1} dw	0.49	0.61	0.61	0.77
S	g kg^{-1} dw	0.04	0.09	0.10	0.24
Al	g kg^{-1} dw	14.9	29.1	26.4	37.8
Fe	g kg^{-1} dw	22.7	41.7	37.5	53.2
As	**mg kg^{-1} dw**	**2.84**	**3.48**	**3.72**	**4.82**
Cd	mg kg^{-1} dw	0.04	0.12	0.12	0.18
Cu	mg kg^{-1} dw	11.2	25.9	24.0	38.6
Cr	mg kg^{-1} dw	27.4	62.0	55.9	81.2
Mn	mg kg^{-1} dw	309	1000	903	1260
Ni	mg kg^{-1} dw	10.1	24.8	23.7	38.4
Pb	mg kg^{-1} dw	4.91	11.2	11.3	17.0
V	mg kg^{-1} dw	43.6	64.9	66.1	101
Zn	mg kg^{-1} dw	55.8	90.5	91.5	138
Se	mg kg^{-1} dw	0.07	0.16	0,16	0.35

3.5.1.3 Soluble concentrations of arsenic and other elements

Concentrations of AAAc extractable macro-elements and AAAc-EDTA extractable microelements in the plough layer of arable soils studied in the Pirkanmaa region are presented in Table 41. Concentrations of both macro- and micro-elements were close to the respective figures of the national soil material in 1998 (Table 32). As to the fertility status of the cultivated fields investigated, pH, P, K, S, Mg and Mn were mostly at or above the target class (satisfactory), while Ca, Cu and Zn were at or under the target class (Table 42). Fertility of the plough layer of the arable soils studied in the Pirkanmaa region was typical for the mineral soils in plant cultivation zones II and III (Mäkelä-Kurtto *et al.* 2006). There were no marked differences in the soil fertility between wheat, potato and timothy fields.

Table 41. Concentrations of AAAc- and AAAc-EDTA –extractable macro- and micro-elements in plough layer of arable soils (n = 15) studied in the Pirkanmaa region.

Extraction solution	**Minimum**	**Median**	**Mean**	**Maximum**
Element	**mg kg^{-1} dw**	**mg kg^{-1} dw**	**mg kg^{-1} dw**	**mg kg^{-1} dw**
AAAc				
Ca	799	1394	1720	3828
K	58.0	153	164	349
Mg	62.0	266	252	455
P	4.1	13.0	20.0	97.0
S	6.7	10.0	13.0	35.0
AAAc-EDTA				
Al	189	297	286	420
Fe	142	385	368	642
Mn	44	124	135	231
As	**0.003**	**0.039**	**0.047**	**0.094**
Cd	0.051	0.073	0.082	0.139
Cr	0.08	0.15	0.15	0.24
Cu	1.6	3.4	3.8	7.7
Ni	0.42	0.67	0.74	1.64
Pb	1.2	2.0	2.0	2.8
V	0.3	1.1	1.1	2.0
Zn	0.9	1.8	2.1	4.9

Table 42. Fertility status of fields (n = 15) studied in the Pirkanmaa region. Interpretation and classification of soil testing results according to Viljavuuspalvelu (2000)*. Target class 4 (satisfactory).

Site No.	**Fertility class**								
	pH	**P**	**K**	**Ca**	**Mg**	**S**	**Cu**	**Mn**	**Zn**
1	5	3	3	4	5	4	2	5	2
2	3	2	4	3	4	3	3	5	3
3	4	2	2	3	5	4	2	5	4
4	4	3	2	2	4	3	3	4	1
5	2	2	3	2	4	4	2	4	2
6	4	4	4	3	2	5	4	4	3
7	5	5	5	3	4	4	3	4	4
8	4	4	4	3	3	4	3	4	2
9	3	4	4	3	3	5	4	4	4
10	6	5	5	5	4	3	3	4	4
11	5	4	3	4	5	4	3	4	4
12	5	4	4	4	5	3	3	4	3
13	7	7	6	6	6	4	4	4	4
14	6	6	3	6	5	3	4	4	4
15	4	2	2	3	4	3	2	4	1
Median	4	4	4	3	4	4	3	4	3
Mean	4.5	3.8	3.6	3.6	4.2	3.7	3.0	4.2	3.0
Minimum	2	2	2	2	2	3	2	4	1
Maximum	7	7	6	6	6	5	4	5	4

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

According to the results presented in Table 43, arsenic seems to be rather insoluble in slightly acidic arable soils studied in the Pirkanmaa region because only about 1% of total (*aqua regia* extractable) arsenic was extractable in AAAc-EDTA extraction solution. This finding coincides with Fig. 12 (Mäkelä-Kurtto 1994). The most soluble micro-element was Cd and about 40% of total Cd could be extracted with AAAc-EDTA. About 15% of soil Mn, Cu and Pb was, on average, soluble. Only some percentages of the other micro-elements and macro-elements occurred as a soluble form in the arable soils studied.

Table 43. Percentages (%) of AAAc and AAAc-EDTA extractable concentrations of macro- and micro-elements from respective *aqua regia* extractable contents in plough layer of arable soils (n = 15) studied in the Pirkanmaa region.

Extraction solution	**Minimum**	**Median**	**Mean**	**Maximum**
Element	%	%	%	%
AAAc				
P	0.5	1.3	1.9	8.7
S	2.6	4.0	5.3	16.0
AAAc-EDTA				
Al	0.7	1.2	1.3	2.8
Fe	0.6	1.1	1.1	1.8
Mn	5.4	15.0	14	20.0
As	**0.1**	**1.0**	**1.2**	**3.1**
Cd	30.0	38.0	39.0	47.0
Cr	0.2	0.3	0.3	0.4
Cu	7.4	16.0	17.0	33.0
Ni	1.8	3.4	3.7	5.7
Pb	12.0	16.0	16.0	23.0
V	0.6	1.5	1.7	2.8
Zn	0.9	1.7	2.0	4.5

Solubility of many trace elements in the soil and availability to plants depends on the soil pH to some extent (Fig. 12). According to a literature review made by Mäkelä-Kurtto (1994), solubility of arsenic in the soil and availability to plants gradually increases under pH 5 and above pH 6 (Fig. 12). In addition to this, arsenic mobility in the soil may be increased by phosphate fertilization, as a result of the competitive behavior of phosphorus and arsenic with respect to binding on soil constituents (Polemio & Bufo 1984).

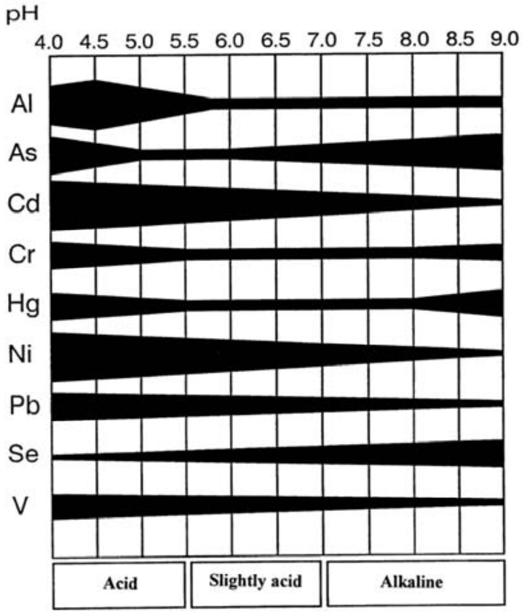


Figure 12. Solubility of some trace elements and availability to plants at different pH levels (Mäkelä-Kurtto 1994).

Table 44. Arsenic concentrations of cultivated soils and crops by sampling sites and by geological subdivisions (TB = Tampere Belt; PB = Pirkanmaa Belt).

Sampling site Nr	**Plant cultivation zone**	**Geological subdivision**	***Aqua regia*** **As mg kg^{-1}dw Subsoil**	***Aqua regia*** **As mg kg^{-1} dw Plough layer**	**AAAc-EDTA As mg kg^{-1} dw Plough layer**	**As mg kg^{-1} dw**				
						Wheat grains	**Potato tubers**	**Potato peeled**	**Timothy grass**	**Red clover**
1	III	TB	4.07	3.50	0.07				0.016	
2	III	TB	4.04	4.45	0.09				0.014	
3	III	TB	3.92	4.48	0.09				0.012	
4	III	TB	3.43	2.97	0.09				0.018	0.01
7	III	TB	3.08	3.36	0.03	0.005				
6	III	TB	3.09	3.31	0.06		0.008	0.002		
8	II	TB	4.31	4.42	0.01	0.005				
9	II	TB	3.44	3.87	0.003		0.008	0.004		
10	II	TB	3.48	3.09	0.02	0.005				
11	III	TB	3.38	3.90	0.09				0.011	
12	II	TB	3.26	4.77	0.04	0.005				
15	III	TB	2.84	3.94	0.004		0.006	0.003		
		Mean, TB	**3.53**	**3.84**	**0.05**	**0.005**	**0.007**	**0.003**	**0.014**	**0.01**
		Std.	0.42	0.63	0.035	0.00	0.00	0.001	0.003	
5	III	PB	4.82	2.90	0.02	0.004				
13	II	PB	4.54	6.80	0.07		0.011	0.006		
14	II	PB	4.10	5.20	0.02		0.009	0.004		
		Mean, PB	**4.49**	**4.97**	**0.037**	**0.004**	**0.010**	**0.005**		
		Std.	0.37	1.96	0.029		0.001	0.001		
		Mean, all	**3.72**	**4.06**	**0.047**	**0.005**	**0.008**	**0.004**	**0.014**	**0.01**
		Std.	0.58	1.03	0.034	0.00	0.002	0.001	0.003	

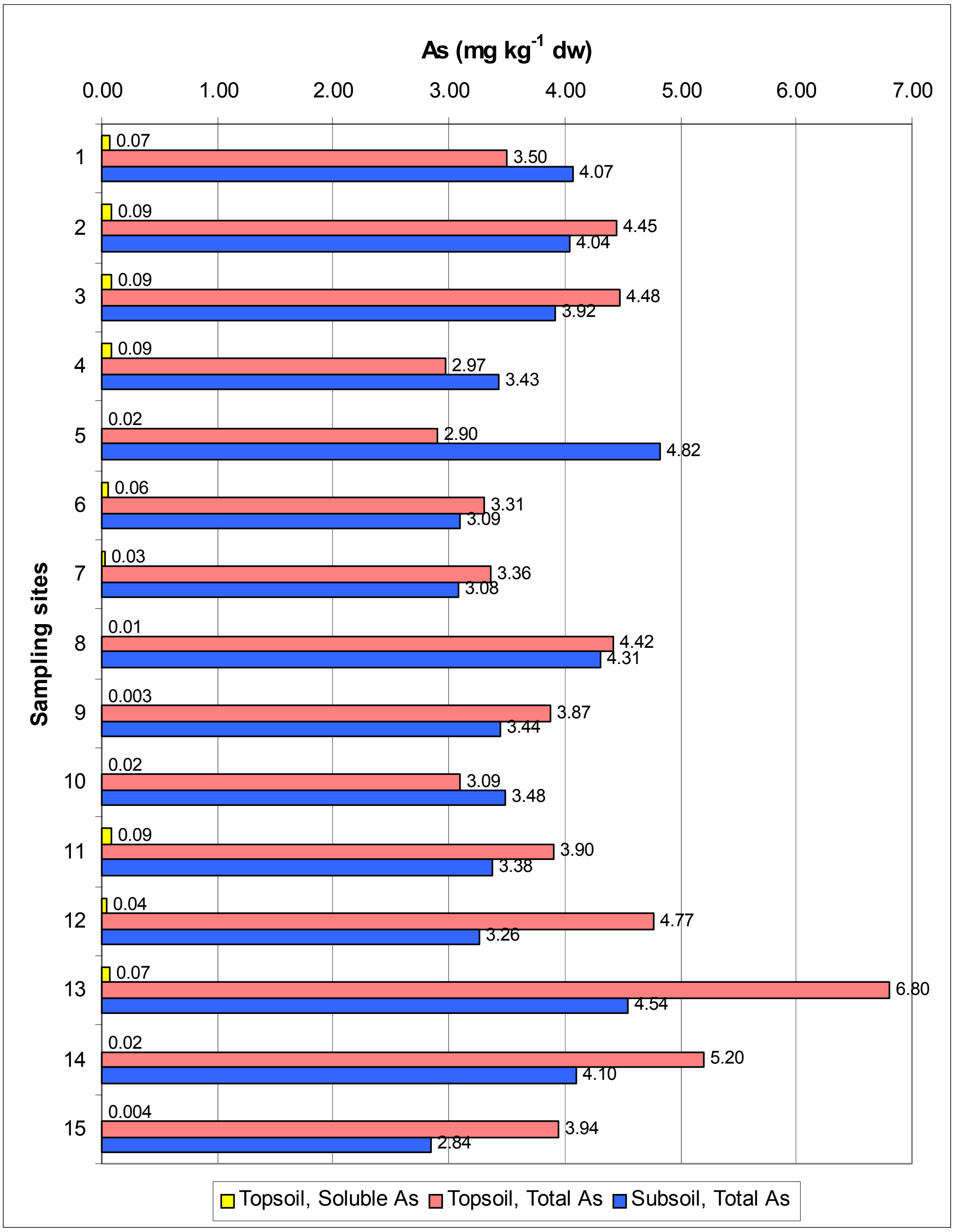


Figure 13. Concentrations of soluble (AAAc-EDTA extractable) and total (*aqua regia* extractable) arsenic in topsoils and total (*aqua regia* extractable) arsenic in subsoils of arable land by sampling sites (1-15).

3.5.2 Forest soils

3.5.2.1 Soil types and general characteristics of forest soils

The forest soils data consist of 11 soil profiles, nine of which were from clay and two from fine sand areas. Each profile was composed of four different sampling levels so that the whole dataset consists of 11 humus samples, 27 clay samples, and six fine sand samples. Podzol is the type of forest soils in this area and is characterized by a poorly decomposed organic layer (O or humus) on top, a light eluvial layer (E-horizon), brown illuvial layer (B-horizon) that is enriched in amorphous Fe, Al, Si and organic matter leached from the E-horizon and an underlying yellowish-grey or greenish-grey geogenic subsoil (C-horizon) (Fig. 11). The humus layer is the most significant sink for trace elements in contaminated soils (Salminen *et al*. 2005). The sampling depths were approximately 0 to 5 cm in humus, 5 to 20 cm in the eluvial layer, 10 to 40 cm in the illuvial layer and 50 to 80 cm in the subsoil layer (C-horizon). The depths of the sampling pits vary depending on the thickness of the podzolic layers at the particular sampling site. The organic matter (OM) and clay contents in soil samples were determined in the GTK Geolaboratory and the methods are described in chapter 3.4.3.

In general, the soil types in the forest soil profiles in Pirkanmaa are humus, clay and fine sand. The highest contents of OM are found in the humus layer, ranging from 18.1 to 63.5% with a median of 41.2% (Tables 45 and 46). The OM contents are about 9 to 17 times lower in the mineral soil samples than in the humus layer. The median OM contents in clays and fine sands are 4.6 and 2.3%. The percentage of clay content (the grain size < 0.002 mm) in the clay soil samples were as high as expected, varying from near 37 to 77% and in the fine sand samples, from 2.5 to 17%.

Table 45. The amount of organic matter (%) dw in the soil samples.

Soil type	Unit	Minimum	Median	Mean	Maximum	N_valid
Humus	%	18.1	39.5	41.2	63.5	11
Clay	%	1.35	4.60	6.20	16.4	27
Fine sand	%	7.90	2.30	2.90	7.90	6

Table 46. The clay content < 0.002 mm (%) of the soil samples.

Soil type	Unit	Minimum	Median	Mean	Maximum	N_valid
Clay	%	36.8	58.0	57.7	77.0	27
Fine sand	%	2.50	8.90	9.20	17.2	6

3.5.2.2 Total concentration of arsenic and other elements

Humus: The total elemental concentrations in humus samples were analysed using the ICP-method from samples extracted with nitric acid (HNO_3). The method is described in chapter 3.4.3. The analyses are presented in Table 44. The arsenic contents in the humus layers varied from 2.17 - 8.58 mg kg^{-1} with a median value of 4.67 mg kg^{-1} (n=11). This value is higher and the range was narrower than observed in south and central Finland where the arsenic contents in the humus layer varies from 0.52 to 17.8 mg kg^{-1} and median is 1.56 mg kg^{-1} (n=163) (Salminen *et al*. 2004).

The concentrations of other elements in humus were also elevated in comparison to south and central Finland (Table 47). For example, the median values of data from Salminen *et al*. (2004) for Ca, K and Mg were 3 170, 1 040 and 571 mg kg^{-1}, respectively. Also, Cu and Cr medians were low, 9.29 and 4.16 mg kg^{-1}, respectively. Only S, Pb and Cd medians were lower in the recent data than those in south and central Finland. This trend was also observed in the study of annual atmospheric deposition of heavy metals in moss samples in northern Europe (Rühling *et al*. 1992). The Pirkanmaa region has a long industrial history, and five mines have been in operation in the central and southern part of the Pirkanmaa region during the late 1900's (Ylöjärvi: Cu-W, Vammala: Ni-Cu, Kylmäkoski: Ni-Cu, Haveri: Au-Cu, Orivesi: Au, Backman et al. 2006). The dust and other emissions related to mining activities are known to influence the surrounding areas and the effects are readily seen in the elevated concentrations in the humus layer. In addition, the Harjavalta smelter in Pori, approximately 60 - 80 km southwest of the sampling sites, is one of the greatest sources of atmospheric deposited heavy metals in the region. Spatial distribution of air pollutant emissions is presented by EMEP squares provided by the UNECE (Finnish Environment Institute 2004). According to this data, the arsenic emissions in 2004 were as follows: in Tampere 10,1-25,9 kg a^{-1}, in Valkeakoski 3.0-10,1 kg a^{-1} and in the other areas in the Pirkanmaa region 0.01-3.0 kg a^{-1}

The contents of arsenic and other elements in humus and soil profiles of all eleven sample sites are presented in Fig. 16 and Fig. 17. The majority of those elements show similar distribution patterns between the sampling site locations and their variable elemental contents and the total contents are more or less in the same range as the below mineral soil samples. For example, high total concentrations of As, Al, Cr, Cu, Fe, Mn, Ni, V and Zn were found mainly in sampling sites 14 and 13 in the Lempäälä area, while the lower concentrations of those elements were measured in sampling sites 4, 6 and 9 in Ylöjärvi and Hämeenkyrö areas. Total concentrations of S, P, and Pb in humus at all sampling sites show, however, higher values than the underlying mineral soils. Moreover, the highest total concentrations were in sampling sites 4, 6, 9 and 12, in Ylöjärvi and Hämeenkyrö areas. The humus layer strongly illustrated the anthropogenic input of S, P, and Pb in the forest area, especially in sampling sites 4, 6, 9 and 12, which have higher anthropogenic contamination levels than the other sampling sites.

Table 47. Concentrations of HNO_3 - extractable elements (mg kg^{-1}) in humus (O horizon) layer in forest soil samples. Number of samples was 11. Median values of 163 samples in study of Salminen *et al.* (2005) as comparison.

Parameter	**Unit**	**Mean**	**Median**	**Minimum**	**Maximum**	**Salminen *et al.* 2004**
Ca	mg kg^{-1}	6 187	5 590	4 080	10 800	3 170
K	mg kg^{-1}	2 435	1 920	923	4 440	1 040
Mg	mg kg^{-1}	4 954	4 550	1 120	9 030	571
P	mg kg^{-1}	1 061	1 090	754	1 350	818
S	mg kg^{-1}	1 133	1 050	667	1 710	1 380
Al	mg kg^{-1}	15 291	14 700	2 970	30 100	2 230
Fe	mg kg^{-1}	22 046	20 500	5 700	40 600	2 560
Mn	mg kg^{-1}	864	882	373	1 230	268
As	**mg kg^{-1}**	**4.84**	**4.67**	**2.17**	**8.58**	**1.56**
Cd	mg kg^{-1}	0.39	0.35	0.11	1.03	0.36
Cr	mg kg^{-1}	38.1	35.7	7.82	73.1	4.16
Cu	mg kg^{-1}	21.8	19.8	13.5	41.2	9.29
Ni	mg kg^{-1}	20.9	17.5	7.72	38.0	5.04
Pb	mg kg^{-1}	32.7	24.3	19.5	68.0	34.0
V	mg kg^{-1}	49.8	51.2	15.8	84.6	7.99
Zn	mg kg^{-1}	115	95.2	46.4	255	48.4

Correlation analysis of arsenic and other elements of humus samples from the forest soil were carried out using cross plots and the Pearson correlation method from SPSS statistical software. Correlation coefficients ranged in value from –1 (a perfect negative relationship) to +1 (a perfect positive relationship). The probability (p) was also calculated for each correlation coefficient. When p is less than 0.05, the relationship between the two variables is significant at the 95% confidence level. The most significant correlation result with p-value <0.05 was marked with a star (*) and a significant linear correlation is counted at the correlation coefficient >±0.7. Correlation coefficients of As and other elements from the HNO_3-extractable elements of the humus samples are shown in Table 48.

Table 48. Pearson correlation of arsenic and other elements of humus samples from the forest soils (HNO_3 extract).

Humus (N=11)

Elements	As	Al	Cr	Cu	Fe	Mn	Ni	P	Pb	S	V	Zn
As	**1**											
Al	**0.41**	1										
Cr	**0.541**	.940*	1									
Cu	**0.368**	.740*	.739*	1								
Fe	**0.565**	.900*	.973*	.723*	1							
Mn	**-0.08**	0.24	0.36	0.04	0.35	1						
Ni	**0.39**	.953*	.963*	.810*	.926*	0.37	1					
P	**-0.39**	-0.07	-0.22	0.08	-0.19	-0.02	-0.07	1				
Pb	**-0.21**	-.733*	-.660*	-0.27	-.633*	-0.22	-.639*	0.48	1			
S	**-0.46**	-.703*	-.758*	-0.32	-.692*	-0.17	-.648*	0.54	.631*	1		
V	**0.563**	.926*	.987*	.654*	.942*	0.37	.934*	-0.24	-.653*	-.820*	1	
Zn	**0.499**	0.09	0.26	0.02	0.38	0.02	0.08	0.03	0.04	-0.07	0.26	1
OM	**-0.971***	-0.52	-.604*	-0.08	-0.55	-0.07	-0.42	0.49	0.5	.819*	-.691*	-0.45

Arsenic has a high negative correlation coefficient to the amount of organic material in the samples (correl. coeff. = -0.971, also Fig. 14). This indicates that the major load of arsenic is bound to minerogenic material. Samples with low organic material content are mainly composed of mineral material. This implies that despite documented arsenic emissions (UNECE), most of the arsenic in the humus layer is not airborne but of local geogenic origin. Arsenic has a high positive correlation, though not significant, with Cr, Fe, and V.

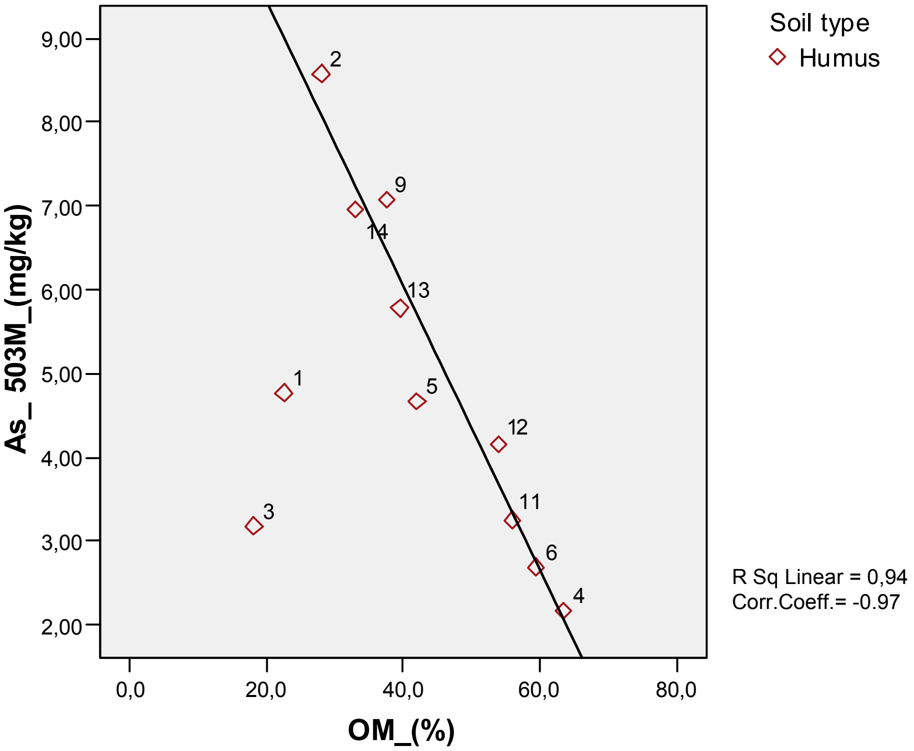


Figure. 14. Correlation of arsenic and organic material contents in humus layer of the forest soil samples. As_503M= HNO_3 leach, OM= organic matter.

Mineral soil samples: The total element contents of mineral soil samples were determined by ICP-method from *aqua regia* extracted samples. The method is described in chapter 3.4.3. The data was classified based on the soil type (clay and fine sand) and the sampling layers. There was no marked variability of total concentration in all elements between the eluvial and illuvian layers. For correlation purposes, the data from the eluvial and illuvian layers (E and B horizons) was combined. This approach also facilitates the correlation between the forest soils and the arable soils, since the combined E+B horizons correspond approximately to the plough layer in arable soils while the subsoils are comparable to each other. (See also Fig. 11. in chapter 3.4.1). The statistical analysis results are presented in Tables 49-52.

The total concentrations of As and other elements in the mineral soils samples are assumed to have a less altered level in the eluvial and illuvial layers and still represent the geologic background level in the subsoil layer. Concentrations of *aqua regia* extracted arsenic were higher in deeper samples taken from the subsoil layer (c horizon) than those taken from upper layers from eluvial and illuvial layers (E and B horizons). The average arsenic contents were higher in clay soil samples than in fine sand soil samples.

The arsenic contents in the soil profile of all eleven sample sites are presented in Fig. 15. In general, the arsenic content increases with depth. However, the arsenic concentrations in eluvial and illuvial layers were rather constant with the maximum arsenic contents less than 5 mg/kg, while a strong increase is observed in the subsoil (C horizon). This pattern suggests that despite of some geochemical reworking, the arsenic levels in eluvial and illuvial layers still reflect the baseline values typical for the area. However, two samples taken from sites 14 and 2 show different trends. The clay content seems to be one of the main factors for the diverse trends, as it is higher than the average. For example, the clay content in sampling site 2 was 58-59% and in sampling site 14 it was 64 - 75.5% (Table 46). Samples taken from fine sand areas contained low arsenic concentrations (less than 5 mg kg^{-1}) for all layers.

The median concentration of arsenic for both soil types in C-horizon is 4.9 mg kg^{-1}. Some comparisons with the nationwide survey (Koljonen *et al.* 1992) can be done despite the difference in the fraction analysed (<0.06 mm fraction was used in Koljonen *et al.* 1992). According to Tarvainen (1995), concentrations of elements are commonly greater in the <0.06 mm than the <2.0 mm fraction. The reported As content of the fine fraction of till in the nation wide survey is only slightly higher with median value of 5.35 mg kg^{-1} for the whole Pirkamaa region (Backman *et al.* 2006). The median value for 15 samples located closest to the forest sampling sites is 9.44 mg kg^{-1}, indicating that the selected test areas are located within a regional arsenic anomaly.

The arsenic medians in the present study were higher compared to the data reported by Salminen *et al.* (2004) from south and central Finland (median 1.61 mg kg^{-1}, n=163), but lower compared to the clay-rich samples collected from the vicinity of the southern coast of Finland.

Concentrations of other elements (Al, Cr, Cu, Fe, Mn, Ni, P, Pb, S, V, Zn and OM) in the soil profile are illustrated in Fig. 16. In general, the concentrations of those elements show the same trends as arsenic, which is, increasing trends with depth and higher concentrations in clay than in fine sand or humus. The concentrations in P, Pb, and S, and the amount of OM, on the other hand, decrease with depth. These elements and OM are enriched in the humus as pointed out above. The concentration of Cd is generally low for all soil layers (not present in the soil profile) and the contents agree well with the values reported by Koljonen *et al.* (1992) and Salminen *et al.* (2004). In comparison to the reference data of C horizon samples from south and central Finland (Salminen *et al*. 2004), the concentrations of the studied elements (with the exception of S) from Pirkanmaa were higher in both clay and fine sand samples.

Table 49. Concentrations of *aqua regia*-extractable elements in eluvial and illuvail layers (E and B horizons) in forest clay soil samples.

Clay from eluvial and illuvial layers (N=18)

Parameter	Unit	Mean	Median	Minimum	Maximum
Ca	mg kg^{-1}	3908	4180	2780	4570
K	mg kg^{-1}	3104	3130	1430	4980
Mg	mg kg^{-1}	8876	8685	5820	11600
P	mg kg^{-1}	709	680	457	1010
S	mg kg^{-1}	244	190	50.6	543
Al	mg kg^{-1}	25328	24550	17200	34400
Fe	mg kg^{-1}	39494	39400	26000	59100
Mn	mg kg^{-1}	1111	1240	406	1940
As	**mg kg^{-1}**	**5.07**	**3.84**	**2.80**	**14.2**
Cd	mg kg^{-1}	.	<0.50	<0.50	0.56
Cr	mg kg^{-1}	57.5	55.6	35.7	79.7
Cu	mg kg^{-1}	22.1	18.5	12.9	51.9
Ni	mg kg^{-1}	30.2	28.6	18.8	46.1
Pb	mg kg^{-1}	22.6	21.7	14.3	32.7
V	mg kg^{-1}	74.5	75.4	52.3	109
Zn	mg kg^{-1}	163	144	71.9	271

Table 50. Concentrations of *aqua regia* -extractable elements in subsoil layer (C horizon) in the forest clay soil samples. Median values of 163 samples in the study by Salminen *et al.* (2005) as a comparison.

Clay from geogenic background (N=9)

Parameter	Unit	Mean	Median	Minimum	Maximum	Salminen *et al.* 2005
Ca	mg kg^{-1}	5641	5760	4260	6700	1330
K	mg kg^{-1}	6593	6240	3410	11300	1085
Mg	mg kg^{-1}	12430	11300	8100	18100	2810
P	mg kg^{-1}	597	610	422	751	366
S	mg kg^{-1}	<50.0	<50.0	<50.0	<50.0	50.5
Al	mg kg^{-1}	26667	27300	18600	41900	9350
Fe	mg kg^{-1}	49233	47300	33000	76700	12000
Mn	mg kg^{-1}	845	902	311	1060	105
As	**mg kg^{-1}**	**6.97**	**6.50**	**4.50**	**11.7**	**1.61**
Cd	mg kg^{-1}	<0.50	<0.50	<0.50	<0.50	0.038
Cr	mg kg^{-1}	67.4	67.9	45.4	107	15.5
Cu	mg kg^{-1}	33.6	27.0	17.0	67.9	7.58
Ni	mg kg^{-1}	35.3	33.1	20.4	68.2	7.95
Pb	mg kg^{-1}	18.4	17.8	12.5	31.3	2.47
V	mg kg^{-1}	89	90.3	65.5	129	22.9
Zn	mg kg^{-1}	99	86.1	62.5	148	22.5

Table 51. Concentrations of *aqua regia* -extractable elements in eluvial and illuvail layers (E and B horizons) in forest fine sand soil samples.

Fine sand from eluvial and illuvial layers (N=4)

Parameter	Unit	Mean	Median	Minimum	Maximum
Ca	mg kg^{-1}	1275	1300	1050	1450
K	mg kg^{-1}	640	550	302	1160
Mg	mg kg^{-1}	3178	3115	1620	4860
P	mg kg^{-1}	481	352	180	1040
S	mg kg^{-1}	106	104	<50.0	166
Al	mg kg^{-1}	10233	9750	5130	16300
Fe	mg kg^{-1}	17000	15700	10500	26100
Mn	mg kg^{-1}	199	217	116	245
As	**mg kg^{-1}**	**2.50**	**2.15**	**1.40**	**4.30**
Cd	mg kg^{-1}	<0.50	<0.50	<0.50	<0.50
Cr	mg kg^{-1}	16.8	15.9	7.22	28.4
Cu	mg kg^{-1}	5.34	5.47	2.09	8.31
Ni	mg kg^{-1}	5.67	5.63	2.61	8.83
Pb	mg kg^{-1}	11.2	11.3	7.71	14.5
V	mg kg^{-1}	35.8	35.2	18.7	54.1
Zn	mg kg^{-1}	34.2	32.2	22.4	49.9

Table 52. Concentrations of *aqua regia*-extractable elements in subsoil layer (C horizon) in forest fine sand soil samples. Median values of 163 samples in the study by Salminen *et al.* (2005) as a comparison.

Fine sand - geogenic background (N=2)

Parameter	Unit	Mean	Median	Minimum	Maximum	Salminen *et al.* 2005
Ca	mg kg^{-1}	2720	2720	2660	2780	1330
K	mg kg^{-1}	4085	4085	3250	4920	1085
Mg	mg kg^{-1}	8415	8415	7140	9690	2810
P	mg kg^{-1}	512	512	501	523	366
S	mg kg^{-1}	87.0	87.0	<50.0	124	50.5
Al	mg kg^{-1}	17000	17000	13300	20700	9350
Fe	mg kg^{-1}	28400	28400	23900	32900	12000
Mn	mg kg^{-1}	289	289	270	308	105
As	**mg kg^{-1}**	**3.00**	**3.00**	**2.40**	**3.60**	**1.61**
Cd	mg kg^{-1}	<0.50	<0.50	<0.50	<0.50	0.038
Cr	mg kg^{-1}	33.0	33.0	24.6	41.3	15.5
Cu	mg kg^{-1}	20.2	20.2	15.9	24.4	7.58
Ni	mg kg^{-1}	14.0	14.0	10.4	17.6	7.95
Pb	mg kg^{-1}	8.9.0	8.90	7.10	10.7	2.47
V	mg kg^{-1}	54.7	54.7	44.5	64.8	22.9
Zn	mg kg^{-1}	58.8	58.8	50.1	67.4	22.5

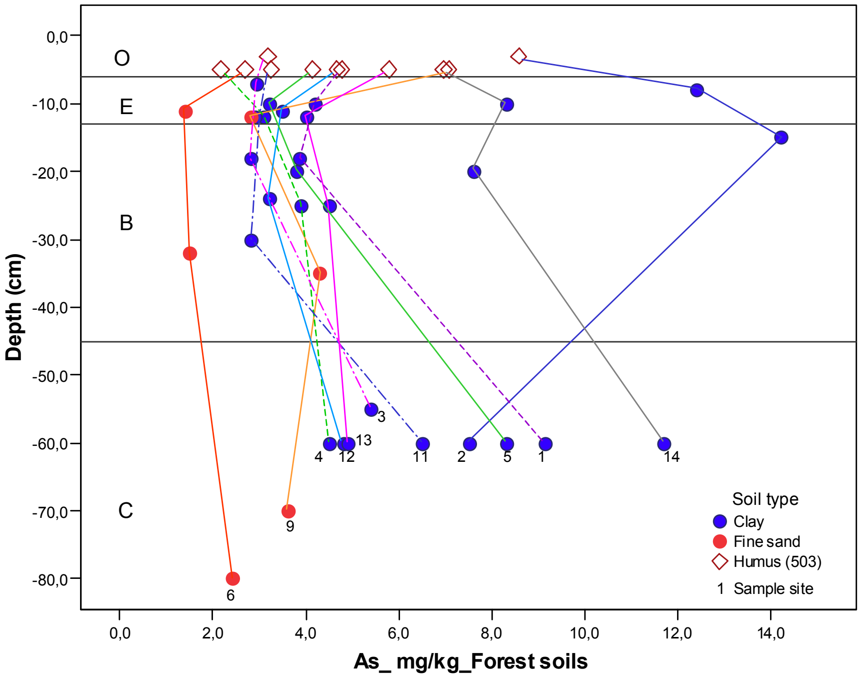


Figure 15. Arsenic contents in soil profiles in eleven different forest soil areas. Soil type is marked with the colour of the marker and sampling sites with a number. O= organic layer, E= eluvial layer, B=illuvial layer and C=subsoil layer.

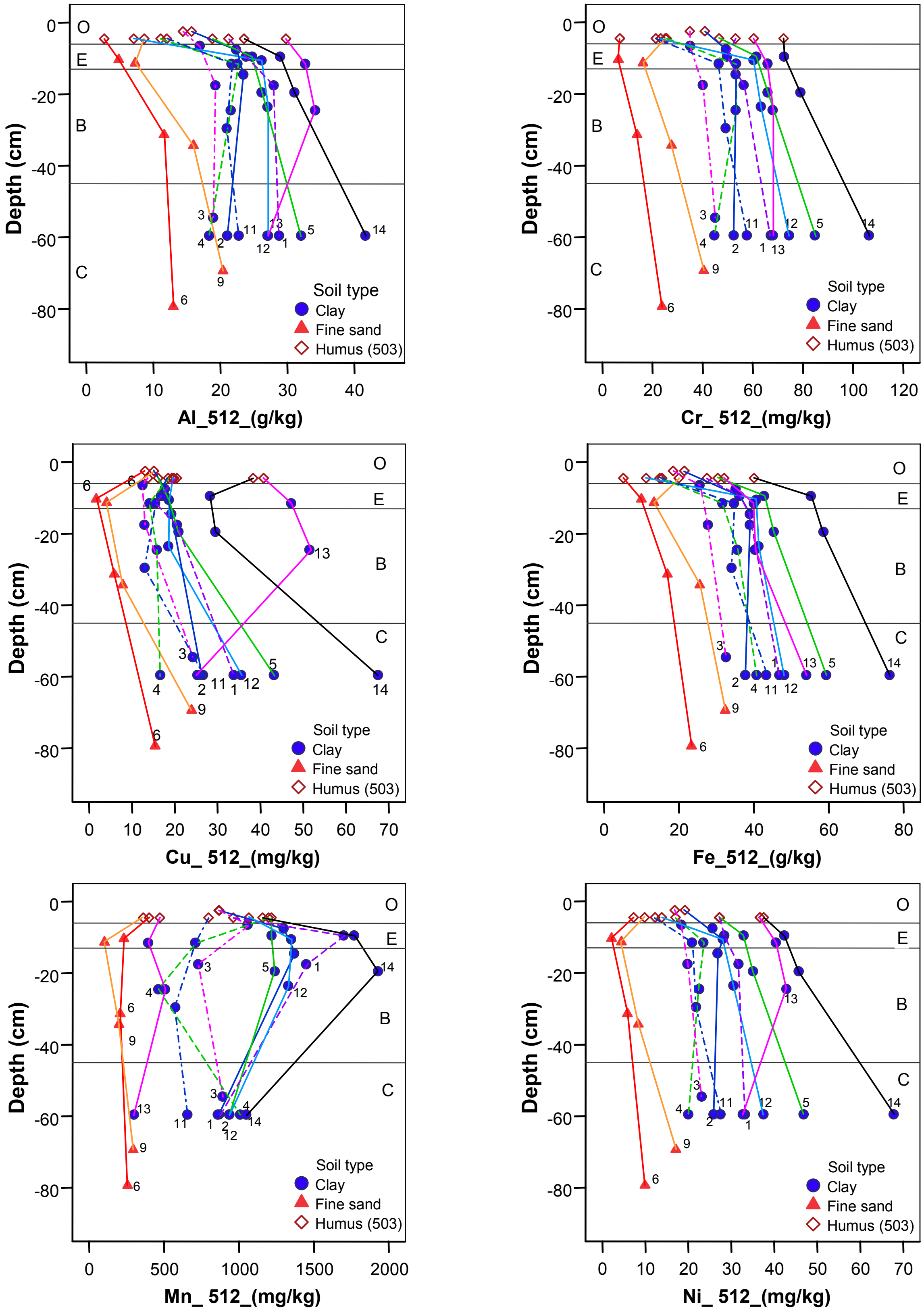


Figure 16. Concentrations of elements in soil profiles in eleven different forest soil areas. Soil type is marked with colour and sampling sites (farms) with number. O= organic layer, E= eluvial layer, B=illuvial layer and C=subsoil layer.

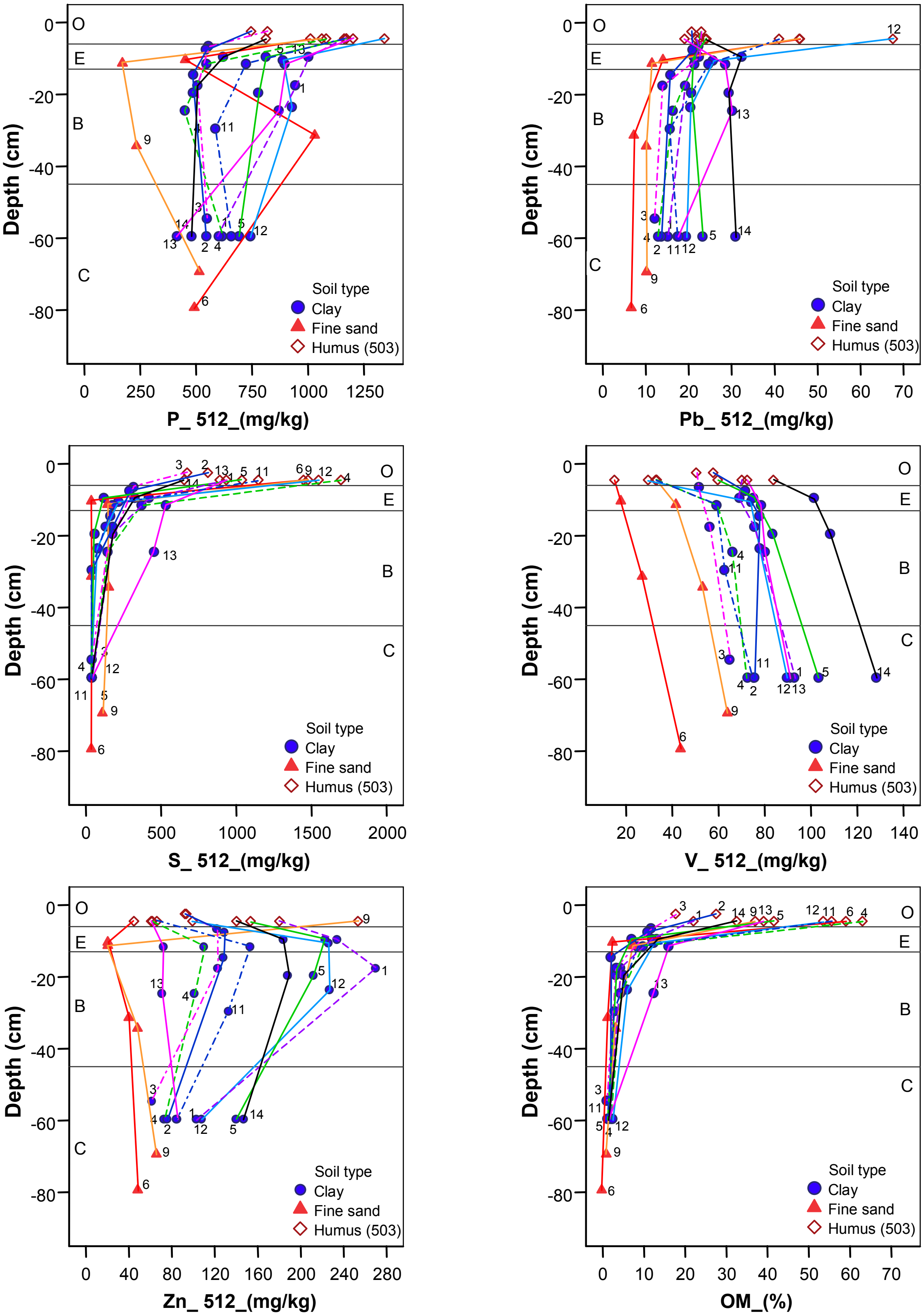


Figure 16 (cont'). Concentrations of elements in soil profiles in eleven different forest soil areas. Soil type is marked with colour and sampling sites (farms) with number. O= organic layer, E= eluvial layer, B=illuvial layer and C=subsoil layer.

Correlation analysis of arsenic and other elements of mineral soil samples from the forest soil was done for two groups: samples from E and B layers together and samples from the C layer. The latter data was not divided according to the soil type due to the small amount of fine sand samples. Correlation coefficients of arsenic and other elements from the AR-extractable elements of mineral soil samples in forest soils are shown in Table 53. Arsenic has stronger correlations to other elements in the deeper horizon (C horizon) than in the upper part (E+B horizons). The correlations in these two groups are quite different because of the different geochemical evolution after deposition. Elements in the subsoil represent the geogenic background, which reflects the local geology of the area, and the elements are in geochemical balance with each other. In contrast, the topsoil is subjected also to atmosperic and anthropogenic factors. E and B layers are specific for certain elements (e.g. Fe, Al, and organic matter) because of the evolution of soil geochemistry in those layers.

Table 53a-b. Pearson's correlation of arsenic and other elements of mineral soil samples from the forest soils (*aqua regia* extract).

a. E+B horizons in Forest soils (N=22)

Elements	As	Al	Cr	Cu	Fe	Mn	Ni	P	Pb	S	V	Zn
As	**1**											
Al	**0.37**	1										
Cr	**0.41**	.958*	1									
Cu	**0.31**	.861*	.759*	1								
Fe	**.493***	.898*	.962*	.659*	1							
Mn	**.529***	.582*	.671*	0.25	.766*	1						
Ni	**0.42**	.959*	.966*	.849*	.934*	.670*	1					
P	**-0.18**	.493*	0.36	0.39	0.314	0.31	.425*	1				
Pb	**0.28**	.789*	.792*	.781*	.760*	.562*	.850*	0.345	1			
S	**0.22**	.514*	0.39	.683*	0.276	0.15	.486*	0.217	.651*	1		
V	**.564***	.894*	.954*	.694*	.976*	.750*	.934*	0.214	.745*	0.342	1	
Zn	**0.15**	.592*	.657*	0.17	.695*	.848*	.600*	.523*	.443*	-0.01	.642*	1
OM	**-0.07**	.431*	0.35	.549*	0.255	0.193	0.42	0.312	.708*	.865*	0.295	0.137

b. C horizon in Forest soils (N=11)

Elements	As	Al	Cr	Cu	Fe	Mn	Ni	P	Pb	S	V	Zn
As	**1**											
Al	**.866***	1										
Cr	**.852***	.983*	1									
Cu	**.867***	.948*	.927*	1								
Fe	**.833***	.967*	.974*	.891*	1							
Mn	**.643***	0.47	0.544	0.519	0.485	1						
Ni	**.874***	.979*	.985*	.972*	.964*	0.561	1					
P	**0.14**	0.05	0.156	0.05	0.039	0.542	0.09	1				
Pb	**.855***	.975*	.989*	.936*	.981*	0.58	.988*	0.16	1			
S	**-0.28**	-0.18	-0.29	-0.17	-0.29	-0.48	-0.28	-0.2	-0.29	1		
V	**.862***	.983*	.992*	.918*	.979*	0.574	.977*	0.129	.986*	-0.26	1	
Zn	**.879***	.946*	.959*	.913*	.927*	0.582	.949*	0.309	.963*	-0.26	.952*	1
OM	**0.48**	0.58	.640*	0.338	.673*	0.331	0.526	0.109	0.588	-0.31	.662*	0.523

3.5.2.3 Soluble concentration of arsenic and other elements

The mobile fraction of elements in the humus and mineral soil samples were determined by ICP-method from samples extracted with acid ammonium acetate – ethyldiamine tetracetic acid (AAAc + EDTA). The method of analysis is described in chapter 3.4.3. The ammonium acetate leach analyses of all studied elements are presented in Tabels 54-56, where the results are classified according to the sampling layer. The results of samples from the eluvial and illuvial layers (E and B horizons) are combined and they correspond to the plough layer in arable soil samples. The subsoil samples (C horizon) correspond to the subsoil sample in arable soils (See also Fig. 11. in chapter 3.4.1). The data was not classified further, for example, according to the soil type because of the low arsenic contents.

Unlike the total concentration data (*aqua regia* leach), the soluble elements have higher contents in the humus layer and the values decrease with depth (Tabels 54-56). Soluble arsenic content in all soil samples was low. In all mineral soils, the concentrations were less than the detection limit (3 mg kg^{-1}) and the concentration was above the detection limit in only a few samples taken from the humus layer. This is the case for Cd, Cr, Cu, Pb, S, and Zn as well. The soluble concentrations of Ca, Mg, Mn and V are generally lower in the E and B horizons than in other horizons. Contents of most of the studied elements were clearly higher in the studied area than in the coast area of Porvoo, south Finland, where AAAc- extract of forest soils was done by Tarvainen *et al.* (2003). Only S, Al, Cr, V, and Zn contents were on the same level or lower in this recently studied data than in the data collected from the district of Porvoo (Tables 55-56).

The mobility rate (% leach) of each element can be defined from a percentile proportion of the concentration of a soluble element (ammonium acetate extract) from its total concentration (*aqua regia* extract). For most of the As, Cd, and Cr results, this procedure was prevented due to the fact that concentrations were below the detection limits (e.g. <3.0 mg kg^{-1} for As). Arsenic in humus and mineral soils seems to be in an insoluble form, except in three humus samples from sites 5, 9 and 12 (4.1-7.1 mg kg^{-1} As in total), which have a high proportion of soluble arsenic.

The solubility of other elements varies from site to site, and for the majority, except S, the mobile fraction tends to decrease with depth. The higher solubilities are measured in the humus layer and the lower solubilities in the C horizon. The proportions of soluble fractions for each element for selected sampling sites are shown in Fig 17. This suggests the same sources. For all sampling sites, Al (except from sites 9 and 6 in Ylöjärvi area), Cr, Fe, K, Mg, Ni, P, V and Zn from mineral soil samples have very low mobility rate for all soil profiles. Aluminium in sampling sites 9 and 6 has leach 8% higher in E and B horizons than in the C horizon. Calcium, Cr, Mn and Pb in mineral soils are generally more soluble than the previously mentioned elements. Higher solubilities were measured in sites 1, 2 and 3 in Orivesi area, where the highest solubility for Mn (48% in site 3) was observed. The mobility rate is generally highest in the eluvial horizon (E horizon), then it drops in the illuvial soil (B horizon) and finally remains constant or slightly increased in the C horizon. An exception is Ca, which generally has much higher solubility in the C horizon than in the B horizon (illuvial layer), up to 15% leach higher in soil sample from site 11. Compared the others, the soluble portion of S is lowest in the humus layer and then it increases with depth. The highest measured solubility for S is 70% in the C horizon at sampling site 9. The high mobility rates can increase more contamination in the soils or sediments. Overall, the mobile fraction of arsenic and other elements in forest soils (except S in mineral soils) are quite low or the elements are only in insoluble form. This suggests that the mineral soil from the forest areas in the study areas is still less contaminated due to the low soluble and less mobility of those elements. This suggests that the elements in the forest soils are not easily mobilised and transported away and, on the other hand, the deeper forest soils have not gained any significant addition of mobile components from other sources. The extremely high soluble proportions of all elements measured in the humus layer, however, suggests the contamination of the surface sediment, especially in the sampling sites 6, 12, 11 and 4 in Ylöjärvi and Hämeenkyrö areas.

Table 54. Concentrations of AAAc+EDTA-extractable elements in humus layer (O horizon) in forest soil samples.The number of samples was 11.

Parameter	Unit	Mean	Median	Minimum	Maximum
Ca	mg kg^{-1}	2909	2410	1270	6090
K	mg kg^{-1}	422	415	194	674
Mg	mg kg^{-1}	521	417	223	1230
P	mg kg^{-1}	136	120	62.1	247
S	mg kg^{-1}	98.0	102	54.1	139
Al	mg kg^{-1}	842	816	361	1260
Fe	mg kg^{-1}	1773	1850	1100	2250
Mn	mg kg^{-1}	498	507	117	916
As	**mg kg^{-1}**	**.**	**<3.00**	**<3.00**	**3.70**
Cd	mg kg^{-1}	0.34	0.26	0.19	1.03
Cr	mg kg^{-1}	.	<0.30	<0.30	0.52
Cu	mg kg^{-1}	5.38	5.34	<3.00	9.28
Ni	mg kg^{-1}	3.64	3.54	1.91	5.60
Pb	mg kg^{-1}	20.6	11.2	8.92	49.1
V	mg kg^{-1}	2.19	2.17	1.46	3.28
Zn	mg kg^{-1}	50.8	23.9	4.70	326

Table 55. Concentrations of AAAc+EDTA-extractable elements in eluvial and illuvial layers (E & B horizons) in forest soil samples. The number of samples was 22. Median values of 72 samples from Tarvainen *et al.* (2003) were used as a comparison.

Parameter	Unit	Mean	Median	Minimum	Maximum	Tarvainen *et al.* 2003
Ca	mg kg^{-1}	429	301	14.5	1250	30.7
K	mg kg^{-1}	117	101	16.1	335	21.2
Mg	mg kg^{-1}	141	147	3.12	335	3.70
P	mg kg^{-1}	26.5	23.2	4.55	61.3	14.0
S	mg kg^{-1}	41.8	36.5	<20.0	94.5	36.3
Al	mg kg^{-1}	826	707	374	1620	671
Fe	mg kg^{-1}	834	856	244	1750	158
Mn	mg kg^{-1}	126	80.8	0.39	458	6.00
As	**mg kg^{-1}**	**<3.00**	**<3.00**	**<3.00**	**<3.00**	**-**
Cd	mg kg^{-1}	.	<0.10	<0.10	0.20	0.02
Cr	mg kg^{-1}	.	<0.30	<0.30	0.85	0.32
Cu	mg kg^{-1}	.	<3.00	<3.00	7.32	<0.10
Ni	mg kg^{-1}	1.57	1.06	0.11	6.04	<0.10
Pb	mg kg^{-1}	3.95	3.57	<2.00	7.00	0.90
V	mg kg^{-1}	1.09	1.03	<0.70	2.30	21.3
Zn	mg kg^{-1}	2.24	1.57	<0.80	7.02	0.80

Table 56. Concentrations of AAAc+EDTA-extractable elements in subsoil (C-horizon) layer in forest soil samples. Number of samples was 11. Median values of 72 samples in study of Tarvainen *et al.* (2003) as comparison.

Parameter	**Unit**	**Mean**	**Median**	**Minimum**	**Maximum**	**Tarvainen *et al.* 2003**
Ca	mg kg^{-1}	1119	1250	14.2	2090	23.2
K	mg kg^{-1}	85.5	52.5	24.8	259	12.4
Mg	mg kg^{-1}	643	620	1.80	1470	2.40
P	mg kg^{-1}	21.8	17.6	<2.00	75.9	5.50
S	mg kg^{-1}	.	<20.0	<20.0	87.0	22.2
Al	mg kg^{-1}	124	102	57.5	390	351
Fe	mg kg^{-1}	375	366	15.4	702	66.3
Mn	mg kg^{-1}	93.3	104	0.28	240	1.10
As	**mg kg^{-1}**	**<3.00**	**<3.00**	**<3.00**	**<3.00**	**.**
Cd	mg kg^{-1}	<0.10	<0.10	<0.10	<0.10	0.006
Cr	mg kg^{-1}	<0.30	<0.30	<0.30	<0.30	0.18
Cu	mg kg^{-1}	.	<3.00	<3.00	3.48	0.16
Ni	mg kg^{-1}	1.02	0.83	<0.10	2.30	<0.10
Pb	mg kg^{-1}	.	<2.00	<2.00	2.07	0.40
V	mg kg^{-1}	2.07	2.02	<0.70	3.68	20.1
Zn	mg kg^{-1}	.	<0.80	<0.80	0.96	0.30

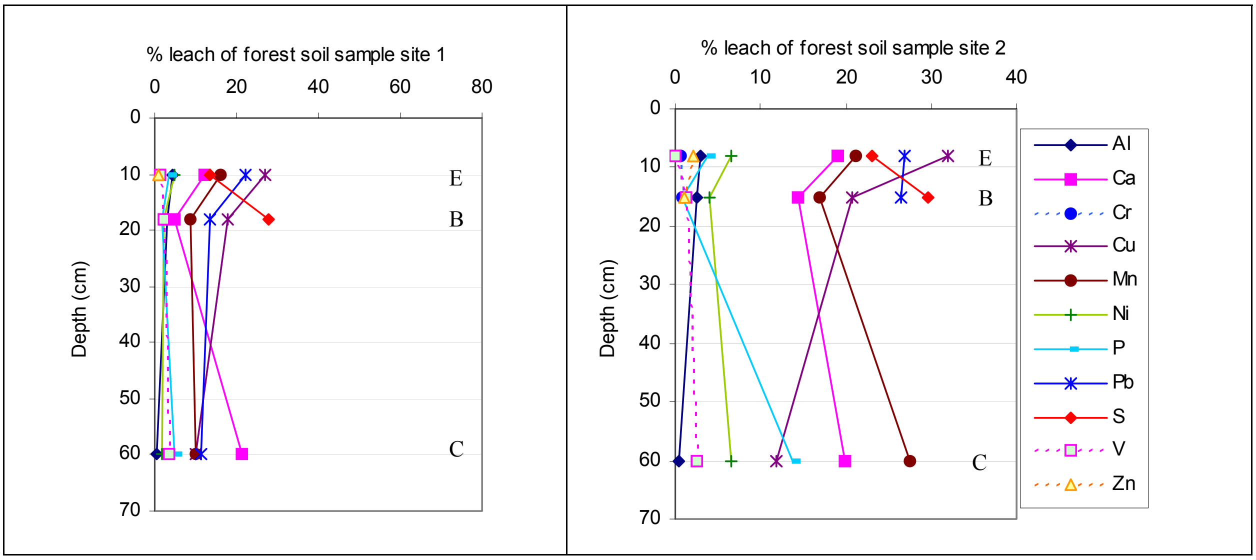


Figure 17. Distributions of the proportion (%) of leach of elements in soil profiles at sampling sites 1 and 2 (Orivesi); 6 and 9 (Ylöjärvi); 11and 12 (Hämeenkyrö); and 13 and 14 (Lempäälä. Each break in the soil profile represents the depth taken from each horizon, from top: eluvial (E), illuvial (B) and C horizons. Cont.

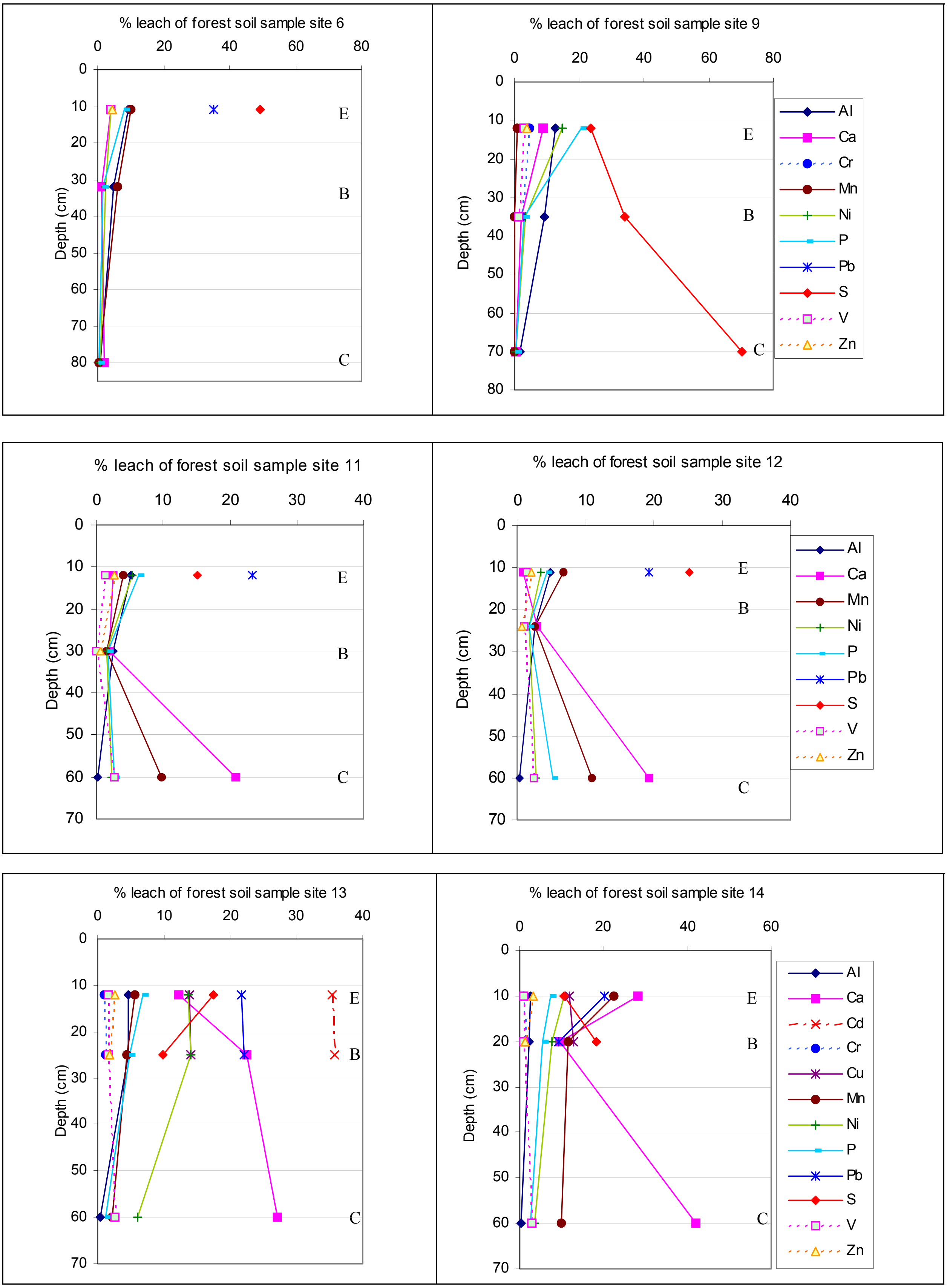
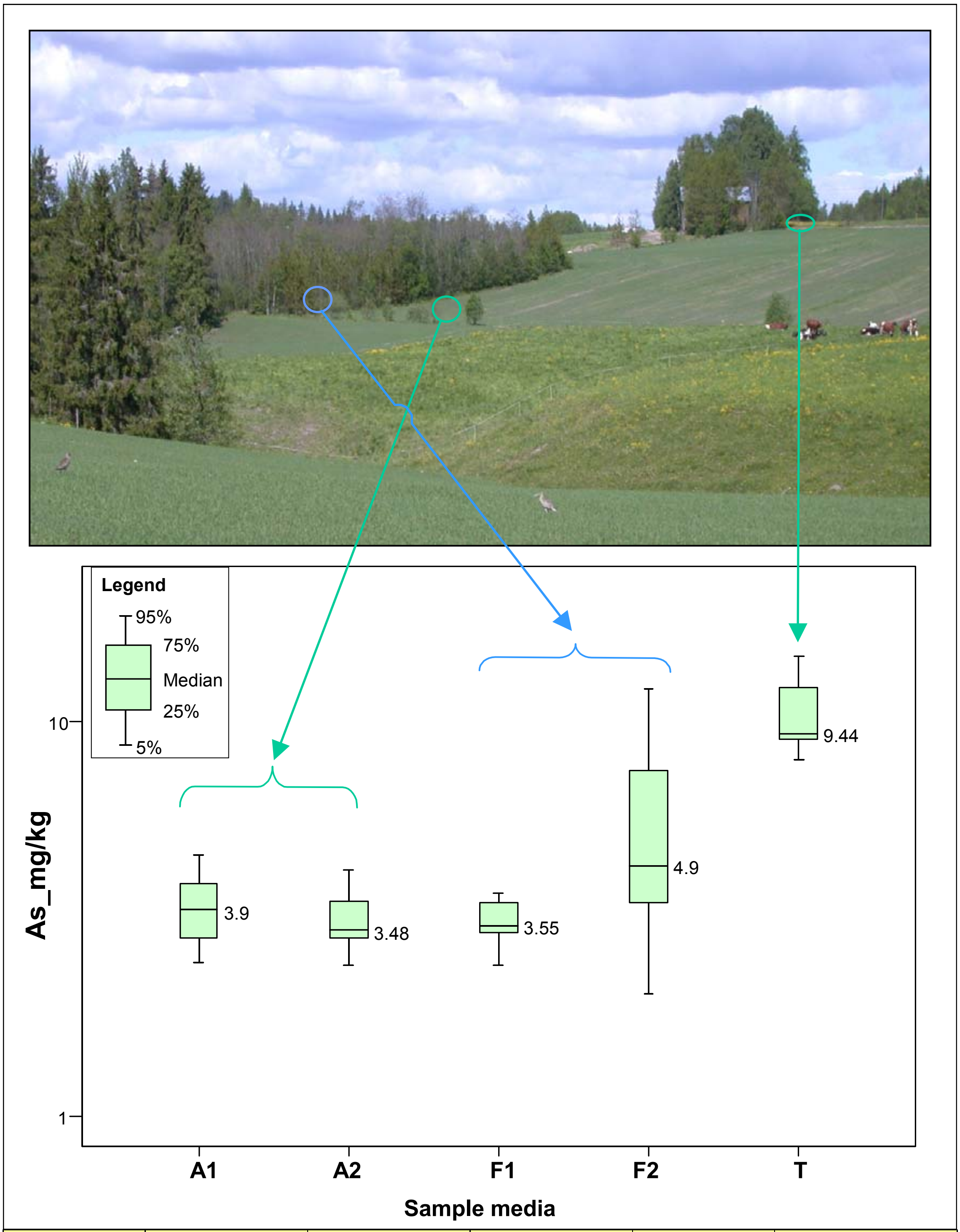


Figure 17. (Cont). Distributions of proportion (%) leach of elements in soil profiles in sampling sites 1 and 2; (Orivesi); 6 and 9 (Ylöjärvi); 11 and 12 (Hämeenkyrö); and 13 and 14 (Lempäälä). Each break in the soil profile represents the depth taken from each horizon, from top: eluvial (E), illuvial (B) and C horizons.

3.5.3 Comparison of arable soils and forest soils

The sampling principle was to take the samples in pairs so that the soil type was the same in both of the sampling sites, in arable land and forest. This principle came valid at the farms, but in three sampling pairs the soil type was same according to the map and field observation, but according to the grain size analyse at laboratory the soil types were determined to be different soil types. The differences were, however, small. The results of samples from eluvial and illuvial layers (E and B horizons) are combined and coincide with the plough layer in arable soil samples and the subsoil samples from arable land and forest land constituted the other pairs (see also Fig. 11 in chapter 3.4.1). The sampling principle and the arsenic content in different sampling materials are displayed in Fig. 18. The average arsenic contents are about the same in arable topsoil and subsoil and also in forest topsoil. The contents of arsenic in samples taken from forest subsoil are, however, higher and the range is wider. The reference data from till deposits is taken from the nationwide survey data (Koljonen *et al*. 1992), so that each farm is relative to the nearest sampling sites. Thus, the number of till data is the same as the number of farms. As mention in the previous section, a comparison between these results and the nationwide survey data can be partially done due to the different fraction analysed (<0.06 mm fraction was used in Koljonen *et al.* 1992) and greater concentrations of elements are expected in the nationwide survey data because till was the study material.



	A1	A2	F1	F2	T
Sample media	Arable_Topsoil	Arable_Subsoil	Forest_Topsoil	Forest_Subsoil	Forest_Subsoil
N_valid	15	15	11	11	15
Soil type	Clay & Fine sand	Clay & Fine sand	Clay & Fine sand	Clay & Fine sand	Till
Data source	RAMAS	RAMAS	RAMAS	RAMAS	National wide survey

Figure 18. Sampling sites and box-plot comparison of As variations in till, arable and forest soils (Photo A. Pullinen).

Grouping the samples from eluvial and illuvial layers together allowed correlation analysis of arable and forest soils to be carried out and this data was compared to the plough sample from arable soil samples. The geogenic background samples from the C horizon were compared to the subsoil samples from the arable area. Correlation coefficients of the As and other elements from the AR-extractable elements of arable and forest soils are shown in Table 57.

Table 57 a-b. Correlation coefficients for regression of AR-extractable elements of arable and forest soils (AR extract).

a. E+B horizons (N=15)

Elements	**As_Fr**	**Al_Fr**	**Cr_Fr**	**Cu_Fr**	**Fre_Fr**	**Mn_Fr**	**Ni_Fr**	**P_Fr**	**Pb_Fr**	**S_Fr**	**V_Fr**	**Zn_Fr**	**OM_Fr**
As_Ar	**0.291**	0.511	0.392	.744*	0.364	0.142	0.489	0.202	.598*	.615*	0.438	-0.021	.779*
Al_Ar	0.21	**.554***	.678*	0.333	.720*	0.513	.615*	0.202	.544*	0.111	.668*	0.509	0.119
Cr_Ar	0.223	.573*	**.719***	0.385	.741*	0.442	.634*	0.116	.588*	0.119	.690*	0.416	0.149
Cu_Ar	0.051	0.409	0.505	**0.509**	.532*	0.045	0.489	-0.038	.525*	0.105	0.506	-0.025	0.195
Fe_Ar	0.151	0.484	.599*	0.287	**.653***	0.475	.557*	0.158	0.486	0.103	.612*	0.467	0.086
Mn_Ar	0.064	0.345	0.4	0.18	0.367	**0.303**	0.352	0.062	0.328	0.218	0.355	0.333	0.207
Ni_Ar	0.247	.685*	.804*	0.495	.833*	.564*	**.751***	0.266	.706*	0.188	.777*	.534*	0.264
P_Ar	-0.288	-0.323	-0.326	-0.125	-0.328	-.565*	-0.346	**-0.385**	-0.253	-0.165	-0.296	-0.512	-0.118
Pb_Ar	0.164	0.503	.657*	0.311	.677*	0.348	.543*	0.047	**0.502**	-0.012	.642*	0.377	0.119
S_Ar	0.078	0.139	0.188	0.264	0.19	-0.144	0.157	-0.187	0.242	**-0.023**	0.203	-0.205	0.157
V_Ar	0.244	.520*	.657*	0.411	.714*	0.397	.606*	0.017	.596*	0.137	**.686***	0.301	0.171
Zn_Ar	0.224	0.335	0.432	0.248	0.443	0.117	0.345	-0.088	0.339	0.09	0.422	**0.11**	0.073
OM_Ar	0.185	.630*	.538*	.797*	0.509	0.217	.626*	0.362	.662*	.564*	.542*	0.156	**.705***

b. C-horizon (N=15)

Elements	**As_Fr**	**Al_Fr**	**Cr_Fr**	**Cu_Fr**	**Fre_Fr**	**Mn_Fr**	**Ni_Fr**	**P_Fr**	**Pb_Fr**	**S_Fr**	**V_Fr**	**Zn_Fr**	**OM_Fr**
As_Ar	**0.295**	0.426	0.418	0.378	0.42	-0.026	0.415	-0.23	0.383	0.021	0.392	0.381	0.37
AL_Ar	0.396	**.580***	.703*	.535*	.776*	0.489	.698*	0.339	.754*	-0.505	.685*	.700*	0.51
Cr_Ar	0.395	.583*	**.691***	0.513	.755*	0.512	.669*	0.357	.734*	-0.402	.690*	.679*	.583*
Cu_Ar	0.276	.571*	.671*	**.522***	.731*	0.384	.659*	0.294	.715*	-0.311	.651*	.663*	.550*
Fe_Ar	0.395	.579*	.704*	.548*	**.777***	.535*	.707*	0.344	.764*	-0.51	.689*	.698*	0.492
Mn_Ar	0.446	0.441	.526*	0.371	.535*	**0.502**	0.509	0.145	.529*	-0.42	.526*	0.43	.544*
Ni_Ar	0.501	.684*	.786*	.617*	.835*	.540*	**.771***	0.303	.820*	-0.457	.776*	.760*	.616*
P_Ar	-0.009	0.182	0.159	0.072	0.285	-0.077	0.136	**-0.227**	0.189	0.209	0.219	0.149	0.331
Pb_Ar	0.442	.596*	.721*	.520*	.771*	.583*	.695*	0.397	**.757***	-0.484	.714*	.691*	.637*
S_Ar	0.067	0.258	0.166	0.337	0.236	-0.309	0.239	-.548*	0.195	**0.341**	0.165	0.132	-0.103
V_Ar	0.372	.625*	.683*	.615*	.743*	0.433	.693*	0.191	.737*	-0.187	**.694***	.663*	0.481
Zn_Ar	0.475	.661*	.720*	.568*	.809*	0.356	.703*	0.079	.749*	-0.299	.733*	**.683***	.600*
OM_Ar	.672*	.765*	.730*	.728*	.803*	0.242	.770*	-0.399	.752*	-0.248	.755*	.632*	**0.396**

Ar = Arable soils, Fr = Forest soils.

There were very small differences in the correlation coefficients of the upper and deeper soil samples for As, Al, Cr, Cu, Ni, and Zn. Arsenic has shown poor correlations between the arable and forest soils in both layers. However, some discrepancies between the correlation coefficients of the upper and deeper soil samples are found for Fe, Mn, P, Pb, S, Zn and OM. In general, the deeper part has a stronger correlation than the upper part, except for P. Phosphorus shows a negative correlation between the arable and forest soils in all profiles, and the upper part has a stronger (negative) correlation. This is probably due to the continued use of phosphorus fertilizers. Moreover, P has shown a negative correlation with arsenic in both sections and stronger correlations were found in clay than in fine sand. The cross plot correlations of arsenic and other elements in arable and forest soils are shown in Figs. 19 and 20. In topsoil samples, arsenic contents in arable soil are slightly higher than in forest sites (see also Fig.18). In contrast, in samples taken from subsoil, the arsenic contents are higher in the forest areas. One of the reasons for this is that the subsoil samples from the forest were taken from a deeper level than those from the arable land. Arsenic contents generally tend to increase with depth (Backman *et al.* 2006). The clay contents are also higher in forest soil samples (especially from the subsoil layer) than in arable land samples (Table 1 and Annex 2). Clay content has a positive correlation with the arsenic content. Slightly higher arsenic content in the top soils from arable land may be due to the use of fertilizers in the arable land soil.

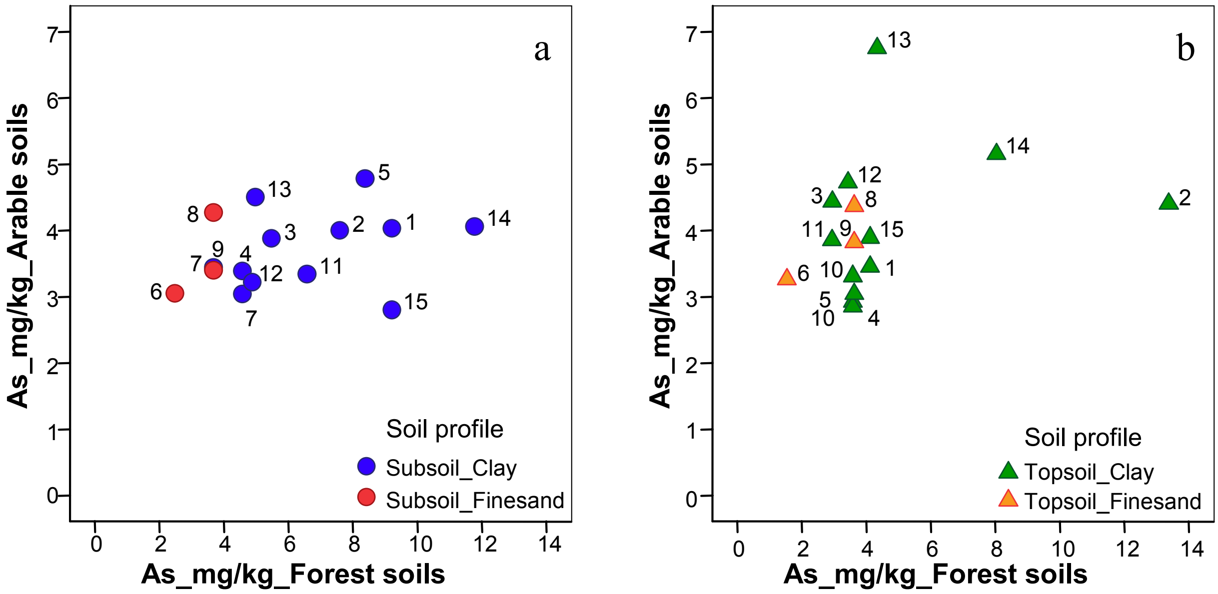


Figure 19. Correlation of arsenic in arable and forest soils in Pirkanmaa. Soil type is marked with colour and sampling sites (farms) with number, a = subsoil data and b = topsoil data.

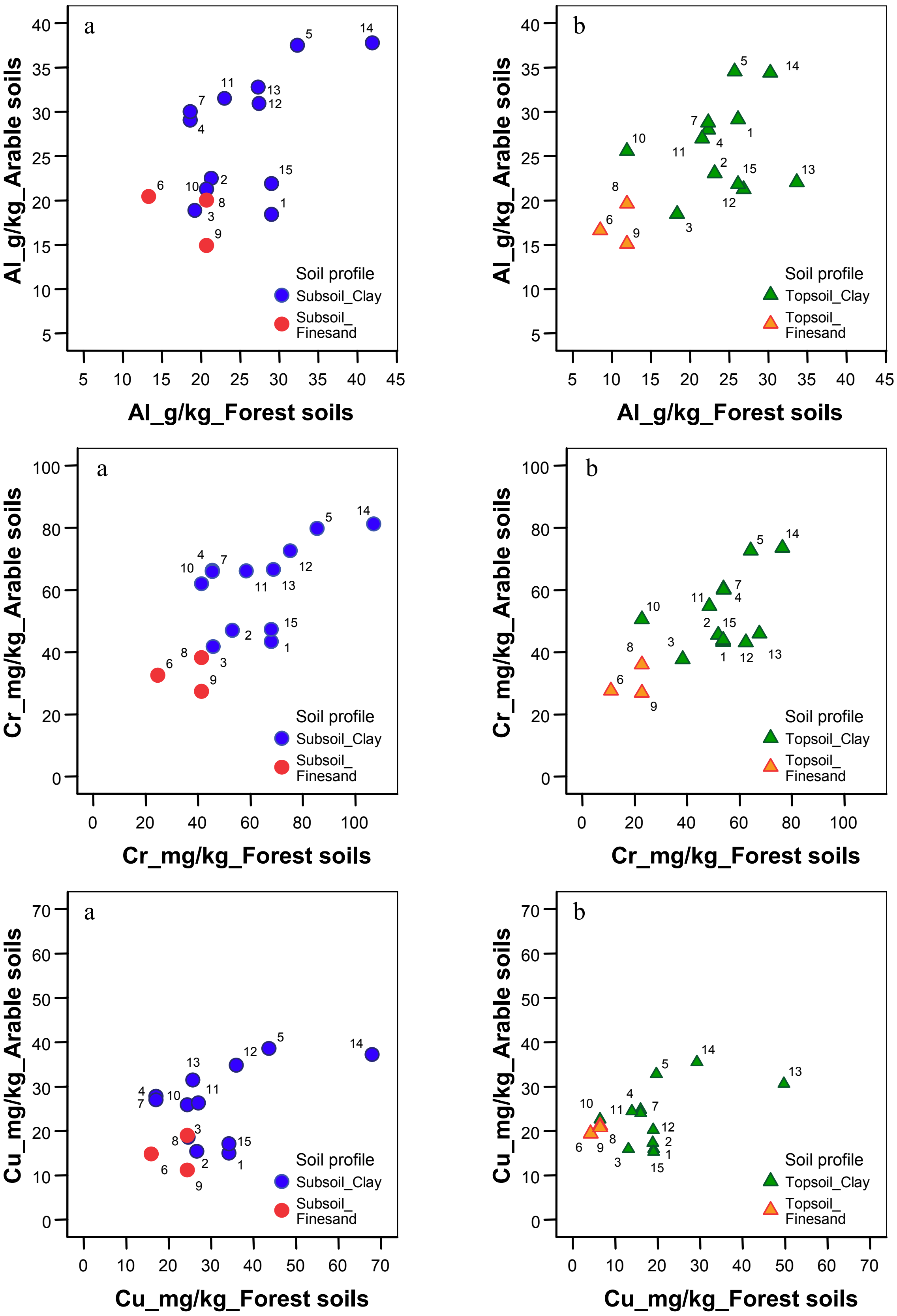


Figure 20. Correlation of other elements in arable and forest soils in Pirkanmaa. Soil type is marked with colour and sampling sites (farms) with number, a = subsoil data and b = topsoil data.

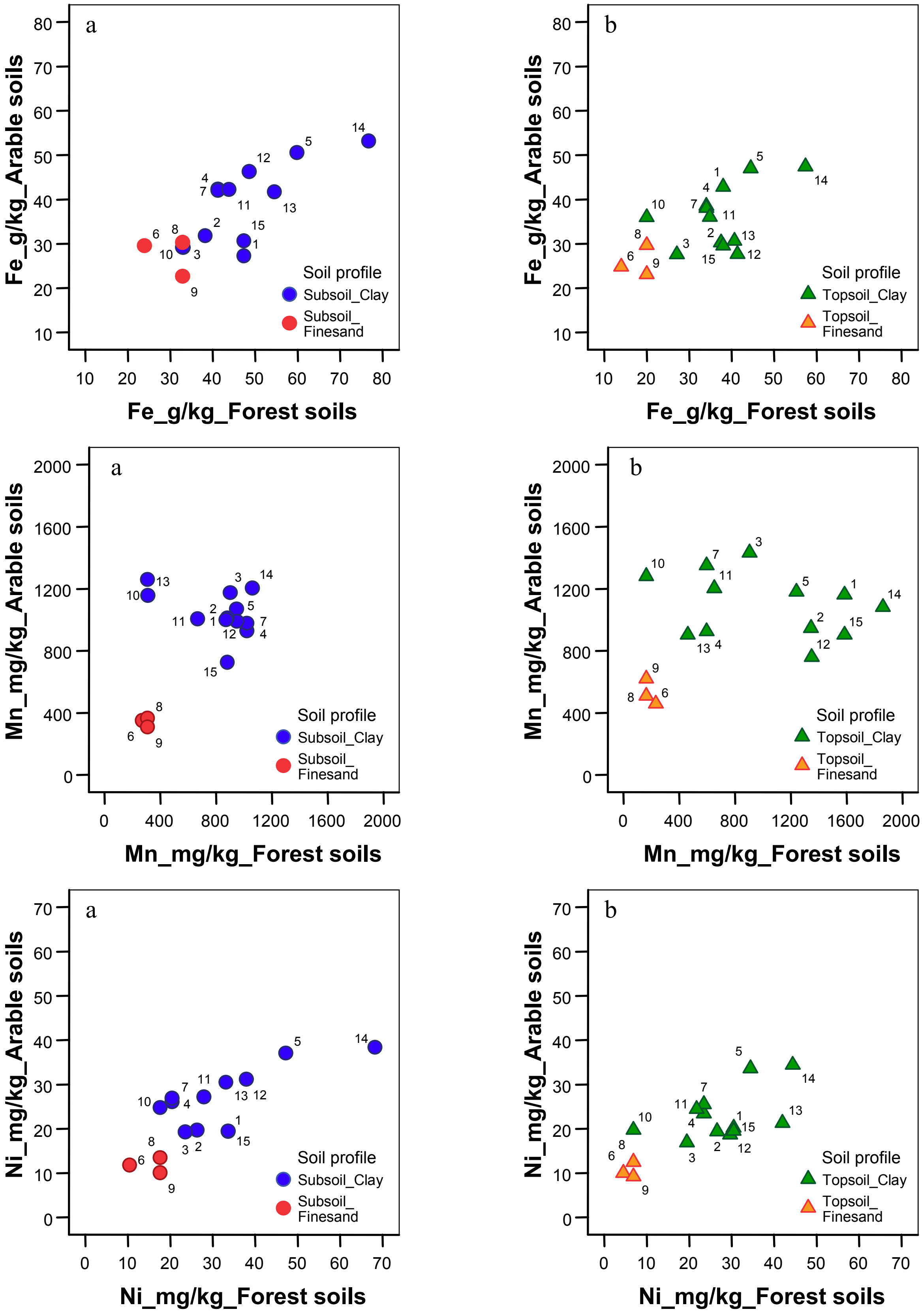


Figure 20 (cont'). Correlation of other elements in arable and forest soils in Pirkanmaa. Soil type is marked with colour and sampling sites (farms) with number, a = subsoil data and b = topsoil data.

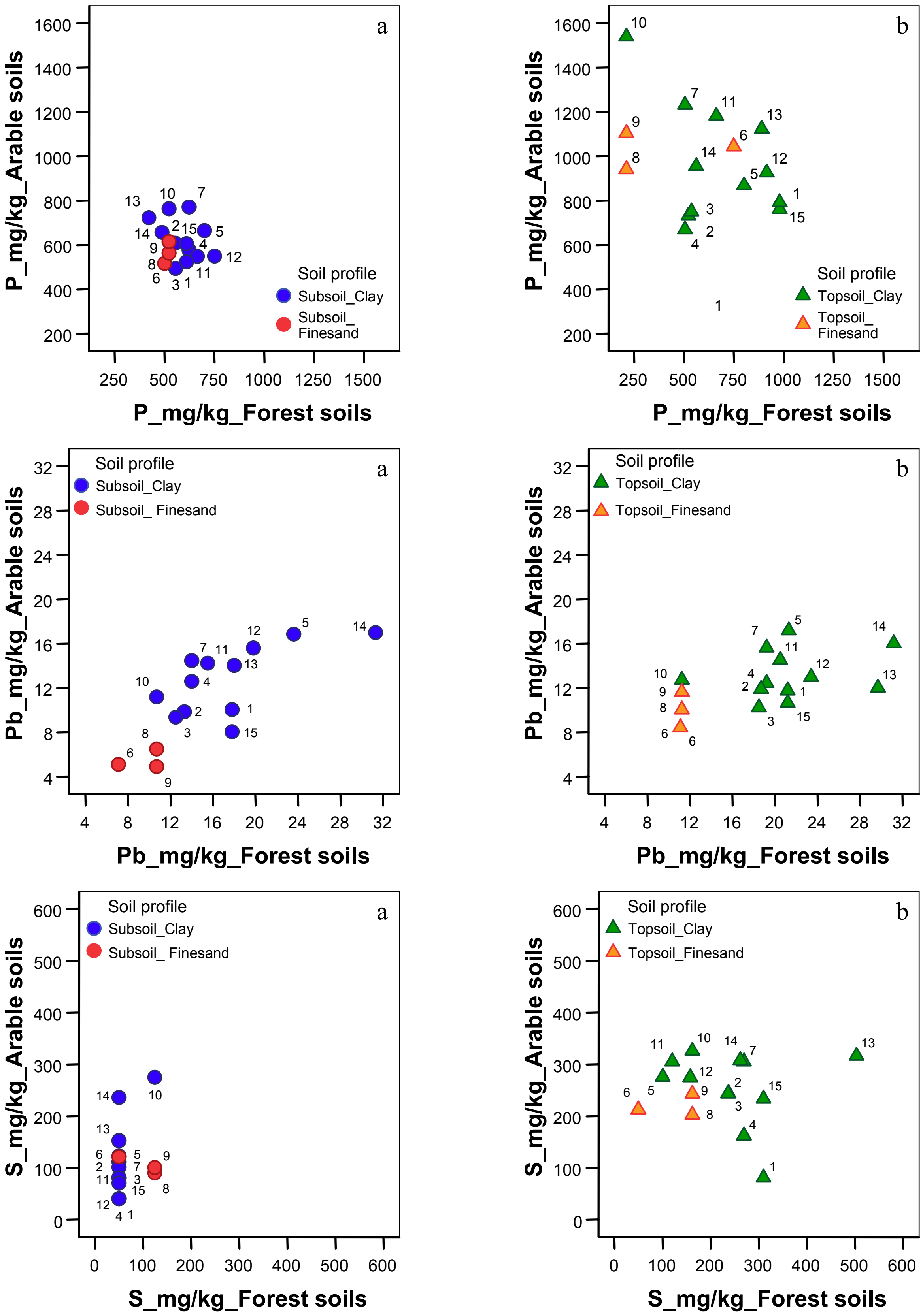


Figure 20 (cont') Correlation of other elements in arable and forest soils in Pirkanmaa. Soil type is marked with colour and sampling sites (farms) with number, a = subsoil data and b = topsoil data.

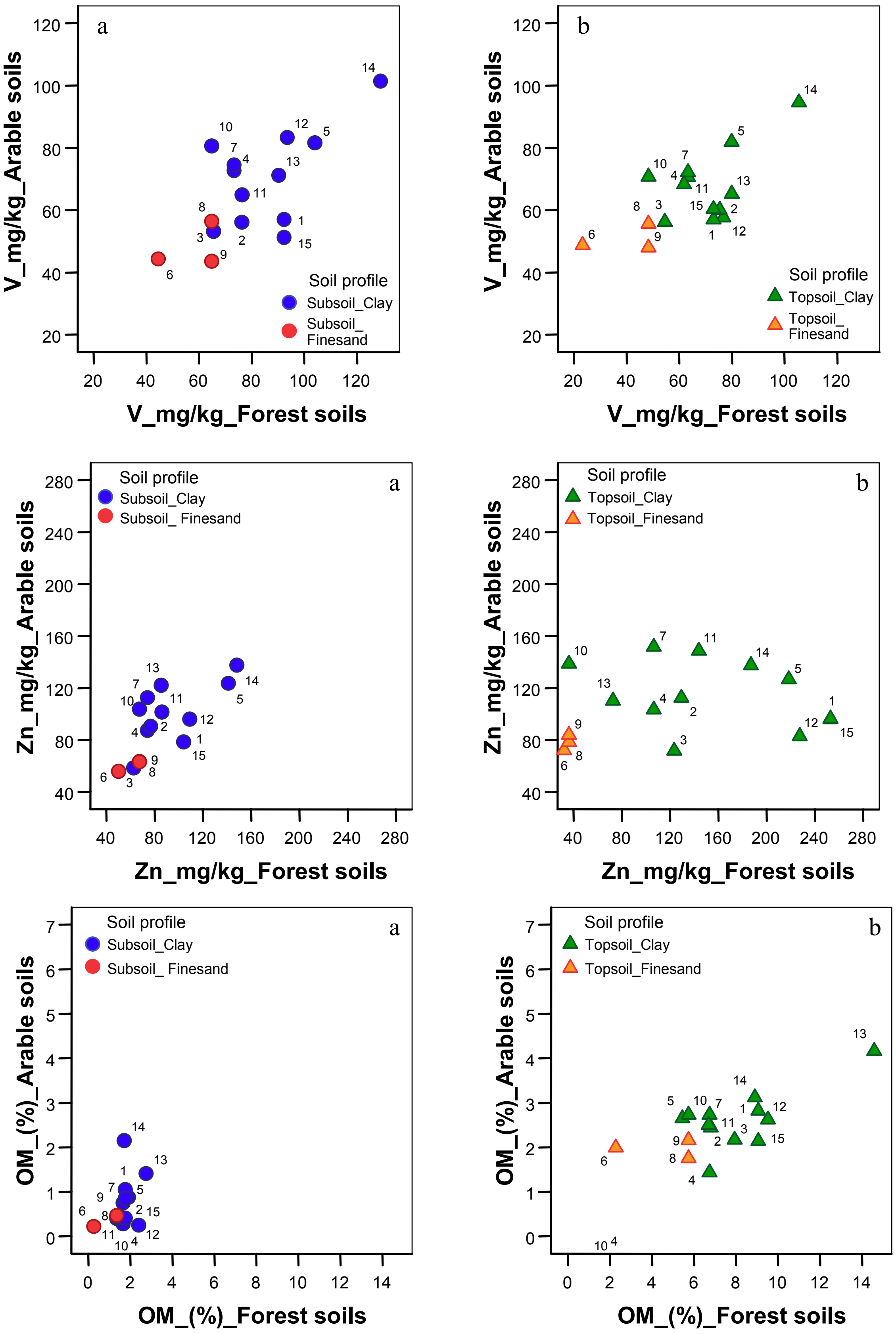


Figure 20 (cont') Correlation of other elements in arable and forest soils in Pirkanmaa. Soil type is marked with colour and sampling sites (farms) with number, a = subsoil data and b = topsoil data.

3.5.4 Plant crops

3.5.4.1 Arsenic and other elements in crop plants

In this study, elemental concentrations in crop plants coincided with the national level for each plant species (Table 58). Plant species and even cultivars may differ genetically in their ability to take up elements and transfer them from roots to shoots. In addition, soil, climate, weather and atmosphere factors and also cultivation practices affect elemental concentrations in plants. Together, these factors explain the differences in elemental patterns in crop plants in this study.

The EU has set maximum limits for toxic Pb and Cd concentrations in certain foodstuffs (Commission regulation No 466/2001). The maximum Pb level for cereals is 0.2 mg kg^{-1} wet weight and for peeled potato 0.1 mg kg^{-1} wet weight. The same levels are applied to Cd in wheat grain and peeled potatoes. In the present study, Pb and Cd concentrations in all crop samples were well below these limits. The highest Pb content in wet weight basis was 0.030 mg kg^{-1} in wheat grain which is about 15% of the maximum limit value. Also, the highest Cd content on a wet weight basis was in wheat grain, 0.062 mg kg^{-1}, which is about 31% of the maximum permitted concentration.

Table 58. Phosphorus and trace element concentrations (mg kg^{-1} dw) in wheat grains, potato tubers, and timothy grass, the second cut.

Element	**Wheat (n=5)**				**Potato, unpeeled (n=5)**				**Timothy (n=5)**			
	Min.	**Median**	**Mean**	**Max**	**Min.**	**Median**	**Mean**	**Max**	**Min.**	**Median**	**Mean**	**Max**
P	3800	4160	4170	4590	1880	2260	2320	2750	2510	3040	3480	5070
Al	2.3	2.5	2.5	2.6	22.0	52.0	46.0	73.0	12.0	16.0	16.0	23.0
As	0.004	0.005	0.005	0.005	0.006	0.008	0.008	0.011	0.011	0.014	0.014	0.018
Cd	0.003	0.025	0.031	0.072	0.019	0.041	0.039	0.056	0.009	0.016	0.015	0.023
Cr	0.03	0.04	0.04	0.05	0.04	0.07	0.09	0.15	0.04	0.06	0.06	0.08
Cu	2.9	5.7	5.2	6.1	2.5	3.6	3.8	6.2	4.4	5.5	6.1	8.8
Fe	29.0	27.0	35.0	41.0	36.0	49.0	49.0	6.2	79.0	87.0	85.0	88.0
Mn	20.0	31.0	34.0	48.0	9.0	6.2	6.8	7.1	30.0	44.0	43.0	51.0
Ni	0.078	0.098	0.153	0.349	0.091	0.137	0.234	0.51	0.468	0.646	0.062	0.732
Pb	0.014	0.015	0.019	0.035	0.029	0.031	0.032	0.036	0.027	0.09	0.078	0.104
Se	0.081	0.19	0.16	0.21	0.004	0.043	0.036	0.077	0.028	0.089	0.092	0.18
V	0.01	0.02	0.01	0.02	0.07	0.09	0.1	0.13	0.03	0.03	0.03	0.05
Zn	22.0	24.0	26.0	31.0	7.4	9.5	9.1	10.7	17.0	22.0	22.0	25.0

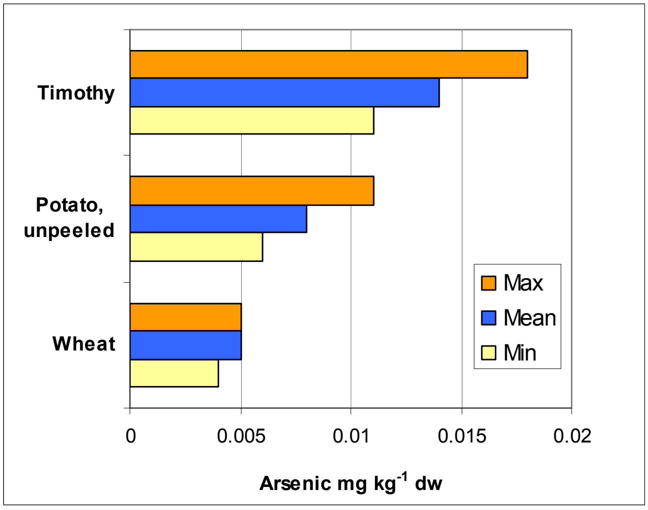


Figure 21. Arsenic concentrations in timothy grass, wheat grains and potato tubers.

Trace element concentrations were generally slightly higher in unpeeled potato samples compared to peeled potatoes (Fig. 22). The largest difference was in Al, Fe and V concentrations which were 61–89 % higher in unpeeled potato indicating contamination from the soil. The mean and median arsenic concentration in a peeled potato was 0.004 mg kg^{-1} dw (range 0.002-0.006 mg kg^{-1} dw).

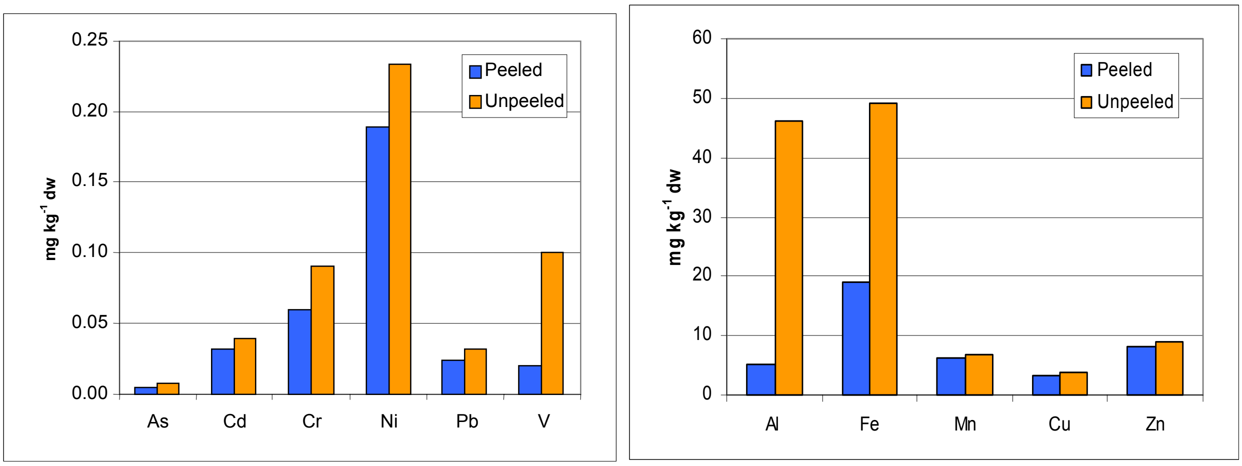


Figure 22. Trace element contents in potato tubers (unpeeled) and peeled potatoes.

The EU has not set maximum limits for arsenic content in foods. In this study, arsenic concentrations in wheat grains, potato tubers and timothy grass were low and represented typical international levels in uncontaminated areas (see chapter 2.4.1). The highest concentrations were in timothy grass. In general, leafy plant parts are more susceptible to atmospheric depositions and soil dust than seeds and grains. Timothy also grew on the soils of with the highest soluble arsenic concentrations found in this study (Fig. 23). Except for the RAKAS-project (2004-2007, unpublished data), no literature data on the arsenic contents of timothy grass were available. Wheat grains and potato tubers showed lower arsenic concentrations and were grown on soils with lower soluble arsenic concentration than timothy. Of the crop plants studied here, potatoes clearly had the highest P demand. Arsenic concentrations of plant crops in the Tampere and Pirkanmaa Belt (Table 44) were similar. From each plant species, a different plant part was sampled (root, shoot and fruit), which makes comparisons difficult. It is genetically determined how the elements are translocated into various plant parts and usually contents decrease from the roots to the shoots and from the shoots to fruits.

The correlation coefficient between AAAc-EDTA extractable arsenic in soil and arsenic in plants was 0.81. However, correlations are misleading or only indicative because the plant species differed and the amount data was very small (Fig. 23). *Aqua regia* extractable As or AAAc extractable P in soils did not correlate with arsenic in plants. A mean AAAc extractable P in soils was lowest in the timothy fields and highest in potato fields. There were no significant correlations between arsenic and other mineral or trace elements in plants.

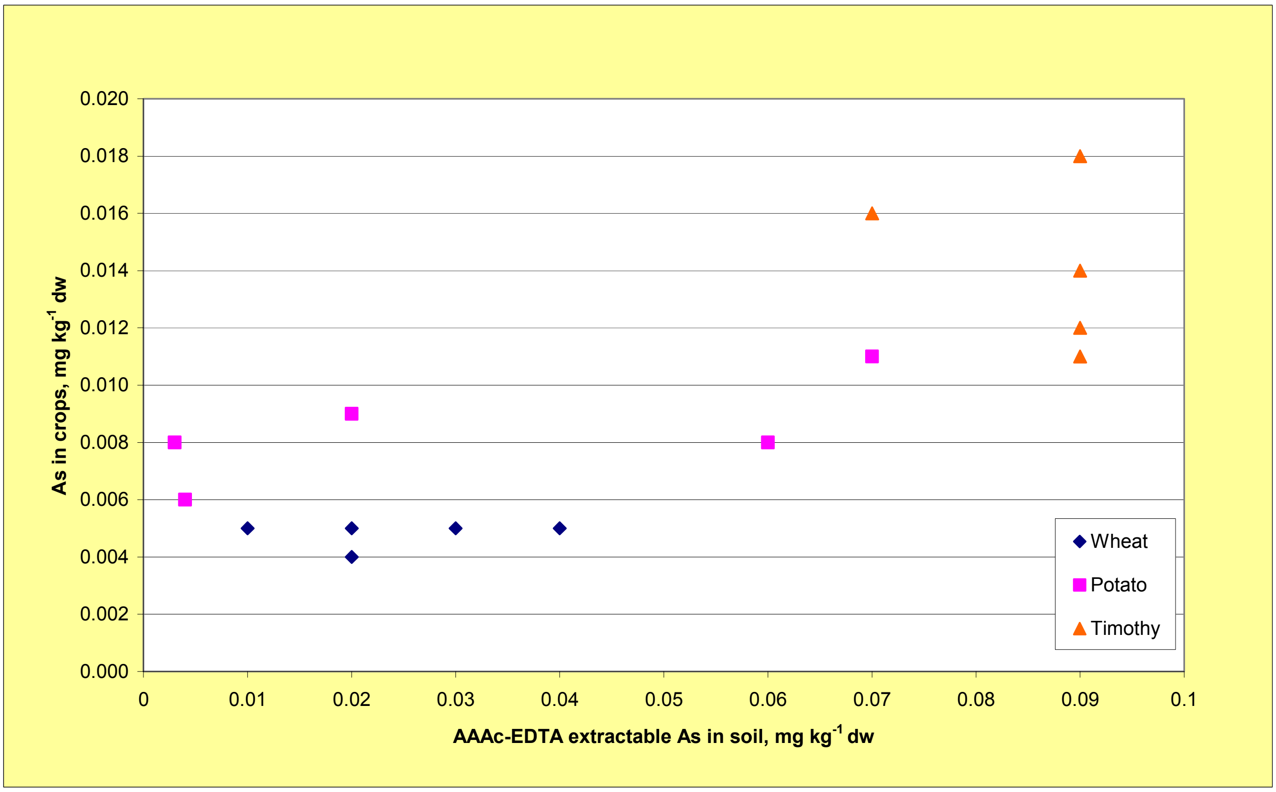


Figure 23. Arsenic (As) contents (mg kg^{-1} dw) in timothy grass, unpeeled potato (tubers) and wheat grains according to concentrations of soluble (AAAc-EDTA extractable) arsenic in the soil plough layer.

3.5.5 Assessments of the migration of arsenic in agricultural soils and crop from arsenic-rich till and/or bedrock

Migration of arsenic in agricultural soils. To assess the migration of arsenic in the arable land studied in the Pirkanmaa region, ratios of arsenic in the plough layer to arsenic in the subsoil were calculated. Table 59 shows that arsenic contents in the plough layer were only slightly higher than those in the subsoils. This may be a sign that arsenic inputs to the topsoil have been, to some extent, higher than the arsenic outputs from the topsoil. Obviously, arsenic additions from fertilizers, feed preparations, manure, and the atmosphere have been larger than arsenic uptake by plants, arsenic leaching and erosion. Also, mass balance calculations at a national and farm level, as presented earlier in this report, are in line with this opinion. Migration of arsenic between the two soil layers seems to be minimal.

Transfer of arsenic from soil to plants. One part of the element content in the plant is taken up from the soil via the roots and the other part from the air via the leaves. Plants and crops with large leaves or shoots may receive a relatively large amount of elements on their surfaces through deposition. Roots and tubers growing in the soil may have arsenic containing soil particles on their surfaces. Arsenic is mainly taken up by plants via the roots, but the relation between arsenic in the soil and plant uptake is not clear. Many complex factors like soil type and chemical composition affect the bioavailability and uptake of arsenic by plants as shown below.

Table 59. Ratios of general soil characteristics and *aqua regia* extractable elements in the plough layer to respective soil parameters in subsoil for fields (n = 15) studied in the Pirkanmaa region.

Element	**Ratios (n = 15)**			
	Minimum	**Median**	**Mean**	**Maximum**
Clay	0.51	0.91	1.21	2.92
Org. C	1.45	4.55	4.83	10.3
Humus	1.46	4.61	4.81	10.1
pH	0.90	1.02	1.01	1.13
P	1.16	1.55	1.59	2.15
S	1.30	2.74	3.19	6.75
Al	0.65	0.96	0.92	1.04
Fe	0.60	0.91	0.89	1.02
Mn	0.77	1.15	1.16	2.01
As	**0.60**	**1.10**	**1.10**	**1.50**
Cd	1.23	1.82	1.90	3.16
Cr	0.59	0.91	0.88	1.00
Cu	0.58	0.93	1.01	1.85
Ni	0.60	0.90	0.88	1.04
Pb	0.83	1.09	1.22	2.37
V	0.69	1.00	0.99	1.18
Zn	0.86	1.23	1.19	1.46

General factors affecting the uptake of trace elements by plants can be summarized shortly as follows (modified from McLaughlin *et al.* 1996, Chaney & Hornick 1978):

* Plant factors
  - plant species
  - plant cultivar
  - plant part and its distance from the roots
  - age of the plant or plant part
  - root excretes
  - depth of roots in the soil

* Soil factors
  - soil parent material (age, texture, $CaCo_3$)
  - total amount and solubility of soil trace element
  - amount and nature of clay
  - amount and nature of organic matter
  - soil salinity
  - soil pH
  - redox potential
  - cation exchange capacity
  - interactions between other elements

* Weather and climate factors
  - temperature
  - precipitation

* Atmospheric factors
  - deposition, dry and wet

* Cultivation practices
  - fertilization (N, P and their forms)
  - liming agents
  - soil improving agents (wastes: ashes sludges, composts etc.).

Elements are transferred into the plants in different ways:
- via root uptake – constituents available from the soil and then transferred to the aboveground portion of the plant;
- via deposition of particles – dry deposition of particle-bound constituents on plants;
- via vapour transfer – uptake of vapour-phase constituents by plants through their foliage (U.S.EPA 1999).

Uptake of arsenic by the plants from the soil can be described by a soil-to-plant uptake factor that is often calculated from empirical data on constituent concentrations (mg kg^{-1} dw) in plant tissue and in the plough layer *(aqua regia* extractable As, mg kg^{-1} dw) of the soil in which the plants were grown. The highest soil-to-plant uptake factor of arsenic among the crops collected from the Pirkanmaa region was for timothy grass (Table 60). Foliage must have received substantial arsenic from the air, as well. However, all the uptake factors for arsenic were very low. Uptake factors were clearly higher for macronutrients than for other elements while those of micronutrients, like copper and zinc, were higher than for the other trace elements.

Table 60. Soil-to-plant uptake factors of arsenic and other elements by plant crops studied.

Element	**Soil-to-plant uptake factor**											
	Wheat grains (n = 5)				**Potato tubers, unpeeled (n = 5)**				**Timothy grass, 2nd cut (n = 5)**			
	Min	**Med**	**Mean**	**Max**	**Min**	**Med**	**Mean**	**Max**	**Min**	**Med**	**Mean**	**Max**
P	2.98	4.38	3.94	4.84	1.84	2.06	2.29	3.18	3.43	4.30	4.24	4.97
Al	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.001	0.001	0.001
Fe	0.001	0.001	0.001	0.001	0.00	0.001	0.001	0.001	0.002	0.003	0.003	0.003
Mn	0.02	0.04	0.04	0.08	0.00	0.01	0.01	0.01	0.03	0.04	0.04	0.05
As	**0.001**	**0.001**	**0.001**	**0.002**	**0.001**	**0.001**	**0.001**	**0.001**	**0.003**	**0.003**	**0.004**	**0.006**
Cd	0.01	0.13	0.15	0.37	0.11	0.15	0.18	0.28	0.04	0.07	0.07	0.10
Cr	0.001	0.001	0.001	0.001	0.00	0.001	0.002	0.004	0.001	0.001	0.001	0.002
Cu	0.12	0.23	0.22	0.30	0.07	0.13	0.17	0.37	0.21	0.35	0.35	0.42
Ni	0.003	0.008	0.007	0.01	0.003	0.009	0.011	0.025	0.019	0.031	0.03	0.038
Pb	0.001	0.001	0.002	0.003	0.001	0.002	0.002	0.003	0.002	0.006	0.006	0.009
V	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.001	0.001	0.001
Zn	0.14	0.24	0.25	0.36	0.06	0.10	0.09	0.11	0.15	0.20	0.22	0.36

Also, according to the review done by Mahimairaja *et al.* (2005), accumulation of arsenic in the edible parts of most plants is low which is attributed to a number of reasons, including low bioavailability of arsenic in soil, restricted uptake by plant roots, limited translocation of arsenic from roots to shoots and phytotoxicity and subsequent premature plant death at relatively low arsenic contents in plant tissues. Most plants do not accumulate enough arsenic to be toxic to animals and humans. Growth reductions and crop failure are the main results of soil arsenic contamination. Thus, the major hazard for animal and human systems is derived from direct ingestion of arsenic contaminated soil or water.

Arsenic may be a beneficial element for plants at very low concentrations. With increasing concentrations, it becomes toxic and affects productivity of crop plants (Bhumba & Keefer 1994, Lamont 2003). Arsenic is not readily transferred from the roots to shoots. Plants differ in their sensitivity to arsenic (Bellows 2005). For example, peas and beans are very sensitive to arsenic in the environment, while some species of ferns accumulate large quantities of arsenic without apparent adverse effects. Some plants are arsenic-resistant or can block arsenic uptake by their root systems. Still other food crops accumulate arsenic at levels that raise human health concerns. Such plant species include wild rice, alfalfa and pasture grasses (Bhumba & Keefer 1994, Lamont 2003).

Since plants take up arsenic primarily by their roots, the highest level of arsenic accumulation is usually in roots and tubers, such as carrots and potatoes (Bellows 2005). Signs of arsenic phytotoxicity vary among plant species, but these typically include leaves dying back from their tips, stunting, and sterile or abnormal fruits and seeds, similar to phosphorus deficiencies. Plants react to arsenic at much lower doses than those needed to have an impact on human health. Thus, most plants die before they produce a food product that is toxic when consumed in normal amounts. In 1993, the National Food Authority set the current health limits for human consumption of arsenic at 1 mg per kilogram of food (dry weight).

Also, according to the Ministry of the Environment in Ontario (2001), the highest arsenic concentrations tend to be in root crops, particularly beets and radishes. Fruit crops, such as tomatoes, berries and apples, present a much lower risk because they take up and store very little arsenic. Green beans are good indicators of arsenic in soil, since bean plants are particularly sensitive to arsenic. If green beans grow well in a garden, it is unlikely that the uptake of arsenic into other vegetables will be high enough to pose a health risk.

To minimize human exposure to arsenic, Canadian guidelines (Ministry of the Environment in Canada 2001) recommend thoroughly washing all vegetables and peeling root crops before eating. Washing has been shown to greatly reduce the levels of arsenic on vegetables. Also, in the present study, peeling potatoes reduced arsenic content substatially. The Canadian guidelines for handling vegetables before eating are in agreement with the current Finnish recommendations given by Evira, the national control authority for food stuffs (Niskanen 2006).

Arsenic concentrations in crops in high- and low-arsenic areas could not be compared because no high-arsenic plant crop was among the study material and no plant crop sample was available from a high-arsenic area.

3.5.6 Recommendations for fertilizing and liming practices of fields with elevated arsenic content

If the arsenic content of the soil is >50 mg kg^{-1}, the soil is most probably polluted and if the content is >100 mg kg^{-1}, the soil possibly has to be remediated (Ministry of Environment in Finland 2006). Among all Finnish fields, only one field (Table 7, MTT Soil Monitoring Study 1998, Chapter 2.3.1) containing arsenic at 166 mg kg^{-1} has been found, indicating that the soil was clearly polluted. This site has been labelled a “hot spot”. This field contained coarse-grained mineral soil (with org. C 7.02% and pH 5.71) and the contents of most other elements (Cd 0.456, Cr 55.92, Cu 27.55, Ni 26.53, V 73.26, Zn 89.29, Se 0.40, Hg 0.091 and Pb 9.3 mg kg^{-1}dw) were above the national mean levels. Reasons for the pollution have not been clarified. The field is located in the municipality of Kärkölä in the Tavast province. Obviously, this field is not suitable for food production. If the pollution occurs over large areas, we will recommend remediation of this soil *in situ* with phytoremediation processes possibly together with physical, chemical, microbiological, mycorrhizal and agronomical techniques. If the pollutant contents in non-food crops grown in this field do not exceed the quality requirements for incineration, the plants could be used for bioenergy production by burning. Otherwise, the crops should be transported to a waste incineration plant. Phytoremediation is a slow process, but an environmental-friendly and a cheap way to clean large land areas, like large fields.

In general, mean and median contents in Finnish arable soils were low. Globally, natural arsenic contents of soils are below 10 mg kg (PennState 2001, Mahimairaja *et al.* 2005). Mäntylahti and

Laakso (2002) suggested an arsenic concentration of 10 mg kg^{-1} as a target value for "Clean Soil" in Finland. The Canadian limit value for arsenic in agricultural soil is 12 mg kg^{-1} (Environment Canada 2002). Hence, in Finnish arable soils, the concentrations exceeding values of 10 or 12 mg kg^{-1} can be considered as elevated. From Table 61, we can see that in Finland, there are a small number of fields that contain more than 10 or 12 mg $kg^{-1}$of arsenic.

Fields with elevated arsenic content (>10 mg kg^{-1}) did not occur at the RAMAS-farms. Instead, among the national soil monitoring study (Unpublished data, RAKAS-project 2004-2007), there were fourteen fields (two in the Pirkanmaa region) that contained more than 10 mg kg^{-1} of arsenic and six fields (one in the Pirkanmaa region) that contained more than 12 mg $kg^{-1}$of arsenic. In the South Savo province, there were two mineral soils and three organogenic soils exceeding the concentration of 10 mg kg^{-1} (Mäntylahti & Laakso 2002). According to Mäntylahti and Laakso (2002) all the farms studied in South Savo province practiced conventional farming, not organic farming which is based on recycling various waste materials in plant cultivation. It is difficult to know the real reasons for elevated arsenic contents found in some cultivated soils in Finland. However, we know that elevated arsenic concentrations in the cultivated soils may occur after applying arsenic-containing waste materials, such as fertilizer preparation, to the soil. Also, the use of arsenic-containing commercial feed preparations for animal nutrition is known to increase arsenic inputs to the soil via farm animal manure (Bellows 2005). In addition, elevated arsenic contents in the soil may occur in the vicinity of metal (copper and other metals, too) smelters or mining areas due to the release of inorganic arsenic into the air (Ministry of the Environment, Ontario 2001). Elevated arsenic contents in soils are possible for geological reasons, too. To avoid an increase in arsenic contents in cultivated soils, low-arsenic fertilizer preparations and low-arsenic feed preparations are recommended for use on all farms.

Table 61. *Aqua regia* extractable arsenic contents in topsoils of arable land in Finland.

Area	**n**	**Range**
Whole Finland	338	0.3 – 18.0 (166*)
Southwestern Finland	23.0	3.1 – 12.0
Ostrobothnia	21.0	1.0 – 11.0
South Savo, min. soils	274	1.0 – 35.0
South Savo, org. soils	38.0	1.0 – 28.0
Pirkanmaa, 1998	35.0	2.2 – 17.0
Pirkanmaa, 2005	**15.0**	**2.9 - 6.8**
Total range in Finland	**744**	**0.3 – 35.0 (166*)**
Value for clean agricultural soil, Finland	-	10.0
Limit for agricultural soil, Canada	-	12.0
Background value, Finland**		2.6 (0.3-20.0)
Value for possibly polluted soil, Finland**	-	50.0
Value for polluted soil, Finland**		100

* Exceptionally high value, hot spot field
** Ministry of Environment in Finland 2006

Since there are cultivated soils with elevated arsenic contents in Finland, too, the authors need to give recommendations for cultivation practices to manage human and animal exposure to arsenic. Based on arsenic chemistry and soil science reviewed by Bellows (2005) recommendations for fertilizing and liming the fields with elevated arsenic content were discussed. Recommendations will help manage the soil to favour arsenic bonding to soil particles and minimize arsenic movement and availability to plants. When arsenic is bound to soil minerals, it is relatively immobile. However, it may be transported by erosion. When arsenic is dissolved in water, it may damage the environment, affect crop growth, or endanger animal and human health versus arsenic that is bound to soil particles (Bellows 2005).

To reduce human exposure to arsenic, we have to recognise the arsenic exposure pathways from soil to humans. The routes are many as described by U.S.EPA (1999):

soil -> human ingestion
soil -> air-> human inhalation
soil -> air -> plant -> human ingestion (above-ground vegetable, fruit)
soil -> air -> plant -> cattle -> human ingestion -> (beef and dairy through forage and silage)
soil -> plant -> human ingestion (above-ground vegetable, fruit, root vegetable)
soil -> plant -> cattle -> human ingestion (beef and dairy through grain, forage and silage)
soil -> soil erosion -> stream -> fish -> human ingestion
soil -> air -> stream -> fish -> human ingestion

Recommendations for cultivation practices to manage Finnish fields with elevated arsenic content

The recommendations for cultivation practices to manage Finnish fields with elevated arsenic content are mainly modified from by Bellows (2005).

Drying of the soils. In wet soils, arsenic occurs as the toxic form arsenite. Since it bonds poorly to soil particles, it is more mobile in the environment than arsenate. Finnish cultivated soils are mostly field-moist or dry. However, the fields located in the lake or sea shorelines and river banks may be wet and muddy as a result of flooding, particularly in springs when the snow and ice has melted, and also in other seasons that have had heavy rains. Also, other fields may stay wet throughout the growing season, if the rains continue through the whole summer. Floods can be best managed by keeping the dykes unbroken. In the other fields, good drainage, both surface and subsurface drains, is a way to transport excess water from the fields to the surface waters and prvent soil from becoming too wet. Drying of the soils is especially important for soils with elevated arsenic contents. It is also important if the fields are sandy, because the sandier or wetter the soil, the greater the potential for arsenic toxicity.

Fertilization. Arsenate replaces and competes with phophorus for plant uptake. Since phosphorus is much more abundant in agricultural soils than is arsenic, it crowds arsenic offbinding sites, increasing the solubility and mobility of arsenic. Effects of the P-fertilization on the behaviour of arsenic depend on the soil type of the fields. For sandy soils, phosphorus additions stimulate plants to take up additional arsenic. Thus, low rates of P applications are recommended for sandy soils with elevated arsenic content. However, for silt or clay soils, phosphorus applications mobilize arsenic but decrease arsenic uptake by the plants. During the last decade, the use of mineral fertilizers, particularly the use of phosphorus, has been decreased radically in Finland. Many mychorrhizal fungi facilitate plant uptake of phophorus and increase plant uptake of arsenic. In evaluating arsenic uptake in crop plants the key factors are arsenic availability, P availability and obviously plant P demand (Meharg *et al.* 1994, Gulz *et al*. 2005). Plant species differ in their P demand which may explain differences in arsenic content of various crop plants.

N-fertilizers also affect the solubility of arsenic in the soil, but the effects depend on the form of nitrogen. Arsenic is more likely to be soluble in soil, if it contains relatively high concentrations of nitrate (NO_3^-). In addition, various N-forms have various effects on soil pH. NH_4^+ fertilizers release through nitrification of H^+ ions and nitrates to the soil, thereby decreasing pH. This reaction may have long-term effects on soil pH. As for NH_3 fertilizers, the conversion of NH_3 to NH_4^+ “takes up”

H^+ from the soil solution, thereby temporarily increasing soil pH. For the cultivated soils with elevated arsenic content, NH_3 fertilizers are preferrable to NH_4^+ fertilizers. Also, the use of nitrogen in agriculture has dimished in Finnish agriculture over the past few years.

Liming. Soil phosphate and pH are the most important factors that control the desorption of arsenic (Mahimairaja *et al.* 2005). Finnish cultivated soils are in general rather acidic and the use of lime has decreased in agriculture over the past few years. However, by keeping the soil pH neutral or slightly acidic, arsenic is more likely to bind to soil particles. By increasing the soil pH by liming with limestone we can possibly reduce the mobility of arsenic into the surface and ground waters and reduce the availability of arsenic to the plants. Liming is very useful for agronomical reasons, especially, if the field has an elevated arsenic content.

Addition of iron, aluminium or manganese. Soil arsenic binds to iron, aluminium and manganese oxides that are the major components of clay coatings on soil aggregates. If the soil is deficient or poor in iron, aluminium or manganese, arsenic in the soil may be rather soluble. By adding these elements into the soil, it is possible to decrease the solubility of arsenic in soil with low clay content.

Addition of organic matter. In general, arsenic and organic matter repel each other because they are both negatively charged and compete with each other for binding sites on positively-charged soil minerals. However, certain types of organic matter, such as humic acid, can decrease the absorption of arsenic. Arsenic will be bound to organic complexes. In sandy soils, the uptake of arsenic will be greatest if the organic matter level is low or moderate. Increasing organic matter content in soil reduces the uptake of arsenic by plants.

Selection of a proper plant species. If the soil contains excessive amounts of arsenic, the field has to be remedied in some way. If the soil contains an elevated arsenic content (>10-12 mg kg $^{-1}$), it may not necessarily be harmful for the crops or for human health. The farmer can make a simple test by growing green beans, which are very sensitive to arsenic. If green beans grow well in the soil, it is unlikely that the uptake of arsenic into vegetables or other crops will be high enough to pose a health risk. To make sure, it is better to send a crop sample to the laboratory for arsenic analysis. However, analytical results from the crop sample are difficult to interpretate because in the EU or in Finland, we have no limit value for food stuffs. If the leafy vegetables or roots cannot be grown in the field, cereals are the next possibility, because arsenic is not readily translocated into the grains. The next possibility is to cultivate non-food crops for fiber industry or energy production.

Use of low-arsenic fertilizer preparations and low-arsenic feed preparations. To control additional accumulation of arsenic in the soil with elevated arsenic content, all the material flowing into the farm must be of the best quality available. This means that the farmer should always select the material with the lowest arsenic content. This includes all the fertilizer preparations and feed preparations, as well. In this way, the potential arsenic risk will not increase over the long term, but will decrease in the future. Particularly, in organic farming based on recycling of various waste materials, arsenic contents of fertilizer preparations and of feed prepartions should be monitored carefully and only the best ones selected for use.

Arsenic found in Finnish cultivated soils is arsenate, which is less toxic than arsenite. Also, arsenate bonds more readily to soil particles than arsenite. In addition, in intensive agricultural areas of Finland, there are often silt soils and clay soils in which phosphorus applications mobilize arsenic but decrease its uptake by the plants. Obviously, the transfer of arsenic from average Finnish cultivated soils to the crop is minor and does not pose a big risk for food chains and human health.

4. CONCLUSIONS

Arsenic in the Pirkanmaa soils is of geologic and/or anthropogenic origin. The question, which one is dominant at a particular site, can be addressed by studying the concentration pattern in the soil profile. In general, when the content increases from the top to the subsoil, the source is likely to be geologic. However, when the top soil or the humus layer has a higher content, an anthropogenic source is suspected. It is reasonable to conclude that both sources frequently contribute to the arsenic budget. However, the geological materials and processes have a strong role and control of the occurrence of arsenic on a regional scale. Except for some localised, heavily contaminated sites, the spatially extensive arsenic enrichments in Pirkanmaa have a natural origin.

Arsenic is not particularly enriched in fine sediment formations, not even in areas where the concentrations are known to be high in bedrock, till, or in groundwater. This is due to the origin of the material in the clay and silt sediments. The fine-grained material is deposited after long transport distance and, therefore, does not reflect the local geology as does the coarser material in till. However, in soil profiles the arsenic concentrations seem to increase when the grain size gets smaller. The soil type in all the studied samples was either clay or fine sand, because the large majority of the cultivated land in the Pirkanmaa region is within the fine sediments region.

The highest arsenic value was found in the clay soil in the subsoil (C horizon) layer with the clay content of 58-75%. The average arsenic content in clayey subsoil was 6.97 mg/kg (median 6.5 mg kg^{-1}) and in fine sand 3.00 mg/kg (median 3.0 mg kg^{-1}). Arsenic has a positive correlation with sampling depth. In average, the arsenic content was higher in humus layer (median 4.67 mg kg^{-1}) than in the eluvial or illuvial layer (median 3.55 mg kg^{-1}). The highest arsenic content was in forest subsoil samples (median 4.9 mg kg^{-1}).

Arsenic contents in the plough layer (median 3.9 mg kg^{-1}) were slightly higher than in the subsoil in arable land (median 3.48 mg kg^{-1}) and also higher than in the forest topsoil (median 3.55 mg kg^{-1}). Thus, the fertilizers and/or atmospheric deposition seem to have an influence on arsenic concentrations of the topsoil of arable land. The arsenic content in arable subsoil was lower than in forest subsoil. There were no indications that might suggest that arsenic would migrate to the arable soils from the high-arsenic tills or other forest soils.

The main source of arsenic in agriculture seems to be atmospheric deposition, especially in southern Finland. Other sources are fertilizer preparations (including mineral fertilizers and lime among others) and feed preparations. Commercial feed preparations are annually used in agriculture a little more than mineral fertilizers and lime together, about 1.3 million tons in Finland. In the EU and in Finland, the quality of feed preparations is regulated with maximum allowable contents for different feed types. Regulations involve a limit value not only for total contents, but also for the concentration of inorganic arsenic. The greatest output of arsenic from the soil occurred into the waters via eroded soil material. The fate of arsenic transported by the soil particles into the surface waters and the effects of arsenic on the water ecosystems should be studied. The arsenic in humus seems to have some geological base also, because the highest values were found in Lempäälä in the area of an arsenic anomaly in till.

Soil mass balances at a national level and at a farm level indicated that arsenic inputs into arable soil were slightly higher than arsenic outputs from the soil, indicating a small accumulation of arsenic in the plough layer. However, inputs and outputs were rather well balanced, on average.

Arsenic contents in the cultivated soils and food and feed crops studied at the farms were at a low national level. However, there is no limit value for foodstuffs in Finland or in the EU. In 1993, the

National Food Authority in America set the current health limits for human consumption of arsenic at 1 mg per kilogram of food (dry weight). It was proposed that the researchers and decision makers together will elaborate upon safe maximum allowable concentrations for various types of foodstuffs to evaluate and interpret the quality of the plant and animal crops and foodstuffs.

About 1% of total arsenic was soluble in arable soil, and the uptake ratio, which is a ratio of arsenic content in plant crop to arsenic content in soil, was low and varied from 0.001 in wheat grains and potato tubers to 0.004 in timothy grass. Arsenic is also practically insoluble in the forest soils with the exception of few humus samples, which showed slightly higher mobility rates.

On the basis of research results obtained, authors conclude that the farmers, their families and domestic animals that live in the Pirkanmaa region and consume home-grown food and feed crops, ingest cultivated soil or inhale dust originating from cultivated soils, do not seem to be exposed to arsenic any more than the people and animals elsewhere in Finland. Cultivated fields studied at the RAMAS-farms in the Pirkanmaa region seemed to represent typical Finnish arable soils with regards to their fertility and contaminant content.

Both inside and outside the Pirkanmaa region, there are a small number of fields containing elevated contents (>10-12 mg kg^{-1}) of arsenic for unknown reasons. Possible arsenic sources might be arsenic-containing fertilizer preparations (including waste materials), arsenic-containing commercial feed preparations via animal manure, atmospheric depositions of arsenic originating from a metal smelter or a mine in the vicinity, use of arsenic containing pesticides in the past, burning of wood treated with arsenic containing substance on the field or natural geogenic material.

Recommendations for cultivation practices were given to minimise the uptake of arsenic by plants from the soil with elevated arsenic content and to reduce human exposure to arsenic.

The RAMAS-farms and sampling sites studied in the Pirkanmaa region during this study can be joined to the national monitoring network for arable soils and used in the next sampling round, if necessary.

5. SUMMARY

RAMAS is a three-year project (2004-2007) funded by the participating organizations and the LIFE ENVIRONMENT -programme of the European Union. The acronym RAMAS arises from the project title “Risk Assessment and risk Management procedure for Arsenic in the Tampere region”. The project targets the Province of Pirkanmaa, which comprises 33 municipalities, and has 455 000 inhabitants within its area.

The project aims to produce risk area maps from the study area, in which the various sources of arsenic contamination are indicated. Health and environmental risk assessment will be produced for the region. As well, in response to the risk analyses, recommendations for the preventive/remediation measures will be presented.

The main aim of this study was to investigate the contents of arsenic and other elements in arable and forest soils and crops in the Pirkanmaa region in potentially high-arsenic areas selected according to the geochemical map of arsenic concentrations in till. Soil and plant crop sample material already collected in the Agrifood Research Finland (MTT) monitoring programme and in other Finnish projects was used in this study, as well. Other aims were to compare arsenic concentrations between the arable and forest soils, between soil layers, between crop species and between the high- and low-arsenic areas; to study effects of soil factors on the arsenic contents in soils and crops; to collect GIS-based databases to be applied in the risk assessment tasks; and to produce thematic risk maps showing high arsenic areas in agricultural and forest soil. The purpose was to expand recommendations for cultivation practices for the fields with an elevated arsenic content. Wheat grains (*Triticum aestivum* L.), potato tubers (*Solanum tuberosum* L.) and timothy grass (*Phleum pratense* L.) were suggested as selected crop species because they are important in the human food chain in Europe and globally, too.

Sampling and analysing of arable soils and crops were made by the MTT. Fifteen sites on arable land at thirteen farms were selected for sampling: five sites were under wheat cultivation; five under potato cultivation; and five under timothy grass cultivation. Clayey soils were preferred because concentrations tend to be higher in fine-grained soils than in coarse-grained soils. All the samples were collected during the 2005 growing season at the time of their normal harvest. Sampling of arable soils and crops was done at the same site and time. Both the soil and crop samples were collected as four subsamples from the corners of the sampling site, 10 x 10 m area. At each site, a crop sample and its respective soil sample from the plough layer and subsoil were taken. The Geological Survey of Finland (GTK) was responsible for collecting and analysing soil samples from the forest land of the same farms and of the same soil types. The GTK took representative soil samples from the forest soil profile.

In 2005-2006, arable soil and crop samples were analysed for arsenic and 13 other elements, including P, S, Al, Fe, Cd, Cu, Cr, Mn, Ni, Pb, V, Zn and Se. Soil samples were digested in *aqua regia* (AR) (ISO 11 466) and arsenic in plant crops were analysed by wet digestion with concentrated HNO_3 (SFS 3 044). The fertility of arable soils was studied by internationally accepted Finnish soil testing methods, which involve determinations of pH and electrical conductivity from a water solution; easily soluble macroelements from an acid (pH 4.65) ammonium acetate (AAAc) extraction solution; and microelements from AAAc-EDTA (Na_2-ethylenediaminetetracetic acid) extraction solution. The pH of the AAAc extraction solution used by the GTK was 4.8. Arsenic measurements from the soil extracts were made by graphite furnace (GTK) or graphite tube AAS (MTT) and from plant digestates by ICP-MS.

Since fine-grained soils were preferred, arable fields (n = 15) studied in the Pirkanmaa region were mostly classified into fine sand soils or clay soils, with a clay content being higher in the subsoil (a median 34.1%) than in the plough layer (a median 24.6%). The humus content of the plough layer soils was at a medium level of 3-6%, on average. A median and mean pH was 6.30 and 6.38 in the plough layer and 6.44 and 6.33 in the subsoil, respectively. Electrical conductivity was clearly higher in the plough layer than in the subsoil due to long-term applications of fertilizer preparations and farm animal manure. The fertility status of the cultivated fields were typical for Finnish arable soils, on average, with pH, P, K, S, Mg, Fe and Mn being mostly at or above the national target level, but Ca, Cu and Zn were at or under the target level.

Arsenic contents in arable soils collected from the farms in the potentially high-arsenic areas in the Pirkanmaa region were at the national level and even lower than the respective figures observed in the Pirkanmaa region in 1998, on average. Arsenic contents ranged from 2.90 to 6.80 mg kg^{-1} dw in the plough layer and from 2.84 to 4.82 mg kg^{-1} dw in the subsoil. A median and a mean value were 3.90 and 4.06 mg kg^{-1} dw in the plough layer and 3.48 and 3.72 mg kg^{-1} dw in the subsoil, respectively. Only about 1% of total arsenic was in a soluble form in the soil plough layer. Contents of other potentially toxic elements in arable soils were also typical for Finnish cultivated soils and no exceptionally high values occurred. However, other projects showed that there is a small number of Finnish fields containing an elevated arsenic content (>10 mg kg^{-1}). Hence, recommendations for cultivation practices and for reducing human exposure to arsenic were expanded.

Arsenic content in forest soils ranged from 2.17 to 8.58 mg kg^{-1} dw in the humus layer, in the eluvian and illuvial layers in clay from 2.8 to 14.2 mg kg^{-1} dw and in fine sand soils from 1.4 to 4.3 mg kg^{-1} dw. The values in forest soils were highest in subsoil samples in clay areas, varying from 4.5 to 11.7 mg kg^{-1} dw. In fine sand subsoil, the values varied from 2.4 to 3.6 mg kg^{-1} dw.

Correlations of arsenic contents in arable land to other soil factors and to arsenic contents in crops were weak because the number of cases and variation of the parameters were small. However, the soil arsenic seemed to be best correlated to the clay and humus content, on average. Arsenic contents were slightly higher in the plough layer than in the subsoil, on average. In forest land, the highest arsenic content occurred in the deepest soil layer studied, the deeper the mineral soil layer, the higher the arsenic content. The organic soil layer contained more arsenic than the next two mineral soil layers below. These two soil layers, which were comparable to the plough layer of the arable land, had a lower arsenic content than the plough layer. Instead, in the subsoil layer of the forest land contained more arsenic than the respective layer of the arable land.

A major source of arsenic in the soil layers of arable and forest land seemed to be geogenic. Obviously, surface layers have received additional arsenic from anthropogenic sources, like atmospheric deposition and fertilizer preparations.

Contents of arsenic and other elements in the crops collected from the farms in the Pirkanmaa region were at a low national level. Arsenic contents increased in the following order: wheat grains (0.005 mg kg^{-1}dw), potato tubers (0.011 mg kg^{-1} dw) and timothy grass (0.014 mg kg^{-1} dw), on average. Concentration ranges were small. Peeled potatoes contained less arsenic than unpeeled ones. Soil-to-plant uptake factors of arsenic were also low 0.001 for wheat grains and potato tubers and 0.004 for timothy grass, on average. Arsenic had one of the lowest soil-to-plant uptake factors among the elements studied. Since there was no crop sample from a high-arsenic field in Finland, it was impossible to compare the arsenic contents of the crops in high- and low-arsenic areas. According to the literature, elevated arsenic contents in crops may occur in arsenic polluted areas, but the major hazard for animal and human systems seems to be derived from direct ingestion of arsenic contaminated soil or water.

To quantify arsenic sources on arable land, the material flows of Finnish agriculture and of Finnish farms were clarified. Currently, the biggest annual material flow to farms seemed to be commercial feed preparations, which had an annual use of about 1 300 million kg. The total annual use of mineral fertilizers was over 700 million kg, and that of lime less than 500 million kg. Only about 0.4% of mineral fertilizers were imported into Finland. Farm animals produced about 20 000 million kg of manure annually and municipalities about 1 000 million kg of sewage sludge. All manure is applied to the fields and is a part of the internal flow of the farm, but only 12% of sewage sludge was used for agriculture. In addition, small amounts of other waste materials or side-products were used in agriculture. Annual crop yields and spatial atmospheric depositions were presented, too. Arsenic contents of mineral fertilizers and food stuffs are not regulated in Finland or in the EU. Instead, arsenic contents of other fertilizer preparations and feed stuffs are limited.

Net mass balances of arable soils were calculated at a national level and at a farm level. They indicated that arsenic inputs to the soil and outputs from the soil were rather well balanced, on average. On a national level, the annual net balance of arsenic varied from -0.362 to +0.138 g per ha. In southern Finland, the balance was slightly positive indicating that 0.138 g of arsenic will accumulate annually to the soil per ha. That is 0.003% of the current median arsenic content in the plough layer in one ha. If it is assumed that arsenic will continuously be accumulated at the same rate in the future, it will take for about 40 000 years before the current arsenic content in the soil will be doubled. The balance became negative to the north mainly due to the lower atmospheric deposition. There arsenic contents in soil will decrease.

At a farm level, arsenic mass balances ranged between -2.0 and +2.3 g ha^{-1} per annum and were mostly negative in the crop farms in southwestern Finland, but mostly positive on the dairy farms in the Ostrobothnia. Mean annual atmospheric depositions were 1.0 and 0.4 g ha^{-1}, respectively. Use of slag from metal industry as a soil improver was one of the biggest sources of arsenic in the farms that had used it. At the crop farms, an arsenic load from the atmosphere was of the same magnitude as the total load from all fertilizer preparations, on average, but a mean input from the fertilizer preparations was about 60% of that in the dairy farms. Mostly, arsenic inputs from various sources decreased in the following order: fertilizer preparations -> atmospheric depositions -> commercial feed preparations, on average. The major part of the total outputs of arsenic from arable soils occurred to the waters via eroded soil material and to a lesser extent via leaching. The fate of arsenic transported by the soil particles into the surface waters and the effects of arsenic on water ecosystems should be studied further. Outputs via plant and animal crops were negligible because arsenic contents were low and crop yields small in Finland. Exported manure from some dairy farms might be a moderate route for arsenic output.

Based on the present study and relatively large background data material, the authors concluded that farmers, their families and farm animals living in the Pirkanmaa region mostly seem to be exposed to arsenic by consuming home-grown food, feed and forest crops, by ingesting soil or inhaling dust originating from the soils to the same extent as people and animals elsewhere in Finland. However, this study cannot exclude the fact that there may also be some locally naturally high-arsenic arable and forest soils in the Pirkanmaa region.

6. YHTEENVETO

RAMAS on kolmivuotinen projekti (2004-2007), jonka rahoittavat projektiin osallistuvat yhteistyökumppanit ja Euroopan Unionin LIFE ENVIRONMENT –tutkimusohjelma. Lyhenne RAMAS tulee projektin nimestä "Risk Assessment and risk Management procedure for Arsenic in the Tampere region". Projekti kohdistuu 33 kuntaa käsittävään Pirkanmaan alueeseen, jonka asukasluku on 455 000.

Projektin tavoitteena on tuottaa koko Pirkanmaan kattava riskialuekartta, joka osoittaa eri päästölähteiden aiheuttamat arseenilla likaantuneet alueet. Myös terveydelliset ja ekologiset riskit tullaan kartoittamaan. Lisäksi riskianalyysitulosten perusteella tullaan antamaan ennalta ehkäiseviä/korjaavia suosituksia.

Tämän tutkimuksen tavoitteena oli selvittää arseenin ja eräiden muiden alkuaineiden pitoisuuksia pelto- ja metsämaissa sekä sadoissa sellaisilla Pirkanmaalla alueilla, joilla geokemialliset kartat osoittavat olevan suuria arseenipitoisuuksia moreenissa. Maa- ja elintarviketalouden tutkimuskeskuksen (MTT) sekä muiden suomalaisten projektien maa- ja satonäytemateriaaleja oli tarkoitus hyödyntää tausta-aineistona. Tavoitteena oli myös verrata arseenipitoisuuksia pelto- ja metsämaiden välillä, maakerrosten välillä, kasvisatojen välillä sekä puhtaiden ja arseenia runsaasti sisältävien alueiden välillä, tutkia maaperätekijöiden vaikutuksia maan ja kasvien arseenipitoisuuksiin, kerätä GIS-pohjainen tietopankki sovellettavaksi riskinarviointiin ja tuottaa alueellisia arseeniriskejä kuvaavat teemakartat pelto- ja metsämaista. Tutkittaviksi kasvilajeiksi ehdotettiin Euroopan ja myös muun maailman elintarviketuotannon tärkeimpiä satokasveja: vehnää (*Triticum aestivum* L.), perunaa (*Solanum tuberosum* L.) ja timoteita (*Phleum pratense* L.).

Maa- ja satonäytteiden keruun pelloilta suoritti MTT. Kolmeltatoista pirkanmaalaiselta tilalta valittiin 15 näytepistettä, joista viidellä kasvoi vehnää, viidellä perunaa ja viidellä timoteinurmea. Savipitoisia maalajeja pidettiin tutkimukseen sopivimpina, koska alkuaineiden pitoisuudet ovat yleensä suurempia hienojakoisilla maalajeilla kuin karkeilla mailla. Kaikki näytteet kerättiin kasvukauden 2005 aikana ja kunkin kasvin normaaliin sadonkorjuun aikaan. Kustakin tutkittavasta tutkimuspisteestä otettiin näytteet muokkauskerroksesta ja jankosta ja myös sadosta samana päivänä neljänä osanäytteenä kunkin tutkimuspisteen, 10 m x 10 m, kulmista. Geologian tutkimuskeskus (GTK) keräsi samoilta tiloilta profiilinäytteet metsämaasta, joiden maalaji oli sama kuin tilalta otetun peltomaan maalaji.

Vuosina 2005 ja 2006 peltomaa- ja satonäytteistä analysoitiin arseeni ja 13 muuta alkuainetta (P, S, Al, Fe, Cd, Cu, Cr, Mn, Ni, Pb, V, Zn and Se). Alkuaineiden kokonaispitoisuudet maasta määritettiin kuningasvesiuutosta, *aqua regia* (AR) (ISO 11 466), ja kasvinäytteiden pitoisuudet typpihappohajotuksesta (SFS 3 044). Maiden yleiset ominaisuudet sekä helppoliukoiset alkuaineet määritettiin kansallisen viljavuustutkimuksen menetelmillä. Maan pH ja johtoluku mitattiin vesiliuoksesta, helppoliukoiset pääravinteet happamasta ammoniumasetaattiuutosta (AAAc) (pH 4,65 MTT; pH 4,8 GTK), ja hivenaineet AAAc-EDTA (natriumetyleeniamiditetraetikkahappo) –uutosta. Maanäytteistä arseeni mitattiin grafiittiuunniatomiabsorptiospektrometrisesti (GFAAS), kasvinäytteistä plasmaemissiomassa-spektrometrisesti (ICP-MS).

Tutkitut peltomaat (n = 15) olivat enimmäkseen hiesu- tai savimaita, koska jo näytteiden valinnassa suosittiin hienojakoisia maalajeja. Savespitoisuus oli suurempi jankossa (mediaani 34,1%) kuin muokkauskerroksessa (mediaani 24,6 %). Humuspitoisuus muokkauskerroksessa oli keskimääräisellä tasolla (3-6 %). Keskimääräinen pH oli 6,30 ja mediaani 6,38 muokkauskerroksessa ja jankossa vastaavasti 6,44 ja 6,33. Sähkönjohtokyky oli muokkauskerroksessa selvästi korkeampi kuin jankossa johtuen lannoitevalmisteiden ja karjanlannan käytöstä. Maan pH, P, K, S, Mg, Fe ja Mn olivat viljavuustutkimuksen tulkinnan mukaan useimmiten kansallisen tavoitetason yläpuolella, mutta Ca, Cu ja Zn tavoitetason alapuolella.

Peltomaiden arseenipitoisuudet tutkituilla pirkanmaalaisilla tiloilla olivat kansallista tasoa ja jopa pienempiä kuin oli todettu Pirkanmaalta vuonna 1998 kerätyistä maanäytteistä. Arseenipitoisuudet vaihtelivat välillä 2,90 ja 6,80 mg kg^{-1} ka muokkauskerroksessa ja välillä 2,84 ja 4,82 mg kg^{-1} ka jankossa. Mediaani oli 3,90 ja keskiarvo 4,06 mg kg^{-1} ka muokkauskerroksessa ja vastaavasti 3,48 ja 3,72 mg kg^{-1} ka jankossa. Noin 1 % maan arseenista oli liukoisessa muodossa. Myös muiden tutkittujen alkuaineiden pitoisuudet olivat tyypillisiä suomalaisille viljelymaille eikä poikkeuksellisen korkeita arvoja tavattu. Kuitenkin muiden projektien mukaan Suomessa on joitakin peltoja, joissa on kohonneita arseenipitoisuuksia (>10 mg kg^{-1}). Tästä syystä annettiin suosituksia viljelytoimenpiteistä, joilla voidaan vähentää ihmisten altistumista arseenille ravintoketjun kautta.

Arseenipitoisuudet metsämaissa vaihtelivat välillä 2,17 ja 8,58 mg kg^{-1} ka orgaanisessa eli humuskerroksessa, eluvian- ja illuvial-kerroksessa savessa välillä 2,8 ja 14,2 mg kg^{-1} ka ja hiesuissa välillä 1,4 ja 4,3 mg kg^{-1} ka. Arvot olivat suurimmillaan pohjamaanäytteissä savialueilla vaihdellen välillä 4,5 ja 11,7 mg kg^{-1} ka. Hiesulla pohjamaan arvot vaihtelivat välillä 2,4 ja 3,6 mg kg^{-1} ka.

Peltomaiden arseenipitoisuus korreloi heikosti muihin maaperätekijöihin ja satojen arseenipitoisuuksiin, koska sekä tutkittujen tapausten lukumäärä että vaihtelu parametrien välillä oli pieni. Kuitenkin maan arseenipitoisuus korreloi parhaiten, ja positiivisesti, saves- ja humuspitoisuuteen. Arseenipitoisuudet olivat keskimäärin hiukan suurempia muokkauskerroksessa kuin jankossa. Metsämaassa korkeimmat arseenipitoisuudet esiintyivät syvimmissä maakerroksissa. Mitä syvemmällä mineraalimaakerros sijaitsi, sitä suurempi oli arseenipitoisuus. Orgaanisen kerroksen arseenipitoisuus oli korkeampi kuin seuraavan kahden alapuolella olevan mineraalimaakerroksen keskimääräinen pitoisuus. Nämä kaksi maakerrosta, joiden katsottiin vastaavan peltomaan muokkauskerrosta, sisälsivät arseenia vähemmän kuin muokkauskerros. Sen sijaan jankkoa vastaavan kerroksen arseenipitoisuus oli metsämaassa suurempi kuin jankon.

Sekä pelto- että metsämaan maakerrosten pääasiallinen arseeni lähde näytti olevan kallioperä. Ilmeisesti lisää arseenia on tullut pintamaahan ihmisen toimintojen seurauksena, kuten laskeumista ja lannoitevalmisteista.

Myös pirkanmaalaisilta tiloilta kerättyjen kasvisatojen arseenipitoisuudet, ja myös muiden tutkittujen alkuaineiden pitoisuudet, olivat pieniä. Keskimääräiset arseenipitoisuudet kasvoivat seuraavasti: vehnän jyvät (0,005 mg kg^{-1} ka), perunan mukulat (0,011 mg kg^{-1} ka) ja timoteikasvusto (0,014 mg kg^{-1} ka). Pitoisuuksien hajonta oli pientä. Kuorituissa perunoissa oli arseenia vähemmän kuin kuorimattomissa. Satojen arseenipitoisuuksien suhde maan arseenipitoisuuteen oli vehnälle ja perunalle keskimäärin 0,001 ja timoteille 0,004. Arseeni oli yksi niistä alkuaineista, joiden siirtyminen maasta kasveihin oli erittäin vähäistä. Satojen arseenipitoisuuksia puhtaiden ja arseenirikkaiden alueiden välillä ei voitu verrata, koska peltojen arseenipitoisuuksissa ei ollut suuria eroja. Kirjallisuuden mukaan kohonneita arseenipitoisuuksia kasveissa voi esiintyä arseenilla saastuneilla mailla, mutta ihmisille ja eläimille suurin vaara tulee arseenilla kontaminoituneen veden käytöstä ja kontaminoituneen maan syömisestä.

Peltomaiden arseenilähteiden merkittävyyden määrittämiseksi selvitettiin Suomen maatalouden ja suomalaisten maatilojen materiaalivirtoja. Nykyisin maatilojen suurimman materiaalivirran muodostavaa kaupalliset rehuvalmisteet, joita käytetään vuosittain noin 1300 miljoonaa kg. Kivennäislannoitteita levitetään pelloille vuosittain yhteensä yli 700 miljoonaa kg ja kalkkia alle 500 miljoonaa kg. Noin 0,4 % kivennäislannoitteista on tuontitavaraa. Kotieläimet tuottavat vuosittain noin 20 000 miljoonaa kg lantaa ja kunnalliset jätevedenpuhdistamot lietettä noin 1 000 miljoonaa kg. Käytännöllisesti katsoen kaikki karjanlanta levitetään pelloille ja on siten osa maatilan sisäistä kiertoa, mutta vain 12 % jätevesilietteestä käytetään maanviljelyssä. Tämän lisäksi pieniä määriä muita jätteitä tai sivutuotteita hyödynnetään maataloudessa. Vuotuisia kasvisatoja ja alueellisia laskeumia esitetään raportissa. Kivennäislannoitteiden ja elintarvikkeiden arseenille ei ole säädetty enimmäispitoisuuksia Suomessa eikä Euroopan Unionissa. Sen sijaan muille lannoitevalmisteille ja rehuvalmisteille on säädöksissä esitetty arseenille suurimmat sallitut enimmäispitoisuudet.

Peltomaiden massataseita laskettiin sekä kansallisella että maatilatasolla. Tulokset osoittivat, että arseenilisäykset maahan ja arseenipoistumat maasta olivat keskimäärin melko hyvin tasapainossa. Kansallisella tasolla arseenin nettotase vaihteli välillä -0,362 ja +0,138 g hehtaaria kohti. Eteläisessä Suomessa tase oli lievästi positiivinen osoittaen, että arseenia kerääntyy maahan hehtaarille vuosittain 0,138 g. Se on 0,003 % maan hehtaarin alalla olevasta arseenivarastosta, joka on laskettu maan nykyiseen mediaanipitoisuuteen perustuen. Jos arseenin kertymisen maahan oletetaan jatkuvan samalla nopeudella tulevaisuudessakin, kestää noin 40 000 vuotta, ennen kuin maan nykyinen arseenipitoisuus kaksinkertaistuu. Pohjoisempana arseenin nettotase oli negatiivinen johtuen pääasiassa pienemmästä arseenilaskeumasta. Siellä maan arseenipitoisuudet tulevat laskemaan.

Maatilatasolla arseenin vuotuiset nettotaseet vaihtelivat välillä -2,0 ja +2,3 g hehtaaria kohti ja olivat useimmiten negatiivisia kasvintuotantotiloilla eteläisessä Suomessa ja useimmiten positiivisia maidontuotantotiloilla Pohjois-Pohjanmaalla. Arseenin keskimääräiset vuotuiset laskeumat olivat vastaavasti 1,0 and 0,4 g hehtaarille. Terästeollisuuden kuonan käyttö maanparannusaineena oli yksi suurimmasta arseenilähteistä niillä tiloilla, joilla kuonaa käytettiin. Kasvinviljelytiloilla kaikista lannoitevalmisteista yhteensä tuleva kuormitus oli keskimäärin samaa suuruusluokkaa kuin ilmasta tuleva arseenikuormitus, mutta noin 60 % siitä, mitä se oli vastaavasti maidontuotantotiloilla. Arseenilisäykset eri lähteistä olivat suurimmasta pienimpään keskimäärin seuraavat: lannoitevalmisteet -> ilmasta tulevat laskeumat -> kaupalliset rehuvalmisteet. Suurin osa arseenista poistuu viljelymaista vesiin erodoituneen maa-aineksen mukana ja vain vähäisessä määrin huuhtoutumalla. Maahiukkasten mukana vesiin kulkeutuneen arseenin käyttäytymistä ja vaikutuksia vesiekosysteemeihin tulisikin jatkossa selvittää. Arseenin poistuminen kasvi- ja eläinsadoissa oli vähäistä, koska Suomessa satomäärät ja arseenipitoisuudet olivat pieniä. Maidontuotantotilalla lannan vienti toiselle tilalle saattoi olla kohtuullisen hyvä keino vähentää arseenikuormitusta omalla tilalla.

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ANNEX 1

Quality control

The uncertainties were calculated using the following formula (FINAS 1996):

Uncertainty:

$$B = z * U, where$$

z = confidence factor, number 2 in 95 % confidence limit
U= Combined uncertainty

$$U = \sqrt{Usystematic^2 + Urandom^2}, where$$

$Usystematic$ = Systematic error
$Urandom$ = Random error

In the MTT Laboratories, every tenth sample is generally analysed as a duplicate. The systematic and random errors were calculated according to FINAS (1996). For non accredited methods, detection limits and uncertainties have been calculated from the results of blanks and samples analysed in RAMAS-project. This means that data for the calculations is very small and not representative generally. Most of the analytical results that were above detection limits. AAAc-EDTA extractable arsenic measurements gave results that were very low and indicated only the general concentration level. Also, arsenic concentrations in plant samples were low (Table 1).

Table 1. Uncertainties (%) in 95% confidence limit of analytical methods used in MTT Laboratories (all exept accredited methods calculated from the data of RAMAS-project).

Element	**AR extraction**	**HNO_3 digestion**	**AAAc or AAAc-EDTA extraction**
	Uncertainty %	**Uncertainty %**	**Uncertainty %**
Al	4.0	20.0	10.0
As	20.0	20.0	160
Cd*	15.0	8.0	20.0
Cr	20.0	90.0	30.0
Cu*	10.0	6.0	9.0
Fe	4.0	9.0	20.0
Mn	5.0	5.0	4.0
Ni	20.0	9.0	30.0
P	5.0	5.0	20.0
Pb*	20.0	40.0	14.0
Se	27.0		
V	20.0	70.0	4.0
Zn*	15.0	4.0	40.0
S**	10.0	7.0	10.0

* method accredited for soil analyses, *aqua regia* extraction

** Total S in soils, method SFS 3044:1980

The accuracy of the analytical methods was tested by determining certified or in-house reference materials depending on the analysed element and matrix. Also, interlaboratory comparison test materials were used as it was difficult to find certified references for V, Cr and As determinations from soil and various food matrices. The relative differences between the theoretical value and test results were generally below ±10%. Only Cr, Ni, and V showed higher relative differences in some reference materials (-39-15%). Results of the references were also used in the calculation of systematic error (FINAS 1996).

According to the MTT Laboratory’s quality system, the laboratory participates regularly in suitable interlaboratory comparison tests. However, for soil matrices not many comparison tests have been organized. Therefore, in spring 2005 the MTT itself organized a small comparison test for trace element analyses from soil matrices. Four laboratories participated in the test that included 3 soil samples: coarse mineral soil, clay soil and organic soil and 10 trace elements: Cd, Pb, Hg, Cr, Cu, Ni, Zn, V, As and Se. The results of the MTT Laboratory’s results were acceptable (z-value below ± 2) with the exception of the V measurement in coarse mineral soil sample.

According to the GTK Quality Control System, the duplicated analyses were made for 5% of the soil samples. In addition, at least one duplicated analysis per indent was also made. The results of duplicated analyses for the Pirkanmaa region soil samples taken in 2005-2006 were gathered and standard deviations (SD) of the measurements of different parameters were calculated. These values were converted into relative standard deviations (RSD, %) and the results were used to evaluate random error. Uncertainties (%) have been evaluated for all accredited analyzing methods, so these values calculated for soil samples of Pirkanmaa can be compared to those uncertainties calculated in 2004-2006.

Uncertainties (%) for the multi-elemental analyses of *aqua regia* (AR) extracted soils by ICP-AES technique are presented in Table 2. Uncertainties (%) for the multi-elemental analyses of HNO_3 extracted soils done by the ICP-MS technique are presented in Table 3. Systematic error is evaluated by analysis of domestic and international collaborative test soil samples and Certified Reference Materials. Random error is evaluated by the analyses of CRM s and real duplicated soil samples.

The uncertainty (U*2) for the AR extracted arsenic measurements by the GFAAS technique can be 60% when the concentrations are at a low level (As 0.1 - 1.0 mg kg^{-1}). Uncertainty decreases to 40% at 1.0 - 5.0 mg kg^{-1} level and continuously to 25% at a concentration level of 5.0 - 40.0 mg kg^{-1} (calculated in Kuopio, 2006). Uncertainties (U*2) are not available for AAAc-EDTA extracted soil sample’s multielemental analysis because it is not a very common method at the GTK Geolaboratory.

Otherwise, the reproducibilities (%) of real duplicate analyses were calculated for all three methods (AR, HNO_3 and AAAc-EDTA extracted elements) used during the RAMAS-project from 16th Sep 2005 to 27th Sep 2006 at the Geolaboratory, GTK in Espoo. The results of other soil samples taken by GTK’s own field workers (sampling method is the same as the RAMAS soil samples) and also a few collaborative test soil samples are included in data during the period of time mentioned above. This evaluation was done to get more duplicate pairs since the amount of duplicate pairs is quite small only for the RAMAS soil samples. The results of the reproducibilities are presented in Tables 4, 5 and 6.

The reproduciblities of AR extracted soil samples are good for arsenic (6.5%) and other elements (<10%) analysed at the GTK Geolaboratory. The reproducibility is quite good by HNO_3 extraction for As (12%) and good for other elements (<10%). The reproducibility is good by AAAc-EDTA extraction for As (5.8%), but more than 15% for Mn, Ni and P. This might indicate that the sample has not been homogeneous enough or there are some specific problems in measurements of AAAc-EDTA extracted manganese and phosphorus by ICP-AES. The reason for poor reproducibility of Ni is because the results are very near detection limit for some duplicate pairs and the relative error is abnormously high. Total uncertainties of all three methods are at a reasonable level and one must keep in mind that the relative (%) errors always increase when dealing with low concentrations near detection limits.

Table 2. Uncertainties (%) in 95% confidence limit of the accredited ICP-AES method of analyzing AR extracted soil samples (calculated in 2004 at the GTK Geolaboratory, Espoo).

Element	Detection limit mg kg^{-1}	Concentration area mg kg^{-1}	Uncertainty %	Concentration mg kg^{-1}	Uncertainty %	Concentration mg kg^{-1}	Uncertainty %
Al	15.0	5 000-20 000	60				
As	5.0	5.0-10.0	40	10.0-50.0	30		
Ca	50.0	50.0-400	90	400-6 000	50	6 000-50 000	20
Cd	0.5	0.5-2.0	40				
Cr	1.0	1.0-25.0	50	50.0-100	40		
Cu	1.0	1.0-4.0	200	10.0-100	30		
Fe	50.0	4 000-10 000	30	10 000-30 000	20		
K	100	500-1 500	60				
Mg	10.0	500-10 000	40				
Mn	1.0	100-800	30	800-1200	20		
Ni	2.0	2.0-6.0	70	6.0-40.0	20		
P	50.0	50.0-200	30	200-1500	15		
Pb	5.0	5.0-10.0	95	10.0-30.0	75	30.0 - 200	20
S	50.0	50.0-100	100	100-300	30	300-800	20
V	1.0	1.0-5.0	80	5.0-50.0	50		
Zn	1.0	10.0-50.0	40	50.0-100	30	100-500	20

Table 3. Uncertainties (%) in 95% confidence limit of the accredited ICP-AES/MS method of analyzing HNO$_3$ extracted soil samples (calculated in 2006 at the GTK Geolaboratory, Espoo).

Element	Concentration area	Uncertainty
	mg kg-1	%
Al	200-12 000	20
As	0.1-5.0	20
Ca	400-3 000	15
Cd	0.01-0.5	30
Cr	0.02-25.0	25
Cu	45 658	20
Fe	400-20 000	15
K	50.0-4 000	15
Mg	100-5 000	20
Mn	1.0-150	20
Ni	42 005	25
P	50.0-400	20
Pb	1.0-100	20
S	500-10 000	20
V	0.5-30.0	20
Zn	14732	20

Table 4. Reproducibilities of AR extracted soil samples' analyses by ICP-AES technique at the GTK Geolaboratory, Espoo between 19.10.2005 – 27.9.2006. All results below detection limits were ignored and reproducibilities were calculated by taking the square root of the sum of $(RSD)^2$ (divided with number of pairs) values (Nordtest 2005).

Parameter	**Reproducibility, %**	**Number of duplicates**
Al	2.2	28
As	6.5	12
Ca	3.5	26
Cd	2.1	8
Cr	2.5	27
Cu	5.8	29
Fe	3.8	28
K	3.2	26
Mg	2.6	26
Mn	3.0	28
Ni	2.5	29
P	2.5	26
Pb	9.1	25
S	6.5	21
V	3.0	28
Zn	3.4	29

Table 5. Reproducibilities of HNO_3 extracted soil samples analysis by ICP-AES/MS technique at the GTK Geolaboratory, Espoo between 16.9.2005 – 19.6.2006. The calculations were similar to those in Table 4.

Parameter	**Reproducibility, %**	**Number of duplicates**
Al	5.7	19
As	12	13
Ca	2.8	17
Cd	5.9	14
Cr	7.8	13
Cu	5.0	13
Fe	6.3	19
K	5.8	15
Mg	3.6	17
Mn	9.0	17
Ni	5.4	13
P	3.1	17
Pb	5.2	14
S	8.5	17
V	6.1	13
Zn	2.3	15

Table 6. Reproducibilities of AAAc-EDTA extracted soil samples analysis by ICP-AES technique at the GTK Geolaboratory, Espoo between 30.9.2005 – 28.8.2006. The calculations were similar to those in Table 4.

Parameter	**Reproducibility, %**	**Number of Duplicates**
Al	5.7	24
As	5.8	13
Ca	7.2	24
Cd	8.5	13
Cr	13.0	12
Cu	5.3	15
Fe	7.5	24
K	6.8	23
Mg	3.4	24
Mn	**20.0**	24
Ni	**22.0**	19
P	**17.0**	20
Pb	14.0	14
S	7.6	14
V	15.0	14
Zn	12.0	19

ANNEX 2.

Table 1. Soil types and particle size (mm) distribution (%) of soil samples collected from the plough layer (1) and subsoil (2) of arable land in 15 sampling sites of study farms in the Pirkanmaa region and the difference in distribution between the two soil layers.

Sampling site	Soil layer	Particle size distribution, %									Soil type
		Clay	Silt		Finesand		Sand		Gravel		
Nr	Nr	<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	2 - 6	6 - 20	
			Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	
1	1	23.0	34.1	28.4	7.7	2.5	2.4	1.9	0	0	Hs 4)
1	2	24.1	32.4	31.4	7.1	2.3	2.0	0.7	0	0	Hs 4)
Difference		-1.1	1.7	-3.0	0.6	0.2	0.4	1.2	0	0	
2	1	25.2	40.3	26.0	4.1	1.7	1.9	0.8	0	0	Hs 4)
2	2	24.6	38.8	26.9	4.3	2.5	2.3	0.6	0	0	Hs 4)
Difference		0.6	1.5	-0.9	-0.2	-0.8	-0.4	0.2	0	0	
3	1	16.4	24.7	34.1	13.0	4.6	4.0	3.2	0	0	Hs 4)
3	2	18.0	28.1	33.3	12.1	3.9	3.1	1.5	0	0	Hs 4)
Difference		-1.6	-3.4	0.8	0.9	0.7	0.9	1.7	0	0	
4	1	33.1	39.2	17.1	5.4	2.2	1.9	1.1	0	0	HsS 6)
4	2	37.5	40.9	15.3	3.1	1.1	1.4	0.7	0	0	HsS 6)
Difference		-4.4	-1.7	1.8	2.3	1.1	0.5	0.4	0	0	
5	1	50.8	33.2	7.1	3.2	2.5	2.3	0.9	0	0	HsS 6)
5	2	54.9	30.0	5.6	4.6	2.8	1.8	0.3	0	0	HsS 6)
Difference		-4.1	3.2	1.5	-1.4	-0.3	0.5	0.6	0	0	
6	1	5.0	1.9	6.0	21.2	51.9	13.2	0.8	0	0	KHt 2)
6	2	1.8	1.2	5.1	21.2	59.3	11.0	0.4	0	0	KHt 2)
Difference		3.2	0.7	0.9	0.0	-7.4	2.2	0.4	0	0	
7	1	33.1	37.1	14.6	6.0	4.5	3.1	1.6	0	0	HsS 6)
7	2	36.9	36.6	12.1	6.9	3.9	2.6	1.0	0	0	HsS 6)
Difference		-3.8	0.5	2.5	-0.9	0.6	0.5	0.6	0	0	
8	1	5.5	4.5	8.3	31.4	46.4	3.3	0.6	0	0	KHt 2)
8	2	2.5	2.3	7.4	33.3	52.4	1.9	0.2	0	0	KHt 2)
Difference		3.0	2.2	0.9	-1.9	-6.0	1.4	0.4	0	0	
9	1	7.0	3.4	6.8	21.4	56.4	4.4	0.6	0	0	KHt 2)
9	2	2.4	2.0	5.0	18.2	68.5	3.4	0.5	0	0	KHt 2)
Difference		4.6	1.4	1.8	3.2	-12.1	1.0	0.1	0	0	
10	1	28.0	22.2	11.9	15.9	14.8	4.2	3.0	0	0	He 3)
10	2	34.1	32.2	8.6	11.0	8.3	3.7	2.1	0	0	HsS 5)
Difference		-6.1	-10.0	3.3	4.9	6.5	0.5	0.9	0	0	
11	1	28.8	35.9	15.5	5.8	4.3	5.9	3.8	0	0	Hs 4)
11	2	37.8	31.5	15.8	8.8	3.3	2.1	0.7	0	0	HsS 6)
Difference		-9.0	4.4	-0.3	-3.0	1.0	3.8	3.1	0	0	
12	1	23.4	21.2	9.0	8.8	18.1	15.5	4.0	0	0	He 3)
12	2	46.2	34.1	9.4	3.7	3.4	2.6	0.6	0	0	HsS 6)

Difference		-22.8	-12.9	-0.4	5.1	14.7	12.9	3.4	0	0	
13	1	23.8	15.9	8.6	8.4	11.5	23.4	8.4	0	0	HHk 1)
13	2	37.1	24.7	10.8	8.4	6.9	9.4	2.7	0	0	HeS 5)
Difference		-13.3	-8.8	-2.2	0.0	4.6	14.0	5.7	0	0	
14	1	46.4	22.0	5.7	4.8	4.7	10.4	6.0	0	0	HeS 5)
14	2	52.2	23.2	6.8	4.0	3.7	7.0	3.1	0	0	HeS 5)
Difference		-5.8	-1.2	-1.1	0.8	1.0	3.4	2.9	0	0	
15	1	24.6	36.5	29.0	5.5	1.7	1.7	1.0	0	0	Hs 4)
15	2	25.2	42.1	26.6	3.5	1.1	1.1	0.4	0	0	Hs 4)
Difference		-0.6	-5.6	2.4	2.0	0.6	0.6	0.6	0	0	
All 15 sites											
Mean difference		**-4.1**	**-1.9**	**0.5**	**0.8**	**0.3**	**2.8**	**1.5**	**0.0**	**0.0**	
Std		7.0	5.2	1.8	2.3	6.1	4.5	1.6	0.0	0.0	

1) HHk = Sand
2) KHt = Finesand
3) He = Loam
4) Hs = Silt
5) HeS = Loamy clay
6) HsS = Silty clay

ANNEX 3.

Table 1. Correlations between general soil characteristics and *aqua regia* extractable (ISO 11 466) macro- and micro-elements in topsoil of 15 fields studied in the Pirkanmaa region (plough layer/plough layer).

	Clay, %	Org C, %	Humus, %	pH(H_2O)	El. cond	P	S	Al	As	Cd	Cu	Cr	Fe	Mn	Ni	Pb	V	Zn
Clay, %	1.00																	
Org C, %	0.35	1.00																
Humus, %	0.35	1.00	1.00															
pH(H_2O)	0.39	0.64	0.64	1.00														
El. cond.	-0.16	0.54	0.54	0.31	1.00													
P	-0.04	0.36	0.36	0.40	0.10	1.00												
S	0.43	0.83	0.83	0.57	0.39	0.64	1.00											
Al	0.95	0.26	0.25	0.41	-0.26	0.05	0.38	1.00										
As	-0.10	0.64	0.64	0.39	0.29	-0.03	0.30	-0.15	1.00									
Cd	0.40	0.43	0.43	0.48	0.09	0.69	0.78	0.40	-0.05	1.00								
Cu	0.67	0.48	0.48	0.49	-0.08	0.25	0.41	0.74	0.24	0.20	1.00							
Cr	0.97	0.28	0.28	0.44	-0.22	0.00	0.37	0.99	-0.11	0.39	0.73	1.00						
Fe	0.92	0.22	0.22	0.39	-0.26	0.07	0.34	0.99	-0.16	0.34	0.78	0.97	1.00					
Mn	0.92	0.22	0.22	0.39	-0.26	0.07	0.34	0.99	-0.16	0.34	0.78	0.97	1.00	1.00				
Ni	0.98	0.40	0.40	0.44	-0.09	-0.06	0.46	0.96	0.01	0.38	0.71	0.98	0.93	0.61	1.00			
Pb	0.88	0.39	0.38	0.32	-0.11	0.20	0.57	0.88	-0.10	0.52	0.72	0.88	0.85	0.54	0.88	1.00		
V	0.92	0.36	0.36	0.54	-0.17	0.12	0.45	0.96	0.02	0.39	0.81	0.96	0.97	0.52	0.94	0.84	1.00	
Zn	0.74	0.42	0.42	0.53	-0.05	0.49	0.67	0.79	-0.12	0.79	0.57	0.77	0.75	0.61	0.74	0.81	0.76	1.00

Table 2. Correlations of general soil characteristics and *aqua regia* extractable (ISO 11 466) macro- and micro-elements between topsoil and subsoil of 15 fields studied in the Pirkanmaa region (plough layer/subsoil).

	Clay, %	Org C, %	Humus, %	P	S	Al	As	Cd	Cu	Cr	Fe	Mn	Ni	Pb	V	Zn
Clay, %	0.92															
Org C, %	0.52	0.69														
Humus, %	0.52	0.69	0.69													
P	0.45	0.52	0.52	0.63												
S	0.49	0.65	0.65	0.08	0.55											
Al	0.86	0.48	0.47	0.19	0.53	0.87										
As	0.29	0.41	0.40	-0.21	0.16	0.29	0.36									
Cd	0.70	0.79	0.79	0.29	0.78	0.63	0.37	0.65								
Cu	0.78	0.45	0.45	0.15	0.45	0.78	0.20	0.35	0.81							
Cr	0.88	0.46	0.46	0.13	0.51	0.87	0.13	0.48	0.75	0.89						
Fe	0.85	0.43	0.43	0.20	0.50	0.87	0.10	0.47	0.79	0.88	0.85					
Mn	0.85	0.43	0.55	0.07	0.62	0.61	0.20	0.63	0.35	0.65	0.56	0.56				
Ni	0.90	0.55	0.54	0.06	0.55	0.86	0.21	0.43	0.76	0.88	0.82	0.82	0.91			
Pb	0.87	0.53	0.53	0.08	0.57	0.83	0.18	0.50	0.70	0.86	0.78	0.78	0.89	0.86		
V	0.80	0.45	0.45	0.21	0.53	0.82	0.15	0.44	0.75	0.83	0.81	0.81	0.81	0.78	0.87	
Zn	0.86	0.69	0.69	0.28	0.69	0.85	0.26	0.53	0.82	0.85	0.81	0.81	0.87	0.85	0.88	0.80

Table 3. Correlations of general soil characteristics and *aqua regia* ectractable (ISO 11 466) macro- and micro-elements in subsoil of 15 fields studied in the Pirkanmaa region (subsoil/subsoil).

	Clay, %	**Org C, %**	**Humus, %**	**P**	**S**	**Al**	**As**	**Cd**	**Cu**	**Cr**	**Fe**	**Mn**	**Ni**	**Pb**	**V**	**Zn**
Clay, %	1.00															
Org C, %	0.45	1.00														
Humus, %	0.45	1.00	1.00													
pH	0.50	0.57	0.57													
El. cond.	-0.14	0.39	0.39													
P	0.42	0.36	0.36	1.00												
S	0.38	0.97	0.96	0.41	1.00											
Al	0.95	0.46	0.46	0.48	0.41	1.00										
As	0.22	0.56	0.56	0.09	0.56	0.26	1.00									
Cd	0.72	0.69	0.69	0.70	0.66	0.67	0.33	1.00								
Cu	0.89	0.42	0.42	0.42	0.37	0.96	0.33	0.57	1.00							
Cr	0.97	0.44	0.44	0.47	0.38	0.99	0.23	0.69	0.96	1.00						
Fe	0.94	0.55	0.44	0.48	0.40	0.99	0.25	0.65	0.97	0.99	1.00					
Mn	0.94	0.44	0.44	0.35	0.38	0.66	0.30	0.83	0.61	0.72	0.67	1.00				
Ni	0.98	0.55	0.55	0.43	0.49	0.97	0.34	0.73	0.95	0.98	0.96	0.76	1.00			
Pb	0.97	0.49	0.49	0.40	0.43	0.96	0.29	0.73	0.92	0.97	0.94	0.77	0.98	1.00		
V	0.88	0.54	0.54	0.50	0.50	0.93	0.26	0.69	0.92	0.93	0.96	0.68	0.92	0.89	1.00	
Zn	0.89	0.68	0.68	0.68	0.65	0.92	0.34	0.86	0.85	0.91	0.90	0.69	0.92	0.89	0.87	1.00

Table 4. Correlations of general soil characteristics and AAAc or AAAc-EDTA extractable macro- and micro-elements in topsoil of 15 fields studied in the Pirkanmaa region (plough layer/plough layer).

	Clay, %	**Org C, %**	**Humus, %**	**pH**	**El. cond**	**P**	**S**	**K**	**Ca**	**Mg**	**Al**	**As**	**Cd**	**Cu**	**Cr**	**Fe**	**Mn**	**Ni**	**Pb**	**V**	**Zn**
P	0.07	0.81	0.81	0.73	0.40	1.00															
S	-0.59	-0.21	-0.21	-0.40	0.29	-0.08	1.00														
K	0.15	0.63	0.62	0.51	0.23	0.71	-0.06	1.00													
Ca	0.53	0.79	0.79	0.92	0.32	0.75	-0.34	0.52	1.00												
Mg	0.83	0.52	0.52	0.60	0.13	0.42	-0.56	0.20	0.68	1.00											
Al	-0.32	-0.26	-0.26	-0.57	-0.31	-0.32	0.55	-0.01	-0.41	-0.63	1.00										
As	0.03	0.03	0.03	0.07	0.29	0.03	-0.22	-0.18	-0.04	0.29	-0.54	1.00									
Cd	0.26	0.32	0.32	0.36	0.18	0.17	-0.15	0.51	0.31	0.15	-0.03	0.17	1.00								
Cu	-0.21	0.43	0.43	0.39	0.26	0.74	0.46	0.51	0.47	0.04	0.15	-0.10	-0.02	1.00							
Cr	0.83	0.55	0.55	0.39	-0.13	0.21	-0.57	0.21	0.60	0.66	-0.17	-0.12	0.17	-0.05	1.00						
Fe	0.78	0.53	0.52	0.60	-0.03	0.31	-0.62	0.25	0.69	0.74	-0.44	0.14	0.37	0.01	0.89	1.00					
Mn	0.23	0.27	0.27	0.39	0.56	0.08	-0.41	0.04	0.25	0.40	-0.71	0.62	0.51	-0.36	0.11	0.38	1.00				
Ni	0.68	0.45	0.45	0.31	0.17	0.13	-0.27	0.08	0.59	0.62	-0.13	-0.07	0.14	0.09	0.77	0.69	0.16	1.00			
Pb	0.62	0.75	0.75	0.64	0.25	0.53	-0.36	0.58	0.72	0.64	-0.25	0.15	0.73	0.20	0.66	0.78	0.44	0.49	1.00		
V	0.72	0.49	0.49	0.73	0.07	0.42	-0.49	0.50	0.72	0.75	-0.52	0.07	0.43	0.14	0.67	0.84	0.38	0.56	0.74	1.00	
Zn	0.08	0.75	0.75	0.55	0.47	0.81	0.03	0.56	0.65	0.38	-0.20	0.19	0.45	0.66	0.26	0.43	0.27	0.33	0.68	0.36	1.00

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The project will produce a number of Technical Reports. The following reports have been published:

1. Natural Occurrence of Arsenic in the Pirkanmaa Region in Finland
2. Anthropogenic Arsenic Sources in the Pirkanmaa Region in Finland
3. Arseenista aiheutuvien riskien hallinta Pirkanmaalla – Esiselvitys ohjaus keinoista ja teknisistä menetelmistä riskien vähentämiseksi (Management of arsenic risks in the Pirkanmaa region – Survey of available risk management instruments and tools)
4. Arsenic and other elements in agro-ecosystems in Finland and particularly in the Pirkanmaa region

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