



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



# Natural Occurrence of Arsenic in the Pirkanmaa Region in Finland

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## Abstract

**Backman, B., Luoma, S., Ruskeeniemi, T., Karttunen, V., Talikka, M. & Kaija, J. 2006. Natural Occurrence of Arsenic in the Pirkanmaa region in Finland. Geological Survey of Finland, Miscellaneous Publications, 82 pages, 34 Figures, and 20 Tables.**

This report aims to describe the distribution and occurrence of natural arsenic in the study area. The information from different sources, research institutes, municipalities and regulatory authorities, has been combined. In addition, some studies were conducted to fill in knowledge gaps in the case of inadequate or lacking data.

Natural arsenic in the area is derived from the arsenic bearing minerals, which are locally enriched in the bedrock. Due to the action of geologic and geochemical processes, arsenic has transferred to groundwater and soils. In Finland, the glaciogenic events were particularly important in dispersing arsenic into the surrounding areas. The study area was divided into three units based on geological grounds and the geochemical data was reviewed according to the division. In the northern half of the area, the Central Finland Granitoid Complex (CFGC), the arsenic concentrations in all geologic media were at the average level encountered in the country. The arsenic problem is clearly focused in the Tampere Schist Belt (TB) and the Pirkanmaa Belt (PB), where metamorphosed volcanites comprise a major part of the bedrock. Based on 603 lithogeochemical samples, the arsenic concentrations varied from 0.1 to 377 mg/kg. The median in the TB was 2.2 mg/kg, 1.9 mg/kg in the PB and 1.0 mg/kg in the CFGC.

Arsenic concentrations in shallow groundwater and surface waters are generally below 1 µg/L. Hence, arsenic is not an issue for the public water supply, which is based on these shallow water reserves. The major concern is focused on drilled wells, which are used by private households and other small units. Altogether, 1272 arsenic analyses from drilled wells were available. In 22.5 % of the wells the limit value, 10 µg/L, was exceeded. All these arsenic wells are located in the southern part of the study area. The median value for drilled wells in the TB was 5.5 µg/L, 1.6 µg/L in the PB and 0.61 µg/L in the CFGC. Most of the samples that had arsenic speciation analysis were arsenate ( $\text{As}^{5+}$ ) dominated.

As many as 10 869 arsenic analyses were available from the till, which is the main soil type in Pirkanmaa. Most of the samples were collected during ore exploration from areas known to be enriched in heavy metals. Part of the data has been produced by the nationwide survey to characterize the geochemistry of tills. The regional arsenic anomaly extending from Pirkanmaa towards south was already recognized in this data. The median value for arsenic in Pirkanmaa was double compared to the rest of the country (5.3 mg/kg vs. 2.6 mg/kg). The highest median values in tills are encountered in the TB (5.92 mg/kg) and the PB (11.5 mg/kg). Arsenic concentrations tend to increase downwards in the soil profile and the highest concentrations were generally in the basal part of the sequence. The highest encountered concentrations (max. 9 280 mg/kg) from the area clearly exceeded the limit value for contaminated soil (50 mg/kg).

Locally high arsenic concentrations in bedrock groundwater may pose a risk for public health and environment in the southern part of the Pirkanmaa region, if the exposure is not limited by appropriate measures. In shallow groundwater and surface water the arsenic concentrations were low and there is no risk for use of them. In some cases the high arsenic content in bedrock and soil may give rise to environmental problems in long-term. However, much can be done if the problem is recognized and the land use practices are planned accordingly.

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Keywords (GeoRef, Thesaurus): arsenic, geochemical surveys, bedrock, soils, till, groundwater, surface water, water quality, risk assessment, Pirkanmaa, Finland.

## Tiivistelmä

**Backman, B., Luoma, S., Ruskeeniemi, T., Karttunen, V., Talikka, M. & Kaija, J. 2006. Natural Occurrence of Arsenic in the Pirkanmaa region in Finland. Geologian tutkimuskeskus, Erikoisjulkaisut, 82 sivua, 34 kuvaa ja 20 taulukkoa.**

Tässä tutkimuksessa on selvitetty luonnollista alkuperää olevan arseenin pitoisuuksia Pirkanmaan alueella. Kaikki aikaisemmin tuotettu arseenipitoisuustieto eri tutkimuslaitoksista, viranomaisilta ja kunnista on koottu tietokantaan ja tehty tarvittavissa kohteissa täydentävää näytteenottoa. Luontainen arseeni on peräisin kallioperän arseenipitoisista mineraaleista, useimmiten arseenikiisusta. Kalliosta arseenia on siirtynyt geologisten ja geokemiallisten prosessien seurauksena maaperään, pintavesiin ja pohjavesiin.

Tutkimuksessa Pirkanmaan alue jaettiin geologisen ja geofysikaalisen tiedon perusteella kolmeen vyöhykkeeseen. Suuria arseenipitoisuuksia havaittiin kahdessa eteläisemmässä osassa: Tampereen liuskevyöhykkeellä (TB) ja Pirkanmaan migmatiittivyöhykkeellä (PB). Pirkanmaan pohjoisosan granitoidivyöhykkeellä (CFGC) pitoisuudet olivat samalla alhaisella tasolla, kuin koko maassa keskimäärin. Kallioperästä on otettu 603 näytettä, joissa arseenipitoisuus vaihteli <0,1–377 mg/kg, TB vyöhykkeellä mediaani oli 2,22, PB vyöhykkeellä 1,9 ja CFGC vyöhykkeellä mediaan oli samaa suuruus luokkaa, 1,0 mg/kg, kuin koko maassa. Myös kalliopohjaveden pitoisuudet olivat suuria TB ja PB vyöhykkeen porakaivovesissä. Porakaivovesistä oli kaikkiaan käytettävissä 1272 arseenimääritystä. Näiden mediaani oli 2,5 µg/L. TB vyöhykkeen porakaivovesien mediaani oli 5,5 ja PB vyöhykkeellä 1,6 µg/L. Pohjoisosan graniittivyöhykkeellä mediaani oli 0,61 µg/L ja koko maan vastaava luku oli 0,16 µg/L. Suurimmassa osassa näytteissä, joissa tehtiin arseenin spesiaatiomäärittäminen oli arsenaatti ( $\text{As}^{5+}$ ) hallitseva. Maaperän pohjavedessä arseenipitoisuudet olivat huomattavasti alhaisempia, mutta mediaanit olivat kuitenkin suurempia TB (0,32 µg/L) ja PB (0,22 µg/L) vyöhykkeillä, kuin CFGC vyöhykkeellä, jossa mediaani (0,15 µg/L) oli lähes sama kuin koko maan mediaani (0,14 µg/L). Talousvedelle sallittu raja-arvo 10 µg/L ylittyi 22,5 % porakaivovesissä ja 1 % maaperän rengaskaivo- ja lähdevesissä.

Pintavesissä arseenipitoisuudet olivat alhaisia: purovesien mediaani oli 0,9 ja järvivesien <1,0 µg/L. Ainoastaan pintavesissä, jotka tulivat kaivosalueilta, joissa louhittiin ja läjitettiin arseenipitoisia kiviä, oli kohonneita arseenipitoisuuksia. Kaikki Pirkanmaalla olevat vedenottamot käyttävät raakavetenä maaperän pohjavettä tai pintavettä. Kaikissa tutkituissa vedenottamovesissä oli hyvin alhaiset arseenipitoisuudet, kaikki tulokset olivat määrittämissä tunteissa.

Alueelta on otettu kaikkiaan 10 869 maaperänäytettä moreenimailta. Suurin osa näytteistä on otettu malminetsintää varten, joten ne sijoittuvat alueille, joissa on korkeita metallipitoisuuksia. Osa maaperänäytteistä liittyy koko maan kattavaan geokemialliseen moreenikartoitukseen ja tämän aineiston arseenipitoisuuden mediaani on Pirkanmaalla 5,35 mg/kg ja koko maan mediaani on 2,6 mg/kg. TB ja PB vyöhykkeellä on arseenipitoisuudet suurempia (mediaanit 5,92 ja 11,5 mg/kg) kuin granitoidivyöhykkeellä (mediaani 3,72 mg/kg). Luonnollista alkuperää oleva arseenipitoisuus maaperässä suurenee alaspäin mentäessä ja lähellä kalliopintaa pitoisuudet ovat suurimmat. Malminetsintään liittyvissä näytteissä pitoisuudet olivat paikoin hyvin suuria, suurin pitoisuus oli 9 280 mg/kg. Pilaantuneen maan raja-arvo 50 mg/kg ylittyi monin paikoin.

Kalliopohjaveden suuret arseenipitoisuudet aiheuttavat Tampereen liuskevyöhykkeellä ja Pirkanmaan migmatiittivyöhykkeellä kohonneen terveys- ja ympäristöriskin. Maaperän pohjavedessä ja pintavedessä arseenipitoisuudet ovat sitä vastoin pieniä, eikä riskiä käytön suhteen ole. Kallioperän ja maaperän suuret arseenipitoisuudet voivat aiheuttaa ympäristöriskin pitkällä aikavälillä ja tämä ongelma on tarpeen huomioida maankäyttösuunnittelussa.

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Asiasanat (Geosanasto, GTK): arseeni, geokemialliset tutkimukset, kallioperä, maaperä, moreeni, pohjavesi, pintavesi, veden laatu, riskin arviointi, Pirkanmaa, Suomi.



## PREFACE

RAMAS (LIFE04 ENV/FI/000300) is a three-year project that 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 Centre (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), comprised of 33 municipalities, and 455 000 inhabitants within its area. Tampere, Finland's third largest city, is the economical and cultural centre of the region.

The goal of the project is 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 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 will produce a number of Technical Reports, which will be published as a special series by GTK. Each report will be an independent presentation of a topic of concern. More comprehensive conclusions will be published in the Final Report of the RAMAS project, which will summarize the projects results. Most of the reports will be published in English with a Finnish summary.

This is the first report in the series. In the future, a cumulative list of reports published so far will be located on the back cover of each report. All documents can be also downloaded from the project's home page: [www.gtk.fi/projects/ramas](http://www.gtk.fi/projects/ramas)

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## 1. INTRODUCTION

The history of arsenic research in Pirkanmaa is a good example of the common interests, which seemingly contradicting activities may have. In this case, environmental research benefits from the work done for ore exploration. The Pirkanmaa region (also called the Tampere region) was the target of intensive gold exploration in the 1980's. During the exploration phase, high arsenic concentrations were observed in accompany with the gold deposits. Thus, after 1992 when the Geolaboratory of the Geological Survey of Finland (GTK) began to routinely analyse arsenic from groundwaters, the regional hydrogeochemical mapping was focused in southern Finland. The results of the mapping showed that arsenic concentrations in the drilled bedrock wells near the gold findings were elevated in some cases. Most of the wells were used as a private water supply. Likewise, anomalous arsenic concentrations were observed in the soil cover (Koljonen *et al.* 1992). At the same time, some alarming findings – mainly from Taiwan and Bangladesh – were published concerning the toxic effects of arsenic in drinking water. For example, the 'Black Foot Disease' was connected to high arsenic content in drinking water. In 1993, as a consequence of these findings the WHO recommended that the health limit value of arsenic in drinking water should be reduced from 50 µg/L to 10 µg/L (WHO 1993). The Finnish Ministry of Social Affairs and Health (STM) followed the recommendation and set the limit value of 10 µg/L for arsenic in water for water plants and private wells (STM 1994a, 1994b). A decree on arsenic in soil is in process at the moment. According to the draft document (Valtioneuvoston asetus maaperän pilaantuneisuuden ja puhdistustarpeen arvioinnista, draft 2.2.2006), the national baseline value in soil will be 2.6 mg/kg, with a range of 0.3 – 20 mg/kg depending on the type of soil. A lower limit value of 50 mg/kg for populated areas and an upper value of 100 mg/kg for industrial areas will be established. The proposed standard values are based on ecotoxicological information. The decree is expected to be established in 2006.

In 1994, the GTK conducted a study funded by the STM, to survey the arsenic contents in drilled wells in southern Finland (Backman *et al.* 1994). Due to this study, the arsenic problem was highlighted in the Pirkanmaa and other areas. Over the next past several years, some basic risk assessment was carried out in certain municipalities of Pirkanmaa in conjunction with the local authorities and the GTK.

In 1999, the GTK carried out a countrywide groundwater quality mapping. This mapping project further confirmed that the high arsenic in groundwater was focused in certain regions of Finland, and one of the major anomalies was located in the highly populated region between the cities of Tampere (the capital of the Pirkanmaa region) and Helsinki. A comprehensive volume of arsenic in Finnish nature was published in 2004 (Loukola-Ruskeeniemi & Lahermo 2004). The publication describes the distribution of arsenic in Finnish bedrock, ore deposits, overburden, vegetation and natural waters.

Based on the above-mentioned studies, the Pirkanmaa region was appraised as a very important test area for risk assessment and risk management procedures. The urgent need and the extensive background information led to a development of a proposal to EU for more detailed risk evaluation. The proposal was successful and in 2004, the EU-Life Environment program granted 50 % support funding for the research project “**Risk assessment and Risk Management for Arsenic in the Tampere region**” or 'RAMAS' (LIFE04 ENV/FI/000300).

Over the few years, more and more findings concerning environmental arsenic problems have been documented in other European countries, such as Hungary, Slovakia, and Romania. The new

information and know-how acquired from the RAMAS-project can be applied to other regions in Finland and, with some modifications, in other European countries suffering from arsenic problems.

## 2. ARSENIC IN NATURE

### 2.1 General properties of arsenic

Elemental arsenic (As) is a member of Group 15 of the periodic table, along with nitrogen, phosphorus, antimony and bismuth. The atomic weight is 74.9216 and the atomic number is 33 (CRC 1986). Arsenic is the 20<sup>th</sup> most abundant element in the Earth's crust at a concentration of 1.5 - 2 mg/kg (Reimann & Caritat 1998). Elemental arsenic is steel grey, very brittle, crystalline, semi-metallic solid. It tarnishes in air and when heated, it is rapidly oxidised to arsenous oxide (As<sub>2</sub>O<sub>3</sub>). Arsenic and its compounds are poisonous (CRC 1986).

Globally, natural arsenic is found native, as oxides (*e.g.* arsenolite: As<sub>2</sub>O<sub>3</sub>), sulphides (*e.g.* realgar: As<sub>4</sub>S<sub>4</sub>), as arsenides (*e.g.* nickeline: NiAs) and sulfarsenides of heavy metals (*e.g.* arsenopyrite: FeAsS). In addition, traces of arsenic may be present in numerous other minerals. Arsenopyrite (FeAsS) is the most common arsenic mineral (Fig. 1).

Arsenic is a redox sensitive element, which means that it may be present in a variety of redox states. The common oxidation states are -3, 0, +3, and +5. Arsenic species in aqueous systems consist principally of arsenite, (As<sup>3+</sup>), and arsenate (As<sup>5+</sup>) oxyanions. Rarely, in strongly reducing environments, elemental arsenic (As) and gaseous arsine (AsH<sub>3</sub>) can exist. Under oxidising conditions, the predominant form of arsenic in water and soil is the oxidised form, arsenate (As<sup>5+</sup>), while under more reducing conditions, arsenite (As<sup>3+</sup>) may be the dominant arsenic species. At a near neutral pH, which is common for groundwaters, arsenate is present as negatively charged oxyions, H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> or HAsO<sub>4</sub><sup>2-</sup>, whereas arsenite remains in the form of uncharged H<sub>3</sub>AsO<sub>3</sub> until the pH is raised to 9. The geochemical properties of these dissolved arsenic forms differ, and this combined with the prevailing conditions in the water- rock/soil system has significant implications on the behaviour of arsenic in the environment.

The major factors affecting the dispersion of arsenic into the environment are:

- Release of arsenic from the primary source (*e.g.* dissolution of As minerals)
- Adsorption/desorption on the positively charged surfaces of solid phases and precipitation/dissolution of arsenic phases are the major mechanisms controlling the mobility of arsenic
- The presence of other ions (mainly phosphate) competing for the sorption sites
- The reduced arsenic species (arsenite) is reported to be more toxic than arsenate



Figure 1. Arsenopyrite (FeAsS) dikes (grey colour) in rock sample from Nokia. Photo J. Väättäinen, GTK.

## 2.2 Natural arsenic sources

Arsenic is a natural component in bedrock, originally introduced into the rock-forming minerals or in specific arsenic-bearing minerals during their initial crystallisation from magma. Numerous geological processes have reworked the bedrock and released and again re-deposited components, including arsenic. The more recent low temperature processes have dispersed arsenic to locations where it is more susceptible to dissolution and transport to biosphere, such as, water-conducting fractures in bedrock and the soil cover. In Nordic countries, the wearing of bedrock due to the action of the continental ice sheet has been particularly important and has resulted in widespread arsenic anomalies in till.

Arsenic is ubiquitous in nature and it ranks twentieth among the elements in abundance in the Earth's crust. The abundance of arsenic in the continental crust is generally given as 1.5-2 ppm (NRC 1977, Reimann & Caritat 1998). Thus, it is relatively scarce. Nevertheless, it occurs as a major constituent in more than 200 minerals (NRC 1977, Smedley & Kinniburgh 2002). Arsenic is found in high concentrations in sulphide deposits, where it is present as the native element or alloys (four minerals), arsenides (27 minerals), sulphides (13 minerals), sulphosalts (sulphides of arsenic with metals, 65 minerals) and the oxidation products of the foregoing (two oxides, 11 arsenites, 116 arsenates and seven silicates) (NRC 1977). The greatest concentrations of these minerals occur in ores or mineralised areas and are found in close association with the transition metals, as well as Cd, Pb, Ag, Au, Sb, P, W and Mo (Smedley & Kinniburgh 2002). Of these minerals, arsenopyrite (FeAsS) is by far the most common (NRC 1977, Smedley & Kinniburgh 2002). It is generally believed that arsenopyrite, together with the other dominant As-sulphide mineral realgar and orpiment, are only formed under the high temperature conditions of the Earth's crust (Smedley & Kinniburgh 2002). However, Rittle *et al.* (1995) have reported authigenic arsenopyrite in sediments and orpiment can be formed by microbial precipitation (Newman *et al.* 1998).



### 2.2.1 Arsenic in bedrock

Arsenic is incorporated into primary rock-forming minerals only to a limited extent, for example, by the substitution of  $\text{As}^{3+}$  for  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$ . Therefore, arsenic concentrations in silicate minerals are typically about 1 mg/kg or less (Smedley & Kinniburgh 2002). Silicate minerals are generally very resistant to weathering and therefore, the elements incorporated in their crystal lattices are released only slowly. However, arsenic is also present in many non-arsenic sulphide minerals as a substitute for sulphur (S). Pyrite ( $\text{FeS}_2$ ) is the most abundant of these sulphides and is found as a minor component in most common rock types and a major component in many ore types. Pyrite is not stable in aerobic systems and oxidises to Fe oxides with the release of large amounts of sulphate, acidity and associated trace constituents, including arsenic.

High arsenic concentrations are also found in many oxide minerals and hydrous metal oxides. Absorption of negatively charged arsenate ion on hydrous Fe oxides is particularly strong and the sorbed loadings can grow appreciable, even at very low arsenic concentrations in solution (Goldberg 1986, Manning & Goldberg 1996, Hiemstra & Van Riemsdijk 1996). Adsorption on hydrous Al and Mn oxides may also be important if these oxides are present in quantity. Arsenic concentrations in phosphate minerals are variable but can reach high values up to 1000 mg/kg in apatite, for example. This may become an issue if the phosphate is quarried to produce fertilizers. However, phosphate minerals are usually much less abundant than oxide minerals and therefore they make only a small contribution to the arsenic concentration in most sediments. Carbonate minerals usually contain less than 10 mg/kg of arsenic.

Arsenic concentrations in igneous rocks, like granites, are generally low. An average value of arsenic in all undistinguished igneous rock types is 1.5 mg/kg (Ure & Berrow 1982). The arsenic concentration average of basic rocks (basalt) is 2.3 mg/kg and acidic rocks (granite) 1.3 mg/kg, but generally less than 5 mg/kg. Volcanic glasses are only slightly higher with an average of around 5.9 mg/kg (Smedley & Kinniburgh 2002).

The concentration of arsenic in sedimentary rocks is typically in the range of 5-10 mg/kg. Average arsenic contents in sediments originally from eroded igneous rocks, like sand and sandstones, tend to have the lowest arsenic concentration, reflecting the low concentrations in their dominant minerals (quartz and feldspars) (Smedley & Kinniburgh 2002). Average arsenic concentrations in sandstones are around 4 mg/kg. Significantly higher concentrations up to 900 mg/kg are found in argillaceous (clay rich) sedimentary rocks including shales, mudstone and slates. Up to 200 mg/kg of arsenic has been reported in phosphate rocks (O'Neill 1995).

Arsenic concentrations in metamorphic rocks tend to reflect the concentrations in their igneous and sedimentary precursors. Most metamorphic rocks contain around 5 mg/kg or less. Pelitic rocks (slates, phyllites and other metamorphic equivalents for clay rich sediments) typically have the highest concentrations, with an average of around 18 mg/kg (Smedley & Kinniburgh 2002).

#### 2.2.1.1. Arsenic in Finnish bedrock

Arsenic concentrations in the Finnish bedrock are generally low. The median value of 6544 lithogeochemical bedrock samples was 0.9 mg/kg and all the contents were between <0.2 and 729 mg/kg (Lahtinen *et al.* 2005a). Only about 1-2 % of the bedrock contains more than 10 mg/kg of arsenic (Eilu & Lahtinen 2004). In general, metasedimentary rocks (metamorphosed rocks of sedimentary origin) have higher arsenic concentrations than other rock types, and values higher than

10 mg/kg are commonly found in graphite- and sulphide- rich metasedimentary rocks. Generally, the high arsenic concentration in the bedrock is directly related to natural processes, like hydrothermal fluid activity. In such cases, extensive zones of arsenic enrichment may have been formed. In addition, the arsenic enriched zones typically contain narrow shear and fracture zones where further enrichment may have taken place.

In a number of ore-potential and mine areas in Finland, the arsenic concentrations are 10 – 1 000 times higher around the ore deposits and occurrences than in the surrounding bedrock (Eilu & Lahtinen 2004). Arsenic values above background are particularly common in the bedrock close to gold occurrences. The most common arsenic mineral found in Finland is arsenopyrite ( $\text{FeAsS}$ ), and to a lesser extent, loellingite ( $\text{FeAs}_2$ ), which are mostly confined to hydrothermally altered areas and other late-stage units in bedrock. Ni-bearing sulphosalts and arsenides, such as gersdorffite ( $\text{NiAsS}$ ), nicceline ( $\text{NiAs}$ ) and maucherite ( $\text{Ni}_7\text{As}_8$ ) may be locally abundant, especially in ultramafic rocks. Small amounts of arsenic may also replace sulphur in the lattice of common sulphide ore minerals, although this apparently has little significance with respect to arsenic concentrations in groundwater compared to the presence of arsenic sulphides (Backman *et al.* 1994). When arsenopyrite is disseminated in bedrock or in quartz veins, it is enclosed into a silicate matrix and arsenic does not easily leach out into the groundwater. However, when such rocks are deformed, arsenopyrite may become exposed in fracture zones, where it is more accessible to groundwater, and arsenic may then be released into the water.

### 2.2.2 Arsenic in soils and sediments

Arsenic is present in all soils and unconsolidated sediments. The natural arsenic content in uncontaminated mineral soils varies from 0.1 - 170 mg/kg. The average is 5–11.3 mg/kg, and it varies considerably among geographic regions (Boyle & Johansson 1973, Ure & Berrow 1982, Cook *et al.* 1995). The lowest concentrations of arsenic are found in sandy soils and those derived from granites, while higher levels are observed in alluvial soils and those rich in organic matter (Kabata-Pendias & Pendias 1984). Mud and clays usually have higher concentrations than sands. Values are typically 3–10 mg/kg, depending on texture and mineralogy (Smedley & Kinniburgh 2002).

High arsenic concentrations tend to reflect the amount of pyrite or iron oxides present in the soil for example, in the mineralised areas. Soils close to or derived from sulphide ore deposits may contain up to 8000 mg/kg of arsenic (NRC 1977). Under oxidising conditions, inorganic arsenate ( $\text{As}^{5+}$ ) occurs as negatively charged oxyions and may be bound to positively charged iron and aluminium cations or oxides or any other cations present such as calcium, magnesium, lead and zinc (Smedley & Kinniburgh 2002).

A recent geochemical survey, the FOREGS Geochemical Baseline Mapping Programme in Europe, reports, among others, the arsenic content in soil, stream water, stream sediment, and floodplain sediments (Salminen *et al.* 2005). The soil samples were taken from two depths; topsoil from 0 – 25 cm, and the subsoil from 50 – 200 cm. A soil sampling site in Pirkanmaa is presented in Fig 2. The *aqua regia* leach was done from grain size <2 mm. The arsenic content in topsoil was on average 9.88 mg/kg (med. 6.00 mg/kg) in 840 samples. In subsoil, the values were 9.75 mg/kg (mean), and 5.00 mg/kg (median) in 784 samples, respectively (Fig. 3).

The arsenic content in stream sediments was on average 9.58 mg/kg, and the median was 6.00 mg/kg in 794 samples with *aqua regia* leach.

According to another recent geochemical study in eastern Barents region, the median value of arsenic in the subsoil of the Middle Taiga region was 1.71 mg/kg; range 0.05 – 19.5 mg/kg, N=410 (Salminen *et al.* 2004). In this survey, a grain size of <2mm and an *aqua regia* leaching were applied.

Peat and bog soils can have higher arsenic concentrations, specifically due to the increased prevalence of sulphide mineral phases under reduced conditions. High concentrations are also found in soils and groundwater affected by geothermal activity (Welch *et al.* 2000).

During the last glaciation in high latitude regions, the advancing glacier eroded bedrock and transported glacial sediments in a down-ice direction. In the glacial till, the arsenic concentrations are 1.9-170 mg/kg (median 9.2 mg/kg) and the highest concentrations are found in tills down-ice from mineralised areas (Cook *et al.* 1995). Arsenic concentrations in lake sediments range between 0.9 and 44 mg/kg (median 5.5 mg/kg) (Cook *et al.* 1995).



Figure 2. A pit for profile soil sampling in Pirkanmaa. Photo M. Eklund.

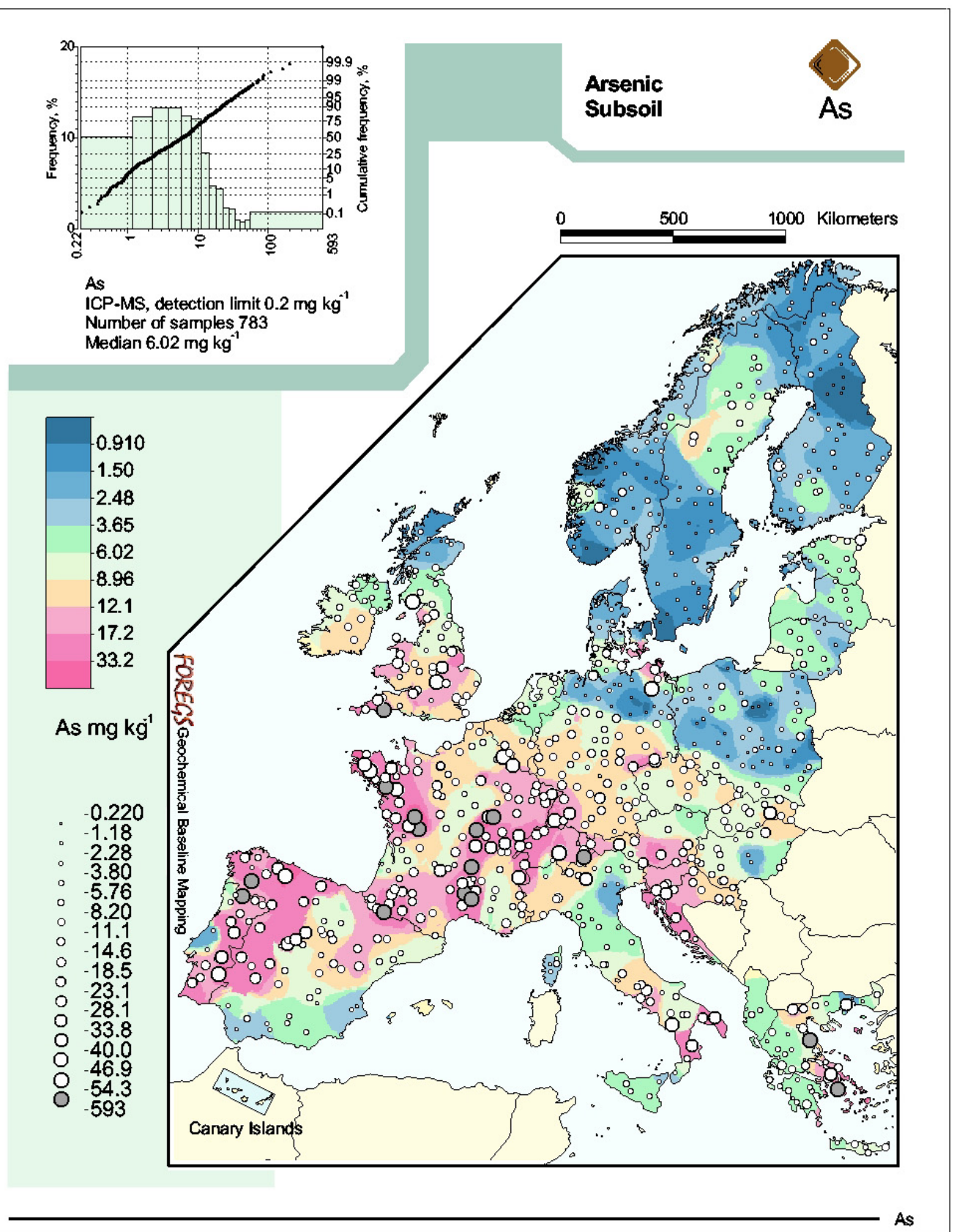


Figure 3. Arsenic in subsoil (50 – 200 cm) in Europe (Salminen *et al.* 2005).



### 2.2.2.1. Arsenic in Finnish soils and sediments

Till has been generated through the grinding of Precambrian bedrock by the thick glacial ice sheet, with minor changes in the chemical composition and with relatively short transport from the place of origin. Thus, till has a chemical composition that corresponds to the composition of the bedrock. The total arsenic concentrations in the fine fraction of till (<0.06 mm) in Finland are between 0.5 and 10 mg/kg, with an average 3.4 mg/kg and median 2.6 mg/kg (Koljonen *et al.* 1992). Arsenic concentrations are generally low (<1 mg/kg) in the areas of Archaean gneisses in eastern and northern Finland. The highest values occur in the centre of the greenstone belt in central Lapland, northern Finland (4-8 mg/kg) and in the Proterozoic volcanic sedimentary schist and gneiss rocks in southwestern Finland (10 mg/kg) (Koljonen *et al.* 1992).

The median concentrations of acid soluble arsenic in the top (0-25 cm from the surface level) and sub (50-75 cm from the surface level) layers of agricultural till soils were 1.24 mg/kg (N = 136) and 1.28 mg/kg (N = 138), respectively (Tarvainen 2004). Arsenic concentrations tend to be higher in the fine-grained agricultural soils. The median values for topsoil and subsoil are 2.4 mg/kg and 2.3 mg/kg, while the median arsenic concentrations for coarse-grained agricultural soils are distinctly lower, 0.51 mg/kg for topsoil and 0.6 mg/kg for subsoil, respectively. Agricultural soils show higher arsenic concentrations in southwestern Finland and lower concentrations in the east and northeast parts of the country, which correlates well with the distribution of arsenic observed in till.

Tarvainen *et al.* (2005), studied the arsenic concentrations in three different soil types in two municipalities, Hyvinkää and Sipoo, in southern Finland. The samples were taken from the topsoil 0-25 cm and from the subsoil (50-75 cm). The analysed material was fine fraction <2 mm and the leach method was *aqua regia*. The median values in topsoil in gravel were 2.38 mg/kg (N=60), in till 2.84 mg/kg (N=60) and in clay 6.59 mg/kg (N=60). The values in subsoil were 2.71 mg/kg (N=60), 2.98 mg/kg (N=60) and 7.22 mg/kg (N=60), respectively. The concentrations in clay are clearly higher than those in other soil types. Similar arsenic concentrations in clay have been reported in the Porvoo area, southeast Finland (Tarvainen *et al.* 2003).

Arsenic concentrations in organic stream sediments are 0.8-15 mg/kg (median 2.9 mg/kg, mean 5.4 mg/kg) (Tarvainen & Mannio 2004). The regional distribution pattern of arsenic in stream sediments resembles the pattern in till and stream water. This kind of information is valuable because it provides a means to evaluate the routes and rates of arsenic transport from the source areas.

Natural arsenic concentrations in Finnish lake sediments are 8 mg/kg on average, as determined from 130 profiles (Mäkinen 2004). Most of these sediments are clay-rich sequences deposited 9 000-10 000 years ago, after the retreat of the continental ice sheet. The portion of organic matter in the sediment varies from 6 to 15 %. The highest arsenic concentrations (maximum 35 mg/kg) are found in rather large lakes of central and southern Finland, ranging from 10 to 400 km<sup>2</sup> in size. Sedimentation of arsenic occurs in both oxidation and reduction environments. The reduced conditions are generally found in small (<10 km<sup>2</sup>) and in deep lakes. The highest arsenic concentrations are found in larger lakes in sediments where sedimentation occurs under oxic conditions.

### 2.2.3 Arsenic in surface waters and groundwaters

Natural waters normally contain arsenic as arsenate (oxidised form) and, if the water is anaerobic, as arsenite (reduced form). Methylated species (monomethylarsonic-MMA and dimethylarsinic-DMA-organic arsenic) are present in water only if special circumstances exist, such as pollution by arsenical herbicides or high biological activity (Irgolic 1994, Irgolic *et al.* 1995). Concentrations of arsenic in clean surface waters and groundwater are typically in the range of 1-10 µg/L. Elevated arsenic concentrations (>1000 µg /L) of natural origin in groundwater have been found in many areas such as in Taiwan (Chen *et al.* 1994), West Bengal, India and Bangladesh (Islam *et al.* 2000, BGS & DPHE 2001, Ahmed *et al.* 2004), in Mexico (Rodriguez *et al.* 2004), several areas of Argentina (Bundschuh *et al.* 2004), and the USA (California, Utah, Nevada, Washington and Alaska) (Welch *et al.* 2000)).

Arsenic is a widespread problem throughout most EU countries. High arsenic concentrations have been observed, for example, in groundwater from alluvial sediments in the southern part of the Great Hungarian Plain of Hungary and neighbouring parts of Romania. Varsa'nyi *et al.* (1991) reported concentrations up to 150 µg/L (average 32 µg/L, 85 samples) and Gurzau & Gurzau (2001) reported arsenic concentrations up to 176 µg/L in the associated aquifers of Romania. In the recent Phare-project 'Survey on the chemical status of groundwaters, Hungary', the highest arsenic content reported in shallow groundwater observation well was 344 µg/L (GTK *et al.* 2006). From all data gathered during the Phare-project (N=1314 samples), the percentages of arsenic analyses above the recommended value for drinking water (10 µg/L) was 12.9 %. High arsenic concentrations in surface waters and groundwater up to 100-5000 µg/L are typical in areas of sulphide mineralization and mining areas in Spain and Portugal.

Geothermal waters can contribute to arsenic in groundwater, particularly in the western United States. High arsenic concentrations in groundwater within the Madison and upper Missouri River valleys appear to be directly or indirectly related to the Yellowstone geothermal system (Nimick *et al.* 1998, Welch *et al.* 2000).

#### 2.2.3.1. Arsenic in Finnish surface waters and groundwater

According to the decree by the Ministry of Social Affairs and Health, the limit value of arsenic for household water and for water plant water in Finland is 10 µg/L (STM 1994, STM 2001). In the first comprehensive groundwater investigation completed in 1993, the highest arsenic concentrations were found from wells drilled into bedrock. The observed arsenic concentrations ranged between 0.05-2230 µg/L with an average value of 17.7 µg/L and the median 0.61 µg/L (Backman *et al.* 1994). Exceptionally high concentrations, above 1000 µg/L, were found from wells drilled into the mafic and ultramafic plutonic rocks in the southern part of the Pirkanmaa area (Backman *et al.* 1994, Backman & Lahermo 2004). The high average and median values of arsenic concentrations reported in this study were distorted by the numerous samples from the case study areas exceptionally rich in arsenic. From a survey carried out in 1999, and by applying a more even nationwide sampling grid (Lahermo *et al.* 2002), the average and median of arsenic concentrations were considerably lower, 1.00 µg/L and 0.16 µg/L, respectively. Only 3 % of the 263 drilled wells studied exceeded the limit value of 10 µg/L. The average and median arsenic concentrations from 739 sampled springs and dug wells throughout all of Finland are 0.35 µg/L and 0.14 µg/L, respectively.

In 2002, an investigation of drilled wells was carried out in five municipalities in Pirkanmaa (Tampere, Nokia, Pirkkala, Lempäälä and Vesilahti). The average and median arsenic



concentrations in groundwater from 237 household wells were 9.7 µg/L and 1.8 µg/L, respectively, and in 17 % of the wells, the arsenic concentrations were above 10 µg/L (Juntunen *et al.* 2004).

All the groundwater chemistry data at the GTK are stored into the same database. The values of statistical parameters of the arsenic data depend on the search key or access time. Therefore, the median values, for example, are varying a little between different studies. In Finland, the arsenic concentrations are generally low in spring water and in water from shallow ring wells dug into overburden. The average arsenic contents are 0.58 µg/L (median 0.10 µg/L) in 741 spring water samples and 0.52 µg/L (median 0.20 µg/L) in shallow dug wells (N=1721) (Backman & Lahermo 2004).

According to Lahermo *et al.* (1996), the arsenic concentrations in stream waters in Finland are between 0.06-1.60 µg/L (median 0.36 µg/L and average 0.53 µg/L). The concentrations in the south (0.2-0.4 µg/L) are higher than in northern Finland (0.1-0.2 µg/L). Elevated arsenic concentrations are especially observed in southwestern Finland (0.5-1.5 µg/L), where the main part of the bedrock is composed of Proterozoic schists and gneisses of volcanic and sedimentary origin. Lower arsenic concentrations are found in the granitoid areas of eastern and northern Finland. The distribution of arsenic concentrations in stream waters correlate well with the distribution of arsenic in till.

Arsenic concentrations in lake waters are in the same order of magnitude (median 0.29 µg/L, mean 0.34 µg/L in 464 samples) than the stream waters according to a survey done in Finland in 1995 (Tarvainen & Mannio 2004).

### **2.3 Arsenic as an environmental risk**

Aquatic and terrestrial biota show a wide range of sensitivities to different arsenic species. Their sensitivity is modified by biologic and abiotic factors. In general, inorganic arsenic compounds are more toxic than organic compounds and arsenite (reduced inorganic form) is more toxic than arsenate (oxidised form). The mode of toxicity and mechanism of uptake of arsenate by organisms differ considerably. This may explain why there are interspecies differences in organism response to arsenate and arsenite. The primary mechanism of arsenite toxicity is thought to result from its binding to protein sulfhydryl groups. Arsenate is known to affect oxidative phosphorylation by competition with phosphate. In environments where phosphate concentrations are high, arsenate toxicity to biota is generally reduced. As arsenate is a phosphate analogue, organisms living in elevated arsenate environments must acquire the nutrient phosphorous yet avoid arsenic toxicity (WHO 2001).

Arsenic compounds cause acute and chronic effects in individuals, populations and communities at concentrations ranging from a few micrograms to milligrams per litre, depending on species, time of exposure and end-points measured. These effects include lethality, inhibition of growth, photosynthesis and reproduction, and behavioural effects. Arsenic-contaminated environments are characterized by limited species abundance and diversity. If levels of arsenate are high enough, only species that exhibit resistance may be present (WHO 2001).

In practice, the effects of contaminants on living organisms may be difficult to observe if the exposure level is low or moderate. When the stress factor originates from natural sources, then it is assumed that natural selection favours tolerant life forms. Many invertebrates, for instance, can live in a soil with a relatively wide range of arsenic. Thus, in areas with elevated arsenic concentrations, the vegetation or organisms may be distributed in a manner that is not much different from the surroundings. Further, the harmful components may have been flushed away from the topsoil by

runoff or recharging water. In glaciated areas, it has taken at 10 000 years or more to achieve the present balance. However, a major impact on the environment may be generated when the concentration levels are suddenly changed due to an increase in the supply of the harmful component or due to migration into an environment not adapted to that component. Such situations may occur when arsenic-bearing bedrock or soil is exposed and handled, or when arsenic-rich water is drained into a watercourse. In time, even very low loads may create extensive contamination in the accumulation area.

## 2.4 Arsenic in the human body and the health risk

Arsenic is present in all living organisms and the total human body content, for example, varies between 3 and 4 mg and tends to increase with age (NRC 1977). With the exception of hair, nails, and teeth, analyses have revealed that most body tissues contain less than 0.3 mg/kg. In the United States, the median arsenic content in 1 000 samples of human hair was 0.51 mg/kg and the median concentrations for males and females were 0.62 and 0.37 mg/kg, respectively (NRC 1977). Nails clippings from a patient with acute polyneuritis from arsenic poisoning contained arsenic 20-130 mg/kg, while the normal arsenic content of nails is 0.43-1.08 mg/kg.

Human exposure to arsenic in the environment is primarily through the ingestion of food and water. Of these, food is generally the principle contributor for the daily intake of total arsenic. The arsenic content of urine normally varies from 0.1-1.0 mg/L. Great daily variations exist and depend on the amount of arsenic in various foodstuffs (like seafood). When arsenic is ingested, the amount excreted increases over several days to a maximum and then declines to normal. Drinking water by far represents the greatest hazard since the species present in groundwater are predominantly the more toxic, inorganic forms. In 1993, WHO reduced its recommended limit for arsenic in drinking water from 50 µg/L to 10 µg/L in response to evidence from toxicological studies (WHO 1993).

Long-term exposure to arsenic in drinking water is causally related to increased risks of cancer in the skin, lungs, bladder and kidney, as well as skin changes such as pigmentation changes and thickening (hyperkeratosis). In Taiwan, for example, inhabitants exposed to high arsenic contents from drinking deep artesian well water have been shown to cause a severe disease of blood vessels leading to gangrene, or “black foot disease” (Chen *et al.* 1994). Moreover, a very serious problem of arsenic contamination of groundwater, in terms of largest population exposed, was found in the alluvial and deltaic sedimentary aquifers of the Bengal Delta Plain in Bangladesh and neighbouring West Bengal, India (Nickson *et al.* 1998, BGS & DPHE 2001, Smedley & Kinniburgh 2002, Ahmed *et al.* 2004). Arsenic concentrations in groundwater from the affected areas have a very large range (<0.5 to ca. 3200 µg/L). It is estimated that worldwide at least 500 million people might consume water with arsenic over the present WHO, US and EU limits of 10 µg/L.

In Finland, Kurttio *et al.* (1999) reported that despite the very low concentrations of arsenic in drilled wells that were used by the study populations (61 bladder cancer cases, 49 kidney cancer cases and 275 random reference samples) during 1967-1980 (median 0.1 µg/L, maximum 64 µg/L, 1% of samples were >10 µg/L), there was some evidence of an association between arsenic and bladder cancer risks. Bladder cancer tended to be associated with arsenic concentration and daily dose during the third to ninth years prior to the cancer diagnosis. No association between arsenic and kidney cancer risk or skin cancer have been reported. However, muscle cramps, mainly in the legs, have been reported in people who have been drinking water with high arsenic contents (min-max: 17-980 µg/L) in southwest Finland (Kurttio *et al.* (1998). In the same group of people, the mean concentration of arsenic in the urine was 58 µg/L (N = 17). The mean concentration of 5 µg/L was measured for a reference group whose drinking water contained less than 1 µg/L of arsenic

(N = 9). Absorption of arsenic through the skin is minimal and thus hand washing, bathing, and laundry, for example, with water containing arsenic do not pose a human health risk ([www.who.int/mediacentre/factsheets/fs210/en](http://www.who.int/mediacentre/factsheets/fs210/en)).

### 3. STUDY MATERIALS AND METHODS

#### 3.1. The study area

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 (Figs. 4 - 5.) In 2006, this 14 700 km<sup>2</sup> area with 450 000 inhabitants consisted of 33 municipalities. The industrial and commercial centre of the area is the city of Tampere ([www.pirkanmaa.fi/english/](http://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 escalate towards northern Pirkanmaa. Surface water bodies cover approximately 15 % of the area of Pirkanmaa.

According to Köppen's climate classification, Finland belongs to the temperate coniferous-mixed forest zone with cold winters and warm summers (Essenwanger 2001). A typical feature is that the four seasons are distinct. In the Pirkanmaa region, the annual air temperature varies from +3 to +5°C. The annual precipitation is around 700 mm, which is obtained during the winter months as snow.

The public water supply in the area is based on surface water (50 %) and groundwater (50%). The total number of water plants is 122. Most of the inhabitants (89 %) are connected to the public water distribution network and only 11 % use their own private wells. The average daily consumption of water at Pirkanmaa is 234 L/person/d. (Pirkanmaan ympäristökeskus 2004).



Figure 4. The study area of Pirkanmaa in southern Finland. (Base map data © National Land Survey of Finland).



Figure 5. Typical scenery in the southern part of the Pirkanmaa region. Photo M.Eklund

### 3.2. Overview of the geology in Finland and Pirkanmaa

In Finland, the contact between bedrock and overburden is very sharp. A geological discontinuity prevails between the bedrock, which is at least 1,000 million years old, and the young sediments, which are about 10,000 years old. Nearly all sediments and rocks formed during this time interval have been eroded away (Koljonen & Tanskanen 1992). The crystalline bedrock in Finland is part of the Precambrian Fennoscandian craton and consists mainly of Archean (3.8–2.5 Ga) and Paleoproterozoic (2.5–1.6 Ga) rocks that are exposed at the current erosional level. The two major collisions of tectonic plates that lead to the formation of the Finnish bedrock occurred at 2.8–2.7 Ga and 1.9–1.8 Ga ago. Major tectonic events have not taken place thereafter, and the bedrock has been subjected to erosion for an extensive period of time. The current erosional level was, for the first time, reached already 600 Ma ago. During the Phanerozoic eon (570–0 Ma), the bedrock in Finland formed a basement for the accumulation of sediment deposits that still overlay the Fennoscandian craton in areas to the south and east of Finland.

Within the last 2.4 Ma, numerous glacial and interglacial periods have occurred and thick continental ice sheets have repeatedly covered northern Europe. During the glacial maximum of the Weichselian glaciation some 18 000 years ago, the ice cover extended to central Europe. As a result, the loose sedimentary material on top of the bedrock has been reworked and glaciogenic moraines were commonly deposited directly on unweathered crystalline bedrock. Scars and grooves produced by the moving ice sheets are typical features on bedrock surface. The majority of the overburden observed today was deposited about 10 000 years ago, during and after the last glaciation. The average thickness of the overburden that comprises moraine, sand, gravel, silt, and clay deposits is 3–4 m. The time scale for the geological history for the Pirkanmaa region is in Fig. 6.

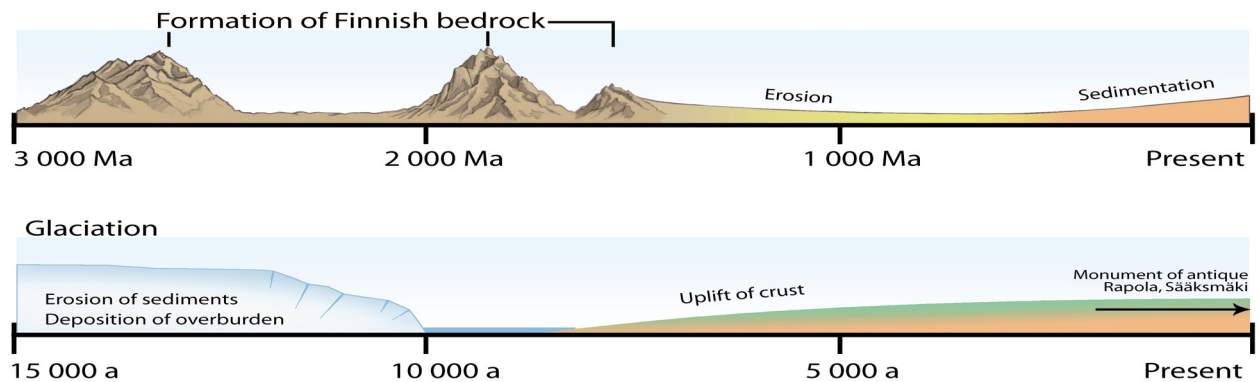


Figure 6. Time scale for the history of Pirkanmaa geology. Picture prepared by H. Kutvonen.

### 3.2.1. Bedrock in the Pirkanmaa region

The Pirkanmaa area is located in the middle of the Paleoproterozoic Svecofennian domain, which formed 1920-1870 Ma ago as a result of several orogenic and extensional events (Lahtinen *et al.* 2005b). The bedrock of the domain is predominantly composed of metasedimentary rocks, metavolcanic rocks of island-arc type 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 metamorphism after their formation. Plutonic rocks, such as granitoids, form deep within the crust when rock material melts under high temperature and pressure, and molten magma rises upwards until it crystallizes as the temperature decreases.

The Tampere region can be divided in three geologically distinct units based on the dominant rock types encountered in the area. The main geological subdivisions in the study area are (Fig. 7): the Central Finland Granitoid Complex (CFGK) in the north, the Tampere Belt (TB) in the centre, and the Pirkanmaa Belt (PB) in the south (Nironen *et al.* 2002). The air-borne geophysical electromagnetic measurement data support this division (Fig. 8).

The CFGK 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).

All the rock types encountered in the area are metamorphosized, crystalline hard rocks. Primary sedimentary or volcanic textures have been only sporadically preserved. The low porosity of these rocks, generally <0,5%, allows conductive groundwater flow only along a fractured network formed during numerous tectonic events. The fracturing is relatively abundant within the upper 150 m of the bedrock and becomes more sporadic with depth. This feature, accompanied by the flat topography in the major part of the country constrains the mixing of the groundwater in the overburden with the water in bedrock. Thus, the surface of the bedrock below the overburden marks an interface between the younger, fresh, shallow waters and the older, chemically more evolved groundwater.

The volcanic-sedimentary belt (TB & PB) of the Pirkanmaa region is bordered by the granitoids (CFGC). The belt is enriched in gold, arsenic, silver, cobalt, copper, lithium, molybdenum, phosphor, antimony, uranium, and zinc (Koljonen *et al.* 1992). The abundance of the sulphide-forming elements Ag, As, Cu, Mo, Sb, and Zn are above average in comparison with other sites in Finland.

### 3.2.2. Quaternary geology in the Pirkanmaa region

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 from Hämeen kangas via Kyröskoski to the south part of Kuorevesi, was formed within one hundred years, between 11000 – 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 (Fig. 9).

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. Till deposits are more common in northern Pirkanmaa than in the southern Pirkanmaa. The average thickness of the till deposits is 3 – 4 metres. Fine-grained sediments – clays and silts deposits - located especially in southern part of the region, cover about 14 % of the whole Pirkanmaa area. Almost all of these areas are in agricultural use. The analyses of the agricultural soils are presented in a separate report compiled in late 2006.

There are two large and important glaciofluvial sand and gravel formations in the study area; the Central Finland End Moraine and the Pälkäne – Tampere - Hämeenkyrö esker. These formations are important for groundwater recharge but also for sand and gravel extraction. Both of these formations are important nationally. There are, also, many smaller sand and gravel formations in the area, with about 5,4 % of the whole Pirkanmaa region covered by these deposits. The sand and gravel formations have been extensively exploited for construction purposes and they are of major importance for the groundwater supply.



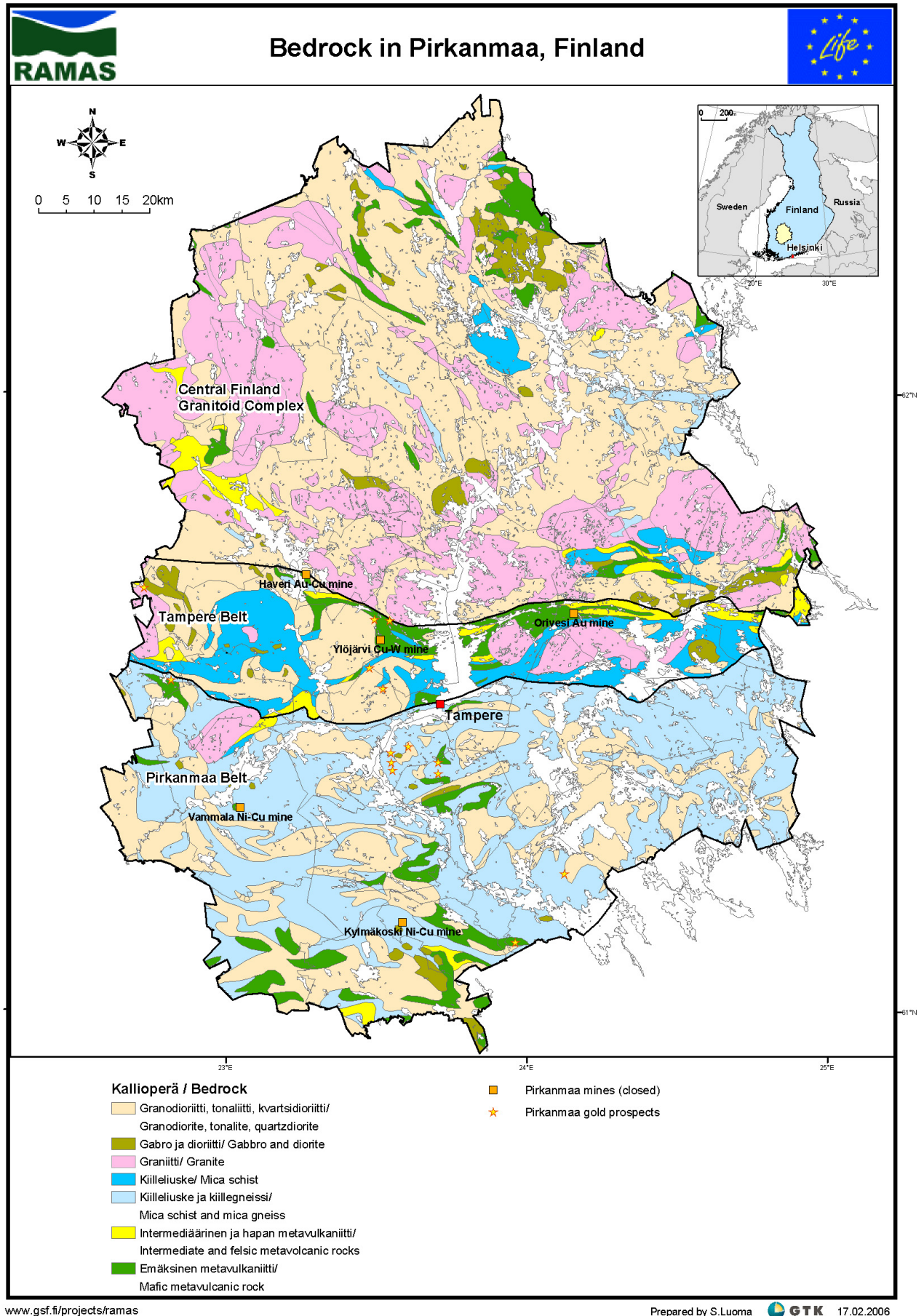


Figure 7. Bedrock in the Pirkanmaa region processed from the GTK data (Geological mapping data © Geological Survey of Finland, Base map data © National Land Survey of Finland).

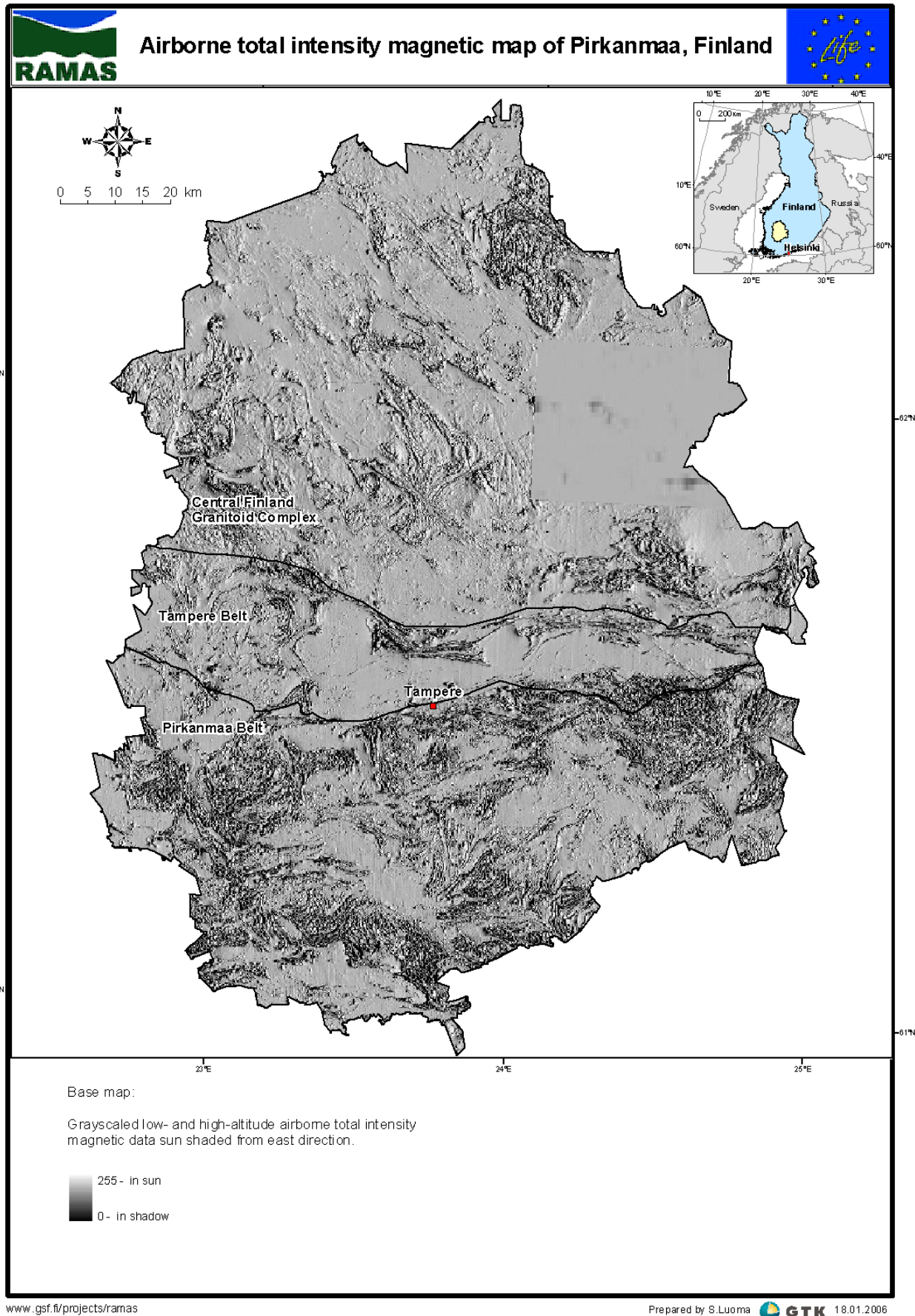


Figure 8. The air-borne geophysical electromagnetic map in the Pirkanmaa region. Data processed from the GTK air-borne geophysical data (Geophysical data © Geological Survey of Finland).



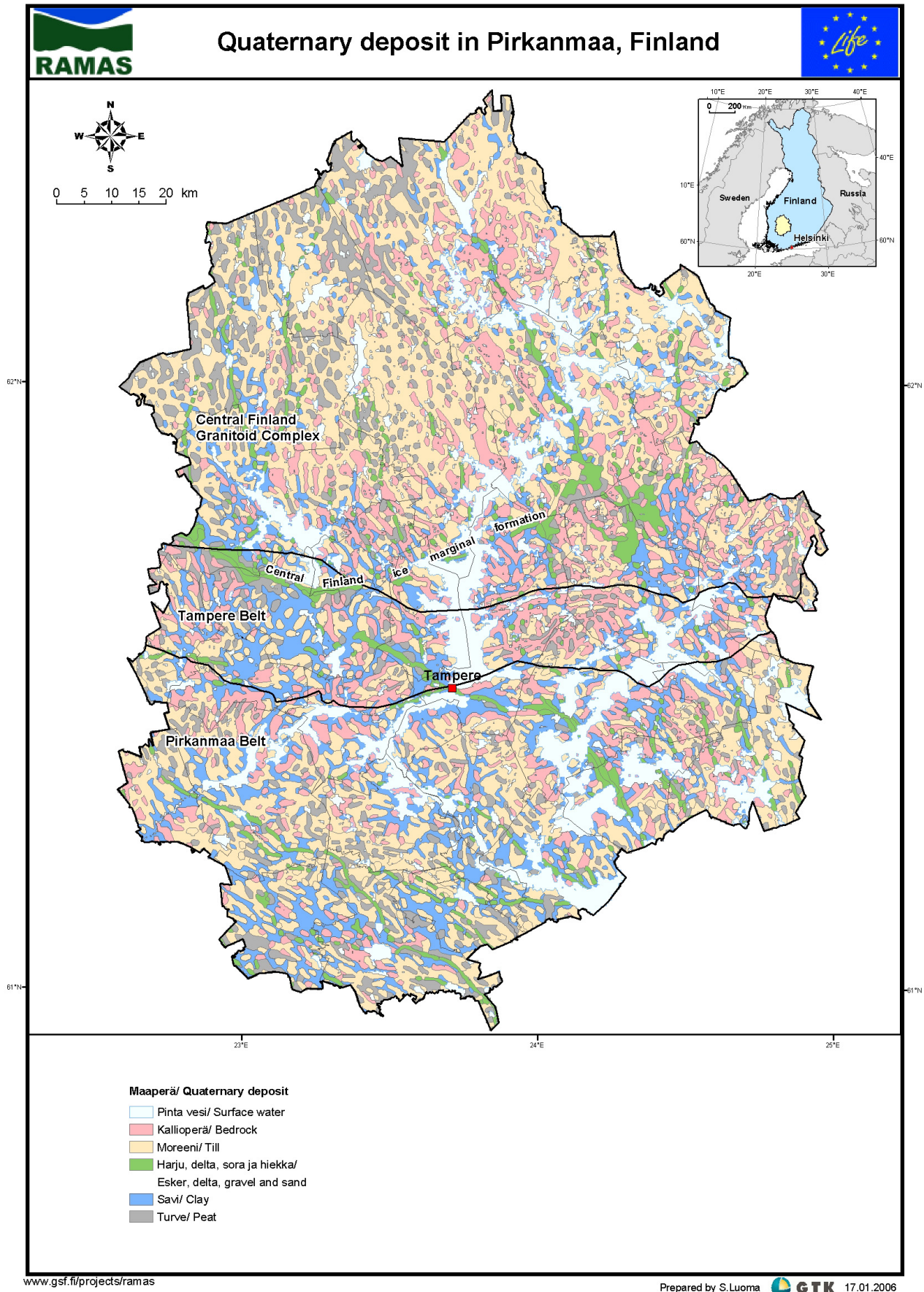


Figure 9. Quaternary deposits in the Pirkanmaa region processed from GTK data (Quaternary mapping data © Geological Survey of Finland, Base map data © National Land Survey of Finland).

### 3.3. Study materials and sampling

The material applied in this study consists of geological, geophysical, geochemical and environmental data from the Pirkanmaa region. All the available arsenic data previously collected during different site surveys and local municipalities have been used. Supplementary sampling of groundwater and soils has been carried out in 2005 within the RAMAS project. A summary of the data exploited in this study is described in Table 1.

Table 1. Arsenic content data used in this study.

Sampling materials	Sampling year	Sampling density	Sampling number	Sampling depth
<b>Rock samples:</b>				
Lithogeochemical sampling	1989-1995	1/20 km <sup>2</sup> -1/100 km <sup>2</sup>	603	Bedrock (non-weathered rock surface)
<b>Soil samples:</b>				
Nation-wide geochemical till fines data	1980-1985	1/300 km <sup>2</sup>	46	0.5 - 2.0 m
Geochemical till fines data for ore exploration	1980's-2000's	1/300 km <sup>2</sup> - 400/1 km <sup>2</sup>	10 823	0.5 m - until bedrock
<b>Water samples:</b>				
Bedrock groundwater data, GTK	1992-2005	Varied	965	Sample from a tap
Bedrock groundwater data, municipalities	1994-2004	Varied	307	Sample from a tap
Shallow groundwater data, GTK	1992-2005	Varied	283	Sample from a tap or directly from the well or spring
Water plant data, KTL	2002	Water production > 1000 m <sup>3</sup> /d	122	Sample from a tap from the water system
Stream water, GTK	2002	Varied	32	0.2-0.5 m from surface
Stream water, PIR	1994-2002	Varied	100	0.2-0.5 m from surface

**The lithogeochemical bedrock samples** were collected during the rock geochemistry program, which was established in 1991 by the Geochemistry Department of the GTK (Lahtinen 1996). Sampling in the Pirkanmaa region was carried out during a pilot project for this research program in 1989 and later in 1991-1995, during the main research phase. The sampling strategy was based on stratified sampling where the number of samples per area depends on the lithological variation seen on geological maps. The sampling density varies from one sample per 100 km<sup>2</sup> in homogenous granitoid areas to one sample per 20 km<sup>2</sup> in areas of variable lithology (Lahtinen 1996). In the Pirkanmaa area, the number of bedrock samples was 603. Sampling was done in a distinct lithological unit by a mini-drill with a diamond bit (sample diameter 2.5 cm) from the non-weathered rock. The analysed sample was composed of 4-6 drill cores (12-15 cm) from the same geological unit and sub-samples were also analysed. To control the representativeness of the collected bedrock samples, duplicate outcrop samples were taken. The distance between original samples and duplicate samples was 1-2 metres. Duplicate outcrop samples were chosen to represent the same rock types as the original samples (Lahtinen 1996, Sandström 1996). The data selection for the Pirkanmaa region was done based on the Rock geochemistry database (Lahtinen *et al.* 2005a).

**The soil sampling** in the Pirkanmaa region took place on many occasions (Fig. 10). The main part of the soil sampling focused on till and all 10 869 samples discussed here are collected from till deposits.

The till samples for the Geochemical Atlas data of Finland - **a nation-wide geochemical survey** - were collected using a uniform grid that covered the whole country (Koljonen *et al.* 1992). The average sampling density was one sample per 300 km<sup>2</sup>. The sampling depth was 0.5 – 2 m and the samples were from non-weathered till, mostly from the C-horizon. The samples were collected in



the beginning of the 1980's. The number of nation-wide survey samples in the Pirkanmaa area was 46. Most of the samples were collected using a spade, and some with a lightweight percussion drill. Every effort was made to obtain chemically unaltered samples, and especially to avoid contamination through sampling devices.

**Geochemical mapping and ore exploration** have a long history in Finland. However, the scale of the  $1/300 \text{ km}^2$  or  $1/4 \text{ km}^2$  sampling density are not enough for ore exploration, therefore sampling in some ore potential areas has been much more frequent, 100 – 400 samples/ $\text{km}^2$ . Soil sampling for ore exploration has been repeatedly conducted in the Pirkanmaa area between 1980 and 2000. Most of the ore exploration in the area has been gold prospecting. Samples were collected either from the topsoil (below the humus layer) or deeper below the non-weathered basal till. Till samples were mostly collected with light percussion drills or from a pit made by an excavator (Hartikainen & Nurmi 1993). Sampling was often done from the whole soil profile. The sample treatment was more or less the same as described above, but the drying of the samples began at the field camp. The number of till samples collected and analysed for ore exploration in Pirkanmaa area was 10 823.



Figure 10. Soils sampling in Pirkkala in 2006. Photo B. Backman

**Groundwater sampling** in Pirkanmaa region has been carried out many times as well (Fig. 11). The first large-scale groundwater study related to arsenic in drilled wells was conducted in the Pirkanmaa area in 1994 (Backman *et al.* 1994). Since then, there has been sampling campaign in the area almost every year. The supplementary sampling by the RAMAS-project was carried out in 2005, and 22 arsenic speciation samples were also taken. The total number of groundwater samples at Pirkanmaa is 1272.



The field measurements at the sampling site included temperature, pH, electric conductivity (EC), redox potential (Eh), dissolved oxygen, and dissolved carbon dioxide. Untreated water samples were taken to determine physico-chemical parameters and anions in the laboratory. A filtered (0.45  $\mu\text{m}$ ) and acidified (0.5 ml concentrated suprapure  $\text{HNO}_3$  /100 ml water) sample was taken for metal and trace element analyses. The number of analyzed chemical components has varied over the years from 38 to 54. All field measurements and main anion and cation analyses have been continuously done but the selection of heavy metal and trace element analyses has varied according to research targets. Also, the number of control and duplicate samples varied during different years.

The municipalities of Tampere and Orivesi delivered groundwater data produced by their own public cost for the research. The sampling of these samples was not documented.



Figure 11. Water sampling from a well in Lempäälä. Photo A. Pullinen.



### 3.4. Laboratory analyses

#### 3.4.1. Bedrock samples

##### 3.4.1.1. Pre-treatment and extraction

The original samples and duplicate samples were crushed to <5 mm with the jaw crusher Retsch BK1 (with Fe-Mn plates). About 200 g of the crushed samples was separated with a riffle splitter (stainless steel) and ground in a carbon steel grinding vessel in a vibrating disc mill, to a grain size <0.06 mm. The original samples were split twice to make laboratory sub-samples, but duplicate outcrop samples were split once (Sandström 1996).

Powdered bedrock samples were extracted with aqua regia ( $m:V = 1:6$ ) during the pilot research (Sandström 1996) and later, during the main research phase (1:10) (Virtasalo 2006, personal communication) for one hour at 90°C and diluted before analyses. A more detailed description of the method is shown in Figs. 12 - 13.

##### 3.4.1.2. Analyses

The total arsenic concentrations of the bedrock samples could not be analyzed because the concentrations were too low for the XRF (X-ray fluorescence spectrometer) method. Therefore, arsenic was analyzed with *aqua regia* extraction and the GAAS (graphite furnace atomic absorption spectrometer, Perkin Elmer SIMAA 6000) technique at the GTK's Geolaboratory in Rovaniemi.



Figure 12. Analysing work at laboratory. Photo J. Väättäinen.

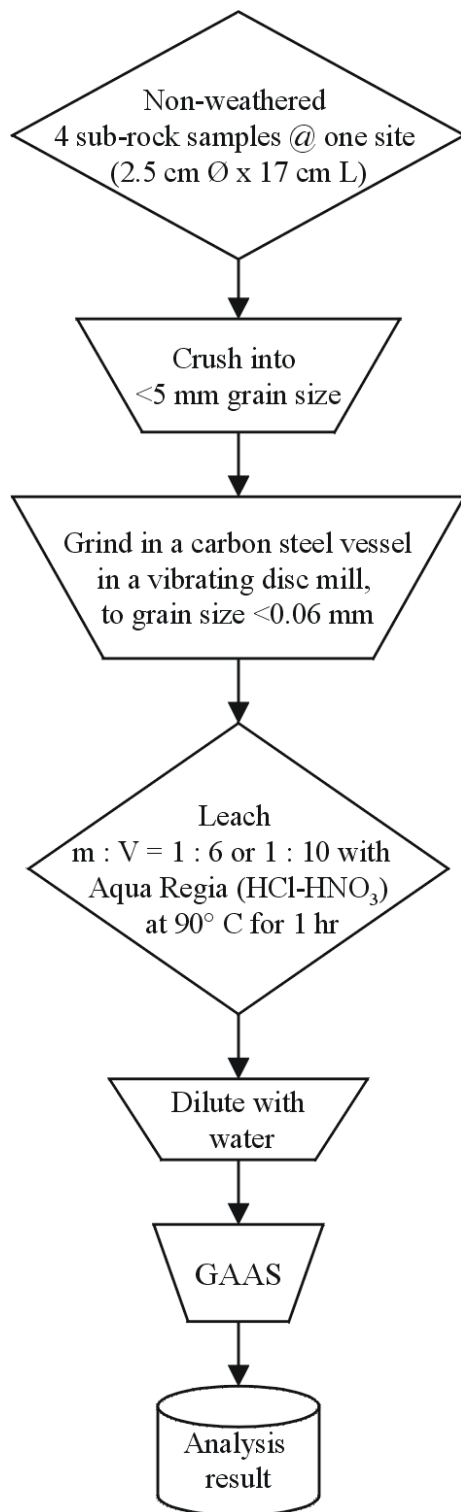


Figure 13. Rock sample pre-treatment and analysis for the regional Rock Geochemistry Research Project (RGRP)

### 3.4.2. Soil samples

#### 3.4.2.1. Pre-treatment and extraction

In the nation-wide geochemical survey (Koljonen *et al.* 1992), the till samples were homogenized and dried in paper bags for 3 days at 70-80°C. If they cemented during drying period, the samples were rehomogenized with light hammering. Afterwards, the original samples were divided into two sub-samples. The samples were sieved with a multi-screen shaker (made of PVC plastic and nylon cloth) and only the fine fraction (<0.06 mm) was analyzed. The pre-treatment is presented in Fig. 14.

Comparison of the chemical data of the soil samples is complicated because of the different extraction methods used in different projects. In nation-wide geochemical survey, the arsenic analyses were done using the NAA (Neutron activation analysis) method (Koljonen *et al.* 1992).

In the ore exploration survey, the till samples were treated following the procedure described above, but were dried at 70 °C (Hartikainen & Nurmi 1993).

The extraction method used for arsenic analyses was *aqua regia* dissolution. The extraction ratio of *aqua regia* dissolution for till samples was 1:3 (m:V) for most of the ore exploration projects in late 1980's and 1990's (Hämäläinen 2006, personal communication). These samples were analyzed at GTK's Geolaboratory in Kuopio and Rovaniemi. *Aqua regia* extraction has been done at room temperature and over night. The more detailed scheme of the process is presented in Fig. 15.

#### 3.4.2.2. Analyses

Around 10 800 soil samples from the Pirkanmaa region were collected and analysed between 1980-2005. However, the analytical methods have changed quite a lot over the past 25 years. The main techniques used in 1980's for metal analyses were atomic absorption spectrometry (AAS) and neutron activation analysis (NAA). From 1990's to the present, the main techniques for multi-elemental analyses are inductively coupled plasma (ICP) atomic emission spectrometry and mass spectrometry (ICP-AES/MS). The arsenic concentrations presented in the geochemical nation-wide survey (Koljonen *et al.* 1992) are analyzed by NAA (Triga Mark II reactor) technique at the Reactor Laboratory of the Technical Research Centre of Finland in Espoo. A more detailed description of the method is shown in Fig. 14.

Arsenic concentrations from *aqua regia* extraction solutions were analyzed by graphite furnace AAS or by flame AAS (hydride generation) (Hartikainen & Nurmi 1993) (Fig. 15). In the late 1990's and at present, arsenic in soil samples is mostly analyzed using the ICP-AES/MS technique. The differences between these arsenic analysis techniques are discussed in the quality control section.

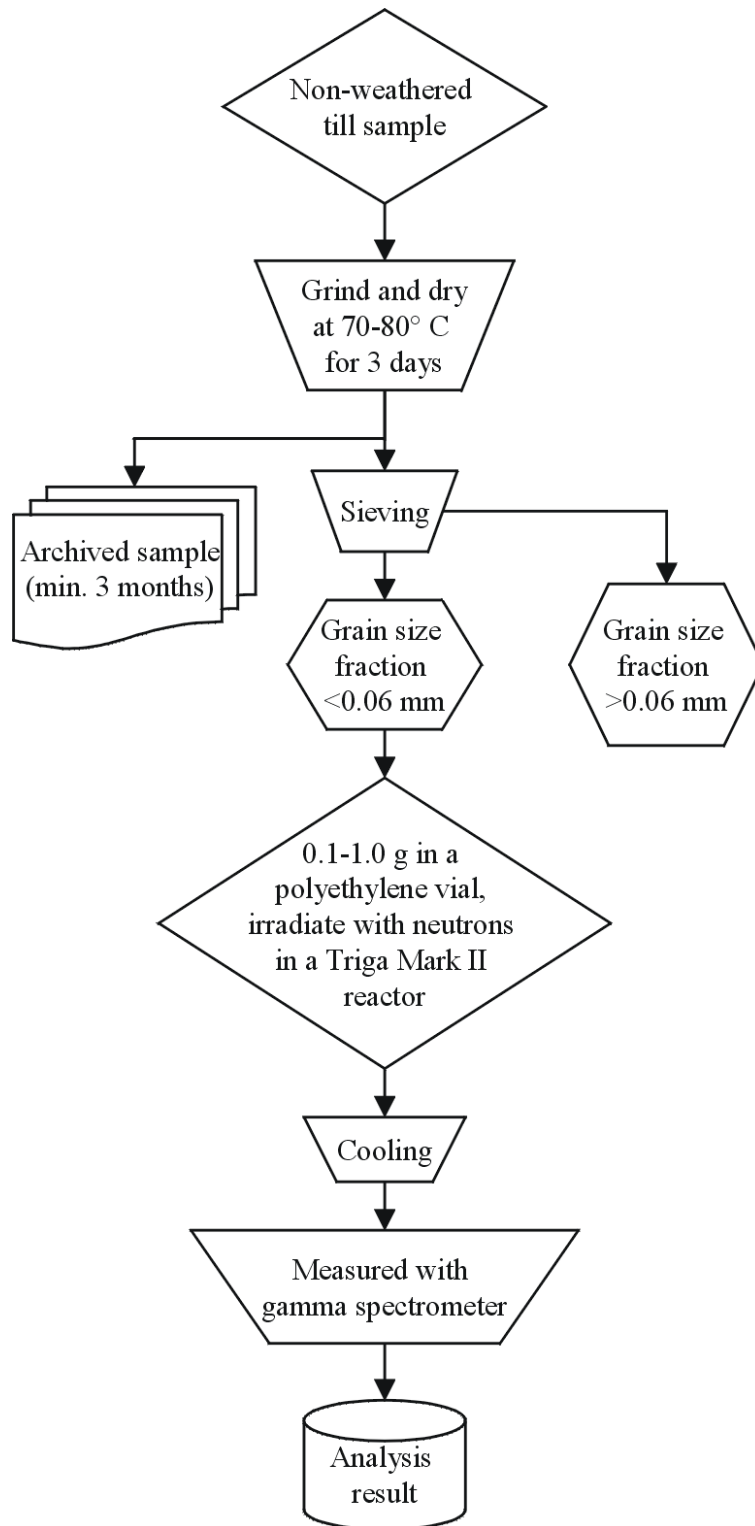


Figure 14. Soil sample pre-treatment and analysis for the nation-wide geochemical survey (According to Koljonen *et al.* 1992).

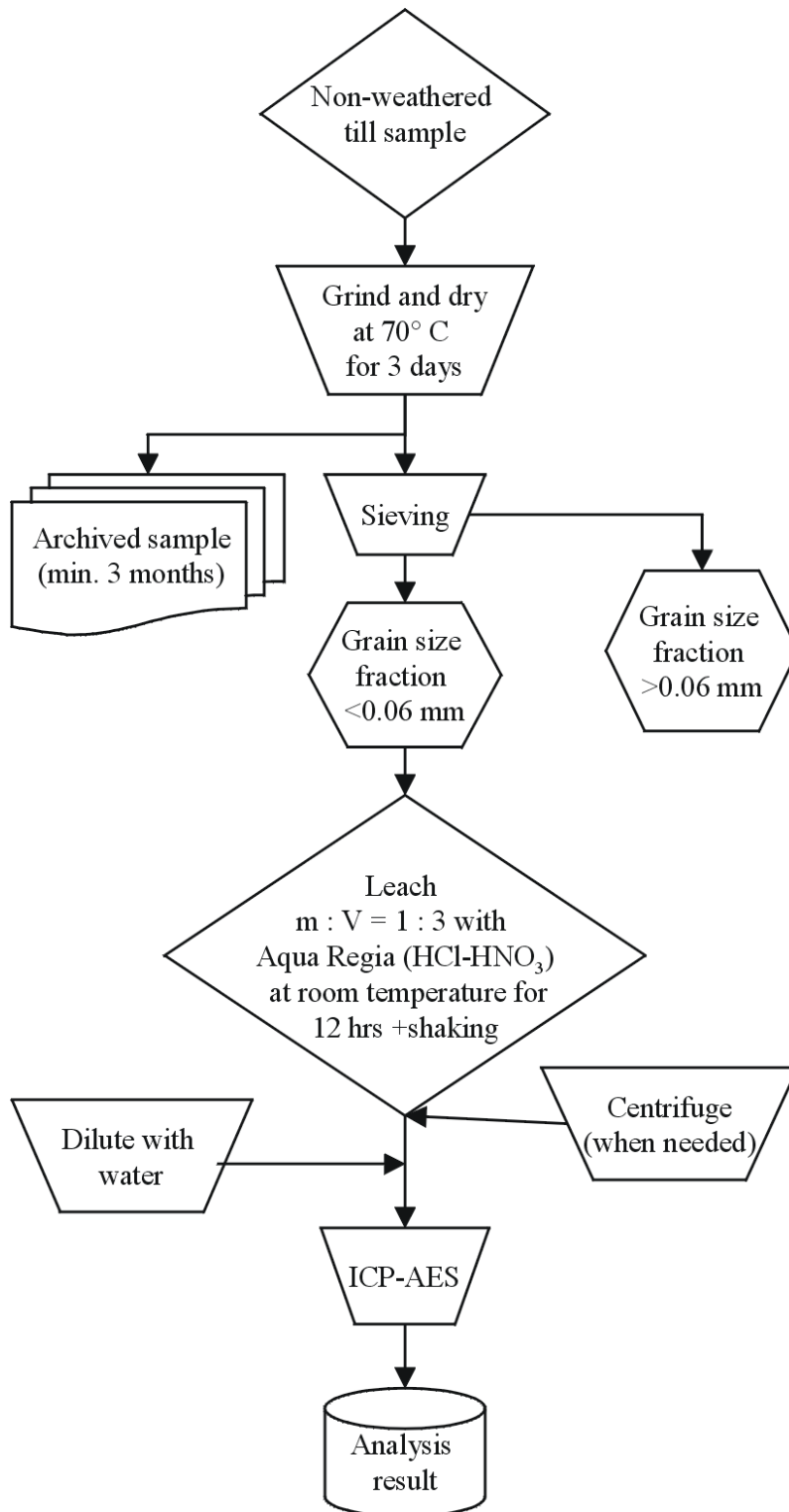


Figure 15. Soil sample pre-treatment and analysis for ore exploration studies.

### 3.4.3. Water samples

#### 3.4.3.1. Analyses

Electric conductivity and pH were measured both in field and laboratory conditions. In the Geolaboratory of the GTK, pH, conductivity and total alkalinity (as mmol HCO<sub>3</sub><sup>-</sup>/L) were

determined using an automatic titrator. The main anions  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ , and  $SO_4^{2-}$  were analysed using the ion chromatographic (IC) technique and  $PO_4^{3-}$  by spectrophotometric method. Chemical oxygen demand of groundwater samples was determined using the titrimetric method with  $KMnO_4$ .

All cations and other elements (for example total sulphur content) were analysed by ICP-AES or ICP-MS technique. A more detailed description of the analysis techniques is presented in Table 2.

Table 2. Chemical analytical methods of the groundwater samples from the Pirkanmaa region.

Chemical Parameter	Analysing Method	Equipment, Model
pH, electric conductivity	Potentiometric and conductive measurement with an automatic titrator	Mettler Toledo DL 70
Alkalinity ( $HCO_3^-$ )	End point titration with 0.05 M HCl to pH 4.5	Mettler Toledo DL 70
Fluoride, chloride, bromide, nitrate, sulphate	Ion chromatographic determination with suppressed $NaCO_3/NaHCO_3$ elution	Dionex DX 120
Phosphate	Spectrometric method using Ammonium-molybdate complexation	Shimadzu UV-150-02 spectrophotometer
$KMnO_4$ number	Manual titration with $KMnO_4$ to the equivalent point	
Ca, Mg, Na, Fe, Si and S (B, Mn and K occasionally)	Inductively coupled plasma (ICP) atomic emission spectrometric (AES) analysis. The calibration for each element is performed using a blank and one calibration standard. The calibration is checked by independent Certified Reference Material water samples.	Thermo Jarrell Ash Corp. (TJA), an ICP-AES dual detector system, IRIS Advantage
Ag, Al, <b>As</b> , B, Ba, Be, Bi, Cd, Co, Cr, Cu, I, K, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, U, V and Zn	Inductively coupled plasma (ICP) mass spectrometric (MS) analysis. The same principle is used in the calibration as in ICP-AES analyses. Furthermore, Rh is added to all samples as an inner standard.	Perkin Elmer PE-SCIEX ICP-MS system, ELAN 6000

### 3.4.3.2 Arsenic speciation

$As^{3+}$  and  $As^{5+}$  species were determined using the ion-exchange technique and measured as arsenic with ICP-MS equipment. The water sample was first filtered ( $0.45\ \mu m$ ) and then acidified with a  $Na_2$ -EDTA (Ethylene diaminetetraacetic acid) solution for the speciation analysis (0.5 ml 0.25 M EDTA solution /100 ml water).

The ion-exchange of the arsenic speciation sample was done with 1-X8 resin (in acetic form) in single used plastic columns under field conditions. The first fraction was separated in the field and the others in laboratory (Fig. 16). A separation of different fractions was, in most cases, done within a few days of speciation sampling. Arsenic measurements from the ICP-MS technique were done in about one week of the speciation sampling. A more detailed description of the method and the results will be published in 2006.



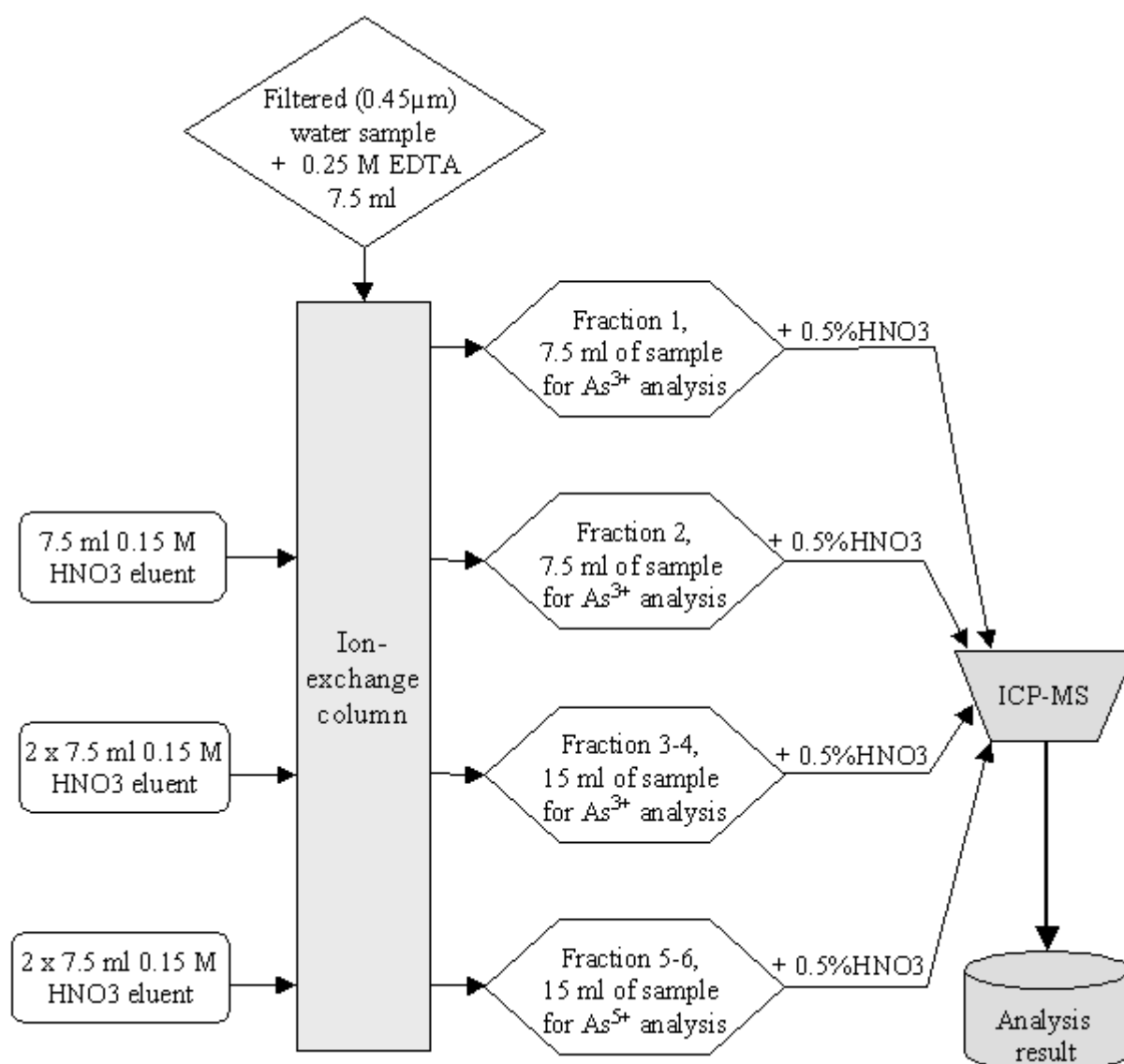


Figure 16. A microscale method for the separation of As<sup>3+</sup> and As<sup>5+</sup> species from RAMAS water samples by ion-exchange with 1-X8 resin and elution with 0.15 M HNO<sub>3</sub>.

### 3.5. Quality control

Quality control was established especially for water samples, but also for soil samples. For water samples, the approach has been to analyse duplicate samples and to calculate the charge balance error. For soil samples, quality control will be discussed later this year because the results of Ramas-project soil samples are not yet ready.

#### 3.5.1 Bedrock samples and soil samples

Sandström (1996) reported the precision of the element determinations used in the "Bedrock geochemistry in the Tampere-Hämeenlinna area" project. Arsenic concentrations of the original bedrock samples and duplicate samples (sampling discussed in section 3.4.1.1.) were analyzed using the GAAS technique. The systematic error was estimated by the analyses of reference materials (RM) and subsamples. For arsenic analyses, the laboratory precision was about 50 % in the 95 % confidence level and the sample precision was about 80 % (in the 95 % confidence level, N=45). The conclusion of the quality control was that arsenic (also Se and Sb) is only partly dissolved with

*aqua regia* extraction, but the arsenic results can clearly be used as indicators of the anomalous areas and rock types because the precision is satisfactory (Sandström 1996).

The uncertainties of the analyzing methods of the till samples from the geochemical nation-wide survey and the ore exploration projects of Pirkanmaa region in 1980's and 1990's were not reported in detail (Koljonen *et al.* 1992, Salminen *et al.* 1995, Nurmi *et al.* 1993). In fact, interest in uncertainties in chemical analyses was not common in 1980's. Laboratories began to use statistical tools to evaluate the quality of their analyses as interest in uncertainties increased in the 1990s.

Mäkinen (1995) presented an evaluation of the analytical reliability of chemical results. He presents relative errors and the rank correlation coefficients for the duplicate analyses of soil samples between 1984 – 1990. According to correlation coefficients, the elements were divided into four classes. The best class ( $r > 0.953$  and relative error  $< 8\%$ ) contained analyses of following elements: Al, Ba, Ca, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Na, P, Sc, Sr, Ti, V, Y, Zn and Zr. Class II contained analyses of As, Pb, Si and Th ( $0.877 < r > 0.737$  and relative error 8-38 %). In the two last classes, the relative error is more than 76 % and the  $r$  value is also poor. In this report, it is noticeable that the relative error in duplicate analyses diminishes when only the last few years (1988 – 1990) are taken into account. In arsenic analyses, there must be a major change in analyzing technique because the relative errors are around 35 % from 1988 – 1990 (in 1984 – 1987  $> 100\%$ ), probably due to a change into hydride formation technique in AAS.

### 3.5.2. Water samples

According to the Quality System of the GTK, duplicate analyses were made for 5 % of the water samples. In addition, at least one duplicate analysis per indent was also made. The results of duplicate analyses for the drilled well water samples from the Pirkanmaa region taken in 2005 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 for evaluation of random error. The GTK has evaluated uncertainties (%) for every accredited analyzing methods, so these values calculated for drilled well waters of Pirkanmaa can be compared to those uncertainties calculated in 2004 by chemists at GTK.

Uncertainty was calculated according to following formula:

$$B = z * U, \text{ where}$$

$z$  = confidence factor, number 2 in 95 % confidence limit

$U$  = Combined uncertainty

$$U = \sqrt{U_{\text{systematic}}^2 + U_{\text{random}}^2}, \text{ where}$$

$U_{\text{systematic}}$  = Systematic error

$U_{\text{random}}$  = Random error

Uncertainties (%) for the multi-elemental water analyses using the ICP-AES/MS technique are presented in Table 3. Analyses of domestic and international collaborative test water samples and Certified Reference Materials evaluate systematic error. Random error is evaluated by analyses of CRM waters and real duplicate water samples (includes groundwater and surface waters).

Table 3. Uncertainties (%) in 95 % confidence limit of the accredited ICP-AES/MS method of analyzing natural waters (calculated in 2004 at the Geolaboratory, GTK, Espoo).

Element	Concentration area (µg/l)	Uncertainty %	Concentration (µg/l)	Uncertainty %	Concentration (µg/l)	Uncertainty %
Ag	0.01-1	20	1-10	15		
Al	1-100	20	100-1000	15	1000-20000	10
As	0.05-1	20	1-30	10		
B	1-200	15	200-1500	10		
Ba	0.04 –5	15	5-150	10		
Be	1-40	20				
Bi	0.5 – 10	20				
Br	2-30	30				
Ca	0.1-200 mg/l	15				
Cd	0.02-1	20				
Cl	0.3-3 mg/l	40	3-10	20		
Co	0.5 – 50	15	50 – 1700	10		
Cr	0.2-1	20	1 – 20	15		
Cs	0.01 – 1	20				
Cu	0.04 – 1	20	1 – 200	15		
Fe	0.03 –20 mg/l	15				
I	2-3	50				
K	0.01-10 mg/l	15	10-50 mg/l	10		
Li	1-50	20	50 – 600	15		
Mg	0.05-50 mg/l	15	50 – 250 mg/l	15		
Mn	0.02-10	15	10-10000	10		
Mo	0.03-15	15				
Na	0.4-500 mg/l	15				
Ni	0.06-50	20	50-2000	15		
Pb	0.03-50	20	50 – 250	15		
Rb	1 – 20	20	20 – 120	15		
S	1 – 1000 mg/l	15				
Sb	0.02-5	15				
Si	0.06-10 mg/l	20	10 – 50 mg/l	15		
Sr	0.1-50	15	50-2000	10		
U	0.1 – 25	15				
V	1 – 25	10				
Zn	0.1-100	15	100 – 14000	10		

The values presented in Table 3. are calculated from several years of measurements with the Thermo Jarrell Ash ICP-AES plasma emission spectrometer and Perkin ELAN6000 ICP mass spectrometer at Geolaboratory, GTK in Espoo. The reproducibility of RAMAS drilled well water chemical analyses is presented in Fig. 17. These values are comparable to the other half of the combined uncertainty (U), or to the random error. This set of analyses includes ICP-AES/MS analyses, potentiometric analyses, spectrometric analysis of  $\text{PO}_4^{3-}$ , and analyses of the main anions by ion chromatographic (IC) technique for example. All values are presented in Table 4. Only a few data points are named in this figure (Fig.17), but this figure provides an overview to reproducibility of the chemical analyses of drilled well samples. For arsenic analysis, the reproducibility is 10 % and this should be multiplied by 2 in 95 % confidence limit. All values are at a reasonable level (around 0 – 10 %), except Ni and Pb (15 – 30 %), which may contain contaminations of single water samples. Reproducibility is not presented if the number of duplicate sample pairs was less than 6.

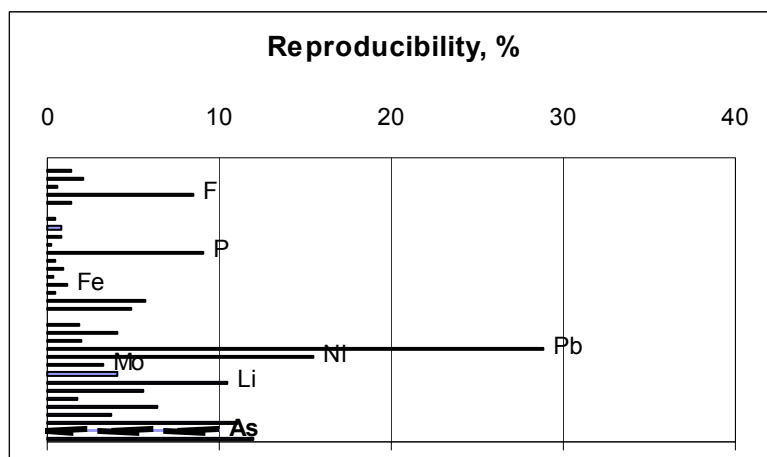


Figure 17. The reproducibility of RAMAS drilled well water sample analyses in 2005.

Table 4. Datapoints of reproducibility presented in Figure 17. Total number of duplicate pairs was 21 for the RAMAS drilled well waters. All results below detection limits were ignored and reproducibility was calculated by taking the square root of the sum of  $(RSD)^2$  values. Chemical parameters methods are presented in Table 2.

Parameter	Order number in Figure 17	Reproducibility, %	Number of duplicates
Al	1	12	14
As	2	10	21
B	3	11	21
Ba	4	3.7	21
Co	5	6.4	19
Cu	6	1.7	9
K	7	5.6	21
Li	8	10	21
Mn	9	4.1	21
Mo	10	3.3	20
Ni	11	15	12
Pb	12	29	21
Rb	13	1.9	21
Sb	14	4.1	19
Sr	15	1.8	21
Tl	16	0.0	14
U	17	4.9	21
Zn	18	5.7	21
Ca	19	0.5	21
Fe	20	1.1	19
Mg	21	0.4	21
Na	22	0.9	21
Si	23	0.5	21
P	24	9.1	17
S	25	0.3	21
PO <sub>4</sub> <sup>3-</sup>	26	0.8	15
PH	27	0.8	21
EC	28	0.5	21
Br	29	0.0	7
Cl	30	1.4	20
F	31	8.4	18
SO <sub>4</sub> <sup>2-</sup>	32	0.6	20
Alkalinity	33	2.1	20
KMnO <sub>4</sub>	34	1.3	20
Colour number	35	0.0	17

The ratio of cation and anion amounts, Balance Error (BE), analyzed from the water samples is a good indicator of the data's reliability. A difference of  $\pm 5\%$  is generally accepted (Drever 1997). Ion balance is calculated as meq/L units according to the following formula:

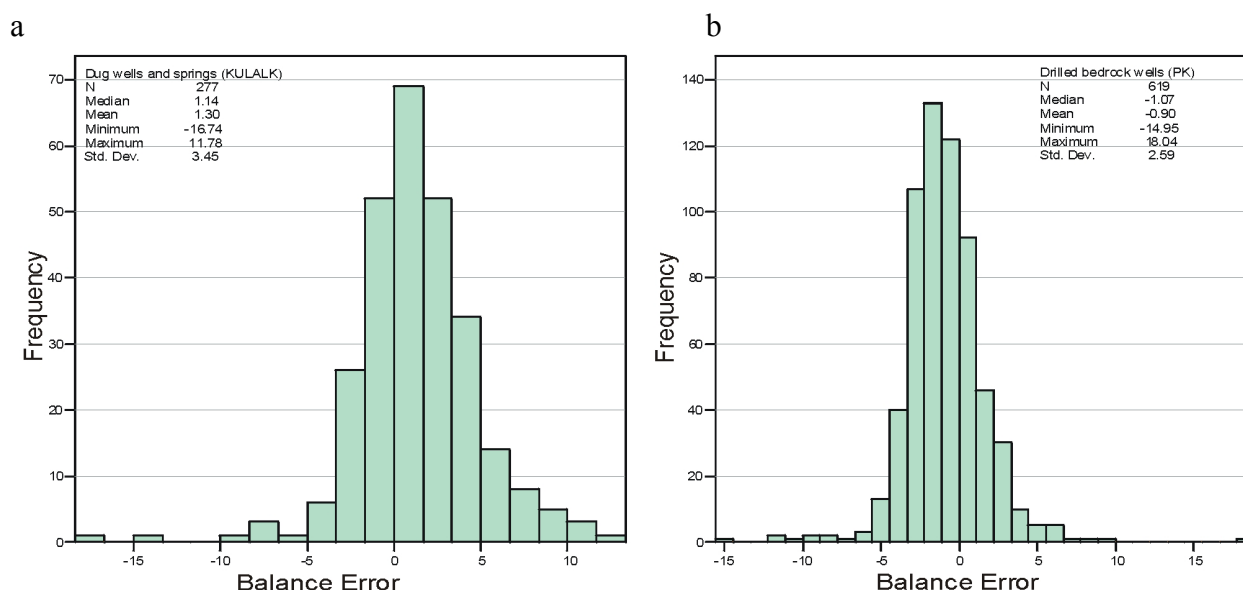
$$\text{BE (\%)} = \frac{(\text{HCO}_3^- + \text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-) - (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)}{(\text{HCO}_3^- + \text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-) + (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)} \times 100$$

Data quality controls were made for the water samples from drilled wells, dug wells, captured wells, and springs. The Balance Error analysis results are shown in Table 5 and the histogram presentations of the BE value distributions for those dug and spring well and drilled well water samples are presented in Figs. 18a-b, respectively. The anion and cation sums differed from each other by less than  $\pm 1.3\%$  on the averages for both water sample groups, which signifies that the  $\pm 5\%$  criterion was well met.

The high BE values ( $\text{BE} > 5\%$ ) in drilled well waters were negative, with about 60 % of these samples having a negative value. In these cases, the reported amount of cations was certainly higher than that of anions. Many of these water samples had a high level of electrical conductivity in comparison with average values. The concentration of Na, Cl, Al, and Fe were also high. Samples where the anions amounts were higher than that of cations had higher concentrations of Al and Fe and the pH values were low. The high BE value ( $\text{BE} > 5\%$ ) in dug wells and spring waters were mainly positive. About 80 % of the exceeded values had higher amounts of anions than cations. These waters mainly had very low pH and high aluminium concentrations.

Table 5. The statistical parameters of Balance Error analysis. PK= Wells drilled into bedrock, KULALK=Dug wells, captured springs and springs.

Elements	N Valid	Minimum	2 %	Median	Mean	Std. Dev	98 %	Maximum
BE_Drilled wells (%)	619	-15.0	-5.70	-1.07	-0.90	2.59	4.99	18.0
BE_Dug wells, springs (%)	277	-16.7	-6.81	1.14	1.30	3.45	9.36	11.8



Figures 18a - 18b. Balance Error (BE) histogram of water samples from dug wells and springs (a), N=277; and from drilled wells, N=619 (b).

### 3.6. Data processing

All geochemical data produced at the GTK was stored in the Alkemia-VAX database (Ahlsved *et al.* 1991). Data from other surveys (for example from municipalities) were stored in Excel files. The statistical and graphical processing of the data was performed using SPSS 14, Aqua Chem 3.6.2, and Excel 2000 software. Corel Draw 12 software was used for the final editing of the graphs. The geological and geochemical data based on maps used in this study were prepared using the ArcGIS 8.3 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. There was some variation in detection limits in different laboratories, especially in the data obtained from the municipalities. However, this was not an issue in this study because the emphasis was not on the small concentrations.

The number of samples, especially groundwater samples, in different calculations, statistical processing and map production is not always the same. This is because the data in this study was compiled from different surveys and the number of analysed quality variables has not always been the same.

## 4. ARSENIC IN THE PIIRKANMAA REGION

### 4.1. Arsenic in the bedrock

On the basis of the data presented by Lahtinen (1996) and Lahtinen *et al.* (2005a), 5.3 % of the 603 bedrock samples from the Pirkanmaa area have arsenic values  $\geq 10$  mg/kg (Figs. 19 - 20). In the three geological subdivisions, the corresponding proportions of arsenic values  $\geq 10$  mg/kg are 0.9 % in the CFGC (Central Finland Granitoid Complex), 10.9 % in the TB (Tampere Belt), and 6.3 % in the PB (Pirkanmaa Belt) (Table 6). The northern half of the study area is mainly composed of granitoids of the CFGC, and the southern half metasedimentary and metavolcanic rocks of the TB and PB and plutonic rocks that cut the supracrustal rocks (Korsman *et al.* 1997). The arsenic values exceeding 10 mg/kg are measured from both supracrustal and plutonic rocks. This indicates regionally elevated arsenic content in southern Pirkanmaa, particularly in the TB area. The bedrock sampling was not equally distributed but the results, however, reflect the overall high arsenic content of the bedrock in the southern part of the study area. The average arsenic content in 6544 bedrock samples in the whole country was 2.69 mg/kg as mean and the median was 0.9 mg/kg (Lahtinen *et al.* 2005a). The maximum value in the data was 729 mg/kg.

Pirkanmaa has a long history of mining including the Ylöjärvi Cu-W-As, Kylmäkoski Ni-Cu, Vammala Ni-Cu, Haveri Au-Cu and Orivesi Au mines (Fig. 7). Arsenic is one of the enriched elements in most of these mined ore deposits (Table 7). It has been difficult to obtain sufficient information from the historical mine sites, but the occurrence of arsenic is somewhat unpredictable. Generally, arsenic concentrations are insignificant in mafic and ultramafic Ni-Cu ores, as in the Vammala mine (Eilu & Lahtinen 2004). However, the Kylmäkoski Ni-Cu ore is atypical in this respect. Some parts of the ore contain more than 1000 mg/kg of arsenic. The arsenic may have assimilated from the surrounding sediments when the intrusion forced its way through. However, the two gold ores are relatively poor in arsenic. Both in Haveri and Orivesi mines the arsenic levels are variable, but generally well below 100 mg/kg. The Ylöjärvi Cu-W-As mine is the only mine in Finland that has produced arsenic concentrate. The highest reported concentrations were around 6000-8000 mg/kg (Clark 1965). The major environmental concerns are related to the tailings area of



this mine and, therefore, the runoff has been monitored for years by the local environmental authority. Currently, there are no metal mine operations in the study area, but exploration is active and is carried out by several companies.

Table 6. Arsenic concentrations in the bedrock of the three geological subdivisions in Pirkanmaa (Lahtinen *et al.* 2005a). See the map in Fig. 7

Rock type	N_ Valid	Mean (mg/kg)	Median (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)
Central Finland Granitoid Complex (CFGC), 218 samples	218	1.73	1.00	0.1	84
Tampere Belt (TB), 128 samples	128	10.41	2.22	0.1	377
Pirkanmaa Belt (PB), 257 samples	257	4.50	1.90	0.1	270

Table 7. Arsenic contents of ores and ore-related rocks in Pirkanmaa.

Mine, commodities	Arsenic content (mg/kg)		Rock type	Reference
	Ore	Ore-related rock		
Haveri, Au-Cu		0-470	Metavolcanic rocks	Mäkelä 1980
Kylmäkoski, Ni-Cu		0-100 (mean)	Mafic-ultramafic plutonic rocks	Papunen 1980
Orivesi, Au		61 (mean)	Sericite-quartz schist	Luukkonen 1994
Vammala, Ni-Cu	27 (mean)		Ultramafic rocks, Ni 0.9% (mean)	Lamberg 2005
Ylöjärvi, Cu-W	4600 (mean mill feed)		Tourmaline breccia	Himmi et al. 1979

Table 8. Arsenic concentration of groundwater from exploration drill holes in Paroistenjärvi mine area in Ylöjärvi municipality.

Elements	Unit	N_ Valid	Median	Mean	Minimum	Maximum
As	µg/L	20	160	2841	0.20	10100

A number of copper, zinc, nickel and particularly gold mineralizations are known in the study area (GTK Active map explorer, <http://maps.gtk.fi/gtk/eexpert.asp>, 15.12.2005). Arsenic is presumably one of the enriched elements in many of these metal occurrences. The majority of the Ni-Cu and Au mineralizations are located in the southern half of the study area where arsenic values of  $\geq 10$  mg/kg in the bedrock are frequent. Elevated arsenic concentrations are especially found in the Tampere-Hämeenlinna region where several gold occurrences exist. Arsenic concentrations in groundwater from selected GTK exploration drill holes are presented in Table 8.

A dozen dimension stone quarries are currently in operation, and there are tens of quarries more or less actively used in aggregate production (Ruokonen, 2006, personal communication). Rock types used for dimension stones and aggregates generally do not contain enriched metal contents.

In general, the bedrock does not cause any significant environmental risk for arsenic dispersion. Even if arsenic rich rocks are exposed to the surface, the dissolution rate of arsenic minerals is slow and the natural processes are able to retain much of the released arsenic. The major concern is related to the arsenic in groundwater. However, the situation is different when arsenic rich bedrock is excavated and crushed as in mining areas or unintentionally during the construction of road cuts or tunnels. Enormous amounts of fresh rock surface are exposed to oxic conditions and the dissolution rate of arsenic may increase significantly. Therefore, appropriate care should be taken when major excavation is carried out in areas where the bedrock may contain harmful elements.



Figure 19. Bedrock quarry in Lempäälä. Photo A. Pullinen.



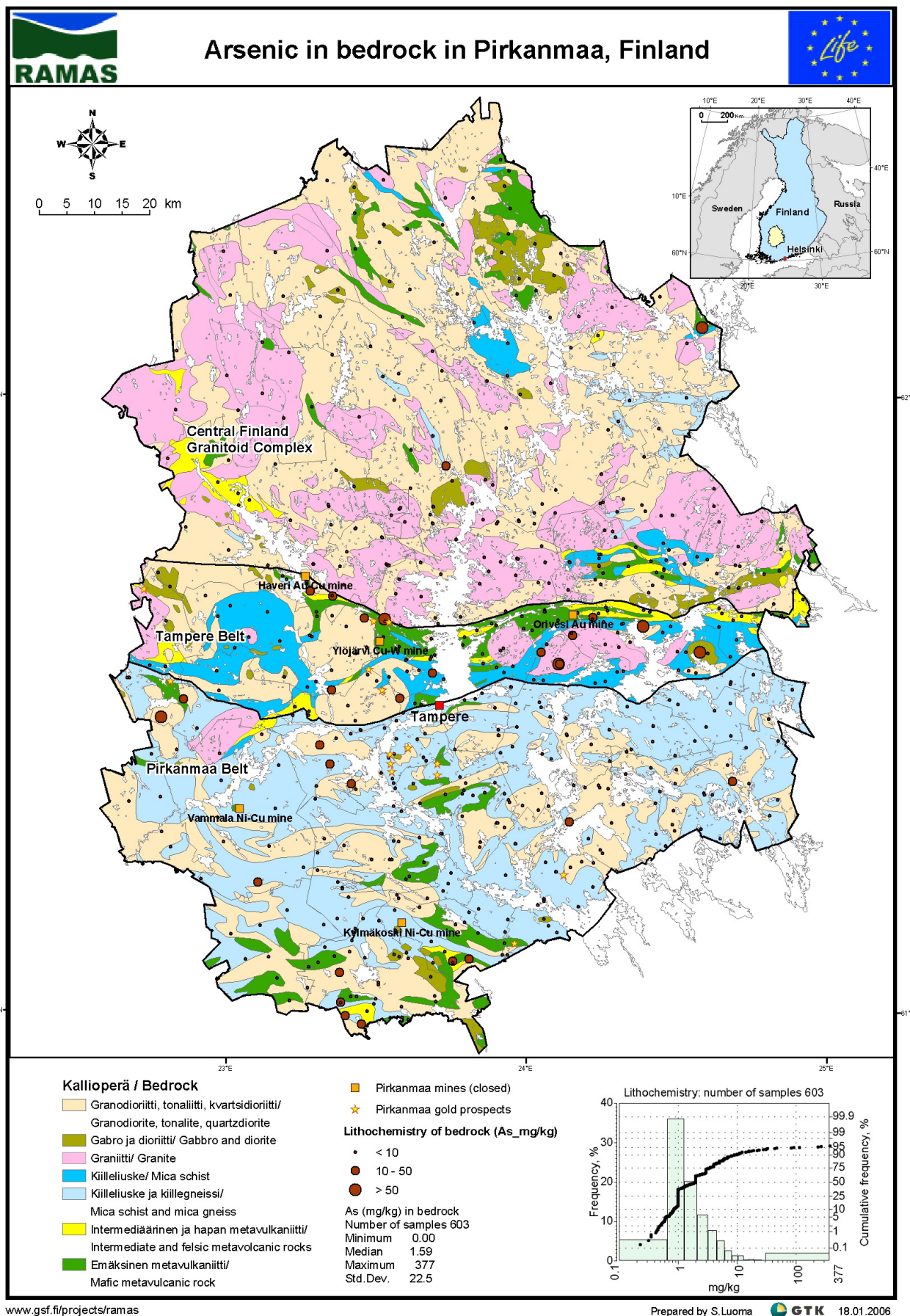


Figure 20. The arsenic content in bedrock. The ground colour is bedrock type and the red symbols are arsenic content in bedrock. The yellow symbols are mines and gold prospecting sites. (Geological mapping data © Geological Survey of Finland, Base map data © National Land Survey of Finland).



## 4.2. Arsenic in glacial till

The available data on arsenic concentrations in soils in the Pirkanmaa region includes the geochemistry of till fines (Fig. 21). So far, geochemical sampling of other soil types in the area has not been done. The results of the agricultural soil and related till sampling performed by the RAMAS project in 2005 will be discussed in the forthcoming report concerning agricultural soils and crops.

All the available data has now been compiled and the database contains 10 869 analyses. There are some issues that demand special attention when the data is evaluated. First, the coverage of the sampling varies according to the targets of the specific campaign. In the nation-wide geochemical survey, the sampling of till fines has been done with a uniform grid over Pirkanmaa, while the soil sampling in the ore exploration has been strongly focused on the surroundings of anticipated mineralizations. The latter approach has resulted in a large number of samples from a relatively small, geochemically anomalous area. Second, the sampling depth has not been the same in all surveys and the grain size of the analysed till fraction has changed from <0.06 mm to <0.2 mm. Finally, the dissolution and analysis methods have varied as well. Therefore, the analytical results are presented below in different tables.

All the soil samples discussed here are leached with *aqua regia* leach. In environmental chemistry, a non-specific term, 'near total', is often used to describe the maximum concentration of an element that can be liberated from a material in its natural environment. An *aqua regia* leach is normally used for simulating this characteristic in the laboratory (Salminen *et al.* 2005). An ammonia acetate leach method for soil samples simulates a natural state in a slightly acid environment. In the supplementary soil sampling of the RAMAS project in 2005 this ammonia acetate leach was also used.



Figure 21. A typical till soil profile in Pirkkala in southern part of Pirkanmaa. (Photo B. Backman)

The ore exploration data has been divided into two subsets according to the sampling depth: samples taken from the upper part (0.5-2 m) and samples taken from deeper part of the till deposit, frequently from the basal till right on the bedrock surface. The nation-wide data is collected only from the upper part of the till layer.

All the arsenic data from the Pirkanmaa region is presented in Table 9. The median arsenic value of the nation-wide till data from the Pirkanmaa region (46 sampling points) is 5.35 mg/kg, which is little higher than that of the whole country (2.57 mg/kg). In the ore exploration till data, the median values are much higher and the arsenic content tends to increase with depth. As one might expect, the maximum values in this data are very high.

In order to show the areal variations in the Pirkanmaa region, the nation-wide till data is presented separately for each of the three geological subdivisions of Pirkanmaa (Table 10). The values are higher in samples taken from the TB (Tampere Belt) and PB (Pirkanmaa Belt) subdivisions than those of the CFGC (Central Finland Granitoid Complex) subdivision. The ore prospecting data has been collected only from the TB and PB areas. The arsenic concentrations from the upper and deeper part of the till layer are presented in Tables 11 - 12.

Table 9. Summary of the arsenic contents in till fines from the Pirkanmaa region.

As_mg/kg	Nation-wide survey Whole Finland	Nation-wide survey Pirkanmaa region	Ore prospect data Deeper part of glacial till	Ore prospect data Upper part of glacial till
N_Valid	1054	46	9392	1431
Minimum	0.10	2.10	<0.05	4.00
2 %	0.16	2.10	2.00	12.0
Mean	3.59	7.78	38.7	22.3
Median	2.57	5.35	14.0	15.0
Std. Dev.	4.60	8.02	227	42.3
98 %	18.3	44.0	198	105
Maximum	44.0	44.0	9280	1050

Table 10. Arsenic statistics from the nation-wide survey data for each of the three geological subdivisions: the Central Finland Granitoid Complex (CFGC) in the north, the Tampere Belt (TB) in the centre, and the Pirkanmaa Belt (PB) in the south. See the map in Fig. 7.

As_mg/kg	Nation-wide survey Pirkanmaa region	CFGC	TB	PB
N_Valid	46	24	6	16
Minimum	2.10	2.10	3.72	4.25
2 %	2.10	2.10	3.72	4.25
Mean	7.78	4.09	6.91	14.2
Median	5.35	3.72	5.92	11.5
Std. Dev.	8.02	1.42	3.44	10.9
98 %	44.0	7.33	12.1	44.0
Maximum	44.0	7.33	12.1	44.0

Table 11. Arsenic in the deeper part of the till layer sampled for ore prospecting in the geological subdivisions TB and PB.

As_mg/kg	Ore prospecting data Pirkanmaa region	TB	PB
N_Valid	9392	2827	6565
Minimum	<0.05	1.00	<0.05
2 %	2.00	2.00	2.00
Mean	38.7	30.4	42.2
Median	14.0	10.1	16.0
Std. Dev.	227	209	234
98 %	198	150	224
Maximum	9280	7860	9280

Table 12. Arsenic in the upper part of the till layer sampled for ore prospecting in the geological subdivisions TB and PB.

As_mg/kg	Ore prospecting data Pirkanmaa region	TB	PB
N_Valid	1431	817	614
Minimum	4.00	15.0	4.00
2 %	12.0	15.0	8.00
Mean	22.3	21.6	23.1
Median	15.0	15.0	15.0
Std. Dev.	42.3	43.8	40.3
98 %	105	79.3	152
Maximum	1050	1050	596

Figures 22 and 23 give the arsenic contents in till from ore prospecting areas (dots) on a map based on the nation-wide arsenic data. The arsenic content in the fine fraction of till in the deeper part of the till layer is presented in Fig. 22 and the arsenic content in the fine fraction of the till in the upper part of the till layer is presented in Fig. 23.

The concentration of arsenic in till fines is locally high. The highest concentrations are closely related to arsenic bearing mineralizations or ores. Analyses of the *aqua regia* leachate (75 % concentrated hydrochloric acid and 25 % concentrated nitric acid) give the near total concentrations of arsenic in a soil sample. The *aqua regia* leaching is strong and is able to dissolve the secondary precipitate minerals, sulphide minerals and most of the minerals like apatite, titanite, biotites, talc and clay minerals, but not feldspars, pyroxenes and amphiboles. In the natural environment of Finland, conditions corresponding to the aquaregia leach are not likely to occur. This method gives the hypothetical concentration for an element that can possibly be released under extreme conditions.

The limit value for arsenic in contaminated soils is 50 mg/kg in populated areas and 100 mg/kg in industrial areas (Valtioneuvoston asetus, Draft 2.2.2006). When comparing the concentrations observed in the naturally rich arsenic soils in the TB and PB subdivisions with these standards, it is obvious that the soils should be treated as contaminated. These areas may pose an ecological risk or a health risk for the population, if the risk in construction sites with major excavations is not recognized and managed properly.



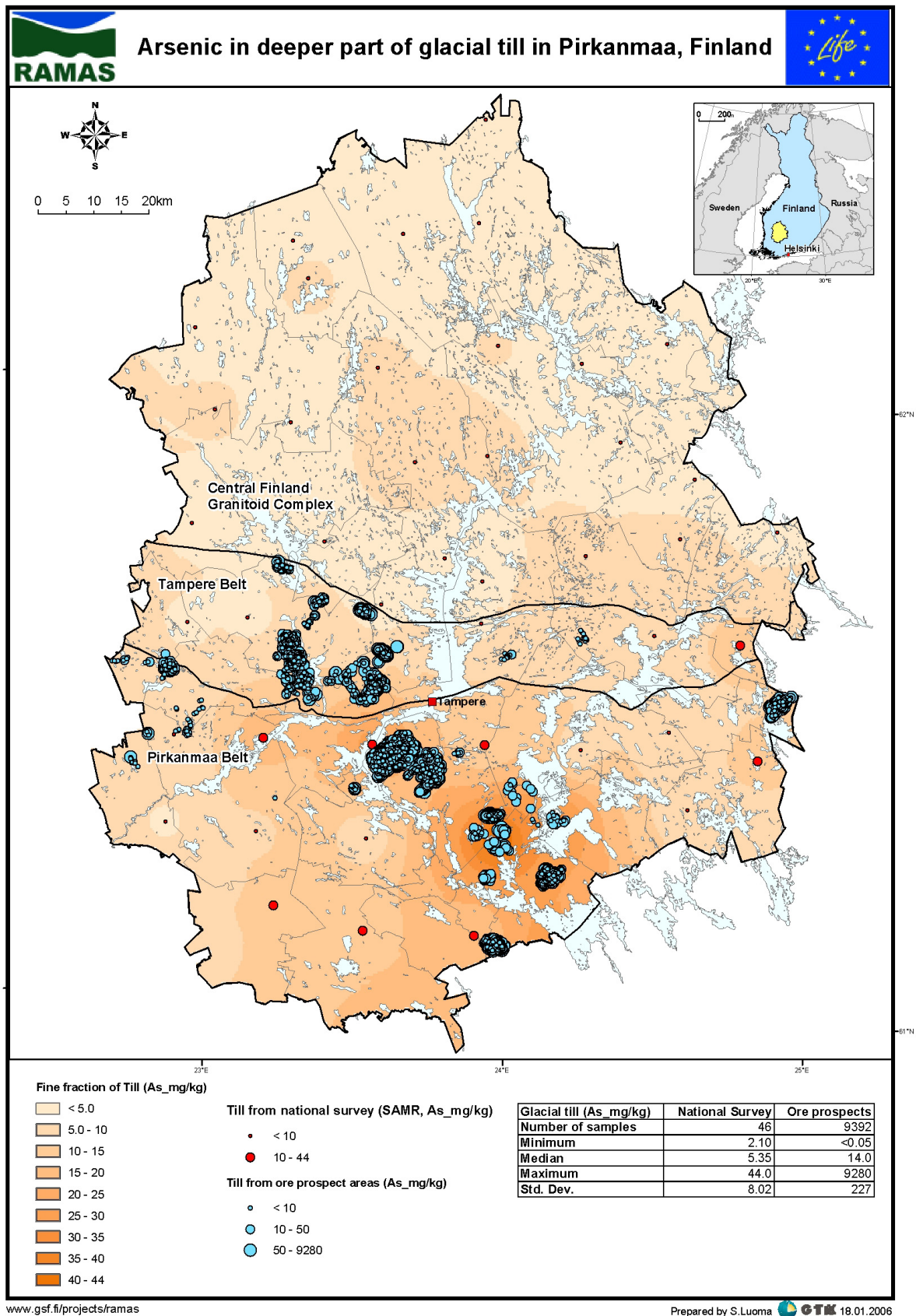


Figure 22. The arsenic content of the deep till samples taken for ore prospecting (blue dots) compared to the regional arsenic data. The concentration contours are based on the data from the nationwide survey. The black (As <10 mg/kg) and red (As 10 – 44 mg/kg) dots indicate the sampling points. (Geological mapping data © Geological Survey of Finland, Base map data © National Land Survey of Finland).

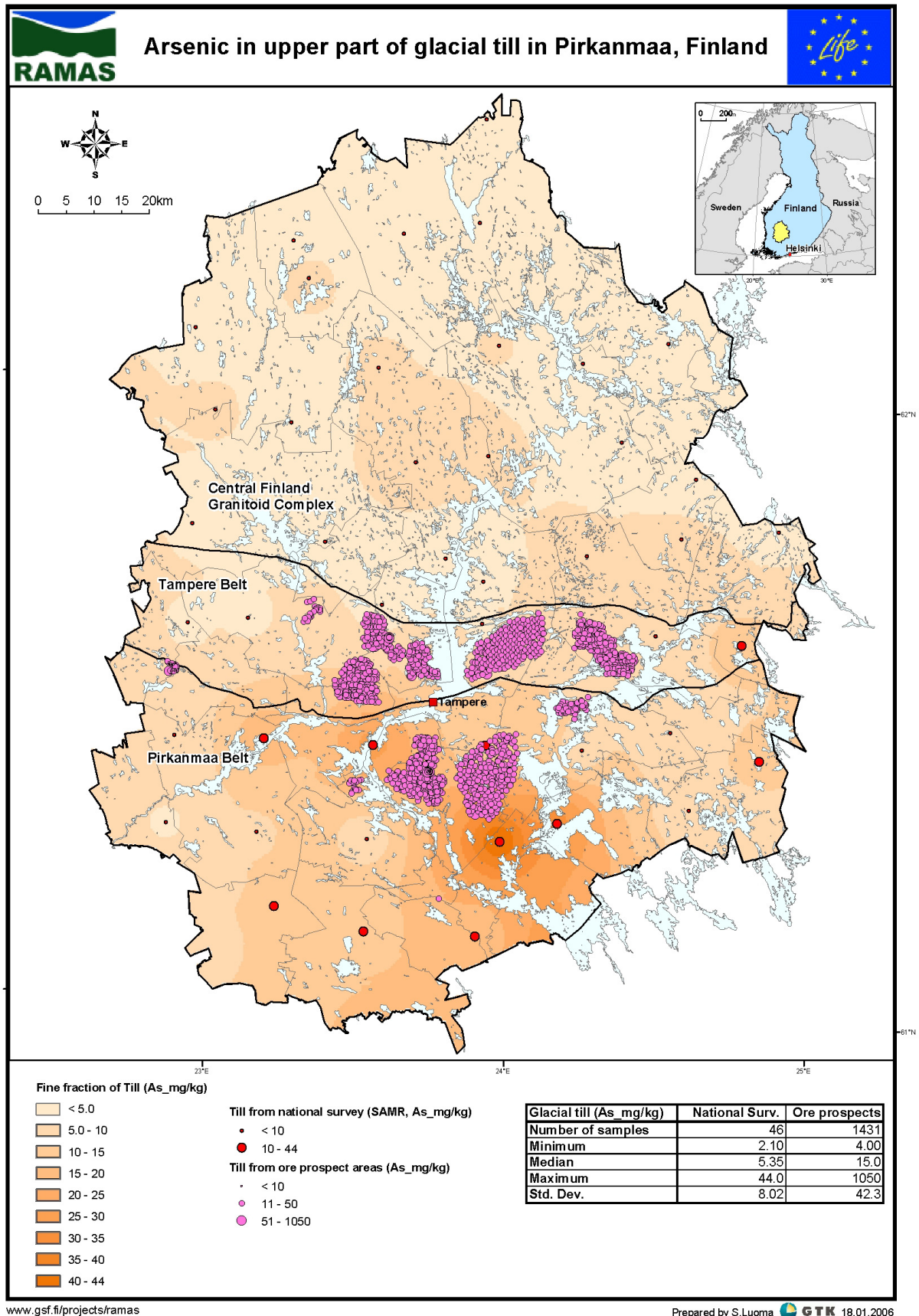


Figure 23. The arsenic content of the upper till samples taken for ore prospecting (pink dots) compared to the regional arsenic data. The concentration contours are based on the data from the nationwide survey. The black (As < 10 mg/kg) and red (As 10 – 44 mg/kg) dots indicate the sampling points. Geological mapping data © Geological Survey of Finland, Base map data © National Land Survey of Finland).

### 4.3. Arsenic in water

The Pirkanmaa region groundwater data will be discussed in two parts. First, the arsenic in the groundwater of crystalline Precambrian bedrock will be discussed followed by the arsenic content in the shallow groundwater of the Quaternary overburden. This due to the fact that the groundwater chemistry is quite different in these two geological formations in Finland as well as in other glaciated Precambrian areas.

#### 4.3.1. Arsenic in bedrock groundwater

All the available bedrock groundwater data from the Pirkanmaa region has been compiled in a database that now contains 1 272 arsenic analyses. The data was collected between 1992 and 2005. Most of the data was collected by the GTK, but also by some municipalities. The Pirkanmaa Regional Environment Centre also provided analyses for the database (see Table 1). Some of the wells (35 wells) have been sampled repeatedly. The hydrogeochemical data received was not uniform as the number of water quality variables varied in different datasets. The major part of the data was complete enough, including the physico-chemical parameters, the main ions and the analyses of trace elements and heavy metals. However, the data obtained from the municipalities contained only arsenic analyses, and some other datasets contained arsenic and part of the main ions. This fact limited the usability of this data in the statistical processing. Therefore, the number of analyses included in the statistical processing and map presentations may vary.

The statistical parameters of groundwater concentrations in drilled wells in Pirkanmaa are presented in Table 13. The data in the table also includes one representative sample from the 35 monitoring wells. The whole chemical composition of the water samples are presented here, because it is essential an overall view of the chemistry of Finnish crystalline bedrock groundwater to understand the geochemical association of the arsenic rich waters.

The median of arsenic content is 1.57 µg/L and the mean 36.1 µg/L. The median and mean values in the wider data, including the results from the municipalities, are 2.5 µg/L and 34.79 µg/L, respectively. The big difference between the median and the mean indicates that in the major part of the dataset, the arsenic content is low and only in a small group of samples was the content high.

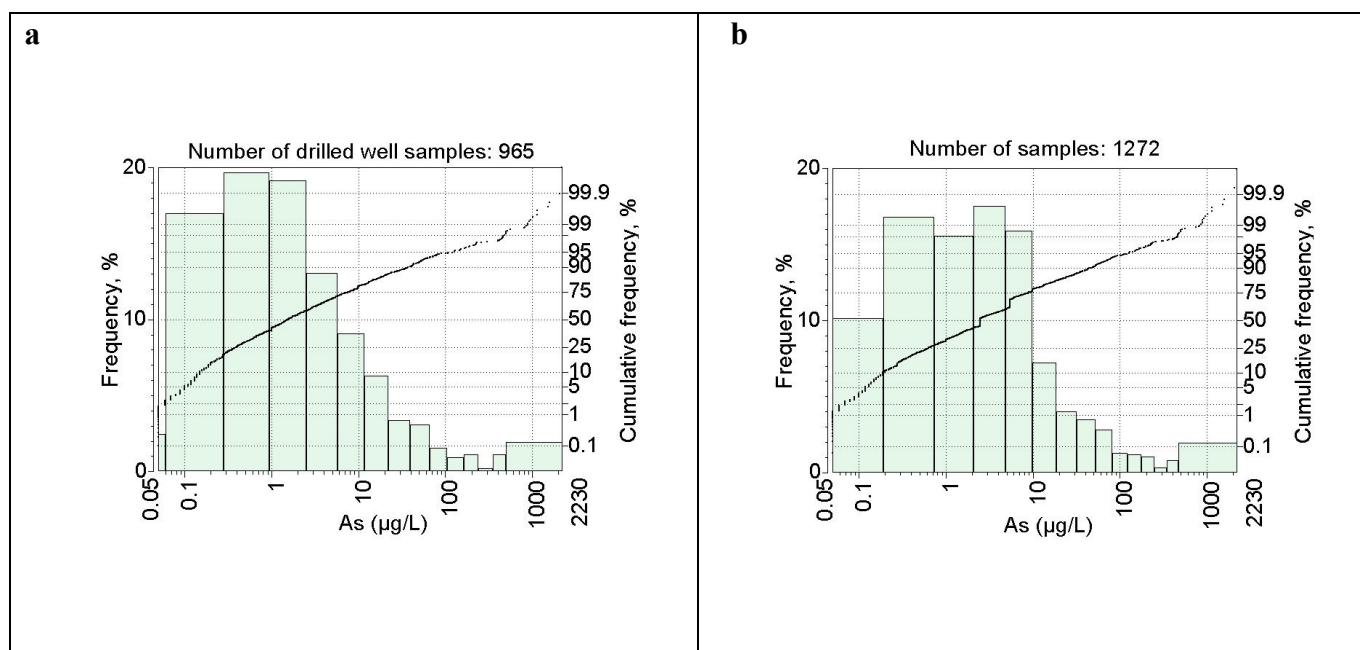
In general, the predominantly Ca-HCO<sub>3</sub> –type groundwater in the drilled wells in the Pirkanmaa region measure up to the quality standards for drinking water. The pH values were close to neutral and the electric conductivities were not too high, meanwhile, the hardness was. Nitrate content and KMnO<sub>4</sub>-numbers were low. The contents of trace elements and heavy metals were also low.

The cumulative concentration curve of arsenic is given in Fig 24. About 22.5 % of the drilled well waters of the GTK data in the Pirkanmaa region exceeded the limit value of 10 µg/L (Fig 24a). In the other diagram (Fig. 24b), the data received from the municipalities is included. From the shape of the curve, it is possible to see that the detection limit of arsenic has been either 5 µg/L or 10 µg/L for many samples. This results a high median value for arsenic (Table 13). The maximum content of arsenic in the data was 2230 µg/L.

Table 13. Minimum, median, mean, standard deviation, maximum and 2 % and 98 % percentiles of water variables from wells drilled into bedrock. The second row of As (marked with \*) also includes the analyses received from municipalities.

Elements	Unit	N_Valid	Minimum	2 %	Median	Mean	Std. Dev	98 %	Maximum
Depth	m	851	10.0	21.0	75.00	81.46	40.8	180.00	270.00
pH, field		517	5.10	5.80	7.40	7.36	0.71	8.76	9.50
EC, field	mS/m	522	5.20	8.69	26.30	28.78	15.12	65.91	149.20
T	°C	714	3.60	5.00	7.80	8.18	2.12	14.00	19.00
CO <sub>2</sub>	mg/L	430	0.00	0.00	10.00	16.14	19.31	65.00	165.00
O <sub>2</sub>	%	467	8.4	9.14	44.45	46.46	24.40	108.80	143.80
Eh	mV	137	-133.00	-65.68	215.00	206.87	127.29	475.22	492.00
PH_LAB		637	5.40	6.05	7.55	7.43	0.62	8.42	9.34
EC_LAB	mS/m	771	4.73	8.40	25.50	28.40	16.48	74.46	162.00
KMnO <sub>4</sub>	mg/L	639	0.44	0.80	3.30	4.34	3.65	17.00	28.00
Hardness	dH	823	0.04	1.19	4.85	5.34	3.02	12.60	33.00
Alkalinity	mmol/L	639	0.11	0.28	1.90	1.93	0.92	4.01	6.79
HCO <sub>3</sub> <sup>-</sup>	mg/L	639	6.71	17.10	116.00	117.44	55.85	245.00	414.00
SO <sub>4</sub> <sup>2-</sup>	mg/L	873	<0.30	2.25	15.90	20.18	15.76	63.50	143.00
Cl <sup>-</sup>	mg/L	873	0.70	1.48	7.43	17.15	39.89	148.00	478.00
NO <sub>3</sub> <sup>-</sup>	mg/L	873	<0.20	<0.20	0.20	2.55	6.34	25.20	66.70
F <sup>-</sup>	mg/L	873	<0.10	<0.10	0.45	0.65	0.59	2.41	4.50
Br <sup>-</sup>	µg/L	873	<0.10	<0.10	0.10	11.63	43.05	107.00	582.00
I	µg/L	376	2.00	2.00	3.67	6.10	6.95	33.06	44.70
PO <sub>4</sub> <sup>3-</sup>	mg/L	470	<0.02	0.02	0.02	0.05	0.11	0.37	1.06
SiO <sub>2</sub>	mg/L	819	3.53	9.85	18.90	19.28	5.37	30.80	37.50
Ca	mg/L	873	<0.10	5.34	21.75	25.05	15.55	64.50	162.00
Mg	mg/L	873	<0.10	1.28	6.95	7.86	4.99	19.75	74.10
Sr	µg/L	869	0.11	30.34	100.00	122.39	97.00	349.74	1410.00
Ba	µg/L	873	0.05	0.35	7.25	20.42	55.80	131.00	858.00
Na	mg/L	852	2.21	3.49	14.00	19.92	19.97	71.97	221.00
K	mg/L	873	0.08	0.74	2.78	3.60	4.69	12.25	74.00
Li	µg/L	869	<0.30	0.30	5.29	6.73	6.44	21.93	84.90
Rb	µg/L	835	0.08	0.25	1.96	2.67	3.43	10.75	42.70
Ag	µg/L	873	<0.01	<0.01	0.01	0.01	0.01	0.02	0.10
Al	µg/L	873	<1.00	<1.00	2.12	16.88	53.54	175.50	953.00
<b>As</b>	<b>µg/L</b>	<b>965</b>	<b>0.05</b>	<b>0.06</b>	<b>1.57</b>	<b>36.10</b>	<b>167.77</b>	<b>499.18</b>	<b>2230.00</b>
<b>As*</b>	<b>µg/L</b>	<b>1272</b>	<b>0.05</b>	<b>0.07</b>	<b>2.50</b>	<b>34.79</b>	<b>152.40</b>	<b>466.54</b>	<b>2230.00</b>
B	µg/L	873	2.86	5.75	27.10	41.13	70.89	160.50	1710.00
Be	µg/L	869	<0.10	<0.10	0.10	0.11	0.04	0.30	0.50
Bi	µg/L	869	<0.03	<0.03	0.03	0.03	0.01	0.03	0.26
Cd	µg/L	873	<0.02	<0.02	0.02	0.04	0.08	0.22	1.48
Co	µg/L	869	<0.02	0.02	0.05	0.49	2.41	3.94	56.50
Cr	µg/L	873	<0.20	<0.20	0.20	0.27	0.19	0.80	2.43
Cu	µg/L	873	0.04	0.04	3.45	23.28	57.46	205.50	873.00
Fe	mg/L	873	<0.03	0.03	0.05	0.57	1.55	6.44	16.80
Mn	µg/L	873	0.05	0.41	53.80	125.10	255.16	661.00	5800.00
Mo	µg/L	873	<0.03	0.05	0.90	1.98	4.49	10.90	72.30
Ni	µg/L	873	<0.06	0.06	0.36	1.89	5.74	14.10	80.30
Pb	µg/L	873	<0.03	0.03	0.10	0.32	0.62	2.11	8.87
S	mg/L	389	0.30	1.30	5.63	7.12	5.36	21.08	51.10
Sb	µg/L	873	<0.02	0.02	0.03	0.11	0.28	0.77	3.61
U	µg/L	869	<0.01	0.01	0.85	5.20	13.68	50.77	149.00
V	µg/L	869	0.02	0.02	0.17	0.47	1.20	3.01	23.30
Zn	µg/L	873	<0.20	0.61	15.25	75.78	367.43	503.00	8750.00





Figures 24a - 24b. The cumulative concentration curve for arsenic in water from drilled wells. Figure a consists of GTK data and Figure b consists of the results received from municipalities.

The close association of the arsenic in drilled wells and the arsenic source in bedrock is readily seen in Fig. 25, where the data is presented on the geological map of the region. Practically all elevated arsenic concentrations are from wells located in the Tampere and Pirkanmaa Belts, where gold (and arsenic) potential rock types dominate. The low arsenic levels in the Granitoid Complex rocks in the north are reflected in low concentrations in the well waters.

Tables 14-16 give the chemical compositions of the drilled well waters in the different parts of the Pirkanmaa region. A noteworthy point here is that the high arsenic concentrations do not unequivocally correlate with the water chemistry.

The waters in the Tampere Belt have higher contents of Ca, Sr, Ba,  $\text{HNO}_3$ , F, Mo, Sb, Cu, U, V, and Zn, while higher levels of  $\text{SO}_4^{2-}$  and S,  $\text{SiO}_2$ , Na, Li, Rb, B, Fe, and Mn characterize the drilled wells in the Pirkanmaa Belt. The average pH and electric conductivity were the same in the well waters in these two geological subdivisions. The average Eh values were lower in the well waters in the Pirkanmaa Belt, which may have some implications for the speciation of arsenic. However, there is not enough data to verify this relationship.

The chemical characteristics of the drilled well waters from all the geological subdivisions are presented in the Piper diagrams in Figs. 26a-d. The data is classified according to the arsenic contents below or above 10  $\mu\text{g/L}$ . Most of the water samples are typical  $\text{Ca-HCO}_3$  waters. In general, the chemistry of the drilled well waters in the Pirkanmaa region is comparable to all of Finland (Lahermo *et al.* 1990). There is no obvious correlation between the water type and arsenic concentration when comparing the chemistry of the wells with high ( $\text{As} > 10 \mu\text{g/L}$ ) and low ( $\text{As} < 10 \mu\text{g/L}$ ) arsenic concentrations. The critical factor seems to be the availability of arsenic from the bedrock. However, there are some samples of Na-Cl type, where the arsenic content is high. These samples represent deeper groundwater in the bedrock.



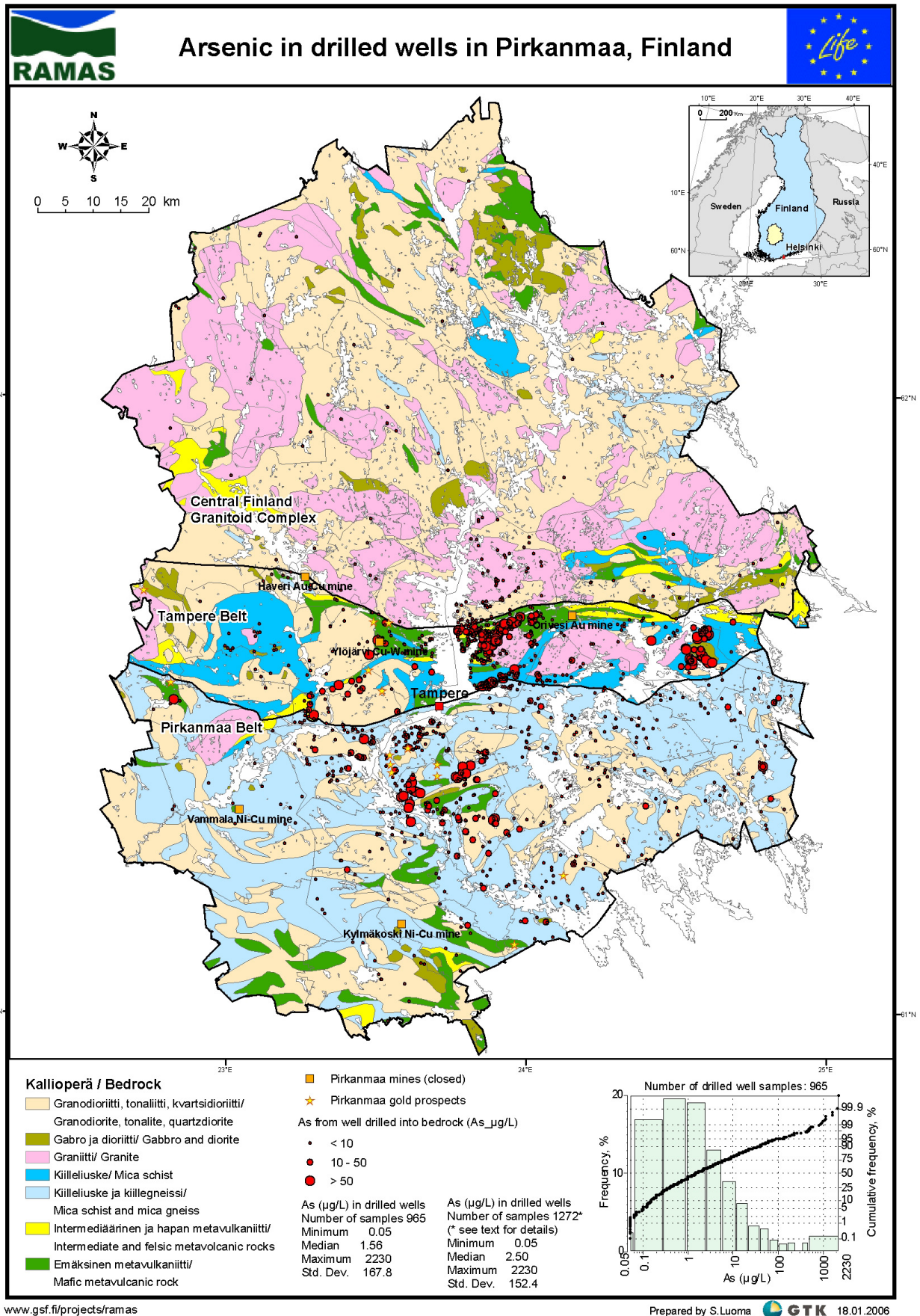


Figure 25. Arsenic concentrations in drilled wells within the main geological subdivisions in the Pirkanmaa region: the Central Finland Granitoid Complex (CFGC) in the north, the Tampere Belt (TB) in the centre, and the Pirkanmaa Belt (PB) in the south. The limit value for arsenic is 10 µg/L.

Table 14. Statistics of groundwater quality in drilled wells located in CFGC. See map in Fig. 7.

**Central Finland Granitoid Complex (CFGC)**

Elements	Unit	N_Valid	Minimum		Median	Mean	Std. Dev	98 %	Maximum
pH, field		84	5.10	5.17	7.35	7.20	0.85	8.63	8.70
EC, field	mS/m	84	5.80	6.78	25.55	26.34	17.32	83.61	149.20
T	°C	84	5.20	5.27	7.75	8.23	1.92	13.18	13.60
CO <sub>2</sub>	mg/L	71	0.00	0.00	11.00	21.32	21.31	70.00	70.00
O <sub>2</sub>	%	72	0.00	0.00	48.30	49.53	22.03	128.43	137.40
Eh	mV	2	135.00	135.00	165.00	165.00	42.43	195.00	195.00
PH_LAB		86	5.47	5.66	7.40	7.28	0.75	8.60	8.60
EC_LAB	mS/m	92	4.82	5.75	25.00	26.13	18.90	92.17	162.00
Hardness	mg/L	92	0.57	0.60	3.40	4.43	4.36	24.42	27.00
	dH	98	0.00	0.66	4.80	4.97	3.78	13.30	33.00
Alkalinity	mmol/L	92	0.15	0.21	1.99	1.79	0.97	3.68	3.83
HCO <sub>3</sub> <sup>-</sup>	mg/L	92	9.15	12.81	121.50	109.25	59.43	224.54	234.00
SO <sub>4</sub> <sup>2-</sup>	mg/L	104	<0.30	1.01	8.60	9.80	5.64	25.44	27.00
Cl <sup>-</sup>	mg/L	104	1.09	1.16	7.40	18.12	50.49	150.80	478.00
NO <sub>3</sub> <sup>-</sup>	mg/L	104	<0.20	<0.20	0.66	3.64	7.74	34.03	54.40
F <sup>-</sup>	mg/L	104	<0.10	<0.10	0.44	0.66	0.66	3.14	3.60
Br <sup>-</sup>	µg/L	104	<0.10	<0.10	0.10	12.71	50.38	59.51	506.00
I	µg/L	65	2.00	2.00	4.50	8.72	9.61	42.12	44.10
PO <sub>4</sub> <sup>3-</sup>	mg/L	74	0.02	0.02	0.02	0.04	0.12	0.61	1.06
SiO <sub>2</sub>	mg/L	98	5.65	6.87	15.70	16.17	5.22	29.17	32.70
Ca	mg/L	104	<0.10	3.16	20.40	21.98	14.84	64.56	114.00
Mg	mg/L	104	<0.10	0.95	7.89	8.66	8.12	23.25	74.10
Sr	µg/L	104	0.26	22.03	115.50	140.68	111.27	421.80	901.00
Ba	µg/L	104	0.22	1.85	24.70	80.11	140.32	569.80	858.00
Na	mg/L	104	2.61	3.36	12.60	16.85	14.58	67.29	68.30
K	mg/L	104	0.08	0.52	2.25	2.57	1.70	9.66	12.40
Li	µg/L	104	<0.30	<0.30	3.10	4.18	3.79	22.06	23.40
Rb	µg/L	92	0.14	0.19	0.97	1.79	2.55	14.17	14.60
Ag	µg/L	104	<0.01	<0.01	0.01	0.01	0.01	0.03	0.06
Al	µg/L	104	<1.00	<1.00	2.77	19.21	51.45	177.80	443.00
As	µg/L	115	0.05	0.06	0.46	0.95	1.72	10.00	10.00
As*	µg/L	133	0.05	0.06	0.61	1.35	1.98	10.00	10.00
B	µg/L	104	3.87	5.14	27.10	34.20	27.55	151.00	158.00
Be	µg/L	104	<0.10	<0.10	0.10	0.11	0.06	0.30	0.30
Bi	µg/L	104	<0.03	<0.03	0.03	0.03	0.01	0.03	0.03
Cd	µg/L	104	<0.02	<0.02	0.02	0.04	0.04	0.22	0.23
Co	µg/L	104	<0.02	0.02	0.03	0.80	5.60	8.10	56.50
Cr	µg/L	104	<0.20	<0.20	0.20	0.30	0.20	0.81	1.36
Cu	µg/L	104	0.04	0.04	6.90	40.35	84.08	371.30	463.00
Fe	mg/L	104	<0.03	<0.03	0.03	0.22	1.00	5.55	8.31
Mn	µg/L	104	0.05	0.15	24.50	121.54	223.46	848.30	1340.00
Mo	µg/L	104	<0.03	<0.03	1.89	2.75	3.19	15.87	17.90
Ni	µg/L	104	<0.06	0.06	0.31	0.85	1.49	7.37	10.80
Pb	µg/L	104	0.03	0.03	0.16	0.47	0.75	3.66	4.11
S	mg/L	65	0.30	0.39	3.22	3.62	1.95	8.46	8.70
Sb	µg/L	104	<0.02	<0.02	0.03	0.05	0.04	0.18	0.21
U	µg/L	104	0.01	0.01	5.25	15.74	26.03	106.66	149.00
V	µg/L	104	0.02	0.02	0.43	1.21	2.66	9.15	23.30
Zn	µg/L	104	0.13	0.62	16.15	85.63	293.59	786.40	2810.00

Table 15. Statistics of groundwater quality in drilled wells located in TB. See map in Fig. 7.

**Tampere Belt (TB)**

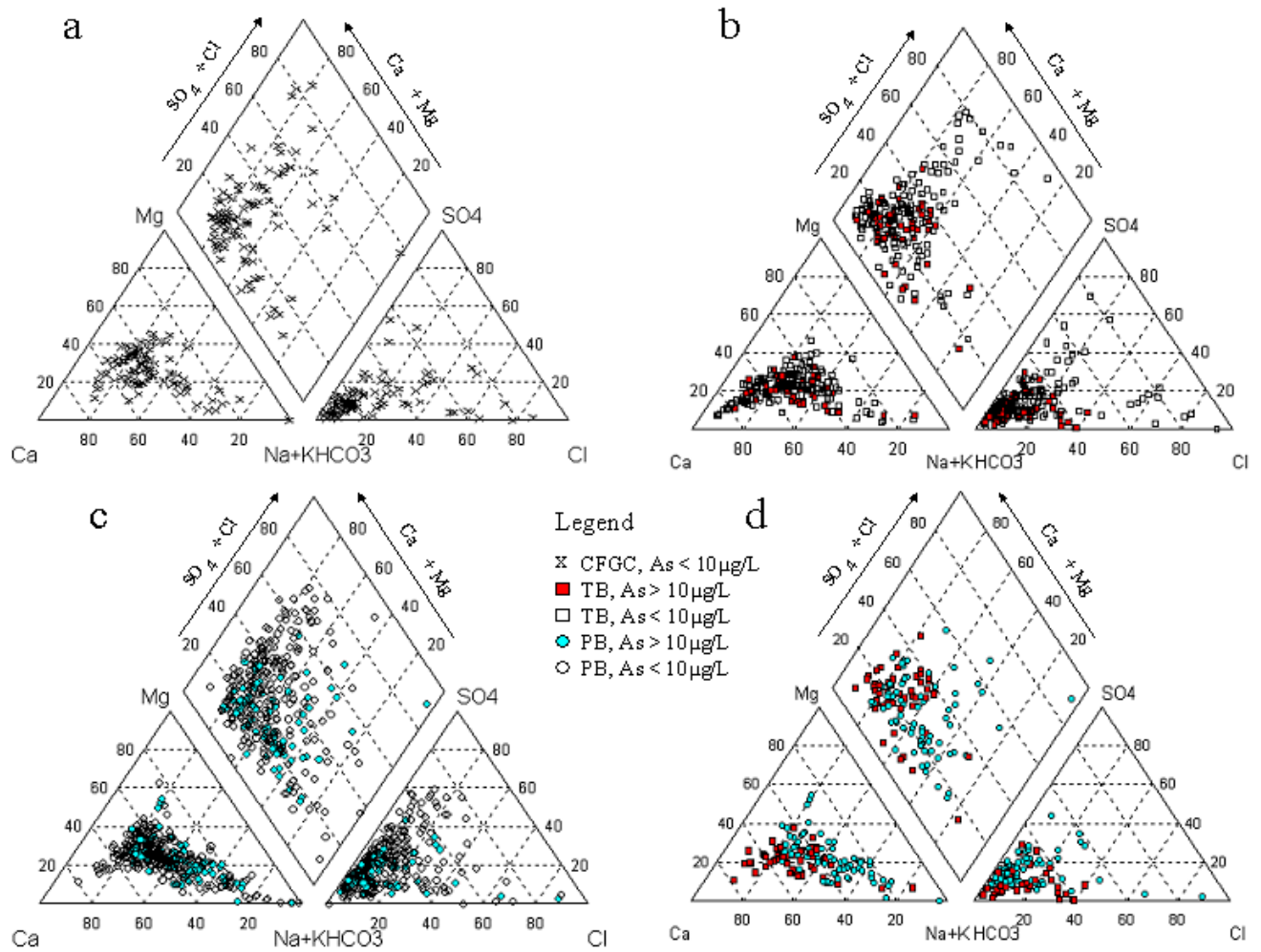
Elements	Unit	N_Valid	Minimum	2 %	Median	Mean	Std. Dev	98 %	Maximum
pH, field		159	5.70	5.92	7.40	7.29	0.57	8.40	8.70
EC, field	mS/m	159	5.20	8.02	26.30	29.49	16.53	69.32	144.50
T	°C	190	4.00	4.40	7.20	7.45	1.57	11.84	13.00
CO <sub>2</sub>	mg/L	121	0.00	0.00	11.00	15.21	17.87	52.80	150.00
O <sub>2</sub>	%	131	8.80	9.29	47.40	50.00	26.81	118.74	143.80
Eh	mV	74	-55.00	-21.50	232.00	249.27	110.29	484.00	492.00
PH_LAB		125	5.50	5.95	7.50	7.38	0.59	8.23	8.31
EC_LAB	mS/m	186	6.80	8.34	25.70	30.06	21.29	123.68	160.00
KMnO <sub>4</sub>	mg/L	182	0.44	0.83	3.73	5.04	4.16	19.05	25.00
Hardness	dH	201	1.03	1.57	5.48	6.24	3.57	17.19	27.60
Alkalinity	mmol/L	182	0.11	0.29	2.01	2.05	1.09	4.86	6.79
HCO <sub>3</sub> <sup>-</sup>	mg/L	182	6.71	17.89	122.50	124.93	66.61	296.58	414.00
SO <sub>4</sub> <sup>2-</sup>	mg/L	245	0.38	1.21	13.70	15.35	9.83	45.14	86.00
Cl <sup>-</sup>	mg/L	245	0.98	1.39	7.70	19.81	49.24	175.12	412.00
NO <sub>3</sub> <sup>-</sup>	mg/L	245	<0.20	<0.20	0.20	3.23	6.51	29.38	37.40
F <sup>-</sup>	mg/L	245	0.10	0.10	0.57	0.73	0.61	2.40	3.22
Br <sup>-</sup>	µg/L	245	<0.10	<0.10	0.10	12.71	50.38	169.84	582.00
I	µg/L	88	2.00	2.00	3.22	5.22	6.82	35.11	44.70
PO <sub>4</sub> <sup>3-</sup>	mg/L	110	<0.02	0.02	0.02	0.04	0.10	0.35	0.93
SiO <sub>2</sub>	mg/L	200	7.30	10.20	17.85	18.18	5.13	29.49	32.70
Ca	mg/L	245	4.95	6.67	26.00	30.73	19.91	85.28	162.00
Mg	mg/L	245	1.23	1.72	6.30	7.22	4.27	20.92	32.40
Sr	µg/L	244	20.50	39.07	114.00	146.74	133.46	443.20	1410.00
Ba	µg/L	245	0.21	0.48	12.90	21.74	26.73	103.08	216.00
Na	mg/L	245	2.21	3.21	11.60	18.22	23.62	76.88	221.00
K	mg/L	245	0.36	0.62	2.43	3.06	3.61	9.27	43.80
Li	µg/L	244	<0.30	0.30	4.59	6.99	8.83	26.82	84.90
Rb	µg/L	243	0.08	0.14	1.71	2.40	3.42	8.85	37.50
Ag	µg/L	245	<0.01	0.01	0.01	0.01	0.01	0.04	0.10
Al	µg/L	245	<1.00	<1.00	2.63	26.78	79.76	291.16	953.00
<b>As</b>	<b>µg/L</b>	<b>320</b>	<b>0.05</b>	<b>0.08</b>	<b>4.05</b>	<b>75.38</b>	<b>248.57</b>	<b>959.00</b>	<b>2230.00</b>
<b>As*</b>	<b>µg/L</b>	<b>588</b>	<b>0.05</b>	<b>0.13</b>	<b>5.50</b>	<b>56.69</b>	<b>194.81</b>	<b>610.68</b>	<b>2230.00</b>
B	µg/L	245	2.87	4.82	24.90	44.05	113.13	161.08	1710.00
Be	µg/L	244	<0.10	<0.10	0.10	0.11	0.05	0.29	0.50
Bi	µg/L	244	<0.03	<0.03	0.03	0.03	0.01	0.05	0.13
Cd	µg/L	245	<0.02	0.02	0.02	0.05	0.09	0.24	0.98
Co	µg/L	244	<0.02	0.02	0.06	0.44	2.07	4.14	29.40
Cr	µg/L	245	<0.20	0.11	0.20	0.27	0.18	0.90	1.71
Cu	µg/L	245	0.04	0.04	6.28	23.10	42.87	165.36	322.00
Fe	mg/L	245	<0.03	0.03	0.04	0.32	0.78	2.58	7.15
Mn	µg/L	245	0.09	0.31	41.00	162.04	418.08	829.00	5800.00
Mo	µg/L	245	0.03	0.08	1.22	3.27	7.77	35.74	72.30
Ni	µg/L	245	<0.06	<0.06	0.36	1.22	3.26	11.22	30.20
Pb	µg/L	245	<0.03	0.03	0.16	0.34	0.63	2.32	5.91
S	mg/L	96	1.25	1.94	4.65	5.52	4.20	27.42	29.30
Sb	µg/L	245	<0.02	0.02	0.06	0.19	0.43	1.85	3.61
U	µg/L	244	0.01	0.02	1.41	5.08	11.36	39.83	104.00
V	µg/L	244	0.02	0.02	0.20	0.46	0.68	2.93	4.65
Zn	µg/L	245	0.26	0.63	15.80	111.03	646.04	451.56	8750.00

Table16. Statistics of groundwater quality in drilled wells located in PB. See map in Fig. 7.

**Pirkanmaa Belt (PB)**

Elements	Unit	N_Valid	Minimum	2 %	Median	Mean	Std. Dev	98 %	Maximum
pH, field		275	5.50	5.90	7.50	7.45	0.72	9.10	9.50
EC, field	mS/m	280	6.70	10.00	26.65	29.11	13.47	67.31	125.10
T	°C	441	3.60	5.00	8.00	8.48	2.28	15.12	19.00
CO <sub>2</sub>	mg/L	239	0.00	0.00	9.00	15.08	19.23	60.40	165.00
O <sub>2</sub>	%	265	0.00	8.86	42.10	43.88	23.52	99.02	114.00
Eh	mV	62	-133.00	-124.42	167.00	157.61	130.77	416.62	420.00
PH_LAB		426	5.40	6.15	7.57	7.48	0.60	8.66	9.34
EC_LAB	mS/m	493	4.73	9.07	25.50	28.19	13.68	63.67	140.00
KMnO <sub>4</sub>	mg/L	365	0.69	1.13	3.03	3.96	3.10	15.54	28.00
Hardness	dH	524	0.04	1.19	4.64	5.06	2.54	11.90	15.50
Alkalinity	mmol/L	365	0.16	0.33	1.87	1.90	0.79	3.90	6.14
CO <sub>2</sub>	mg/L	365	9.76	20.10	114.00	115.66	48.32	237.88	375.00
O <sub>2</sub>	mg/L	524	0.30	4.53	19.30	24.52	17.65	76.30	143.00
Eh	mg/L	524	0.70	1.62	7.27	15.73	31.88	100.30	377.00
PH_LAB	mg/L	524	<0.20	<0.20	0.20	2.02	5.90	21.95	66.70
EC_LAB	mg/L	524	<0.10	0.10	0.41	0.61	0.56	2.49	4.50
KMnO <sub>4</sub>	µg/L	524	<0.10	<0.10	0.10	11.42	34.02	107.00	364.00
Hardness	µg/L	223	2.00	2.00	3.56	5.69	5.88	29.80	37.90
Alkalinity	mg/L	286	0.02	0.02	0.02	0.06	0.10	0.39	0.98
HCO <sub>3</sub> <sup>-</sup>	mg/L	521	3.53	11.10	20.00	20.28	5.20	31.11	37.50
SO <sub>4</sub> <sup>2-</sup>	mg/L	524	0.10	5.34	20.75	23.01	12.41	59.75	89.70
Cl <sup>-</sup>	mg/L	524	0.10	1.15	7.12	8.00	4.43	19.55	24.60
NO <sub>3</sub> <sup>-</sup>	µg/L	521	0.11	30.35	91.50	107.27	66.12	291.24	638.00
F <sup>-</sup>	µg/L	524	0.05	0.29	3.89	7.95	11.06	42.00	89.50
Br <sup>-</sup>	mg/L	503	2.75	3.88	15.50	21.38	18.89	74.25	193.00
I	mg/L	524	0.21	0.92	3.19	4.05	5.43	13.70	74.00
PO <sub>4</sub> <sup>3-</sup>	µg/L	521	0.30	0.41	5.98	7.09	5.33	21.92	44.20
SiO <sub>2</sub>	µg/L	500	0.16	0.35	2.25	2.97	3.55	10.90	42.70
Ag	µg/L	524	<0.01	<0.01	0.01	0.01	0.01	0.02	0.07
Al	µg/L	524	<1.00	<1.00	1.95	11.82	34.96	109.00	409.00
<b>As</b>	<b>µg/L</b>	<b>530</b>	<b>0.05</b>	<b>0.05</b>	<b>1.50</b>	<b>20.07</b>	<b>112.35</b>	<b>214.76</b>	<b>1560.00</b>
<b>As*</b>	<b>µg/L</b>	<b>551</b>	<b>0.05</b>	<b>0.05</b>	<b>1.60</b>	<b>20.07</b>	<b>110.22</b>	<b>213.16</b>	<b>1560.00</b>
B	µg/L	524	2.86	6.14	27.70	41.20	47.48	179.00	549.00
Be	µg/L	521	<0.10	<0.10	0.10	0.10	0.04	0.20	0.45
Bi	µg/L	521	<0.03	<0.03	0.03	0.03	0.01	0.03	0.26
Cd	µg/L	524	<0.02	<0.02	0.02	0.04	0.09	0.22	1.48
Co	µg/L	521	<0.02	0.02	0.06	0.46	1.20	3.71	12.40
Cr	µg/L	524	<0.20	<0.20	0.20	0.27	0.19	0.74	2.43
Cu	µg/L	524	0.04	0.04	2.63	20.02	56.51	178.50	873.00
Fe	mg/L	524	<0.03	0.03	0.07	0.77	1.85	7.43	16.80
Mn	µg/L	524	0.10	0.49	61.95	108.00	127.31	468.50	864.00
Mo	µg/L	524	0.03	0.06	0.71	1.21	1.42	5.52	12.10
Ni	µg/L	524	<0.06	<0.06	0.39	2.42	7.00	18.25	80.30
Pb	µg/L	524	<0.03	0.03	0.08	0.28	0.58	1.83	8.87
S	mg/L	228	0.95	1.97	7.10	8.81	5.76	23.75	51.10
Sb	µg/L	524	<0.02	<0.02	0.03	0.08	0.21	0.56	2.95
U	µg/L	521	<0.01	0.01	0.51	3.14	9.57	37.38	116.00
V	µg/L	521	0.02	0.02	0.14	0.34	0.81	2.03	11.30
Zn	µg/L	524	0.25	0.60	14.45	57.31	112.77	513.00	759.00





Figures 26a-d. The chemical composition of 619 drilled well waters in Pirkanmaa: a) drilled wells in the Central Finland Granitoid Complex ( $As < 10 \mu g/L$ ), b) drilled wells in the Tampere Belt, c) the drilled wells in the Pirkanmaa Belt, and d) all samples with arsenic content more than  $10 \mu g/L$ .

The nature of arsenic rich waters was studied with statistical tools to see if it is possible to characterize and predict the arsenic risk based on the chemical composition of the water. Aqua Chem statistical software was used to produce Stiff diagrams for drilled well waters with the highest arsenic levels (and the complete cation and anion analyses). The diagram is based on the concentrations of selected major components in the water. Basically, it provides a quick way to visualize and compare the chemical compositions. Similar shapes indicate similar chemical ratios in the waters and the wider shape indicates higher concentrations of the dissolved components. The diagrams are displayed in Fig. 27. Three of these wells are located in the Tampere Belt ( $As$  822 – 2230  $\mu g/L$ ) and three in the Pirkanmaa Belt ( $As$  510-1560  $\mu g/L$ ). The wide shape (high calcium and bicarbonate) of the Stiff diagrams from the Tampere Belt indicates a longer contact time between the water and the bedrock. The more narrow shape (low calcium and bicarbonate concentrations) of the diagrams from the Pirkanmaa Belt indicates shorter contact times with the bedrock. The arsenic content shows some correlation with the residence time, that is, longer reaction times increase the amount of dissolved arsenic. However, the wells from the Pirkanmaa Belt demonstrate that arsenic may dissolve in water very quickly when the hydrogeochemical conditions are favourable.



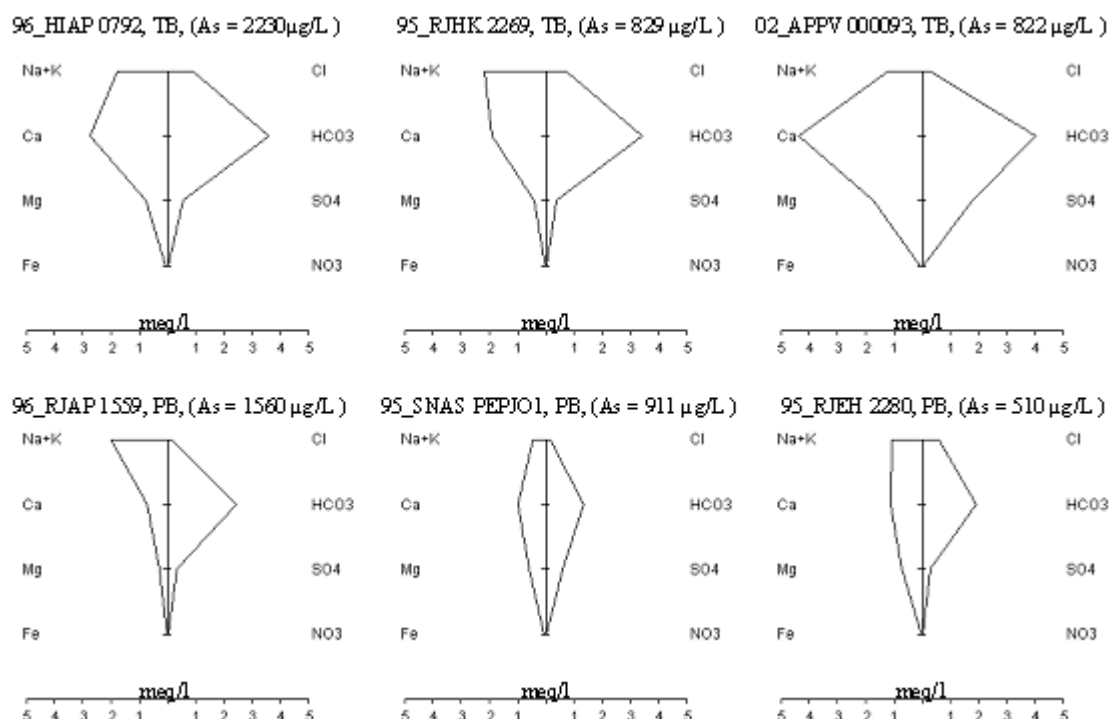


Figure 27. Stiff diagrams for drilled well waters with high arsenic content located in the subdivisions of Tampere (upper row) and Pirkanmaa Belts (lower row). Major ions are given in mill equivalents/L.

Correlation analysis of groundwater chemistry was done in order to find the relationships of arsenic and other elements or parameters. Pearson and Spearman's rho correlation methods (SPSS statistical software) were applied. Cross plots of arsenic and each parameter were also carried out to confirm the validity of the correlation.

Pearson's correlation coefficient is a measure of linear association. Two variables can be perfectly related, but if the relationship is not linear, Pearson's correlation coefficient is not an appropriate statistical method for measuring their association. However, the Spearman's rho correlation method is a nonparametric test that determines a correlation coefficient or the strength of the association when the relationship between two variables is nonlinear. Correlation coefficients range in value from  $-1$  (a perfect negative relationship) and  $+1$  (a perfect positive relationship). A value of  $0$  indicates no linear 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. Most significant correlation results with  $p$ -value  $<0.05$  are shown in Table 17.

For most correlations, the Spearman's method seems to be more suitable, suggesting that the relationship between arsenic and many of the components is nonlinear. Significant linear correlation (coefficient  $>\pm 0.7$ ) is observed only between arsenic and phosphate. This underlines the similar geochemical properties of these elements. The nonlinear Spearman correlations are weaker and more difficult to interpret and are probably related to the differences in the bedrock chemistry, since there are differences between the Tampere and Pirkanmaa Belts (Table 17). Positive correlations are found with pH, EC,  $\text{HCO}_3^-$ , F,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SiO}_2$ , Ca, Sr, Na, Se and hardness, Negative correlations are found with  $\text{O}_2$ ,  $\text{SO}_4^{2-}$ , Ba and Cd. The correlation with iron is contradictory because in the majority of samples, the iron concentration is less than the detection limit. However, cross plots from high arsenic wells show a negative correlation between iron and arsenic.

Table 17. Comparison of correlation coefficients between Pearson and Spearman's rho correlation values for arsenic in drilled wells in Pirkanmaa region.

Elements	All data, As >10 µg/L		All data		CFGC		TB		PB	
	Pearson	Spearman	Pearson	Spearman	Pearson	Spearman	Pearson	Spearman	Pearson	Spearman
Depth	N	N	N	0.116	N	N	N	N	N	0.113
pH	N	N	N	0.343	0.418	0.526	0.178	0.328	N	0.34
EC	0.324	N	N	0.162	N	0.341	N	0.255	N	N
Temperature	N	N	N	N	N	N	N	N	N	N
O <sub>2</sub>	N	N	N	-0.205	N	N	N	-0.358	N	-0.162
Eh	N	N	N	0.357	N	N	N	0.331	N	0.292
KMnO <sub>4</sub>	0.219	0.174	0.085	N	N	N	0.203	N	N	-0.163
Hardness	0.185	N	0.076	0.103	N	0.233	0.162	0.168	N	N
HCO <sub>3</sub> <sup>-</sup>	0.216	N	0.101	0.26	0.223	0.409	0.192	0.325	N	0.202
SO <sub>4</sub> <sup>2-</sup>	N	N	N	-0.085	N	N	N	-0.175	N	-0.193
Cl <sup>-</sup>	N	N	N	N	N	N	N	N	N	N
NO <sub>3</sub> <sup>-</sup>	N	N	N	-0.301	N	-0.428	N	-0.318	N	-0.27
F	N	N	N	0.329	0.498	0.551	N	0.436	N	0.252
PO <sub>4</sub> <sup>3-</sup>	<b>0.838</b>	0.519	0.669	0.374	N	0.392	<b>0.704</b>	0.337	<b>0.780</b>	0.409
SiO <sub>2</sub>	0.248	N	0.139	0.131	N	0.335	0.297	0.244	N	N
Ca	0.226	N	0.094	0.159	N	0.258	0.168	0.265	N	N
Mg	N	N	N	N	N	0.198	N	N	N	N
Sr	N	N	N	0.124	N	0.234	N	0.225	N	N
Ba	0.262	0.207	N	-0.2	N	N	N	N	N	-0.29
Na	N	N	N	0.262	N	0.464	N	0.281	N	0.269
K	N	N	N	N	N	N	N	N	N	-0.101
Cd	N	0.164	N	-0.224	-0.223	-0.391	N	-0.129	N	-0.274
Fe	0.175	0.215	N	N	N	N	0.171	0.181	N	-0.129
Mn	N	0.165	0.123	0.156	N	0.304	N	0.324	0.128	N
Se	N	0.225	0.071	0.111	N	N	N	0.205	N	N
V	N	N	N	0.09	N	N	N	N	N	0.159

N = No or poor correlation ( $p > 0.05$  or coefficient  $< \pm 0.5$ )

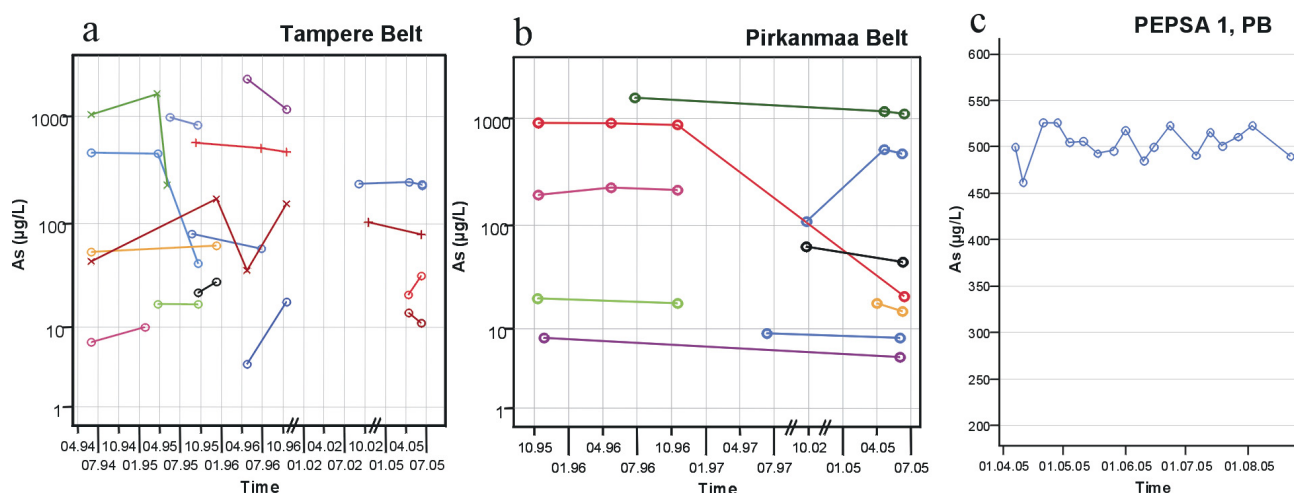
#### 4.3.1.1. Monitored bedrock wells

The number of drilled wells sampled more than once was 35. Twenty-four of these wells, were located in the Tampere Belt (TB) and 11 in the Pirkanmaa Belt (PB). The Säijä well in the Pirkanmaa Belt was monitored 18 times during a 5-month period in 2005. One of the objectives was to observe the seasonal variation of the water chemistry, including the variation in the arsenic concentrations.

In most of the monitored well water, the arsenic content remained on a level typical for that site, but in some cases major changes were observed (Figs. 28a-c). The substantial changes in the arsenic contents in many of the wells may be due to the changes in the water consumption. There are many monitored wells in the Pirkanmaa region where the increased use of well water has substantially increased the arsenic content in the water. This is especially harmful if the limit value is exceeded in a well assumed to be safe. Generally, detailed information on the pumping volume was not available, but it was possible to estimate the approximate historical consumption based on information received from the well owners. An opposite trend occurs when the well is abandoned or the consumption decreases significantly. For example, in one particular well in the Pirkanmaa Belt an arsenic concentration of about 900 µg/L was recorded during 1995-1996, while in 2005 the concentration dropped to 21 µg/L (Fig. 28b). However, some wells are surprisingly stable despite of heavy pumping. This was tested at the project's test site for arsenic removal at the Säijä well in

Lempäälä. The arsenic content in the water fluctuated between 462 µg/L and 538 µg/L over five month's time in 2005 (Fig. 28c). In the beginning of the test in April 2005, the pumped water volume was low (4.1 m<sup>3</sup>/month) and later increased (May: 5.6 m<sup>3</sup>/month; June 263 m<sup>3</sup>/month; July 228 m<sup>3</sup>/month and in August 199 m<sup>3</sup>/month). The pumping test simulated the water consumption of an average family; the use of water was high in the morning, in the afternoon, and again in the evening.

The behaviour of the arsenic concentration is very difficult to predict. It seems that in some cases the effective use of a well results in the exploitation of water from a deep-seated or otherwise more arsenic rich source, while in the opposite case the fresh, recharging waters dilute the arsenic concentrations. The size and yield of the water source area (“aquifer”) is a key issue here. If the pumping rate exceeds the available reserves, the replenishment will be extracted where it is most easily obtained. The well waters should be analysed on a regular basis for arsenic and other harmful components, especially when the water consumption increases.



Figures 28a-c. Changes in arsenic content in monitored well waters in the Tampere Belt (a); in the Pirkanmaa Belt (b); and in a drilled well in Säijä, Lempäälä (c). The monitoring period in the first two diagrams is 11 and 10 years. In the Säijä well (c), the pumping interval was 5 months.

#### 4.3.1.2. Arsenic speciation

The amount of arsenite ( $\text{As}^{3+}$ ) and arsenate ( $\text{As}^{5+}$ ) were analysed from selected drilled wells with high arsenic contents, according to the procedure described in Chapter 3.4.3.2. Arsenic III/V ratio was determined for 20 drilled well waters in 2005. Seven of these samples were collected from the Säijä well in connection with the arsenic removal test. This provided an opportunity to consider the time and rate dependent changes in arsenic concentration and its oxidation state. Speciation is an important issue because arsenite is reported to be more toxic than arsenate.

As discussed above, the arsenic content remained relatively constant in the water of the Säijä drilled well throughout the pumping test (Fig. 29). The groundwater was dominated by arsenite ( $\text{As}^{3+}$ ) during the whole period. The proportion of arsenite varied from 58 % to 74.8 % of the total arsenic.

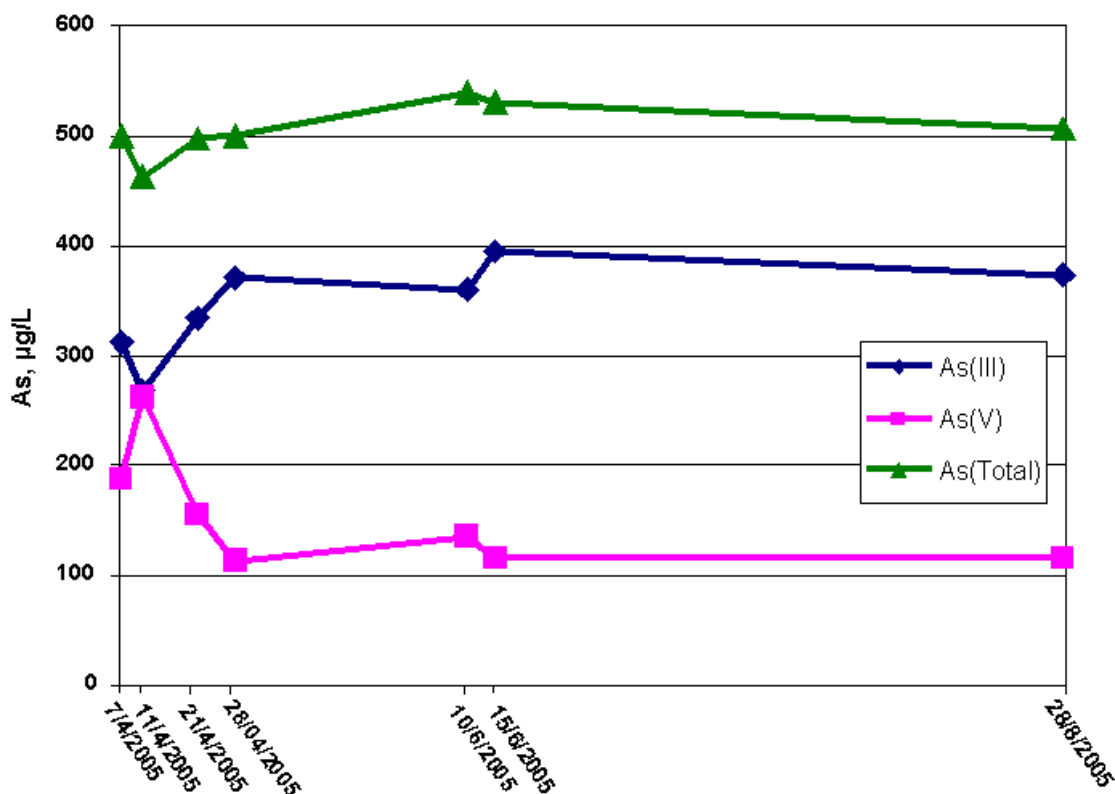


Figure 29. Arsenite ( $\text{As}^{3+}$ ), arsenate ( $\text{As}^{5+}$ ) and arsenic total (EDTA concentrated arsenic) in drilled well water samples at Säijä between 7.4. – 28.8.2005.

The contents of arsenite and arsenate in other 13 drilled wells are presented in Table 18. The total content of arsenic varied from 10.8 µg/L to 1110 µg/L. Except for two wells, all the groundwater samples were clearly dominated by arsenate. The proportion of arsenite varied from 0.66 % to 73.8 % of the near-total arsenic (EDTA concentrated). The speciation does not correlate with the total arsenic content or the depth of the well, but the local hydrogeological conditions are assumed to be decisive.

Table 18. The arsenite (As III), arsenate (As V) and As (EDTA) content in 13 selected drilled wells in the Pirkanmaa region. The dominant species is highlighted with red colour TB = Tampere Belt, PB= Pirkanmaa Belt.

	Geological subdivision	Depth of well, m	As (III), µg/L	As (V), µg/L	As (EDTA), µg/L	As (III) from As (EDTA), %
PEPMH1	PB	40	27.2	27.9	57.4	47.4
PEPJO1	PB	55	13	10	22.3	58.3
PEPRO1	PB	57	501	592	1110	45.1
PEPOJ1	PB	90	69.3	437	508	13.6
PEPEI1	PB	70	3.41	<10	10.8	31.6
PEPTI1	PB	126	3.27	12.3	15.5	21.1
PEPJT1	PB	77	0.64	25	24	2.7
PEPSR1	TB	100	<0.5	12.7	12.8	3.9
PEPMM1	TB	36	2.52	33.3	36.4	6.9
PEPPV1	TB	60	4.35	10.1	13.7	31.7
PEPVA1	TB	43	2.89	12.2	13.3	21.7
PEPMI1	TB	60	0.57	86.2	86	0.66
PEPSS1	TB	84	177	55	240	73.8

#### 4.3.1.3. Factors controlling the mobility and availability of arsenic

The factors to be considered in the control system of availability and mobility of arsenic are: 1) that there is a source – primary or secondary - of arsenic, 2) the processes that release arsenic into the groundwater system. Two main processes that largely control arsenic mobility by releasing arsenic from the aquifer solid phase into the groundwater system are adsorption and desorption reactions and solid-phase precipitation and dissolution reactions.

Arsenic adsorption and desorption reactions are controlled by changes in pH, redox (Eh) reactions, and associated water quality parameters of the aquifer. Arsenic is a redox-sensitive element and it may be present in a variety of redox states. Arsenate ( $\text{As}^{5+}$ ) generally predominates under oxidizing condition and arsenite ( $\text{As}^{3+}$ ) under reducing condition. Redox reaction can control aqueous arsenic concentration by their effect on arsenic speciation, and therefore, arsenic adsorption and desorption. Reduction of arsenate ( $\text{As}^{5+}$ ) to arsenite ( $\text{As}^{3+}$ ), for example, can promote arsenic mobility because arsenite ( $\text{As}^{3+}$ ) is generally less strongly adsorbed than arsenate ( $\text{As}^{5+}$ ). At the pH conditions of most groundwater (acid and near-neutral pH), arsenate ( $\text{As}^{5+}$ ) is present as negatively charged oxyanions ( $\text{H}_2\text{AsO}_4^-$  or  $\text{HAsO}_4^{2-}$ ).  $\text{H}_2\text{AsO}_4^-$  is dominant at low pH (less than about pH 6.9), whilst at higher pH,  $\text{HAsO}_4^{2-}$  becomes dominant.  $\text{H}_3\text{AsO}_4$  and  $\text{AsO}_4^{3-}$  may be present in extremely acidic and alkaline conditions, respectively (Brookins 1988, Smedley & Kinniburgh 2002). Whereas arsenite ( $\text{As}^{3+}$ ) from reducing conditions (<200 mV, pH <9.2) is present at the uncharge species ( $\text{H}_3\text{AsO}_3^0$ ). The ionised form of arsenite ( $\text{As}^{3+}$ ), *e.g.*  $\text{H}_2\text{AsO}_3^-$ , occurs only in alkaline environments at pH >9.2. These different charges control the strength of adsorption and desorption reactions and solid phase surfaces in aquifers. Under this typical pH groundwater condition, absorption of arsenate ( $\text{As}^{5+}$ ) to iron oxide surfaces is particularly strong and sorbed loadings can be appreciable even at very low As concentrations in solution. Adsorption to Al and Mn oxides may also be important if these oxides are present in quantity (Edmunds & Smedley 1996, Smedley & Kinniburgh 2002). On the other hand, the adsorptions of arsenite ( $\text{As}^{3+}$ ) to iron oxide surface are weak under the normal pH conditions of groundwater. However, adsorption of both species decreases when the pH increased. At the pH values above 8, arsenate ( $\text{As}^{5+}$ ) will release from iron oxide surface. In the presence of extremely high concentrations of reduced sulphide, dissolved As-sulphide species can be significant. Reducing, acidic conditions favour precipitation of orpiment ( $\text{As}_2\text{S}_3$ ), realgar ( $\text{AsS}$ ) or other sulphide minerals containing co-precipitated As, hence the As mobility is reduced due to the precipitations of those secondary sulphide minerals.

In addition, reduction in surface area of oxide minerals due to the structural change in solid phase affect also arsenic adsorption and desorption. For example, disordered and fine-grained iron oxides, which may include hydrous ferric oxide, lepidocrocite, schwertmannite and magnetite are commonly formed in the early stages of weathering. These iron oxides are gradually transforms or crystallizes to more ordered forms such as goethite or hematite. As a result the specific surface area of the oxide minerals are reduced and some of the adsorbed ions, such as arsenic, will be desorbed.

Solid-phase precipitation and dissolution reactions are controlled by solution chemistry, including pH, redox reaction and chemistry composition. Arsenic in solid phase is released to groundwater when this solid phase dissolves. Similarly, arsenic is removed from groundwater when solid phase containing arsenic precipitates from aqueous solution. High arsenic concentration in groundwater is often associated with iron oxides and sulphide minerals. Iron oxides frequently dissolve under reducing conditions, and often precipitate under oxidizing conditions. Sulphide minerals are generally unstable under oxidizing conditions, but may precipitate under reducing conditions. Therefore, the result of the redox facilitated precipitation and dissolution reactions of these solid phases may transfer large amount of arsenic into the groundwater system.



The mobility and toxicity of arsenic depend on its species, which have different chemical properties and forms. As mentioned before, the two predominant inorganic species of arsenic are arsenite ( $\text{As}^{3+}$ ) and arsenate ( $\text{As}^{5+}$ ). Arsenite occurs as an uncharged molecule, while arsenate occurs as a negatively charge. The lack of charge on the arsenite enhances the mobility of arsenite relative to arsenate. Additionally, arsenite is 10-60 times more toxic than arsenate and several hundred times higher than that of organic arsenicals (Morrison *et al.* 1989).

These two arsenic species typically occur in different hydrologic environments. Arsenate predominates in oxidizing environment, while arsenite is more abundant in reducing environment. Drinking water normally contains arsenic as arsenate and, if the water is anaerobic (reducing), some arsenite. The arsenic speciation analysed from water of 14 drilled wells in the Pirkanmaa region gave a result that the arsenate was dominated in 8 sites and arsenite in 3 sites. In two cases there was no clear dominant species. Organic arsenic is present in water supplies only if special circumstances exist, such as contamination. Therefore, knowledge the particular species of arsenic in groundwater is necessary for an effective arsenic treatment strategy and management. (Edmunds & Smedley 1996, Smedley & Kinniburgh 2002).

Redox potential was not measured from all the bedrock groundwater samples, but the small data is possible to represent in an Eh-pH diagram (Fig. 30). The most part of the data is located in the block of arsenate ( $\text{HAsO}_4^{2-}$ ), but some of the samples from PB are located in the block of arsenite ( $\text{H}_3\text{AsO}_3$ ), under reducing conditions. All samples from CFGC and almost all samples from TB are located in the block of arsenate.

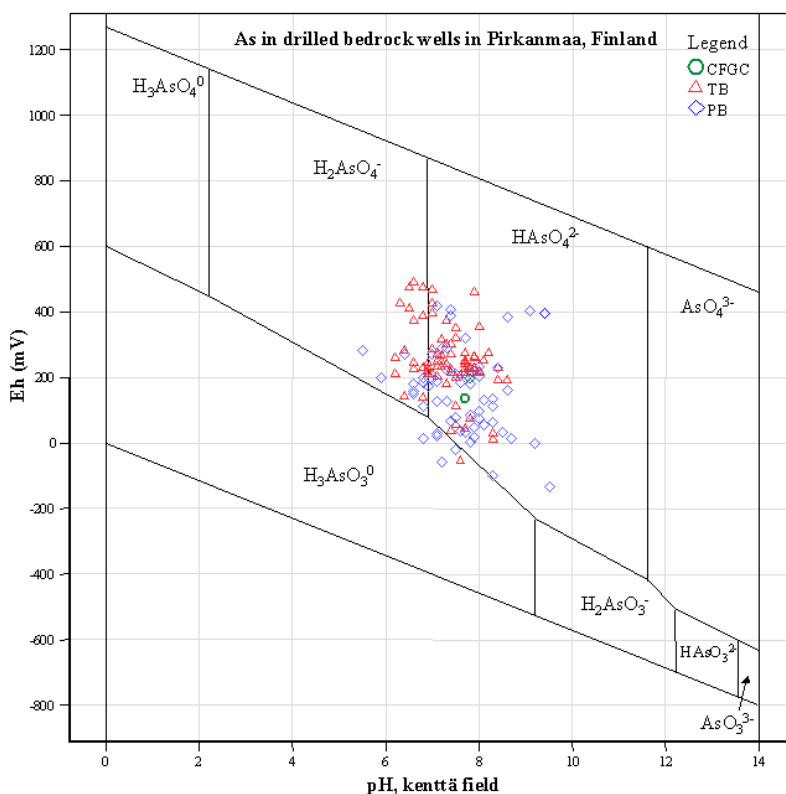


Figure 30. Simplified Eh-pH diagram for arsenic species of drilled well waters in the Pirkanmaa region. Diagram according to Brookins (1988 ).

### 4.3.2. Arsenic in shallow groundwater

All the shallow groundwater sampling sites in the Pirkanmaa region are located in Quaternary deposits. These deposits are composed of silt, sand and gravel formations, and till deposits. Samples were taken from natural springs, captured springs and dug wells with concrete rings. The statistical parameters of the shallow groundwater are presented in Table 19. The cumulative concentrations curve of arsenic in shallow groundwater is presented in Fig 31. The limit value (10 µg/L) was exceeded in 2 shallow groundwater samples in the Pirkanmaa region. The shallow groundwater in the Pirkanmaa is quite acidic with low alkalinity, and the amount of dissolved elements is low.

In comparison to the countrywide data of the study “1000 wells” (Lahermo *et al.* 2002), the geochemical composition of the 283 shallow groundwater samples in the Pirkanmaa region is similar to the rest of Finland. The arsenic concentrations in shallow groundwater in the Pirkanmaa area are, on average, a little bit higher compared to countrywide data.

All the shallow groundwater sites are plotted on the map with the arsenic concentrations in till (Fig. 32). Three main geological subdivisions of the Central Finland Granitoid Complex (CFGC) in the north, the Tampere Belt (TB) in the centre, and the Pirkanmaa Belt (PB) in the south are also marked. The groundwater data has been divided into three groups relative to the sampling location. The statistical parameters of these groups are presented in Table 20. All the main components and many of the heavy metal and trace element concentrations are lowest in the groundwater encountered in the CFGC, and highest in the PB. The arsenic concentrations within CFGC are similar to those reported by Lahermo (2002) for the whole country (0.14 µg/L, N=739). The arsenic concentrations are higher in wells and spring located within the PB and, especially in the TB.

The chemical characteristics of the shallow groundwater are presented in the Piper diagrams in Fig. 33. Most of the waters are of Ca-HCO<sub>3</sub> type, which is typical for shallow Finnish groundwater (Lahermo *et al.* 1990, 2002). The data is classified in two groups using the limit value for arsenic as a threshold value (<10 µg/L and >10 µg/L) and taking into account the location of the sampling site relative to the three geological subdivisions. There are three samples with arsenic concentrations higher than 10 µg/L. One sample from the Tampere Belt lacked water analyse and therefore was dropped in these data processing. Both remaining samples with high arsenic concentrations are located in the PB area. These two samples have more or less similar chemical composition as the samples with lower arsenic concentrations. High calcium and low chloride concentrations are common for these two arsenic enriched waters.

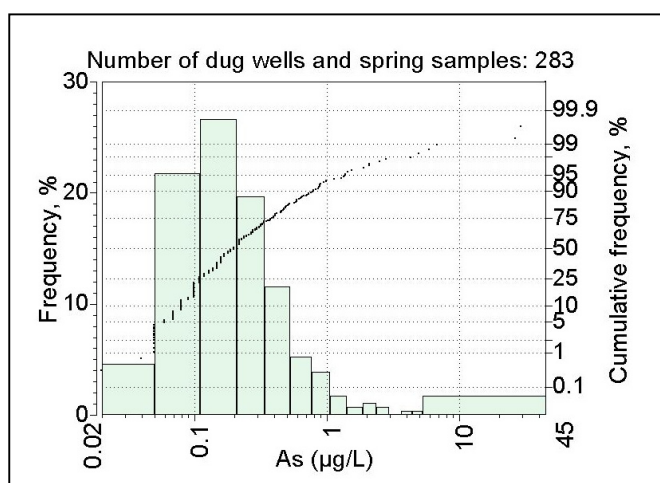


Figure 31. The cumulative concentrations curve of arsenic in dug wells, captured springs and springs. N=283.

Table 19. Minimum, median, mean, standard deviation, maximum and 2 % and 98 % percentiles of variables of water from dug wells, capture springs and springs.

Elements	Unit	N_Valid	Minimum	2 %	Median	Mean	Std. Dev	98 %	Maximum
pH, field		253	5.10	5.30	6.10	6.13	0.40	7.18	7.30
EC, field	mS/m	254	0.40	3.30	12.90	15.85	12.00	49.30	106.00
T	°C	256	3.90	4.63	7.80	8.53	5.14	15.92	81.00
CO <sub>2</sub>	mg/L	254	4.00	5.00	35.00	42.64	34.83	120.00	430.00
O <sub>2</sub>	%	241	0.00	0.00	71.90	73.56	27.31	131.64	145.50
Eh	mV	39	-60.00	-60.00	424.00	347.00	162.08	550.00	550.00
pH_LAB		263	4.80	5.71	6.40	6.43	0.42	7.43	7.85
EC_LAB	mS/m	265	2.20	2.90	12.70	15.09	11.56	47.85	108.00
KMnO <sub>4</sub>	mg/L	277	0.50	0.86	4.30	7.13	8.46	38.44	56.80
Hardness	dH	279	0.28	0.45	2.28	2.85	2.21	9.74	11.70
Alkalinity	mmol/L	277	0.10	0.14	0.48	0.68	0.57	2.65	3.74
HCO <sub>3</sub> <sup>-</sup>	mg/L	277	6.10	8.27	29.30	41.78	34.78	162.08	228.00
SO <sub>4</sub> <sup>2-</sup>	mg/L	279	1.30	2.74	14.00	18.49	16.08	59.68	146.00
Cl <sup>-</sup>	mg/L	279	0.30	0.70	3.60	8.85	19.98	41.28	262.00
NO <sub>3</sub> <sup>-</sup>	mg/L	279	<0.20	<0.20	3.60	8.09	11.58	44.26	73.70
F	mg/L	279	<0.10	<0.10	0.10	0.12	0.08	0.33	0.59
Br	µg/L	279	<0.10	<0.10	<0.10			0.20	0.20
I	µg/L	49	2.00	2.00	3.07	4.45	4.42	30.20	30.20
PO <sub>4</sub> <sup>3-</sup>	mg/L	156	0.02	0.02	0.02	0.04	0.09	0.26	0.92
SiO <sub>2</sub>	mg/L	279	3.77	5.02	14.80	15.16	5.40	27.32	38.70
Ca	mg/L	279	1.38	2.09	11.30	13.21	9.57	40.06	61.00
Mg	mg/L	279	0.18	0.58	2.79	4.34	4.50	20.70	26.00
Sr	µg/L	279	13.00	18.10	56.50	64.36	44.19	194.00	398.00
Ba	µg/L	279	0.47	2.10	14.70	20.20	36.05	74.32	563.00
Na	mg/L	279	1.71	1.89	5.31	7.20	9.47	22.94	141.00
K	mg/L	279	0.01	0.43	3.00	4.06	4.57	19.78	47.80
Li	µg/L	279	<0.30	<0.30	1.22	2.75	4.08	16.10	32.80
Rb	µg/L	176	0.13	0.18	2.55	4.62	6.69	24.16	66.90
Ag	µg/L	279	<0.01	<0.01	0.01	0.01	0.01	0.02	0.07
Al	µg/L	279	<1.00	1.55	26.90	82.53	164.89	694.80	1260.00
<b>As</b>	<b>µg/L</b>	<b>283</b>	<b>&lt;0.05</b>	<b>0.05</b>	<b>0.20</b>	<b>0.75</b>	<b>3.58</b>	<b>5.29</b>	<b>45.00</b>
B	µg/L	279	0.63	1.37	9.52	15.95	22.10	78.96	227.00
Be	µg/L	279	<0.10	<0.10	0.10	0.11	0.15	0.30	2.14
Bi	µg/L	279	<0.03	<0.03	<0.03			0.03	0.33
Cd	µg/L	279	0.02	0.02	0.05	0.09	0.15	0.77	1.10
Co	µg/L	279	0.02	0.02	0.15	0.75	2.89	7.62	41.70
Cr	µg/L	279	<0.20	<0.20	0.23	0.40	0.49	2.32	4.44
Cu	µg/L	279	0.11	0.16	3.41	16.57	40.11	182.40	295.00
Fe	mg/L	279	<0.03	<0.03	0.05	0.16	0.38	1.32	4.39
Mn	µg/L	279	0.20	0.51	6.26	36.93	84.34	376.60	624.00
Mo	µg/L	279	<0.03	0.03	0.16	0.24	0.24	1.03	1.72
Ni	µg/L	279	0.08	0.10	1.93	5.05	12.39	39.70	136.00
Pb	µg/L	279	<0.03	0.03	0.09	0.24	0.35	1.69	2.04
S	mg/L	59	1.09	1.11	4.30	5.23	3.43	16.16	16.80
Sb	µg/L	279	<0.02	<0.02	0.04	0.06	0.08	0.38	0.72
U	µg/L	279	0.01	0.01	0.09	0.24	0.79	1.69	11.90
V	µg/L	279	0.02	0.02	0.19	0.37	0.56	2.09	5.07
Zn	µg/L	279	1.15	1.54	16.90	54.87	135.26	513.20	1480.00

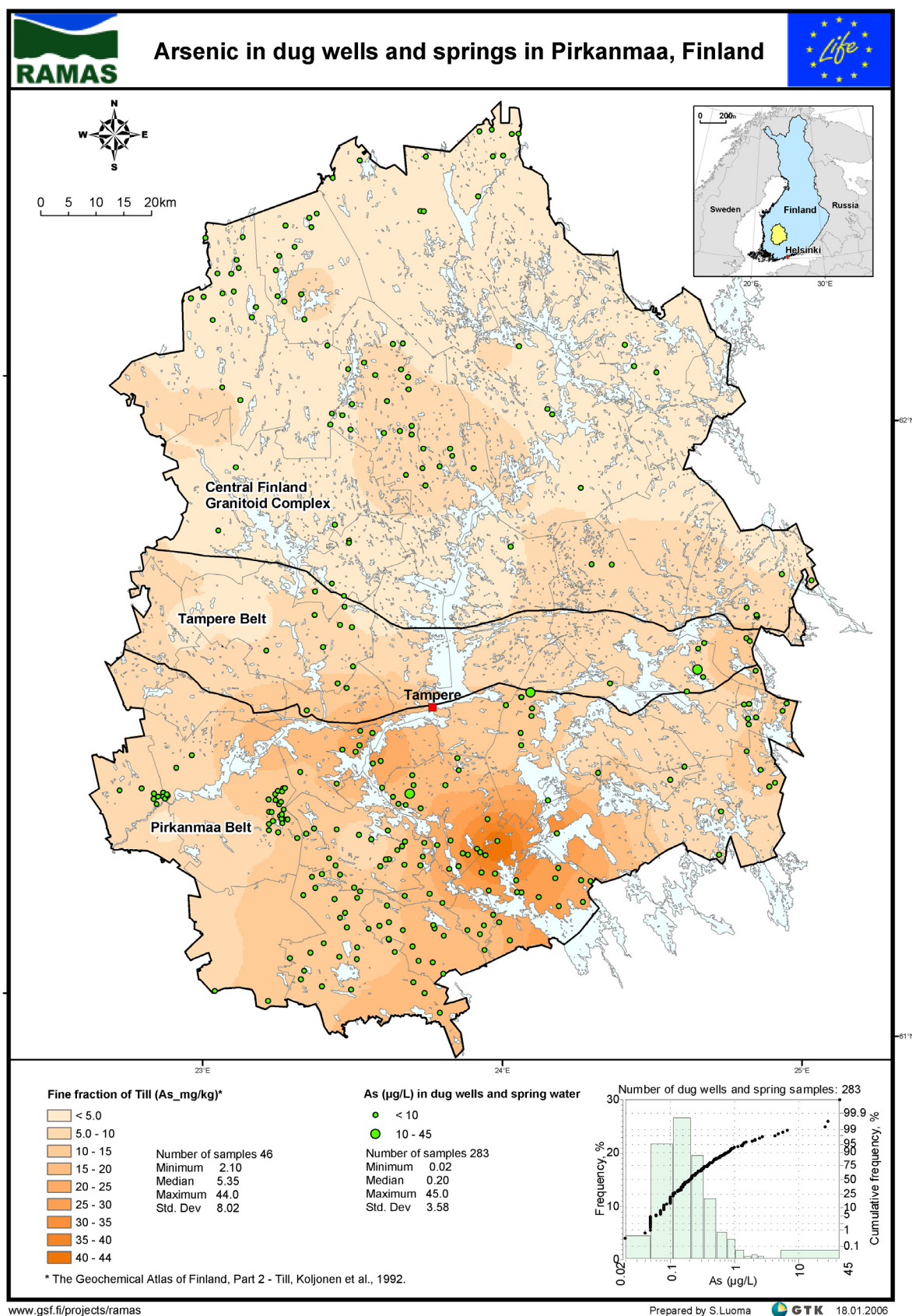


Figure 32. The arsenic concentrations in shallow groundwater within the main geological subdivisions in the Pirkanmaa region: the Central Finland Granitoid Complex (CFGC) in the north, the Tampere Belt (TB) in the centre, and the Pirkanmaa Belt (PB) in the south. The concentration contours are based on the data from the nation-wide survey of GTK.



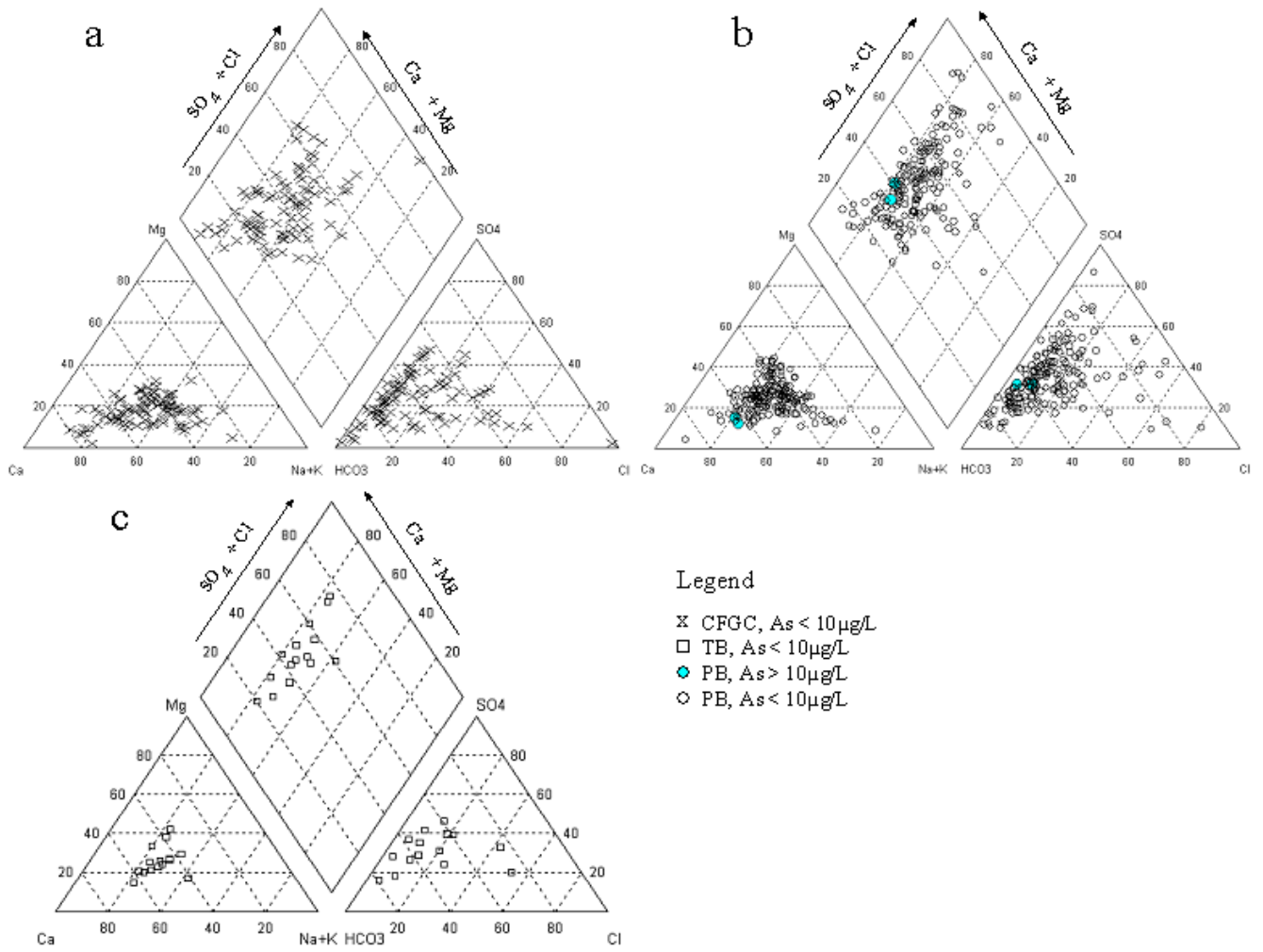


Figure 33. The chemical composition of shallow groundwater in the Pirkanmaa region. The number of samples is 277. a) Samples from the CFGC (As < 10 µg/L); b) Samples from the PB (As < 10 µg/L and As > µg/L); c) Samples from the TB (As < 10 µg/L).

Table 20. Statistics of shallow groundwater quality in wells and springs located in geological subdivisions CFGC, TB, and PB. See map in Fig. 7.

Elements	Unit	CFGC		TB		PB	
		N_Valid	Median	N_Valid	Median	N_Valid	Median
pH, field		82	6.00	11	6.10	160	6.15
EC, field	mS/m	82	8.35	12	11.00	160	15.80
T	°C	82	7.95	12	7.05	162	7.80
CO <sub>2</sub>	mg/L	82	32.00	12	35.00	160	35.00
O <sub>2</sub>	%	82	69.30	11	63.80	148	72.90
Eh	mV	2	169.00	7	160.00	30	444.50
pH_LAB		86	6.45	15	6.00	162	6.40
EC_LAB	mS/m	86	7.97	15	10.00	164	15.05
KMnO <sub>4</sub>	mg/L	87	4.00	15	5.70	175	4.30
Hardness	dH	87	1.39	15	1.95	177	2.80
Alkalinity	mmol/L	87	0.40	15	0.44	175	0.54
HCO <sub>3</sub> <sup>-</sup>	mg/L	87	24.40	15	26.80	175	32.90
SO <sub>4</sub> <sup>2-</sup>	mg/L	87	6.80	15	13.00	177	19.00
Cl <sup>-</sup>	mg/L	87	2.50	15	4.70	177	4.17
NO <sub>3</sub> <sup>-</sup>	mg/L	87	1.10	15	2.00	177	5.20
F	mg/L	87	0.10	15	0.10	177	0.10
Br	µg/L	87	<0.10	15	0.10	177	<0.10
I	µg/L	22	3.58	6	2.44	21	3.20
PO <sub>4</sub> <sup>3-</sup>	mg/L	58	0.02	14	0.02	84	0.02
SiO <sub>2</sub>	mg/L	87	12.20	15	15.70	177	15.60
Ca	mg/L	87	7.43	15	9.33	177	13.60
Mg	mg/L	87	1.30	15	2.79	177	3.86
Sr	µg/L	87	46.40	15	55.90	177	61.50
Ba	µg/L	87	17.80	15	11.30	177	13.20
Na	mg/L	87	3.49	15	4.37	177	5.85
K	mg/L	87	1.96	15	1.36	177	3.45
Li	µg/L	87	0.58	15	1.57	177	1.84
Rb	µg/L	58	1.66	15	1.64	103	3.14
Ag	µg/L	87	0.01	15	0.01	177	0.01
Al	µg/L	87	27.00	15	60.60	177	25.30
<b>As</b>	<b>µg/L</b>	<b>87</b>	<b>0.15</b>	<b>19</b>	<b>0.32</b>	<b>177</b>	<b>0.22</b>
B	µg/L	87	5.57	15	5.09	177	11.20
Be	µg/L	87	0.10	15	0.10	177	0.10
Bi	µg/L	87	<0.03	15	<0.03	177	0.03
Cd	µg/L	87	0.03	15	0.02	177	0.07
Co	µg/L	87	0.06	15	0.08	177	0.22
Cr	µg/L	87	0.23	15	0.28	177	0.23
Cu	µg/L	87	2.99	15	2.55	177	3.72
Fe	mg/L	87	0.03	15	0.03	177	0.06
Mn	µg/L	87	3.34	15	2.91	177	8.57
Mo	µg/L	87	0.09	15	0.17	177	0.22
Ni	µg/L	87	0.91	15	1.43	177	3.20
Pb	µg/L	87	0.11	15	0.05	177	0.09
S	mg/L	24	2.56	11	4.30	24	6.43
Sb	µg/L	87	0.03	15	0.03	177	0.04
Se	µg/L	87	0.50	15	0.50	177	0.50
U	µg/L	87	0.09	15	0.14	177	0.09
V	µg/L	87	0.22	15	0.24	177	0.17
Zn	µg/L	87	10.60	15	13.10	177	19.40

#### 4.3.2.1. Arsenic in water plants

The public water supply in the Pirkanmaa region is based half on shallow groundwater and half on surface water. If the consumption of the city of Tampere is not included in the calculation, the proportion of groundwater increases to 75 % (Pirkanmaan ympäristökeskus 2004). The number of water plants in the Pirkanmaa region in 2006 is 122 (Fig. 34). Also, the classified groundwater areas are presented on the map. The number of areas important for water supply (group 1) is 91, and those suitable for such use (group 2) is 89 (Pirkanmaan ympäristökeskus 2004). The estimated yield of these groundwater areas is 146 000 m<sup>3</sup>/day.

According to the EU-Directive 98/83/EY, all member states of the EU have to report to the EU commission about the quality of drinking water provided by water plants, which produce water more than 1000 m<sup>3</sup>/d or to more than 5000 inhabitants. The health officer of each municipality manages the drinking water sampling and reports the water quality annually to the Ministry of Social Affairs and Health. The data for each municipality is compiled and the Ministry reports to the EU commission. The commitment to analyse arsenic content in drinking water belongs to those parameters that are necessary to analyse and to report only occasionally.

There are 14 water plants in the Pirkanmaa region, which are liable to report to the EU commission. The water production in seven water plants is based on groundwater; four on surface water and in three cases, the raw water is a mixture of groundwater and surface water. The arsenic concentrations in those waters were analysed 24 times in 2004. In 20 out of the 24 samples, the concentration was lower than the detection limit for arsenic and in 4 samples the concentrations were 1 µg/L (Zacheus 2005). The detectable arsenic contents were from the Ylöjärvi and Lempäälä water plants, which both are located in area where the arsenic concentrations in soil samples are elevated. However, arsenic is clearly not a problem in the public water supply.

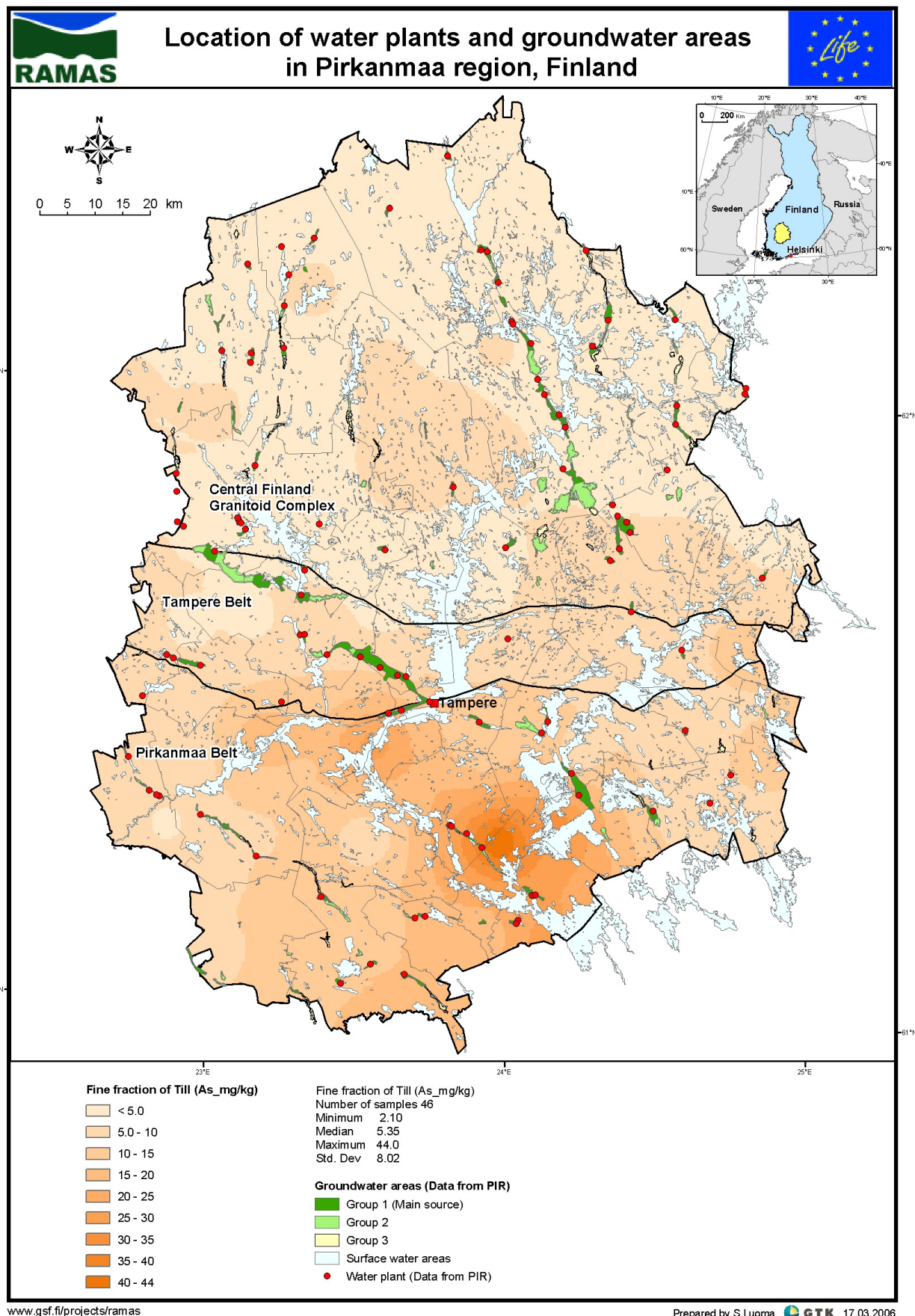


Figure 34. Water plants and groundwater source areas in the Pirkanmaa region. The classification of the groundwater areas: Group 1= the area is important for groundwater supply; Group 2= the area is suitable for groundwater supply; Group 3= other groundwater area. The concentration contours are based on the data from the nation-wide survey of GTK.

### 4.3.3. Arsenic in surface waters and in stream and lake sediments

#### 4.3.3.1. Stream water and sediments

There are about one hundred arsenic analyses from stream waters in the Pirkanmaa Regional Environment Centre (PIR) database. Most of these samples were collected in 1994 - 2004 from drainage streams in peat bogs. The arsenic concentrations in the stream waters were low. The highest concentrations were in stream water from a peat bog in Juupajoki, where the mean value of 77 samples was 0.9 µg/L and the maximum value was 3.67 µg/L.

The number of stream and lake water samples from Pirkanmaa in the GTK database is 32. Twenty-six samples were collected around the closed Ylöjärvi Cu-W mine in 2002, 14 are from small lakes and 12 from streams. The average arsenic concentration in lakes near the mine was 35.1 µg/L and in streams 475.8 µg/L. In 1998, 6 stream water samples were taken from south-eastern Pirkanmaa. The average arsenic concentration in these samples was 0.44 µg/L. A comparison of the above values clearly demonstrates the impact a mine or some other major source area may have on the environment. This issue is discussed in more detail in the forthcoming Ramas reports on the anthropogenic arsenic sources in Pirkanmaa and the transport modelling of arsenic from the Ylöjärvi mine site, both due later in 2006.

#### 4.3.3.2. Lake water and sediments

According to the PIR database, 56 water samples were taken from lakes in different parts of Pirkanmaa between 1994-2004. The arsenic concentrations were less than 1.0 µg/L except for one sample from Urjala Lahmajärvi in 1995 with an arsenic content of 1.3 µg/L. The only lake sediment profiles from the Pirkanmaa region were collected in the vicinity of mine sites to investigate the arsenic transport from the tailings area. These results will be published in another report this year.

## 5. DISCUSSION

### *Availability of arsenic data*

Arsenic is a natural and even relatively common component in Finland's geosphere and hydrosphere. Until early 1990s, it has been largely neglected and only sporadic information on its occurrence is available. The reasons behind this situation are partly related to analytical difficulties. Prior to the introduction of mass spectrometers, the analyses were so laborious that arsenic was not included in routine analytical procedures. Due to this historical burden, arsenic is still left out of many studies where it most definitely should be included in analyses. Despite the well-known toxicity of arsenic and arsenic compounds, it was long time before arsenic was considered a particular risk to people and the environment in Finland. Arsenic does not cause taste or colour defects in water or soil, which would attract attention and there are no cases reported where an environmental or health problem could have been linked directly to arsenic. Thus, there has been no collective pressure to analyse arsenic.

The only exception to the above situation has been ore exploration, which applies arsenic anomalies to trace gold occurrences. Ore exploration is often considered a threat to the environment. However, it also produces valuable information for environmental research by revealing areas where potentially harmful elements (heavy metals, sulphur, arsenic) have been strongly enriched. Much of



the exploration is focused on geochemically exceptional areas, but they can may represent the environmental “hot-spots” and the worst-case scenarios, at least when the natural occurrence of elements is considered. Another thing is how this information is obtained to benefit environment and the society. In the private sector, the economical interest and the desire to protect the competitive edge against other exploration companies may hinder the access to data. In countries like Finland where the governmental Geological Survey has carried out ore exploration in addition to the countrywide, basic geological and geochemical mapping, there is lots of information that is more readily accessible. Whether it is concern of private or public information, it is always possible to negotiate and if the terms of usage are agreed, there is good chance for data transfer, especially when interests are not contradicting.

In combining information from different sources, research institutes, municipalities and regulatory authorities, the RAMAS project was able to get a relatively clear picture of the distribution of natural arsenic in the Pirkanmaa region and to identify the areas where the risk for arsenic exposure may be elevated. Some additional studies have been conducted to fill gaps in the knowledge in the case of inadequate or lacking data. The actual environmental or health risks will be evaluated in the forthcoming reports produced by the RAMAS project. There are several noteworthy observations directly related to the geologic occurrence of arsenic, which may help to avoid or reduce the risk if duly recognized. These issues are shortly discussed below.

### ***Arsenic in bedrock***

The Pirkanmaa region is distinctly dimidiated as to the occurrence of arsenic. Virtually all anomalous arsenic concentrations, either in bedrock, soil or groundwater, are observed in the southern half of the area. There are clear geologic grounds for this distribution. The rock types encountered in the Tampere and Pirkanmaa Belts are such that they contain arsenic bearing minerals, basically arsenopyrite, and they are also ore potential. Within these belts, however, the distribution of high arsenic concentrations are much more difficult to predict. There are other factors that have controlled the redistribution and enrichment of elements since the formation of the bedrock some 2000 Ma ago. This implies that geologically similar, nearby locations may be different in this respect. This should be particularly emphasized when the quality of groundwater is considered.

In general, the bedrock does not provoke any significant environmental risk for arsenic dispersion. Even in the case that arsenic rich rocks are exposed to the surface, the dissolution rate of arsenic minerals is low and natural processes are able to retain much of the released arsenic. This is demonstrated, for example, by the low arsenic levels in surface waters and stream sediments. In undisturbed conditions, the major concern is related to the long-term interaction of arsenic bearing rocks and groundwaters. However, the situation is different when arsenic rich bedrock is excavated and crushed in mining areas and quarries or unintentionally during construction of road cuts or tunnels. Enormous amounts of fresh rock is exposed to oxic conditions and the dissolution rate of arsenic may increase significantly. Therefore, appropriate care should be taken when major excavation is carried out in areas where the bedrock may contain harmful elements.

### ***Arsenic in Quaternary deposits***

The major part of the overburden deposited on the bedrock in Finland is composed of material that the continental ice sheets have abraded from the local bedrock. Along with the common rock-forming constituents, the potentially harmful components have been released to the geochemical and geological cycles. Due to the subsequent transport of the loose material, the geochemical anomalies in the soil and bedrock may be displaced. In the glaciogenic processes, the material is strongly reworked and the elemental concentrations tend to decrease, but at the same time, the

components are dispersed over a wider area. The transport distance and the dilution of the concentrations depend on soil type. The source area for clay, sand and gravel is further away than for till. The basal till is deposited closer to the source than the top upper part of the till. The transport distance has an impact on the maturity of the material, which means the response to the mechanical and geochemical stress. Longer transport is followed by more intense mechanical disintegration and geochemical dispersion.

Thus, the overburden in glaciogenic terrains is not homogenous, but it is comprised of layers with contrasting mechanical and geochemical characteristics. This has important implications in environmental studies. There should be a sufficient understanding of the structure of the soil cover when geochemical sampling is planned and the sampling strategy should be scaled to the size and the foreseen use of the area. For example, sampling of the topsoil is hardly sufficient, if the target is to evaluate the risks related to a construction project where major excavation and moving of soil is necessary.

The observed distribution of arsenic in soil at Pirkanmaa reflects the patterns outlined above. The highest concentrations are found in the southern half of Pirkanmaa, on the anomalous bedrock units. Elevated concentrations are strongly related to the till. The lower concentrations in other soil types can be attributed to arsenic-poor source areas and/or to higher geochemical dispersion during the longer transport period. In the anomalous areas, the highest natural arsenic concentrations are thousands of mg/kg. The limit for arsenic in contaminated soil is 50 mg/kg in populated areas and 100 mg/kg in industrial areas. When comparing these concentrations, it is obvious that some of the natural soils should be treated as contaminated. These soil areas may pose an ecological risk or a health risk for the population, if the risk is not recognized and managed properly.

### ***Arsenic in groundwater and surface water***

Arsenic concentrations in shallow groundwater and surface waters in the study area are, with few exceptions, well below the limit values (10 µg/L). Hence, arsenic is not an issue for the public water supply, which is based on these shallow water reserves. The major concern is focused on drilled wells, which are exploited by private households and other small units.

Again the correlation with the bedrock is clear. The arsenic in the rock is readily transferred to the deep groundwater. There is little information about the geochemical processes related to the dissolution of the primary phases and the possible retention of arsenic compounds along the groundwater flow route, or the rate these reactions take place under subsurface conditions. In any case, arsenic concentrations exceeding the limit value (10 µg/L) by ten- or hundred-folds are rather common. It is relatively easy to define the areas where the risk to come up against an arsenic well is high. However, the arsenic concentrations are very difficult to predict in detail. Nearby wells may have very different arsenic levels and most of wells in the risk area are healthy. The explanation for this is probably found from the nature of the “aquifers” in crystalline bedrock. All the rock types encountered in the area are metamorphosized, crystalline hard rocks. The low porosity of these rocks allows the storage and conductive flow of groundwater only along a fracture network. The fracturing is relatively abundant within the upper 150 m of the bedrock and becomes more sporadic with depth. The fractures may cross from one rock mass to another, but compartmentalization is also common. For example, wells close to each other may preferentially gain their water from independent, unconnected aquifers. In relation to this, there is evidence that the changes in the consumption are reflected in the quality of the water. Increased pumping can result in the exploitation of water from another, deep-seated or otherwise more arsenic rich source. The size and yield of the water source area (“aquifer”) is a key issue here. If the pumping rate exceeds the available reserves, the replenishment will be extracted where it is most easily obtained. It is

recommended that well waters should be analysed on regular basis for arsenic and other harmful components, especially in the areas where arsenic wells are known to exist and when the water consumption increases.

An additional issue related to the dissolved arsenic is its capability to occur under different oxidation states. The two main arsenic species occur in different hydrologic environments. Arsenate ( $\text{As}^{5+}$ ) is predominant in an oxidizing environment, while arsenite ( $\text{As}^{3+}$ ) is more abundant in a reducing environment. Drinking water normally contains arsenic as arsenate and, if the water is anaerobic (reducing), some arsenite. These arsenic species have different chemical properties, which affect their mobility in the environment, for example. It is also reported that arsenite would be more toxic than arsenate. If this is the case, then the arsenic concentration alone is not enough to assess the health and environmental risks. Prior to RAMAS, the data on arsenic speciation from Finland was practically non-existent because the whole analytical chain from the sampling and pre-treatment of the samples to the actual analysis is challenging and demands know-how, which is not available in most water laboratories.

The arsenic speciations from 14 drilled wells in the Pirkanmaa region showed that arsenate was dominant in 9 sites and arsenite in only 3 sites. In two cases, there was no clear dominant species. This is in accordance with the field measurements, where the pH and Eh were recorded. The diagram below shows that the physiochemical conditions in the wells favour the presence of arsenate (See Fig. 30). The speciation does not correlate with the total arsenic content or the depth of the well, but the local hydrogeological conditions are assumed to be decisive.

However, the same caution, which is related to the changes in the total arsenic concentrations when the water consumption is increased, is valid for the speciation data as well. There is a risk that the surplus is gained from more reduced sources, which may lead to a high proportion of arsenite. Therefore, knowing the particular species of arsenic in groundwater is necessary for an effective arsenic treatment strategy and management. The applied treatment method should be checked to ensure that it does not preferentially remove arsenate and concentrated arsenite in the water.

As a final remark, one of the observations made during the compilation of the available data from the Pirkanmaa area was that much relevant research and investigations have been done through the years for various purposes, but unfortunately the data sets are incomplete and many important parameters are missing. For future environmental investigations, at least the public bodies, should look to the future, review their analytical procedures and collect as much comprehensive analytical data as possible. Currently, the analytical methods are advanced and a large number of elements can be analysed concurrently and the saving of analytical cost gained by restricting the list of elements is not significant compared to the sampling costs.

It is also interesting to notice how well the nationwide geochemical survey of till has been able to identify the regional risk areas, despite of the relatively coarse sampling grid.

## 6. SUMMARY

This investigation is part of a comprehensive environmental RAMAS project, which is jointly funded by the EU LIFE ENVIRONMENT program and other research partners. The final goals of the project are to assess the environmental risk induced by the natural and anthropogenic arsenic, and to present recommendations for risk management procedures for the Pirkanmaa region,

southern Finland. This report aims to describe the distribution and occurrence of natural arsenic in the study area.

The study of the natural occurrence of arsenic in the Pirkanmaa region was to investigate and summarize the natural occurrences and sources of arsenic in the bedrock, glacial till, surface water and groundwater.

Arsenic in Pirkanmaa is natural in origin, derived from bedrock by natural geological and geochemical processes. Concentrations of arsenic in bedrock samples in Pirkanmaa range from less than the detection limit to 377 mg/kg (N = 603). The median arsenic concentration is 1.59 mg/kg, which correspond to the average arsenic concentration of the continental crust (1.5 - 2.0 mg/kg) (NRC 1977). Elevated arsenic concentrations were found in bedrock that contains arsenic minerals, mainly arsenopyrite (FeAsS), which are associated with gold-bearing quartz veins in synorogenic Svecofennian intermediate intrusive and several mineralization *e.g.* Cu-W, Ni-Cu, Ni-Cu and Au-Cu. The distributions of arsenic are scattered, vary within short distances and are strongly related to distinct geologic units. Elevated arsenic concentrations in the bedrock were encountered in the middle and southern parts of Pirkanmaa. The highest concentrations were found in the narrow volcanic-dominated Tampere Schist Belt (TB), in the middle of the region, with a median value of 2.22 mg/kg. The average values were also high in the Pirkanmaa Migmatite Belt (PB), in the southern part, with a median value of 1.9 mg/kg. The average arsenic content in bedrock in the Central Finland Granitoid Complex (CFGC), north of the region, is similar to the average value for the whole country, with the median values of 1.0 and 0.90 mg/kg, respectively.

The highest average arsenic concentration in the glacial tills is also found in the middle and southern parts of the Pirkanmaa region, with a median arsenic concentration of 5.35 mg/kg. The concentrations increase with depth. In gold prospect areas, the deeper part of the glacial till, which reflects the geochemistry of the nearby bedrock, has a median arsenic concentration of 14.0 mg/kg and a maximum of up to 9 280 mg/kg.

Concentrations of arsenic in the surface water are generally low, except in those watercourses that are located in the vicinity of mine areas. The median arsenic concentrations of stream and lake waters in Pirkanmaa are 0.9 and less than 1.0 µg/L respectively. The concentrations increase up to 475.8 and 35.1 µg/L respectively in the stream and lake water near the mines. Similar to the surface water arsenic concentrations are generally low in dug wells, capture springs and springs. The concentrations vary from less than detection limit (<0.05 µg/L) to 45 µg/L, with the median value of 0.20 µg/L. Less than 1.1 % of a total of 283 wells exceeded the WHO guideline (STM 2001) limit value of 10 µg/L for arsenic in drinking water. Here it can be also emphasized that arsenic is not an issue for the public water supply, which is based on the shallow groundwater and surface water reserves. The water quality in the water plants is controlled on a regular basis and arsenic is one of the elements monitored.

In contrast to the shallow groundwater, the arsenic concentrations reach the higher levels (up to 2 230 µg/L, median 1.57 µg/L) in the wells drilled into bedrock. About 23 % of the 965 wells exceeded the limit value of 10 µg/L. High arsenic concentrations in the drilled wells are derived from the nearby bedrock and the arsenic concentrations in drilled bedrock wells correspond very well with the geological units. The median arsenic concentrations in groundwater in the TB, PB and CFGC areas are 4.05, 1.50 and 0.47 µg/L, respectively.

Groundwaters in Pirkanmaa are predominantly Ca-HCO<sub>3</sub> – type. Bicarbonate (HCO<sub>3</sub><sup>-</sup>) indicates the degree of water-rock interaction in the aquifer. The drilled well water with high arsenic content has much the same anion-cation ratio than well waters in Finland in general. The amount of HCO<sub>3</sub><sup>-</sup> and

Ca are, however, higher in water from the TB subdivision than in that of PB. This indicates a slightly longer groundwater residence time in bedrock in the former area. The arsenic content is high in both these areas. Arsenic concentrations tend to increase with increasing  $\text{HCO}_3^-$  concentrations, which suggests that arsenic mobilization is achieved through greater aquifer residence times. These waters, which have longer time to be in contact with aquifer material, have undergone greater water-rock interaction with As-bearing mineral phases. However, the drilled well water quality is generally good and measure up to the standards for drinking water. The pH values were close to neutral and the electrical conductivities were not too high, and the hardness and  $\text{KMnO}_4$ -numbers were low. There is also little evidence of significant agricultural pollution since concentrations of  $\text{NO}_3$ , K and P were usually low. The contents of trace elements and heavy metals were also low on average. Trace metals, which are associated with sulphide oxidation and gold deposit, like Ag, Co, Cu, Ni, Pb, Sb, except Zn, are generally below the WHO guideline for the maximum values in drinking waters.

Groundwater in Pirkanmaa is predominantly oxic and clearly dominated by arsenate ( $\text{As}^{5+}$ ). This is confirmed both by the redox potential measurements in field and arsenic speciation analyses. Nine of the 14 studied drilled wells contain mainly arsenate. Arsenite dominant wells were found in a few reduction condition areas and are mainly in the PB area. The proportion of arsenite ( $\text{As}^{3+}$ ) varied from 0.66 % to 73.8 % of the near-total arsenic (EDTA). Arsenite is known to be more toxic than arsenate. Although the dominant arsenic species in the Pirkanmaa wells seem to be arsenate, special care should still be taken for wells that contain high arsenic levels. The seasonal variation of arsenic concentrations are still difficult to predict and the mechanisms involved are still not well understood. From the monitoring wells results, it seems that in some cases the effective use of a well results in the exploitation of water from a deep-seated or otherwise more arsenic rich source, while in the opposite case the fresh, recharging waters dilute the arsenic concentrations. A detail study of the arsenic mobilization in the groundwater aquifer would be an interesting topic for further research.

Locally high arsenic concentrations in deep groundwater, soils and bedrock may pose a risk to public health and the environment in the southern part of the Pirkanmaa region, if the exposure is not limited by appropriate measures. Much can be done if the problem is recognized and the land use practices are planned accordingly. A good example for such actions, already implemented in many municipalities, is the construction of a public water supply for the areas suffering from arsenic.

## 7. YHTEENVETO

Pirkanmaalla on tehty malminetsintään liittyen geokemiallista tutkimusta 1980-luvulta lähtien. Tutkimuksissa havaittiin, että alueen malmeihin, etenkin kultamalmeihin liittyi usein korkeita arseenipitoisuuksia. Alueella tehdyissä pohjavesitutkimuksissa ilmeni, että korkeita arseenipitoisuuksia oli myös pohjavedessä. Arseenin haitallisuuden ja useiden kuntien alueella Pirkanmaalla esiintyneiden kohonneita pitoisuuksia vuoksi, päätettiin tehdä laaja, alueellinen riskinarviointi ja -hallinta selvitys. Vuonna 2004 EU-Life Environment ohjelma myönsi rahoituksen Ramas-projektille vuosiksi 2004 - 2007. Ramas-lyhenne tulee projektin englanninkielisestä nimestä 'Risk Assessment and Risk Management Procedure for Arsenic in the Tampere Region'. Tutkimuksen tarkoituksena ja tavoitteena on koota tietokantaan kaikki olemassa oleva tieto luontaisista ja antropogeenisistä arseenipitoisuuksista Pirkanmaan alueella ja laatia alueelle riskihallintaohjelma. Aineistoa koottiin tutkimuslaitoksista, viranomaisilta ja kunnista. Koottujen arseenitietojen käsittelyn perusteella laadittiin täydentävä näytteenotto-ohjelma alueille, joilta vielä



puuttui tietoa. Yksi työn monista haasteista oli erilaisilla tutkimusmenetelmillä ja erilaisilla analyysimenetelmillä pitkän ajan kuluessa tuotetun aineiston yhteensovittaminen.

Luonnollista alkuperää oleva arseeni Pirkanmaalla on peräisin kallioperän arseenipitoisista kivistä ja mineraaleista. Arseeni esiintyy Suomen kallioperässä yleisimmin arseenikiisu-nimisenä mineraalina ja sitä siirtyy kallioperästä maaperään ja veteen erilaisten geologisten ja geokemiallisten prosessien seurauksena. Näin ollen arseenia esiintyy kallioperän lisäksi myös maaperässä, pohjavedessä sekä pintavesissä ja järvi- ja purosedimenteissä. Kallioperän arseenipitoisuudet vaihtelevat Pirkanmaalla 603 kallionäytteessä  $<0,1 - 377$  mg/kg. Mediaaniarvo on 1,59 mg/kg, joka on lähellä maankuoren keskipitoisuutta  $1,5 - 2,0$  mg/kg. Suuria arseenipitoisuuksia esiintyy kallioperässä, jossa on arseenikiisua tai kupari-volframi, nikkeli-kupari ja kulta-kupari mineralisaatioita.

Tutkimuksessa Pirkanmaa jaettiin geologisin ja geofysikaalisin perustein kolmeen vyöhykkeeseen: Keski-Suomen granitoidivyöhykkeeseen (CFGK), Tampereen liuskevyöhykkeeseen (TB) ja Pirkanmaan migmatiitti vyöhykkeeseen (PB). Kallioperän kohonneet arseenipitoisuudet keskittyvät TB ja PB vyöhykkeisiin, jossa kallioperän arseenipitoisuuden mediaaniarvot ovat 2,22 mg/kg ja 1,9 mg/kg. Grantoidivyöhykkeellä arseenipitoisuuden mediaaniarvo on 1 mg/kg, joka on hyvin lähellä koko maan mediaaniarvoa 0,9 mg/kg.

Pirkanmaalta on määritetty arseenipitoisuus kaikkiaan 10 869 maaperänäytteestä, pääasiassa moreenialueiden näytteistä. Suurin osa näytteistä on otettu malminetsintään liittyvien tutkimusten yhteydessä, siten näytteenotto on kohdentunut alueille, joissa on korkeita metalli- ja arseenipitoisuuksia. Osa maaperänäytteistä liittyy koko maan kattavaan geokemialliseen moreenikartoitukseen ja tämän aineiston arseenipitoisuuden mediaani on Pirkanmaalla 5,35 mg/kg ja koko maan mediaani on 2,6 mg/kg. Tässä aineistossa arseenipitoisuudet ovat suurempia TB ja PB vyöhykkeillä (mediaanit 5,92 ja 11,5 mg/kg) kuin granitoidivyöhykkeellä (mediaani 3,72 mg/kg). Luonnollista alkuperää oleva arseenipitoisuus maaperässä suurenee alaspäin mentäessä ja lähellä kalliopintaa pitoisuudet ovat suurimmat. Malminetsintään liittyvissä näytteissä arseenipitoisuudet ovat paikoin hyvin suuria, suurin pitoisuus on 9 280 mg/kg, joka on moreenin alaosasta, alueelta, jossa on kultamineralisaatio. Pilaantuneen maan raja-arvo 50 mg/kg ylittyi useilla alueilla Pirkanmaalla.

Pirkanmaan alueen pintavesissä arseenipitoisuudet ovat pieniä. Purovesien keskimääräiset arseenipitoisuudet ovat 0,9 µg/L ja järvivesien  $<1,0$  µg/L. Ainoastaan kohteissa, joissa vesi tulee kaivosalueelta, jossa on louhittu ja rikastettu arseenipitoista kiveä, on kohonneita arseenipitoisuuksia: purovesissä 475,8 µg/L ja järvivesissä 35,1 µg/L.

Maaperän pohjavedestä on otettu näytteitä lähteistä, lähdekaivoista ja rengaskaivoista. Keskimääräiset arseenipitoisuudet ovat pieniä, 283 näytteen mediaaniarvo on 0,2 µg/L. Arvojen vaihteluväli on  $<0,05 - 45$  µg/L. Juomaveden sallittu enimmäisraja 10 µg/L ylittyi vain kolmessa kohteessa. Pirkanmaalla olevat vedenottamot käyttävät raakavetenä maaperän pohjavettä tai pintavettä. Missään tutkitussa vedenottamovedessä ei todettu kohonneita arseenipitoisuuksia. Kalliopohjavesissä on sitä vastoin korkeita arseenipitoisuuksia ja juomaveden sallittu enimmäisraja ylittyi 22,5 %:ssa 965:sta porakaivovesinäytteestä. Korkeita arseenipitoisuuksia todettiin alueilla, joissa kallioperässä oli arseenipitoisia mineraaleja, erityisesti arseenikiisua. Arseenipitoisuudet olivat korkeita Tampereen sekä Pirkanmaan vyöhykkeillä, joissa porakaivovesien arseenipitoisuuksien mediaaniarvot olivat 4,05 ja 1,5 µg/L. Grantoidivyöhykkeellä mediaaniarvo oli 0,47 µg/L ja koko maassa 0,16 µg/L. Suurimmat arseenipitoisuudet esiintyivät porakaivovesissä ja siksi tutkimus painotettiin niiden tutkimiseen.

Pirkanmaan alueen kalliopohjavedet ovat keskimäärin pH-arvoltaan lähes neutraaleja,  $\text{Ca} - \text{HCO}_3$  valtaisia vesiä, joiden kokonaiskovuus ja  $\text{KMnO}_4$ -luku on pieni. Raskasmetalli- ja hivenainepitoisuudet sekä ravinnepitoisuudet ovat pieniä. Tämän kaltainen kemiallinen koostumus on suomalaiselle kalliopohjavedelle tyypillinen ja ainoastaan suuret arseenipitoisuudet ovat alueen kalliopohjavesille ominainen piirre. Tampereen ja Pirkanmaan vyöhykkeiden porakaivovesien keskimääräinen koostumus erosi jossain määrin toisistaan: rauta- ja mangaanipitoisuudet ovat suurempia Pirkanmaan vyöhykkeen vesissä kuin Tampereen vyöhykkeellä. Tampereen vyöhykkeellä happipitoisuus ja Eh-potentiaali ovat suurempia, samoin Cu-, Mo-, Sb- ja V-pitoisuus. Myös suhteelliset  $\text{HCO}_3^-$  - ja Ca-pitoisuudet ovat suurempia Tampereen vyöhykkeen vesissä, kuin Pirkanmaan vyöhykkeellä, mikä viittaa pitempään viipymään ja siten pitempään kiven ja veden väliseen kontaktiaikaan. Arseenipitoisuudet ovat kuitenkin suuria molempien vyöhykkeiden vesissä. Tämä viittaa siihen, että kun arseenia on kallioperässä ja hydrogeokemialliset olosuhteet ovat suotuisat, niin arseeni liukenee herkästi pohjaveteen.

Arseeni esiintyy pohjavedessä joko viiden arvoisena arsenaattina ( $\text{As}^{5+}$ ) tai kolmen arvoisena arseniittina ( $\text{As}^{3+}$ ). Pirkanmaalla 14 kaivovedestä tehtiin arseenispesiaatiomääritys ja yhdeksässä kaivovedessä oli vallitseva muoto vähemmän myrkyllinen arsenaatti, kolmessa vallitsevan muotona oli arseniitti ja kahdessa kohteessa molempia muotoja oli lähes yhtä paljon. Arseniitin osuus tutkituissa vesissä vaihteli 0,66 – 73,8 %.

Kalliopohjavesien arseenipitoisuuden ajallista vaihtelua seurattiin 35 eri kaivoissa eri pituisten jaksojen ajan. Osassa kaivoja arseenipitoisuus pysyi vakaasti tietyllä tasolla veden käyttömäärästä riippumatta, osassa kaivoja veden arseenipitoisuus oli selvästi riippuvainen veden käyttömäärästä. Mitä enemmän vettä käytettiin, sitä suuremmat olivat arseenipitoisuudet.

Tampereen ja Pirkanmaan vyöhykkeillä kalliopohjavedessä on kohonnut arseeniriski. Porakaivoveden arseenipitoisuuden tutkiminen on mahdollisten terveyshaittojen kannalta välttämätöntä. Mikäli veden arseenipitoisuus osoittautuu suureksi, on syytä ryhtyä toimenpiteisiin, joko arseenin poistoon tai toiseen vesilähteeseen siirtymiseen. Maaperän pohjaveden arseenipitoisuus on alueella vain vähän kohonnut, joten sen käyttö ei aiheuta riskiä. Arseenipitoisuus on kuitenkin hyvä tutkia myös näistä kaivoista. Tutkittujen vedenottamoiden veden arseenipitoisuudet olivat pieniä, aivan määrittämissä tuntumassa, joten vedenottamoveden käyttö ei aiheuta arseeniriskiä.

Kallioperän arseenipitoisuus saattaa aiheuttaa riskin tilanteessa, jossa kalliota louhitaan, joko tieleikkauksen vuoksi tai kivimateriaalin tuottamiseksi. Tuoreesta kallio- tai kivipinnasta, jossa on arseenipitoisia mineraaleja, voi liueta arseenia ympäristöön. Tämä voi aiheuttaa tarpeen ohjeistaa uudelleen kivimateriaalin käyttöä tai välivarastointia ja läjitystä. Maaperässä todettiin suuria pitoisuuksia ja pilaantuneen maan raja-arvo ylittyi Tampereen ja Pirkanmaan vyöhykkeillä. Maankäytön turvallisuutta tullaan selvittämään tulevissa Ramas-raporteissa.

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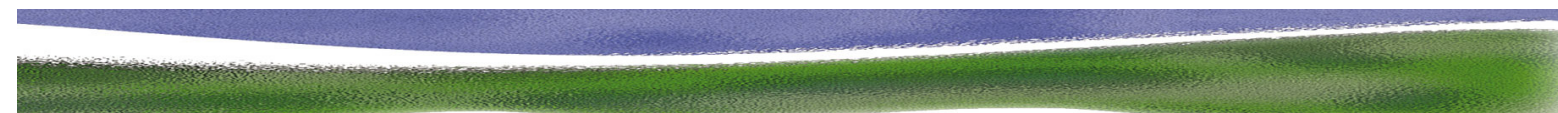
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The project will produce a number of Technical Reports. The following reports have been published:

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 ohjauskeinoista ja teknisistä menetelmistä riskien vähentämiseksi (Management of arsenic risks in the Pirkanmaa region – Survey of available risk management instruments and tools)

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