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

Anthropogenic Arsenic Sources in the Pirkanmaa Region in Finland

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ABSTRACT

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This paper is the final report of TASK 2 which is part of the RAMAS project, in which scientists from the Helsinki University of Technology (TKK), Pirkanmaa Regional Environment Centre (PREC) and the Geological Survey of Finland (GTK) participated. The work was performed during 2005/2006. In this report, information about anthropogenic sources of arsenic in the Pirkanmaa region (also called the Tampere region) was gathered and RAMAS performed complementary sampling and analyses in potentially contaminated areas. Data was acquired about chemicals containing arsenic (wood preservative agents, pesticides etc.), the metal industry and metallic products containing arsenic (*e.g.* gunshots), mining and waste management. Available data was gathered from the Chemical Register (KETU), the Register of Contaminated Land Areas and the Register of Surface Waters maintained by the Finnish Environment Institute (SYKE) and the Regional Environment Centers of Finland, from environmental authorities and other very diverse sources. Dozens of unpublished file reports on the risk assessments and remediation of contaminated soils provided by consulting companies and previous studies made by the Regional Environment Centers of Finland were studied to gather information about arsenic contamination. Information about environmental impacts of mining industry was obtained from geological publications. The data acquisition was difficult because information about contamination, concentrations and risk assessments of arsenic is scattered in unpublished reports and informal papers. RAMAS studied areas affected by soil and surface water contamination in one wood preservative plant (52 field analyses and 5 samples analyzed in laboratory), two mines (6 tailings samples analyzed for geochemical composition, leachability and toxicity, 6 lake and stream sediment samples and over 60 surface water samples), waste treatment and municipal waste water treatment plants. In total, over 100 samples were analyzed.

The acquired data as well as sampling and analyses performed by RAMAS confirmed that wood preservation plants are the major source for arsenic in the Pirkanmaa region. They may pose a risk to nearby residents, surface waters and groundwater, but only affect rather small areas. Shotgun shooting ranges are possible arsenic contaminated areas though lead is the main concern in these sites. The mining industry may affect vast areas through air and especially through surface waters, which was shown in the RAMAS studies in the former Ylöjärvi mine. Arsenic is transported from the mine area along a seven kilometers long watercourse to Lake Näsijärvi. The mining activities can be traced from the lake and stream sediments as high concentrations of arsenic and other heavy metals. The studies of waste management also show that, in general, waste material does not contain high concentrations of arsenic. However, point source pollution from wood preservative product wastes or disposed CCA-treated wood can be a contamination risk in the surroundings of older, poorly isolated landfills.

In addition to old landfills, the area around of scrap yards, closed factories, old refineries, foundries and tanneries are potentially arsenic contaminated areas. Animal shelters, like fur ranges, and the plastic industry among many other human activities are also probable contaminants though arsenic is not the main detrimental element. However, all of the contaminated sites in the Pirkanmaa region are relatively small compared to other European countries, such as extensive mining areas in southern Spain.

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Keywords (AGI, GeoRef, Thesaurus): environmental geology, arsenic, soil pollution, water pollution, wood preservatives, shooting ranges, mines, tailings, leaching, stream sediments, lake sediments, ecotoxicity, waste management, Pirkanmaa, Finland.

TIIVISTELMÄ

Parviainen, A., Vaajasaari, K., Loukola-Ruskeeniemi, K., Kauppila, T., Bilaletdin, Ä., Kaipainen, H., Tammenmaa, J. and Hokkanen, T., 2006. Anthropogenic Arsenic Sources in the Pirkanmaa Region in Finland. Geologian tutkimuskeskus, Erillisjulkaisut, Ramas-projektisarja, 72 sivua, 23 kuvaa, ja 8 taulukkoa.

Tämä TASK2-loppuraportti kuuluu RAMAS-projektiin. Raporttia on valmistelu vuosina 2005 ja 2006, ja siihen osallistui tutkijoita Teknillisestä korkeakoulusta (TKK), Pirkanmaan ympäristökeskuksesta (PIR) ja Geologian tutkimuskeskuksesta (GTK). TASK2-loppuraportissa kerättiin tietoa ihmisen toiminnan aiheuttamista arseenin lähteistä Pirkanmaan alueella. RAMAS-projektissa tehtiin myös täydentävää tutkimusta arseenin saastuttamilla alueilla. Tietoa koottiin arseenipitoisista kemikaaleista (kuten puunkyllästeistä ja pestisideistä), metalliteollisuudesta ja arseenia sisältävistä metallituotteista (esim. haulit), kaivosteollisuudesta sekä jätehuollosta. Suomen ympäristökeskuksen ja muiden viranomaisten ylläpitämät rekisterit ja tietokannat kemikaaleista (KETU), pilaantuneista maa-alueista (MATTI-järjestelmä) ja pintavesistä (PIVET) antoivat hyödyllistä tietoa pääasiallisesta arseenin aiheuttamasta pilaantumisesta. Lisätietoja saatiin insinööritoimistojen tekemistä kymmenistä julkaisemattomista ympäristöteknisistä tutkimuksista, riskiarvioinneista ja kunnostussuunnitelmista sekä PIRin omien tutkimusten tuloksista ja julkaisuista. Kaivostoiminnan ympäristövaikutuksista etsittiin tietoa lisäksi geologisista julkaisuista. Tiedon hankinta osoittautui hankalaksi, sillä tieto arseenisaastumisesta, pitoisuuksista ja riskinarvioinnista on ripoteltu epävirallisiin tai julkaisemattomiin raportteihin. RAMAS tutki entisen suolakyllästämön pilaamaa maa-aluetta (52 kenttäanalyysiä ja 5 laboratoriossa analysoitua näytettä), kahden suljetun kaivosalueen ympäristöä (6 rikastehiekkanäytteestä tutkittiin geokemiallinen koostumus, liukoisuus ja toksisuus, 6 järvi- ja purosedimenttinäytettä sekä yli 60 pintavesinäytettä), sekä kunnallisia ja teollisuusjätevesiä ennen ja jälkeen jäteveden puhdistusta. Kaikkiaan yli 100 näytettä analysoitiin.

Sekä tiedonkeruu että näytteenotto osoittivat, että puunkyllästämöt ovat merkittävin arseenilähde Pirkanmaalla. Ne aiheuttavat riskiä lähialueen asukkaille, pinta- ja pohjavesille, mutta niiden vaikutusalue on kuitenkin verrattain pieni. Ampumaradat ovat mahdollisia arseenin saastuttajia, vaikkakin lyijy on pääongelmana näillä kohteilla. Kaivosteollisuus vaikuttaa ympäristöönsä ilma- ja vesipäästöjen kautta, mikä käy ilmi RAMASin tutkimalla Ylöjärven kaivosalueella. Arseeni kulkeutuu kaivosalueelta aina seitsemän kilometrin pituisen vesiväylän päähän Näsijärveen, ja kaivostoiminnan vaikutukset näkyvät korkeina arseeni- ja raskasmetallipitoisuuksina järvi- ja purosedimenteissä. Jätehuollon tutkimukset osoittavat, että yleisesti erilaisten jätteiden arseenipitoisuudet ovat alhaiset. Kuitenkin pistekuormitus esim. kyllästämöjätteistä tai kyllästetystä puujätteestä voi aiheuttaa kontaminaatioriskiä vanhoilla, huonosti eristetyillä kaatopaikoilla.

Vanhojen kaatopaikkojen lisäksi, romuttamojen, suljettujen tehtaiden, öljynjalostamojen, sulattojen ja nahkatehtaiden ympäristöt ovat potentiaalisia arseenin saastuttamia kohteita. Turkistarhat ja muoviteollisuus sekä monet muut antropogeeniset lähteet voivat olla mahdollisia arseenisaastuttajia, vaikka arseeni ei olekaan pääasiallinen haitallinen aine. Pirkanmaan saastuneet alueet ovat kuitenkin pieniä verrattuna muihin Euroopan maihin, kuten esimerkiksi Etelä-Espanjan laaja kaivostoiminnan vaikuttama alue.

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PREFACE

RAMAS (LIFE04 ENV/FI/000300) is a three-year project, which is jointly funded by the LIFE ENVIRONMENT – program, by the beneficiary, the Geological Survey of Finland (GTK), and by the partners: the Helsinki University of Technology (TKK), the Pirkanmaa Regional Environment Center (PREC), 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 is targeting the whole Province of Pirkanmaa (also called the Tampere Region), which comprises 33 municipalities, and has 455 000 inhabitants within its area. The Finland's third largest city of Tampere is the economical and cultural center of the region.

The project aims to identify the various sources of arsenic in the target area, to produce a health and environmental risk assessment for the region and to present recommendations for the preventive/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 (PREC), Kati Vaajasaari until 30.4.2006; Ämer Bilaletdin since 1.5.2006
3. Risk assessment (SYKE), Eija Schultz
4. Risk Management (SYKE), Jaana Sorvari
5. Dissemination of results (TKK), Kirsti Loukola-Ruskeeniemi
6. Project management (GTK), Timo Ruskeeniemi

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

The report at hand is the first one in the series. In future, a cumulative list of the reports published so far will be given in the back cover of each report. All documents can be also downloaded from the project's home page: www.gtk.fi/projects/ramas .

1. INTRODUCTION

Arsenic (As) has been known for thousands of years and it has been used as medicine to treat such ailments as purulent wounds, cancer and psoriasis. Arsenic was commonly used in medical purposes until the beginning of the 20th century, even though as early as the late Middle Age, awareness of the toxicity became evident. As a result arsenic was used in assassinations and in carrying out death sentences. Until recently, arsenic has commonly been used in numerous chemicals appearing in paints, tanning agents of leather, metal alloys, and wood preservative agents for example. In general, arsenic has an antibacterial, conserving effect, but is classified as a toxic and hazardous element because it is cancerous, deteriorates the nervous system, fertility and development of embryo. Therefore its use is limited nowadays. However, its use in chemicals in the past has caused a contamination risk for a long period of time.

To understand the environmental risks of arsenic, its behavior in nature and its tendency to form compounds must be understood. Arsenic (As) is a metalloid that can be present in four oxidation states: As^{3-}, As^0, As^{3+} and As^{5+}. Arsenic commonly exhibits oxidation states +III and +V (the former being more toxic than the latter) forming weak or moderate strength acids: arsenious acid H_3AsO_3 and (ortho)arsenic acid H_3AsO_4. The inorganic salts of these acids are arsenite (+III) and arsenate (+V), respectively. Arsenate forms in aerobic conditions in nature, whereas in anaerobic wetlands it is reduced to arsenite. Complex ions of arsenic bind with secondary iron oxides and hydroxides, and in varying degrees with manganese and aluminum precipitates. Clay and humus are also known to be good absorbents of arsenic. In plants, arsenic appears as organic compounds that are catalyzed by bacterial processes. Arsenic appears at oxidation state -III in hydrogen arsenide (AsH_3). When arsenic is heated it sublimates. As well, microbial activity can transform arsenic into gaseous arsine even though arsenic concentrations in the contaminated soil were not high. Microorganisms are able to methylate inorganic arsenic trivalent arsenic (+III) to less toxic monomethyl arsenic acid (MMAA) and dimethyl arsenic acid (DMAA). (Decree of Ministry of Social Affairs and Health 509/2005 (List of hazardous substances))

To assess the ecological harmfulness of arsenic in nature, a set of limit values have been established. In Finland, 10 mg/kg of arsenic in soils is set as a lower guideline value indicating mildly contaminated land and 50 mg/kg of arsenic is an upper guideline value indicating the threshold value for soil remediation requirement (Puolanne *et al.* 1994). In the proposal of the decree of Council of State, new lower and upper guideline values are set to 50 mg/kg and 100 mg/kg, respectively, which will be implemented during the following year (http://www.ymparisto.fi/download.asp?contentid=46769&lan=fi). Risk assessment, based on future land use purposes of the contaminated soil, guides the remediation requirement and the new guideline values that will be used. For instance, the new lower guideline value is meant for remediation in inhabited areas, whereas the upper guideline value is intended for areas planned for industrial activities. The limit value of water for household consumption is 10 µg/l. Solid wastes are classified as hazardous waste if arsenic concentration in solid matter exceeds the limit value of 1000 mg/kg (Finnish Waste Degree 1128/2001, Hazardous Waste Directive 1991/689/EC). According to waste acceptance criteria (Council Decision 2003/33/EC) of the EU Landfill Directive, leaching of arsenic into water at liquid to solid -ratio of 10 l/kg should not be greater than 0.5 mg/kg for inert waste, 2.0 mg/kg for non-hazardous waste, and 25 mg/kg for hazardous waste, respectively.

The aims of this research were to gather up existing material and information about the anthropogenic sources of arsenic, and to conduct complementary sampling and analyses in some of the major contaminant sites in the Pirkanmaa region (Figure 1). The focus will be on soil and water contamination, not on airborne emissions of arsenic. The data acquisition has been difficult because in many studies there is no analyzed arsenic concentration data. Information about arsenic contamination is scattered in unpublished reports and sometimes its reliability can be questioned. While arsenic is known to be harmful for the environment and for human beings, it is surprising how often it is left out from analyzed elements. For instance, the leachate waters and surface waters monitored from landfills are commonly analyzed for agents inducing eutrophication, but not for arsenic and other heavy metals. Analyses focus on pH, nitrogen and oxygen contents to assess eutrophication of the surface waters. Nowadays, arsenic is increasingly added to the list of analyzed elements. In many cases, the surface water monitoring established at old mining sites constitutes only analyses of the main exploited elements, leaving other possible contaminants out of the inspection. To complement the information collected from previous studies, RAMAS measured arsenic from contaminated soils of a former wood preservation plant and from waste waters and purified waste waters of several waste water treatment plants in the Pirkanmaa region. In addition, contaminated soils, lake and river sediment samples and water samples were studied from two closed mining areas.

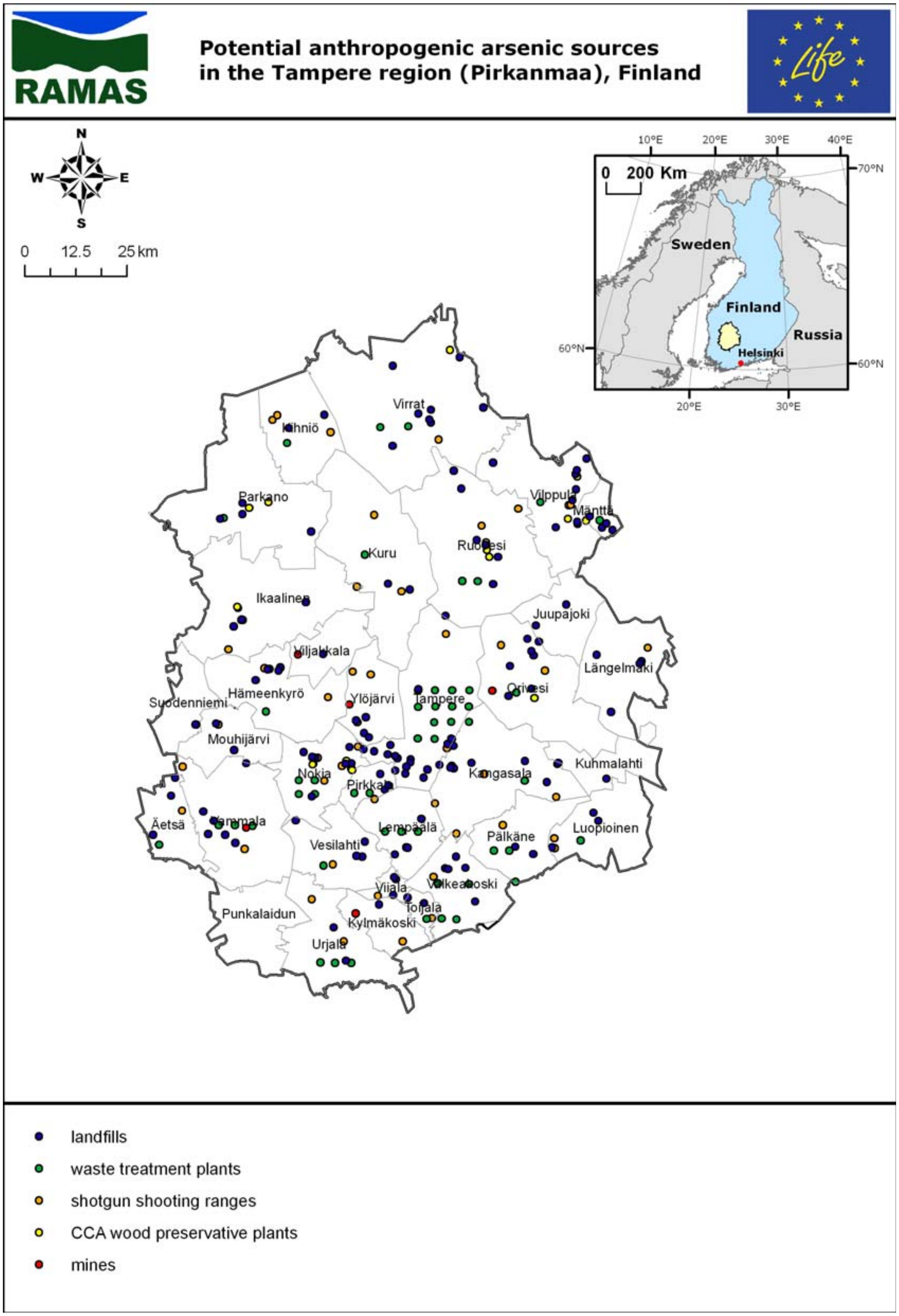

Figure 1. Potential anthropogenic arsenic sources in the Pirkanmaa region presented in this RAMAS project report (Anu Peltonen, PREC).

2. ANTHROPOGENIC SOURCES OF ARSENIC

Arsenic is a common element in the nature and it is among the twenty most common elements on the Earth. Backman *et al.* (2006, report of TASK1) studied the natural sources of arsenic in the Pirkanmaa region (also called the Tampere region) and found that arsenic is a natural constituent of the bedrock, topsoil and groundwater. Since arsenic is prevalent in the Earth, it is easy to understand that it appears in raw materials derived from the earth’s crust, *e.g.* gold and copper-nickel ores, heating oil, coal and peat to mention a few sources. When ore is extracted, otherwise stable arsenic bearing minerals are exposed to oxidizing conditions and sulfide minerals weather releasing arsenic into surface waters and top soils. The metal industry generates blast-furnace cinder and airborne emissions containing arsenic. In fact, the metal industry is considered the major airborne pollutant of arsenic (90 % in 1997) in Finland (Melanen *et al.* 1999). In the burning process of the fossil fuels arsenic accumulates in the ashes and part of it is also released in the air as small particles or gases. The total airborne emissions are difficult to calculate, but it was estimated to have decreased 90 % from 1990 to 1995 because of better technologies in the industrial and burning processes. The airborne contamination of arsenic is not examined in detail in this report.

Other anthropogenic sources of arsenic are As containing chemicals which have been used diversely in the past century. Their application and extent of usage has been restricted in the last decades because of health and environmental problems. Pesticides, agricultural products, textile chemicals, tanning agents of leather, anti-corrosive agents, glass and ceramic products and paints are known to have contained arsenic in the past, but nowadays the use of arsenic is forbidden in most of those chemicals. However, arsenic is still used as arsenicpentoxide in wood preservative agents and found as a side product in sulphuric acid production. In plastics, arsenic is used as an antibacterial additive as Phenoxarsine oxide and 10,10'-Bis(phenoxyarsinyl) oxide (KETU database from Finnish Environment institute, SYKE).

Chromated copper arsenates (CCA) are probably the most well-known anthropogenic contaminants of arsenic. They are used in wood treatment to increase the usage time and to protect wood from humidity, mold, bacteria and insects. CCA treated wood is used in buildings, bridges, power transmission line and phone line supports and in many other places requiring durable wooden material. CCA’s are the most common wood preservative products used in humid conditions. Other inorganic preservatives are ammonia copper arsenates (ACA) and acid copper chromates (ACC). Creosote oil is an organic wood preservative consisting of coal oils and cancerous organic agents. CCA products are classified into three groups according to the amount of arsenic: A containing 16.4 % As; B 45.1 %; and C 34.0 % (Vihavainen 1989). CCA-C is the most used internationally, including Finland. In Finland, CCA preservatives have been used since the 1950’s and as an example 96 % of the treated wood was impregnated with CCA agents in 1989 (Vihavainen 1989).

The environmental impacts of the treatment plants and treated wood are well acknowledged nowadays. According to the Chemical Law (744/1989), all chemicals used in wood preservatives must be approved by SYKE before they can be produced, marketed and used. In the past decade, the CCA treatment has been restricted in Finland, while the use and waste disposal of CCA-treated wood has been limited. Since 2004, all products treated with the arsenic bearing preservatives are forbidden for household use, but are only allowed for professional purposes, including building bridges, piers and noise barriers (http://www.ymparisto.fi/default.asp?node=1700&lan=fi). CCA-treated wood can only be cut in longitudinal direction to avoid exposure to cancerous arsenic and chromium. Creosote oil is used restrictedly in professional use, and in 2003, it was prohibited in playgrounds, parks and in items in contact with food (http://www.ymparisto.fi/default.asp?node=1700&lan=fi). While the wood preservative industry has tried to develop products that have less impact on the environment and the use of CCA has been restricted, the arsenic and chromium free, copper-based products have not really broken through. Most of the wood preservation plants are committed to mark the impregnated wood with information about the used preservative agents and about the producers, and since 2002 it is required for all CCA-treated wood. One main source of arsenic contamination in Finnish soils has typically been caused by the spills of the CCA preservatives into the ground in many old wood impregnation plants (Ruokolainen *et al.* 2000, Vaajasaari *et al*. 2002, Turpeinen 2002). Metal pollution originating from the CCA agents spread to the water bodies close to plants situated in groundwater areas or near waterways (Ruokolainen *et al.* 2000, Turpeinen 2002). Recent studies showed that leaching of preservative components from CCA treated wood also caused harmful effects to the environment, for example in coastal water bodies (Lebow *et al.* 1999, Hingston *et al.* 2001). Other contaminated soil sites are in shooting ranges affected by the load of widespread gunshots and bullets. Lead (Pb) is the main problem in shooting ranges, but other harmful elements like antimony (Sb), arsenic (As), copper (Cu), zinc (Zn) and nickel (Ni) burden the environment (Naumanen 2002). Arsenic contamination can arise in the aquatic or terrestrial environment from several other human activities such as animal shelters, steel and metal industry, paint industry, graphic industry and glass industry (see Appendix 1).

A number of different pesticides have been used in greenhouse cultivations containing about 120 effective agents (Jaakkonen 2003). It is difficult to track down all the pesticides used in closed nursery gardens because there are a variety of pesticides applied depending on the cultivated plants and the authorities did not control their use. Stability, migration, accumulation and toxicity are main qualities of pesticides that determine their behavior in the environment. A cold climate enhances the stability of most pesticides in our environment compared to warmer climates and the ability to migration is a function of the products solubility in water and type of the soil. Accumulation ability measures biological concentrations in living organisms while toxicity indicates the harmfulness of the products on organisms. Inorganic, arsenic-bearing compounds like arsenic acids and copper, zinc, lead and calcium arsenates were used as vermin pesticides from the early 1900 until the late 1950's. In Finland, synthetic organic pesticides were introduced in late 1940's, and soon after chlorinated hydrocarbon DDT and lindane were marketed many other synthetic pesticides were available like tecnazene, thiram and paradichlorobenzol (Jamalainen and Kanervo, 1948). In the second half of the 20th century people became aware of the health and environmental problems caused by pesticides and some of them (*e.g.* DDT) were prohibited. All arsenic bearing pesticides were prohibited in 1964 (Markkula 1990). Therefore, concerning arsenic contamination, the problematic gardens are the ones that occurred before the prohibition. While the slowly degradable pesticides causing health problems are forbidden today, after being applied for decades ago, they keep contaminating soils and groundwater.

In agriculture, arsenic bearing disinfection solution for cloven hoofs has also been used. This copper sulfate biocide containing 0.02-0.008 % of arsenic is allowed until 1.9.2006 (Oral notification by

Virpi Virtanen from SYKE). Nevertheless, anthropogenic sources of arsenic from agriculture are not examined in this report. In later RAMAS reports, this topic will be reviewed in detail by Agrifood Research Finland (MTT).

Arsenic is a minor constituent in some products like lead batteries, gunshots and other metal products. If these products end up in municipal landfills, scrap yards or pile up in the forests at shooting ranges, arsenic can cause an environmental contamination risk to the terrestrial or aquatic environment. Arsenic contamination can also be detected in landfill leachates when impregnated wood, incineration ashes and various other types of wastes are sited into landfills. The most common cleanup method for the metal-contamination of soils is excavation. The traditional method of dealing with excavated contaminated soils is landfill disposal. In landfills, arsenic from soils contaminated by the wood preservative agents can arise in terms of landfill leachates (Cooper 1991, Pohlandt-Schwandt 1999, Clausen 2000).

3. DATA ACQUISITION AND SOURCES OF INFORMATION

Data available in the Register of Contaminated Land Areas (database MATTI) maintained by SYKE and Regional Environment Centers of Finland were used to list the risk areas and possible arsenic contaminants. The Register of Surface Waters (database PIVET) was also checked. Further, more detailed information about the contaminants was acquired from very diverse sources. Environmental authorities were questioned to determine other anthropogenic sources of arsenic and possible contaminants that had not yet been considered.

Consulting companies are mainly responsible for the risk assessments and remediation of contaminated soils in wood preservation plants. The research data are found in unpublished file reports in the Pirkanmaa Regional Environment Centre (PREC). The information about arsenic concentrations in wood preservation plants given in this report was gathered from file reports concerning the risk assessment and soil remediation.

Information about shooting ranges in the Pirkanmaa region was collected from the PRECs unpublished reports and from a thesis by Sami Mustajoki (Häme Polytechnic) done in co-operation with the PREC. Researches from other Regional Environment Centers in Finland were also reviewed.

Information about the geology and mining history of old mining sites in the Pirkanmaa region (Pirkanmaa) is found in numerous geological articles and mining engineering publications. However, information concerning piling and banking of tailings and acid mine drainage is rarely given. Waste management and environmental problems are delicate matters and unwanted publicity is often avoided. Surface water monitoring of old mining areas is performed in few places but in general there is little information about environmental risks or contamination. It has been especially difficult to find information about arsenic because in some cases surface water monitoring includes only analyses of the main exploited elements. Recently published risk assessment reports from Haveri and Ylöjärvi mine are reviewed in this paper.

General information about waste management is gathered from Pirkanmaa Waste Management Plan for 2005 to 2010 (Blinnikka 2004) and the waste management database VAHTI. Arsenic concentrations in different types of solid wastes and their eluates (landfill disposability or re-use studies) were gathered from different research studies and laboratory test results from the Pirkanmaa Regional Environment Centre (LIMS database). Until recently, surface water monitoring in landfills has not covered analyzed data on arsenic, which makes the long-term risk assessment impossible. However, some reports on old landfills reviewed in this paper exhibit that arsenic is a contaminant in landfills.

Data about other possible sources of arsenic, like in commercial nursery gardens, was difficult to obtain, because there is no published data and unpublished reports do not comment on the appearance of arsenic in the soils of gardens in the Pirkanmaa region. Studies from other Regional Environment Centers were used as reference cases.

4. ARSENIC IN CONTAMINATED SOILS

In the European Union, there are around 300 000 – 1.5 million contaminated soil areas in 15 different member states that have been reported to European Environment Agency (EEA). For example, in Flanders (BE) the number of potentially contaminated soil sites is 76 000, in Austria 2265, and in France 300 000 – 400 000. In Finland, around 20 000 soil sites may be contaminated. In the Pirkanmaa region, the total number of potentially contaminated areas is over 1400. Different anthropogenic sources of soil contamination and the potential contaminants released into the environment have been listed twice in Finland in the beginning of the 1990 and during 1998 and 1999 (see Appendix 1). The inorganic or organic contamination of Finnish soils has typically been caused by the spills of the CCA preservatives in many old wood impregnation plants or gasoline leaks into the ground at old petrol distribution stations. Other main sources of soil contamination are scrap yards, garages, timber mills and shooting ranges (see Appendix 1). At the moment, around 400 soil sites are remediated every year in Finland, and the amount of money spent annually for remediation procedures is around 50 - 70 million euros. In the Pirkanmaa region, 259 soil sites have been remediated to date (Blinnikka 2004). Most of these soil sites were old petrol distribution stations.

In Finland, the guideline values are set for preliminary risk assessment of contamination, which can also be used to monitor the site after remediation. Target values are set to achieve good ecological state of the ground soil. To assess the risk at a contaminated soil site, the natural occurrence of the contaminant is considered to be a target value for soil cleanup. If the concentrations exceed the target value, there is a contamination risk and remediation actions are needed. If the concentrations of contaminants are greater than guideline values, contamination is considered to be a human and environmental risk and minimization of the risk is needed. In Finland, a lower guideline value is set to 10 mg/kg and an upper guideline value to 50 mg/kg for arsenic to assess soil remediation requirement.

Remediation can be done in many ways: isolating, excavating, washing and solidifying the contaminated ground. The method used depends on concentration and property of harmful agents and on soil type. The most common remediation method is excavation of landmasses and removal to landfills, stabilizing or solidifying them. The amount of excavated soil mass is annually around 500 000 tons in Finland. In the Pirkanmaa region, the main source of arsenic contamination is the old CCA wood preservative plants (16) and timber mills (3) where wood impregnation with CCA preservatives has been practiced (Table 1). In all of these sites, at least preliminary characterization of arsenic contamination has been done and four of these sites have already been completely or partly remediated.

Other soil sites where contamination is frequent are shooting ranges. Shotgun, rifle and pistol shooting causes mainly lead contamination because of the scattered gunshots and bullets on the ground, but small amounts of arsenic in gunshots also pose a contamination risk. Remediation in these sites is complicated due to the vast area exposed to gunshot residues and due to the nature of soils in forestry areas. In the Pirkanmaa region, there are 72 active shooting ranges, 47 of which include shotgun practice. At present, only three ranges are supervised under an environmental permit.

4.1. Wood preservatives

In the Pirkanmaa region, there are 16 wood preservation plants, three of which, are still working (Figure 2). Soil remediation has been conducted in three closed plants and in one of the working plants. One of the active impregnation plants uses arsenic free copper-based impregnation agents. Timber mills often have diverse contamination problems because in many cases, wood preservation plants and timber mills worked together. Since the 1930’s, chlorophenols containing KY-5 wood protective liquids have been used in timber mills, and in the Pirkanmaa region, there are three closed timber mills that had a mixed use of CCA and KY-5 wood preservatives. Only two impregnation plants are situated in 1st class groundwater areas[1], both of which have been closed since the late 1960’s (Table 1). RAMAS studied one of these old impregnation plants in Ruovesi commune and an earlier study of another plant in 1st class groundwater area from Ruovesi commune is also reviewed in this report. In the latter location soil remediation was conducted because of soil contamination and an evident risk for groundwater contamination. Two other cases from Vilppula and Virrat communes are also reviewed later in this paper.

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[1] Finland's environmental administration classifies ground water areas in three classes according to the usability and need for protection: I = important for groundwater intake, II = suitable for groundwater intake, III = other ground water area.

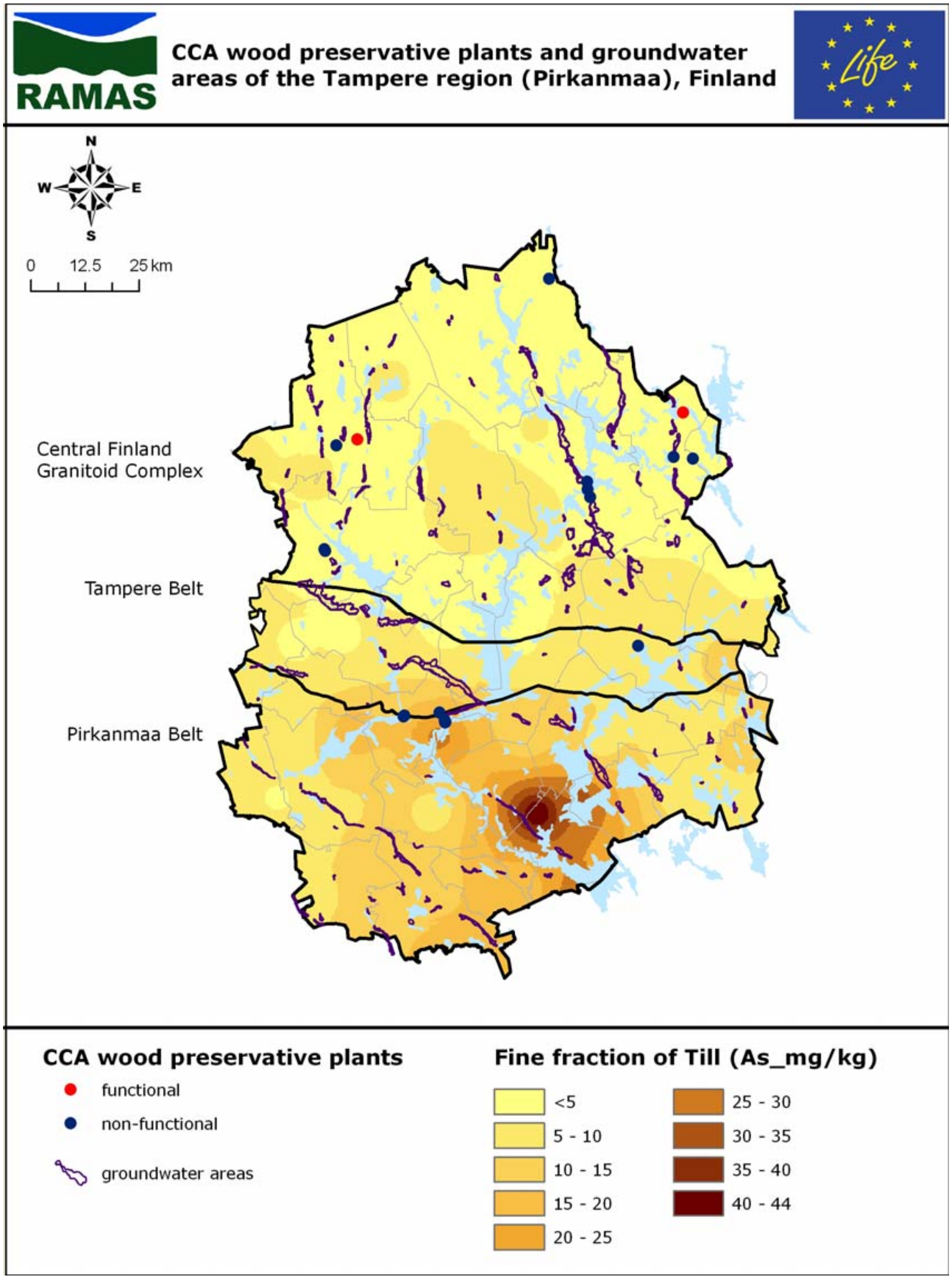


Figure 2. **A map showing arsenic concentration in glacial till in the Pirkanmaa region, with the locations of former and active wood preservation plants. Important groundwater resources are also shown in the map (Anu Peltonen, PREC).**

Table 1. Arsenic concentrations characterized in the soils of eleven wood preservation plants and three timber mills where CCA- impregnation was practiced in the Pirkanmaa region. Distances (m) to various sources used for the preliminary risk assessment are also presented.

Commune	State	Min	Max	Average	Median	Number of Analysis	Year of commencement
Ruovesi[1]	Remediated	23	6700	1474	320	15	1957
Ruovesi[1]	Studied in RAMAS	66	4200	1152	440	7	1960
Ruovesi	Preliminary studied	11	250	54	26	15	1954
Parkano	Preliminary studied	6	860	54	13	49	–
Parkano	*	–	–	–	–	–	1990
Ikaalinen	Preliminary studied	23	110	53	33	5	–
Ikaalinen	Preliminary studied	0	209	32	21	39	–
Vilppula[1]	Remediated	2	730	82	18	20	1953
Vilppula	Remediated *	< 10	4930	100	14	65	1955
Virrat[1]	To be remediated in 2006	3	1000	220	140	39	1956
Nokia	Preliminary studied	< 5	1060	75	10	51	1931
Orivesi[2]	Preliminary studied	3	5900	859	5	10	–
Nokia[2]	Preliminary studied	7	2780	465	33	19	1955
Nokia[2]	Preliminary studied	3	4200	235	19	38	1965

Commune	Year of closure	Distance to groundwater area	Groundwater classification	Distance to groundwater intake	Distance to Lake	Distance to River	Distance to residential area
Ruovesi[1]	1968	0	1	1058	105	2240	100
Ruovesi[1]	1968	0	1	145	169	424	100
Ruovesi	1965	270	3	762	614	1373	50
Parkano	1971	1776	1	2095	524	450	100
Parkano	*	2470	3	3402	777	50	500
Ikaalinen	1976	2035	1	2597	750	120	100
Ikaalinen	1976	2466	1	3025	950	10	100
Vilppula[1]	1963	330	2	3600	80	10	0
Vilppula	*	2253	1	2538	100	250	200
Virrat[1]	1967	11477	1	12221	< 50	–	100
Nokia	1955	530	3	2453	600	490	100
Orivesi[2]	–	2921	1	3040	50	738	100
Nokia[2]	1984	895	1	2170	50	50	100
Nokia[2]	1988	8600	1	9000	100	100	50

[1] wood preservative plants viewed in this paper, [2] timber mills where impregnation has been practised, * active wood preervative plants at the present

Imprudent handling of impregnation products has given rise to soil and water contamination. Impregnation plants were commonly built near lakes because in the past, logs were transported along waterways. Wood is impregnated with diluted preservative agents (2 %) in closed pressure chambers and dried in open-air stocks or artificially in warehouses over one year. The treated sap wood contains about 12 to 15 kg/m^3 preservative salts, which means that it contains 1.2-1.4 kg/m^3 copper, 2.1-2.3 kg/m^3 chromium and 1.8-2.2 kg/m^3 arsenic (Vihavainen 1989). While the wood dries, preservative agent attaches as a very poorly soluble compounds. The end products can not be delivered to clients before completely drying up to prevent any exposure to toxic agents. Despite the precautionary measures, wood preservation plants pose a risk of contaminating soils and groundwater, and remediation of the soils is required in closed impregnating plants. Older impregnation plants are especially problematic areas because decades ago, when the toxicity of chromium, copper and arsenic was not acknowledged, attention was not paid to the spilling of impregnation products. Treated wood was stocked directly on the ground allowing the product to penetrate the soil, and spills from the impregnation chamber were not controlled. Impregnated waste wood, *e.g.* sawdust and chips, were mixed with soil and dumped in the plant area, as well as CCA containing bark was left laying on the ground. Groundwater is at risk when wood preservatives are allowed freely to penetrate the soils. For example, chromates are able to easily penetrate to the groundwater supply because it is hardly absorbed by soils, whereas copper is absorbed effectively in soils thus diminishing the water contamination risk (Melcher and Peek 1997). Arsenic moves easily in soils, but is absorbed in iron hydroxides, organic matter and clay minerals.

4.2. End products of impregnated wood

The contamination risk of arsenic, chromium and copper is not limited to the treatment plants because impregnated wood causes health and environmental problems also when it is consumed. Treated wood is used in supporting structures in constant contact with soil and water. Piers, bridges, supporting columns for buildings, power transmission line and phone line supports are common destinations for humidity tolerating CCA-treated wood. At present, CCA-treated wood is not allowed in toys or parts of playgrounds, any items in contact with food (*e.g.* package material), garden furniture and greenhouses (http://www.ymparisto.fi/default.asp?node=1700&lan=fi). However, the material employed before the restriction is still in use in terrace boarding or wooden panels and sandboxes for children. Information about contamination in playgrounds or private gardens is rarely available but there are strong suspicions about contamination and the probable health effects. It is known that while playing children are exposed to arsenic, chromium and copper in the sand through skin contact and also through ingestion because children often put their fingers in their mouth (Jantunen *et al.* 2005). Metals are also leached from CCA treated wood used in piers built in contact with salty ocean water (Lebow, *et al.* 1999, Hingston, *et al.* 2001).

The waste management of impregnated wood is problematic. Nevertheless, impregnated wood from demolished buildings is classified as hazardous waste some of it ends up in municipal landfills because of poor sorting. The disposal of treated wood by burning is not allowed except in power plants with an environmental permit for hazardous waste incineration. It is difficult, however, to control the private consumers. Burning of these products accumulates arsenic, chromium and copper into the incineration ashes, but part of the arsenic is carried out as small particles along with the smoke. The produced ashes are assessed and deposited in hazardous waste landfills if necessary. In the Pirkanmaa region, there are plans to establish a power plant intended for district heating and electricity production powered by impregnated waste wood, other recycled wood and forest processed chips.Citizens have expressed their opposition to the plan and the environmental impact assessment (EIA) of the future power plant is currently in process. The waste management will be discussed more in chapter 6.

4.3. Case studies of former wood preservation plants in the Pirkanmaa Region

Four wood preservation plants are reviewed in this chapter. Two plants situated in 1st class groundwater area in Ruovesi commune were reviewed. Both plants are situated close to groundwater intake plants and lakes. The two other case studies are from Vilppula and Virrat communes. The land of the former plant in Vilppula is currently owned by a private person and contamination poses a risk for the family living in the vicinity. In Virrat, residential buildings are very close to the former impregnation plant as well.

4.3.1. Ruovesi I

The RAMAS project studied the ground of a former impregnation plant located in 1st class groundwater area (Figure 3). The distance to the nearest ground water intake plant is 145 meters and the nearest lake is situated 169 meters from the former plant. This plant was active for eight years after commencing in 1960. The aims of the study were to determine total contents of the detrimental agents, their leaching properties and to investigate the ecotoxicity of the soil samples to help assess risk in the former wood preservation plants. Additionally, Ground Penetrating Radar (GPR) measurements were performed to assess topography and depth of the bedrock below soil cover. The contaminated area was divided in to squares of 2*2 meters (Figure 3 and Figure 4). Heavy metal contents were measured with X-ray fluorescence field analyzing instrument (INNOV-X). Five samples were chosen for laboratory analysis. At first, soil samples were sieved to particle size < 4 mm. For analyzing total arsenic and metal concentrations, samples were ground to a particle size of < 0.250 mm and then extracted with nitric acid by microwave-assisted digestion and the metal concentrations of the extracts were analyzed using ICP-MS (inductively coupled plasma mass spectrometry) and ICP-OES (inductively coupled plasma optical emission spectrometry) techniques.

Using field analyzer, arsenic concentrations of 52 samples were analyzed and the concentrations varied between 8 to 4400 mg/kg (average 610 mg/kg) whereas copper concentrations ranged from 13 to 5900 mg/kg (average 440 mg/kg) and chromium concentrations from 68 to 3700 mg/kg (average 580 mg/kg). The laboratory results also showed high concentrations of arsenic ranging from 66 to 4200 mg/kg (Table 2). The leaching ability of detrimental agents was studied with a two-stage batch leaching test (EN 12457-3) intended for waste compliance testing. First, a soil sample was agitated with water at a liquid to solid -ratio of 2 l/kg (L/S 2), and the mixture was separated by filtration. In a similar manner, the same solid sample was agitated with fresh water at a L/S-ratio of 8 l/kg. The eluates of different stages were used for chemical and ecotoxicological analyses. The concentrations of substances analyzed from the leaching test eluates were expressed as the leached amounts (mg/kg) relative to the total mass of the test sample at L/S 2 and cumulative L/S 10 ratio (Table 2). The leaching tests were conducted for three samples showing the leachability of arsenic less than one percent for L/S 2 and 0.8-2.0 % for L/S 10. This indicates that the leachability of heavy metals is low in the pH range of the water-soil mixture (pH 3.4-3.9). The toxicity of the solid soil samples was tested using a seed germination test and Enchytraeid worm survival and reproduction tests, and leaching test eluates with the luminescent bacteria test (EN-ISO-11348-3) and reverse electron transport assay (RET). Five solid samples were toxic to luminescent bacteria in the solid-phase assay (FLASH, Lappalainen 2001), whereas the leaching test eluates did not cause any acute toxicity to luminescent bacteria and enzyme activity (RET). Ecotoxicity test results are discussed in more detailed in the TASK 3 report. As well, surface water samples from a nearby stream showed that arsenic, copper and chromium are most likely transported to a lake in the vicinity: the water entering the area contains less than 3 μg/l of As whereas the water running downstream from the contaminated area showed concentrations of 49 μg/l As.

Table 2. Total arsenic concentrations (tot) and the leached portion of arsenic from contaminated soil samples collected from a wood preservation plant in Ruovesi I. L/S 2 and L/S 10 means liquid to solid -ratio at first and second stage of the leaching test method EN-12457-3.

	Content and amount leached (mg/kg)				Leached portion from the total content		
Point		As	Cr	Cu	As	Cr	Cu
R1.3	tot	440	260	200			
R2.1	tot	310	120	150			
R2.4	tot	270	160	160			
R2.4	L/S2	2.1	0.05	0.59	0.8 %	0.03 %	0.4 %
R2.4	L/S10	5.3	0.14	1.21	2.0 %	0.1 %	0.8 %
R3.2	tot	680	300	280			
R4.4	tot	2100	940	1000			
R4.4	L/S2	10.5	1	1.69	0.5 %	0.11 %	0.2 %
R4.4	L/S10	28.4	2.3	5.4	1.4 %	0.24 %	0.5 %
R5.3	tot	4200	2200	1100			
R5.5	tot	66	77	33			
R5.5	L/S2	<0.1	0.03	0.06	<0.2 %	0.04 %	0.2 %
R5.5	L/S10	<0.5	0.09	0.13	<0.8 %	0.12 %	0.4 %

Figure 3. Sampling in a former wood preservation plant in Ruovesi commune (Kati Vaajasaari).

Figure 4. The area of an old wood preservation plant in Ruovesi was divided into squares of 2 x 2 meters, and samples were systematically picked (Kati Vaajasaari).

The Geoenvironmental technology laboratory at the Helsinki University of Technology within the RAMAS project made experimental measurements with Ground Penetrating Radar (GPR) at wood preservation plant at Ruovesi I to assess the topography of the area and the probable runoff direction of the detrimental agents. The test measurements were made on appropriate lines that were not marked in the field and the altitudes of the test lines were not measured either. Therefore, the exact locations of the lines are not known and the topographic correction could not be done.

Ground Penetrating Radar (GPR) is one type of echo sounder that sends an electromagnetic pulse into the ground and measures the arrival times of reflected echoes. Knowing the arrival time of the reflected pulse and its speed in the ground the depth of the reflecting surface can be calculated. The speed of the GPR-pulse depends on the type of soil and rock. When determining the speeds, certain assumptions can be made about the soils and rocks through which the pulse passes. Figure 5 explains the principle of the method and visualizes the results. The higher the frequency of the GPR pulse, the faster it dies out when penetrating the soil or rock. The conductivity of the medium has the same effect. The lower the frequency, the deeper the volume of investigation and vise versa. As well, the resolution increases with the frequency. The antenna determines the frequency whereas the problem to be solved determines the antenna to be used. In this study a 100 MHz antenna and a 500 MHz antenna were used.

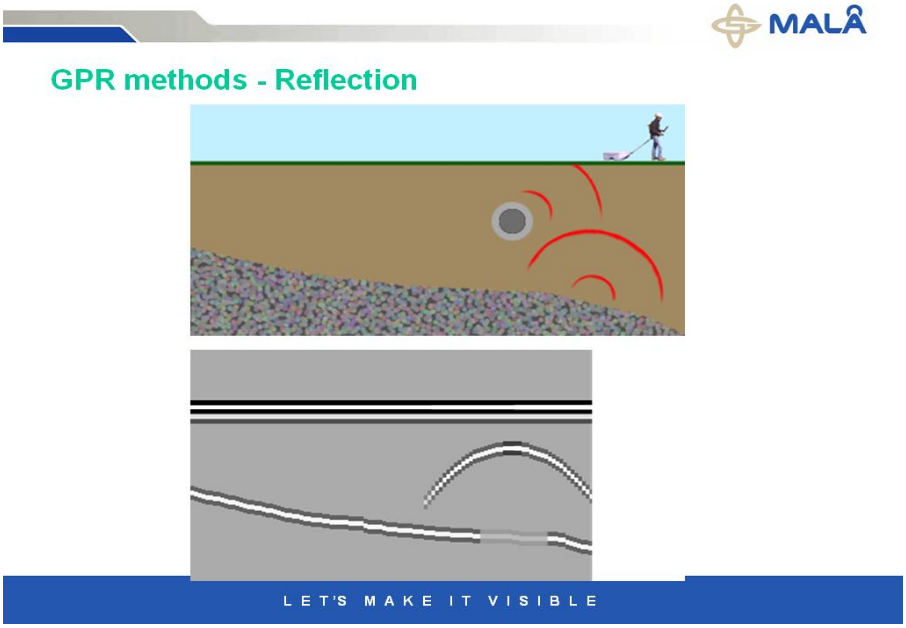


Figure 5. In the upper illustration, the GPR antenna sending pulses is dragged along the surface of the earth. The bedrock dipping to the right is covered with a soil layer in which there is a small reflecting target (reflected pulses are marked with red color). In the illustration below, the distance - time image of the result is shown in grey scale on the computer screen. The surface of the flat rock looks the same in the image but the response of the small object forms a hyperbola. The sharpness of the hyperbola is dependent on the speed of the GPR pulse in the soil. (Malå GeoScience)

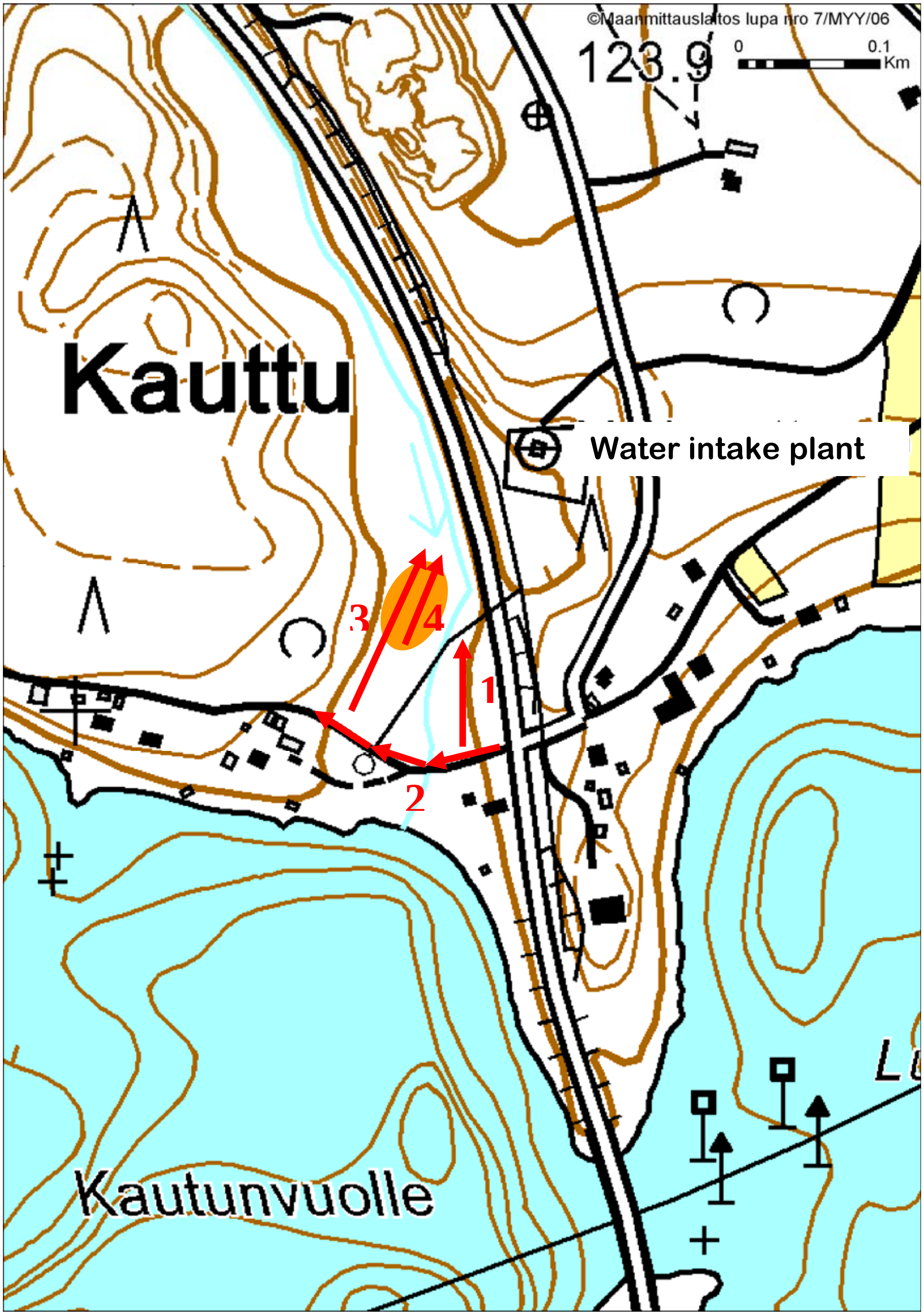


Figure 6. The test lines are marked with red lines on the scheme of Ruovesi I wood preservation plant area (orange circle).

A small stream runs through the study area and the wood preservation plant is situated on the northern side of the stream. The altitude of the plant area is a few meters above the water surface of the stream, and to the northeast of the contaminated site is a cliff. Thus one can assume that the surface of the bedrock runs steeply in the direction of the stream.

Line 1 is on even ground southeast of the plant and line 2 runs along the road south of the plant (Figure 6). Line three runs through dense bushes to the contaminated site and over it. A 100 MHz antenna was used in measuring the lines 1, 2 and 3, whereas a 500 MHz antenna was used to measure the line 4 over the contaminated site.

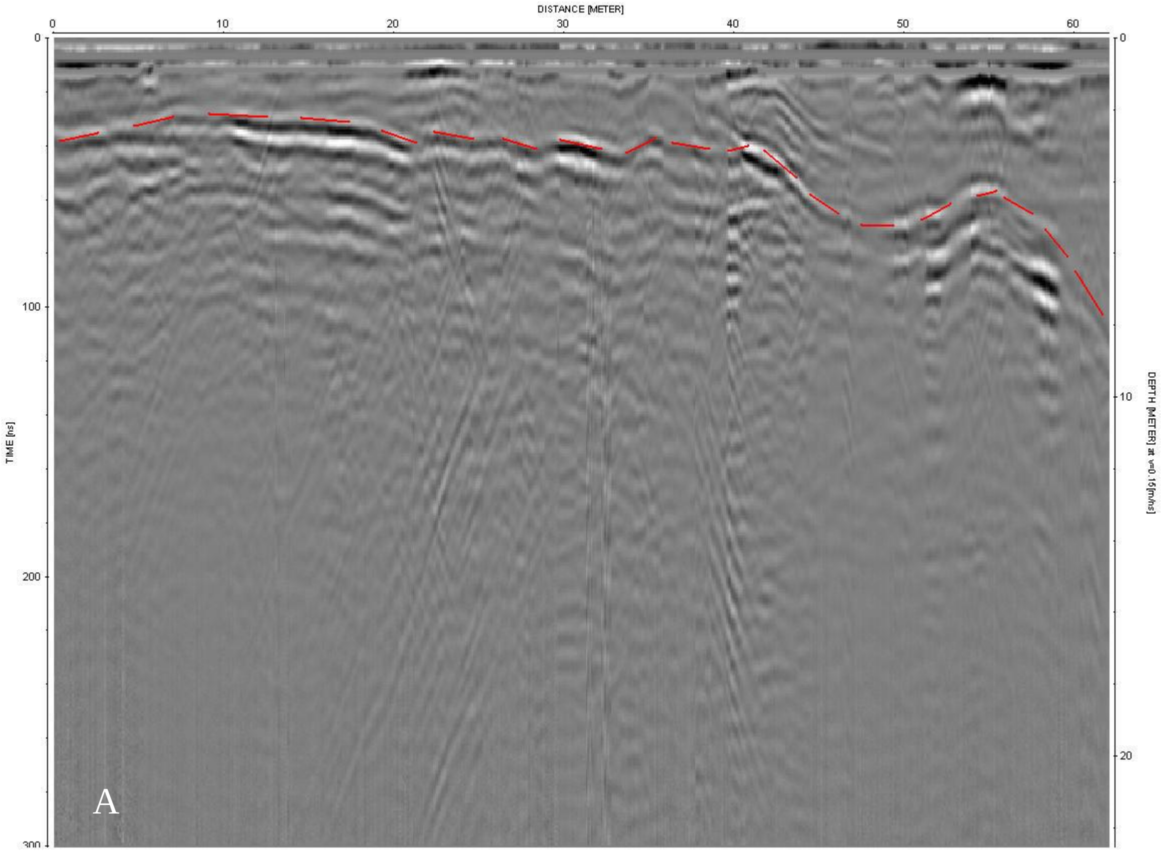
The red dashed line in Figure 7A indicates the interpreted surface of the bedrock in the measurement of line 1 which shows a south inclined topography. The tails of the hyperbolas seen in the Figure 7A indicates a speed of 0.1 m/ns, which is characteristic for shales.

The red dashed line in Figure 7B indicates the interpreted surface of the bedrock in line 2, which runs along the road. The green dashed line indicates the boundary of saturated and dry sand. The blue line marks a distinct boundary in the texture, indicating the road pavement. Black hyperbolas are fitted on the hyperbolas seen in the Figure 7B to estimate the speed of the GPR pulse in the medium. A bridge over the stream is at 12 m. The line first went downward and after about 25 m started to run steeply upward. With topographic corrections the green dashed line in Figure 7B would be horizontal to mark the surface of the water table, but no topographic data was available. Hyperbolas A, B, C and D over the green line indicate a speed of 0.15 m/ns, which is typical for dry sand. Hyperbola E gives a speed of 0.06 m/ns, which is typical for water saturated sand. Hyperbola F gives the speed of 0.1 m/ns indicating shales of the bedrock.

Line 3 runs through a dense bush from the road to the wood preservation plant and over it. The rough terrain and difficult access to the study site made it difficult to move the antenna and distance measuring equipment in the field resulting in disruption of the distance information. The red dashed line in Figure 7C marks the interpreted surface of the bedrock. A sharp discontinuity at 72 meters shows that there is a very strong reflection in the plant area close to the surface of the ground, which is emphasized with a blue line. The wood preservative agents change the electrical properties of the soil, making it a better reflector for the GPR pulses. The reflector could have something to do with the remains of the substances used for wood preservation. A topography correction would make the reflecting surface horizontal.

Line 4 runs over the wood preservation plant parallel to the last 30 meters of line 3 (Figure 7D). The red dashed line in Figure 7D marks the interpreted surface of the bedrock. The blue dashed line marks the same strong reflecting horizon as in Figure 7C although it has much more detail.

The field observations and the Ground Penetrating Radar measurements confirmed the interpretation of the detrimental agent runoff in the direction of the stream to the adjacent lake. The cliffs on the northwestern side and on the eastern side of the wood preservation plant, together with a relatively steeply dipping southern edge form a runoff path ending in the lake about 169 meters south of the former plant.


DISTANCE [METER]
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TIME [ns]
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300
DEPTH [METER] at v=0.15[m/ns]
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10
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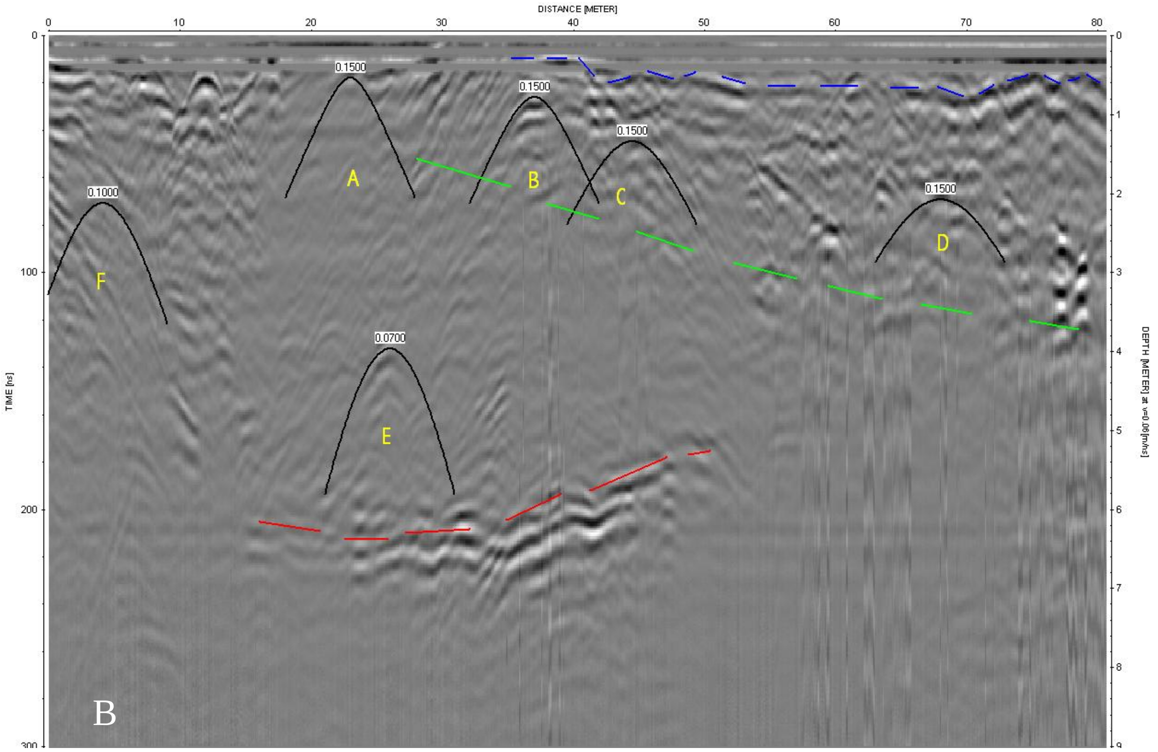
A


DISTANCE [METER]
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80
TIME [ns]
0
100
200
300
DEPTH [METER] at v=0.06[m/ns]
0
1
2
3
4
5
6
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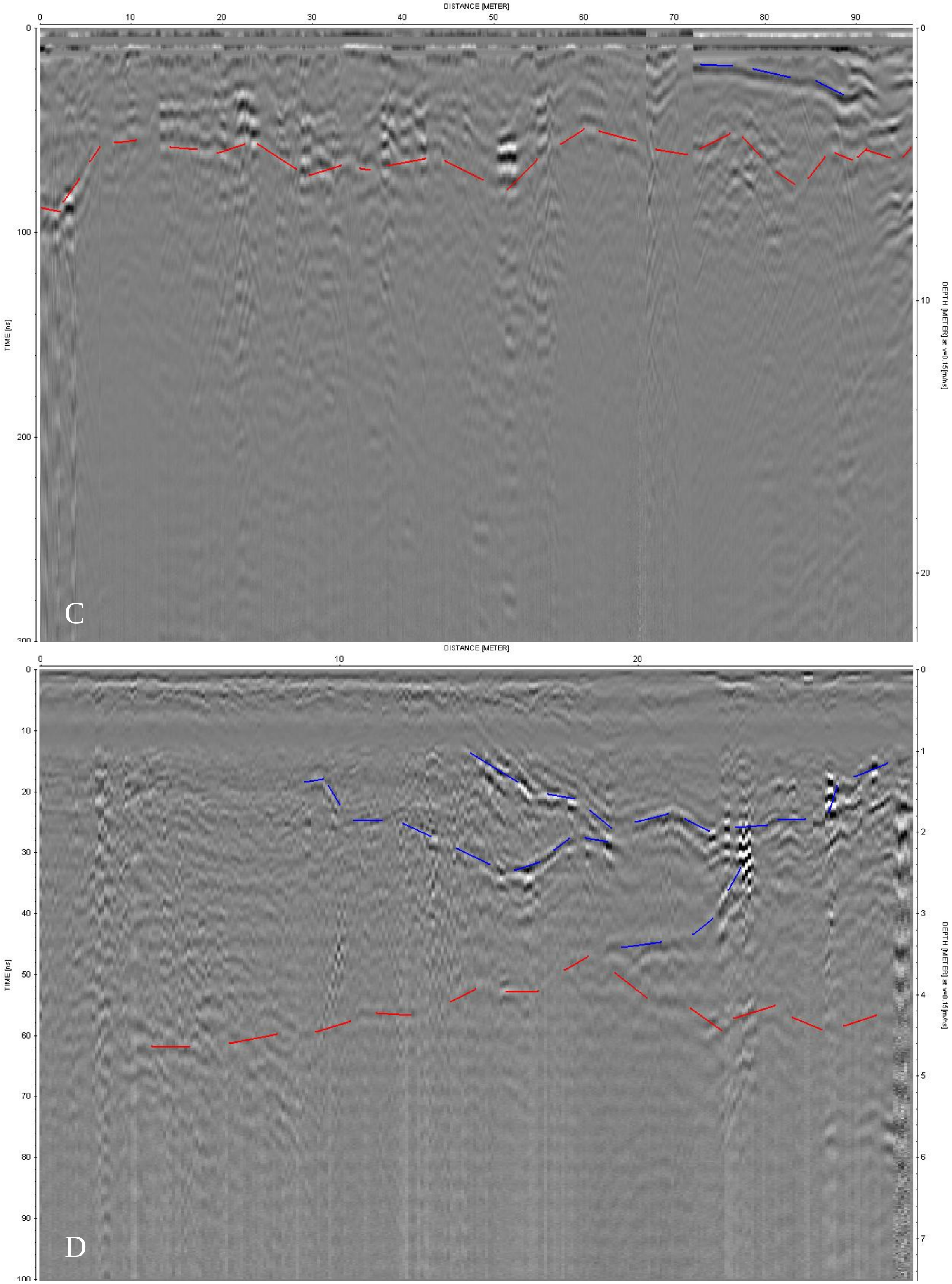

Figure 7. Ground Penetrating Radar measurement lines in Ruovesi I wood preservation plant. A) Line 1 measured with a 100 MHz antenna, B) Line 2 measured with a 100 MHz antenna, C) Line 3 measured with a 100 MHz antenna, and D) Line 4 measured with a 500 MHz antenna.

4.3.2. Ruovesi II

The ground at an old wood preservation plant in Ruovesi commune that closed in 1968 was first studied in the early 1990's. The soil of the wood preservation plant was situated on a 1st class groundwater area and close to a groundwater intake plant and was confirmed to be contaminated with high concentrations of arsenic, copper and chromium. The contaminated area was relatively small, though heavy metal concentrations were elevated. Arsenic concentrations ranged from 23 to 6700 mg/kg with a median of 320 mg/kg (average 1474 mg/kg). Soil remediation was conducted in two phases in 2001 and 2004. In the first phase of the remediation, highly contaminated soils (332 tons) were excavated and removed to a hazardous waste disposal plant, whereas mildly contaminated soils (80 m^3) were transported to an adjacent landfill. In 2004, the rest of the contaminated land (840 m^3) was removed and encapsulated in a hazardous waste capsule in the same landfill area. A small area of about 2m x 10m was left without remediation because of the risk of breaking underlying power lines. In this area, the highest arsenic concentration was up to 160 mg/kg.

In 2002, PREC and SYKE performed further sampling to assess ecotoxicity and leachability of arsenic, chromium and copper from the soil samples at Ruovesi II area. Samples were collected from study pits using a spade for a composite sample from a depth of 0.05–0.5 m. The two samples selected for ecotoxcity and leaching tests were sandy soils. Sample A was collected from the 'hot-spot' area, which was highly contaminated with chromium, copper, arsenic and zinc, and sample B from the less contaminated spot of the area. Total concentrations of arsenic, copper and chromium and zinc in the soil samples were analyzed from nitric acid extracts with ICP-MS. A Dutch percolation test (NEN 7343) was used to study the percolation of metals and arsenic of wood preservative agents from the contaminated soil samples into water under laboratory conditions. The soil samples were sieved to a particle size < 2 mm. Humidity of the soil samples was determined before the pretreated soil sample was weighed and packed to fill up the column. The pH of de-ionised water was adjusted to pH 4 with 1 mol/L nitric acid. Water was then pumped up-stream through the column at a constant flow. Filters were placed into the lower and upper part of the column. Filtered fractions were collected at different liquid to solid –ratios (L/S) 0.1; 0.1; 0.3; 0.5; 1; 3 and 5. In addition to chemical analyses, the aquatic toxicity of the leaching test eluates were determined by water flea (*Daphnia magna)* immobilization, onion (*Allium cepa*) root growth, luminescent bacteria (*Vibrio fischeri*) bioluminescence, and reverse electron transport (RET). The terrestrial toxicity of the soil samples was tested by *Enchytraeus albidus* survival and reproduction assays, and by lettuce seed germination assay. (Vaajasaari *et al*. 2002)

The soil samples collected from this old impregnation plant predicted a constant and relatively low leaching compared to the total metal concentrations in soil. The test represents long term leaching of the elements, as the testing period was 25 days for the sample A containing 12000 mg/kg As and 32 days for the sample B containing 89 mg/kg As. The leached amount of arsenic as a percentage of the total arsenic content was 0.1 and 0.6 % in the samples with total arsenic contents of 89 and 12 000 mg/kg, respectively. (Figure 8, Vaajasaari *et al.* 2002).

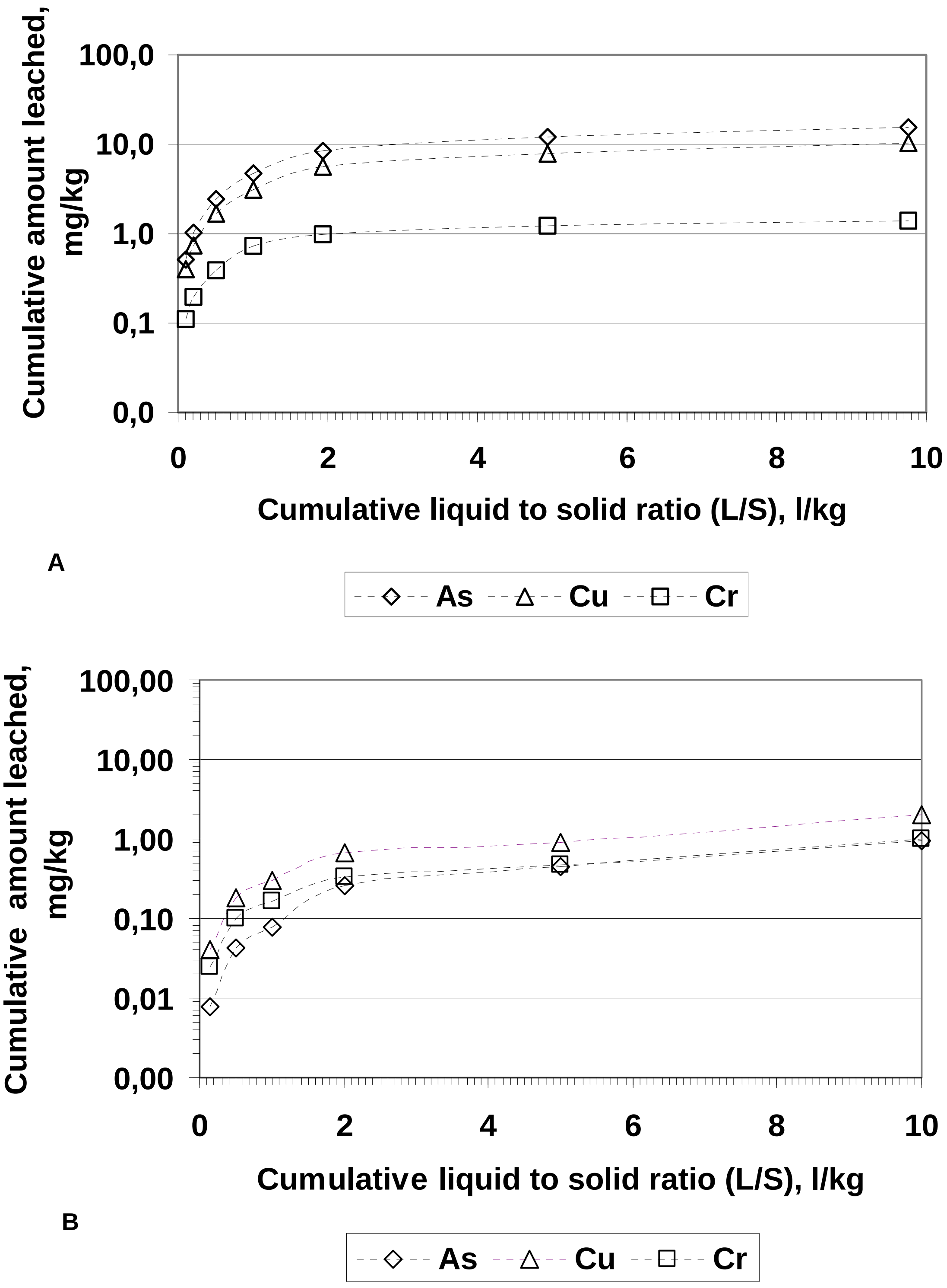

Figure 8. Cumulative leached amount of wood preservative agents from the soil samples collected from an old impregnation plant in Ruovesi II as a function of cumulative liquid to solid -ratio (L/S) of the column test (NEN7343). The results of the soil sample containing 12 000 mg/kg of arsenic are shown in the Figure 8.A, and the results of the soil sample with 89 mg/kg of arsenic in the Figure 8.B. (Vaajasaari *et al.* 2002)

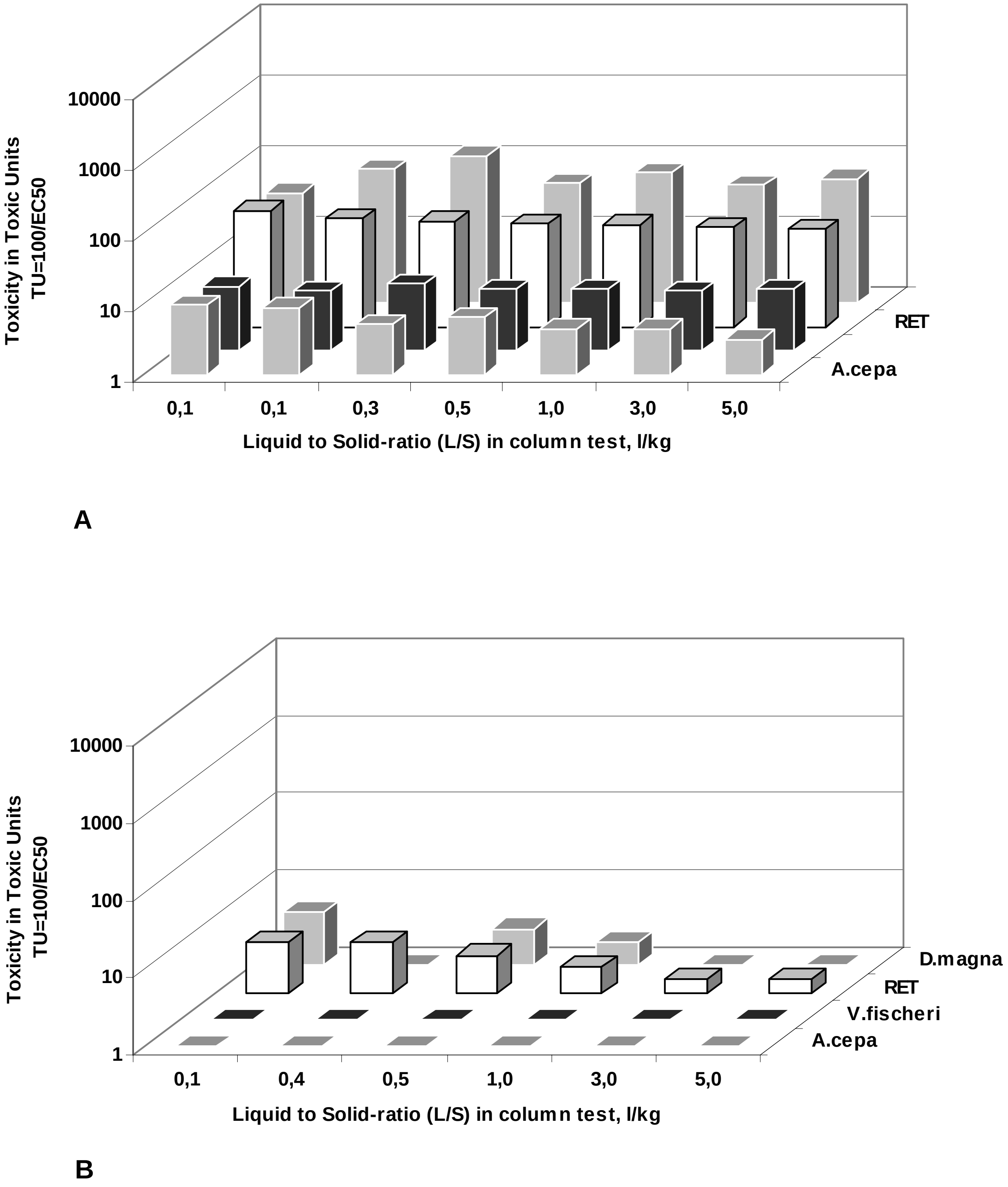

Figure 9. Aquatic toxicity of the leaching test eluates in TUs (100/EC50) as a function of liquid to solid –ratio (L/S) of the column test (NEN7343). The results of the soil sample with an initial arsenic concentration of 12 000 mg/kg are shown in the Figure 9.A, and the results of the soil sample with 89 mg/kg of arsenic is shown in the Figure 9.B. (Vaajasaari *et al.* 2002)

However, the soil samples contaminated by wood preservative agents from the Ruovesi II case study area exhibit harmful, long-term effects on the terrestrial and aquatic environment. According to the ecotoxicity tests, at the high contamination level (As 12000 mg/kg, Cr 7500 mg/kg, Cu 4400 mg/kg, Zn 7500 mg/kg), the soil sample was lethal to *E. albidus* already at a test soil concentration of 5 %, and remained toxic after leaching. In addition, the percolation test eluates of this soil material were clearly toxic to all the aquatic test biota (Figure 9.A). The sample with an arsenic concentration of 89 mg/kg was not toxic in terrestrial tests and only slightly toxic in aquatic environment (Figure 8.B). The germination of lettuce seeds was not strongly inhibited in these soil samples, but the toxic effects could be observed as decreased growth and unhealthy roots. (Vaajasaari *et al*. 2002)

4.3.3. Vilppula

In 2005, an old CCA-treatment plant in Vilppula commune was remediated because according to preliminary characterization of the site done by PREC indicated that the CCA agents heavily contaminated the soil. The plant was closed in 1963 after being active for ten years, and at present the land is privately owned residing on the owners' back yard. The studied land is not located at an important groundwater area, but caused a health risk to the family living in the vicinity. In 2002 and 2003, PREC studied the area to establish the need for soil remediation. According to these studies, arsenic concentrations exceeded the guideline values in several samples, with arsenic concentrations ranging from 1.5 to 730 mg/kg (82 mg/kg As on average). Overall, strongly contaminated ground was limited to the old impregnation area and chemical warehouse, where contaminated soils covered an area of approximately 850 m^2 and, in general, extended to a depth of less than one meter. Water samples from a household used well, nearby gutter and groundwater pipe were analyzed and showed elevated arsenic values in the gutter (250 µg/l) and groundwater (57 µg/l). In the well, arsenic content (11 µg/l) was barely over the guideline value of water for household consumption (10 µg/l). Excavation of the contaminated soils was the proper remediation method. In 2005, a total of 1810 m^3 (2353 tons) of contaminated soils were removed and transported to a hazardous waste disposal site and encapsulated in a disposal capsule.

4.3.4. Virrat

The wood preservation plant in Virrat commune was active from 1956 to 1967 resulting in soil contamination. Arsenic was the main contaminant, but copper and chromium values exceeded the guideline values in many samples as well. The average arsenic content was 219 mg/kg in 39 soil samples from which 24 samples exceeded the upper guideline value for As (50 mg/kg). The contaminated land area covers about 11600 m^2 and in places reaches a depth of two meters. The old CCA-treatment plant is only fifty meters from the residential building. This treatment plant does not pose a risk for important groundwater areas.

Excavation and isolation of the contaminated masses were chosen for as remediation methods, and the land will be remediated in 2006 by a consulting company. The excavated soil masses will be removed to a proper treatment or disposal site or contaminated land masses can be isolated from the clean soils *in situ*.

4.4. Shooting ranges

High concentrations of heavy metals, mainly lead, are measured in the humus layer of shooting ranges. The soil in shooting ranges is affected by the load of widespread gunshots and bullets. Lead (Pb) is the main problem in the shooting ranges, but other harmful elements like antimony (Sb), arsenic (As), copper (Cu), zinc (Zn) and nickel (Ni) burden the environment. The shots for shotguns contain 97 % lead, 1 to 3 percent antimony, 0.1 to 0.5 percent arsenic and lesser amounts of other metals, whereas bullets, used in rifles and pistols, contain 89 % lead, 9 % copper and 1 % of zinc and antimony each, but no arsenic (Naumanen *et al.* 2002). The gunshots spread throughout the shooting area and pile up on the mulch layers, thus exposed to rain and air (Figure 10). The metals are leached, and arsenic as well as antimony, tend to form soluble salt complexes that percolate into the groundwater. Scattered clay pigeons also release PAH-compounds (Figure 10). The areas affected by the shooting residues depend on the type of shooting that is practiced, and can cover many hectares. Rifle and pistol shooting aim at a still or moving target, and the bullets accumulate in the banks behind the targets in a relatively small area. In some ranges, the shooting distances and therefore the burdened areas, are up to 300 meters long. Clay pigeon shooting with shotguns requires more space as the gunshots spread over an area of up to 10 hectares. In Figure 11, the schemes of two types of shotgun ranges are illustrated. Clay-pigeons are launched in the air in trap and skeet shooting, which produces a dispersion area covering about 250 meters at an angle of 90° in trap ranges, whereas in skeet ranges gunshots accumulate in a radius of 200 meters, at an angle of 150°.

In the Pirkanmaa region, there are more than 110 shooting ranges with approximately 72 active sites (Mustajoki 2004, MATTI database). There are 47 active shooting ranges with shotgun practice. Most of the ranges are privately owned. Almost half of all shooting ranges in the Pirkanmaa region have practiced shotguns leading to the risk of lead contamination while arsenic poses a minor risk. A total of 29 ranges are situated in 1st class groundwater areas, and 19 of these ranges are still actively used (Figure 12).

Figure 10. Scattered gunshots and pieces of clay-pigeons on the humus layer in a shooting range (Kati Vaajasaari).

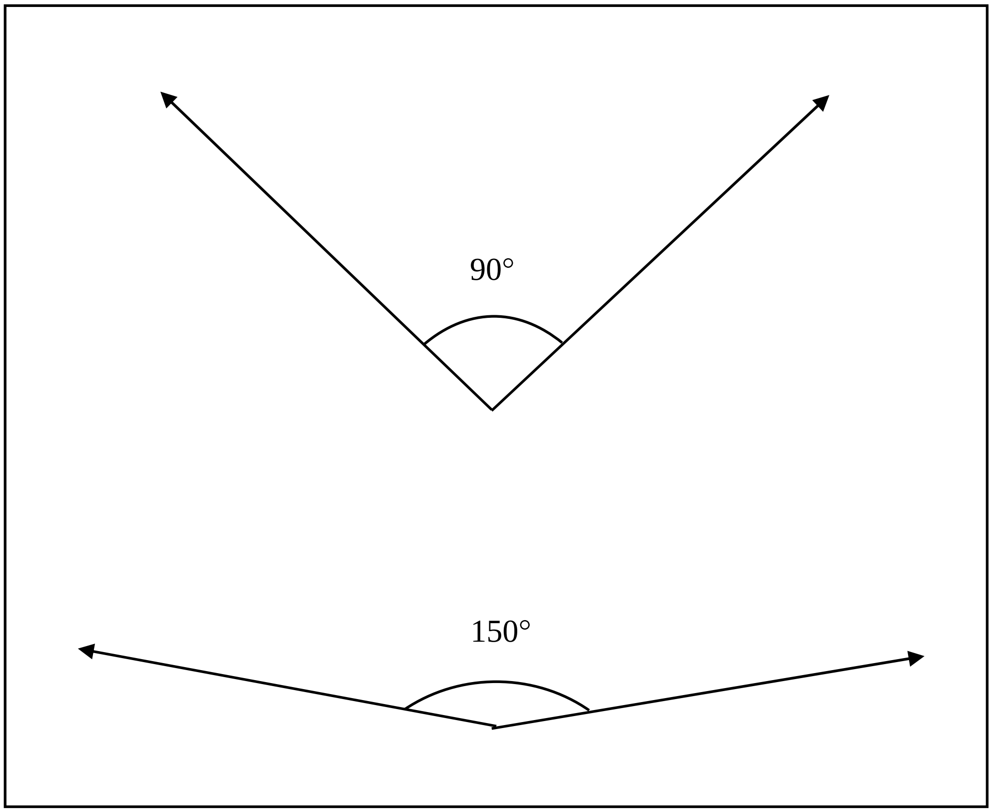

Figure 11. Dispersion of gunshots in trap and skeet ranges. The gunshots scatter in a radius of 200 to 250 meters, and at an angle of approximately 90° in trap ranges and 150° in skeet ranges. (Modified from Naumanen *et al.* 2002)

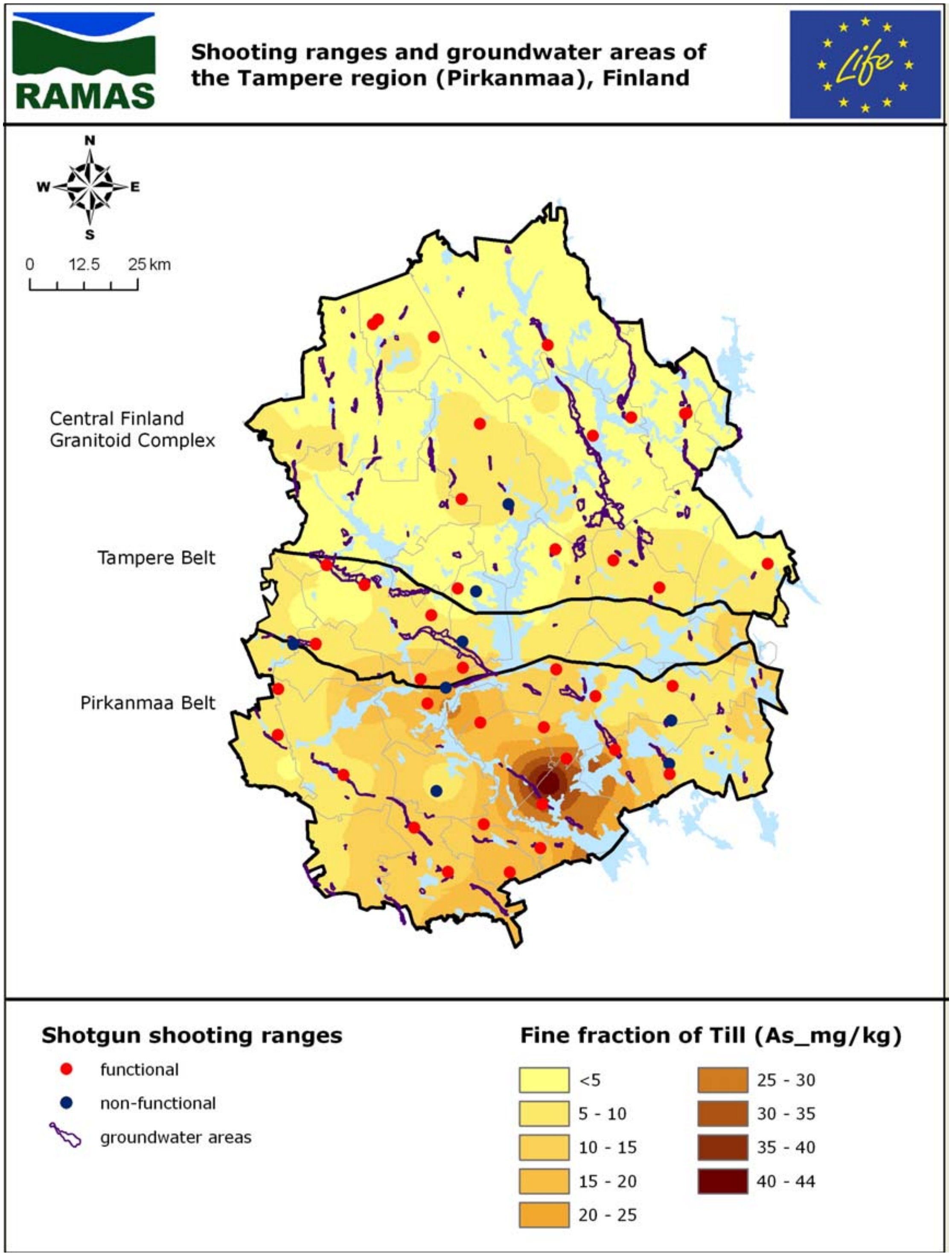

Figure 12. A map showing arsenic concentration in glacial till in the Pirkanmaa region, with the location of shotgun shooting ranges (Anu Peltonen, PREC).

4.4.1. Case studies of six shooting ranges in the Pirkanmaa region

In 2004, Pirkanmaa Regional Environment Centre (PREC) completed a study regarding soil contamination at six shooting ranges in the Pirkanmaa region. In all of the studied areas, both shotgun and rifle shooting were practiced over approximately 30 years and two ranges were located on mires with another four on coniferous forests where the humus layer is thick. Depending on the amount of shotgun firings in the studied shooting ranges, about 60 to 600 kg (on average 310 kg) of lead is spread on the ground every year, and on average one kilogram of arsenic is accumulated annually at each range. (Mustajoki 2004)

PREC studied the extent of contaminated soils by analyzing lead and other heavy metal concentrations in systematic sampling lines with an INNOV-X field analyzer. Samples were collected from the humus layer and from the sandy layer just below humus layer in shotgun ranges to analyze heavy metal contents, and their leachability and ecotoxicity in laboratory. Lead is the main cause of soil contamination. The lower guideline value for lead contamination in soil is 200 mg/kg and upper guideline value is 750 mg/kg. The target value is between 0.1 to 20 mg/kg depending on the natural background concentration. The concentrations of lead in the humus layer from mineral soils ranges from less than 10 mg/kg to up to 14 000 mg/kg, whereas in the deeper sandy layer lead, contents were less than 60 mg/kg indicating that lead is effectively absorbed in the humus layer of the topsoil. In the mires, lead appears in higher concentrations in the topsoil, and at the depth of 0.4 meters high concentrations (up to 800 mg/kg) were also measured. The absorption of lead in humus layer in mires is weaker than in the mineral soils. This study shows also that in the depth of 0.1-0.2 meters arsenic content ranges from 1.1 to 5.8 mg/kg in mineral soils and from 1.1 to 28 mg/kg in mires. In mineral soils, arsenic did not show concentrations exceeding 10 mg/kg, whereas in mires only one sample exceeded the lower guideline value. However, Naumanen *et al.* (2002) measured higher concentrations of arsenic from deeper mineral soils, and found up to 200 mg/kg As (14 mg/kg on average) in the Anttonen shooting range in eastern Finland. The water samples from nearby rivers and ponds showed elevated lead and antimony contents, but arsenic appeared in concentrations lower than the limit value for drinking water (10 µg/l). In one mire studied by PREC, lead and arsenic concentrations measured from surface waters showed that lead (4.2 - 221 µg/l) and arsenic (1.2 - 4.1 µg/l) were leached to the aquatic environment from the shooting range activity. The study from the Pirkanmaa region can be considered preliminary research and thorough assessment of arsenic and heavy metal contamination requires further investigation and sampling from deeper mineral soils and from surface waters.

4.4.2. Environmental permit for shooting ranges – an example from Nokia

Since 2002, shooting ranges must apply for an environmental permit. At present, there are three shooting ranges monitored by environmental permits in the Pirkanmaa region. The first permit in accordance with the environmental legislation was given to a shooting range in Nokia commune in the Pirkanmaa region. According to this environmental permit, there are limitations on shotgun shooting for example on holidays. In the construction of new shooting ranges, noise barriers are to be considered or silencers ought to be used if possible. As well, the topsoil of the new shotgun ranges needs to be covered to avoid soil and groundwater contamination. In Nokia, with the help of a fabric coating, accumulated gunshots can be removed. On the other hand, in rifle ranges the environmental permit requires that the banks must be made up of material that can be sieved or otherwise cleaned to sort out the bullets. The drainage of rainwater and melt water in the banks must also be minimized.

5. MINING INDUSTRY

Old sulfide mines are a risk to surrounding surface waters and groundwater because of the acid mine drainage from mining waste consisting of wall rock, tailings and sludge. Acid mine drainage is formed by a series of complex geochemical and microbial reactions that occur when water comes in contact with sulfides. The open pits and the tailings contain sulfides and arsenides formed in reducing conditions that tend to weather in contact with air and oxidizing surface water, releasing heavy metals, arsenic and sulfates to the drainage waters. The resulting water is usually high in acidity and dissolves more metals, leading to elevated concentrations of heavy metals and arsenic in the nearby rivers and lakes. Acidic waters also leach silicate minerals in the tailings, releasing silica, potassium, sodium and calcium from feldspars and plagioclase, as well as magnesium, iron and manganese from mafic minerals like amfibols. The metals stay dissolved in solution until the pH rises to a level where precipitation occurs. Commonly, the iron hydrolyzes and forms goethite, schwertmannite or jarosite depending on the pH. This process further increases the acidity of the drainage water. Some heavy metals, especially arsenic, are retained in these iron hydroxides and their concentrations decrease in drainage waters. Furthermore, pH increases and arsenic content decreases by mixing of surface water.

Many sulfides, *e.g.* pyrite, chalcopyrite, pyrrhotite, can contain several weight percentage of As in their structure. The arsenic content in arsenides (nickeline, maucherite) and sulfarsenides (arsenopyrite, glaucodite, cobaltite, gersdorffite) is considerable higher than in sulfides, and is therefore abundant in the exploited ore assemblages, resulting in high risk of As contamination.

Backman *et al.* (2006, report of TASK1) divided the Pirkanmaa region into three distinctive geological belts, which are from, north to south, the Central Finland Granitoid Complex (CFGC), the Tampere Belt (TB) and Pirkanmaa Belt (PB). The Ni-Cu and gold mines are situated in the Tampere Belt and Pirkanmaa Belt comprising mainly metasediments, metavulcanites and granitoids. Mica schist, island arc type metavulcanites characterize the TB. Together with granitoids mica schist and mica gneiss are the main rock types in the PB. In Figure 13, natural occurrences of arsenic in the glacial tills and five mines are shown.

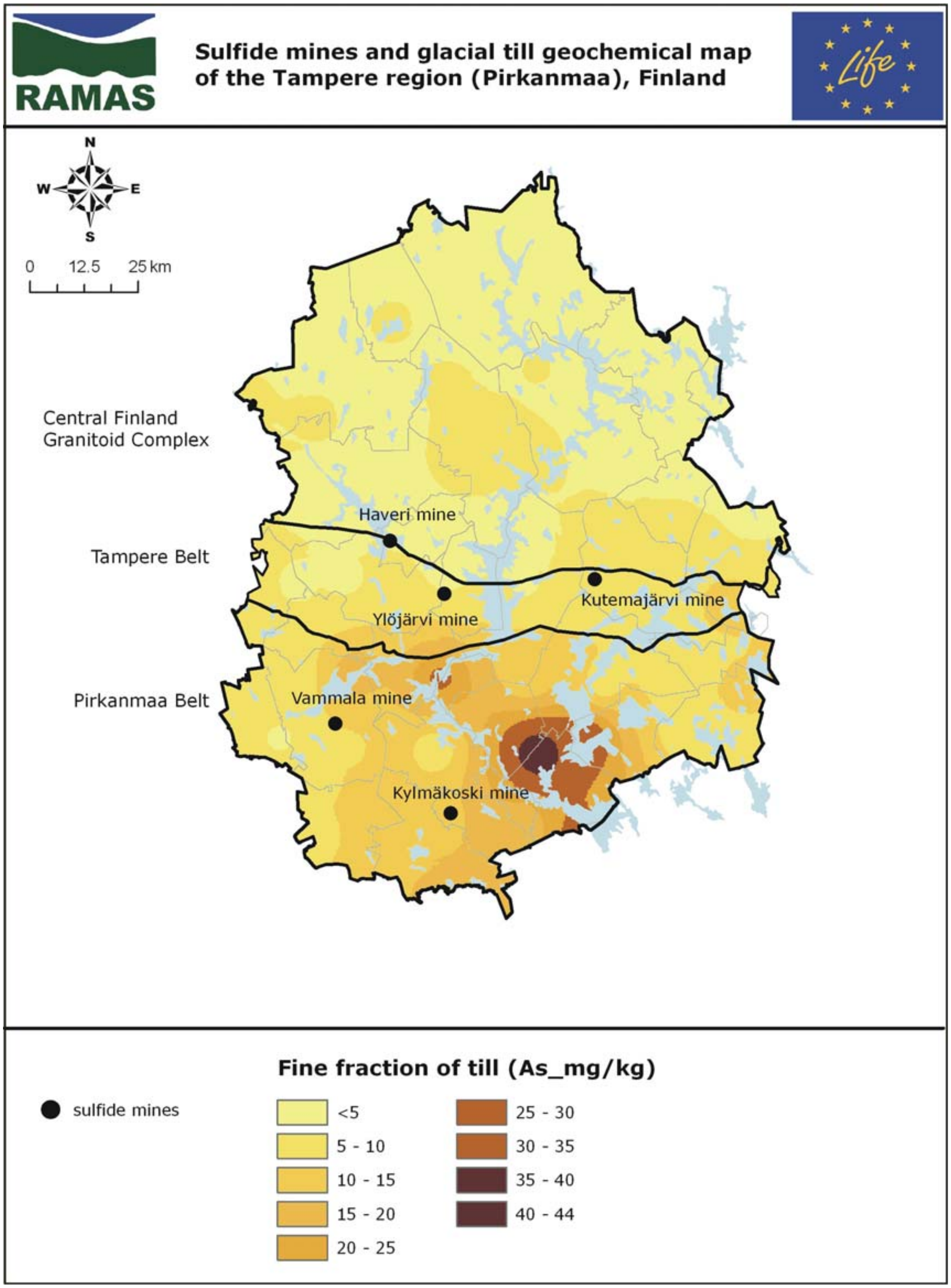

Figure 13. A map showing arsenic concentration in glacial till in the Pirkanmaa region, with the location of sulfide mines (Anu Peltonen, PREC)

5.1. The Haveri mine

The Haveri mine is located in Viljakkala commune, roughly 35 kilometers north-west of Tampere, between two lakes: Lake Kyrösjärvi to the west and Lake Kirkkojärvi to the east of Haveri. The Haveri Au-Cu deposit is situated within the Haveri formation in the western part of the Tampere Schist Belt and consists of tholeiitic basic metalavas, metalava breccia, metatuff and metatuffite, (Mäkelä 1980). The metalavas occasionally present flow and pillow structures; some pillow lavas are brecciated. Chemical sediments, such as limestone and chert, appear in Haveri formation. Other main rock types described in the surrounding area are calc-alkaline intermediate metavolcanic rocks, graywacke-slate and mica schist and granite.

5.1.1. Ore body and ore minerals

The proper ore body, consisting of from 20 to 80 % sulfides, appears together with metalava breccia and metatuff. Sulfide minerals comprise mainly pyrrhotite, chalcopyrite and minor pyrite. Sulfarsenides, cobaltite, glaucodote, gersdorffite and arsenopyrite, are found as accessory minerals. Native gold exhibits small grains along grain boundaries of the sulfarsenides, and fine-grained, nebulous disseminations in cobaltite. Gold is mainly concentrated in metalavas and metalava breccias. In addition, sphalerite, molybdenite, scheelite, tellurobismutite and hessite are found (Paarma 1947). The only oxide minerals found are magnetite and ilmenite. Sulfarsenides are the main source of arsenic, but other sulfides can also contain arsenic in the mineral structure.

5.1.2. History of the mine

The Haveri iron deposit was found in the 18th century and iron was exploited in a small-scale open-pit mine until the mid 19th century. Oy Vuoksenniska Ab discovered the Haveri Au-Cu deposit in 1935, which led to a mine that was active from 1942 to 1961. Gold was extracted by cyanide process and copper by flotation. A total of 1.5 million tons of ore containing 2.85 g/t Au and 0.39 % Cu was mined from an open pit and underground (Puustinen 2003). The tailings were piled up in the vicinity of Lake Kirkkojärvi in an area of about 19 ha.

5.1.3. Present situation

The old mine area, owned by Viljakkala commune, is to be converted into a museum and recreation area. One consulting company performed a risk assessment of contaminated soils in the mine area, excluding the open pit and tailings area in 2004. The heavy metal and cyanide contents and their solubility were investigated from the topsoil in the areas covering the enrichment plant, cyanide processing plant, storage and other buildings. The results indicated that the topsoil in the mine area contains concentrations of cadmium, vanadium and mercury exceeding the lower guideline values, whereas arsenic, copper, zinc and lead showed concentrations higher than the upper guideline values. According to the risk assessment, some remediation is required and the groundwater pipes should be put in the ground for further studies on groundwater movements and quality.

Glenmore Highlands, a Canadian mining exploration and development company, acquired Haveri in 1996, and studied the area in detail performing drilling and gathering old mining data. In 1997, they planned to dewater the open pit and the mining shafts to allow for a detailed examination of the geological controls on the mineralization that sustained the old mine. Before the dewatering, water quality was shown to be good, except for high concentrations of aluminum and iron. Other heavy metals were not detected in excess, and the pH was 3.6. Water was treated with liming to precipitate aluminum and oxidized for the precipitation of iron. The water was further clarified in a settling basin before conducting it to the Lake Kyrösjärvi. The analyses of the iron precipitates showed that copper (91-760 mg/kg), zinc (230-1100 mg/kg) and nickel (440-1300 mg/kg) precipitated along with iron and aluminum, but arsenic was present in very small concentrations (1.9-3.0 mg/kg) (Unpublished reports from archives of PREC). The water conducted to the Lake Kyrösjärvi was not analyzed.

Another Canadian mining exploration company, Northern Lion, which is continuing vast exploration studies, now owns Haveri. According to Northern Lion, the Haveri deposit is expected to have considerable gold and copper resources grading 3.5 g/t gold and 0.50 % copper. The inferred gold resource is approximated to 742,682 ounces.

To prevent dusting, the tailings area is now partly covered by exported land masses and asphalt. Random users practiced motorcross on top of the tailing area, which caused dusting of the finest particles. RAMAS will take some dust samples from the area in summer 2006 which will be reported in the final report of RAMAS. Furthermore, lake and stream sediment samples were taken from Kirkkojärvi in spring 2006 as well. The results of the sediment samples will be discussed in a separate report later this year.

Water samples from the Haveri mine area, taken in November 2005 by RAMAS, will be presented in this study. Three water samples were collected from a stream deriving from the tailings to Lake Kirkkojärvi, one from Lake Kirkkojärvi close to the shoreline and one from an impound basin that is connected with the lake. In May 2006, RAMAS took complementary water samples to assess the possible seasonal changes. Samples were taken from the same sampling points as in November 2005, and an additional three samples were taken from a stream on the southern edge of the tailings area, from a ground water intake plant and from the Haveri open pit. RAMAS also conducted a drill core sampling in the Haveri tailings and the results will be reported together with the water sample results in the final report of RAMAS.

5.1.4. Results

The analyses with ICP-MS showed that arsenic concentrations ranged from 0.50 to 3.20 μg/l (average 1.50 μg/l As) in the five water samples taken from the surroundings of the Haveri tailings. However, other elements show significantly higher concentrations, *e.g.* copper ranged from 7.06 to 2430 μg/l; cobalt from 0.62 to 2180 μg/l; manganese from 18.3 to 5540 μg/l; and iron from 0.131 to 299 mg/l. The higher concentrations correspond to the stream originating from the tailings, whereas lower concentrations represent the values in the lake.

5.2. The Ylöjärvi mine

The Ylöjärvi copper-tungsten deposit in the western end of Tampere Schist Belt is hosted by tourmaline breccia. The surrounding rocks are mainly tuffites with porfyrite intercalations. The mine is close to Lake Parosjärvi and Lake Saarijärvi. Lake Parosjärvi is connected with Lake Näsijärvi by a river (
Figure 16).

5.2.1. Ore type and ore minerals

Economically significant sulfide grades are encountered in the northeastern section of the tourmaline breccia where the ore bodies form four subparallel and vertical zones (Himmi *et al.* 1979). The ore is characterized by two types of mineral assemblages: the arsenopyrite assemblage appearing in the chloritized parts of the wall rocks and breccia fragments, and the chalcopyrite-arsenopyrite-pyrrhotite association present in the breccia matrix. Other sulfides (pyrite, sphalerite, galena, cubanite, molybdenite) and oxides (magnetite, ilmenite, cassiterite) are found in minor amounts together with the main ore minerals. Even though, randomly distributed scheelite exhibited modest concentrations it became an important side product. Native bismuth, silver and gold were found in minor amounts as well.

5.2.2. History of the mine

Outokumpu Oy claimed the Ylöjärvi area in 1940 and studied the deposit. The Ylöjärvi mine was exploited for Cu, W and As between 1943-1966. The exploitation began south of Lake Parosjärvi in an open pit and continued on the east side of the lake in 1945. The mining operations went underground in 1951. A total of 4 million tons of ore was processed to produce 28 322 tons of copper (0.75 %), 894 tons of scheelite enrichment product (containing 47.8% of WO_3), 2112 tons of arsenopyrite concentrate (containing 26.66 % As), 49 502 kg of silver (13.68 %) and 270 kg of gold (0.04 %) (Puustinen 2003). The tailings area, of about 4 ha, was first situated at the southern end of the Lake Parosjärvi, whereas the second waste area (17 ha) opened in 1952 further south in a marsh. The lake was used as a settling pool. Part of the smaller waste area, the open pit and the underground galleries were covered under the water masses of Lake Parosjärvi after the mine was closed, leaving a lot of material containing arsenic, heavy metals and sulfides in the bottom of the lake.

Figure 14. The tailings of Ylöjärvi mine (Kati Vaajasaari).

Figure 15. Very little vegetation grows in the tailings of Ylöjärvi mine. Water horsetail, *Equisetum fluviatile,* is shown in this figure (Kati Vaajasaari).

5.2.3. Present situation

The mining area was sold to the Finnish government after the ore was exhausted. The land is now used as the Technical Research Center of the Finnish Defence Forces. Since 1975, local consulting companies have carried out surface water monitoring of the Lake Parosjärvi and nearby streams and rivers, and the monitoring continues to the present day. The monitoring is done according to environmental permits under the supervision of the Pirkanmaa Regional Environment Centre (PREC). Arsenic content is measured from six stream and river samples and from one lake water sample showing elevated concentrations of arsenic (Figure 16).

In 2002, the Geological Survey of Finland (GTK) and PREC studied the state of the old Ylöjärvi mine area. Geophysical measurements and water, iron precipitate and peat sampling were performed. According to this study, acid mine drainage spills in all directions from the southern waste area, and from the spill points water flows to nearby rivers and to a peat bog causing high concentrations of arsenic and heavy metals in upper layers of the peat where iron oxide is deposited (Carlson *et al.* 2002). The formed iron precipitates retain arsenic and some heavy metals, diminishing their concentrations in rivers. However, in the stream leading from the tailings area to Lake Parosjärvi iron does not oxidize that effectively and arsenic ends up in the lake (150 µg/l As in the stream water). According to Carlson *et al.* (2002), about 1.5 kilometers downstream in the Stream Parosjärven Oja high concentrations of arsenic were measured (29 µg/l). According to the results of surface water monitoring supervised by PREC, arsenic concentrations in the Stream Parostenjärven Oja have varied from 1 to 130 µg/l (63 µg/l As on average).

RAMAS is developing an arsenic transport model in surface waters in Ylöjärvi mine area, which will be discussed in detail in a separate report released in 2006. The surface water monitoring according to environmental permits provides long-term data from 1977, which now comprises around 600 arsenic analyses along the whole length of the transport route from Lake Parosjärvi to Lake Näsijärvi. To demonstrate the dynamic changes in arsenic transport, RAMAS collected water samples monthly from close to the annual monitoring points from March to December in 2005. Many other elements were analyzed from these water samples as well. The complementary samples were taken from the Lake Parosjärvi (sampling point 1), the Parosjärven Oja (2 and 3) and Vähä-Vahantajärven Oja streams (4 and 5) and Lake Näsijärvi (6) (Figure 16 and Figure 17). The aim of the arsenic transport model is to develop an empirical model using monitored data and to take into account the discharge of small rivers and the sub-catchments of the Vahantajoki river basin. However, in this report only statistical results of the sampling performed in 2005 will be reviewed.

In March 2005, RAMAS collected lake sediment and stream sediment samples from the same watercourse as the water samples to analyze the arsenic content in the sediment load (Figure 16). Stream surface sediment samples were collected from six locations extending from the foot of the Lake Parosjärvi dam through Lake Vähä-Vahantajärvi to Lake Näsijärvi. In addition to these surface sediment samples, sediment cores were analyzed in more detail from three locations: from the wetland below Lake Parosjärvi dam; from Lake Vähä-Vahantajärvi; and from Lake Näsijärvi. Core samples can depict temporal changes and recent trends in arsenic transport from the mine area. The samples were extracted with a microwave-assisted HNO_3 leach and analyzed for arsenic and other elements using ICP-AES and ICP-MS. In addition, the core samples from Lake Vähä-Vahantajärvi were analyzed for two phosphorus fractions (NaOH-leach and HCl-leach). The latter analyses were performed to obtain information on nutrients because the aim was to try to separate the possible ecological effects of arsenic transported to the lake from the effects of nutrient enrichment. To achieve this aim, the core levels sampled for chemical analyses were also analyzed for sediment diatom (Bacillariophyceae) assemblages.

In September 2005, five composite samples from the southern tailings area of the Ylöjärvi mine were collected from the depth of 0.05-0.3 m to study leaching and ecotoxicity of arsenic and heavy metals from the mine tailings (Figure 14 and Figure 15). Arsenic and heavy metal concentrations were first measured with X-ray fluorescence field analyzing instrument (INNOV-X), and then extracted with nitric acid by microwave-assisted digestion and analyzed using ICP-MS and ICP-OES techniques. The leaching properties of arsenic and other contaminants were studied from three selected samples using a two-stage batch leaching test (EN 12457-3). Ecotoxicity of these samples was measured from the solid and aquatic phases.

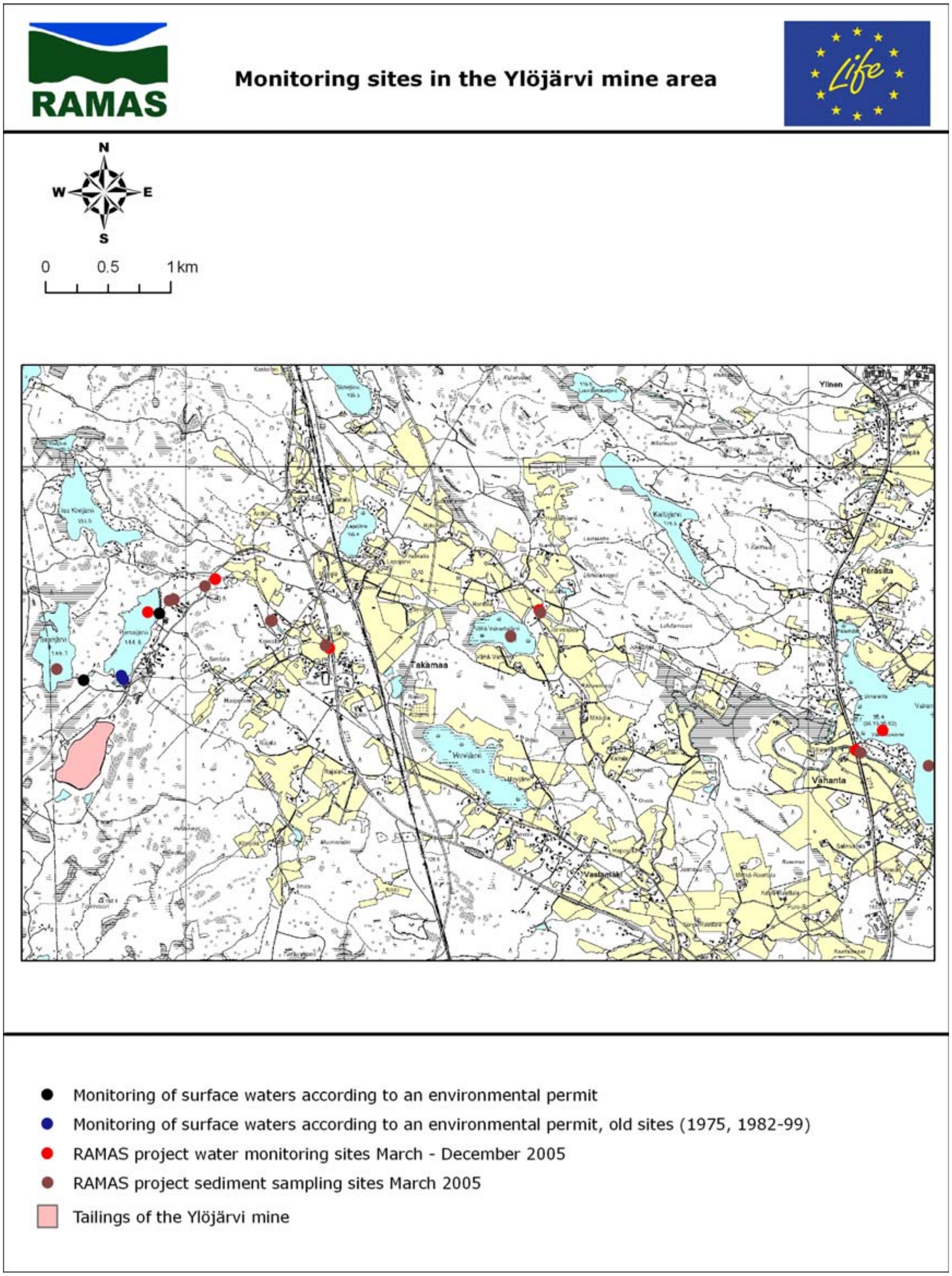

Figure 16. RAMAS sampling points at the Ylöjärvi mine area (Anu Peltonen, PREC).

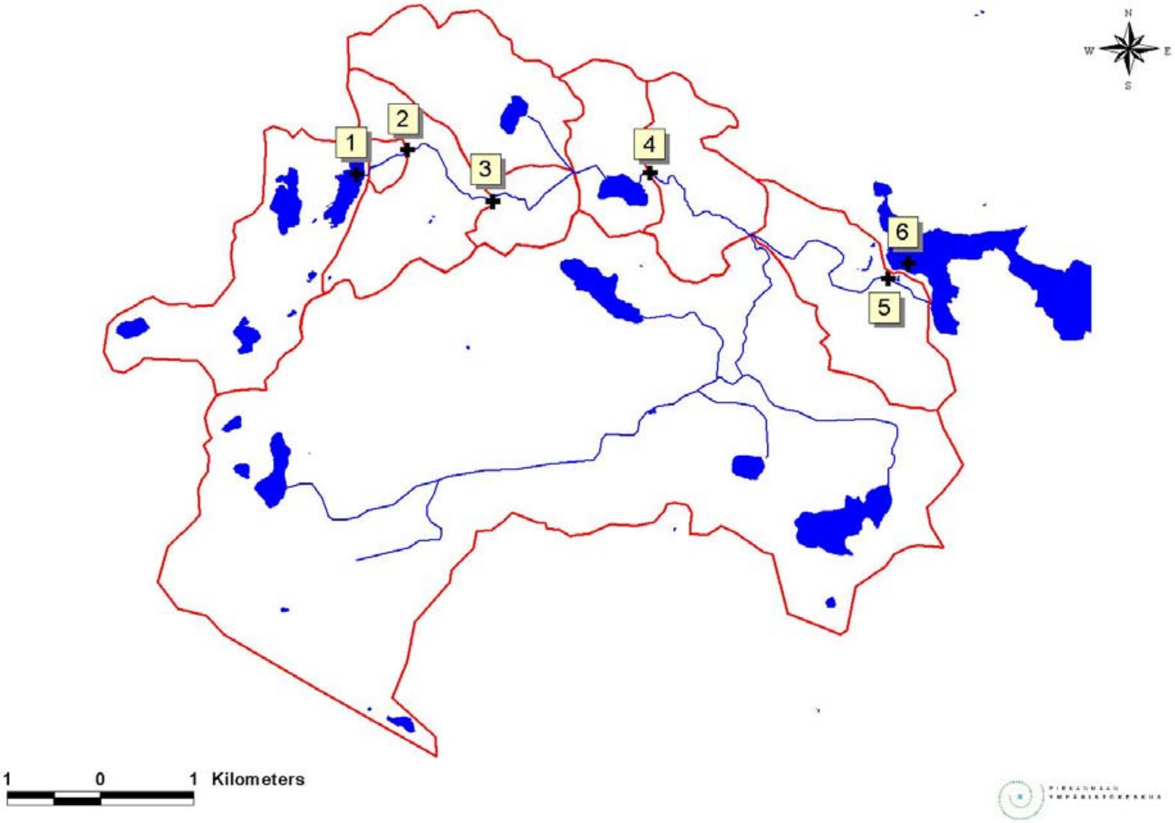

Figure 17. The RAMAS surface water sampling points and the sub-catchments of River Vahantajoki (Ämir Bilaletdin, PREC).

5.2.4. Results

According to the surface water sampling, the total arsenic values progressively decreased from the Lake Parosjärvi to the Lake Näsijärvi which is considered logical. The average arsenic concentrations in the different sampling points were 99.6 μg/l in the sampling point 1; 97.1 μg/l in sampling point 2; 75.6 μg/l in sampling point 3; 18.2 μg/l in sampling point 4; and 6.0 μg/l in the sampling point 5. The main explanation for the decreasing values is dilution along the stream course. Total arsenic concentrations are shown in the Figure 18, and concentrations of As, Cu and Fe as well as pH values are shown in Table 3. Filtered arsenic analyses were also made.

Dilution, sedimentation and chemical processes are presumable processes regards to arsenic transport. The general form of the model is an advection-dispersion model. In Figure 19, the advection-dispersion model has been used to simulate the total arsenic concentration in different sampling points in 2005. The starting point in developing the arsenic loss model is to assume that the loss obeys first order kinetics with a constant reaction rate coefficient. The discharge values of small rivers in the study site can be calculated using the VESISTÖMALLI runoff model developed by the Finnish Environment Institute. Before doing so, the sub-catchments of the Vahantajoki river basin are specified using a Digital Elevation Map. The simulation will also be done separately for particle bounded arsenic and soluble arsenic to possibly consider different processes in the simulation.

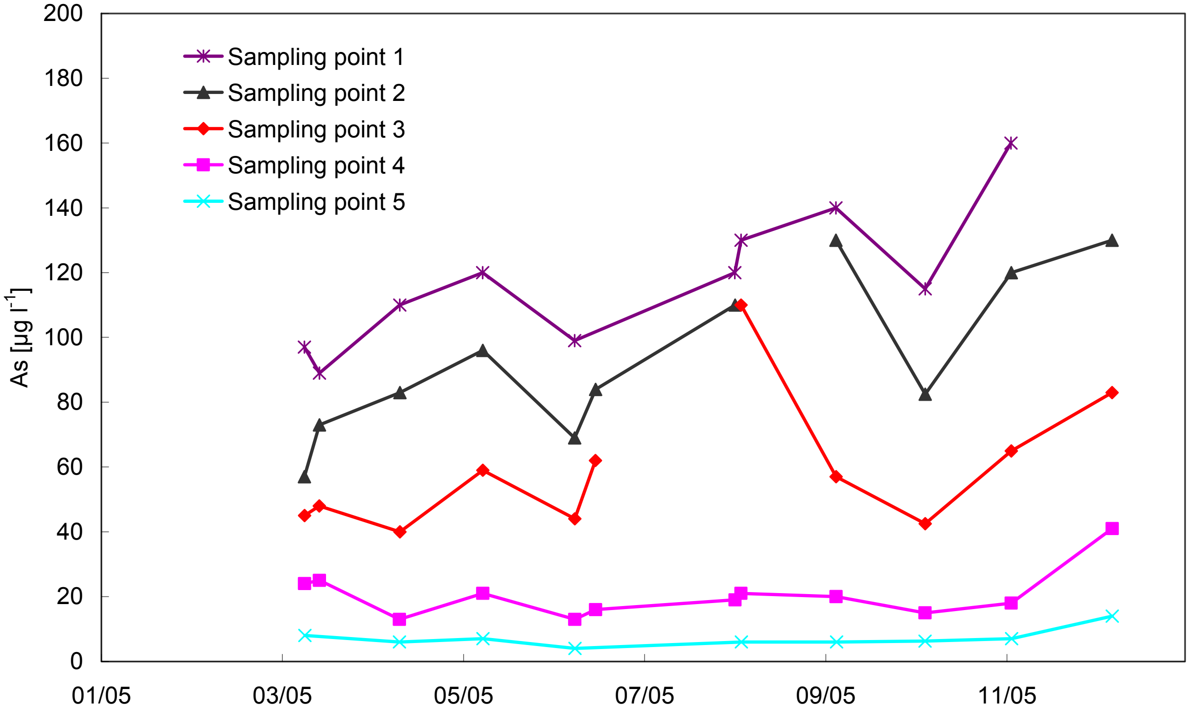

Figure 18. The total arsenic values in different surface water sampling points in the Ylöjärvi mine area in 2005.

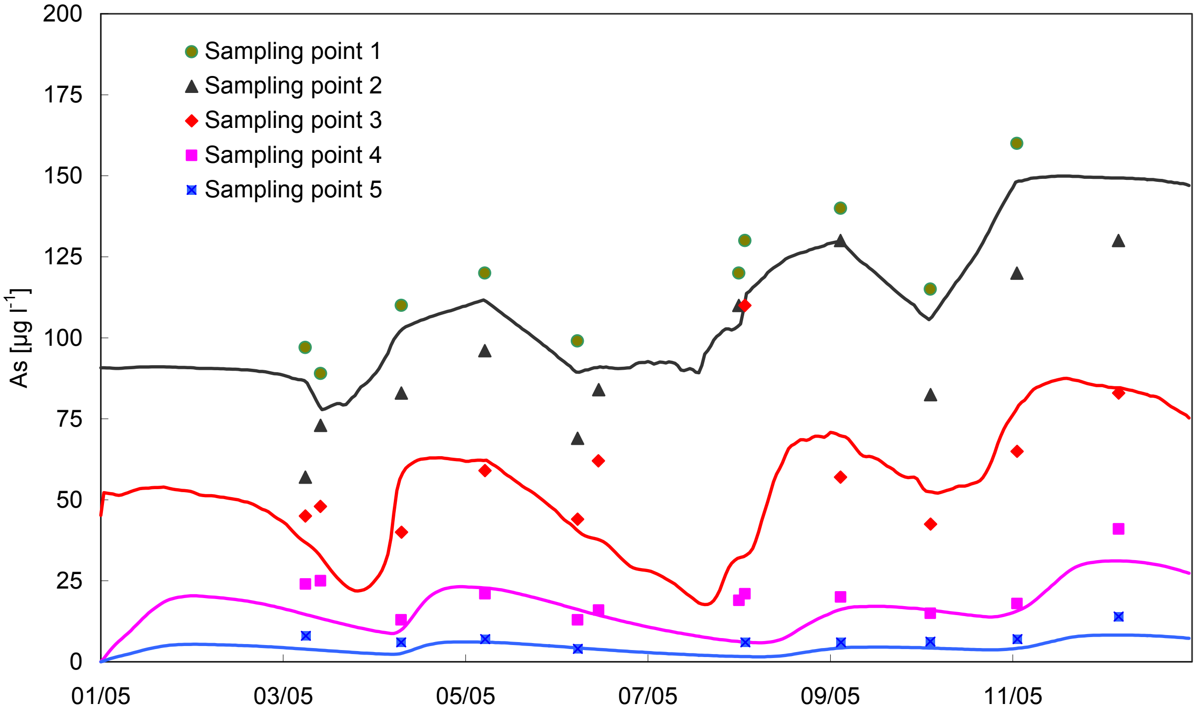

Figure 19. The simulation results of total arsenic concentration in different surface water sampling points in the Ylöjärvi mine area using an advection-dispersion model and first order kinetics.

Table 3. Some main analyses of the RAMAS surface water sampling points in 2005. AAG = Atomic adsorption spectroscopy (graphite furnace), F = filtered sample with 0.45 μm membrane filter.

Sampling point 1

Date	As AAG μg/l	As F;AAG μg/l	Cu μg/l	Fe μg/l	pH
10.3.2005	97	78		1000	5.4
15.3.2005	89		37	920	5.4
11.4.2005	110	98		920	5.5
9.5.2005	120	50		1100	5.5
9.6.2005	99	44		820	5.7
2.8.2005	120		73	550	5.8
4.8.2005	130	79		600	5.8
5.9.2005	140	69		630	5.9
5.10.2005	110			720	5.8
3.11.2005	160			930	5.9

Sampling point 2

Date	As AAG μg/l	As F;AAG μg/l	Cu μg/l	Fe μg/l	pH
10.3.2005	57	39		1500	5.7
15.3.2005	73		32	1200	5.2
11.4.2005	83	52		1000	5.9
9.5.2005	96	52		990	6.0
9.6.2005	69	30		720	6.1
16.6.2005	84		75	700	5.6
2.8.2005	110		74	520	5.8
4.8.2005	380	170		4100	6.4
5.9.2005	130	45		1500	6.2
5.10.2005	86			880	6.2
3.11.2005	120			990	6.2
7.12.2005	130	39		1000	5.9

Sampling point 3

Date	As AAG μg/l	As F;AAG μg/l	Cu μg/l	Fe μg/l	pH
10.3.2005	45	29		2000	6.3
15.3.2005	48		39	1200	5.8
11.4.2005	40	24		3700	6.4
9.5.2005	59	29		1300	6.6
9.6.2005	44	20		920	6.9
16.6.2005	62		690	660	6.0
2.8.2005	560		47	7300	6.5
4.8.2005	110	59		1800	7.1
5.9.2005	57	22		980	6.8
5.10.2005	45			900	6.8
3.11.2005	65			980	6.6
7.12.2005	83	36		1100	6.4

Sampling point 4

Date	As AAG μg/l	As F;AAG μg/l	Cu μg/l	Fe μg/l	pH
10.3.2005	24	16		1100	6.3
15.3.2005	25		16	1200	6.5
11.4.2005	13	6		2200	6.5
9.5.2005	21	14		650	7.0
9.6.2005	13	11		220	7.0
16.6.2005	16		10	270	7.1
2.8.2005	19		6	230	7.0
4.8.2005	21	18		460	7.0
5.9.2005	20	15		270	6.8
5.10.2005	14			320	6.8
3.11.2005	18			440	7.0
7.12.2005	41	21		750	6.6

Sampling point 5

Date	As AAG μg/l	As F;AAG μg/l	Cu μg/l	Fe μg/l	pH
10.3.2005	8	5		1300	6.6
11.4.2005	6	1.5		3600	6.6
9.5.2005	7	5		1300	6.9
9.6.2005	4	3		720	7.0
4.8.2005	6	6		580	6.9
5.9.2005	6	4		520	6.9
5.10.2005	7			660	6.8
3.11.2005	7			670	6.9
7.12.2005	14	7		890	6.7

Stream surface sediment and core sample arsenic concentrations give indications of As transport and retention in the Vahantajoki River. All core samples from the overgrown pond located immediately below the dam at Lake Parosjärvi have high arsenic concentrations (1130 - 4480 mg/kg). The lowermost sample, a clay sample from below the mine-derived sediments at 180-183 cm, had an arsenic concentration of 179 mg/kg whereas the mining-related silts and clays between 178 and 107 cm had concentrations between 1760 and 3690 mg As/kg. In the sandier sediment section, between 107 and 51 cm, concentrations were lower (1130-1590 mg/kg) whereas the uppermost 50 cm of sediment, mostly consisting of macrophyte remains, had arsenic concentrations between 2600 and 4480 mg/kg.

These high concentrations suggest that considerable amounts of arsenic may be retained in this wetland. The lithological and chemical stratigraphies also show that particulate matter rich in arsenic has been released to the Vahantajoki River from the mine area in the past. Arsenic concentrations of stream sediment samples taken downstream from the mine area depend largely on sediment characteristics. Some 300 m downstream from the wetland, at Stream Site 2, a surface sediment sample consisting of clay, silt and organic remains had an arsenic concentration of 110 mg/kg (90 % of Finnish stream sediments between 0.8 and 15 mg/kg). Further downstream, in a pond excavated in the stream (Stream site 3), sediments contained 228 mg/kg (fine-grained, organic-rich top sediment, 0-8 cm) and 128 mg/kg (clay between 8 and 13 cm) of arsenic, demonstrate the effect of organic matter in arsenic retention. At the next sampling location (Stream site 4) 500 m further downstream, clayey surface sediments had an arsenic concentration comparable to the previous clay samples (134 mg/kg).

While the origin and age of the clay samples in the stream are somewhat uncertain (the site may be erosional and the clay may be reworked), the organic-rich, fine-grained surface sediment samples most likely represent recent deposition. The topmost samples in Lake Vähä-Vahantajärvi have arsenic concentrations of 200-250 mg/kg, which is comparable to the top sediment sample from the pond 2 km upstream (228 mg/kg). However, in organic-rich samples furthest away from the mine area, taken from Stream Site 6 (~6 km away) and Lake Näsijärvi (~7 km away), top sediment arsenic concentrations were only 25 and 37 mg/kg, respectively. (No samples were analyzed from Stream Site 5, downstream from Lake Vähä-Vahantajärvi, because of the coarse grain size.)

The Lake Näsijärvi core, located roughly seven kilometers away from the mine area, was analyzed at three depths (30-29 cm, 21-20 cm, and 5-4 cm). These levels were selected to represent sediments deposited before, during and after the operation of the mine. To select the samples, deposition rates were estimated based on the clear 1986 Chernobyl nuclear fallout peak of ^{137}Cs found at 7-8 cm in the sediment. Chemical analyses showed that sediment arsenic concentrations increased more than ten fold from the background levels of 17 mg/kg to 235 mg/kg during the operation of the mine. Concentrations have since declined to 37 mg/kg at 5 cm (~year 1990-1995).

In the Lake Vähä-Vahantajärvi sediment core, the arsenic concentration profile resembles that of Lake Näsijärvi (Figure 20). Concentrations increase from 54 mg/kg at 30 cm to 583 mg/kg at 8 cm, a ten-fold increase. However, the ^{137}Cs peak between 3 and 4 cm in sediment suggests that sediments below 10-15 cm in sediment should have been deposited before the operation of the mine. These samples showed a large variation in arsenic concentrations (54-246 mg/kg), depending largely on sediment organic matter content. Despite this variation, an increase in arsenic concentrations similar to that found in Lake Näsijärvi is evident in Lake Vähä-Vahantajärvi as well. In the Lake Vähä-Vahantajärvi core, elements that also peak at 8 cm include arsenic, molybdenum, silver, copper, and selenium. In contrast, concentrations of cobalt, zinc and sulfur increase above 10 cm as well but decline only slightly in the upper part of the profile. Nutrient concentrations follow changes in mineral matter inputs. Apatitic phosphorus (HCl-P) is closely related to mineral matter inputs while the Fe, Mn, Al –bound phosphorus fraction (NaOH-P) diminishes with increasing sediment mineral matter content. Mineral matter is largely derived from fertile arable land areas in the catchment of the lake and the lake. Therefore it is no surprise that lake water phosphorus concentrations modeled by using diatom assemblage results appear to follow sediment concentrations of mineral matter and apatite phosphorus.

Lake Vähä-Vahantajärvi was used for analyses of biotic remains (diatoms) because it is the first larger basin downstream from the mine area. The aim was to see if changes in diatom species composition coincide with changes in sediment chemistry, mainly nutrient (phosphorus) and arsenic concentrations. Changes in sedimentary diatom assemblages are indeed seen at e.g. 12 cm and 8 cm in sediment (Figure 21). However, from 15 cm downwards, diatom-inferred lake water total phosphorus concentration (DI-TP) increases, suggesting nutrient enrichment. It was, therefore, necessary to try to separate the ecological effects of arsenic from those caused by eutrophication, as expected. This was done using redundancy analysis (RDA), a linear-based canonical ordination method. In RDA, no statistically significant effect of arsenic on diatom species compositions was found and the relationship was insignificant for mineral matter as well. The latter was used as a surrogate variable for nutrient inputs to the lake because of its good correlation with diatom-inferred TP concentrations.

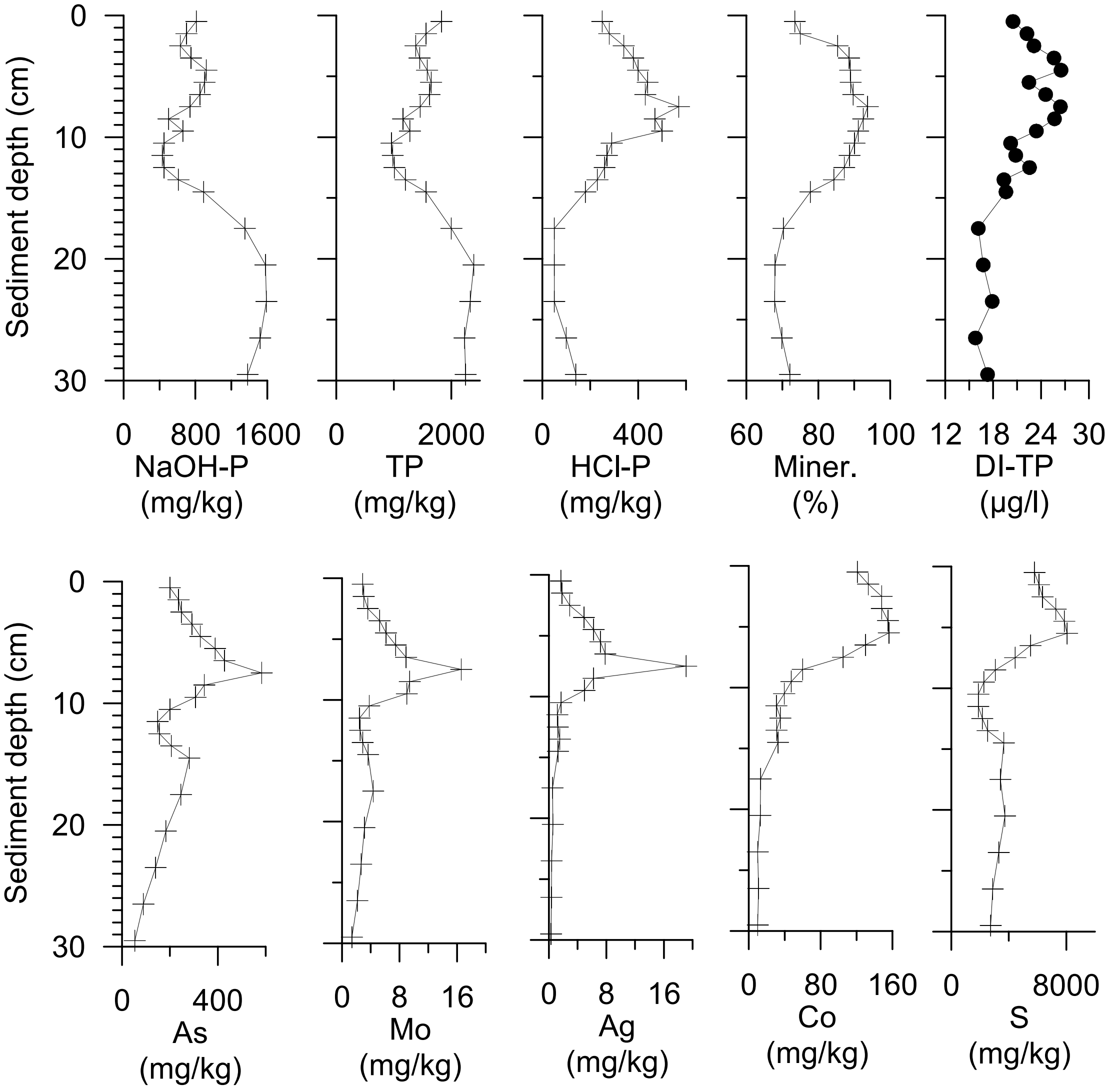

Figure 20. Concentration profiles of selected elements in the Lake Vähä-Vahantajärvi core. Past lake water total phosphorus concentrations, modeled from diatom assemblages, are also shown (DI-TP).

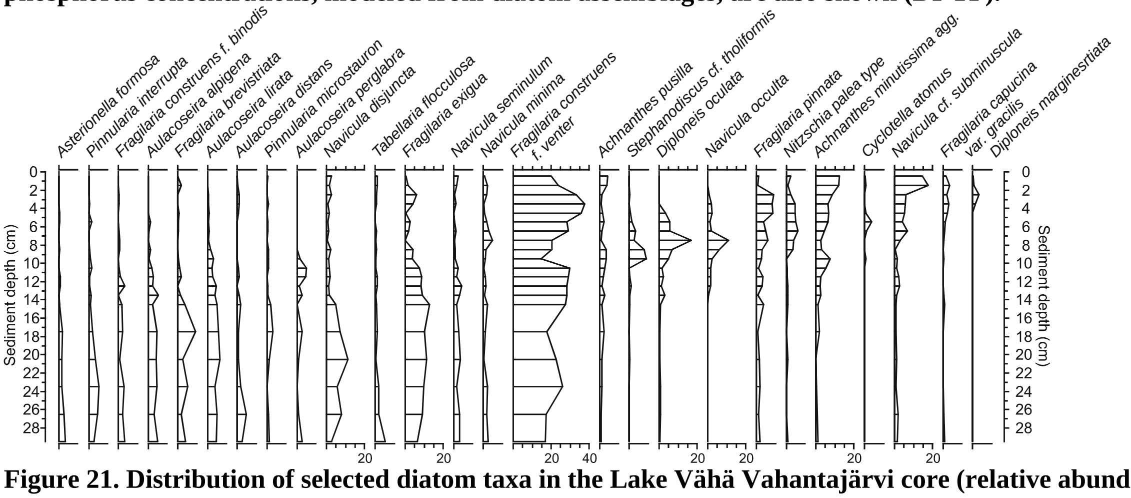

Figure 21. Distribution of selected diatom taxa in the Lake Vähä Vahantajärvi core (relative abundances). Taxa are arranged according to their abundance weighted average depth of occurrence.

The soil samples from the Ylöjärvi tailings collected by RAMAS showed high concentration of arsenic ranging from 1000 to 2200 mg/kg (Table 4). However, the leaching of arsenic was relatively low in the pH range of the water-soil mixture (pH 3.9 - 5). The leached arsenic portion of the total content was between 0.01 and 0.45 %. The leachability was highest in the sample collected near the margin of the tailings area (leached portion of arsenic 0.11-0.45 %). The leaching test eluates of the batch leaching test were non toxic to luminescent bacteria. Only one sample with the highest sulphate concentration (Table 4) was acutely toxic in the reverse electron transport assay (RET). The results of waste analyses are discussed in more detailed in the TASK3 RAMAS report.

Table 4. Total concentrations of contaminants (tot) and leached amount of substances (L/S 2 and L/S 10) performed by a two-stage batch leaching test (EN-12457-3) in the samples collected from Ylöjärvi mine tailings.

	Content and leached amount in mg/kg							leached portion of the total content
	Al	**As**	**Ba**	**Fe**	**Ti**	**Zn**	**sulfate**	**As**
tot	50200	2100	400	116000	2400	220		
L/S2	6.51	0.2	0.07	0.02	<0.02	0.79	260	0.01 %
L/S10	9.91	<0.5	0.25	0.06	<0.1	1.2	350	<0.02 %
tot	48100	1000	530	114000	2500	180		
L/S2	0.14	0.1	0.04	<0.01	<0.02	0.04	18	0.01 %
L/S10	<0.37	0.6	0.14	<0.05	<0.1	0.15	38	0.06 %
tot	41300	2200	480	91300	2200	170		
L/S2	0.36	2.5	0.29	0.2	<0.02	0.28	10	0.11 %
L/S10	0.85	10	0.72	0.7	<0.1	0.7	<21	0.45 %

5.3. The Kylmäkoski mine

The Kylmäkoski Ni-Cu deposit is located in the Pirkanmaa Belt, about 40 km south of the Tampere Schist Belt, where there are other considerable Ni deposits, like Vammala, Sääksjärvi, Harjunpää, Hyvelä and Korkeakoski. The Kylmäkoski deposit is a 260 meter long and about 80 meters deep ultramafic intrusion hosted in migmatized gneiss (Papunen 1980). It is limited on the northern side of the ultramafic body by quartz diorite. The Kylmäkoski deposit is composed mainly of equigranular and nodular peridotite grading into pyroxenite, perkinite and hornblendite. Other rock types appearing in the ultramafic body are cummingtonite rocks and gabbros.

5.3.1. Ore type and ore minerals

The sulfide ores exhibit three texture types: dissemination, breccia and massive vein (Papunen, 1980). Disseminated and breccia ores contain pyrrhotite, pentlandite and chalcopyrite, whereas cubanite is present in the breccias rich in Cu. Rare gersdorffite-cobaltite grains are found within disseminated sulfides. Molybdenite and argentian pentlandite appear as minor constituents in breccia ores in the basal contact with gneiss and the latter one also occurs in sulfide veins. Sulfide veins grade in composition to sulfarsenide and eventually to a Ni arsenide hosted vein. The sulfarsenide grains are made up of zoned gersdorffite-cobaltite, and the Ni arsenides comprise nickeline and maucherite (Papunen 1980). The following minerals are also found in the arsenide veins: chalcopyrite, argentian pentlandite, pentlandite, and minor wehrlite, galena and PGM.

5.3.2. History of the mine

The first indications of the Ni-Cu sulfide ore were discovered in 1962, and between 1971 and 1974, the Outokumpu Mining Oy exploited this deposit. The Kylmäkoski mine began as an open pit, and after a year and a half a year mining continued underground. The tailings were removed to a storage area (8 ha) half a kilometer from the pit. A total of 689 616 tons of ore were removed out of which the total recovery of nickel (0.36 %) and copper (0.27 %) was 1829 and 579 tons, respectively (Puustinen 2003).

5.3.3. Present situation

The Kylmäkoski mine is not under surface water monitoring. There are no records available of the condition of the nearby rivers or lakes. In 1974, the period the mine effluents were conducted, Outokumpu Oy monitored the effluent and the Tarpianjoki River. Cu, Ni, Fe, Ca and SO^{-}_{4} contents, pH and electrical conductivity were measured. The monitoring showed that the pH ranged from 6.4 to 10.5 and sulphate concentrations ranged from 2.5 to 50 mg/l. The conductivity was generally 100 μS/cm. Nickel and iron concentrations were elevated.

5.4. The Vammala mine

The Vammala nickel deposit is part of the Pirkanmaa Belt. A sulfide bearing peridotite sample found in Stormi (Vammala) in 1960 gave the first hint about the deposit. Outokumpu Oy performed a thorough exploration in the area and found a profitable ultramafic body. This ultramafic body, embedded in garnet-cordierite gneiss, consists of layers of peridotite in the lower and upper part with hornblendite in the intermediate portion. Orbicular peridotite appears in the basal layer.

5.4.1. Ore type and ore minerals

The Ni sulfide ore resides in the basal layer of the ultramafic body. The sulfides appear as matrix ore or massive veins that occasionally tend to extend from the peridotite basal layer to the gneiss. The more massive matrix ore grades into a sulfide dissemination from the basal contact inward. The main ore minerals are pyrrhotite, pentlandite, chalcopyrite and mackinawite (Häkli and Vormisto 1985). In some assemblages, violarite, cubanite and vallerite are present. Small amounts of native gold are found in the basal contact with mica gneiss, together with a pyrrhotite-chalcopyrite assemblage.

5.4.2. History of the mine

Outokumpu Oy began operating at the Vammala Stormi mine in 1974 and the main exploited elements were Ni (0.68 %) and Cu (0.42 %) (Puustinen 2003). A total of 7.5 million tons of ore was processed until 1995 when the mine closed. The tailings area (21 ha) is located about 300 meters from the concentrator behind the old open pit (Vanha-Honko *et al.* 1984). Nickel ore was processed until 1996, but the gold ore from Kutemajärvi mine (Orivesi) was processed in Vammala between 1994 - 2003.

5.4.3. Present situation

After the closure of the Ni-Cu mine in 1995, part of the underground galleries and open pits were filled with land, but the tailings are maintained for future enrichment processing from other deposits reasonably close to the processing site. The Pirkanmaa Regional Environment Centre (PREC) supervises surface water monitoring in the Vammala mine area. Monitoring began in 1996 and includes only nickel, copper, chloride and sulphate analyses from nearby rivers. The drainage waters are contaminated by the mining activity; the nickel concentration is especially high in river water. When the Kutemajärvi gold mine in Orivesi commune is reopened, the ore will be processed the Vammala enrichment plant and the tailings will be carried to the old mining galleries. The current holder is Australian Polar Mining Oy. There are also other ore prospects in the Pirkanmaa region that could be enriched in the Vammala processing plant.

5.5. The Kutemajärvi mine

The Kutemajärvi gold deposit is located in Orivesi 25 kilometers northeast of Tampere and is embedded in sericite-quartz schist within the Tampere Schist Belt. The critical gold seam is situated in the northern contact of the sericiteschist, where it is limited by granite batholite (Ollila *et al.* 1990). The intermediate metatuffs around the hydrothermally altered schist also contain sulfides.

5.5.1. Ore type and ore minerals

The gold is disseminated between the silicate minerals in pipe-like formations. Gold appears also in quartz veins. Sulfide minerals (pyrite, pyrrhotite, chalcopyrite, sphalerite and galena) are common in the gold seam, as well as small amounts of rutile, cassiterite and tellurides. Scarce arsenopyrite is found together with the sulfides. (Ollila *et al.* 1990)

5.5.2. History of the mine

The deposit was first studied for its sericite and quartz content but in the mid 1980’s the gold anomaly was found and Outokumpu Mining Oy began investigating the gold prospect. Over a million tons of ore was processed in the Vammala enrichment plant during the time that the mine was active from 1994 to 2003. The ore content was 9.54 g/t Au.

5.5.3. Present situation

In 2003, Outokumpu Mining Oy sold the mine to an Australian company called Polar Mining Oy. The current holder is planning to reopen the gold mine and the permit application is been considered in the environmental permit bureau of western Finland. A statement of environmental impacts on the Natura area south and west of the mining area is included in the application. The Kutemajärvi mine should be opened in the near future. When the mine reopens the enrichment processing will continue in the Vammala enrichment plant because of the relatively short service life of the mine. Since the mining ceased operations in 2003, the mine has been dewatered for future exploitation. Water is being monitored for phosphorous, sulfate, oxygen and nitrogen contents, and for acidity and electrical conductivity. The water is highly acid due to the oxidizing sulfides and it is neutralized before being conducted to Lake Ala-Jalkajärvi.

6. WASTE MANAGEMENT

6.1. Waste legislation demands

The present European Union policy on hazard classification and landfill disposal of waste materials requires stricter control over the release of contaminants into the environment. Hazardous Waste Directive 1991/689/EC defines a set of 14 properties to be used in waste hazard classification. According to EU Landfill Directive 1999/31/EC, the waste criteria for acceptance impose requirements for waste classification and quality monitoring. The basic requirements for waste classification are: (1) source and origin of the waste, (2) information about the waste producing process, (3) data on its composition and on its leaching behaviour and appearance. The management of waste from extractive industries is regulated by the newly prepared directive 2004/35/EC. The changes to the national legislation of the member states will be needed in spring 2008.

The Finnish national waste legislation is based on EU directives and regulations. The list of wastes and hazardous wastes is presented in the statutory regulations of the Finnish Ministry of Environment (1129/2001). For hazard classification, all the possible substances present in waste have to be identified on the basis of the hazardous properties (H) given in the Waste Decree (1128/2001). Solid wastes are classified as hazardous waste if the arsenic concentration in solid matter exceeds the limit value 1000 mg/kg (Finnish Waste Degree 1128/2001, Hazardous Waste Directive 1991/689/EC).

According to EU regulations, the acceptance of wastes into landfills consists of (1) basic characterization, (2) compliance testing and (3) on-site verification (Official Journal of the European Communities 2003). The basic characterization tests focus on understanding the long-term leaching behavior and the parameters influencing leaching (*e.g.* pH). When waste has been deemed acceptable for a landfill class of inert, non-hazardous or hazardous waste landfills on a basic characterization, the quality of the waste is determined by a compliance test periodically for waste streams that are produced regularly in the process (Official Journal of the European Communities 2003).

The EU criteria for landfills for non-hazardous waste was established only for inorganic wastes with low organic content, which is disposed in the same cell with stable, non-reactive hazardous waste. At the moment, this work is in process, and the changes to the Finnish national landfill legislation (861/1997) will be announced in September 2006.

6.2. Waste management in the Pirkanmaa region

In Finland, the total amount of wastes ending up in landfills was over 10 million tons in 2003 of which the amount of household waste was around 1.4 million tons (Finnish Ministry of the Environment, Waste statistics 2003). In the same year, the total amount of wastes from energy production was over 727 000 tons, from different other industries around 6.7 million tons, and the amount of construction and demolition waste was 520 000 tons. The recent regional waste management planning session in the Pirkanmaa region was done for the amounts and management practices of solid wastes from 1999 to 2001 (Blinnikka 2004). In 2000, the total amount of waste produced in the Pirkanmaa region was over 3 million tons and most of the waste produced ended up in landfills (Table 5). The sludge from municipal waste water treatment and wastes produced in the mechanical forest industry are the most recycled or re-used. The most typical waste materials from the forest industry are de-inking wastes from paper recycling, wood and barking wastes and saw dust, but these factories also produce incineration ashes, metal waste, household wastes and various kinds of hazardous waste (Blinnikka 2004). In year 2000, the total amount of hazardous waste produced in the Pirkanmaa region was around 14 800 tons of which 171 tons were situated in the hazardous waste landfill.

Table 5. The amount of different types of waste materials and their waste management in the Pirkanmaa region in 2000. Data was collected from the regional waste plan of PREC (Blinnikka 2004).

Waste type	Total amount tons	Landfilled	Re-used for energy production	Re-used as material	Re-used as energy or material
Municipal solid waste (MSW)	266 800	53 %	9 %	34 %	4 %
Sludge from municipal waste water treatment	103 000	1 %	-	19 %	80%***
Wastes from forest industry	410 700	28 %	23 %	44 %	5 %
Wastes from mechanical forest industry	1 008 600	76 %	3 %	21 %	-
Wastes from metal industry	53 400	61 %	4 %	35 %	-
Wastes from chemical industry	41 800	14 %	66 %	17 %	3 %
Wastes from food production	34 700	50 %	40 %	10 %	
Construction and demolition wastes	85 600	66 %	10 %	24 %	-
Wastes from mining	247 800	80%*	-	0,01 %	20%**
Wastes from energy production	60 500	91 %	-	-	9 %
Other wastes	122 000	-	-	-	-
Total	3 827 700	-	-	-	-

* contains mining wastes stored in quarries, ** waste rocks from mining, *** composed

The location of landfills and prevailing conditions in the surrounding area contribute to the contamination risk of the environment. Former landfills were constructed without any knowledge of groundwater areas causing evident risk for surface and groundwater. Old landfills are especially problematic because of poor isolation and lack of protecting structures thus affecting the surrounding environment through soil, air, surface water and groundwater contamination. Rainwater and groundwater migrate through the waste dump leaching harmful agents, *e.g.* heavy metals, organic detrimental elements (dioxin, furan etc.) and different nitrogen compounds. The damages can also include harmful gases and unpleasant odors, toxic leachates, fire risk or esthetic problems. In the old landfills, the dumped waste was not controlled and practically anything could end up in municipal landfills. Therefore, a number of landfills have been closed over the past few years in Finland. For example, in 2004 the total number of landfills was 188 while five years earlier it was 300. In 2004, there were 151 non-hazardous waste landfills, 17 hazardous waste landfills and 20 inert waste landfills in the whole country. In the Pirkanmaa region, there have been more than 130 landfills, though only seven of them are currently in use.

There are four waste management companies collecting and handling municipal solid wastes in the Pirkanmaa region (Figure 22). At the moment, three non-hazardous municipal waste landfills are in use in Tampere, Nokia and Virrat communities, and four non-hazardous waste landfills owned by industries. Currently, 16 landfills are also in use for slightly contaminated soils in the Pirkanmaa region. Typical industrial waste managed in the industry owned landfills consists of incineration fly ash and bottom ash, forest industry waste such as fiber sludge, waste from castings of ferrous pieces, dregs and green liquor sludge and construction waste or wastes from the production of construction materials. Other activities practicing waste management (number of companies 38 monitored by PREC) in the Pirkanmaa region are municipal sludge composting companies, companies collecting and storing hazardous wastes, waste management companies handling and pre-treating mainly oil contaminated soils, and companies reusing construction wastes in civil engineering.

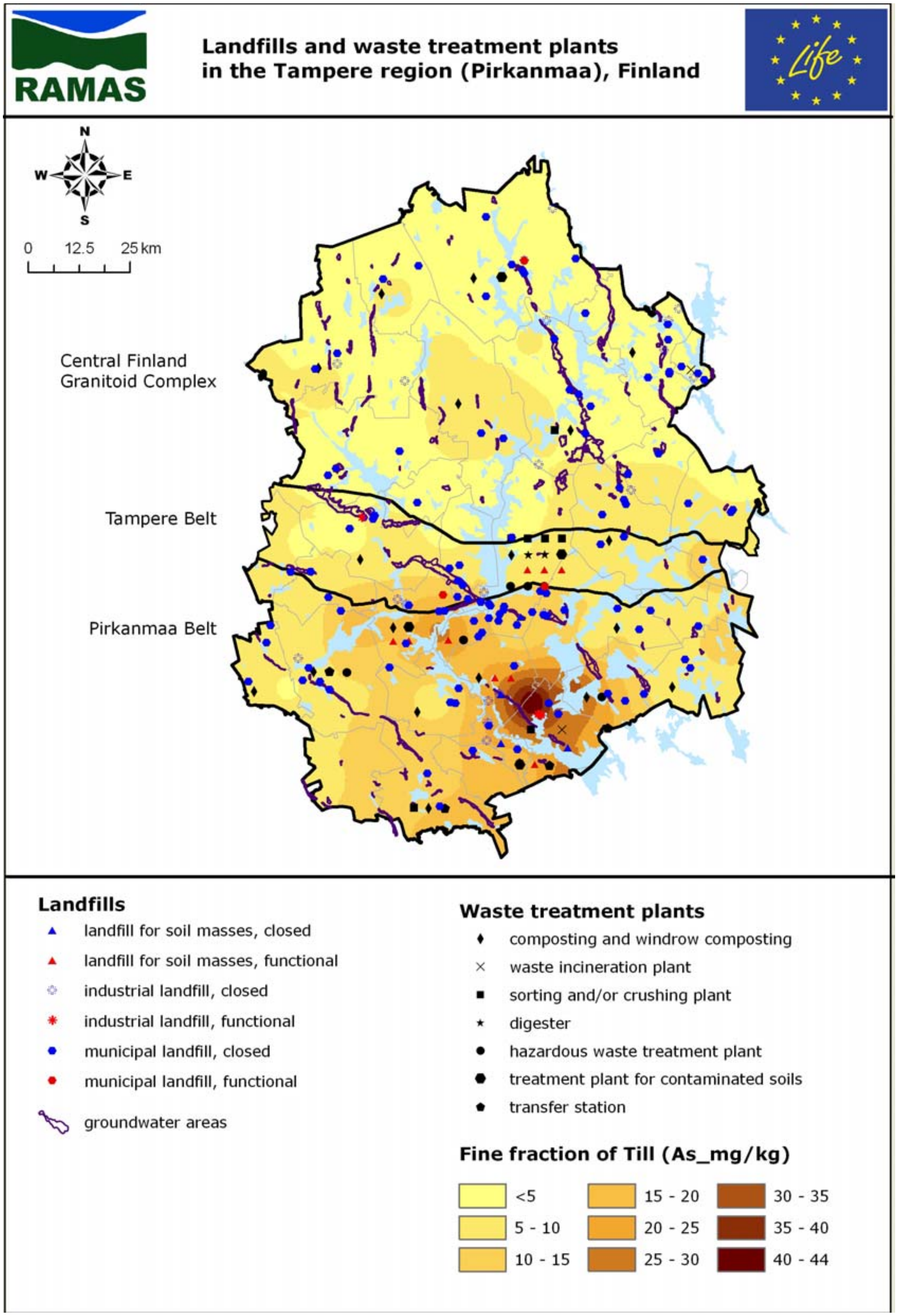

Figure 22. A map showing arsenic concentration in glacial till in the Pirkanmaa region, with the location of landfills and waste treatment plants (Anu Peltonen, PREC).

6.3. Solid wastes in the Pirkanmaa region

According to EU Landfill Directive 1999/31/EC, waste acceptance criteria impose requirements for waste classification and quality monitoring. The location, ground water protection and monitoring of the landfill environment are regulated and an environmental permit is needed for landfill activities. The basic requirements for waste classification are: (1) source and origin of the waste, (2) information about the waste producing process, (3) data on its composition, its leaching behaviour and appearance. The proposed leaching limit values at L/S-ratio 10 l/kg for arsenic should not be greater than 0.5 mg/kg for inert waste, 2.0 mg/kg for non-hazardous waste, and 25 mg/kg for hazardous waste, respectively. Recent studies on waste materials show that high concentrations of arsenic are not found in different waste types (Table 6). The most significant waste containing high amounts of arsenic are end products of inorganic wood preservatives and soil masses contaminated by CCA preservatives (Table 6). In van Eetvelde (1994 cited in van der Sloot *et al.* 1997), the maximum cumulative proportional leached quantities of copper, chromium and arsenic from the CCA treated wood after the tank-leaching test (NEN 7345) of 64 days were 2.0 %, 0.05 % and 0.63 %. The leaching of CCA treated wood was studied in relation to the temperature. Nevertheless, impregnated wood from building demolition wastes are classified as hazardous waste and some of this waste ends up in municipal landfills because of poor sorting.

Table 6. Examples of arsenic concentrations in various types of waste materials. EWC = European Waste Code, N = number of results.

Type of waste	EWC-code	Concentration in solid waste mg/kg			N	Leaching test results L/S 10 mg/kg			N	Reference
		min	average	max		min	average	max		
de-inking waste from paper recycling	03 03 05	1	-	11		-	0,1	-	1	3, 4
leather waste from dressing and finishing	04 01 99	-	3,1	-	1	-	<0.01	-	1	1
calcium-based reaction waste from flue gas desulphurisation	10 01 05	-	1,6	-	1	-	0,2	-	1	1
jarosite slag	11 02 02*	-	-	-	-	0,07	-	0,3	1	4
wastes from shaping of metals	12 01 01	0,75	4	10	3	<0.01	0,01	0,03	4	1, 4
wastes from surface treatment of metals, residues	12 01 99	-	1,3	-	1	-	0,01	-	1	1
sludge from municipal waste water treatment	19 06 04	3,1	3,4	3,6	2	0,06	-	0,2	1	1
sludge from forest industry waste water treatment	19 08 12	<3	5,8	12	18	-	0,02	-	1	1, 3
concrete construction waste	17 01 01	0,05	5,2	12	11	<0.01	0,02	0,07	10	1,2
construction waste, painted wood waste	17 02 01 or 17 02 04*	-	4,9	-	1	-	-	-	-	1
residues from soil washing	17 05 03* or 17 05 04	8,6	12	15	2	0,17	0,19	0,21	2	1
Soil contaminated by CCA wood preservatives	17 05 03* or 17 05 04	13	1700	12000	380	<0.5	11	28	5	1

* hazardous waste, 1) PREC laboratory results (LIMS database), 2) Sorvari 2000, 3) Toikka 1999, 4) Vaajasaari 2005

6.4. Wastes from thermal processes

The burning of coal, peat and heating oil in power plants generates arsenic and heavy metal emissions over an extensive area. Arsenic and heavy metals can disperse into the environment through flue gas emissions from the solid fuel burning process. The total emission is difficult to estimate. Lyyränen *et al.* (2004) gathered information from recent studies and estimated the heavy metal emissions produced by power production in Finland. According to this paper, the arsenic content in the fuels is not very high (Table 7). Recycled residues used as burning fuels may contain greater amounts of arsenic according to the origin of the wastes. Recycled burning fuels may contain CCA-treated wood, old printing ink, tanning agents for leather or corrosion inhibitor, all of which are sources for arsenic. Therefore, depending on the burned material heavy metal and arsenic contents may vary greatly (from 3 to 34 mg/kg of arsenic). In Europe, municipal solid wastes (MSW) and wastes from different industrial sectors are incinerated to a larger extent than in Finland. In 1997, the percentage of incinerated MSW out of the total amount of waste produced in Germany was 50 % and in Netherlands 62 %, and in France it was 30 %, whereas in Finland it was 2 % (Laine-Ylijoki *et al*. 2005). The amount of bottom ash and fly ash produced annually is around 575 000 t to 814 000 t in Denmark, Germany, and Netherlands. Waste incineration and the amounts of ash produced is also expected to increase in Finland.

In the Pirkanmaa region, most of the power plants use natural gas for energy production. Oil and peat are also used as additional fuels. According to discussions with PREC environmental authorities, five forest industrial power plants also use wood waste, bark and saw dust as burning fuel. There are only two industrial power plants in the Pirkanmaa region that have an environmental permit to burn waste water sludge, and one pilot plant burning different types of waste materials.

Table 7. Minimum, average and maximum contents of arsenic (mg/kg) in different types of fuels (Lyyränen *et al.* 2004).

Fuel	Min	Average	Max
Coal	1.0	5.0	13.0
Peat	0.2	2.2	9.3
Heating oil	–	5.0	–
Recycled fuels	3.0	12.0	34.0

In Finland in general, the majority of wastes from thermal processes are produced in the coal burning process. Coal burning generates about 10 to 15 percent of its original weight in ashes. Annually, 500 to 900 thousand tons of ash is produced, of which *ca*. 500 000 tons is fly ash and 90 000 tons is bottom ash (http://www.energia.fi/page.asp?Section=4540). The arsenic concentration in fly ash varies according to the pyrite content of the coal, assuming that arsenic appears in the mineral structure of pyrite, and the average concentration of arsenic in the fly ash generated in Finnish coal-fired power plants is 40 mg/kg (Table 8). The European waste list (94/904/EC) classifies typical waste materials as either hazardous or non-hazardous, and the European waste codes (EWC) are given in this waste catalogue (Table 8). The Finnish national waste legislation is based on EU directives and regulations. The list of wastes and hazardous wastes is presented in the statutory regulations of the Finnish Ministry of Environment (1129/2001). Oil fly ash is classified as hazardous wastes according to the waste list. Bottom ash from MSW incineration can either be hazardous or non-hazardous (EWC-code in Table 8). More than 90 % of the energy production waste and ash produced in the Pirkanmaa region ends up to the landfills (Table 5). Ash can be used as an alternative raw material in the building industry for example for making cement and gypsum plates, in civil engineering and in road construction. There are restrictions on the use of ash to prevent any exposure to the environment and groundwater. The use of ash is forbidden in close contact with important groundwater areas and water supply source. Furthermore, ash-containing materials must be covered with other materials to prevent it from weathering and other types of erosion. To use ash in civil engineering purposes an environmental permit is usually required (http://www.energia.fi/attachment.asp?Section=4521&Item=15038). At the moment, ash from thermal processes is not re-used to a great extent in the Pirkanmaa region. Concentrations of arsenic in solid ash materials and their leaching test eluates gathered from different research studies and laboratory results of the PREC laboratory shows that arsenic concentrations vary depending on the burnt fuel. Leaching of arsenic into the water from various types of ash is quite low (Table 8).

Table 8.Some examples of arsenic concentrations in ashes and arsenic leachability from various types of ashes. EWC = European Waste Code, N = number of results.

Type of waste	EWC-code	Concentration in solid waste, mg/kg			N	Leaching test results L/S 10, mg/kg			N	Reference
		min	average	max		min	average	max		
coal bottom ash	10 01 01	5	16	27	8	0,049		0,2	16	2
coal fly ash	10 01 02	21	40	98	28	0	0,09	0,3	19	2
peat and untreated wood fly ash	10 01 03	1,98	23	72	62	0,02	0,1	1	27	2
oily fly ash	10 01 04*	<0.4	5,9	20	4	<0.02	0,3	1,3	4	1
fly ash from municipal waste incineration	10 01 14* or 10 01 15	49	-	320	-	-	-	-	-	3
bottom ash from municipal waste incineration	10 01 16 * or 10 01 17	0,12	-	189	-	<0.01	-	0,34	-	1,3

* hazardous waste, 1) PREC laboratory results (LIMS database), 2) Sorvari 2000, 3) Laine-Ylijoki *et al.* 2005

6.5. Liquid discharge from landfills

Liquid discharges from landfills, referred to here as landfill leachates, can be classified as a mixture of thousands of soluble and solid compounds. Heavy metal concentrations in landfill leachates are generally rather low, but a broad range of xenobiotic organic compounds has been detected in landfill leachates (Kjeldsen *et al.* 2002, Wintgens *et al.* 2003). Arsenic is not leached from the municipal landfills to a large extent. The average arsenic concentration in Finnish municipal landfill leachates is 9.5 µg/l whereas the maximum concentration has been 760 µg/l (Wahlström *et al.* 2004). In one of the municipal non-hazardous waste landfills in the Pirkanmaa region, arsenic concentrations in landfill leachates ranged from 1.8 to 317 µg/l with a mean concentration of 37 µg/l As (number of results 17, LIMS database).

Due to poor isolation and negligent sorting of waste in former landfills, leachates can contain varying concentrations of arsenic. For example, in a former landfill in the Pirkanmaa region where CCA treated waste wood was sited, the arsenic concentrations in the landfill leachates varied from 4 to 236 µg/l with an average value of 88 µg/l As (number of results 10, LIMS database). In the leachates of former municipal landfills, where mainly household wastes were situated, the arsenic concentrations varied from 0.21 to 14.6 µg/l with an average value of 4.6 µg/l As (number of results 17, LIMS database). More examples of arsenic discharge from one closed municipal and one closed industrial landfill are presented in the following chapter.

6.6. Case studies of former landfills in Pirkanmaa region

6.6.1. Municipal landfill of Ikuri in Tampere commune

The Ikuri landfill in Tampere was used from 1963 to 1983, and is located near the Myllypuro Natura area where the Myllypuro River flows into Lake Vihnusjärvi. The Nokia commune uses Lake VIhnusjärvi as a water supply for groundwater recharging. The distance from the nearest groundwater intake plant is 1.5 km, and the closest population center with residential buildings is situated approximately 100 to 200 meters away. The base of the landfill is poorly isolated and the underlying soil is mainly silt soil. The northern and eastern ends of the waste pile are two points where leachate water discharges. The distance from the discharge points to the nearby river is 0.2 km and to Lake Vihnusjärvi about 3.9 km. The Ikuri landfill was used as a mixed waste area for municipal and industrial wastes where material from a paint and surface treatment factory, glasshouse and leather and fur factory were carried. Solvent substances, organic halogen compounds, metals and other hazardous wastes may have ended up in the landfill. (Montonen 2005)

In summer 2005, Montonen studied the Ikuri landfill area through analyses on soil, waste, leachate water and groundwater samples were performed, and the toxicity was studied with luminescent bacteria, water fleas and green algae. According to Montonen (2005), the Ikuri landfill poses an environmental risk due to the elevated levels of detrimental elements in the surface and groundwater, waste and soil samples as well as in gas emissions. The leachate water analyzed from the discharge points of the landfill was toxic to all tested organisms. The worst contaminants were solvents, but heavy metals exhibited high values. Arsenic concentrations in the solid waste ranged from 3.2 to 20 mg/kg. The water sample taken from the interior of the landfill contained 80 μg/l arsenic and other heavy metals (Cr, Fe and Pb), whereas the leachate water contained only 11 μg/l As. The groundwater was analyzed from two groundwater wells, and showed values up to 150 μg/l of arsenic. Cr, Pb, Mn, Ni and Fe also had high values in the groundwater.

6.6.2. Industrial landfill of Pollarinkangas in Vilppula commune

The Pollarinkangas Industrial landfill was remediated in 2000. The landfill was active from 1962 to 1972, and was situated on a 3rd class groundwater area. Creosote oil and CCA agent residues from wood preservation plants and phenolic resin distillation water from a factory manufacturing laminated timber slabs were delivered to Pollarinkangas landfill. It is possible that KY5 chlorophenols from nearby timber mills were also dumped. The landfill had a detrimental environmental impact on the soil, groundwater and air. The soil underlying the waste tip was contaminated all the way to the bedrock. The landfill was not covered or protected in any way, allowing the rainwater to wash and leach the wastes. Due to lack of fine fractions and organic carbon the mineral soil, the underlying soil was not able to absorb the detrimental agents, and leached water percolated to the groundwater. The contaminated soils contained elevated values of arsenic ranging from 13 to 450 mg/kg (128 mg/kg on average). The soil remediation was conducted by excavating all the land masses, which were removed from above the bedrock surface, then replaced by clean soil and landscaped with trees. Contaminated soils were classified according to the concentration of detrimental agents (PAH compounds, chlorophenols, arsenic, chromium and copper). Heavily contaminated soils were stored in a landfill before stabilization with cement, whereas mildly contaminated soils were carried away and piled up in a landfill. (Unpublished report by local consulting company)

7. ARSENIC IN OTHER HUMAN ACTIVITIES

There are around 137 large or medium-sized factories that are monitored according to environmental permits from the Pirkanmaa Regional Environment Centre (PREC). The main portion of the industrial activities in the Pirkanmaa region are factories producing chemicals such as paints, glues, printing inks, viscose fibers and medicines, and metal industry factories providing basic metal products or metal surface treatment or metal finishing and forging (Figure 23).

Currently, arsenic is not used to a great extent in these industrial sectors and therefore, only a little monitoring data for arsenic is available. For example, arsenic concentrations in waste water and surface water discharges from the three different factories producing glues, textile and construction products have varied from 0.1 to 4.8 µg/l with an average of 1.4 µg/l As (number of results 19, LIMS database) whereas in timber mills and wood preservation plants using CCA preservatives, waste waters contain from 59 to 160 µg/l of arsenic (LIMS database). The arsenic concentrations in surface waters near one working timber mill have varied from 0.43 to 13.1 µg/l with an average value of 5 µg/l As (number of results 12, LIMS database). In 2006, RAMAS additionally sampled wastewaters from 36 wastewater treatment plants in the Pirkanmaa region. The results showed that arsenic is found neither in municipal wastewaters nor in purified waters. Almost all of the 65 analyses exhibited values less than 3 µg/l of arsenic and only one sample exhibited arsenic concentration of 6 µg/l. The average value was 1.5 µg/l of arsenic.

The majority of airborne emissions of arsenic are derived from the metal industry (Melanen *et al.* 1999). The total amount of arsenic emissions diminished radically (90 %) from the beginning of 1990 to 1995. In 1997, a total of 12.3 tons of arsenic emissions were released, out of which 90 % came from metal industry processes. In the production of copper, iron and steel, arsenic may be a minor element (Table 6). For instance, copper concentrates contain As, Cd, Pb, Hg, Se, Ni and Zn as impurities. PREC supervises a total of 26 facilities and metal industry plants including approximately seven foundries, five metal surface treatment plants, three forging plants and other various facilities laboring metal, *e.g.* motors service centers and factories producing metallic devices. These plants mainly treat iron and steel. Arsenic can appear in wastes and drainage waters of these facilities, but also in airborne emissions. However, as shown in Table 5, Arsenic concentrations in wastes from shaping of metals are not high (0.75 - 10 mg/kg) and leached amounts of arsenic from these metal industry wastes is low (< 0.01 - 0.03 mg/kg).

Arsenic is not the major contaminant in the forest industry wastes either. As an example, one factory in the Pirkanmaa region is using recycled paper as raw material. Typical arsenic concentrations in the de-inking wastes from that kind of paper production vary between 1 to 11 mg/kg. Sludge from forest industry waste water treatment has also low arsenic concentrations (biosludge between 0.1 - 10 mg/kg and chemical sludge 0.5 - 13 mg/kg). (Toikka 1999)

As mentioned earlier, the use of arsenic is restricted to minimum and the concern is the past practices. For example, in 1908, a famous gunshot factory was established in Tampere city and it produced lead gunshots for hunting purposes. Arsenic was used to improve the elasticity of the gunshot products. Nowadays, only the tower of this factory remains and it is a cultural monument. In preliminary studies by PREC in 2002, the ground near this former factory proved to be heavily contaminated by lead and arsenic. The arsenic concentrations in the soil ranged from 41 to 100 000 mg/kg with a median of 305 mg/kg (average 11 300 mg/kg As) whereas lead concentrations in this area ranged from 250 to 230 000 mg/kg.

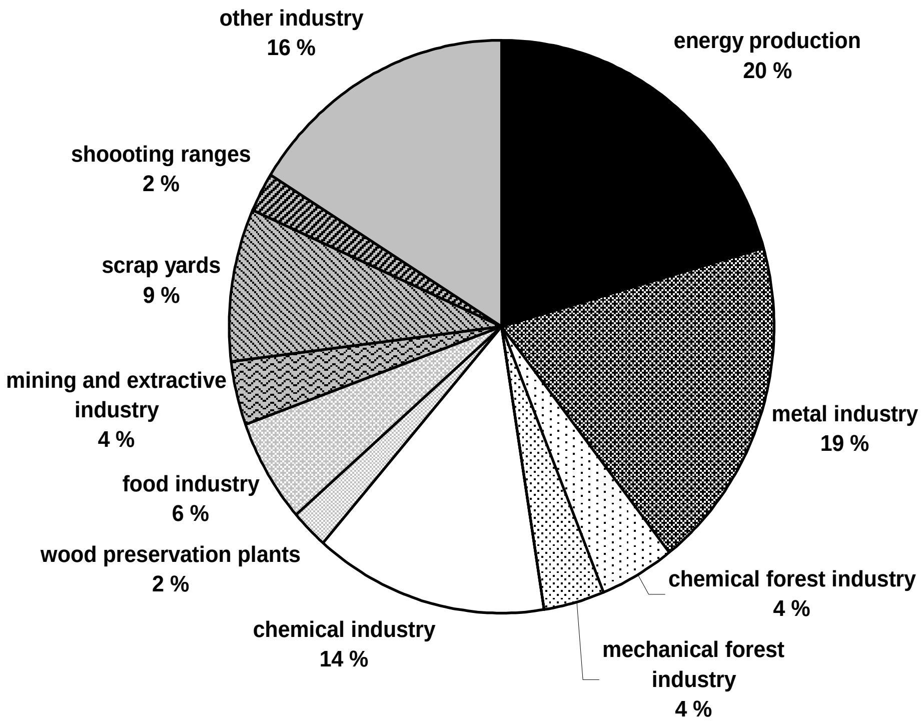

Figure 23. The main portions of the present industrial activities in the Pirkanmaa region monitored according to environmental permits by Pirkanmaa Regional Environment Centre. Factories monitored by municipalities are not included.

Commercial nursery gardens may also be possible anthropogenic contaminant sources of arsenic. A number of different pesticides have been used in greenhouse cultivations containing over 120 effective agents (Jaakkonen 2003). Inorganic, arsenic bearing compounds *e.g.* arsenic acids, copper, zinc, lead and calcium arsenates were used as vermin pesticides from the early 1900 until the late

1950's. However, in the Pirkanmaa region arsenic is not a probable contaminant in commercial nursery gardens because of the prohibition of As-bearing pesticides in the mid 1960, after which time most of the gardens in the region were built. In the Pirkanmaa region, there are 45 commercial gardens 15 of which have ceased operations. In 2000, the Pirkanmaa Regional Environment Centre (PREC) released a questionnaire for garden owners to determine the state of the operational and non-operational nursery gardens in the Pirkanmaa region. The response rate was low. Four commercial gardens in Pirkanmaa have had soil remediation because of contaminated soil, and landmasses have been removed for the remediation. In all four locations the contamination was due to an oil leak from a heating fuel container. Research into commercial gardens has shown that analyzed matters are ususally organic pesticides and possible oil damage thus omitting inorganic compounds like arsenates. Therefore, analyzed results of arsenic are seldom available.

In 2003, the Uudenmaa Regional Environmental Centre conducted a study into soil contamination in closed commercial nursery gardens in the Uudenmaa area, of southern Finland. The content of heavy metals and arsenic in soil samples was measured only in one of the 15 gardens studied in the Uudenmaa region. Cadmium, lead and vanadium exhibited elevated concentrations, but the arsenic concentration was less than 10 mg/kg. However, arsenic concentration exceeded 10 mg/kg in pond sediments close to one of the gardens. Generally, the detected pesticides were DDT, heptochlorine, endosulfate, lindane and dieldrine. (Jaakkonen 2003)

8. SUMMARY

In this TASK 2 report of RAMAS project, information about anthropogenic sources of arsenic in the Pirkanmaa region was gathered and RAMAS performed complementary sampling and analyses in potentially contaminated areas. Data was acquired about chemicals containing arsenic (wood preservative agents, pesticides etc.), the metal industry and metallic products containing arsenic (*e.g.* gunshots), mining and waste management. RAMAS studied areas affected by soil and surface water contamination caused by wood preservative plants, mining and waste treatment and municipal waste water treatment plants. The airborne contamination of arsenic was not covered in this report.

The measurement of total chemical concentrations of individual elements in soils can either underestimate or overestimate the environmental impacts of pollutants. Aging and bioavailability also affect the overall environmental risk of pollutants in soils (Alexander 2000). From an environmental hazard assessment perspective, the bioavailability of substances has to be distinguished from the total concentration of chemicals in wastes or in contaminated soils (Turpeinen 2002, Lanno *et al.* 2004). Chemical analyses cannot provide information about bioavailability, effects on biota, antagonism or interactions between chemicals. In addition, ecotoxicological properties are not easy to characterize or quantify using just chemical data. This emphasizes the importance of studying the leaching and ecotoxicological properties of contaminated soils and wastes along with the total concentrations of key hazardous substances. Therefore, RAMAS has taken into consideration leaching and toxicity properties of arsenic in this study.

The wood preservative plants proved to be the major arsenic pollutors. The negligent use of chromated copper arsenate (CCA) products, inappropriate storage of CCA-treated wood and the use of the impregnated wood in the past has caused soil, surface water and groundwater contamination. Concentrations of arsenic in the contaminated soils of wood preservative plants range from 3 up to 12000 mg/kg, although only minor leaching of arsenic and other heavy metals was detected (from < 0.2 to 2.0 %, Table 2). The majority of detrimental agents from the contaminated soils of old wood preservative plants have already leached and migrated over time, and at present the leaching of heavy metals is slow but continuous. Ruokolainen *et al.* (2000) and Turpeinen (2002) have presented similar results. According to their studies, the percentage of leached arsenic from the CCA contaminated soils of old impregnation plants were around 0.3–0.6 %. Schultz *et al*. (2004) also showed that the easily leachable fractions of As to 0.01 M barium chloride were around 0.1 to 2 % of the total concentration of 752 – 4340 mg/kg arsenic in contaminated soils. According to Van Eetvelde *et al.* (1998), the maximum leachability of Cr and As from soil samples was detected under neutral conditions. Pantsar-Kallio and Manninen (1997) showed in their study that less than 2 % of the total arsenic (600 mg/kg) was extracted at pH 3–9 from the sandy soils contaminated by CCA preservatives, whereas the pH changes would have had to be dramatic, either pH 1 or pH 13, to release high amounts of arsenic. As well, RAMAS found that heavily contaminated soils at the Ruovesi I site appeared to be toxic to some organisms and the analyzed ground had greenish stains and only little vegetation (Figure 3). On the basis of the chemical characterization of the soil samples from Ruovesi II impregnation plant, arsenic was considered to be the major detrimental element, but comparisons between leached concentrations of preservative agents and aquatic ecotoxicity in the leaching test eluates showed that copper rather than arsenic caused the environmental hazard.

Shooting ranges are problematic contaminated areas where lead (up to 14000 mg/kg) is the major contaminant, whereas arsenic appears in minor concentrations in the soils (from 1.1 to 28 mg/kg). However, large amounts of accumulated gunshot residues in the old shooting ranges are left in nature and keep degrading thus heavy metals, including arsenic, dissolve contaminating the soils and surface waters. Since 2002, new shooting ranges require an environmental permit that regulates and supervises the activity.

The mining industry is one anthropogenic source of arsenic producing huge quantities of country rock and tailings. The environmental impacts of arsenic depend on the amount of arsenic bearing minerals in the exploited rock. Arsenic minerals and As-bearing sulfides leach in contact with rainwater and air, giving rise to acid mine drainage. Arsenic and other heavy metals end up in nearby rivers and lakes, as well as in the groundwater. Surface water monitoring of old mining areas is performed in a few places including the commonly analysed main exploited elements. In general, there is little information about environmental risks or arsenic contamination in mine areas in the Pirkanmaa region. The RAMAS surface water and lake and stream sediment results show that mining activities in Ylöjärvi have affected the surface waters and the active period of the mine can be traced from the sediment layers of nearby lakes and streams. Even today, As concentrations are high (75.6 µg/l of As ca. two kilometers from the mine) upstream of the studied watercourse from Lake Parosjärvi to Lake Näsijärvi. As far as Lake Näsijärvi, about seven kilometers from the Ylöjärvi mine, sediment layers accumulated during exploitation contain 235 mg/kg of arsenic, whereas background levels were 17 mg/kg. The soil samples from the Ylöjärvi tailings collected by RAMAS showed high concentration of arsenic ranging from 1000 to 2200 mg/kg (Table 4). However, the leaching of arsenic was relatively low, from 0.01 to 0.45 % of the total arsenic content.

The total amount of waste produced in the Pirkanmaa region was over 3 million tons in 2000 and most of it ended up in landfills. In general, high concentrations of arsenic are not found in different waste types, but occasional disposal of CCA wood preservative waste may cause local contamination. For example, arsenic concentrations in wastes from metal shaping is low (0.75-10 mg/kg) and leached amounts of arsenic from this metal industry wastes is low (<0.01-0.03 mg/kg), whereas end products of inorganic wood preservatives and soil masses contaminated by CCA preservatives can contain up to 12000 mg/kg of arsenic. Poor isolation and negligent sorting of waste (*e.g.* some of the CCA-treated wood ends up in municipal landfills) in former landfills, has resulted in leachates that can contain varying concentrations of arsenic. The average arsenic concentration in a Finnish municipal landfill leachate is 9.5 µg/l. However, in one of the municipal non-hazardous waste landfills in the Pirkanmaa region, arsenic concentrations in landfill leachates ranged from 1.8 to 317 µg/l with a mean concentration of 37 µg/lAs. The majority of the older landfills are now closed and new ones are constructed and supervised in a more environmentally aware manner, thus major contamination is prevented.

Arsenic and heavy metals accumulated in the ash of solid fuel burning process vary in concentration depending on the burnt fuel, but usually leaching of arsenic into the water from various types of ash is low. In the Pirkanmaa region, most of the power plants use natural gas for energy production. Oil and peat are used as additional fuels. There are only two industrial power plants in the Pirkanmaa region that have an environmental permit to burn waste water sludge, and one pilot plant burning different types of waste materials. Ash from thermal processes is not re-used to a great extent in the Pirkanmaa region. More than 90 % the energy production waste and ash produced end up in landfills.

There are other point source polluters of arsenic, such as old tanneries, refineries and scrap yards which were active in the past. Factories processing arsenic containing raw materials or chemicals caused environmental risks through poor waste management, drainage or negligent handling of detrimental agents. Reliable data on these kinds of contaminated sites is very difficult to acquire.

9. CONCLUSIONS AND SUGGESTIONS FOR FOLLOW-UP ACTIVITIES

The results of RAMAS show that wood preservation plants are the major anthropogenic source of arsenic in the Pirkanmaa region. High concentrations, low but constant solubility and high toxicity of arsenic are a risk for nearby residents and possibly for groundwater. The end products of impregnated wood cause environmental and health problems and waste management of CCA treated wood is problematic.

Arsenic contamination in the Pirkanmaa region is restricted to small, local sites, and at present the contamination risk is relatively small. The Geochemical Atlas of Europe provides insight into the arsenic contamination risk across Europe (Salminen *et al.* 2005). The data collected form 26 countries shows arsenic concentrations in soils and surface waters. The geochemical maps highlight the problematic areas where arsenic soil content is elevated in southern Great Britain, northern Spain and in central Europe in France and Switzerland, whereas the arsenic stream water content is elevated in southern Portugal and Spain, France and Hungary (Salminen *et al.* 2005).

There is no well-established database or source of information about sources, appearance or concentrations of arsenic in soils, surface water and groundwater. The information is scattered in informal papers and unpublished reports. Even though the ecological risk of arsenic is well acknowledged, it is often left out of analyses. Generally, heavy metal contents are not studied in landfills or commercial nursery gardens. It is easy to depict all possible anthropogenic contamination sources of arsenic and the risks they pose. In addition to measurements of arsenic concentration in aquatic or terrestrial environmenst, it is also important to understand other aspects such as leaching and ecotoxicity. Chemical analyses often focus on the determination of concentrations of key hazardous substances. Thus, analyzing a limited set of key hazardous substances in matrices may not provide sufficient data to reflect the overall environmental risk of contaminated areas. This emphasizes the importance of studying the leaching and/or ecotoxicity properties of contaminated soils and surface waters in addition to the concentrations of the key hazardous substances.

More research and data about arsenic contamination is needed because generally other detrimental agents are the main focus. For example, arsenic could be a standard analyzed element in surface water monitoring according to environmental permits and in the landfill leachate monitoring. Continuous monitoring and graduated information would increase the environmental consciousness of arsenic related problems. In many occasions, one detrimental element does not solely cause environmental contamination. Knowledge of the interactions between contaminants is important. Chemical analyses alone cannot provide information about bioavailability, effects on biota, antagonism or interactions between chemicals. Therefore, ecotoxicity testing is a useful tool to be used for risk assessment properties. The RAMAS project will also use leaching and ecotoxicity test results produced during this TASK 2 report for risk assessment studies in the TASK 3 portion of the RAMAS project.

Besides increasing environmental consciousness and knowledge about the effects of detrimental elements, prevention is a good method to minimize anthropogenic contamination. Environmental permits control different facilities and polluters. For example, to prevent soil contamination new shooting ranges need to build soil coatings to collect the spread gunshots from the ground.

The remaining question is what kind of arsenic contaminants will arise in the future. Currently, the use of arsenic is restricted and the concern past practices. Many times, inappropriate waste management has caused environmental problems that are discovered when old landfills, scrap yards or surroundings of closed factories are assessed for contamination risk. Equally difficult cases are old refineries and foundries where the environmental impacts are not detected until a thorough risk assessment is conducted. For example, there are only few working tanneries in the Pirkanmaa region, but the old factories using leather tanning agents might have consumed arsenic bearing chemicals prior to the arsenic ban. The problems remain in the backyards of the old factories or in the landfills. Animal shelters like fur ranges and the plastic industry among many other human activities may also be potential contaminant sources though arsenic is not the main detrimental element. The consequences of mistakes and negligence in the past still emerge and have an impact on the environment today.

10. YHTEENVETO

Tämä TASK2-loppuraportti on osa kolmevuotista RAMAS-projektia. Raporttia on valmisteltu vuosina 2005 ja 2006, ja siihen osallistuivat Teknillinen korkeakoulu (TKK), Pirkanmaan ympäristökeskus (PIR) ja Geologian tutkimuskeskus (GTK). TASK2-loppuraportin tavoitteina oli kerätä tietoa ihmisen aiheuttamista arseenin lähteistä Pirkanmaan alueella ja tehdä täydentävää tutkimusta arseenin saastuttamilla alueilla. Tässä työssä koottiin tietoutta ihmisen toiminnasta aiheutuvista arseenipäästöistä pääasiassa kokoamalla yhteen eri tutkimuslaitosten ja viranomaislaitosten jo olemassa olevat tiedot maa- ja vesiympäristöä pilaavista kohteista. Ilmapäästöjä ei tässä työssä tarkasteltu. Olemassa olevia tietoja mahdollisista ihmisen toiminnasta aiheutuvista arseenipäästöistä etsittiin selvittämällä minkä tyyppisessä teollisuudessa arseenia käytetään ja mitä käytössä olevia tai käytöstä poistettuja arseenipitoisia kemikaaleja on ollut markkinoilla. Arseenia on käytetty mm. puunkyllästeissä, tietyissä kasvintorjunta-aineissa sekä muoviteollisuudessa mikrobien torjunnassa. Myös tietyt metalliteollisuuden tuotteet sisältävät sivuttuotteena arseenia (lyijyakut ja haulit). Projektissa tarkasteltiin myös laajemmin teollisuusjätteistä ja energiantuotannosta sekä jätehuollosta, kuten toiminnassa olevista tai suljetuista kaatopaikoista sekä kaivostoiminnasta toiminnasta aiheutuvista arseenipäästöistä.

Projektin aikana tehtiin myös pienimuotoisia lisätutkimuksia entisen suolakyllästämön pilaamalla maa-alueella sekä kahden suljetun kaivosalueen ympäristössä. Lisäksi arseenipitoisuuksia mitattiin myös kaivoksien läheisyyteen sijoittuvista pintavesistä sekä kunnallisista ja teollisuusjätevesistä ennen ja jälkeen jäteveden puhdistuksen.

Suomen ympäristökeskuksen ja muiden viranomaisten ylläpitämät rekisterit ja tietokannat kemikaaleista (KETU), pilaantuneista maa-alueista (MATTI-järjestelmä) ja pintavesistä (PIVET) antoivat hyödyllistä tietoa pääasiallisesta arseenin aiheuttamasta pilaantumisesta. Lisätietoja saatiin myös insinööritoimistojen tekemistä ympäristöteknisistä tutkimuksista, riskiarvioinneista ja kunnostussuunnitelmista sekä PIRin omien tutkimusten tuloksista ja julkaisuista. Kaivostoiminnan ympäristövaikutuksista etsittiin tietoa lisäksi geologisista julkaisuista. Pirkanmaan ympäristökeskuksen ympäristöviranomaisilta tiedusteltiin mahdollisista arseenin saastuttamista kohteista ja muiden paikallisten ympäristökeskusten ja kuntien tutkimuksia on käytetty tietolähteinä raporttia laadittaessa.

Tämän hetken tiedon perusteella ihmisen toiminnasta aiheutuvaa maaperän pilaantumista arseenilla on eniten aiheuttanut sahatavaran kyllästystoiminta sekä ampumaratatoiminta. Puunkyllästämöt, joissa on käytetty CCA-kyllästettä eli arseenia, kromia ja kuparia sisältävää puunkyllästeainetta, osoittautuivat suurimmaksi arseenisaastuttajaksi myös Pirkanmaalla. Ongelma on suurin vanhoilla kyllästämöillä, joissa kyllästettä käsiteltiin huolimattomasti, ja CCA-käsiteltyä puuta saatettiin varastoida suoraan maaperän päälle, jolloin kylläste pääsi valumaan suoraan maaperään. Kyllästämön maaperän arseenipitoisuudet voivat olla jopa 6700 mg/kg (keskiarvo 373 mg/kg). Ampumaradoilla arseenin pilaantumista aiheuttaa maaperään jäävät haulit, missä ne ilman ja sadeveden vaikutuksesta rapautuvat ja vapauttavat raskasmetalleja maaperään ja pohjaveteen. Haulikkoampumaradoilla kuitenkin lyijy (jopa 14000 mg/kg) on päähaitta-aineena arseenin aiheuttaessa pienemmän ympäristöriskin (1.1 - 28 mg/kg). Muita arseenin kuormittajia voivat olla vanhat nahan parkitustehtaat, öljynjalostamot ja romuttamot.

Kaivosteollisuus on yksi merkittävistä arseenin lähteistä. Malminlouhinta tuottaa suuria määriä sivukiveä ja rikastehiekkaa. Louhittavan malmin koostumuksesta ja sen arseenipitoisuudesta riippuen, arseenimineraalien tai arseenipitoisten sulfidien päästessä kosketuksiin ilman ja sadeveden kanssa, muodostuu raskasmetallipitoisia happamia kaivosvesiä, jotka pilaavat ympäröiviä pinta- ja pohjavesiä. Pirkanmaan kaivosalueilla on hyvin vähän tietoa arseenipäästöistä. RAMAS-projektissa Ylöjärven rikastehiekka-alueelta kerätyissä maaperänäytteissä arseenipitoisuus oli korkea (1000 - 2200 mg/kg), mutta arseenin liukoisuus alhaista (0.01 - 0.45 % kokonaispitoisuudesta). RAMAS tutki myös arseenin kulkeutumista Ylöjärven Cu-W kaivoksesta lähialueen pintavesiin sekä arseenin esiintymistä puro- ja järvisedimenteissä. Vesinäytteet osoittivat, että kaivostoiminnalla on vielä nykyäänkin vaikutusta pintavesien arseenikuormaan (75.6 µg/l As noin kaksi kilometriä kaivoksesta alavirtaan). Puro- ja järvisedimenttien avulla puolestaan kaivostoiminnan aikaiset sedimenttikerrostumat voitiin erottaa korkean arseenipitoisuuden avulla jopa Näsijärvestä, missä tausta-arvot olivat 17 mg/kg, mutta kaivostoiminnan aikaiset arvot olivat 235 mg/kg.

Vanhojen kaatopaikkojen huono eristys ja huolimaton jätteenlajittelu ovat aiheuttaneet saastumista kaatopaikkojen ympäristössä. Suurin osa vanhoista kaatopaikoista on suljettu nykyään, ja uudet rakennetaan ympäristönormeja noudattaen. Yleisesti arseenin pitoisuudet kaatopaikkojen suotovesissä ovat olleet alhaisia (keskimäärin 9.5 µg/l As suomalaisilla yhdyskuntakaatopaikoilla), kun Pirkanmaalla yhden tavanomaisen jätteen kaatopaikan suotoveden arseenipitoisuus on vaihdellut välillä 1.8 - 317 µg/l (keskiarvo 37 µg/l). Arseenipitoisuudet eivät ole yleensä korkeita eri teollisuuden jätteissä. Esimerkiksi metallinteollisuuden jätteissä arseenia on ollut vain <0.01 - 0.03 mg/kg, kun taas kyllästetty jätepuu tai CCA-kyllästeillä pilaantuneet maamassat voivat sisältää jopa 12000 mg/kg arseenia. Energiantuotannosta syntyy tuhkaa ja polttoaineesta riippuen niiden arseenipitoisuudet voivat vaihdella (3 - 34 mg/kg). Yleensä jätteen poltosta syntyvissä tuhkissa arseenipitoisuudet voivat olla korkeita (49 - 320 mg/kg). Tutkimustulosten perusteella arseenin liukoisuus tuhkista on kuitenkin melko alhaista.

Muita pistemäisiä arseenin kuormittajia ovat mm. vanhat nahan parkitustehtaat, öljynjalostamot ja romuttamot. Ympäristöriskin saattoi aiheuttaa arseenia sisältävien kemikaalien tai raaka-aineiden käsittely, huolimaton varastointi, jätehuolto tai viemäröinti. Lisäksi esim. turkistarhat ja muoviteollisuus voivat olla arseenin lähteitä vaikkakaan arseeni ei välttämättä ole pääsaastuttaja. On hankalaa saada tietoa tällaisista tapauksista, ja ongelmat tulevat yleensä ilmi vasta, kun alueella suoritetaan kattava riskinarviointi.

Yleisesti ottaen Pirkanmaalla arseenin saastumisriski on pientä ja hyvin pistemäistä verrattuna muuhun Eurooppaan. Euroopan geokemiallinen atlas antaa hyvää tietoa arseeniongelmista Euroopassa. (Salminen *et al.* 2005). Mm. eteläisessä Isossa Britanniassa, Pohjois-Espanjassa, Ranskassa ja Sveitsissä maaperän arseenipitoisuudet ovat koholla, ja Etelä-Portugalissa, Etelä-Espanjassa, Ranskassa sekä Unkarissa purovesien arseenipitoisuudet ovat koholla (Salminen *et al.* 2005).

Tiedonkeruu arseenin pitoisuuksista ja päästölähteistä osoittautui hankalaksi, koska mitään yhtenäistä aineistoa ei ole saatavilla ja usein tuloksia arseenista löytyy julkaisemattomista tai epävirallisista raporteista. Monesti arseenista ei myöskään ollut analysoitua tietoa, ellei sen ole ennalta tiedetty olevan yksi pilaantumista aiheuttavista haitta-aineista tutkittavassa tai kunnostettavassa kohteessa. Tästä syystä jatkotutkimuksia ja lisää tietoa arseenista tarvitaan lisäämään ympäristötietoisuutta kohteiden mahdollisesta arseenipilaantumisesta. Arseeni tulisi systemaattisesti seurata pintavesien ja kaatopaikkojen suotovesistä sekä maaperästä ja erilaisista kiinteistä jätemateriaaleista. Myös eri haitta-aineiden yhteisvaikutuksia ja niistä aiheutuvia ympäristöhaittoja tulisi tutkia enemmän. Ympäristötietoisuuden lisäämisen ja alkuaineiden käyttäytymisen ymmärryksen lisäksi ennaltaehkäisy on hyvä tapa välttyä ihmisen toiminnan aiheuttamalta saastumiselta.

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APPENDIX

Appendix 1. Different anthropogenic sources of soil contamination and the potential contaminants released into the environment.

human activities	**potential contaminants**
animal shelters	nutrients, microbes, heavy metals and arsenic
commercial gardens	pesticides, heating oils
textile industry	color agents, organic solvents, paints, varnishes, glues, chromium
leather and fur industry	chromium, cyanides, aromatic and chlorinated hydrocarbons
timber mills	chlorophenols, dioxins, furans
wood impregnation plants	arsenic, copper, chromium, creosote, PAHs
plywood industry	pesticides, glues, formaldehyde, resins
petrol stations, oil storages	BTEX-compounds, PAHs, MTBE, TAME, lead
foundry	heavy metals, PAHs, dioxins
mine	heavy metals, concentrating agents, cyanide
steel industry	heavy metals, oil hydrocarbons, sulfur compounds
metal producing industry	heavy metals, oil hydrocarbons, chloroparaffins
surface handling industry	heavy metals, cyanides
electronic industry	heavy metals, solvents
rubber and plastic industry	solvents, resins, phtalates, catalytic metals
forest industry	chlorophenols, solvents, oil hydrocarbons, PCBs, mercury
medicine industry	solvents, high molecular compounds
chloroalkali industry	mercury, dioxins, other organochloro compounds
paint industry	heavy metals, VOC, pesticides, arsenic, selenium
other chemical industry	different solvents, catalytic metals
oil product industry	BTEX compounds, PAHs, aliphatic hydrocarbons, arsenic, lead, MTBE
graphic industry	heavy metals, VOC, arsenic, lead, MTBE
glass industry	Lead, arsenic and other heavy metals, phenols
element industry	phenols, PCBs
construction insulation industry	phenols, asbestos, other mineral fibers
shooting ranges	lead, arsenic and other heavy metals, oils
chemical laundries	tri- and tetra-chloroethene, dioxin
food industry	solvents, protection agents
gas plants	PAHs, cyanides, phenols
other energy plants	oils, PAHs
container cleaner plants	solvents, oils, dioxins, organochlorides
landfills	cyanides, PCBs, chlorophenols, heavy metals
garages	VOCs, metals, oil hydrocarbons
rail way field	oil hydrocarbons, heavy metals, VOCs, PAHs, creosote

PAH = polyaromatic hydrocarbons
BTEX compounds = sum of benzene, toluene, ethylbenzene and xylenes
MTBE = methyl-tert-butyl-ether
TAME = tert-amyl-methyl-ether
PCB = polychlorinated biphenyls
VOC = volatile organic compounds

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

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

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