



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



Arsenic removal from groundwater and surface water - Field tests in the Pirkanmaa Region, Finland

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ABSTRACT

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The arsenic removal in field demonstration was conducted in two test sites in relation to the RAMAS project addressing the natural and anthropogenic arsenic risks and their management in the Pirkanmaa region. The tests were conducted using drilled well water at Säijä School and surface water at the Ylöjärvi mine site. Arsenic concentrations in both sites are high with the average above 100 µg/L. The arsenic at the Säijä site is considered to represent natural arsenic occurrence, while the Ylöjärvi mine is described as an anthropogenic arsenic source. The objective of this study was to evaluate the capacity and effectiveness of the arsenic removal using adsorbent filter/filtration, and to investigate the relevant factors that may influence the efficiency of the method under different test conditions. The tests were based on the ferric oxo-hydroxides adsorbent filters, CFH 12 and CFH 0818, developed by Kemira.

A field test with the drilled well water at Säijä applying the CFH 12 filter demonstrated that the treatment process is capable to reduce the arsenic concentrations from 500 µg/L to less than 10 µg/L. With a 36 L of CFH 12 adsorbent, it was possible to treat 54 m³ of water. If the flow rate is optimized to provide longer contact times, the removal capacity can be utilized even more efficiently. In the bedrock groundwater the arsenite (As III) was dominating over As (V). The removal of arsenite was excellent, even better than for arsenate. The filter was effective for heavy metals as well.

The surface water at Ylöjärvi mining site was treated with CFH 0818, which has a better filtering capacity. Although, in the beginning the filter was able to remove 70.4 % of the arsenic (from 123 to 36.4 µg/L), the efficiency was lower than expected. This was probably due to the high contents of organic matter in the water. Organic material may block the filter pores and hence reduce the adsorption capacity. The pre-treatment process using e.g. ferric salt is recommended for raw water that contains high organic matter before the arsenic removal with filtration process is done.

Laboratory experiments were done to define an optimal flow rate and to establish an efficiency baseline for the CFH 12 and CFH 0818 filters. In these tests a water containing 50 µg/L As was used. The experiments showed, that at this arsenic level very large water volumes can be treated with ferric oxo-hydroxide adsorbent to meet the requirements for drinking water.

The arsenic removal method using the ferric oxo-hydroxides adsorbent filter is a simple and efficiency method. The removal cost per household depends strongly on the arsenic concentration in the well water. The arsenic removal cost using CFH 12 adsorbent for a well water containing 500 µg/L of arsenic would be about 3.10 €/m³. For the water containing about 50 µg/L of arsenic, the cost would be 0.094 €/m³ when using the CFH 12 adsorbent and 0.067 €/m³ if using CFH 0818 adsorbent.

The disposal of spent adsorbent media has been evaluated based on TCLP test, which is widely used in USA. Based on this test the leaching rate of arsenic from the CFH adsorbent is within acceptable limits and the used CFH material could be disposed as non-hazardous substance in USA.

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TIIVISTELMÄ

Backman, B., Kettunen, V., Ruskeeniemi, T., Luoma, S., Karttunen, V., 2007. Arseenin poisto pohjavedestä ja pintavedestä – Kokemuksia Pirkanmaan kenttäkokeista. Geologian tutkimuskeskus, Erikaisjulkaisut, 42 sivua, 15 kuvaa, ja 7 taulukkoa.

Pirkanmaan arseeniriskien arviointiin ja riskien hallintaan liittyen tehtiin RAMAS projektin puitteissa arseenin poistokokeita kahdessa eri kohteessa. Säijän koulun porakaivovesi edustaa kohdetta, jossa arseenipitoisuus on kohonnut luontaisista syistä johtuen ja Ylöjärven kaivosalueen pintavesien kohonneen arseenin katsotaan johtuvan ihmisen toiminnasta. Molemmissa kohteissa arseenipitoisuudet ovat varsin korkeita, selvästi yli 100 µg/L. Testien tarkoituksena oli tutkia Kemiran kehittämien granuloitujen ferrihydroksidien, CFH 12 ja CFH 0818, käyttökelpoisuutta arseeninpoistossa ja tarkastella tekijöitä, jotka vaikuttavat suodatinmassan suodatustehoon erilaisissa olosuhteissa.

Porakaivoveden arseenin poistokokeessa käytettiin 36 L:n CFH 12 suodatinta. Porakaivoveden arseenipitoisuus oli noin 500 µg/L. Arseenin poiston jälkeen pitoisuus laski selvästi alle 10 µg/L, mikä on talousveden suurin sallittu pitoisuus. Suodattimen kapasiteetti riitti 54 m³ käsittelyyn. Suodatustehoa voidaan parantaa säätämällä veden virtausnopeutta siten, että veden ja suodatinmassan välinen reaktioaika on optimaalinen. Kaivovedessä vallitseva liukoisen arseenin muoto oli arseniitti (As III), jota suodatin poisti tehokkaasti, jopa tehokkaammin kuin arsenaatti (As V). Suodatin poisti tehokkaasti myös rautaa, mangaania, molybdeenia, fosforia, fosfaattia, antimonia, lyijyä ja uraania.

Ylöjärven pintavesikohteessa käytettiin kapasiteetiltaan tehokkaampaa suodatinta CFH 0818. Aluksi suodatin poisti vedestä noin 70 % arseenista, jolloin pitoisuus laski tasolta 123 µg/L tasolle 36,4 µg/L. Suodatinmassan arseeninpoistokapasiteetti oli kuitenkin odotuksia heikompi. Tämä todennäköisesti selittyy sillä, että pintavedessä on runsaasti orgaanista ainesta, joka täyttää suodattimen huokoset ja estää arseenin kiinnittymisen suodatinmassaan. Pintavesille suositellaankin esikäsittelyä ennen arseeninpoistoa.

CFH 12 ja CFH 0818 suodattimia testattiin myös laboratorio-olosuhteissa, jossa vesijohtoveteen oli lisätty 50 µg/L arseenia. Koe osoitti, että tällä arseenitasolla suodattimien teho riittää suurien vesimäärien käsittelyyn.

Arseeninpoistomenetelmä, joka perustuu ferrihydroksisuodattimeen on yksinkertainen ja tehokas. Arseeninpoiston kustannukset riippuvat talousveden arseenipitoisuudesta. Kun arseenipitoisuus on noin 500 µg/L ovat käsittelykustannukset noin 3,10 €/m³ kun käytetään CFH12 suodatinta. Kun pitoisuus on noin 50 µg/L ovat kustannukset CFH12 suodattimella enää 0,094 €/m³ ja CFH0818 suodattimella 0,067 €/m³.

Suodattimen hävittäminen on testattu USA:ssa käytettävällä TCLP testillä, jonka perusteella CFH suodattimet ovat kaatopaikkakelpoista materiaalia ainakin USA:ssa.

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PREFACE

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

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

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

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

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

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

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

LIST OF ABBREVIATIONS

AA	activated alumina
AR	<i>aqua regia</i>
BV	bed volume
C/F	coagulation/filtration
CCA	Copper-Chromium – Arsenic
CFU	colony-forming unit
cm	centimetre
EBCT	empty bed contact time
EC	electric conductivity
EDTA	ethylene diaminetetraacetic acid
Eh	redox potential
ha	hectare (1 ha = 0.01 km ²)
IC	ion chromatographic
ICP-AES	inductively coupled plasma - atomic emission spectrometry
ICP-MS	inductively coupled plasma – mass spectrometry
IX	ion exchange
km ²	square kilometre
L/min	litre per minute
µg/L	micrograms per litre
µm	micrometer
m ³ /d.	cubic meter per day
MF	microfiltration membrane
mg/kg	milligram per kilogram
ml	millilitre
mmol/L.	millimole per litre
Mt	million ton
NaClO	sodium hypochlorite solution
NF	nanofiltration membrane
NOM	natural organic matter
°C.	degree Celsius
RO	reverse osmosis
SOCs	synthetic organic compounds
SS	suspended solids
TC	toxicity characteristic
TCLP	toxicity characteristic leaching procedure
UF	ultrafiltration membrane
US EPA	United States Environmental Protection Agency
UV	ultraviolet

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1. INTRODUCTION

Arsenic is a world-wide problem, which concerns millions of people. There are many countries where arsenic in drinking-water has been detected at high concentrations. These include Argentina, Australia, Bangladesh, Chile, China, Hungary, India, Mexico, Peru, Thailand, and USA. In many countries adverse health effects have been linked to arsenic despite of the delayed response to the exposure and poorly understood physiological mechanisms. Since 1958 the WHO guideline value for arsenic has declined from 200 µg/L to the present 10 µg/L as more evidence is gained pointing to the health risks related to long-term exposure for relatively low arsenic levels, and there have been discussions about even lower limit values. The health concerns combined with the fact that the arsenic levels in raw waters exceed the guidelines values so frequently, have motivated the development of arsenic removal technologies for decades. The need for effective, reliable, technically simple and cheap water treatment methods has resulted in numerous solutions. However, although many techniques seem to work, further development is still needed.

A relatively new aspect is the concept of ecological risk, which presumes the protection of environment against adverse effects generated by anthropogenic activities. When the treatment of contaminated waters, for example, from an industrial site or a landfill area is considered the volumes are easily in different magnitude compared to drinking-water treatment and the chemical challenges may be more severe due to complex chemistry although the target levels themselves may be higher.

The RAMAS project is addressing the risk assessment and risk management issues related to the natural and anthropogenic arsenic in the Pirkanmaa region. The Pirkanmaa region is located in southern Finland, about 160 km northwest of Helsinki, in the Häme province (Fig. 1). In 2006, this 14 700 km² area with 455 000 inhabitants consisted of 33 municipalities. The industrial and commercial centre of the area is the city of Tampere (www.pirkanmaa.fi/english/). The area is located in the middle of a regional arsenic anomaly revealed in the nation-wide survey on till geochemistry. The arsenic in the till fines originates from the underlying bedrock, which comprises ore potential horizons. Arsenopyrite is a relatively common mineral in these units. A proportion of the arsenic is introduced to the groundwaters, which has provoked concern on the possible ecological and health risks related to the elevated arsenic levels (Backman *et al.* 2006).

Elevated arsenic concentrations in bedrock groundwater in southern part of the Pirkanmaa regions was well known since the early 1990's (Backman *et al.* 1994, Idman 1996, Juntunen *et al.* 2004, Backman *et al.* 2006). Most of the wells with high arsenic content were used as a private water supply, but arsenic is not a problem for public water supply in the Pirkanmaa region. The public water supply there based totally on shallow groundwater from the overburden and on surface water.

In addition to the natural arsenic sources a number of anthropogenic sites have been identified as potential risk areas Parviainen *et al.* (2006). They are mainly abandoned wood preservative plants, where Cu-Cr-As salt spills (CCA) have contaminated the soils. The arsenic concentrations may be high (from 3 up to 12000 mg/kg), but the sites are areally limited.

Another important source of anthropogenic arsenic is mining industry. Mining operations produce huge quantities of country rock and tailings and the environmental impacts depend on the amount of arsenic bearing minerals in the exploited rock. Arsenic minerals and As-bearing sulphides tend to dissolve in contact with rainwater and air, giving rise to acid mine drainage. Unless properly treated, arsenic and heavy-metal bearing waters may end up in the surrounding rivers and lakes, as

well as in the groundwater. At least two out of the five sulphide mines located in the Pirkanmaa region, the closed mines of Haveri and Ylöjärvi, are known to have tailings areas with high arsenic concentrations and also arsenic transport has been observed (e.g. Carlson *et al.* 2002, Parviainen *et al.* 2006, Bilaletdin *et al.* 2007).

The Pirkanmaa region provides an excellent possibility to test various remediation techniques due to the different types of arsenic sources, different arsenic concentration levels and geological context. However, already during the planning stage of the project it was decided to concentrate on the removal of arsenic from ground- and surface waters. It was assumed that the major health and ecological risks would be related to the dissolved arsenic. Since one of the partners, Kemira, is a global company supplying water treatment products, equipment and services and they were already developing water treatment applications based on a granulated ferrihydroxide (Kemira GFH), it was natural to concentrate on water treatment aspects.

The objective of this study was to evaluate the capacity and effectiveness of the arsenic removal using adsorbent filter/filtration, and to investigate the relevant factors that may influence the efficiency of the method under different test conditions.

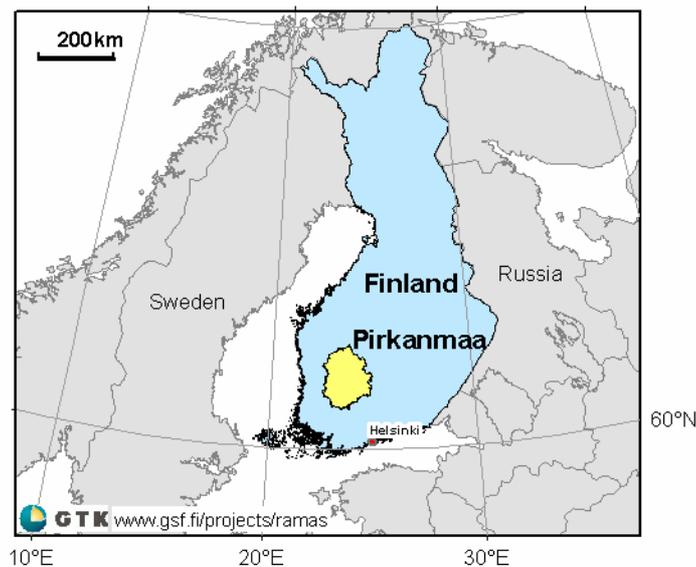


Figure 1. The study area of Pirkanmaa in southern Finland (Base map data ©National Land Survey of Finland).

2. NATURAL ARSENIC IN THE PIRKANMAA REGION

The Pirkanmaa region is distinctly dimidiated as to the occurrence of arsenic (Backman *et al.* 2006). Virtually all anomalous arsenic concentrations, either in bedrock, soil or groundwater, are observed in the southern half of the area. There are clear geologic grounds for this distribution. The rock types encountered in the anomalous area contain arsenic bearing minerals, basically arsenopyrite, and they are also ore potential.

The Pirkanmaa region can be divided in three geologically distinct units based on the dominant rock types encountered in the area (Fig. 2). The main geological subdivisions in the study area are the Central Finland Granitoid Complex (CFGC) in the north, the Tampere Belt (TB) in the centre, and

the Pirkanmaa Belt (PB) in the south (Rasilainen *et al.* 2007, Backman *et al.* 2006). The CFGC mainly consists of tonalites, granites and granodiorites with minor proportions of supracrustal rocks and mafic plutonic rocks (Korsman *et al.* 1997). The TB is mainly composed of turbiditic metasedimentary rocks and felsic-intermediate arc-type metavolcanic rocks and plutonic intrusions that cut the supracrustal sequence (Ojakangas 1986, Kähkönen 1989, Kähkönen & Leveinen 1994). In the PB area, mafic and ultramafic plutons and granitoids cut the migmatitic metasedimentary rocks, sporadically containing graphite-bearing gneiss interlayers (Nironen *et al.* 2002).

All the rock types encountered in the area are crystalline hard rocks. Primary sedimentary or volcanic textures have been only sporadically preserved after metamorphic and tectonic deformations. The low porosity of these rocks, generally < 0.5 %, allows conductive groundwater flow only along a fractured network formed during numerous tectonic events (Backman *et al.* 2006).

The overlying till in the volcanic-sedimentary belts (TB & PB) is enriched in gold, arsenic, silver, cobalt, copper, lithium, molybdenum, phosphorus, antimony, uranium, and zinc (Koljonen *et al.* 1992). The abundance of the sulphide-forming elements Ag, As, Cu, Mo, Sb, and Zn are above average in comparison with other sites in Finland. The arsenic contents in three different geological subdivisions are presented in Table 1 and the spatial distribution of arsenic in bedrock is shown in Figure 2.

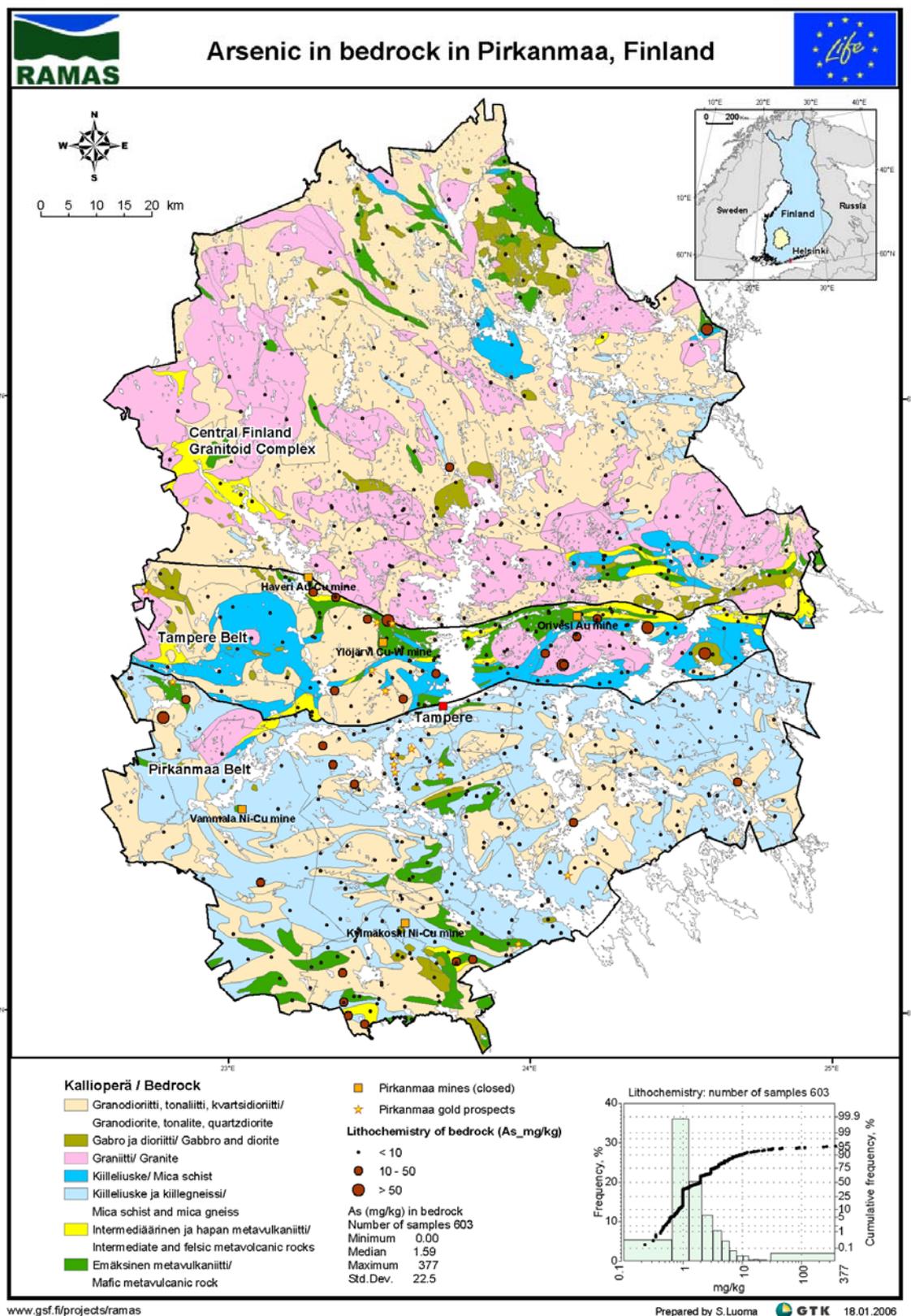


Figure 2. Bedrock in the Pirkanmaa region and arsenic content in bedrock. The ground colour is bedrock type and the red symbols represent arsenic content in bedrock. The yellow symbols are mines and gold prospecting sites. (Geological mapping data © Geological Survey of Finland, Base map data © National Land Survey of Finland).

Table 1. *Aqua regia* leachable arsenic concentrations in the bedrock of the three geological subdivisions in Pirkanmaa. See the map in Figure 2.

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

Based on the 1 272 arsenic analyses from drilled wells available from the Pirkanmaa region the arsenic values vary from < 0.05 to 2 230 µg/L (Backman *et al.* 2006). The median value is 2.5 µg/L and mean value 34.79 µg/L. The studied bedrock wells were 75 meters deep in average. The predominant groundwater type was Ca-HCO₃ and in general the waters conformed the requirements for good drinking water. However, 22.5 % of the wells exceeded the health limit value for arsenic, 10 µg/L. The spatial distribution of arsenic in bedrock groundwater is presented in Figure 3 together with the geological characteristics. The elevated arsenic contents in groundwaters are observed in areas, where the bedrock is composed of intermediate and felsic metavolcanic rocks, mafic metavolcanic and mica schists (Table 2, Fig. 3). The highest arsenic concentration observed exceeded 2 000 µg/L. The arsenic values in the granitoid area in the north are on the same low level as elsewhere in Finland, median 0.16 µg/L, N = 263 (Lahermo *et al.* 2002).

Table 2. Statistics of arsenic concentrations in groundwater in three different geological subdivisions in the Pirkanmaa region. See the map in Figure 2.

	N_valid	Mean (µg/L)	Median (µg/L)	Minimum (µg/L)	Maximum (µg/L)
All	1272	34.79	2.5	<0.05	2230
CGFC	133	1.35	0.61	<0.05	10
TB	588	56.69	5.5	<0.05	2230
PB	551	20.07	1.6	<0.05	1560

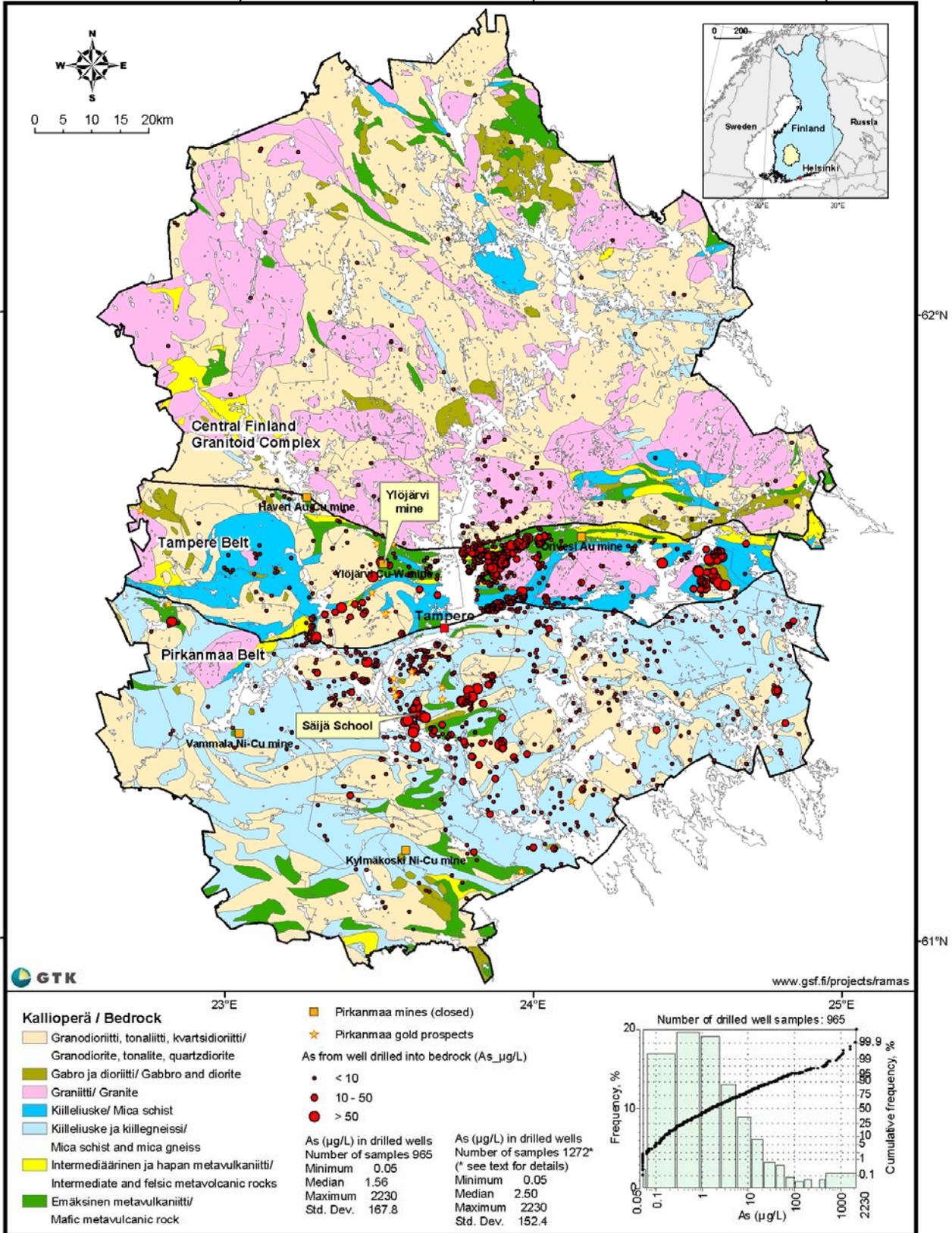


Figure 3. Arsenic concentrations in drilled wells within the main geological subdivisions in the Pirkanmaa region: the Central Finland Granitoid Complex (CFGC) in the north, the Tampere Belt (TB) in the centre, and the Pirkanmaa Belt (PB) in the south. The limit value for arsenic is 10 µg/L. The studied test areas are highlight on the map.

3. ARSENIC REMOVAL METHODS

Different arsenic removal techniques have been evaluated in literatures. One extensive study has been carried out by the US Environmental Protection Agency (US EPA). In this report the principles of some commonly applied arsenic removal methods are described based on quotations from the USEPA report. More detailed evaluation can be found from the USEPA report “Technologies and Costs for Removal of Arsenic from Drinking Water” (US EPA 2000).

3.1 Precipitation process

Coagulation/filtration (C/F) is a treatment process by which the physical or chemical properties of dissolved colloidal or suspended matter are altered such that agglomeration is enhanced to an extent that the resulting particles will settle out of solution by flotation, gravity or will be removed by filtration. Coagulants change surface charge properties of solids to allow agglomeration and/or enmeshment of particles into a flocculated precipitate. In either case, the final products are larger particles, or floc, which more readily filter or settle under the influence of gravity.

The coagulation/filtration process has traditionally been used to remove solids from drinking water supplies. However, the process is not restricted to the removal of particles. Coagulants render some dissolved species [e.g. natural organic matter (NOM), inorganics, and hydrophobic synthetic organic compounds (SOCs)] insoluble and the metal hydroxide particles produced by the addition of metal salt coagulants (typically aluminum sulfate, ferric chloride, or ferric sulfate) can adsorb other dissolved species.

The chemical costs in precipitation process are usually lower compared to adsorption process. However, precipitation and separation process requires much higher investment compared to adsorption system. Major components of a basic coagulation/filtration facility include chemical feed systems, mixing equipment, basins for rapid mix, flocculation, settling, filter media, sludge handling equipment, and filter backwash facilities. Settling may not be necessary in situations where the influent particle concentration is very low. Treatment plants without settling are known as direct filtration plants. For this reason it is usually preferable to use precipitation process when water flow is high and/or when arsenic concentration in raw water is high ($> 100 \mu\text{g/L}$).

As (III) removal during coagulation with alum, ferric chloride, and ferric sulfate has been shown to be less efficient than As (V) under comparable conditions.

Coagulation technology can successfully achieve As (V) removals greater than 90 percent. With this technology it is possible reduce arsenic levels below $5 \mu\text{g/L}$. Moreover, if optimal operating practices are adopted, it is anticipated that effluent levels of less than $3 \mu\text{g/L}$ will be obtainable. Arsenic in the pentavalent arsenate form (As V) is more readily removed than the trivalent arsenite form (As III). At pH 7.6 or lower iron and aluminum coagulants are of equal effectiveness in removing As (V).

However, iron coagulants are advantageous if pH is above 7.6, if soluble coagulant metal residuals are problematic, or if As (III) is present in the raw water. In general, higher arsenic removal efficiencies are achieved with increased coagulant dosages. The effectiveness of iron coagulants in removing As (III) diminishes at pH 6.0. Recent studies have shown that arsenic removal is independent of initial concentration. This contradicts initial findings, which indicate that arsenic removals decrease with increasing initial concentrations. The presence of sulfates significantly

decreases As (III) removal, but only slightly affects As (V) removal. At pH higher than 7.0, removal of As (V) increases in the presence of calcium.

3.2 Adsorption by activated alumina

Activated Alumina (AA) is a physical/chemical process by which ions in the feed water are sorbed to the oxidized AA surface. AA is considered an adsorption process, although the chemical reactions involved are actually an exchange of ions. Activated alumina is prepared through dehydration of $\text{Al}(\text{OH})_3$ at high temperatures, and consists of amorphous and gamma alumina oxide. AA is used in packed beds to remove contaminants such as fluoride, arsenic, selenium, silica, and natural organic matter (NOM). Feed water is continuously passed through the bed to remove contaminants. The contaminant ions are exchanged with the surface hydroxides on the alumina.

When adsorption sites on the AA surface become filled, the bed must be regenerated. Regeneration is accomplished through a sequence of rinsing with regenerant, flushing with water, and neutralizing with acid. The regenerant is a strong base, typically sodium hydroxide; the neutralizer is a strong acid, typically sulfuric acid.

Many studies have shown that AA is an effective treatment technique for arsenic removal. However, arsenic adsorption capacity of activated alumina is significantly lower compared to ferric oxo-hydroxide.

Factors such as pH, arsenic oxidation state, competing ions, empty bed contact time (EBCT), and regeneration have significant effects on the removals achieved with AA. Other factors include spent regenerant disposal, alumina disposal, and secondary water quality.

AA processes may produce changes to the effluent water quality. When pre-treatment is used to reduce the pH to low levels (less than 6.0) to optimize the process, the effluent pH will be less than typically desired in the distribution system. For this reason, post-treatment corrosion control to raise the pH would be necessary for those systems.

3.3 Ion exchange process

Ion exchange (IX) is a physical/chemical process by which an ion on the solid phase is exchanged for an ion in the feed water. This solid phase is typically a synthetic resin, which has been chosen to preferentially adsorb the particular contaminant of concern. To accomplish this exchange of ions, feed water is continuously passed through a bed of ion exchange resin beads in a downflow or upflow mode until the resin is exhausted. Exhaustion occurs when all sites on the resin beads have been filled by contaminant ions.

At this point, the bed is regenerated by rinsing the IX column with a regenerant - a concentrated solution of ions initially exchanged from the resin. The number of bed volumes that can be treated before exhaustion varies with resin type and influent water quality. Typically from 300 to 60 000 BV can be treated before regeneration is required. In most cases, regeneration of the bed can be accomplished with only 1 to 5 BV of regenerant followed by 2 to 20 BV of rinse water.

Important considerations in the applicability of the IX process for removal of a contaminant include water quality parameters such as pH, competing ions, resin type, alkalinity, and influent arsenic concentration. Other factors include the affinity of the resin for the contaminant, spent regenerant and resin disposal requirements, secondary water quality effects, and design operating parameters.

It has been shown, that in optimal operation conditions it is possible to reach 3-5 $\mu\text{g/l}$ As concentration after ion exchange treatment. The drawback in ion exchange process is that it is quite complicated with regeneration equipments and therefore it requires more operation personnel compared to e.g. adsorption processes.

3.4 Nanofiltration and reverse osmosis

Nanofiltration (NF) membranes are capable of removing significant portions of the dissolved arsenic compounds in natural waters due to their small pore size. NF will primarily remove divalent ions (e.g. Ca, Mg), but not monovalent salts (e.g. Na, Cl). Through size exclusion, NF can remove both dissolved As (V) and As (III). This makes NF a reliable arsenic removal process for groundwater, which contains up to 90 % dissolved arsenic. The small pore size, however, makes NF membranes more prone to fouling than ultrafiltration (UF) or microfiltration (MF) membranes. The application of NF for surface water treatment is typically not accomplished without extensive pre-treatment for particle removal and possibly pre-treatment for dissolved constituents to prevent fouling. In ground water treatment membrane fouling may also occur due to Fe and Mn contaminants and therefore it is preferred that these compounds are removed from the water before NF treatment.

Several NF studies for have been undertaken, and the results show that NF processes are effective for the removal of arsenic. Removal however depends on operating parameters, membrane properties, and arsenic speciation. The drawback in NF treatment is that As (III) removal efficiency is quite low. It is possible that only 12 % As (III) removal is achieved. Therefore it is necessary to oxidise As (III) to As (V) before NF treatment.

Reverse osmosis (RO) is the oldest membrane technology, traditionally used for the desalination of brackish water and seawater. RO produces nearly pure water by maintaining a pressure gradient across the membrane greater than the osmotic pressure of the feed water. Osmotic pressure becomes great in RO systems compared to other membrane processes due to the concentration of salts on the feed side of the membrane. The majority of the feed water passes through the membrane, however, the rest is discharged along with the rejected salts as a concentrated stream. Discharge concentrate can be substantial, between 10 % and 50 % of the influent flow depending on influent water quality and membrane properties.

The disposal of arsenic containing concentrate is considered to be major problem in RO treatment. In NF treatment the volume of arsenic containing concentrate is significantly slimmer, but treatment process for concentrate would still be needed.

Both NF and RO treatment remove also Ca and Mg salts from water. RO also removes Na. Due to this, it is possible that salts should be added to water after As removal treatment.

RO and NF equipments are also quite expensive and consume high amount of electricity. These equipments are not widely used for arsenic removal application, because there are many less expensive techniques available.

4. THE TEST SITES AND THE TEST ARRANGEMENTS

4.1 Test sites

The arsenic removal was deliberately tested in two very different cases: arsenic removal from bedrock groundwater and removal from surface waters transporting harmful components from a closed sulphide mining area. Both waters have high arsenic concentrations, but otherwise they constitute different challenges for the applied technology. In the case of drilled well the chemistry and physico-chemical conditions are assumed remain stable throughout prolonged pumping period. No redox reactions are expected to take place within the closed system between the well and filter apparatus. Also the amount of suspended particulates is insignificant. On the other hand, the run-off and precipitation driven surface waters are subject to complex chemical and physical fluctuation. The rate and direction of reactions depends on the flow rates in the catchments area and the suspended particulate load is likely to vary in a broad range.

Drilled well at the Säijä School

Säijä School is located in the Lempäälä municipality, approximately 14 km from the centre of Lempäälä and 22 km southwest of the City of Tampere. The Säijä village with about 400 inhabitants is a Lempäälä's main agriculture area. The bedrock in the area is known to be anomalous for arsenic (Figs. 3 and 4). The bedrocks in the area consist mainly of mica schist and mica gneiss with mafic metavolcanics and plutonic intrusions (e.g. granodiorite, granite). Arsenic is especially enriched in gold-potential showings in the area regardless the bedrock type. In detail the bedrock in the area is mosaic like and the rock types alternate all the time. The drilled well at Säijä School is situated in the contact zone of an ultramafic peridotite intrusion and mica gneiss. The specifications of the well construction are not available, nor the depth or the drilling date is known.

Water in bedrock is moving in faults and joints and water dissolves arsenic minerals from the bedrock and transports them sometimes quite far a way from the original source. Therefore the arsenic concentrations in the bedrock groundwater are unpredictable and variation is large. In the Säijä area, the arsenic concentrations in the drilled bedrock wells vary from 0.19 up to 911 µg/L. The well at Säijä School had very high and constant arsenic concentration, 500 µg/L. Fortunately the well is not used anymore, since a public water supply was established to the area in 2004.

The Ylöjärvi mining site

The Ylöjärvi mine is located about 18 km northeast of the city of Tampere within the Tampere Belt (TB). Low grade ore (0.75 % Cu, 0.11 % W, and 0.12 % As) was excavated from the mine between 1943 and 1966 (Fig. 3). In total 4.01 Mt of ore was processed and Cu, WO₃ and As concentrates were produced, the latter only about five years. The sulphide mineralisation contains chalcopyrite (CuFeS₂) as the main copper mineral, arsenopyrite (FeAsS) and scheelite (CaWO₄). The host rocks are mostly represented by mafic metavolcanics, which typically are strongly altered by tourmalinisation (Himmi *et al.* 1976).

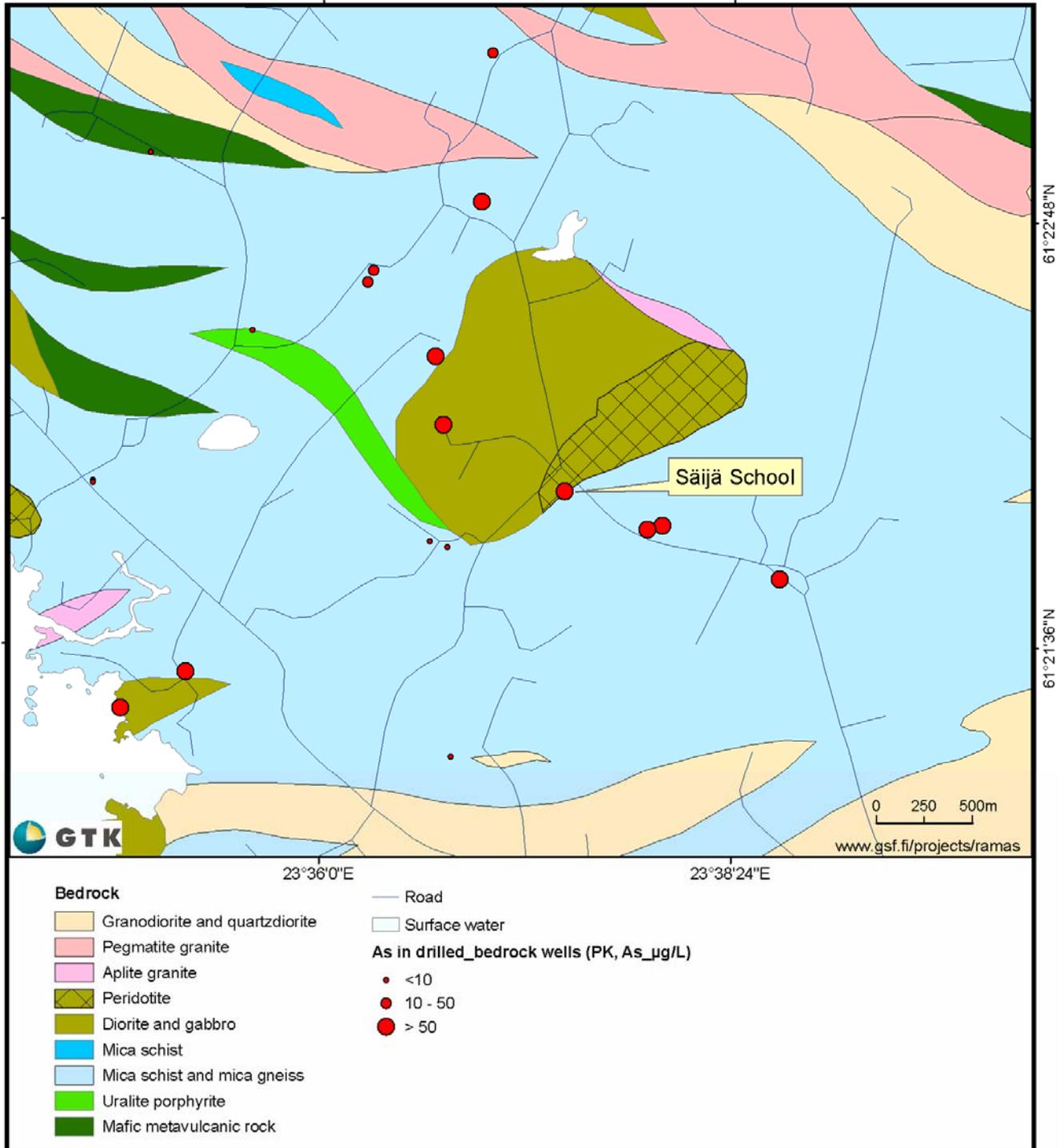


Figure 4. Location of the Säijä test site, the generalised geology of the area and the arsenic concentrations in the nearby drilled wells.

The main tailings area is approximately 17 ha ($\sim 0.17 \text{ km}^2$) and contains both tailings sand and waste rock (Carlson *et al.* 2002). A smaller tailings area ($\sim 4 \text{ ha}$), the open pit and the underground mine workings are located beneath the present Lake Parosjärvi. In total about 4 Mt of tailings is disposed to the area. Parviainen *et al.* (2006) found 1 000 – 2 200 mg/kg of arsenic from the tailings sands. From 1960 the empty galleries were backfilled with the tailings sand and 1.1 Mt of the

tailings was disposed underground. Later on the tailings area was partly covered with a layer of till and vegetated after the closure of the mine and crushed limestone was added to the discharge ditch.

The discharge of the seepage waters from the tailings area is channelled first through a ditch to Lake Parosjärvi and eventually to Lake Näsijärvi via a stream-lake system. Arsenic concentrations in the observation wells drilled in the tailings area is 3 000 – 10 000 µg/L. The long-term surface water monitoring and the stream and lake sediment analyses demonstrate that arsenic is transported and deposited along the whole route down to Lake Näsijärvi, 7 km downstream. The sediments deposited close to the outlet at Lake Näsijärvi during the active mining period contain up to 235 mg/kg of arsenic. The present load is 37 mg/kg, which is more than double to the pre-mine background level (17 mg/kg). (Parviainen *et al.* 2006, Bilaletdin *et al.* 2007). It is also noteworthy that about half of the transported arsenic is in soluble form, while the rest is bound to suspended particulate material.

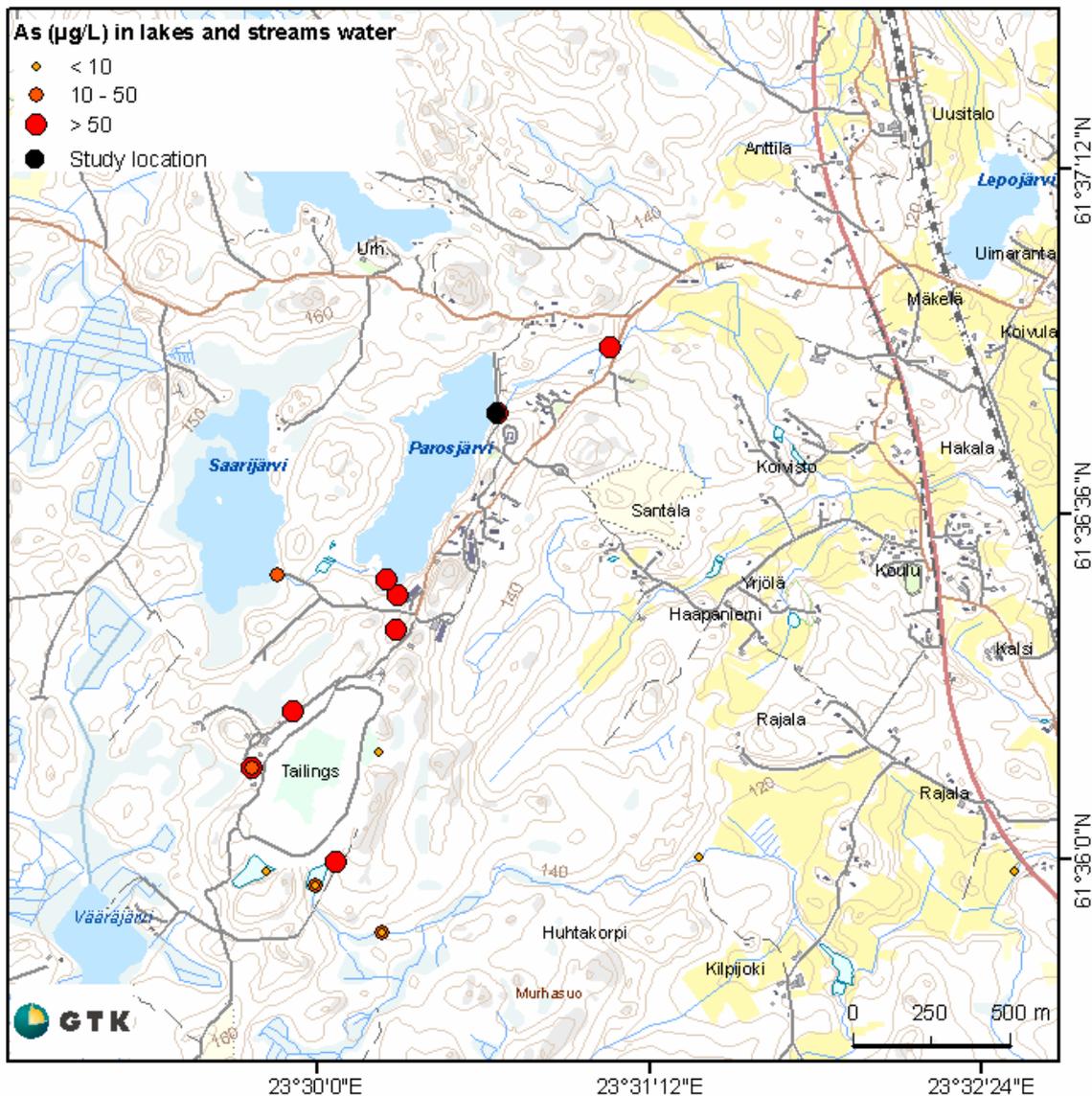


Figure 5. Arsenic concentrations in lake and streams water around the Ylöjärvi mining area. The location of the arsenic removal test site is marked by a black circle. The red symbols represent arsenic concentrations in lakes and streams water.

The arsenic removal test site was set in the Lake Parosjärvi. The raw water was taken directly from the Lake Parosjärvi near the inlet of the stream which discharges the waters to the Lake Näsijärvi. The water intake pipe was sunk about 1 meter below the water surface. The location of the test site is shown in Figure 5. The long-term median arsenic concentrations in the lake water are 68 µg/L for the near surface water and 130 µg/L for the bottom water (Bilaletdin *et al.* 2007).

4.2 The Adsorption process

Arsenic removals in both field tests were conducted using adsorption technique with the ferric oxo-hydroxides. This technique was chosen because the ferric oxo-hydroxide has proven to be highly efficient material, especially for As (V) adsorption, but also in some extents for As (III) adsorption. Adsorption involves the mass transfer of a soluble species (adsorbate) from solution to the surface of a solid phase (adsorbent). When the adsorbent is a porous media, the transport of adsorbate to adsorbent will occur through following basic steps:

Bulk solution transport. - The adsorbate is first transported from the bulk solution to the hydrodynamic boundary layer surrounding the adsorbent.

External (film) resistance to transport – The adsorbate must then pass through the hydrodynamic boundary layer to the surface of the adsorbent. The thickness of the boundary layer will depend on the velocity of the bulk solution.

Internal (pore) transport – This step occurs after the adsorbate has passed through the boundary layer. This intraparticle transport may occur by molecular diffusion through the solution in the pores (pore diffusion) or by diffusion along the adsorbent surface (surface diffusion) after adsorption takes place.

The final step is the attachment of the adsorbate onto the adsorbent surface at available sites. This step is very rapid; therefore the preceding diffusion steps will control the rate of mass transfer.

Arsenic adsorption by hydrous iron oxide follows reactions shown below (FeOH represents oxide surface site).



The adsorption technique is very simple. Arsenic containing water is conducted through adsorbent material and during the seepage arsenic is adsorbed to the solid material. Schematic picture of adsorption tank is presented below (Fig. 6).

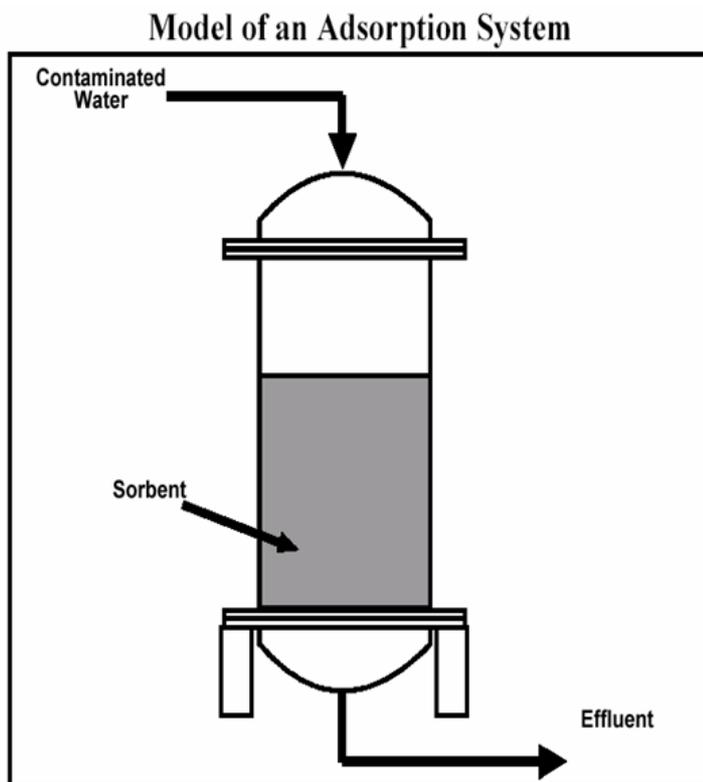


Figure 6. Water flow in adsorption tanks can be either from top to bottom or the opposite.

4.3 Field tests and samplings

Some terms related to adsorption process are widely used. These terms are defined as follows:

Bed volume (BV) is the volume of adsorbent material in the filter. If the filter is filled with 1 m³ of adsorbent material, it means that one bed volume in this filter is 1 m³ of water.

Empty bed contact time (EBCT) describes the time that is available for the contaminant in the filter to transfer from water to adsorbent material. It is calculated so that adsorbent volume (L) is divided by water flow-rate (L/min), thus 1000 L of adsorbent material and the flow-rate of 100 L/min gives the EBCT of 10 min.

4.3.1 The drilled well at Säijä

The arsenic removal test at the Säijä School was carried out between the 7th of April and the 22nd of August in 2005. Groundwater samples were collected 18 times from raw water and from treated water during this period. The arsenic speciation sampling was done seven times in connection to the conventional chemistry sampling. The samplings were carried out by the Geological Survey of Finland (GTK) and the Pirkanmaa Regional Environment Centre (PIR). The field measurements at the sampling site included temperature, pH, electric conductivity (EC), redox potential (Eh), and dissolved oxygen. Untreated water samples were taken for the physico-chemical measurements and anion analyses. A filtered (0.45 µm) and acidified (0.5 ml concentrated suprapure HNO₃ /100 ml water) sample was taken for metal and trace element analyses. Also, the control and duplicate samples were taken.

The water sample for the As (III) and As (V) analyses was first filtered (0.45 µm) and then acidified with a Na₂-EDTA (Ethylene diaminetetraacetic acid) solution (0.5 ml 0.25 M EDTA solution /100 ml water). The ion-exchange of the arsenic speciation sample was done with 1-X8 resin. The first fraction was separated in the field and the others in laboratory. A separation of different fractions was, in most cases, done within a few days of speciation sampling.

The arsenic removal filter apparatus was constructed by Kemira. The adsorbent material in the filter was commercial product of Kemira CFH 12. The product sheet is presented in Appendix 1. The filter was scaled to treat the drilled well water with exceptionally high arsenic concentration.

Water was pumped from drilled well to a pressurized water tank. The pressure in the tank was 2 – 4 bar. The water from this tank was conducted to the CFH 12 adsorbent tank. A commercially available filtration tank was used in the test. Tank height was 150 cm and the diameter 25 cm. The volume of CFH 12 in the adsorbent tank was 45 kg (~36 L). Thin layer of coarse sand was placed under the adsorbent material in order to confirm that turbidity of treated water stays at very low level. Adsorbent was backwashed after installation with water until all dust was removed from adsorbent granules. A 20 - bed volume of water was used in backwashing. The raw water-filtering rate was 10-13 L/min. This gives 3-4 min EBCT.

The filter backwashing was automatically done once a week. Adsorbent materials should be backwashed on regular basis in order to prevent blocking of the filter. Backwashing needs depend strongly on the raw water quality. If there is a high concentration of suspended solids (SS), Si or P in raw water, backwashing frequency should be increased. The correct backwashing frequency should be adjusted in the treatment plant. The frequency should be adjusted so that the needless backwashing is avoided, because in the backwashing a small part of the adsorbent material will escape from the filter.

4.3.2 The Ylöjärvi mining site

The field test at Ylöjärvi was carried out between the 13th of July and the 17th of October 2006. In this test arsenic was removed from surface water pumped from Lake Parosjärvi. Kemira CFH 0818 adsorbent was used in this trial. This adsorbent has been found to be more efficient in groundwater arsenic removal compared to CFH 12 due to the smaller granule size. Kemira CFH 0818 product sheet is presented in Appendix 2. CFH 0818 adsorbent was installed to the adsorption tank. Adsorbent was backwashed with about 100 BV of water after installation in order to remove dust from the product.

The test was carried out with the same pilot equipment that was used in Säijä trial. Adsorbent volume was 36 L and water flow of 10 L/min, which gives EBCT of 3.6 min. The pressure in the adsorption tank was < 1 bar. About 10 cm layer of coarse sand was used under the adsorption material.

The sampling site is located nearby the Technical Research Centre of the Finnish Defence Forces and the water sampling was taken by their staff. The raw water was pumped to the filter directly from the lake. Water intake pipe was about 1 m below lake water surface level. Samples were not pre-treated in Ylöjärvi. Samples from the inlet and outlet waters were delivered to the GTK's Geolaboratory in Espoo by post.

4.4 Laboratory analyses

All the analyses of groundwaters and surface waters were done in the GTK's Geolaboratory. Electric conductivity and pH were measured both in field and laboratory conditions. In the GTK's Geolaboratory, pH, conductivity and total alkalinity (as mmol HCO₃⁻/L) were determined using an automatic titrator. The main anions: F⁻, Cl⁻, Br⁻, NO₃⁻, and SO₄²⁻ were analysed using the ion chromatographic (IC) technique and PO₄³⁻ by spectrophotometric method. Chemical oxygen demand of groundwater samples was determined using the titrimetric method with KMnO₄. For the surface water samples (Lake Parosjärvi) also total suspended solids (mg/L) were gravimetrically determined. All cations and other elements were analysed by ICP-AES or ICP-MS technique. A more detailed description of the analysis techniques is presented in Table 3.

Table 3. Chemical analytical methods of the groundwater samples from the Pirkanmaa region.

Chemical Parameter	Analysing Method	Equipment, Model
pH, electric conductivity	Potentiometric and conductive measurement with an automatic titrator	Mettler Toledo DL 70
Alkalinity (HCO ₃ ⁻)	End point titration with 0.05 M HCl to pH 4.5	Mettler Toledo DL 70
Fluoride, chloride, nitrate, sulphate	Ion chromatographic determination with suppressed NaCO ₃ /NaHCO ₃ elution	Dionex DX 120
Phosphate	Spectrometric method using Ammonium-molybdate complexation	Shimadzu UV-150-02 spectrophotometer
KMnO ₄ number	Manual titration with KMnO ₄ to the equivalent point	
Ca, Mg, Na, Fe, Si (SiO ₂) and (B, Mn and K occasionally)	Inductively coupled plasma (ICP) atomic emission spectrometric (AES) analysis. The calibration for each element is performed using a blank and one calibration standard. The calibration is checked by independent Certified Reference Material water samples.	Thermo Jarrell Ash Corp. (TJA), an ICP-AES dual detector system, IRIS Advantage
Al, As, B, Cd, Co, Cr, Cu, I, K, Mn, Mo, Ni, Pb, P, Sb, Se, U, V and Zn	Inductively coupled plasma (ICP) mass spectrometric (MS) analysis. The same principle is used in the calibration as in ICP-AES analyses. Furthermore, Rh is added to all samples as an inner standard.	Perkin Elmer PE-SCIEX ICP-MS system, ELAN 6000

As (III) and As (V) species were determined using the ion-exchange technique and measured as arsenic with ICP-MS equipment. The first fraction was separated in the field and the others in laboratory. The arsenic concentrations of different fractions were measured with the ICP-MS technique in about one week of speciation sampling. A more detailed description of the method and the results, including the results of quality control samples, is presented in an earlier RAMAS report (Backman *et al.* 2006).

In Säijä school trial the microbiological quality of ground water and treated water was also checked. The analysis was carried out in the Pirkanmaa Environmental laboratory.

4.5 Data processing

All geochemical data produced at the GTK was stored in the Alkemia-VAX database (Ahlsved *et al.* 1991). The statistical and graphical processing of the data was performed using SPSS 14, and Excel 2000 software. Corel Draw 12 software was used for the final editing of the graphs. The geological and geochemical data based on maps used in this study were prepared using the ArcGIS 9.1 software. In this study, numbers below the analytical detection limit for a given element or compound have been processed statistically as the numerical value of the analytical detection limit.

5. RESULTS AND DISCUSSION

5.1 The tests at the drilled well

The drilled well at Säijä School was monitored in a four-month period in 2005 and the number of samples was 36, 18 samples from raw water (PEPSA1) and 18 from treated water (PEPSA3). The median arsenic concentration in Säijä School well water was 503 µg/L and the temperature of the raw water varied from 6.4 to 7.9 °C. Statistic of arsenic and other elements in raw water are presented in Table 4 and Figure 7.

Total coliform bacteria, heat resistant coliform bacteria and Fecal streptococcus bacteria was analysed. No microbiological contamination was found in these analysis and all results were 0 CFU/100 mL. Even though no microbiological contamination was found in the Säijä trial, it is suggested that a disinfection process should be combined with the adsorption process. Disinfection is strongly recommended, if raw water temperature is > 10° C, because above this temperature the potential for microbiological growth starts to increase rapidly. Disinfection can be done with *e.g.* sodium hypochlorite solution (NaClO) or UV method. If NaClO is used, it is preferable to add this solution before adsorbent material. NaClO dose should be adjusted so that Cl₂ content in treated water is 0.1 - 0.3 mg/L.

In comparison to the other drilled well waters located in the test area, the Säijä well water was neutral or low alkaline water with high oxygen content. The iron value was low, but the manganese value was constantly quite high. The electrical conductivity values were much the same as in other well waters in the area, but sulphate, chloride and sodium values were slightly elevated as were also molybdenum and boron values compared to other drilled well waters.

Statistics of the quality of the treated water are presented in Table 5 and Figure 7. In average there is a huge improvement in the water quality after the water treatment. The temperature of the treated water varied from 7.8 to 16.1 °C.

Table 4. Statistics of groundwater quality of raw water in drilled well at Säijä (PEPSA1). The water quality requirements for small-scale household water (Act 401/2001) are given as comparison (STM 2001).

PEPSA1	Unit	N_Valid	Mean	Median	Std. Dev.	Minimum	Maximum	STM recom
Al	µg/L	18.00	8.01	2.22	10.99	1.00	35.80	200.00
As	µg/L	18.00	504.00	503.00	16.80	462.00	526.00	10.00
B	µg/L	18.00	35.68	37.70	7.64	17.90	46.70	1000.00
Ca	mg/L	18.00	25.19	25.25	0.78	24.30	27.40	
Cd	µg/L	18.00	0.02	0.02	0.00	0.02	0.02	5.00
Cl ⁻	mg/L	18.00	23.28	23.50	1.27	22.00	25.00	100.00
Co	µg/L	18.00	0.06	0.06	0.03	0.02	0.10	
Cr	µg/L	18.00	0.20	0.20	0.00	0.20	0.20	50.00
Cu	µg/L	18.00	0.94	0.10	2.99	0.10	12.80	2000.00
EC	mS/m, 25°C	6.00	29.28	29.75	2.04	26.70	31.80	
EC_Lab	mS/m, 25°C	18.00	31.58	31.00	0.98	30.00	34.00	250.00
Eh	mV	6.00	144.00	134.50	39.20	94.00	195.00	250.00
F ⁻	mg/L	18.00	0.34	0.30	0.05	0.30	0.40	1.50
Fe	mg/L	18.00	0.12	0.06	0.10	0.03	0.42	0.40
HCO ₃ ⁻	mg/L	18.00	126.67	124.50	5.63	120.00	140.00	
I	µg/L	12.00	2.02	2.00	0.07	2.00	2.24	
K	mg/L	18.00	4.40	4.41	0.36	3.50	4.88	
KMnO ₄	mg/L	18.00	2.37	2.20	0.47	1.80	3.50	20.00
Mg	µg/L	18.00	10.24	10.20	0.27	9.89	10.80	
Mn	µg/L	18.00	128.33	125.50	13.12	109.00	164.00	100.00
Mo	µg/L	18.00	1.99	1.99	0.06	1.86	2.13	
NO ₃ ⁻	mg/L	18.00	0.20	0.20	0.00	0.20	0.20	50.00
Na	mg/L	18.00	21.36	21.40	0.45	20.60	22.20	200.00
Ni	µg/L	18.00	0.09	0.05	0.05	0.05	0.21	20.00
O ₂	%	6.00	71.30	65.50	32.29	40.10	130.10	
P	µg/L	18.00	41.49	40.30	4.46	33.30	50.40	
PO ₄ ³⁻	mg/L	18.00	0.69	0.71	0.11	0.40	0.92	
Pb	µg/L	18.00	0.67	0.57	0.75	0.13	3.41	10.00
SO ₄ ²⁻	mg/L	18.00	19.44	19.00	1.34	18.00	22.00	250.00
Sb	µg/L	18.00	0.08	0.06	0.06	0.04	0.23	
Se	µg/L	18.00	0.50	0.50	0.00	0.50	0.50	10.00
SiO ₂	mg/L	18.00	15.61	15.70	0.43	15.00	16.50	
U	µg/L	18.00	3.80	3.84	0.46	3.13	4.63	100.00*
V	µg/L	18.00	0.05	0.05	0.00	0.05	0.05	
Zn	µg/L	18.00	60.15	43.75	56.73	9.08	238.00	
pH		6.00	8.00	8.00	0.09	7.90	8.10	6.5-9.5
pH_Lab		18.00	7.54	7.55	0.18	7.30	7.90	6.5-9.6

* The Finnish Ministry of Social Affairs and Health (STM) quality requirement is valid only for public water supplies.

Table 5. Statistics of groundwater quality of treated water in drilled well at Säijä (PEPSA3). The water quality requirements for small-scale household water (Act 401/2001) are given as comparison (STM 2001).

PEPSA3	Unit	N_Valid	Mean	Median	Std. Dev.	Minimum	Maximum	STM recom
Al	µg/L	18	8.20	2.02	11.25	1.00	36.90	200.00
As	µg/L	18	68.94	10.69	83.41	1.18	241.00	10.00
B	µg/L	18	38.49	39.80	7.26	19.20	52.20	1000.00
Ca	mg/L	18	33.14	25.75	21.81	23.50	96.40	
Cd	µg/L	18	0.05	0.02	0.05	0.02	0.16	5.00
Cl ⁻	mg/L	18	24.33	24.00	2.25	22.00	32.00	100.00
Co	µg/L	18	3.30	0.12	3.94	0.03	10.10	
Cr	µg/L	18	0.20	0.20	0.01	0.20	0.24	50.00
Cu	µg/L	18	0.39	0.10	0.51	0.10	1.62	2000.00
EC	mS/m, 25°C	6	72.75	68.30	49.36	27.10	134.00	
EC_Lab	mS/m, 25°C	18	43.85	33.00	30.07	31.00	140.00	250.00
Eh	mV	6	195.67	215.50	45.85	103.00	221.00	250.00
F ⁻	mg/L	18	0.36	0.30	0.32	0.10	1.30	1.50
Fe	mg/L	18	<0.03	<0.03	0.00	<0.03	<0.03	0.40
HCO ₃ ⁻	mg/L	18	77.52	111.50	55.72	8.54	140.00	
I	µg/L	12	2.08	2.00	0.16	2.00	2.50	
K	mg/L	18	4.49	4.46	0.28	3.79	4.92	
KMnO ₄	mg/L	18	1.97	1.80	0.50	1.40	3.20	20.00
Mg	µg/L	18	21.80	10.45	39.41	10.10	176.00	
Mn	µg/L	18	171.24	97.10	118.47	48.90	347.00	100.00
Mo	µg/L	18	0.79	0.39	0.82	0.02	1.90	
NO ₃ ⁻	mg/L	18	0.22	0.20	0.06	0.20	0.40	50.00
Na	mg/L	18	21.61	21.60	0.39	20.90	22.30	200.00
Ni	µg/L	18	14.39	0.52	17.46	0.05	46.90	20.00
O ₂	%	6	27.35	28.05	11.26	11.30	40.00	
P	µg/L	18	11.31	10.00	2.31	10.00	17.00	
PO ₄ ³⁻	mg/L	18	0.09	0.02	0.09	0.02	0.30	
Pb	µg/L	18	0.34	0.21	0.34	0.05	1.04	10.00
SO ₄ ²⁻	mg/L	18	124.67	27.00	200.81	20.00	747.00	250.00
Sb	µg/L	18	0.03	0.02	0.02	0.02	0.08	
Se	µg/L	18	0.50	0.50	0.00	0.50	0.50	10.00
SiO ₂	mg/L	18	8.39	8.96	5.49	1.39	15.30	
U	µg/L	18	0.92	0.28	0.99	0.01	2.41	100.00*
V	µg/L	18	<0.05	<0.05	0.00	<0.05	<0.05	
Zn	µg/L	18	47.59	47.05	33.99	2.35	98.00	
pH		6	6.43	5.90	0.91	5.80	7.70	6.5-9.5
pH_Lab		18	6.63	7.05	0.77	5.60	7.60	6.5-9.6

* The Finnish Ministry of Social Affairs and Health (STM) quality requirement is valid only for public water supplies.

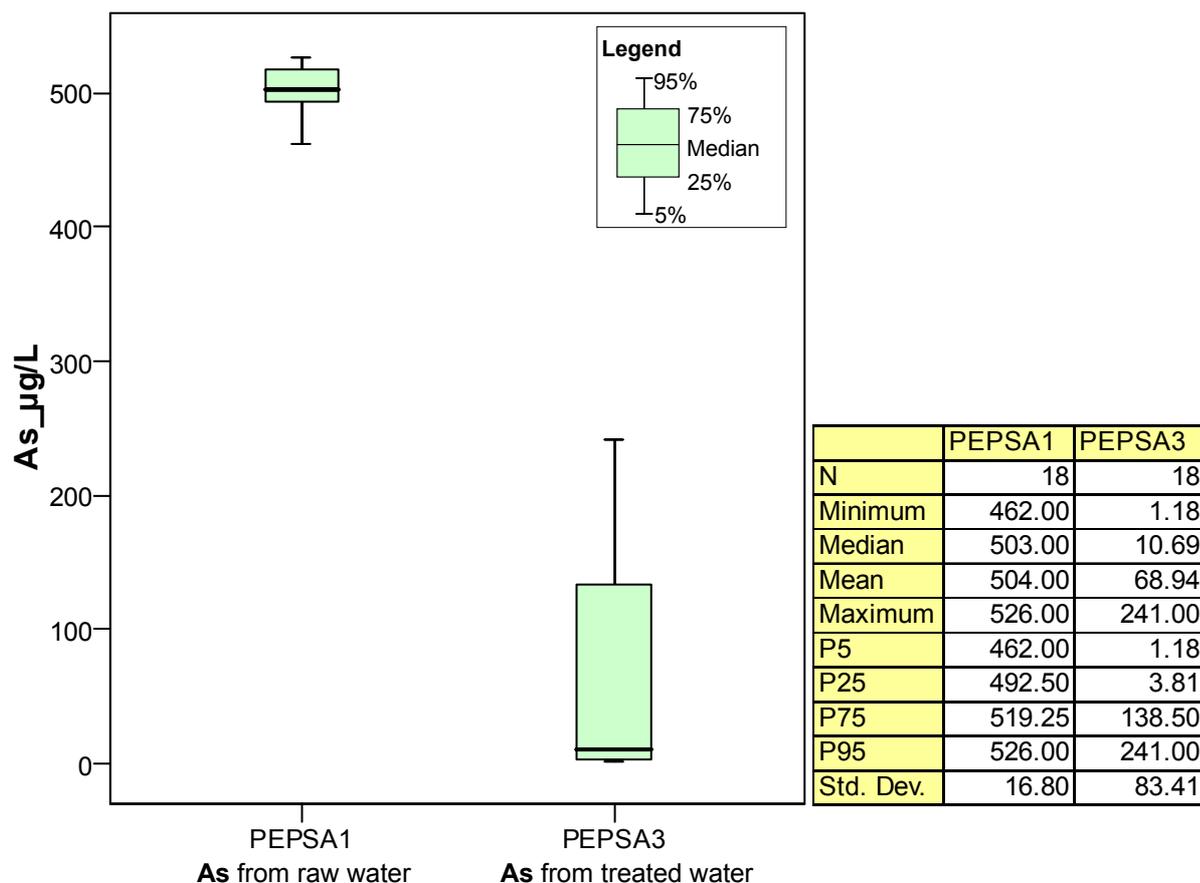


Figure 7. Arsenic content in raw water (PEPSA1) and in treated water (PEPSA3) as box plots and detailed statistic.

Effect on total arsenic concentrations

The arsenic removal results at the Säijä School well are presented as time series in Figure 8. It can be seen that with the applied bed volume (BV) up to about 1 500, the arsenic concentration was reduced to level below 10 µg/L, which is the recommended drinking water quality limit. This means that with 36 L CFH 12, it was possible to treat 54 m³ of water so that the arsenic concentration was maintained within the acceptable level.

After 1 500 BV applied, the level of arsenic concentrations in treated water exceeded the drinking water limit. The reason why only a relatively small volume of safe water (As < 10 µg/L) was obtained was probably due to a very high arsenic concentration in the raw water. Total treated water volume was 15 600 BV and at this time > 50 % arsenic removal was still achieved.

In this test site the EBCT was increased from 3 - 4 min to 9 min after 7 500 BV. As a result, the arsenic removal efficiency was increased as shown that curve was dropped and the arsenic concentration in treated water decreased from 130 µg/L to 100 µg/L for a short time (Figure 8). Based on this result, it can be said that the optimum EBCT for CFH 12 product should be more than 3 – 4 min. It would be most preferable to design the process so that 5 – 10 min EBCT can be reached. Following this specification, the CFH 12 arsenic removal capacity could be utilized more efficiently.

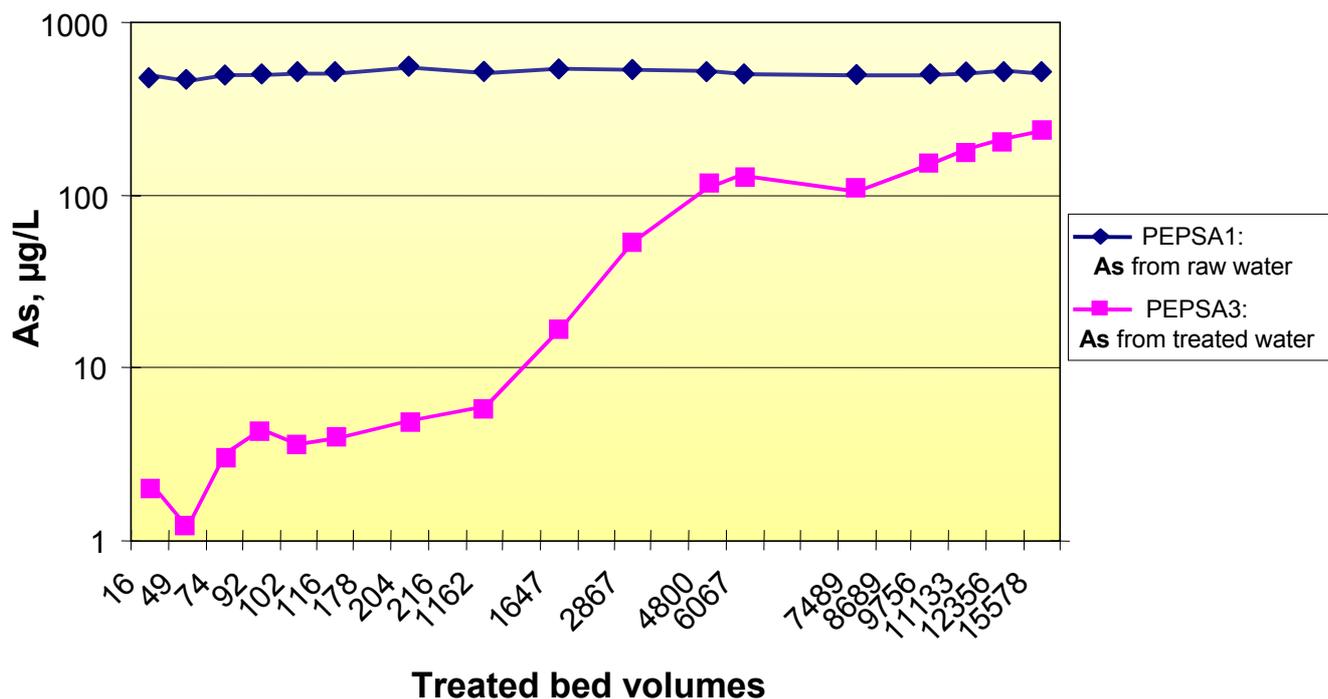


Figure 8. The results of arsenic removal trial at Säjä School well by using adsorption technique with the Ferric oxo-hydroxides of the Kemira CFH 12 filter varies in treated bed volumes.

Effect on arsenic speciation

The arsenic concentrations in the raw water (PEPSA1) remained steadily on a high level during the monitoring period while the values fluctuated from 462 to 526 µg/L (Fig. 8). The increase of pumping volume did not change the total arsenic concentrations, but the arsenate, As (V), and arsenite, As (III), values varied in the beginning of the monitoring (Fig. 9). Later the As (III)/As (V) ratio was stabilized. The dominant arsenic species in the Säjä School well water was arsenite (As III). At the beginning of the test the removal of both, arsenite and arsenate, was very effective (Fig. 10). Later after about 2000 BV applied, the removal was still effective for arsenite (As III). The arsenite values of 360 – 394 µg/L in raw water dropped down to 3.18 – 3.11 µg/L in the treated water (99 % of arsenite was removed). For arsenate (As V) the method was not effective anymore during that time. The concentrations varied from 116 – 135 µg/L of arsenate in raw water and in treated water 14.8 – 51.3 µg/L (11 – 44 % of arsenate was removed). Later, after 15 000 BV applied, neither the removal of arsenite nor arsenate was effective.

Effect on other elements

The removal trial decreased not only the concentration of arsenic, but also many elements and compounds such as iron, manganese, KMnO_4 -number, molybdenum, phosphate and phosphorus, lead, antimony and uranium (Table 5). Also the amount of dissolved oxygen, bicarbonate, and content of silica decreased and the water became more acidic. Concentrations of the selected elements in raw water and treated water are illustrated in Figure 11. The amount of some elements, e.g. Co, Ni, and SO_4 increased during the treatment, especially in the beginning of the test period (PEPSA3 > PEPSA1). This may probably due to the impurity of the filter material.

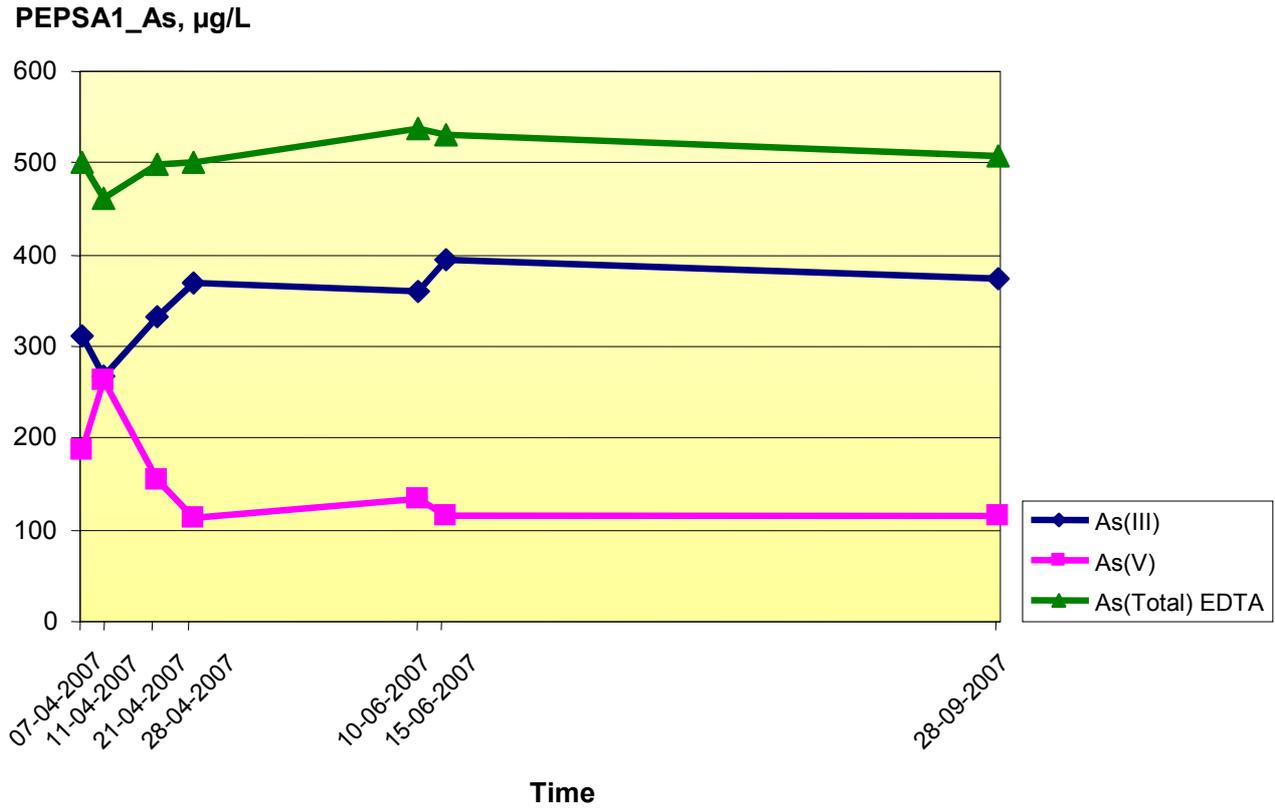


Figure 9. Speciations of arsenic in raw water of Säjä School well (PEPSA1).

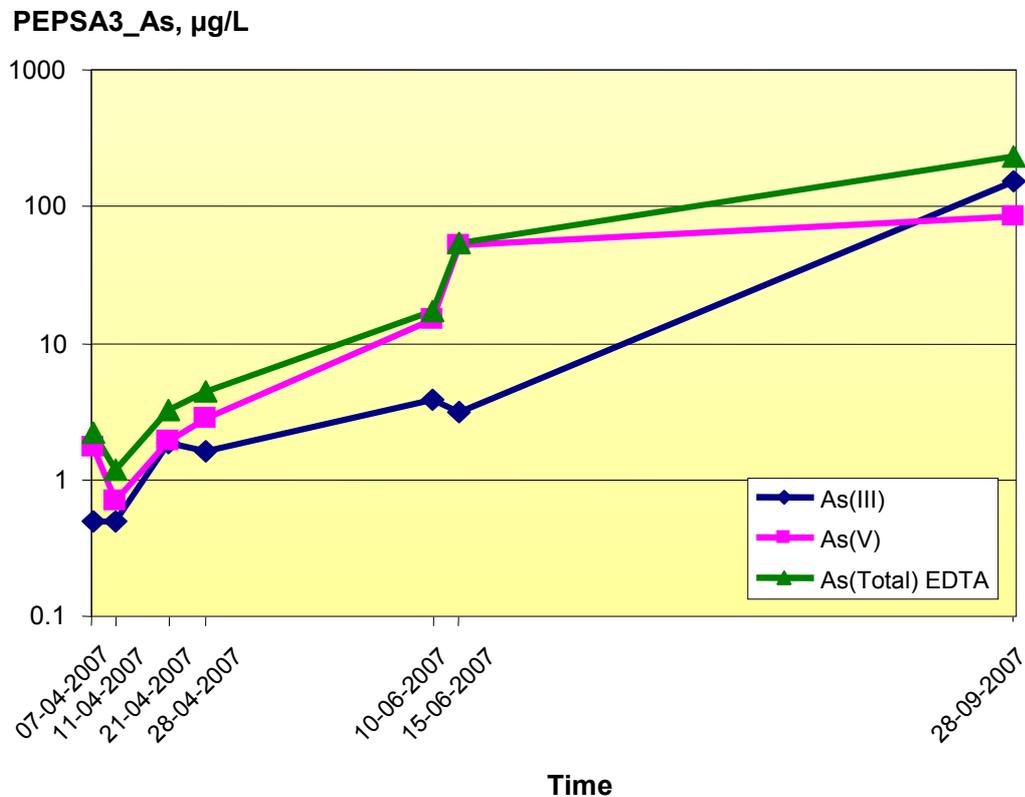


Figure 10. Speciations of arsenic in treated water of Säjä School well (PEPSA3).

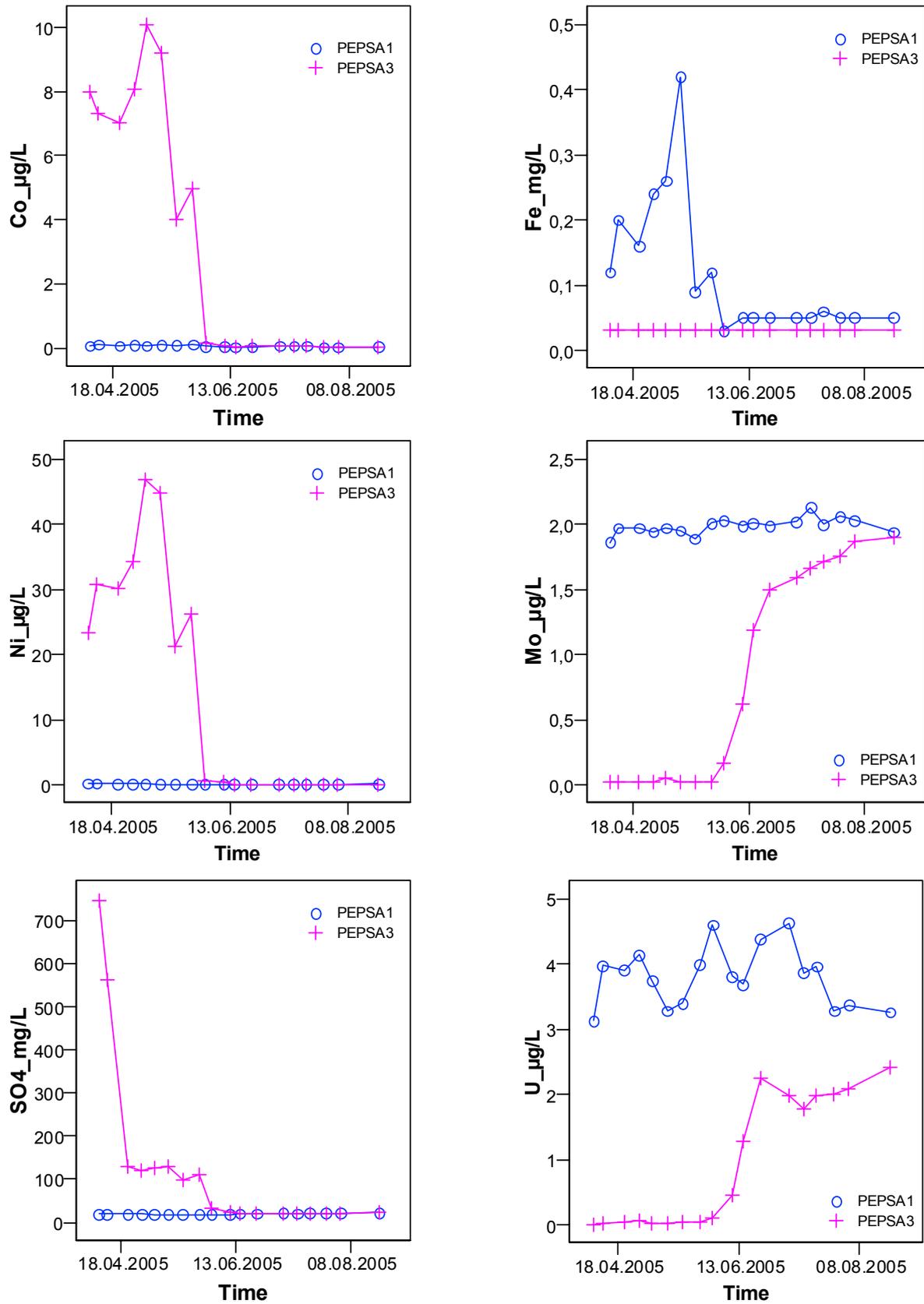


Figure 11 Examples of some elements and compound in raw water (PEPSA1) and in treated water (PEPSA3) at the Säijä School well.

Experience from the tests at Säijä

The arsenic removal efficiency and capacity of the CFH 12 product was somewhat lower than expected in the Säijä test. The main reason was the high arsenic concentration in the Säijä School raw water. Lifetime of adsorbent depends strongly on arsenic concentration in raw water. In small scale, it may be economical to use adsorption method in arsenic removal even if the raw water arsenic concentration is in the range 100 - 500 µg/L. This is due to the fact that adsorption equipments are very simple and cheap to purchase compared to other arsenic removal techniques such as reverse osmosis or iron salt coagulation combined with flotation. In large-scale arsenic removal processes, adsorption technique is usually evaluated to be the most cost efficient option, when arsenic concentration in raw water is < 100 µg/L and when treated water volumes are < 5 000 m³/d.

After the Säijä field test, Kemira developed a new CFH product grade called CFH 0818. The granule size is smaller in this product than in the CFH 12 and therefore higher arsenic removal capacity and efficiency can be reached. This product is preferable especially if the raw water arsenic concentration is > 100 µg/L.

5.2 The tests with the surface waters at the Ylöjärvi mining site

At the Ylöjärvi site the surface water was acid with pH value of 5.6 and alkalinity of 0.1 mmol/L. The water contained a high level of organic matter, but not so much of suspended solids. The total arsenic concentrations in the raw water fluctuated from 120 to 180 µg/L. The chemical composition of the raw water is presented in Table 6 and Figure 12. The oxidized form, arsenate, was dominating in the surface water. The arsenate As (V) and arsenite As (III) concentrations in the raw water were 160 µg/L and 2.45 µg/L and 116 µg/L and 2.02 µg/L, respectively in the treated water.

The arsenic removal at the Ylöjärvi site exploited the same method as in the Säijä case with the exception that a new filter material CFH 0818 was tested. At the beginning of the test, the arsenic removal efficiency was not as high as it was estimated based on Säijä's experiment and in general the chemistry of the water did not change very much during the test. The statistics of the treated surface water of Lake Parosjärvi is presented in Table 7 and Figure 12.

Figure 13 illustrates the results of arsenic removal at the Ylöjärvi mine site. The curves represent total arsenic concentrations in raw water and treated water as a function of treated bed volumes. The arsenic concentration was decreased up to 70.4 % at the beginning of the test, as the arsenic concentration in raw water dropped from 123 µg/L to 36.4 µg/L. After 10 000 BV arsenic removal was about 44 % and then the removal efficiency decreased quite rapidly when the amount of treated bed water volume increased (Fig. 13).

The arsenic removal efficiency at the Ylöjärvi site was significantly worse at the start of the trial compared to Säijä test despite of the lower arsenic concentration in the raw water. It is most likely that rather high concentration of organics in the surface water (KMnO₄-numbers of 30 - 50 mg/L at the Ylöjärvi site compared with 1.8 - 3.5 mg/L at the Säijä School site) was the reason for the adsorbents behaviour. Organic material may be blocked into the pores of ferric oxo-hydroxide and therefore the adsorption efficiency is drastically decreased.

Table 6. Statistics of groundwater quality of the raw water at the Ylöjärvi mine.

Elements	Unit	N_Valid	Mean	Median	Std. Dev.	Minimum	Maximum
Al	µg/L	4.00	271.75	266.50	19.00	255.00	299.00
As	µg/L	4.00	154.25	157.50	23.46	123.00	179.00
B	µg/L	4.00	78.61	99.15	53.13	0.14	116.00
Ca	mg/L	4.00	11.38	11.10	1.54	9.92	13.40
Cd	µg/L	4.00	0.15	0.15	0.01	0.13	0.15
Cl ⁻	mg/L	3.00	1.37	1.40	0.06	1.30	1.40
Co	µg/L	4.00	25.58	25.70	1.71	23.40	27.50
Cr	µg/L	4.00	0.21	0.21	0.01	0.20	0.22
Cu	µg/L	4.00	64.85	64.95	2.94	61.50	68.00
EC	mS/m	4.00	10.98	10.50	1.44	9.90	13.00
F ⁻	mg/L	3.00	0.30	0.30	0.00	0.30	0.30
Fe	mg/L	4.00	0.39	0.38	0.06	0.34	0.46
HCO ₃ ⁻	mg/L	4.00	4.65	4.50	0.57	4.20	5.40
K	mg/L	4.00	2.49	2.33	0.57	2.03	3.28
KMnO ₄	mg/L	4.00	42.00	41.50	5.48	36.00	49.00
Mg	mg/L	4.00	2.36	2.31	0.24	2.15	2.67
Mn	µg/L	4.00	89.60	88.60	103.25	0.18	181.00
Mo	µg/L	4.00	0.30	0.30	0.04	0.26	0.36
NO ₃ ⁻	mg/L	4.00	0.20	0.20	0.00	0.20	0.20
Na	mg/L	4.00	3.00	2.96	0.23	2.79	3.30
Ni	µg/L	4.00	5.36	5.33	0.55	4.82	5.97
P	µg/L	2.00	10.00	10.00	0.00	10.00	10.00
PO ₄ ³⁻	mg/L	4.00	0.19	0.19	0.03	0.15	0.22
Pb	µg/L	4.00	1.26	1.06	0.76	0.59	2.35
SO ₄ ²⁻	mg/L	4.00	38.70	37.20	6.93	32.40	48.00
Sb	µg/L	4.00	0.10	0.10	0.01	0.09	0.11
Se	µg/L	4.00	0.50	0.50	0.00	0.50	0.50
Si	mg/L	4.00	1.88	1.88	0.15	1.71	2.05
U	µg/L	4.00	0.20	0.20	0.01	0.18	0.20
V	µg/L	4.00	0.21	0.21	0.02	0.18	0.23
Zn	µg/L	4.00	37.05	37.10	1.73	35.00	39.00
pH		4.00	5.68	5.70	0.05	5.60	5.70
Total suspended solids	mg/L	4.00	10.00	10.00	0.00	10.00	10.00

Therefore it is recommended that this kind of surface water should be pre-treated before the process of arsenic removal efficiency with FeOOH based adsorbent. Pre-treatment could be done by using ferric salt precipitation followed by flotation, gravitation or filtration. This treatment could decrease KMnO₄-number in the water to about 5 - 10 mg/L. The treatment would also decrease arsenic concentration in the water. The coagulation method for arsenic removal is described in section 3.1. If arsenic level is still too high after pre-treatment, the rest of arsenic could be removed using ferric oxo-hydroxide based adsorption method.

Some other interesting water quality parameters of raw surface water and the treated surface water during the removal period are presented in Figure 14.

Table 7. Statistics of groundwater quality of treated water in the monitoring well at Ylöjärvi mine.

Elements	Unit	N_Valid	Mean	Median	Std. Dev.	Minimum	Maximum
Al	µg/L	4.00	189.25	206.50	60.07	106.00	238.00
As	µg/L	4.00	93.35	108.00	38.77	36.40	121.00
B	µg/L	4.00	77.79	96.00	53.10	0.17	119.00
Ca	mg/L	4.00	11.38	11.10	1.67	9.72	13.60
Cd	µg/L	4.00	0.10	0.12	0.05	0.02	0.14
Cl ⁻	mg/L	3.00	1.37	1.40	0.06	1.30	1.40
Co	µg/L	4.00	19.52	25.05	12.40	1.06	26.90
Cr	µg/L	4.00	0.25	0.21	0.08	0.20	0.36
Cu	µg/L	4.00	49.78	56.70	15.44	26.70	59.00
EC	mS/m	4.00	11.23	10.85	1.38	10.00	13.20
F ⁻	mg/L	3.00	0.30	0.30	0.00	0.30	0.30
Fe	mg/L	4.00	0.36	0.35	0.07	0.29	0.44
HCO ₃ ⁻	mg/L	4.00	6.75	5.40	3.11	4.80	11.40
K	mg/L	4.00	2.36	2.29	0.38	2.04	2.81
KMnO ₄	mg/L	4.00	38.00	37.50	2.45	36.00	41.00
Mg	mg/L	4.00	2.81	2.57	0.71	2.25	3.84
Mn	µg/L	4.00	50.89	5.70	94.21	0.18	192.00
Mo	µg/L	4.00	0.22	0.23	0.03	0.19	0.25
NO ₃ ⁻	mg/L	4.00	0.20	0.20	0.00	0.20	0.20
Na	mg/L	4.00	3.33	3.00	0.80	2.79	4.52
Ni	µg/L	4.00	4.86	5.97	2.71	0.84	6.68
P	µg/L	2.00	10.00	10.00	0.00	10.00	10.00
PO ₄ ³⁻	mg/L	4.00	0.12	0.15	0.06	0.03	0.16
Pb	µg/L	4.00	0.64	0.66	0.27	0.29	0.95
SO ₄ ²⁻	mg/L	4.00	38.98	36.85	5.73	35.00	47.20
Sb	µg/L	4.00	0.07	0.08	0.02	0.04	0.09
Se	µg/L	4.00	0.50	0.50	0.00	0.50	0.50
Si	mg/L	4.00	1.54	1.75	0.66	0.59	2.08
U	µg/L	4.00	0.17	0.17	0.03	0.13	0.19
V	µg/L	4.00	0.16	0.17	0.03	0.11	0.18
Zn	µg/L	4.00	53.14	33.45	61.72	2.64	143.00
pH		4.00	6.05	5.85	0.58	5.60	6.90
Total suspended solids	mg/L	4.00	10.00	10.00	0.00	10.00	10.00

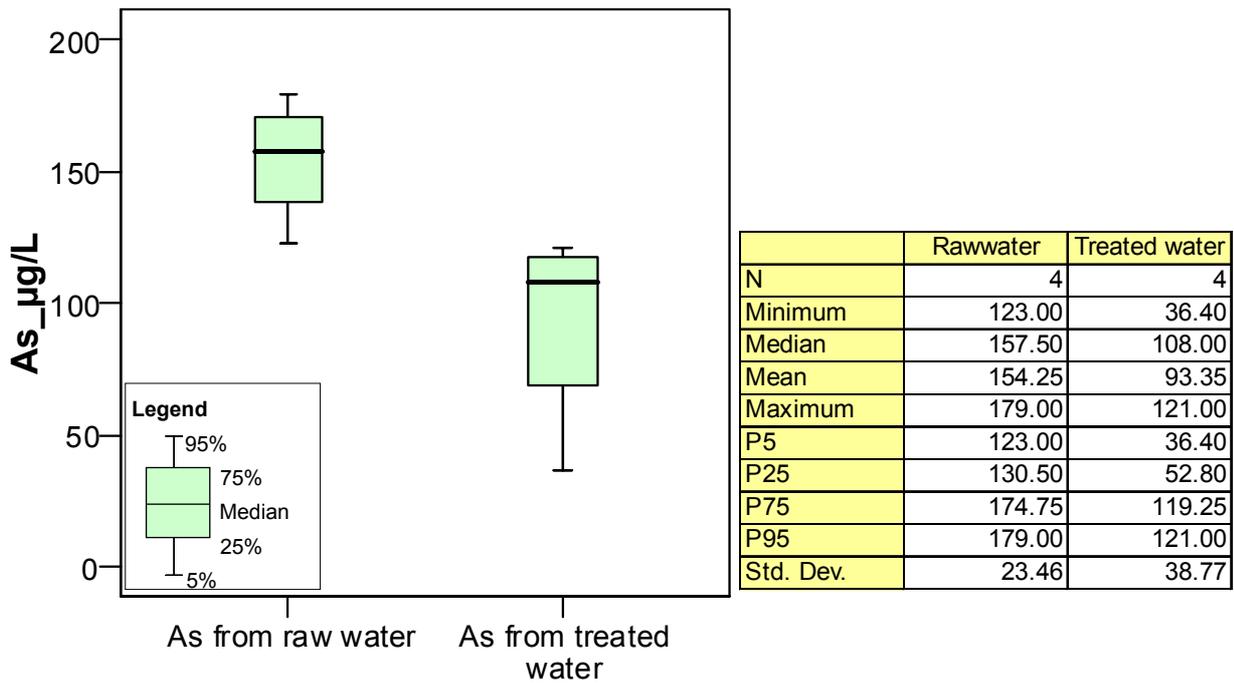


Figure 12. Arsenic content in raw water and in treated water at the Ylöjärvi mine site as box plots and detailed statistic.

Arsenic removal with CFH 0818 in Ylöjärvi trial

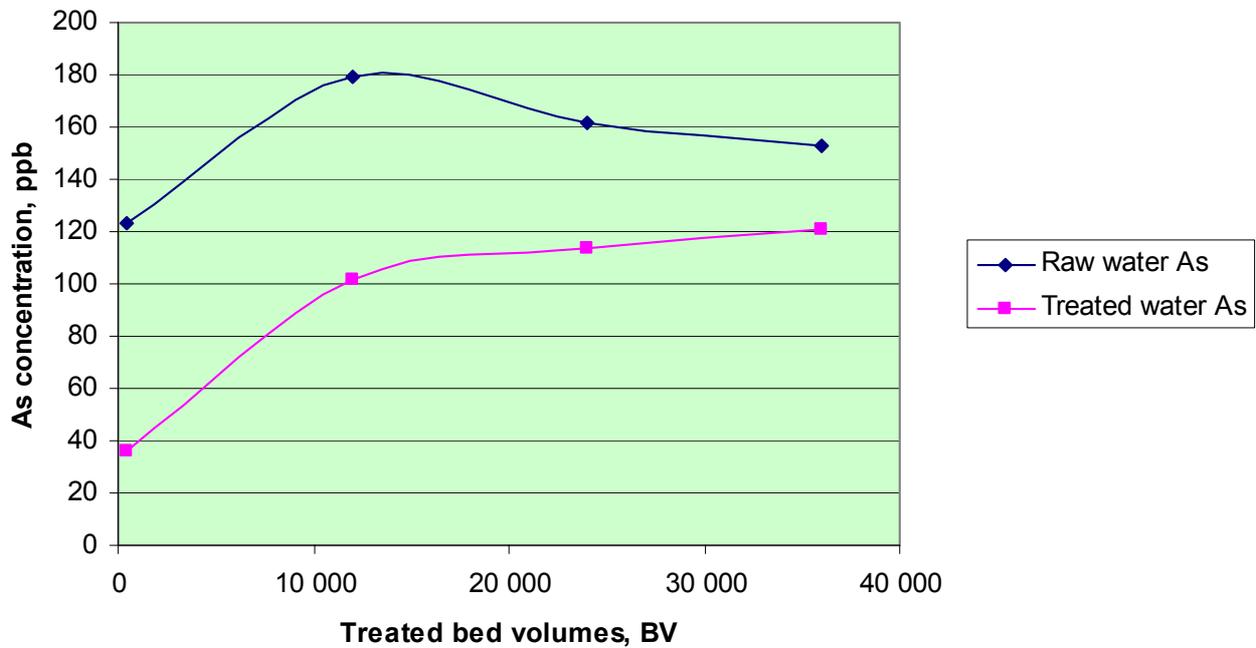


Figure 13. The results of arsenic removal test at Ylöjärvi mine site by using adsorption technique with the Kemira CFH 0818 filter material.

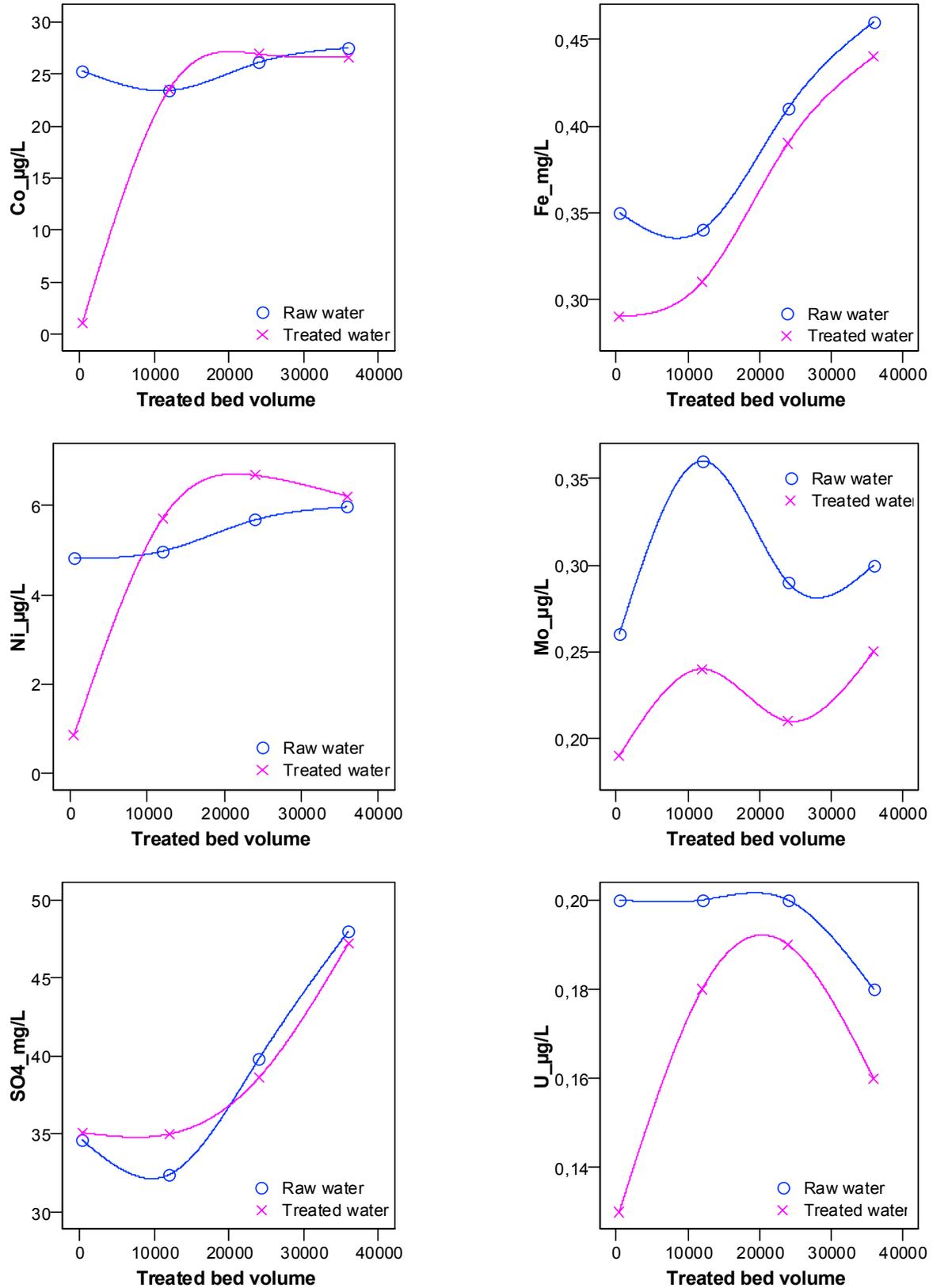


Figure 14. Examples of some elements and compound in raw water and in treated water at the Ylöjärvi mine.

5.3 Laboratory scale arsenic removal tests with CFH 12 and CFH 0818 filters

CFH 12 and CFH 0818 arsenic removal efficiency was also tested in laboratory scale. In this test 50 µg/L of As (V) was added to the normal tap water and the water pH was adjusted to pH 6.5. In this trial the effect of empty bed contact time to the arsenic removal efficiency was tested. The trial results are presented in Figure 15.

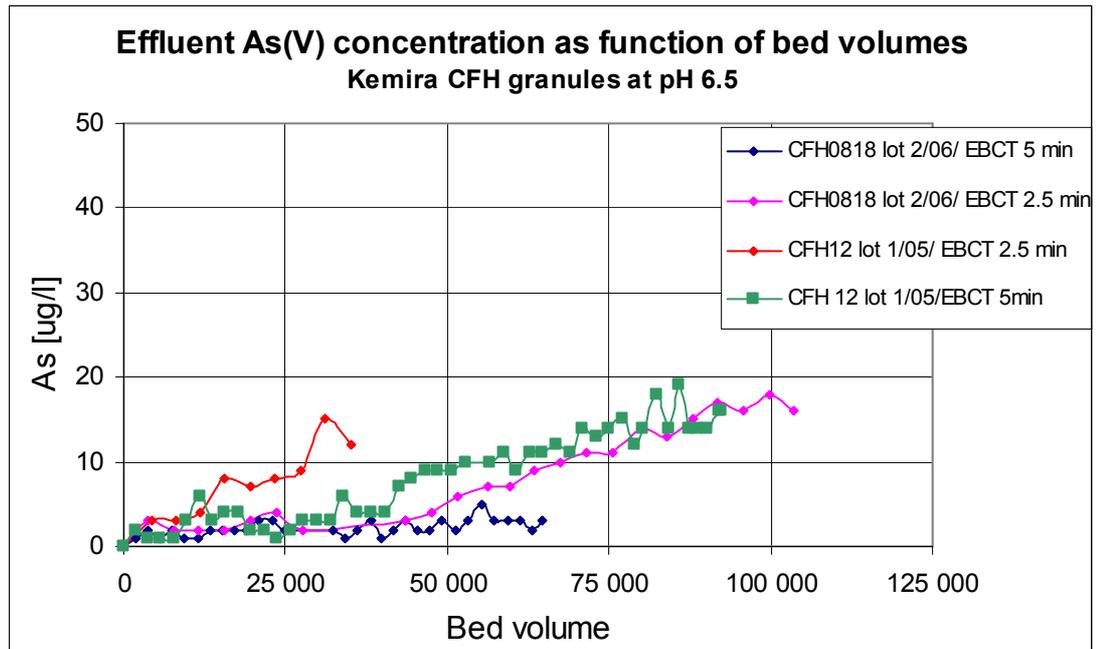


Figure 15. The treatment of a water containing arsenic 50 µg/L with CFH 12 and CFH0818 at pH 6.5.

From the curve it can be seen the 5 min EBCT is more preferable compared to 2.5 min. Especially, if CFH 12 product is used, it is important to have a minimum of 5 min contact time between the raw water and the adsorbent. Too short contact time will result to the overrunning of the 10 µg/L concentration limit significantly earlier.

With CFH 12 product and 5 min EBCT it was possible to treat 50 000BV of water. CFH 0818 has shown to be even more efficient. The trial with CFH 0818 is still ongoing and until now it has been possible to treat > 70 000 BV and arsenic concentration after adsorbent unit is still clearly < 10 µg/L.

5.4 Arsenic removal costs by adsorption technique

Highly contaminated water

Based on results of Säjjä School trial, the arsenic removal costs based on adsorption could be calculated. The cost for individual household, that is using own well water with 500 µg/L As, would be as presented below:

Adsorption tank (max. flow 10l/min)	1 500 € (one time investment)
CFH 12 adsorbent (36 L)	170 €/54 m ³ water
	3.10 €/m³ water

The water treatment cost is quite high in this case is due to the very high arsenic concentrations raw water (500 ppm).

Slightly contaminated water

Based on laboratory scale test, the cost for raw water containing 50 µg/L can be evaluated. The cost for individual household, that is using own well water would be as presented below:

Adsorption tank (max. flow 10l/min)	1 500 € (one time investment)
CFH 12 adsorbent (36 L)	170 € /1.800 m ³ water
	0.094 €/m³ water
CFH 0818 adsorbent	170 € /2.520 m ³ water
	0.067 €/m³ water

The municipal tap water cost for Finnish households varies between 2-3 €/m³. Based on this it can be said that adsorption method may be cost efficient solution for arsenic removal. If there is drilled well available for household, where the water quality is good except for the excess of arsenic, it may be economical to construct a ferric oxo-hydroxide based filtering system. This is especially beneficial if the joining to public water supply is not possible due to long distances and, consequently, high costs.

Based on these cost estimations it is obvious that the amount of arsenic concentration in raw water has a major impact to water treatment cost. However, it is quite rare that raw water contains 500 µg/L arsenic as in Säjjä School case. In many cases raw water arsenic concentrations are between 15-50 µg/L. As shown above, the lower arsenic level means significantly lower treatment costs.

5.5 Disposal of used ferric oxo-hydroxide granules

A standard leaching method used in US, the toxicity characteristic leaching procedure (TCLP) was used in order to evaluate the CFH 12 and CFH 0818 disposal possibilities.

TCLP is a standard method, which is developed by the United States Environmental Protection Agency (US EPA) to provide a means of determining the potential for solid materials to release chemical contaminants into a landfill environment. TCLP is designed to expose the waste to conditions, which are more favourable to toxic leaching than the conditions in landfill.

The procedure mimics, mildly acidic rainwater leaching metals from a sample. The results of the TCLP tests are compared with the maximum concentration of contaminants for toxicity characteristics (TC) to determine if the waste can be disposed in a non-hazardous landfill. The TC value for arsenic is 5 mg/L.

If the used adsorbent material is approved in TCLP test, it can be disposed as non hazardous waste to normal dumping areas. If the material doesn't pass the TCLP test, it should be disposed as hazardous waste.

The procedure is as follows (US EPA 2000):

Sorbent preparation

- a. The sorbent is sieved to the required size range and weighed.
- b. The sorbents is stored in a desiccator or in a dry place to prevent them getting any moisture.

Deciding about which extraction fluid to use

Extraction fluid 1: Add 5.7 mL glacial acetic acid ($\text{CH}_3\text{CH}_2\text{OOH}$) to 500 mL Milli-Q water, add 64.3 mL 1 N NaOH (40 g/L NaOH), and dilute to a volume of 1 liter. When correctly prepared the pH of this fluid will be 4.93 ± 0.05 .

Extraction fluid 2: Dilute 5.7 mL glacial acetic acid with Milli-Q water to 1 L, when correctly prepared the pH of this fluid will be 2.88 ± 0.05 .

Experimental TCLP procedure

- i) 2 g waste and 40 mL extraction fluid is used (solid/liquid = 1/20).
- ii) End-over-end tumbler was used to shake the samples for 18 ± 2 hours at 30 ± 2 rpm.
- iii) After 18 hours of tumbling samples were centrifuged and filtered from 0.45 μM filter, the extract was acidified and kept in the fridge.
- iv) The toxicity was evaluated determining the level of dissolved heavy metals in the extract, if the level of metals exceeds the specified limits; the material was characterized as toxic. The TC limit is 5 mg/L for As.

Following the USEPA procedure it was found out that CFH adsorbents subjected to TCLP experiment do not release arsenic more than TC limit 5 mg/L. Therefore based on TCLP test the used material can be disposed as non hazardous waste.

6. CONCLUSIONS

A field demonstration study has been performed to test the filtration systems using commercial Kemira CFH 12 adsorbent in the Säjjä School well. The treatment process can remove arsenic from approximately 500 $\mu\text{g/L}$ in the well water to less than 10 $\mu\text{g/L}$ up to 1 500 BV treated water, this means that 54 m^3 water can be treated so, that the quality requirements for drinking water are met. It can be concluded that with the CFH 12 adsorbent the drinking water quality can be achieved even for highly contaminated waters. In the tested bedrock groundwater the arsenite (As III) was dominating over As (V). The removal of arsenite was excellent, even better than for arsenate.

The direct adsorption treatment for arsenic removal from surface water was not very efficient. In the treatment of surface water that contains high organic matter it is recommended to have a pre-treatment before the adsorption process. The pre-treatment can be done by, for example, chemical precipitation combined with gravitation, flotation or direct filtration. If this treatment does not decrease arsenic concentration to the targeted level, it is possible to use adsorption method after this treatment.

The ferric oxo-hydroxide adsorption treatment can be very cost efficient method for arsenic removal. Adsorption method is especially economical when water consumption is rather low and/or when arsenic concentration in raw water is $< 100 \mu\text{g/L}$. The process equipments needed for ferric oxo-hydroxide adsorption process are significantly cheaper compared to alternative arsenic removal techniques.

Based on the toxicity characteristic leaching procedure (TCLP) test, the used ferric oxo-hydroxide based adsorbent material can be disposed as none hazardous material to normal dumping places. In the future, the disposal possibilities should still be evaluated also based on the standard leaching methods applied in Finland.

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APPENDIX: 1

kemira

PRODUCT INFORMATION

CFH12 18.10.2006

Kemira

CFH 12

Application

CFH 12 product is suitable for removal of arsenic and phosphorus as well as most metals from aqueous solutions. The product can be used in containers, basins or ground filters. Different impurities adsorb on the ferric hydroxide granules.

Main components (as is)

		Min	Max	Typical
Iron, Fe ³⁺	%	39	48	44
Water soluble content	%	0.5	3.0	2.0
Moisture	%	13	19	16

Inorganic trace substances (on dry basis)

		Max	Typical
Arsenic, As	mg/kg	< 1	
Cadmium, Cd	mg/kg	< 1	
Lead, Pb	mg/kg	< 20	3
Copper, Cu	mg/kg	< 20	5
Chromium, Cr	mg/kg	< 25	10
Nickel, Ni	mg/kg	< 200	140
Manganese, Mn	mg/kg	< 2 500	1 000

Granule density and size

		Min	Max	Typical
Bulk density, kg/l		1.10	1.30	1.20
Granule size				
	D ₅₀ (d50%) mm			1.4
	98% mm			< 2.0

Appearance Brown or reddish brown granule

Other information

Using CFH 12 in a filter:

CFH 12 adsorbent material is first installed to the filter. Filter is then filled with water. Filter backwashing should be carried out with water volume of approximately 20 times the volume of CFH 12. During backwashing dust and most of water soluble content is removed from the adsorbent. Backwashing water should be discharged to the sewer.

APPENDIX: 2

KEMIRA

Kemira

CFH 0818

PRODUCT INFORMATION

CFH0818 18.10.2006

Main components (as is)

	Min	Max	Typical
Iron, Fe ³⁺ , %	39	48	44
Water soluble content, %	0,5	3,0	2,0
Moisture, %	13,0	19,0	16,0

Inorganic trace substances (on dry basis)

	Max	Typical
Arsenic, As, mg/kg	<1,0	
Cadmium, Cd, mg/kg	<1,0	
Lead, Pb, mg/kg	<20	3
Copper, Cu, mg/kg	<20	<5
Chromium, Cr, mg/kg	<25	10
Nickel, Ni, mg/kg	<200	140
Zinc, Zn, mg/kg	<600	400
Manganese, Mn, mg/kg	<2500	1000

Granule density and size

	Min	Max	Typical
Bulk density, kg/l	1,10	1,30	1,20
Granule size			
Effective size, mm (*)			0,7
Uniformity coefficient (**)			1,3
d50%, mm			0,9
Dust, %			0,7

Appearance Brown or reddish brown granule

Other information

CFH 0818 adsorbent material is first installed to the filter. After this, filter is filled with water. Filter backwashing should be carried out with Min. 20 bed volumes of water. In the backwashing the dust and most of water soluble content is removed from the adsorbent. Backwashing water should be pumped to the sewer.

*) Effective size = Diameter of 10 w-% of product

**) Uniformity coefficient = Diameter of 60w-% of product
Diameter of 10w-% of product



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

1. Natural Occurrence of Arsenic in the Pirkanmaa Region in Finland
2. Anthropogenic Arsenic Sources in the Pirkanmaa Region in Finland
3. Arseenista aiheutuvien riskien hallinta Pirkanmaalla – Esiselvitys ohjaus keinoista ja teknisistä menetelmistä riskien vähentämiseksi (Management of arsenic risks in the Pirkanmaa region – Survey of available risk management instruments and tools)
4. Arsenic and other elements in agro-ecosystems in Finland and particularly in the Pirkanmaa region
5. A transport model of arsenic for surface waters - an application in Finland
6. Arsenic Ecotoxicity in Soils
7. Arsenic removal from groundwater and surface water - Field tests in the Pirkanmaa Region, Finland

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