



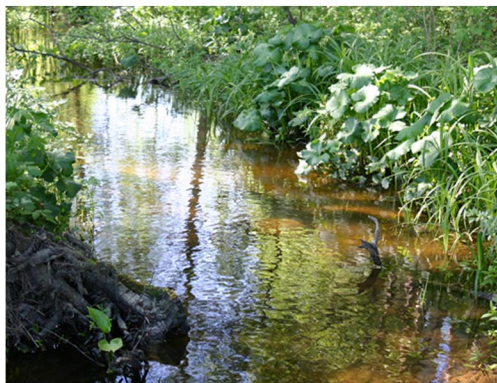
Risk Assessment and Risk Management  
Procedure for Arsenic in the Tampere Region



# A transport model of arsenic for surface waters - an application in Finland

Ämer Bilaletdin  
Heikki Kaipainen  
Annika Parviainen  
Tommi Kauppila  
Timo Ruskeeniemi

Pirkanmaa Regional Environment Center  
Helsinki University of Technology  
Geological Survey of Finland



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Ämer Bilaletdin (PIR)  
Heikki Kaipainen (PIR)  
Annika Parviainen (TKK)  
Tommi Kauppila (GTK)  
Timo Ruskeeniemi (GTK)

## ABSTRACT

RAMAS is a three-year project (2004 - 2007) funded by the participating organizations and the LIFE Environment programme of the European Union. The acronym RAMAS arises from the project title "Risk Assessment and risk Management procedure for Arsenic in the Tampere region". The project is targeting the Province of Pirkanmaa which comprises 28 municipalities, and has 469 000 inhabitants within its area.

Arsenic undergoes a number of changes in response to environmental conditions such as pH, redox potential and other soluble compounds and solid phases present in the system. As exact transfer modelling requires huge amounts of data, a relatively simple calculation method is needed for large sites. A model has to contain enough essential processes, state variables etc. but it should not require too much data, and the running of the model should not be too laborious. This is especially important for modelling tools designed to assist authorities in their tentative environmental reviews.

The study area in the Vahantajoki river basin comprises an approximately seven kilometres long watercourse, here referred to as the transport route of arsenic, originating from the Ylöjärvi mining area.

The aim of this study is to develop a statistical arsenic transport model for surface waters using monitored data and to take into account the discharge of small rivers and the sub-catchments, calculated using a runoff model. Dilution, sedimentation and chemical processes are presumable processes regarding arsenic transport. The general form of the model is an advection-dispersion model and the first order kinetics. The advection-dispersion model, separately for particle bounded arsenic and soluble arsenic, has been used to simulate the total arsenic concentration. The driving process for particle bounded arsenic is sedimentation and the driving state variables for soluble arsenic are pH and iron. The main conclusion of this study is that by using a quite simple mass balance model it was possible to simulate arsenic transport in surface waters for risk assessment purposes.

E-mail: [emir.bilaletdin@ymparisto.fi](mailto:emir.bilaletdin@ymparisto.fi)

**Keywords:** arsenic, transport model, RAMAS, surface water, advection-dispersion, Pirkanmaa, Finland.

## TIIVISTELMÄ

RAMAS on kolmivuotinen hanke (2004-2007), joka on rahoittajina on EU:n LIFE Environment – ohjelma ja hankkeeseen osallistuvat organisaatiot. Akronyymi RAMAS muotoutuu hankkeen nimestä "Risk Assessment and risk Management procedure for ArSenic in the Tampere region". Hankkeen kohdealueena on Pirkanmaan maakunta, joka koostuu 28 kunnasta ja jossa asuu 469 000 asukasta.

Arseenin esiintymismuoto riippuu ympäristöolosuhteista kuten pH:sta, redox-potentiaalista ja metalleista. Arseenin kulkeutumisen yksityiskohtainen prosessikuvaus vaatii valtavan laajan havaintoaineiston. Iso alueen arseenin kulkeutumisen mallintaminen vaatii kuitenkin suhteellisen yksinkertaisen mallikuvauksen. Mallin täytyy sisältää keskeiset prosessit, tilamuuttujat jne., mutta tarvittavan havaintoaineiston määrä ei saa olla liian suuri eikä mallin käyttö liian työlästä. Tämä on erityisen tärkeää niiden mallintamistyökalujen osalta, jotka on suunnattu ympäristöviranomaisten alustavien selvitysten tekemiseen.

Mallinnusalue on Ylöjärven kaivosalueen alapuolinen reitti, joka sijaitsee Vahantajoen vesistöalueella. Kaivosalue kuormittaa jokireittiä mm. arseenilla. Hankkeen tarkoituksena on kehittää tilastollinen arseenin kulkeutumismalli. Mallinnuksessa hyödynnetään kerättyä havaintoaineistoa ja otetaan huomioon valuma-alueen sivujokien vaikutus. Alueen hydrologia lasketaan erillisellä valumamallilla. Arseenin kulkeutumisen mallinnuksessa tärkeimpiä prosesseja ovat laimentuminen, sedimentaatio ja kemialliset prosessit. Mallin yleinen rakenne advektio-dispersio ja ensimmäisen kertaluokan kinetiikka. Advektio-dispersio -mallia käytettiin liukoisen ja kiintoaineeseen sitoutuneen arseenin pitoisuuden simulointiin. Keskeinen prosessi kiintoaineeseen sitoutuneen arseenin kuvauksessa on sedimentoituminen ja liukoisen arseenin osalta tilamuuttujien pH:n ja raudan kemialliset prosessit. Tämän tutkimuksen pääasiallinen johtopäätös on, että suhteellisen yksinkertaisella massatasapainoon perustuvalla, empiirisellä mallilla on mahdollista simuloida arseenin kulkeutumista pintavedessä riskinarvioinnin tarpeisiin.

Sähköpostiosoite: [emir.bilaletdin@ymparisto.fi](mailto:emir.bilaletdin@ymparisto.fi)

**Asiasanat:** arseeni, kulkeutumismalli, pintavesi, advektio-dispersio, RAMAS, Pirkanmaa, Suomi.

## PREFACE

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

The acronym RAMAS arises from the project title "Risk Assessment and Risk Management Procedure for Arsenic in the Tampere Region". The project targets the whole province of Pirkanmaa (also called the Tampere Region), comprised of 28 municipalities, and 469 000 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](http://www.gtk.fi/projects/ramas)

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## 1. INTRODUCTION

All over the world, numerous active or abandoned mine sites and ore processing plants bear potential to contaminate their surrounding soils and waters with metals and other compounds. One of the most harmful and rather common elements is arsenic. Because arsenic in groundwater and water poses a risk to ecosystem and human health, more detailed information is needed on the factors that govern arsenic fate and transport in the environment. In this context, modelling can be used to study the geochemical interactions between elements, the role of physico-chemical conditions and to build transport scenarios where the impacts of the relevant parameters are simulated in spatial and temporal framework. An important call for this kind of models follows from the need to predict future loads, which is further underlined by the expected climate change.

Models are always a simplification of reality (Morgan 1995), they do not offer a substitute for reliable measurements from a well designed and properly equipped field experiment, but help in understanding the cause-effect relationship in a transport modelling. Whatever the choice of the modelling approach, the goal is to meet the objectives defined by the study.

Among the existing predictive transport models, two types are widely used: empirical models and physically-based models. They describe processes by mathematical equations. This description can be simple, often expressing a statistical relationship like in empirical models. Equation may also be more complex, related to the fundamental physics or mechanics of the process like in physically-based models. Models should not be classified as good or bad, it might be said that models are acceptable if they meet their objectives or design requirements and are not difficult to operate. When selecting a model, care needs to be taken to avoid its misuse, for too complex systems or extrapolating it to conditions beyond those of the database from which it was derived.

Arsenic undergoes a number of changes in response to environmental conditions such as pH, and redox potential and other soluble compounds and solid phases present in the system. These factors are important as they determine the fate and biological availability of the arsenic in mine tailings, effluent discharge and affected sediments. Several transport models have been proposed for the geochemical cycling of arsenic. Exact modelling requires huge amounts of data and detailed understanding of the whole system. Since this is rarely the case, relatively simple, but sufficiently sensitive calculation method is needed for large sites. A model has to contain the most essential processes, state variables etc. but it should not require too much input data and the running of the model should not be too laborious. The objective of the work presented in this paper is to develop such a transport model.

All over the world a lot of different methods to purify drinking water from arsenic have been studied, as well as, technologies removing arsenic from contaminated soils and waters (*e.g.* Garelick *et al.* 2005, Thirunavukkarasu *et al.* 2003). These studies, provide useful information on the behaviour of arsenic in process level. Much less studies have been carried out on arsenic transport in large river basins, even though this is a severe problem in many natural and anthropogenic environment *e.g.* Bright *et al.* (1994), Hancock *et al.* (2001), Pettine *et al.* (1992).

## 2. DESCRIPTION AND CONCEPTUALISATION OF THE STUDY AREA

The study area in the Vahantajoki river basin comprises an approximately seven kilometres long watercourse, here referred to as the transport route of arsenic, originating from the Ylöjärvi mining area and ending in the Lake Näsijärvi. The transport route of arsenic begins from the Lake Parosjärvi, which is located in the immediate vicinity of the former mine and the tailings area. The lake is connected to the Stream Parosjärven oja, which flows into the Lake Vähä-Vahantajärvi and into the Stream Vähä-Vahantajärven oja and, finally, into the Lake Näsijärvi, which is the major lake basin in the region (Figure 1). The sub-catchments of the Vahantajoki river basin are specified using a Digital Elevation Map. The areas and mean discharges of the different sub-catchments are given in Table 1. In Figure 2 is presented a topographic map of the study area.

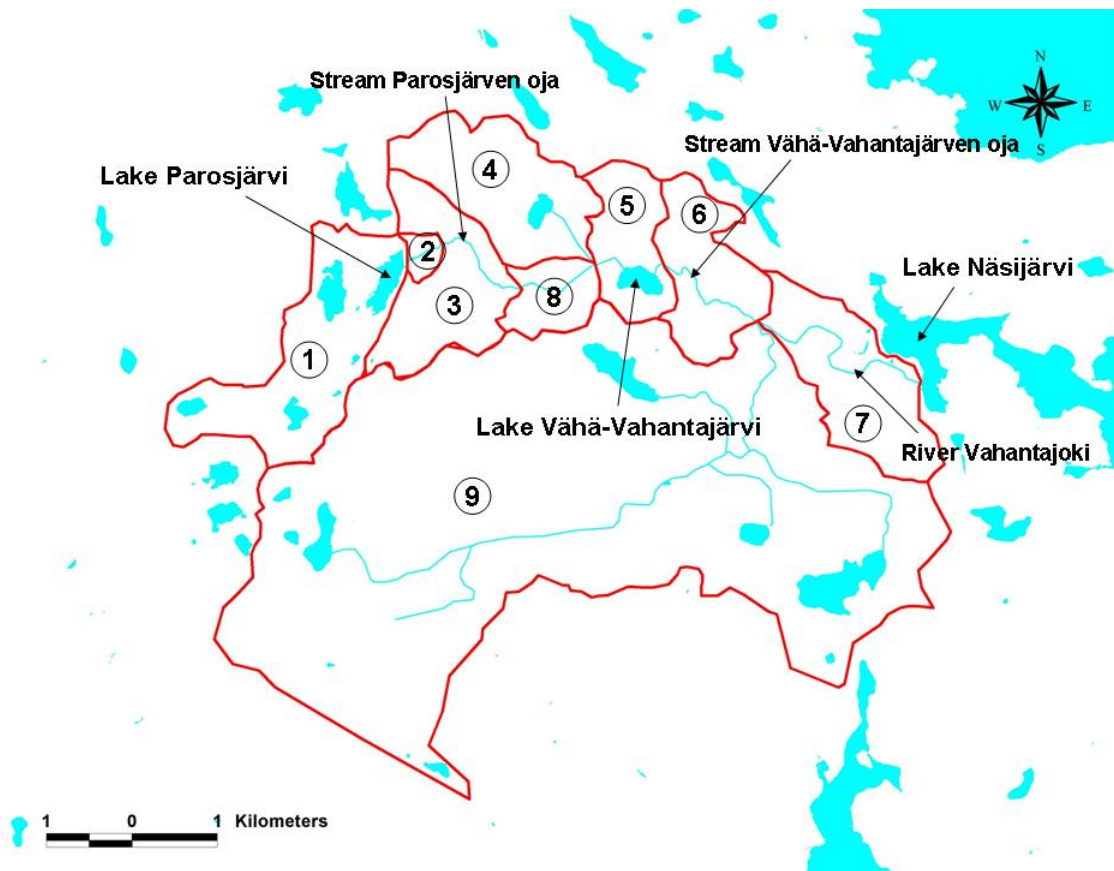


Figure 1. The sub-catchments of Vahantajoki river basin.



Table 1. The areas and mean discharges (mean runoff =  $10 \text{ l s}^{-1} \text{ km}^{-2}$ ) of the sub-catchments of Vahantajoki river basin.

Sub-catchment	Area ( $\text{km}^2$ )	MQ ( $\text{m}^3 \text{ d}^{-1}$ )
1	3.41	2946
2	0.20	173
3	2.21	1909
4	2.58	2229
5	1.42	1227
6	1.86	1607
7	2.45	2117
8	0.83	717
9	25.02	21617

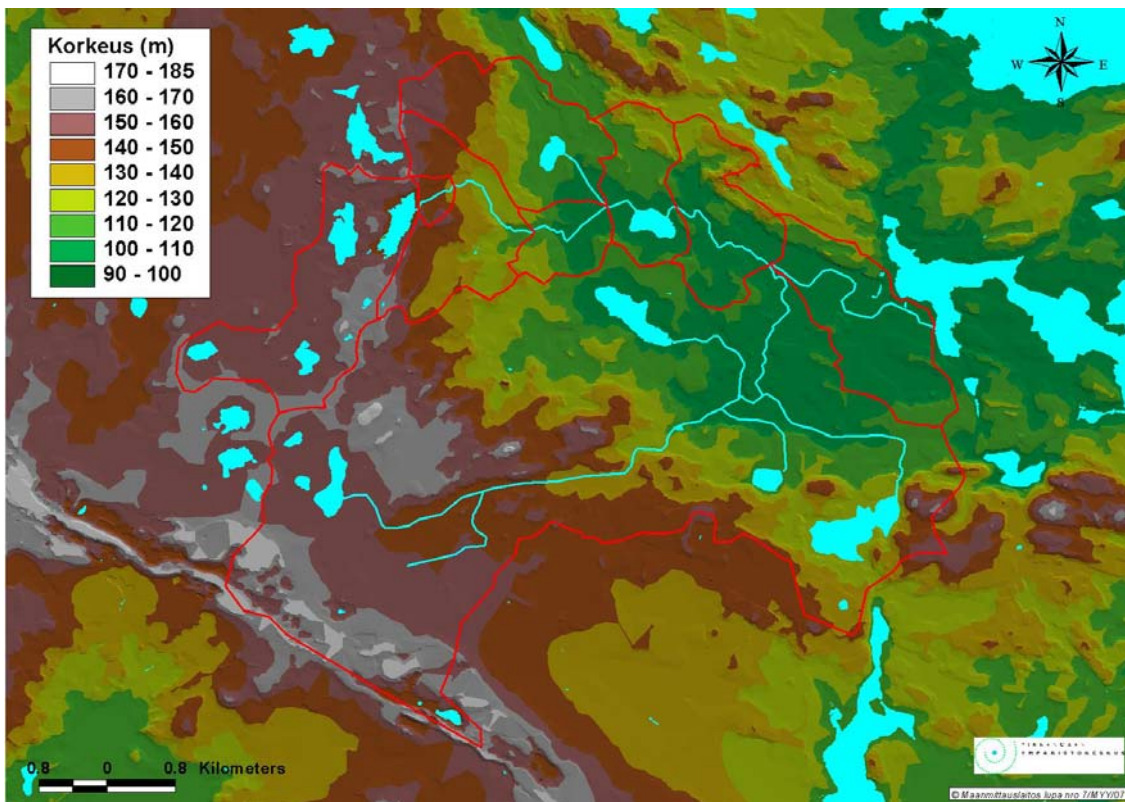


Figure 2. A topographic map of the study area.

The principal origin of the arsenic contamination in the surface waters of the study area is the copper-tungsten-arsenic (Cu-W-As) mine of Ylöjärvi which was active during 1943-1966. This Cu-W deposit is situated in the western end of the Tampere Schist Belt, which consists mainly of metamorphosed supracrustal rocks (volcanics and sediments) and plutonic intrusions. Regionally, this belt contains elevated arsenic concentrations with the median of  $10 \text{ mg/kg}$ , whereas the median of the whole country is  $0.9 \text{ mg/kg}$  (Lahtinen *et al.* 2005). The Ylöjärvi deposit is hosted by a tourmaline breccia, and the surrounding rocks are mainly tuffites with porphyrite intercalations (Himmi *et al.* 1979). The main ore minerals, arsenopyrite ( $\text{FeAsS}$ ), chalcopyrite ( $\text{CuFeS}_2$ ) and pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ), are associated with other minor sulphides [pyrite ( $\text{FeS}_2$ ), sphalerite ( $\text{ZnS}$ ), galena ( $\text{PbS}$ ), cuban-

ite ( $\text{CuFe}_2\text{S}_3$ ), molybdenite ( $\text{MoS}_2$ ), oxides [magnetite ( $\text{Fe}_3\text{O}_4$ ), ilmenite ( $\text{FeTiO}_3$ , cassiterite ( $\text{SnO}_2$ )], scheelite ( $\text{CaWO}_4$ ) and minute concentrations of native bismuth, silver and gold (Himmi *et al.* 1979). The Ylöjärvi mine is the only mine in Finland that produced arsenic concentrate, and the highest reported concentrations were from 6000 to 8000 mg/kg. However, it is worth to notice that arsenic concentrate was recovered only few years implying that most of the arsenic ended up in the tailings.

The mining activities left behind two tailings areas of 4 ha and 17 ha, two open pits and underground galleries. It is estimated that about 4 Mt of tailings and waste rock is stored in the area. Water from the Lake Parosjärvi was used in processing the ore in a closed circulation, and the first open pit as a clarification pool. As the mining works proceeded under the lake, it was dewatered. After closing the mine, the lake filled up again with water, and as a consequence part of the smaller tailings area, the open pits and the underground galleries filled with tailings were flooded, leaving a lot of arsenic, heavy metals and sulphides containing material subject to leaching of surface and groundwater. Reductive conditions are prevailing at the bottom of the lake, but two times a year seasonal temperature changes of the water mix the oxidative surface water with the deeper one, causing degradation and dissolution of the material. However, the main arsenic sources into the surface waters are the arsenic bearing sulphide minerals in the tailings areas. These minerals tend to weather and dissolve in contact with air and oxidizing rain water releasing arsenic and heavy metals into the environment. This process, formed by a series of complex geochemical and microbial reactions, is called acid mine drainage (AMD), and waters affected by it are characterized by high acidity and elevated concentrations of heavy metals and arsenic. According to Carlson *et al.* (2002), AMD spills in all directions from the bigger tailings area.

Besides the anthropogenic environmental impacts of the Ylöjärvi mine, natural occurrence of arsenic in bedrock and soil seems to be an important regional factor. The elevated arsenic concentrations in the bedrock are reflected in the surface waters as well as in the river and lake sedimentary records of the study area. This is demonstrated by the lake sediment cores, which show that already before mining activities, the arsenic content in the sediment load was elevated, from 17 to 54 mg/kg. Other higher values are possibly contaminated (Parviainen *et al.* 2006). The average concentration in Finnish sediments is 4.44 mg/kg (Lahermo *et al.* 1996).



Figure 3. The tailings of Ylöjärvi mine (Kati Vaajasaari).



Figure 4. Lake Vähä-Vahantajärvi in the study area (Arto Paananen).

### 3. MONITORING AND SAMPLING RESULTS DATA SETS

The Ylöjärvi mine area provides a good reference area for developing a transport model of arsenic. The source term (the tailings area) is relatively well defined, there is long-term data on arsenic and heavy metal concentrations along the whole length of the transport route, as well as, studied information about the environmental impacts, which give some support for process level assumptions. To investigate the short-term dynamic changes in the arsenic transport a monthly monitoring of the surface waters was implemented during the RAMAS Project in 2005. The studies conducted depict the gravity of the environmental impacts of the Ylöjärvi mine giving credible background information for further research and transport modelling of arsenic. In the following chapters, these studies are reviewed, as well as, the new results collected during the RAMAS project and employed in this paper. Table 2 summarizes the pretreatment and the analyzing methods used in the previous and current studies.

Table 2. Pretreatment and analyzing methods for different sample types that are referred to in this paper [ICP-AES = inductively coupled atomic emission spectrometry, ICP-MS = inductively coupled mass spectrometry, AAG = atomic adsorption spectroscopy (graphic furnace)].

<b>Water</b>	0,45 µm membrane filter, suprapur HNO <sub>3</sub>	ICP-AES	Carlson <i>et al.</i> 2002
		ICP-MS	
<b>Iron precipitates</b>	63 µm sieving, ammoniumoxalate and aqua regia	ICP-AES	Carlson <i>et al.</i> 2002
<b>Peat</b>	microwave-assisted HNO <sub>3</sub> leaching	ICP-AES	Carlson <i>et al.</i> 2002
<b>River and lake sediments</b>	microwave-assisted HNO <sub>3</sub> leaching	ICP-AES	Parviainen <i>et al.</i> 2006
		ICP-MS	
<b>Water</b>	0,45 µm membrane filter, suprapur HNO <sub>3</sub>	AAG	RAMAS
	non-filtered, suprapur HNO <sub>3</sub>		

#### 3.1. Monitoring of the surface waters in the river basin

Since 1975, local environmental consulting companies have carried out surface water monitoring of the Lake Parosjärvi and nearby streams and rivers. The monitoring, done according to the obligatory monitoring under the supervision of the Pirkanmaa Regional Environment Centre (PIR), provides long-term data, which now comprises around 600 arsenic analyses along the whole length of the transport route from Lake Parosjärvi to Lake Näsijärvi. Arsenic content in water is measured from four stream and river monitoring points and from two lake monitoring points showing elevated concentrations of arsenic (Table 3).

Table 3. Arsenic ( $\mu\text{g/l}$ ) at the various monitoring points of the Vahantajoki river basin. Data from the obligatory sampling under the supervision of the Pirkanmaa Regional Environment Centre reported by Carlson *et al.* (2002) and Parviainen *et al.* (2006).

	Water sampling point	Year	Mean	Min	Max	Med	N
	Ditch from tailings to the Lake Parosjärvi	1982-1999	258.8	43	580	250	25
1	Lake Parosjärvi surface	1975-2005	66.6	0.5	160	68	58
	Lake Parosjärvi bottom	1975-2005	155.3	1.2	910	130	56
2	Stream Parosjärven oja 1	1975-2005	60.2	1	380	60	68
3	Stream Parosjärven oja 2	1975-2005	57.9	0.5	850	31	73
4	Stream Vähä-Vahantajärven oja	1975-2005	16	0.8	65	14	73
5	Stream Vahantajoki alav mts	2005	7.1	4	14	6.3	9
6	Lake Näsijärvi surface	2005	2.9	1.5	6	3	8
	Lake Näsijärvi bottom	2005	23.4	6	66	14	8

### 3.2 Characterisation of the tailings area

Carlson *et al.* (2002) studied the environmental state of the closed Ylöjärvi mine area. Geophysical measurements and water, iron precipitate and peat samplings were performed. According to this study, AMD spills in all directions from the southern tailings area. From these spill points water flows to nearby streams and to a peat bog accumulating high concentrations of arsenic and heavy metals in the soil and in the upper layers of the peat (Carlson *et al.* 2002). Commonly, the dissolved iron hydrolyzes and forms iron(III) precipitates goethite, schwertmannite or jarosite depending on the pH range. The iron precipitates retain arsenic and some heavy metals, diminishing their concentrations in surface waters.

The sampling in the western and northwestern peat bogs showed that arsenic and heavy metal concentrations in the upper layer were elevated, but diminished further away from the spill points and in the intermediate layers of the bog. In the basal minerogenic soils of the northwestern peat bog, As, Fe, Cr, Cu, Ni, Zn and V concentrations were greater than in the overlaying peat and the anomalous concentrations extended further away from the tailings area. This could indicate that the contamination is provoked by groundwater that washes through the tailings (Carlson *et al.* 2002). Arsenic concentrations of the iron precipitates and of the peat are shown in the Table 4. The monitoring sites in the tailings area are presented in Figure 5.

In the ditch leading from the southern tailings area into the Lake Parosjärvi, iron does not oxidize so effectively and arsenic ends up in the lake (average 123  $\mu\text{g/l}$  As in the ditch water). This ditch has been treated with lime, which raised the pH of both the ditch and the lake. Before liming, in 1988, the pH in the lake was 3.8, whereas during 2000-2002 it ranged from 5.2 to 5.3. Despite the liming, iron does not precipitate effectively enough to retain arsenic, because of too high flow rate, which allows too short reaction times. According to Carlson *et al.* (2002), high concentrations of arsenic were measured in the lake as well as in the Stream Parosjärven oja: 62  $\mu\text{g/l}$  in the lake, 60  $\mu\text{g/l}$  about 500 meters downstream (Stream Parosjärven oja 1) and 29  $\mu\text{g/l}$  about 1.5 kilometres downstream from the lake (Stream Parosjärven oja 2).

Table 4. Average concentrations of arsenic, iron and copper and pH of surface waters, iron precipitates and peat (Carlson *et al.* 2002).

	Water sampling point	pH field	As mg/l	Fe mg/l		Iron precipitate sampling point	pH lab	total As mg/kg	total Fe mg/kg
1	N of tailings in a creek flowing to Lake Parosjärvi	6.4	1480	58	A	N of tailings in a creek flowing to Lake Parosjärvi	6.5	18600	379000
2	N of tailings in a creek just before flowing into Lake Parosjärvi	6.2	123	9	B	N of tailings in a creek just before flowing into Lake Parosjärvi	4.2	5955	380250
3	NW of tailings in a seepage water	4.2	2310	13	C	NW of tailings in a seepage water	3.5	44300	297400
4	W of tailings in a seepage water	4.0	54	1.90	D	W of tailings in a seepage water	3.9	96850	312500
5	S of tailings in a seepage water	3.7	109	37	E	S of tailings in a seepage water	3.6	3539	380000
6	S of tailings in a creek further South	5.6	10	0.39	F	S of tailings in a creek further South	5.0	7710	193000
7	E of tailings in a seepage water	4.2	6	2.15					
8	NE Lake Parosjärvi	5.8	62	0.65					
9	Parosjärvenoja Stream about 500m from the lake	6.3	60	0.72					

	Peat bog sampling point	pH field	As mg/kg	Fe mg/kg	Cu mg/kg
1-1	NW, in the bog 1 profile 1 from the depth of 0 cm	?	6130	62000	452
	NW, in the bog 1 profile 1 from the depth of 100 cm	5.2	67	3320	126
1-2	NW, in the bog 1 profile 2 from the depth of 0 cm	?	1020	2440	433
	NW, in the bog 1 profile 2 from the depth of 100 cm	4.3	15	2310	32
	NW, in the bog 1 profile 2 from the depth of 350 cm in mineral	4.6	1290	33100	662
1-3	NW, in the bog 1 profile 3 from the depth of 0 cm	4.8	499	44400	204
	NW, in the bog 1 profile from the depth of 100 cm	4.1	18	2999	63
	NW in the bog 1 profile 3 from the depth of 245 cm in mineral	?	1380	28200	306
2-1	W, in the bog 2 profile 1 from the depth of 0 cm	4.3	96	14800	676
	W, in the bog 2 profile 1 from the depth of 50 cm	4.9	97	4390	84
2-2	W, in the bog 2 profile 2 from the depth of 0 cm	4.9	23	2300	9
	W, in the bog 2 profile 2 from the dept of 100 cm	4.3	< 10	871	7

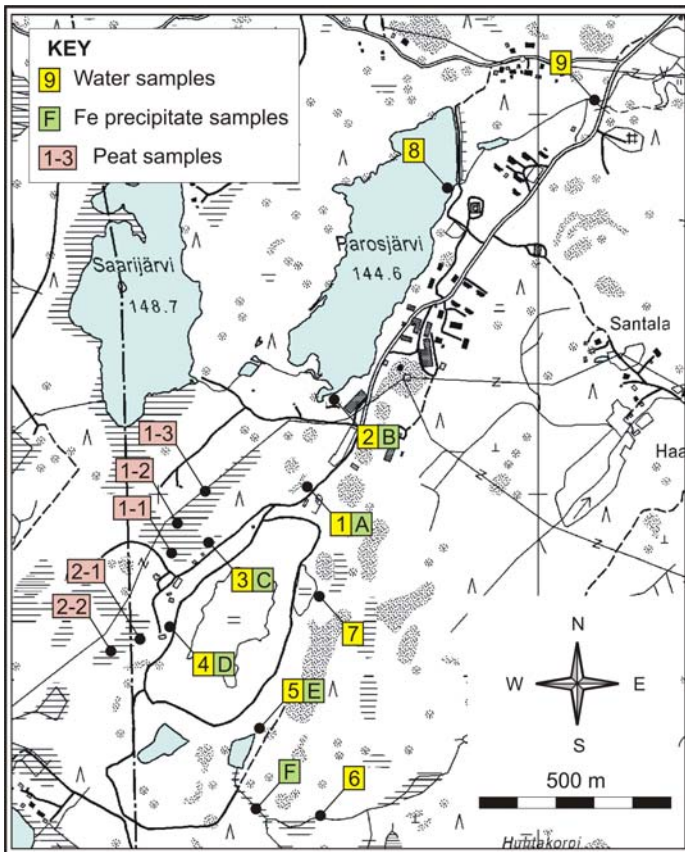


Figure 5. The water, Fe precipitate and peat sampling sites according to Carlson *et al.* 2002.

### 3.3. Stream and lake sediments

In March 2005, RAMAS performed river and lake sediment sampling in the transport route in the Vahantajoki river basin. The aim was to investigate the recent and longer term temporal changes in the transport of arsenic and in the arsenic retention in the sediment load (Parviainen *et al.* 2006). These samples comprise stream sediment samples of the Streams Parosjärven oja and Vähä-Vahantajärven oja, as well as lake sediment cores from a wetland below the Lake Parosjärvi, from the Lake Vähä-Vahantajärvi and from the Lake Näsijärvi (Figure 6). The results are used in verifying the modelling presented in this paper.

The 183 cm composite core from the wetland located close to the mine site was taken with a d-section corer (Jowsey, 1966) and sectioned in the field into consecutive 10 cm samples. The samples from the stream sites were also taken with the d-section corer with the aim of recovering an organic-rich top layer representing recent deposition. Where possible, a sample was also taken below this top layer for comparison. The two lake sediment cores (Lake Vähä-Vahantajärvi and Lake Näsijärvi) were taken with a Kajak-type gravity corer (Renberg 1991) and sectioned in the field to consecutive 1 cm slices.



Figure 6. RAMAS project sediment sampling sites March 2005.

The stream sediment analyses show that the arsenic contents (Table 5) in the recent sediment load are significantly higher than in the Finnish average river sediments (4.4 mg/kg As, Lahermo *et al.* 1996). The radioactive  $^{137}\text{Cs}$  peak inherited from the Chernobyl fallout (1986) has been used to define a reference horizon in the sediment core. The recent sedimentation rate has been estimated based on the 20-year accumulation. This value, together with the geochemical profiling, has been used to divide the lake sediment cores into sections deposited prior, during and after the mining. The recent sediment layers in the lake sediment cores contain higher concentrations of arsenic than those deposited prior to the mining activities. (Table 5). This indicates that inputs from the mining area and redeposition of older, As-rich sediments, keep contaminating the surface waters and the transport of arsenic is continuous. Additionally, the sediment cores reveal that the sediments accumulated during the 20-year active mining period contain tenfold concentrations of arsenic compared to the background values. These peaks exhibit 583 mg/kg and 235 mg/kg of arsenic in the Lakes Vähä-Vahantajärvi and Näsijärvi, respectively (Table 5). In Figure 7, the As concentrations are presented in the sediment of Lake Näsijärvi.



Table 5. Concentrations of arsenic in the river surface sediments and in the lake sediment cores. The distances downstream are average distances from the Lake Parosjärvi (Parviainen *et al.* 2006).

Sediment core sampling point	Depth (cm)	As mg/kg	Surface sediment sampling point	As mg/kg
A wetland below the dam in the Lake Parosjärvi	0-50	2600-4480	The Stream Parosjärven Oja, ~300 m downstream	110
	51-171	1130-1590	The Stream Parosjärven Oja, ~900 m downstream	128-228
	107-178	1760-3690	The Stream Parosjärven Oja, ~1300 m downstream	134
	180-183	179	The Stream Vähä-Vahantajärven Oja, ~6000m downstream	25
The Lake Vähä-Vahantajärvi ~3000 m	top	200-250		
	8	583		
	10-15	54-246		
	30	54		
The Lake Näsijärvi ~7000 m	4-5	37		
	20-21	235		
	29-30	17		

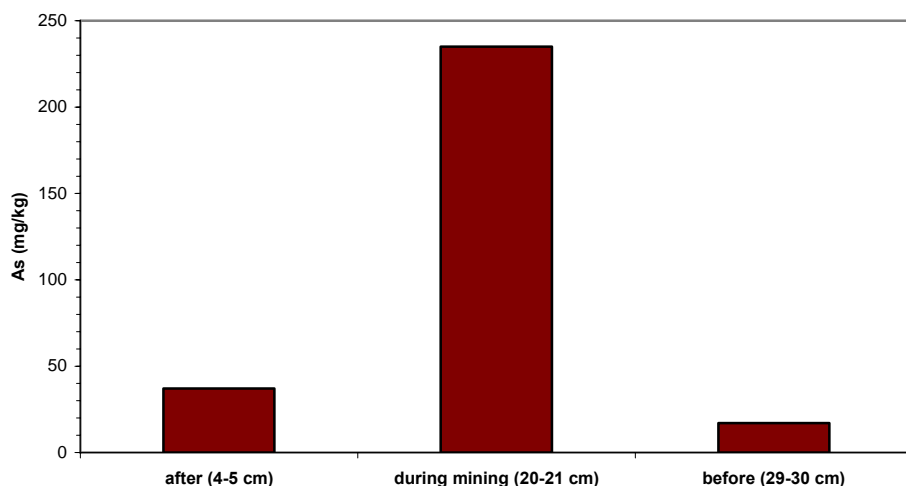


Figure 7. Arsenic concentrations in the sediment of Lake Näsijärvi before, during, and after mining activity.

### 3.4. Monthly surface water monitoring carried out by the Ramas Project

Monthly water samples collected by RAMAS imported new information about the dynamic changes in the arsenic transport complementing the annual, long-term monitoring data (Figure 8.). In addition to arsenic, many other elements were analyzed from these water samples. These water samples used for the actual transport modelling of arsenic were collected from March to December in 2005

from the Lake Parosjärvi (sampling point 1), the Stream Parosjärven oja (sampling points 2 and 3), Stream Vähä-Vahantajärven oja (4), Stream Vahantajoki alav mts (5) and Lake Näsijärvi (6) (Figure 8). Two sets of water samples were collected from each sampling point, filtered (0.45  $\mu\text{m}$ ) and non-filtered, and the 60 ml samples were acidified with 0.3 ml of suprapure nitric acid. The non-filtered samples were used to assess the role of suspended material in the transport. The laboratory analyses were performed with graphite furnace atomic absorption spectrometry (AAG) (Table 6).



Figure 8. RAMAS project surface water monitoring sites March – December 2005.

The total arsenic values progressively decreased from the Lake Parosjärvi towards the Lake Näsijärvi (Figure 9). The average concentrations of total arsenic in the different sampling points were 109  $\mu\text{g/l}$  in the sampling point 1 (surface), 118  $\mu\text{g/l}$  in the sampling point 2, 60  $\mu\text{g/l}$  in the sampling point 3, 19  $\mu\text{g/l}$  in the sampling point 4, 7.2  $\mu\text{g/l}$  in the sampling point 5 and 2.9  $\mu\text{g/l}$  in the sampling point 6 (surface). It is noteworthy that in the lake basins the arsenic concentrations seem to be stratified. The deep waters close to the bottom are clearly more enriched than the upper layer at both ends of the transport route (Figures 9a and 9c). This layering and also the transport rate are sensitive for the climatic conditions. The year 2005 was fairly dry in the Tampere region except for August when the precipitation was almost double compared to the long-term average. Drastically increased run-off due to heavy precipitation generates effective mixing in the Lake Parosjärvi resulting in the homogenisation of the water column. The increased discharge is seen slightly delayed as high arsenic concentrations in the streams and, especially in the deep waters at Lake Näsijärvi.

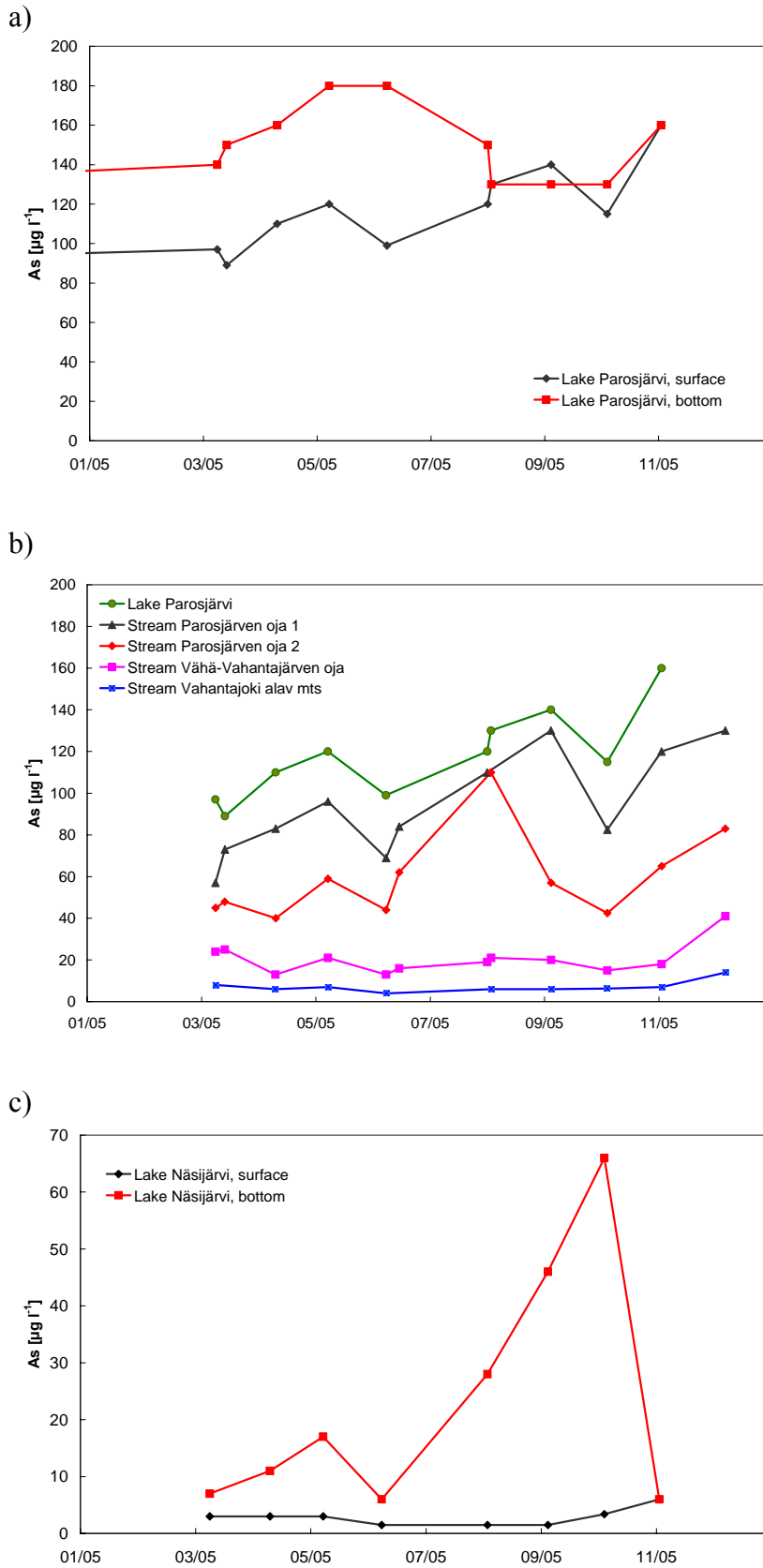
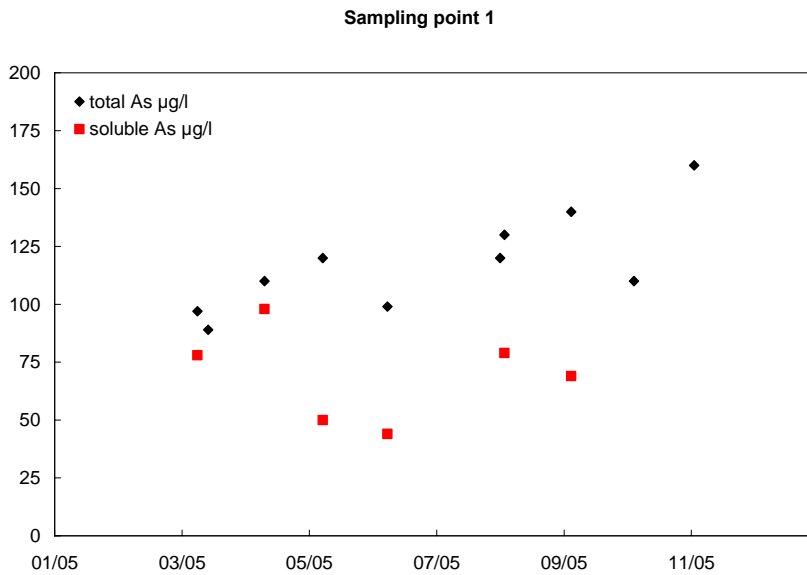


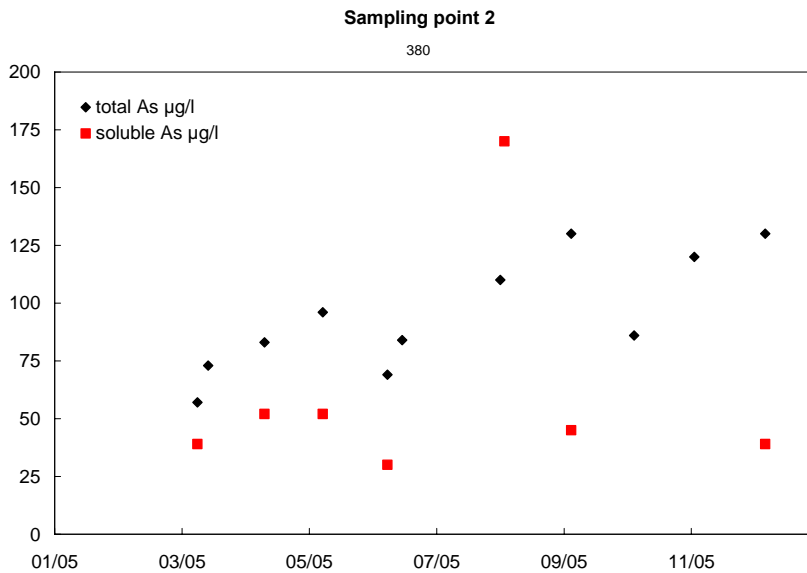
Figure 9. The total arsenic values in different surface water sampling points in the Ylöjärvi mine area in 2005: a) Lake Parosjärvi, surface sample (black) and deep sample (red), b) arsenic in Lake Parosjärvi and in sampling points 2-5 c) Lake Näsijärvi, surface sample (black) and deep sample (red).

Total arsenic (non-filtered sample) and soluble (filtered sample) arsenic concentrations are shown in the Figure 10a-10f. Concentrations of As, Cu and Fe as well as pH values are shown in Table 6. Comparison of filtered and non-filtered samples show that roughly half of the total arsenic is in soluble form and the rest is incorporated in the suspended solids. For example, in the sampling points 1, 2 and 3, the soluble arsenic concentrations were 63  $\mu\text{g/l}$  (total 109  $\mu\text{g/l}$ ), 61  $\mu\text{g/l}$  (total 118  $\mu\text{g/l}$ ) and 31  $\mu\text{g/l}$  (total 60  $\mu\text{g/l}$ ), respectively.

a)

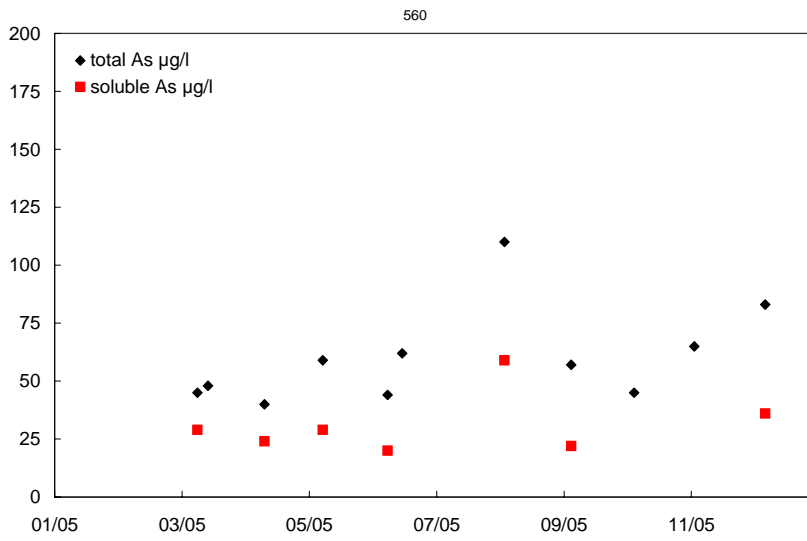


b)



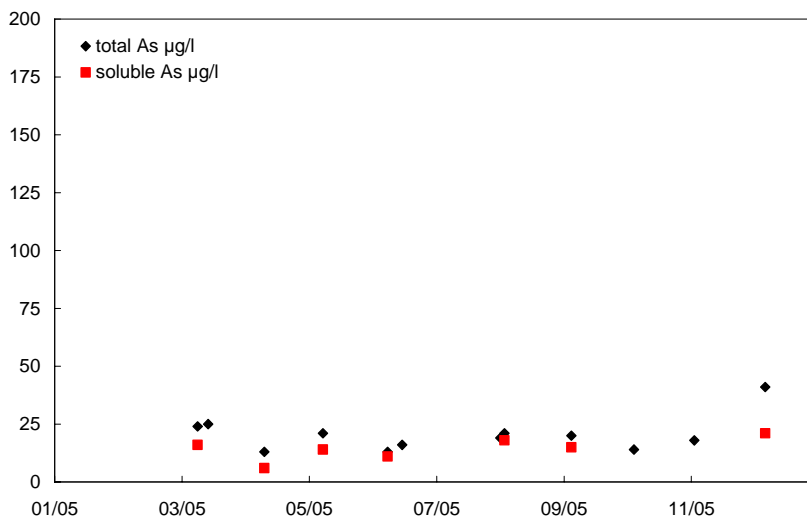
c)

Sampling point 3



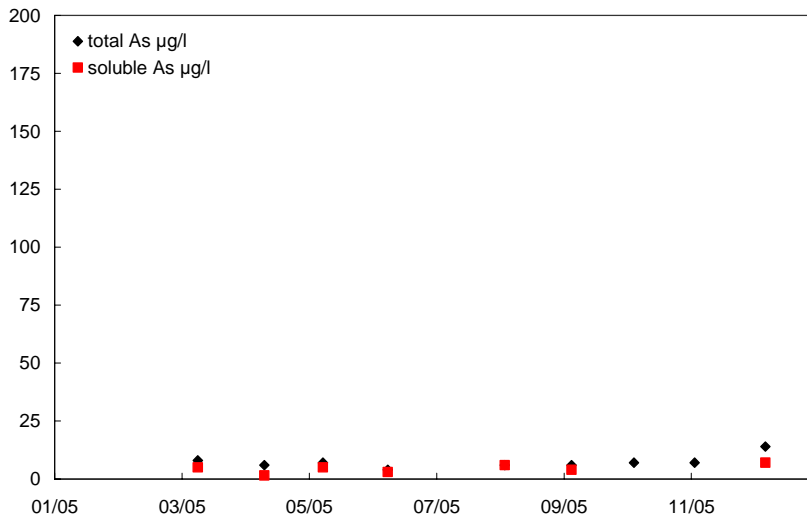
d)

Sampling point 4



e)

Sampling point 5



f)

Sampling point 6

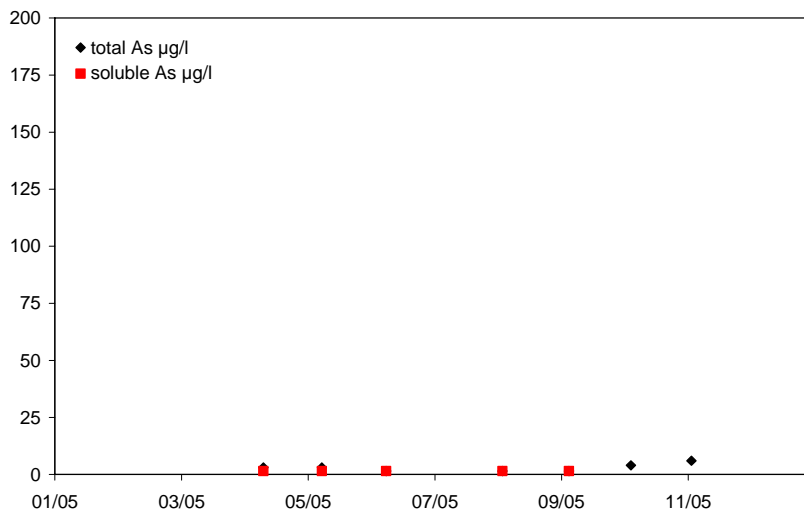


Figure 10. The total arsenic (blue) and soluble arsenic (red) values in different surface water sampling points in the Ylöjärvi mine area in 2005: a) Lake Parosjärvi (surface), b) Stream Parosjärvenoja 1, c) Stream Parosjärvenoja 2, d) Stream Vähä-Vahantajärven oja, e) Stream Vahantajoki alav mts f) Lake Näsijärvi (surface).

Table 6. Total arsenic, soluble arsenic, Cu and Fe analyses and pH of the surface water samples taken in 2005. AAG = atomic adsorption spectroscopy (graphic furnace), F = filtered sample with 0.45 µm membrane filter.

Sampling point 1					
Date	As total µg/l	As soluble 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 total µg/l	As soluble 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 total µg/l	As soluble 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 total µg/l	As soluble 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 total µg/l	As soluble 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

Sampling point 6					
Date	As total µg/l	As soluble µg/l	Cu µg/l	Fe µg/l	pH
11.4.2005	3	1,5		590	6.6
9.5.2005	3	1,5		340	7.2
9.6.2005	1.5	1,5		270	7.4
4.8.2005	1.5	1,5		170	7.3
5.9.2005	1.5	1,5		200	7.4
5.10.2005	4			240	7.2
3.11.2005	6			440	7.1

#### 4. MODEL DEVELOPMENT

The aim of the arsenic transport model was 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, the results of the sampling performed in 2005 were used in the study due to the limitations in the old data, which provided the total arsenic concentrations instead of the separation of dissolved and particulate bounded fractions.

The dynamical discharge values of small rivers in the study area can be calculated using the runoff model, VESISTÖMALLI, developed by the Finnish Environment Institute (Vehviläinen 1994). This model takes into account the meteorological and hydrological variables in the area. The model is based on a conceptual distributed runoff model, which is a Finnish version of the original HBV - runoff model (Bergström 1976), and water balance model for lake, river routing model and flood area models. The input variables for the model are daily precipitation, temperature and potential evaporation (Class A pan). The HBV rainfall-runoff model contains a description of the following processes: areal precipitation, snow accumulation and snowmelt, infiltration and storage of water in soil moisture zone and groundwater storage. In the precipitation model, precipitation is divided into the solid and liquid parts according to the daily mean temperature. The solid and liquid precipitations are then multiplied by different correction factors, which are mainly due to the effect of wind on the catch of precipitation gauges. The areal snow water equivalent and water yield from snow-pack are simulated with a model as well.

Although quite rarely applied to metals, the mass-balance approach offers a useful technique for quantifying the transport of trace elements such as arsenic in surface water. In mass-balance considerations data on both hydrological conditions and chemical quality of water are taken into account simultaneously. Water quality models can be either simple mass balance models or sophisticated conceptual models. However, the distinction between these two model types is not always clear, and it may sometimes be difficult to decide whether a model is "simple" or "conceptual". For example all conceptual models are based on mass balance considerations. Simple mass-balance models are often classified as black-box models because there are statistical components in these models or the basic assumptions are known to be valid in scientific sense, but they can produce results good enough when calibrated using sufficient data. Sophisticated, conceptual models also have statistical (or black-box) components, for all ecological knowledge cannot be included in only one model (Frisk 1989).

#### 4.1 Components of the modelling tool

Dilution, sedimentation and biochemical reactions are presumable processes controlling natural attenuation during arsenic transport. The general form of the model is an advection-dispersion model and first order kinetics using Eq. (1). The traditional advection-dispersion equation is a standard model for contaminant transport (e.g. Kinnunen *et al.* 1982). In the model the river basin is divided into hydraulically homogenous elements parallel to the surface of the river basin. In the elements, water quality changes in vertical direction only. The two basic principles of the model are the conservation of mass and the kinetic principle. The first principle implies conservation of mass even though material is changed in chemical and biological reactions from one form to another, while the kinetic principle states that the rate of change of a concentration is equal to the product of a coefficient and the concentrations of one or more variables that interact to cause the change. Estimation of parameters can be accomplished on the basis of experiments carried out in the field or in the laboratory, or parameters may be taken from the literature or estimated by calibration.

$$A_x \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( A_x D_L \frac{\partial c}{\partial x} \right) - \frac{\partial}{\partial x} (A_x u c) + S(c, Fe, pH \dots) A_x \quad (1)$$

- c = concentration of arsenic
- t = time
- x = distance
- $A_x$  = area of the element
- $D_L$  = dispersion coefficient



u = advective velocity  
 S = transformation processes

The first term on the right-hand side describes diffusion and the second one vertical advection. The third term describes transformation processes, e.g. chemical transformation and settling phenomena. In this application diffusion is a minor factor.

### Step 1

The starting point in developing the arsenic loss model was to assume that the transformation process obeys first order kinetics with a constant reaction rate coefficient. It means that all transformation processes can be defined to constant reaction rate coefficient (Eq. 2), since almost all transformation processes in the nature can be simplified.

$$S = -\rho c \quad (2)$$

$\rho$  = reaction rate coefficient of transformation processes ( $T^{-1}$ )

In Figure 11, the advection-dispersion model (Eq. 1 and Eq. 2) has been used to simulate the total arsenic concentration in different sampling points in 2005.

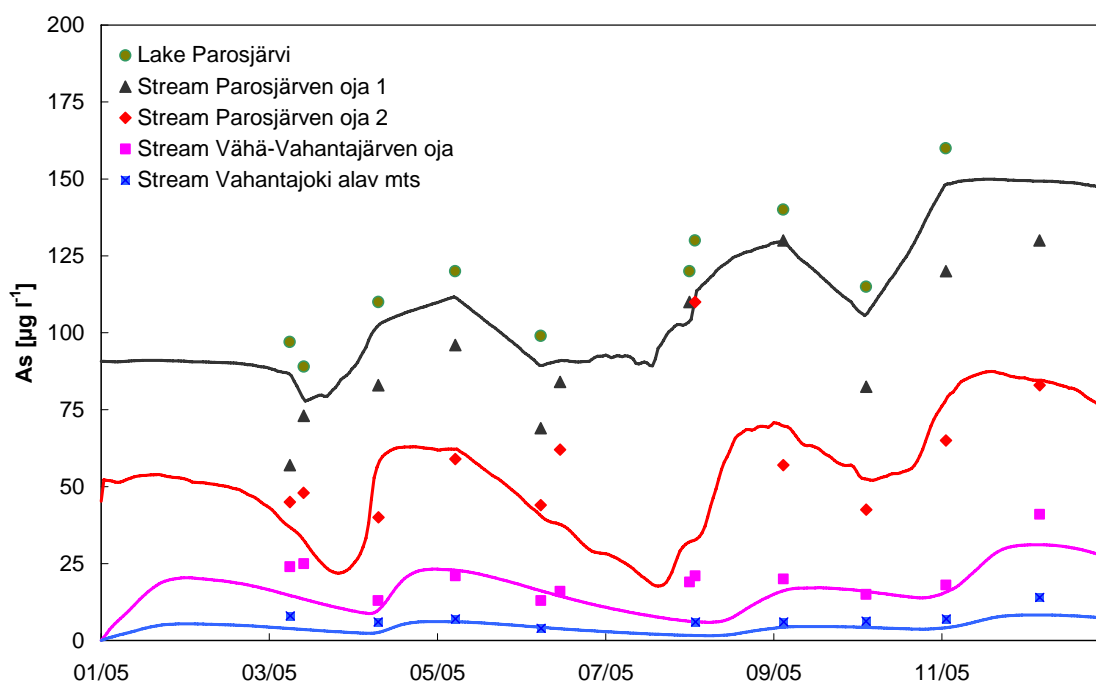


Figure 11. The simulation results of total arsenic concentration in different surface water sampling points from 2005 in the Ylöjärvi mine area using an advection-dispersion model and first order kinetics.

We can see that the results of the simulation are generally moderate in different sampling points but particularly in the beginning of the transport route (sampling point 2, Stream Parosjärven oja 1) a difference between the observations and the simulated results is quite significant. Therefore a more sophisticated description of transformation processes was tested.

## Step 2

It is arguable that particle bounded arsenic is settling better than dissolved arsenic. Therefore it seemed reasonable to divide total arsenic to particle bounded and dissolved arsenic and to consider the different processes affecting the transport of arsenic, Eq. 3.

$$c = c_p + c_s \quad (3)$$

$c_p$  = concentration of particle bounded arsenic

$c_s$  = concentration of soluble bounded arsenic

Particle bounded and soluble arsenic are behaving independently and these fractions have their own characteristic reaction processes. Generally, we can write the following equations (4-6):

$$S = S_p + S_s \quad (4)$$

$$S_p = -\rho_p c_p \quad (5)$$

$$S_s = -\rho_s c_s \quad (6)$$

$\rho_p$  = particle bounded arsenic loss process coefficient

$\rho_s$  = soluble arsenic loss process coefficient

There was no universal equation available and, therefore, for particle bounded arsenic sedimentation process was chosen as a principle factor controlling the arsenic transport in solid phase (Eq. 5). It is known that soluble arsenic reacts chemically in many ways. Complex ions of arsenic interact with secondary iron oxides and hydroxides, and in varying degrees with many manganese and aluminium precipitates. Clay and humus are also known to be good absorbents of arsenic. In this study the different correlations between soluble arsenic and other state variables were checked, but only the correlation of pH turned out to be significant (Figures 12-15). Therefore the equations (7 and 8) are the following:

$$\rho_s = f(\text{pH}) \rho'_s \quad (7)$$

$$f(\text{pH}) = -11.5 \text{ pH} + 12 \quad (8)$$

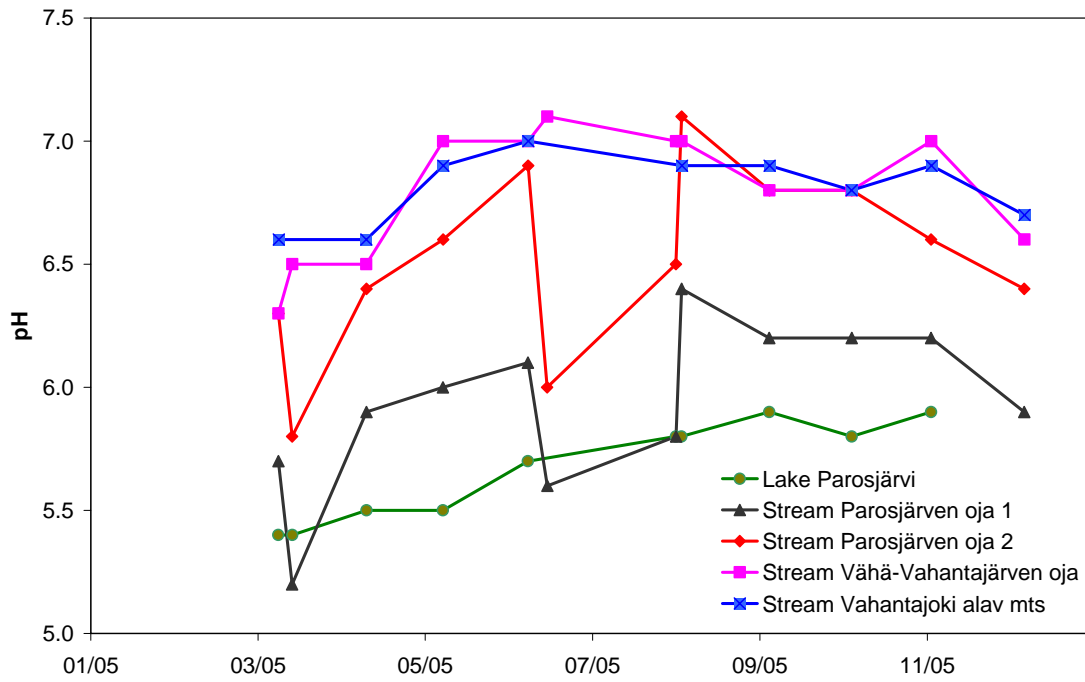


Figure 12. The pH values in different surface water sampling points in the Ylöjärvi mine area in 2005. The pH increases down stream and the variations become less drastic and abrupt.

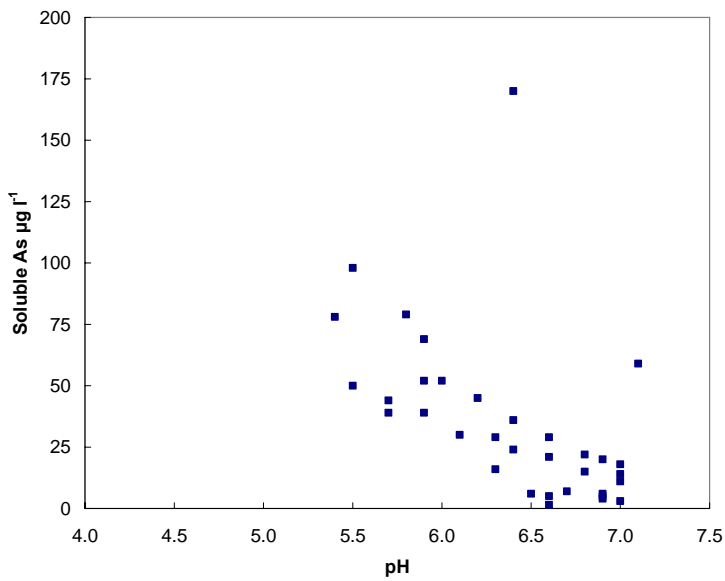


Figure 13. A correlation between pH and soluble As values in different surface water sampling points in the Ylöjärvi mine area in 2005.

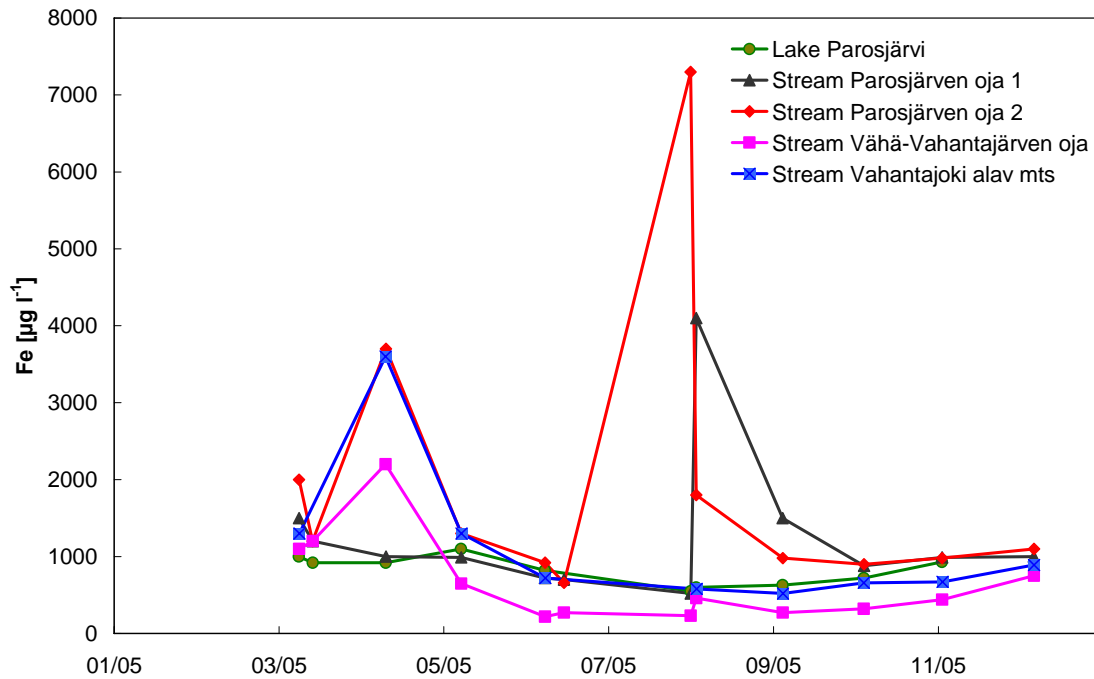


Figure 14. The Fe values in different surface water sampling points in the Ylöjärvi mine area in 2005.

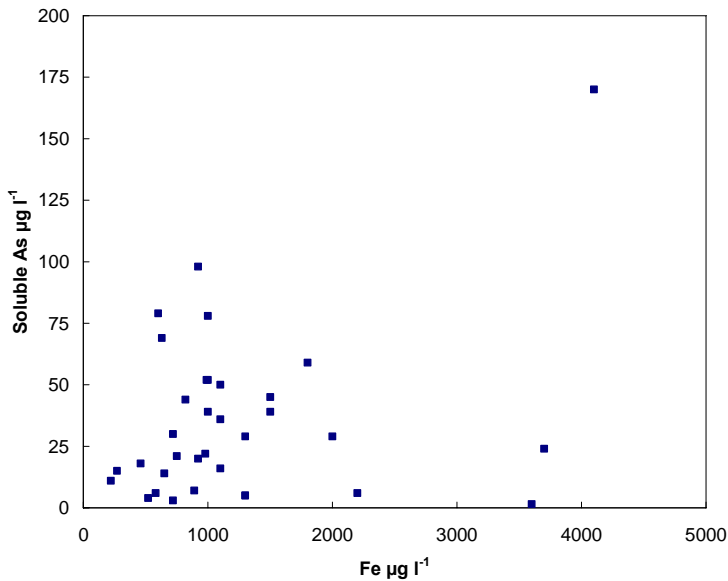


Figure 15. A correlation between Fe and As values in different surface water sampling points in the Ylöjärvi mine area in 2005.

In Figure 16, the advection-dispersion model has been exploited separately for particle bounded and soluble arsenic to simulate the total arsenic concentration in different sampling points. The driving process for particle bounded arsenic is sedimentation and the driving state variable for soluble arsenic is pH. When comparing Figures 10 and 16 it is evident that the simulation result did not get essentially better, which suggests that the system is more complex and probably several factors not considered in this exercise are affecting the behaviour of arsenic. However, the simulation improved the model is capable of producing a fairly good estimate of the arsenic fate in the transport route and the present version provides a sound basis for further developing work. In Figure 17, the

advection-dispersion model has been used to simulate the soluble arsenic concentration in different sampling points in 2005. The driving state variable for soluble arsenic is pH.

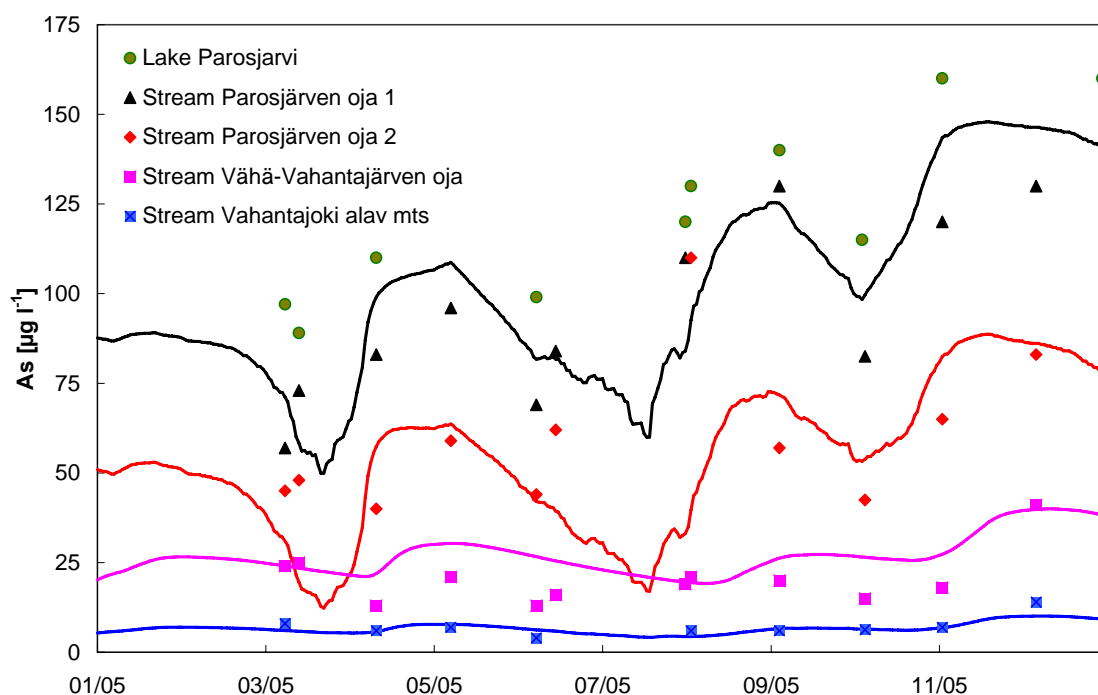


Figure 16. The simulation results of total arsenic in which arsenic has been exploited separately for particle bounded and soluble arsenic in different sampling points.

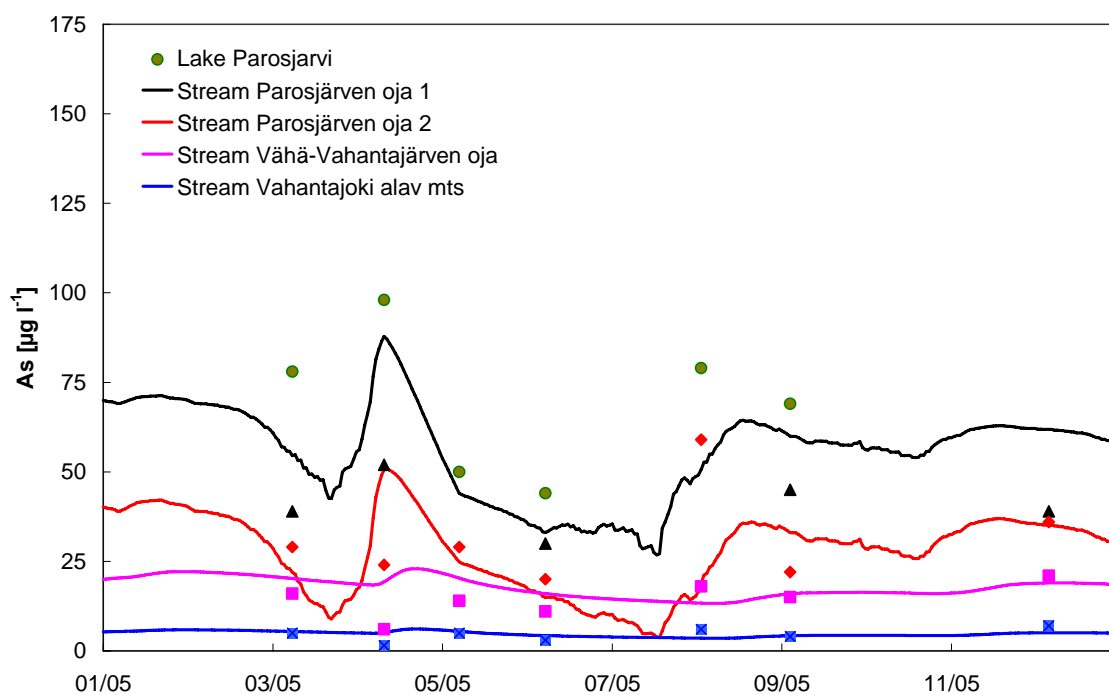


Figure 17. The advection-dispersion model has been used to simulate the soluble arsenic concentration in different sampling points in 2005.

In Figures 13 and 15, we can easily see that there exists a correlation between soluble As and pH but there is no correlation between soluble As and Fe. A chemical process between As and Fe is probably so quick that the observed values from Lake Parosjärvi and from the stream sampling points represent the situation after reaction and As and Fe values do not represent initial situation in the surface water. Therefore, it is not possible to find the correlation between those variables. However, we can assess that Fe is affecting As concentration but it is hard to make numerical modelling using available data. However, it gives reasons to write the equation (7) to the following form (9).

$$\rho_s = f(\text{pH}) f(\text{Fe}) \rho'_s \quad (9)$$

Using the observed As and Fe data from the mining site we can roughly try to study the process between arsenic and iron before the water is moving to the transport route. In Figure 18 is presented a correlation between arsenic and iron values. The data is from the stream leading from the tailings area to Lake Parosjärvi and from the stream after Lake Parosjärvi.

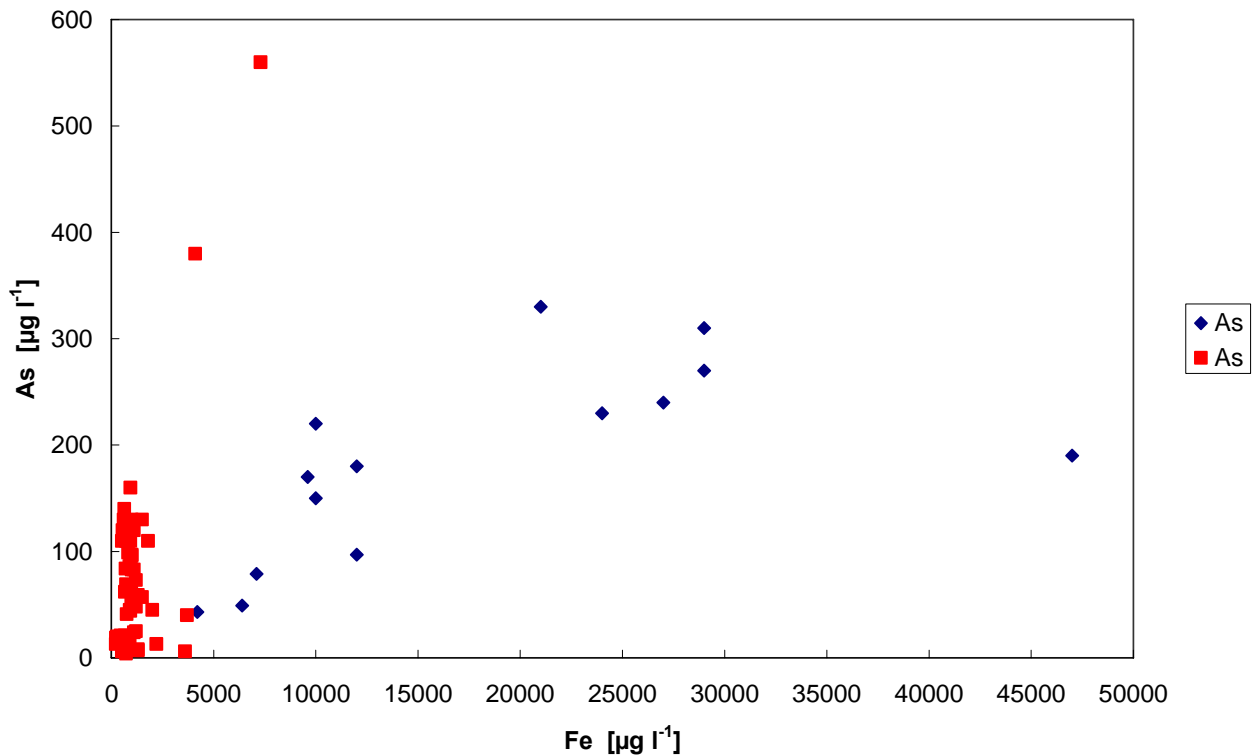


Figure 18. A correlation between arsenic and iron in the stream from the tailings area to Lake Parosjärvi (blue) and in the stream after Lake Parosjärvi (red).

In this study the total arsenic values were used due to the limitations in the old data. It makes an examination more uncertain but general conclusions are still possible. We can come to a conclusion that after Lake Parosjärvi iron is not coupled with arsenic anymore. The decreasing values of arsenic are a consequence of diluting, sedimentation and a reaction of pH. In the tailings area there is a clear correlation between total arsenic and iron. Concerning this figure, a limit in which iron does not react with arsenic seems to be in the range of 1000 – 10000  $\mu\text{g l}^{-1}$ .

The final used simulation equations in this study were Eqs. (10) and (11) for particle bounded and soluble arsenic, respectively.

$$Ax \, dx \, \partial c_p / \partial t = \partial / \partial x (Ax \, DL \, \partial c_p / \partial x) dx - \partial / \partial x (Ax \, u \, c_p) dx - \rho_p \, c_p \quad (10)$$

$$Ax \, dx \, \partial c_s / \partial t = \partial / \partial x (Ax \, DL \, \partial c_s / \partial x) dx - \partial / \partial x (Ax \, u \, c_s) dx - (1.5 \, \text{pH} + 12) \, \rho'_s \, c_s \quad (11)$$

## 5. MODEL EVALUATION

In the transport modelling, the first order reaction coefficient  $\rho_p$  (particle bounded arsenic sedimentation rate) was calibrated for Lake Vähä-Vahantajärvi. It was also possible to assess roughly the sedimentation coefficient in the same lake using lake sediment samples (arsenic concentrations, density, water content, and estimated deposition rate). The sedimentation coefficients values obtained with these two methods were  $0.13 \, \text{g m}^{-2} \, \text{a}^{-1}$  and  $0.07 \, \text{g m}^{-2} \, \text{a}^{-1}$ , respectively. There was, thus, a fairly good agreement between the sedimentation coefficient estimates that were of same order of magnitude. However, the calibrated sedimentation coefficient based on mass balance data was about 2 times greater than the sedimentation coefficient derived from the sediment data. A reason might be that a single sediment sampling point does not adequately describe the average sedimentation area in the lake. Also, the loose upper part of the lake sediment profile is susceptible for flow erosion. The recent sedimentation coefficient was calculated based on the accumulation after the Chernobyl marker (1986).

Besides the quite good calibration results of the transport model in which arsenic has been exploited separately for particle bounded and soluble arsenic, the similarity of sedimentation coefficients determined by different methods suggests that the basic structure of the transport model is accurate.

## 6. CONCLUSIONS

The main result of this model development is that by using a quite simple mass balance model it was possible to simulate arsenic transport in different circumstances. Dilution, sedimentation and biochemical reactions are presumable processes controlling natural attenuation during arsenic transport. One main goal of this approach was that on a catchment scale a relevant data survey should not be too laborious and expensive. The general form of the model is an advection-dispersion model and the first order kinetics. In order to improve the model and to understand the processes of a transport phenomenon, the particle bounded and dissolved fractions were treated separately. A fit of the simulation was better than using only total arsenic. The applied driving process for particle-bounded arsenic is sedimentation and the driving state variable for soluble arsenic is pH. Using this kind of approach the basic features of arsenic transportation can be studied and relevant data for risk assessment purposes can be produced. An advantage of this model is that it does not need very sophisticated data to achieve estimates of arsenic transport for surface waters in large catchments. The present model version provides a good starting point for future development. For instance, it would be interesting to test the model also with background arsenic values in some study areas.

By studying the lake sediment data it is also possible to assess which kind of history and also future is in the study area concerning arsenic concentrations. The sediment sampling indicates that still about forty years after terminating the mining operations the area contaminates the surface waters and the transport of arsenic the investigated transportation route is continuous (Figure 7). The measured arsenic concentrations in the lake sediment at Lake Näsijärvi, 7 km away from the source area, are twice as high as the local baseline value defined from the lower part of the sediment profile. A health limit of drinking water for arsenic is  $10 \, \mu\text{g/l}$  and this limit is overrun in the whole length of the route. This means that some kind of risk exists at least for surface water supply but perhaps also for the lake ecology too.

## 7. SUMMARY

RAMAS is a three-year project (2004 - 2007) funded by the participating organizations and the LIFE Environment programme of the European Union. The acronym RAMAS arises from the project title "Risk Assessment and risk Management procedure for ArSenic in the Tampere region". The project is targeting the Province of Pirkanmaa which comprises 28 municipalities, and has 469 000 inhabitants within its area.

The study area in the Vahantajoki river basin comprises an approximately seven kilometres long watercourse, here referred to as the transport route of arsenic, originating from the Ylöjärvi mine area.

Since 1975, local consulting companies have carried out surface water monitoring of the Lake Parosjärvi (Ylöjärvi mine area) and nearby streams and rivers, and the monitoring continues to the present day. The monitoring, done according to environmental permits under the supervision of the Pirkanmaa Regional Environment Centre (PREC), provides long-term data, which now comprises around 600 arsenic analyses along the whole length of the transport route from Lake Parosjärvi to Lake Näsijärvi. Monthly water samples collected by RAMAS imported new information about the dynamic changes in the arsenic transport complementing the annual, long-term monitoring data. In addition to arsenic, many other elements were analyzed from these water samples. These water samples used for the transport modelling of arsenic were collected from March to December in 2005.

The total arsenic values progressively decreased from the Lake Parosjärvi to the Lake Näsijärvi. The average concentrations of total arsenic in the different sampling points were 109 µg/l in the sampling point 1 (surface), 118 µg/l in the sampling point 2, 60 µg/l in the sampling point 3, 19 µg/l in the sampling point 4, 7.2 µg/l in the sampling point 5 and 2.9 µg/l in the sampling point 6 (surface). Filtered samples exhibited that roughly half of the total arsenic is soluble. For example, in the sampling points 1, 2 and 3, the soluble arsenic concentrations were 63 µg/l, 61 µg/l and 31 µg/l, respectively.

The aim of this study is to develop a statistical arsenic transport model for surface waters using monitored data and to take into account the discharge of small rivers and the sub-catchments, calculated using a runoff model. Dilution, sedimentation and biochemical reactions are presumable processes controlling natural attenuation during arsenic transport. The general form of the model is an advection-dispersion model and the first order kinetics. The advection-dispersion model, separately for particle bounded arsenic and soluble arsenic, has been used to simulate the total arsenic concentration. The driving process for particle bounded arsenic is sedimentation and the driving state variables for soluble arsenic are pH and iron. The main conclusion of this study is that by using a quite simple mass balance model it was possible to simulate arsenic transport in surface waters for risk assessment purposes.

## 8. YHTEENVETO

RAMAS on kolmivuotinen hanke (2004-2007), joka on rahoittajina on EU:n LIFE Environment – ohjelma ja hankkeeseen osallistuvat organisaatiot. Akronyymi RAMAS muotoutuu hankkeen nimestä "Risk Assessment and risk Management procedure for ArSenic in the Tampere region". Hankkeen kohdealueena on Pirkanmaan maakunta, joka koostuu 28 kunnasta ja jossa asuu 469 000 asukasta.



Tämä raportti on osa TASK-3:a, jossa koottiin tietoutta ihmisen toiminnasta aiheutuvista arseenipäästöistä. Tämän osahankkeen tarkoituksena oli kehittää tilastollinen arseenin kulkeutumismalli.

Arseenin esiintymismuoto riippuu ympäristöolosuhteista kuten pH:sta, redox-potentiaalista ja metalleista. Arseenin kulkeutumisen yksityiskohtainen prosessikuvaus vaatii valtavan laajan havaintoaineiston. Iso alueen arseenin kulkeutumisen mallintaminen vaatii kuitenkin suhteellisen yksinkertaisen mallikuvauksen. Mallin täytyy sisältää keskeiset prosessit, tilamuuttujat jne..., mutta tarvittavan havaintoaineiston määrä ei saa olla liian suuri eikä mallin käyttö liian työlästä. Tämä on erityisen tärkeää niiden mallintamistyökalujen osalta, jotka on suunnattu ympäristöviranomaisten alustavien selvitysten tekemiseen.

Mallinnusalue oli Ylöjärven kaivosalueen alapuolinen reitti, joka sijaitsee Vahantajoen vesistöalueella. Kaivosalue kuormittaa jokireittiä mm. arseenilla. Hankkeen tarkoituksena oli kehittää tilastollinen arseenin kulkeutumismalli. Mallinnuksessa hyödynnettiin kerättyä havaintoaineistoa ja otettiin huomioon valuma-alueen sivujokien vaikutus. Alueen hydrologia laskettiin erillisellä valumamallilla. Arseenin kulkeutumisen mallinnuksessa tärkeimpiä prosesseja ovat laimentuminen, sedimentaatio ja kemialliset prosessit. Mallin yleinen rakenne advektio-dispersio ja ensimmäisen kertaluokan kinetiikka. Advektio-dispersio -mallia käytettiin liukoisen ja kiintoaineeseen sitoutuneen arseenin pitoisuuden simulointiin. Keskeinen prosessi kiintoaineeseen sitoutuneen arseenin kuvauksessa on sedimentoituminen ja liukoisen arseenin osalta tilamuuttujien pH:n ja raudan kemialliset prosessit.

Vuodesta 1975 lähtien Parosjärven (Ylöjärven kaivosalue) ja siitä lähtevän joen veden laatua on seurattu Pirkanmaan ympäristökeskuksen koordinoimalla velvoitetarkkailulla. Koko 7 kilometrin mittaiselta vesireitiltä Parosjärvestä Näsijärveen on tehty yhteensä noin 600 arseenianalyysia. RAMAS-hankkeen aikana vuonna 2005 havaintotiheys on ollut noin kerran kuukaudessa, jolloin arseenipitoisuuksien dynaamista vaihtelua on voitu paremmin seurata mm. mallinnuksen tarpeisiin. Havaintotoiminta tehtiin maaliskuun ja joulukuun välillä vuonna 2005.

Kokonaisarseenipitoisuudet laskivat vähitellen Parosjärvestä Näsijärveen mentäessä. Keskimääräiset kokonaisarseenipitoisuudet eri näytepisteissä olivat: 109 µg/l Parosjärven pintavedessä, 118 µg/l jokipisteessä 2, 60 µg/l jokipisteessä 3, 19 µg/l jokipisteessä 4, 7,2 µg/l jokipisteessä 5 ja 2,9 µg/l Näsijärven pintavedessä. Suodatetut näytteet osoittivat, että karkeasti puolet kokonaisarseenista on liukoisessa muodossa. Esimerkiksi näytepisteissä 1,2 ja 3 liukoisen arseenin pitoisuudet olivat 63 µg/l, 61 µg/l ja 31 µg/l.

Tämän tutkimuksen pääasiallinen johtopäätös on, että suhteellisen yksinkertaisella massatasapainoon perustuvalla, empiirisellä mallilla on mahdollista simuloida arseenin kulkeutumista pintavedessä riskinarvioinnin tarpeisiin.

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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
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