# Determination of Arsenic and Arsenic Species in Ombrotrophic Peat Bogs from Finland

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# Determination of Arsenic and Arsenic Species in Ombrotrophic Peat Bogs from Finland

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# Summary

The main goal of this study was to evaluate how faithful arsenic (As) has been preserved in ombrotrophic peat bogs from Finland. The changing rates of atmospheric As deposition have been reconstructed using peat cores from three Finnish bogs: Harjavalta (Har), nearby a Copper (Cu) - Nickel (Ni) smelter, Outokumpu (Out), near a famous Cu-Ni mine, and a peat bog at Hietajärvi (Hie) which is remote from industrial activity.

To study the preservation of As within these cores, firstly several new accurate and sensitive analytical procedures for the reliable and direct determination of As in nitric acid digests of ombrotrophic peat samples at low ng $l^{-1}$ concentrations, namely hydride generation – atomic absorption spectrometry (HG-AAS), hydride generation – atomic fluorescence spectrometry (HG-AFS) and inductively coupled plasma – sector field – mass spectrometry (ICP-SF-MS) were developed. The analytical procedures were critically evaluated by analysing several certified plant and peat reference materials. Results for the determination of As in selected peat samples highly correlated underpinning the accuracy of all adopted analytical protocols (HG-AAS, HG-AFS, ICP-SF-MS).

Secondly, chronologies of atmospheric As accumulation in these cores were compared with historical records of industrialisation. Comparison of anthropogenic and natural As and Pb concentrations showed that anthropogenic As and Pb decreased from ~1000 AD onwards (coal burning) and that additionally the As concentration profiles reflected the atmospheric deposition history of the mining and smelting sites (Out, Har).

As an independent check of the retention of As by the peat cores, As was also determined in the pore waters using ICP-SF-MS. Only 0.02% to 0.05% of the total As concentrations were present in the pore waters, further suggesting that As is well retained in ombrotrophic peat bogs.

As a further check on the preservation of As by the peat cores and to mimic the leaching ability of the natural pore fluids of the peat which are derived exclusively from rainwater, As was extracted from fresh Finnish peat samples using water and the predominant As species were determined using anion-exchange HPLC-ICP-SF-MS. Extraction yields (0.7% to 12% of the total As concentrations) were low. All water extracts from the Finnish peat samples contained arsenic acid, and arsenous acid was present in all but two Finnish peat samples. Dimethylarsinic acid was the dominant organic arsenic species. The low extraction yields together with the low As concentrations in the pore waters indicate, that the arsenic species may react with their functional groups (onium centers, hydroxyl groups, doubly bonded oxygen atoms) and thus become preserved in peat bogs.

# Zusammenfassung

Das Ziel dieser Arbeit war die Untersuchung ob, und in welchem Ausmaß ombrotrophe Hochmoore als Archive atmosphärischer Arseneinträge dienen können. Für die Untersuchung dieser Fragestellung wurden folgende ombrotrophe finnische Hochmoore ausgewählt: Harjavalta (Har) in unmittelbarer Nähe eines Kupfer (Cu) - und Nickel (Ni) Hüttenwerks, Outokumpu (Out), benachbart zu einer ehemaligen Cu-Ni Mine, und Hietajärvi (Hie), in einem Nationalpark und somit frei von industriellen Belastungen.

Die Entwicklung neuer, nachweisstarker, präziser und genauer analytischer Verfahren für die Bestimmung von Arsen (As) in diesen Matrices mittels Hydrid – Atomabsorptionsspektrometrie (HG-AAS), Hydrid – Atomfluoreszenzspektrometrie (HG-AFS) und induktiv gekoppelter Argon – Plasma – Sektorfeld - Massenspektrometrie (ICP–SF–MS) war, augrund der zu erwartenden geringen As Konzentrationen, unumgänglich. Alle neu entwickelten Verfahren wurden durch die Messung zertifizierter Referenzmaterialien auf ihre Richtigkeit überprüft. Als weitere Qualitätskontrolle wurden ausgewählte Proben mittels HG-AAS, HG-AFS, und ICP-SF-MS analysiert, und die Ergebnisse dieser Messungen miteinander verglichen. Die sehr gute Übereinstimmung der Resultate bestätigte zusätzlich die Richtigkeit der entwickelten Verfahren.

Die gemessenen Arsenkonzentrationen der Hochmoorkerne wurden mit den Bleikonzentrationen dieser Profile verglichen. Der anthropogene Arseneintrag begann zeitgleich mit dem anthropogenen Bleieintrag im Zuge der Industrialisierung in Europa (~ 1000 AD, Kohleverbrennung). Außerdem reflektieren die Arsenkonzentrationen die Geschichte der benachbarten Mine und des Hüttenwerks.

Als weitere Bestätigung der Annahme, dass Hochmoore atmosphärische Arseneinträge archivieren, wurden Arsenkonzentrationen der Porenwässer dieser Moore mittels ICP–SF–MS bestimmt. Die geringen gefundenen As Konzentrationen (nur ~ 0.02% - 0.05% der Totalarsenkonzentration) bekräftigen diese Vermutung.

Zuletzt wurden die vorherrschenden Arsenspezies [Arsensäure As(V), arseniger Säure As(III), Dimethylarsinsäure (DMA) und Methylarsonsäure (MA)] mittels Wasser (um die natürlichen Gegebenheiten des Regenwassers und somit der Porenwässer zu simulieren) extrahiert, und mit Hochleistungsflüssigkeitschromatographie (HPLC) gekoppelt an ein ICP-SF-MS detektiert. Die Extraktionsausbeuten waren gering (0.7% bis 12% der enthaltenen Totalarsenkonzentrationen). Arsensäure konnte in allen Proben detektiert werden. As(III) wurde in fast allen Proben gefunden. Die dominierende anorganische Arsenverbindung war DMA. Die geringen Extraktionsausbeuten und die geringen gefundenen Arsenkonzentrationen in den Porenwässern verstärken die Hypothese, dass Arsen in Hochmooren konserviert ist: die Arsenspezies scheinen mit ihren funktionellen Gruppen (Hydroxylgruppen, Doppelbindungen, OH - Gruppen, Onium - Zentren) zu reagieren und bleiben so im Hochmoor erhalten.

**The results presented in this work were published in the following articles:**

**Chapter 3.1**

- J. Frank, M. Krachler and W. Shotyk **(2005)** Direct determination of arsenic in acid digests of plant and peat samples using HG-AAS and ICP-SF-MS. *Analytica Chimica Acta*, **530**, 307-316.

**Chapter 3.2**

- J. Frank, M. Krachler and W. Shotyk **(2005)** Determination of arsenic in peat samples using HG-AFS requires L-cysteine as pre-reductant. *Journal of Analytical Atomic Spectrometry* (submitted).

**Chapter 3.3**

- J. Frank, M. Krachler, A.K. Cheburkin and W. Shotyk **(2005)** Natural and anthropogenic atmospheric arsenic accumulation in ombrotrophic peat bogs from Finland. *Environmental Science and Technology* (manuscript in preparation).

**Chapters 3.6, 3.7, 3.8**

- J. Frank, M. Krachler and W. Shotyk **(2005)** Determination of arsenic species in ombrotrophic peat bogs from Finland using HPLC-ICP-SF-MS. *Environmental Science and Technology* (manuscript in preparation).

**Section 2.6.1**

- N. Givelet, G. Le Roux, A.K. Cheburkin, B. Chen, J. Frank, M.E. Goodsite, H. Kempter, M. Krachler, T. Nørnberg , N. Rausch, S. Rheinberger, F. Roos-Barraclough, A. Sapkota, C. Scholz, and W. Shotyk **(2004)** Suggested Protocol for Collecting, Handling, and Preparing Peat Cores and Peat Samples for Physical, Chemical, Mineralogical and Isotopic Analyses, *Journal of Environmental Monitoring* **6**, 481-492.

**During the period of research the following posters were presented at scientific meetings:**

- Frank J, Krachler M, Shotyk W **(2005)** Development of Extraction Procedures for the Determination of As in Two In-house Peat Reference Materials. *European Plasma Winter Conference on Plasma Spectrochemistry*, Budapest, Hungary, January 29-February 2.

- Frank J, Krachler M, Gonzalez ZI, Shotyk W **(2004)** Speciation of arsenic in peat using HPLC-Sector Field-ICP-MS. *Seventeenth Annual International Ion Chromatography Symposium*, Trier, Germany, September 20-23.

- Krachler M, Rausch N, Frank J, Le Roux G, Kober B, Shotyk W **(2003)** Sektorfeld-ICP-MS für die Bestimmung von Spurenelementen und Isotopenverhältnissen in Torfkernen und Porenwässern. *6. Symposium Massenspektrometrische Verfahren der Elementspurenanalyse/18. ICP-MS Anwendertreffen*, Berlin, Germany, October 6-9.

- Givelet N, Le Roux G, Roos-Barraclough F, Goodsite ME, Rausch N, Frank J, Krachler M, Nørnberg T, Cheburkin AK, Kempter H, Shotyk W **(2003)** Protocol for collecting, handling, and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses. *6th International Symposium on Environmental Geochemistry*, Edinburgh, Scotland, September 7-11.

- Frank J, Krachler M, Shotyk W **(2003)** Accurate Determination of Arsenic in Peat Bogs by HG-AAS and ICP-SF-MS. *6th International Symposium on Environmental Geochemistry*, Edinburgh, Scotland, September 7-11.

- Frank J, Krachler M, Shotyk W **(2003)** Atmospheric Deposition of Arsenic in Ombrotrophic Peat Bogs: Evaluation of Analytical Methods. *12th International Conference on Heavy Metals in the Environment*, Grenoble, France, May 26-30.

- Frank J, Krachler M, Shotyk W **(2003)** Comparison of Different Analytical Procedures for the Reliable Determination of Arsenic in Peat and Plant Materials. *European Plasma Winter Conference*, Garmisch-Partenkirchen, Germany, January 12-17.

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*For my family*

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# 1 Introduction

## 1.1 Arsenic and Arsenic Species

### 1.1.1 A Brief History of Arsenic

Arsenic probably has the worst public relations record of all elements due to the fact that is has been used as a poison since humans first became interested in chemistry. The popularity of arsenic as a poison is due more to its availability, low cost, and the fact that it is tasteless and odourless than to its effectiveness. Common arsenicals cause a slow and painful illness rather than instantaneous and certain death. One of the earliest documented cases of arsenic poisoning was Nero´s poisoning of Britannicus. Through the centuries arsenic has been surrounded by mystery and myth as a synonym for poison. The odourless, tasteless white powder arsenic trioxide was known as the 'king of poisons'. Since 315 B.C., when sulfidic arsenic ores (orpiment, realgar) were first mentioned by Aristotle, numerous arsenic bearing minerals have been fascinating people because of their bright red and yellow colours (Azcue and Nriagu, 1994).

The discovery of elemental arsenic is generally credited to the German Dominican scholar and alchemist Albertus Magnus (1193-1280), although several other people have also been cited as the discoverer. The discovery of several new arsenic species started when chemistry was finally separated from alchemy in the middle of the eighteenth century.

Arsenic´s popularity as a poison declined dramatically in the latter of the 19th century, due to the development of a highly reliable and sensitive assay described by Marsh in 1836.

Until nowadays numerous species have been detected and investigated enhancing the knowledge about the fate of arsenic in the environment and the potential for its use and application (Azcue and Nriagu, 1994).

### 1.1.2 Properties of Arsenic

Arsenic belongs to group 15 of the periodic table, has the atomic number 33 and an atomic mass of 74.92. Arsenic is a metalloid widely distributed in the earth's crust and present at an average concentration of 2 mg/kg. Arsenic has five valence states:-3, 0, +1, +3, and +5 (Welch et al., 1988). At near-neutral pH the solubility of most trace-metals is severely limited by precipitation or copercipitation (e.g. oxide, hydroxide, carbonate or phosphate mineral, strong absorption to hydrous metal oxides, clay or organic matter). In contrast arsenate tends to become less strongly sorbed as the pH increases (Dzombak and Morel, 1990). Under some conditions the anions can persist in solution at relatively high concentrations, even at near-neutral pH. Therefore, oxyanion-forming elements (e.g. As, Cr, U, and Se) are some of the most common trace contaminants in groundwaters.

Arsenate is generally the stable oxidation state in oxygenated environment. Arsenic and its species occur in crystalline, powder, amorphous or vitreous forms. Arsenic is widespread in the environment and can be detected in traces everywhere.

Arsenic speciation is controlled by pH and Eh. $H_2AsO_4^-$ (Fig. 1-1) is the dominant species under oxidising conditions at low pH. At higher pH (> ~ 9.9) $HAsO_4^{2-}$ becomes dominant. $H_3AsO_4^0$ and $AsO_4^{3-}$ may be present in extremely acidic and alkaline conditions, respectively. At pH less than ~ 9.2, $H_3AsO_3^0$ will predominate (Fig. 1-1). In the presence of extremely high concentrations of reduced sulphur, dissolved arsenic-sulphide species can be significant. The precipitation of orpiment ($As_2S_3$), realgar (AsS) or other sulphide minerals may be favoured by acidic, reducing conditions.

Equilibrium thermodynamic calculations predict, that As(V) should dominate over As(III) in all but strongly reducing conditions. However, the theoretical behaviour is not necessary followed because of the affects of biological processes on individual arsenic species. Cullen and Reimer (1989) for example report As(V):As(III) ratios in oxygenated seawater of 0.1-250, driven by biological transformation, although the ratios should be theoretically of the order of $10^{15}$-$10^{26}$.

Organic arsenic forms may be produced by biological activities. The ability of microorganisms to generate volatile arsines was established in 1933 by Challenger (Challenger et al., 1933). The authors reported the production of volatile arsines by strains of *Penicillium brevicaulis* growing on bread.

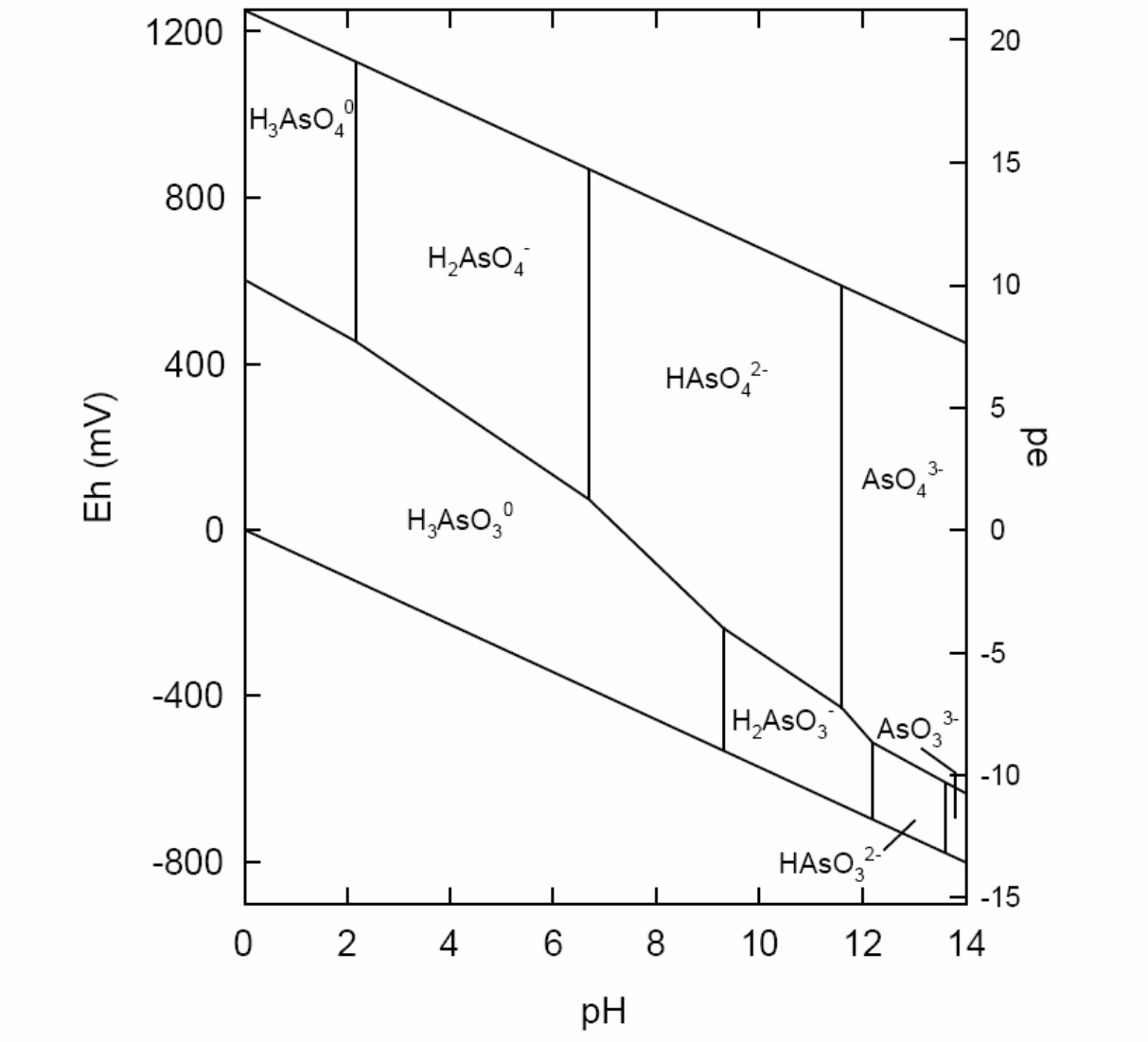



**Fig. 1- 1**: Eh-pH diagram of aqueous As species (World Health Organisation, 2001)

Arsenic is mobilised in the environment through a combination of natural processes. These include weathering reactions, biological activity, and volcanic emissions. Other important sources are anthropogenic including mining activity, combustion of fossil fuels, the use of arsenical pesticides, herbicides and crop desiccants, and the use of arsenic as an additive to livestock feed for poultry and swine. Arsenic is also used as a wood preservative.

### 1.1.3 Natural Occurring Organoarsenic Species

The total arsenic concentration in seawater is almost uniformly (0.5 – 2 mg As $l^{-1}$, Francesconi and Edmons, 1997). Arsenic concentrations in marine organism are sufficiently high to allow the determination of arsenic species: for example marine algae and animals may contain As at mg/kg level due to their ability to accumulate high amounts of arsenic (Francesconi and Edmonds, 1993). Since the organic arsenical arsenobetaine (AB) was first identified by Edmons et al. (1977) in the western rock lobster, arsenic species in the marine environment have been investigated intensively. One of the main subjects was marine algae, and the organoarsenicals so far detected in these organisms are arsenoriboses and traces of methylarsonic acid (MA) and dimethylarsinic acid (DMA). Tetramethylarsonium cation (TETRA), arsenobetaine (AB), and arsenocholine (AC) have not been found in marine algae (Francesconi and Edmonds, 1997). Additionally, Edmons and Francesconi (1981) identified arsenosugars isolated from brown kelp as intermediates in the cycling of arsenic. These species could be subsequently metabolised to arsenobetaine. The following organic arsenic species have been identified in marine ecosystems during the past three decades: Methylarsonic acid (seawater, sediments, sediment pore water, algae), dimethylarsinic acid (seawater, sediments, sediment pore water, algae, animals), trimethylarsine oxide (TMAO, sediments, sediment pore water, animals), the tetramethylarsonium cation (animals), arsenobetaine (animals), arsenocholine (animals), arsenoriboses (algae, animals) (Francesconi and Edmonds, 1997).

The As concentrations in terrestrial organisms are generally lower than the As concentrations in marine organisms, and therefore the determination of As species in these organisms is more difficult, due to a lack of methods with sufficiently low detection limits. For a long time organic arsenic species in terrestrial plants seemed to be restricted to the species MA, DMA, and TMAO (Cullen and Reimer, 1989). Since AB was reported for the first time in a mushroom sample of terrestrial origin in 1995 (Byrne et al., 1995), a variety of organoarsenic species formerly attributed only to marine organisms have been detected also in terrestrial green plants. Uncontaminated green plants usually contain 0.2 to 0.4 mg As/kg dry mass. Green plants from contaminated areas e.g. mine wastes were found to contain arsenic up to the high mg/kg level (Cullen and Reimer, 1989). Structures of organoarsenic species detected in marine and terrestrial environment are shown in Figure 1-2.

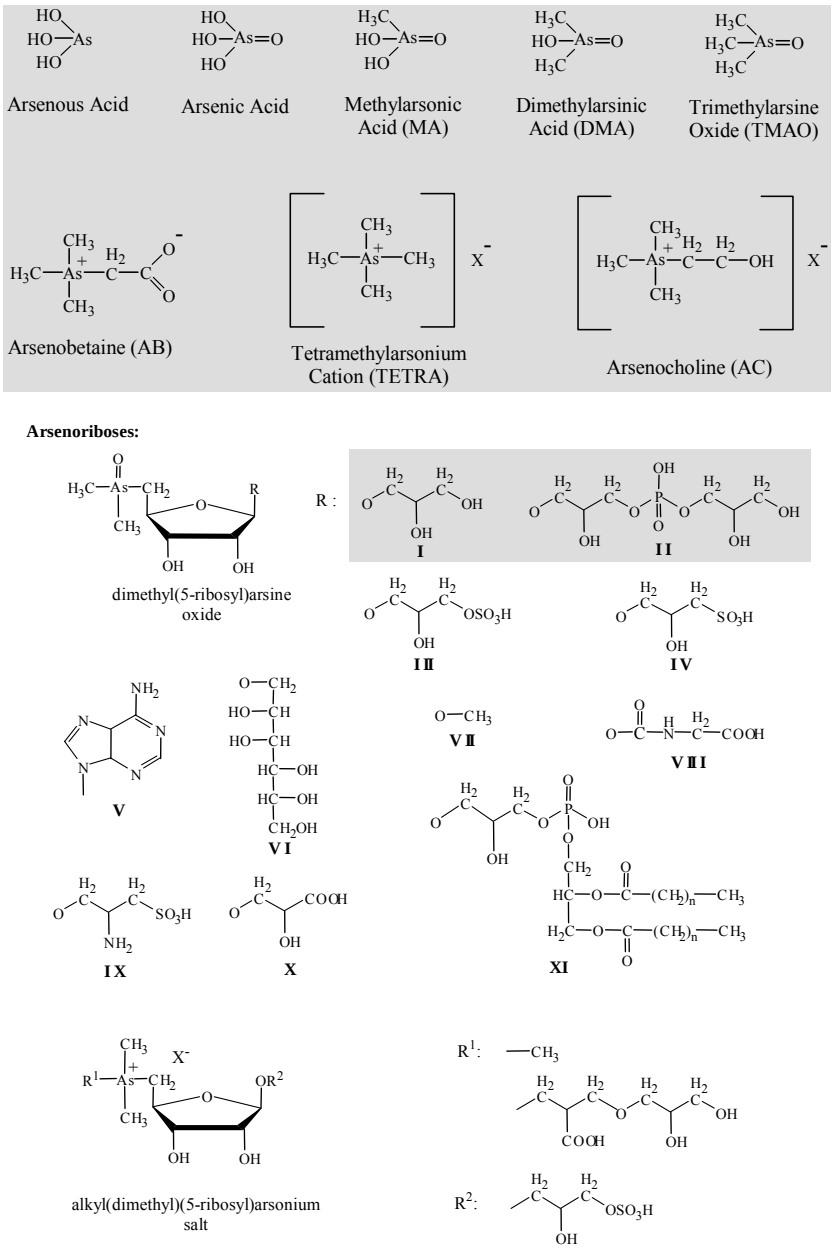



**Fig. 1-2:** Organoarsenic species detected in the marine environment. Shaded species have also been detected in the terrestrial environment (adapted from Kuehnelt 2000).

The identification of organoarsenicals such as AB, AC, TETRA, or arsenoriboses in terrestrial green plants confirmed the theory, that these organoarsenic species are constituents of the terrestrial environment. A variety of different terrestrial samples was reported to contain organoarsenic species: Freshwaters including groundwaters, as well as waters from wells, taps, rivers, ponds and lakes and sediment pore waters; soils and sediments; microorganisms; freshwater algae; mushrooms; lichens; green plants; urine, feces, blood, and tissues of animals; human urine, blood, and tissues have been studied (Kuehnelt, 2000).

## 1.1.4 Occurrence of Arsenic and Arsenic Species

### 1.1.4.1 Earth Crust

Arsenic can be found in more than 200 minerals. About 60% of these are arsenates, 20% sulphides and sulfosalts and the remaining 20% include arsenides, arsenites, oxides and elemental arsenic (Onishi, 1996).

Major arsenic containing minerals are the sulfidic ores of which arsenopyrite is the most common, realgar, and orpiment, as well as arsenides of copper, lead, silver, or gold (World Health Organisation, 1981). Some of the most common naturally occurring arsenic bearing minerals are summarized in Table 1-1. Inorganic arsenate may also be bound to oxides or almost any metal cation present (iron, aluminium, lead, magnesium, and zinc).

Arsenic tends to be found associated with sulphide-bearing mineral deposits, often as separate As minerals due to its ability to bind to sulphur ligands. Concentrations of As in various types of igneous rocks range from >1 to 15 mg As/kg. Concentrations in limestone and sandstone are similar. Concentrations as great as 900 mg As/kg have been found in phosphate rocks (O´Neill, 1990). Concentrations in coals and bituminous deposits are highly variable. In some coals extremely high As concentrations (up to 35 000 mg $kg^{-1}$) have been reported (Belkin et al., 1998), although generally lower concentrations (2.5 – 17 mg $kg^{-1}$) were reported (Palmer and Klizas, 1997).

**Table 1- 1:** Some of the most common naturally occurring arsenic bearing minerals (adapted from Azcue and Nriagu, 1994).

| Name | Formula |
|---|---|
| Arsenargentite | $Ag_3As$ |
| Chloanthite | $(Ni, Co)As_{3-x}$ |
| Domeykite | $(Cu_3As)$ |
| Loellingite | $FeAs_2$ |
| Niccolite | NiAs |
| Skutterudite | $(Co, Ni)As_3$ |
| Orpiment | $As_2S_3$ |
| Realgar | $As_4S_4$ |
| Arsenopyrite | FeAsS |
| Cobaltite | CoAsS |
| Enargite | $Cu_3AsS_4$ |
| Tennantite | $(Cu, Fe)_{12}As_4S_{13}$ |
| Pearcite | $Ag_{16}As_2S_{11}$ |
| Proustite | $Ag_3AsS_3$ |
| Gersdorffite | NiAsS |
| Arsenolite | $As_2O_3$ |
| Adamite | $Zn_2AsO_4OH$ |
| Olivenite | $Cu_2AsO_4OH$ |

#### 1.1.4.2 Air

Today, arsenic is emitted into the atmosphere primarily as $As_2O_3$ or as a volatile organic compound: during the smelting process arsenic is volatized as arsenic trioxide. Arsenic trioxide can also be obtained by the roasting of arsenopyrite. Arsines ($AsH_3$, $CH_3AsH_2$, $(CH_3)_2AsH$, $(CH_3)_3As$, and arsines from arsenoriboses) that are released form microbial

sources in soils or sediments undergo oxidation in the air and settle back to the ground. Arsenic in air exists mainly as particulate matter and is mostly absorbed to particles < 2μm (Coles et al., 1979). The particles return to the earth by wet or dry deposition. The atmospheric residence time of particulate-bound arsenic depends on particle size and meteorological conditions, but a typical value is about 9 days (US EPA, 1982).

Concentrations of arsenic in remote and rural areas range from 0.02 to 4 ng/$m^3$. In urban areas, arsenic concentrations range from 3 to 200 ng/$m^3$. Concentrations up to > 1000 ng/$m^3$ have been measured in the vicinity of industrial sources. Arsenic concentrations vary worldwide as follows: 0.007-1.9 ng/$m^3$ in remote areas; 1-28 ng/$m^3$ in rural locations, and 2-2320 ng/$m^3$ in urban environments (Schroeder et al., 1987).

Arsenic in air is usually a mixture of arsenite and arsenate. Organic species are of negligible importance, except in areas where significant quantities of methylated arsenic pesticides are applied. Some arsenic species are volatile and contribute significant fluxes in the atmosphere. It has been estimated that the atmospheric flux of As is about 73 540 tonnes/year (Chilvers and Peterson, 1987). About 40% is derived from anthropogenic sources. Most important natural sources of arsenic are volcanic emission and low temperature volatilization (microbiological activity).

#### 1.1.4.3 Water

Arsenic enters the atmosphere through several pathways as wind erosion, volcanic emission, low temperature volatilisation from soils, marine aerosols and pollution. Arsenic is returned to the earth's surface by wet and dry deposition.

Arsenic is present in rainwater at mean concentrations of 0.2 - 0.5 μg $l^{-1}$ (Welch et al., 1988). Oxidation states vary according to the arsenic source. When arsenic is derived from combustion processes, such as smelters, coal burning and volcanic sources, $As_2O_3$ is likely to be dominant. Organic species may be derived by volatilisation from soils, arsines from landfills and reducing soils such as peats, and arsenate may be derived from marine aerosols. Reduced forms will undergo oxidation by $O_2$ and reactions with $SO_2$ or $O_3$ are likely (Cullen and Reimer, 1989).

Concentrations of arsenic in seawater range typically from 0.5 - 2 μg/L (Francesconi and Edmonds, 1997). Arsenic in seawater may be present as arsenate, arsenite, MA and DMA (Maher and Butler, 1988). Depletions in phosphate in biologically productive surface waters

are mirrored by depletions in arsenate. Arsenate concentration minima often coincide with photosynthetic maxima evidenced by high concentrations of chlorophyll *a* (Cullen and Reimer, 1989).

Arsenic concentrations in groundwater average about 1-2 µg/L, except in areas with volcanic rock and sulphide mineral deposits where arsenic levels can range up to 3400 µg/L (Welch et al. 1988; Page, 1981; Robertson 1989). Arsenic concentrations up to 48 mg/L have been reported in some mining areas (Welch et al., 1988). The geometric mean of the arsenic concentration in European, and North and South American river water was reported to be 1.4 µg As/L (Cullen and Reimer, 1989). Arsenate is the dominant species in groundwater, although some have been found to contain a high proportion of arsenite. Concentrations of methylated species in natural waters are usually < 0.3 µg/L (ATSDR, 1993).

#### 1.1.4.4 Soil and Sediments

Arsenic concentrations in soils and sediments are dependent on the geological conditions as well as on anthropogenic activities, e.g., the use of pesticides, mining activities, or industrial processes. Average arsenic concentrations of uncontaminated soils were reported to be usually below 15 mg As/kg. In contaminated soils arsenic concentrations of more than thousand mg As/kg can be reached (Smith et al., 1998) Arsenic concentrations up to 27 000 mg/kg were reported in soils contaminated with mine or smelter wastes (US EPA, 1982). Depending on the soil and soil type and the microbial activity, processes involving demethylation, methylation, and reduction can occur in soil (Cullen and Reimer, 1989).

Arsenic may also be bound to the organic matter in soils, in which case it is released into the soil solution as the organic matter is oxidised and is then available for plant uptake or fixation by soil cations. Some arsenic from other inorganic forms is also available for plant uptake, inasmuch as the slightly soluble iron and aluminium arsenates and the soil solution are in equilibrium. The amount released for plant uptake is a function of the particular chemical and physical forms of individual arsenic species. The amount of available arsenic (extracted with 0.05M hydrochloric acid and 0.025 M sulphuric acid) averages in virgin soils about one-tenth of the total arsenic (National Research Council, 1997).

Uncontaminated sediments usually contain below 10 mg As/kg dry mass, whereas contaminated sediments can contain up to 10 000 mg As/kg dry mass (World Health Organisation, 1981).

Methylation and reduction of arsenic in soil is attributed to microbial activity as well as to organic matter. Evolution of arsines from sterilised soil treated with DMA did not occur, whereas generation of DMA from non sterilised soil was observed (Gao and Burau 1997). Turpeinen et al. (1999) investigated the influence of microbes on the biomethylation of arsenic in soil samples collected from a wood impregnation plant in Southern Finland. The main arsenic compound within the four soil samples was arsenate. MA was only found in one sample. After aerobic incubation, MA was detected together with DMA. When the samples were incubated anaerobically, no organoarsenic species were formed. Also AB is reported to be found in incubated soil due to activity of microorganism (Pongratz, 1998).

Organoarsenic species in sediments seem to be restricted to MA and DMA, although Cullen and Reimer (1989) report the detection of MA, DMA and TMAO in culture media of sediments incubated with arsenate or arsenite. Additionally the release of methylarsines was observed.

Whereas the presence of AB in soil and sediments has yet to be confirmed, the presence of MA and DMA due to microbiological activity seems to be well established.

## 1.1.5 Sources of Environmental Pollution

### 1.1.5.1 Industry

The two major industrial processes leading to anthropogenic arsenic contamination of air, water and soil are smelting of non-ferrous metals and the production of energy from fossil fuel. Other sources of contamination are the manufacture and the use of arsenical pesticides and wood preservatives. The largest single anthropogenic input into the atmosphere is generated from smelting activities (Chilvers and Peterson, 1987). Another source of contamination of soil and, because of leaching also of groundwater, are tailings from metal-mining operations.

The total industrial emission of arsenic to the air in the member states of the European Union in 1990 was estimated to be 575 tonnes, of which 492 tonnes came from stationary combustion (mainly coal and oil combustion). The emission of the missing 77 tonnes was

estimated to derive mainly from the iron and steel as well as the non-ferrous metal industry (DG Environment, 2000). Arsenic is also present in the rock phosphate used to manufacture fertilisers and detergents. Hutton and Symon (1986) report the import of 1324 * $10^3$ tonnes of rock phosphate to the United Kingdom in 1982, with an estimated arsenic burden of 10.2 tonnes.

### 1.1.5.2 Agricultural Uses

Before the 1960s mainly inorganic arsenic species, such as lead and calcium arsenate and copper acetoarsenite have been used in agriculture. Nowadays, also organic arsenic species (MA, DMA) are also used.

Woolson (1983) reported arsenical pesticides to be one of the largest classes of biocontrol agents in the USA in 1983. The use of total arsenical pesticides, excluding wood preservatives, was estimated at 7-11*$10^3$ tonnes As/year. Application of lead arsenate to orchards in the USA ranged from 32 to 700 kg As/ha. Residues in orchard soils as high as ~ 2500 mg/kg have been reported.

### 1.1.5.3 Military Uses

The gas lewisite was used during World War I and was highly effective in producing casualties, because it caused skin lesions that were difficult to heal. Arsenic species, that are highly irritating to the skin, eyes, and respiratory tract, thereby causing dermal pain, sneezing and vomiting, may still be used, but chemical and pharmacologic information of these species is difficult to obtain. Several arsenical species are available for use as riot control agents that act as severe irritants to the skin and mucus membranes. Information about their other effects is not available in the literature (National Research Council, 1997). Dimethylarsinic acid (Agent Blue) was used during Viet Nam war as a defoliant.

#### 1.1.5.4 Production and Application

Arsenic species are mainly used in the electronics industry, metallurgy, and in agriculture as pesticides, insecticides, defoliants, debarking agents for trees, wood preservatives and soil sterilants (Azcue and Nriagu, 1994).

Arsenic production is mainly based on its occurrence as a by-product of the smelting of copper, lead, cobalt, and gold ores (Azcue and Nriagu, 1994). It is present in flue dust from the roasting of ores, especially those produced from copper ores, mainly as arsenic trioxide, which can be recovered. Arsenic trioxide can also be obtained by the roasting of arsenopyrite. The world production of arsenic trioxide was 47,632 tons in 1990, with Sweden, the USSR, France, and Mexico being countries of the highest production (Azcue and Nriagu, 1994).

Arsenic species are industrially applied in glass manufacturing, electrophotography, pyrotechnics, ceramics, dyes and soaps, as catalysts, antifouling paints, and pharmaceutical substances.

In electronics gallium and indium arsenide are used in solar cells, optoelectronic devices, semiconductors, and light-emitting diodes. In metallurgy it is added to alloys and battery plates.

Additionally, arsenic is still in use in medicine in some developing countries (Azcue and Nriagu, 1994). In 1998, the complete remission of patients suffering from acute promyelocytic leukemia after treatment with arsenic trioxide was reported (Soignet et al., 1998). This observation offers a new application field of arsenic in medicine in the future.

By 1990, the estimated use of arsenic in the USA was 70% in wood preservatives, 22% in agricultural use, 4% in glass, 2% in non-ferrous alloys and 2% in other uses.

### 1.1.6 Distribution in the Environment

High-temperature processes, such as coal-fired power plants, burning vegetation and volcanism emit As into the atmosphere. Other sources are naturally occurring low – temperature biomethylation and microbial reduction to arsines. Arsenic is present in the atmosphere mainly as $As_2O_3$, adsorbed on particulate matter. These particles are dispersed by

the wind, depending on their size, and return to earth by dry or wet deposition. An average value for the atmospheric residence time of arsenic is about 9 days (US EPA, 1982). Arsenic may be adsorbed from water on to clays, iron oxides, aluminium hydroxides, manganese species and organic material. Additionally methylation and demethylation reactions control the mobilisation and subsequent distribution of arsenicals.

There exist three major modes of arsenic biotransformation in the environment: redox transformation between arsenite and arsenate, the reduction and methylation of arsenic, and the biosynthesis of organoarsenic species.

Dissolved forms of arsenic in the water column include arsenate, arsenite, methylarsonic acid (MA) and dimethylarsinic acid (DMA) (Braman and Foreback, 1973). A detailed study of the seasonal variations of the arsenic species in water of Lake Biwa, Japan, was carried out by Sohrin et al. (1997). They reported that DMA became the major arsenic compound within the euphotic zone of the water in summer. Monomethylarsonous acid ($MA^{III}$), dimethylarsinous acid ($DMA^{III}$), and MA were also detected in the water as minor arsenic species. The authors suggested that the seasonal variations of the arsenic species in the lake water largely depend on biological processes such as the metabolism of phytoplankton, the decomposition of organic matter by bacteria, or the microbial reduction of iron and manganese oxides in the sediments, and that eutrophication affects the arsenic species in the lake water. Pongratz (1998) reported the presence of trace amounts of DMA (0.2 µg As/L) in rain water samples collected in Wolfsberg, Austria. Thus it seems that MA and DMA are the dominating organoarsenic species detected in natural freshwaters. However, in anoxic sediments and anoxic water, As(III) should dominate.

The ability of marine organisms to methylate arsenic is well established. Most macroalgae, and freshwater higher plants release protein-bound arsenic as a result of sequential methylation and adenosylation.

Marine organisms contain much higher levels of arsenic than terrestrial organisms, at the mg/kg level, and some of them even show arsenic concentrations higher than 100 mg As/kg (dry mass). Mc Bride et al. (1978) report that dimethylarsine [$(CH_3)_2AsH$] was mainly produced by anaerobic organisms, whereas trimethylarsine [$(CH_3)_3As$] resulted from aerobic methylation.

Most environmental transformations of arsenic occur in the soil, in sediments, in plants and animals, and in zones of biological activity in the oceans. The most important environmental transformations of the element are biomethylation and bioreduction. These processes can produce organometallic species that are mobile in air and in water. The

biomethylated forms of arsenic are subjected to oxidation and bacterial demethylation back to inorganic forms (World Health Organisation, 2001). Moreover arsenic can undergo a complex series of transformations, including redox reactions, ligand exchange and biotransformation.

Total atmospheric arsenic emissions from both, natural and anthropogenic sources have been estimated to be $31*10^9$ g/year. The total atmospheric arsenic removal was estimated to be $30\text{-}50*10^9$ g/year (Walsh et al., 1979). Global atmospheric emission into the atmosphere and deposition of arsenic was also estimated by Nakamura et al. (1990). They estimated the major source of arsenic being anthropogenic emissions, and the major source of natural arsenic being volcanic activity. Total emissions were estimated at $36*10^9$ g/year. Emissions from anthropogenic sources were estimated at $24*10^9$ g/year, representing 64% of total arsenic influxes. Depositions from the atmosphere to the land and the oceans were estimated at $24*10^9$ and $9*10^9$ g/year, respectively. The total annual transport of arsenic into the Arctic atmosphere was calculated at $285*10^6$g (Akeredolu et al., 1994). Nriagu and Pacyna (1988) estimated that anthropogenic sources of atmospheric arsenic (~18,000 tonnes/year) amounted to around 30% of the global atmospheric arsenic flux.

While anthropogenic sources are known to have an important impact on airborne arsenic compositions, their influence on the overall arsenic cycle is not well established. The global arsenic cycle is presented in Fig. 1-3.

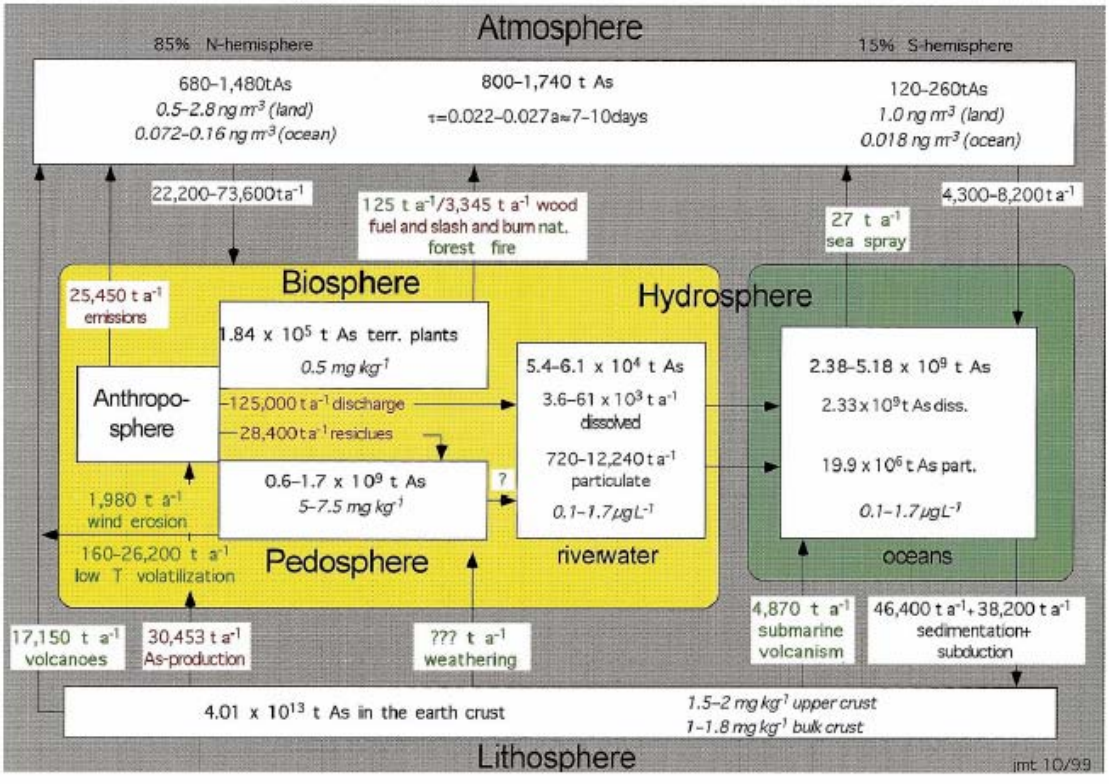



**Fig. 1-3**: Global As cycle (Matschullat, 2000).

### 1.1.7 Toxicology

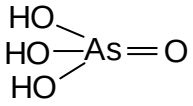
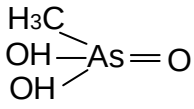
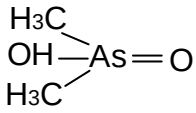
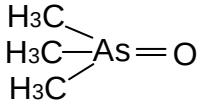
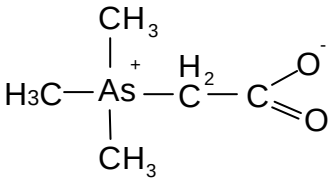
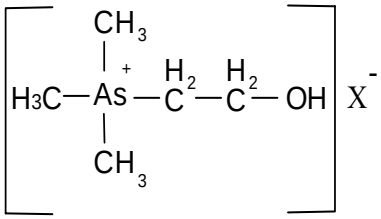
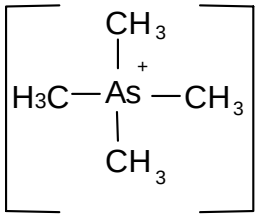
Arsenic toxicity is a property of the specific arsenic species and varies with its composition and structure. Elemental arsenic itself is not appreciably toxic, but is converted readily to toxic species in the organism. Nearly all arsenic species are considerably toxic. The toxicity of the various arsenic species differs significantly and $LD_{50}$ doses for arsenic species frequently found in the environment are given in Table 1-2.

The presence of these species in environmental samples is primarily attributed to biological methylation of inorganic arsenic (Cullen and Reimer, 1989). Methylation of inorganic arsenic mediated by microorganisms can take place in soil and sediment, and in aquatic and terrestrial plants and animals, including humans. According to Challenger (Challenger, 1945), the biomethylation of arsenic involves repeated steps of reductions, methylations, and oxidations. The proposed methylation pathway is outlined in Figure 1-4. Recent studies indicate that the necessary intermediates monomethylarsonous acid ($MA^{III}$) and dimethylarsinous acid ($DMA^{III}$) are more toxic than the inorganic arsenic species (Styblo et al., 1997; Lin et al., 1999; Petrick et al., 2000; Cullen et al.,1989). Methylation in plants and animals was thought to detoxify inorganic arsenic. However, recent studies suggest, that this should be reconsidered in light of the toxicity of $MA^{III}$ and $DMA^{III}$ and their identification in human urine (Le et al., 2000; Aposhian et al., 2000; Del Razo et al., 2000).

Marine animals normally have high arsenic concentrations (mg/kg range). Still they can be consumed without health risks, because they contain the element primarily in the form of arsenobetaine, which is non-toxic. In addition to the acute toxicity of the arsenic species, long-term effects due to the exposure to arsenic have to be considered.

The teratogenicity of inorganic arsenic was monitored in laboratory animals, whereas human data on this topic are limited. Mutagenicity and carcinogenicity (skin or lung cancer) of inorganic arsenic are well described. Effects on the human respiratory system (exposure from airborne arsenic in the smelting industry) and skin (exposure from drinking water) have been reported. Additionally, inorganic arsenic has been related to liver damage, malfunctions of the cardiovascular system (e.g., blackfoot disease, which is observed in areas with high arsenic concentrations in the drinking water) and nervous system (World Health Organisation, 1981).

**Table 1- 2:** $LD_{50}$ doses of eight common arsenic species (Frank, 2001).

| Arsenic Compound | Structure | $LD_{50}$ [g/kg body mass] | Animal/ Administration | Reference |
|---|---|---|---|---|
| **Arsenic Trioxide** | $As_2O_3$ | 0.035<br>0.0045 | mouse/oral<br>rat/intraperitoneal | Kaise et al. (1985)<br>Franke and Moxon (1936) |
| **Arsenic Acid** |  | 0.014 - 0.018 | rat/intraperitoneal | Franke and Moxon (1936) |
| **Methylarsonic Acid ($MA^v$)** |  | 1.8 | mouse/oral | Kaise et al. (1989) |
| **Dimethylarsinic Acid ($DMA^v$)** |  | 1.2 | mouse/oral | Kaise et al. (1989) |
| **Trimethylarsine Oxide (TMAO)** |  | 10.6 | mouse/oral | Kaise et al. (1989)<br>Kaise and Fukui (1992) |
| **Arsenobetaine (AB)** |  | >10 | mouse/oral | Kaise et al. (1985) |
| **Arsenocholine (AC)** |  | 6.5<br>0.19 | mouse/oral<br>mouse/intravenous | Kaise and Fukui (1992)<br>Kaise et al. (1992) |
| **Tetramethyl arsonium (TETRA) Iodide** |  | 0.9 | mouse/ oral | Kaise and Fukui (1992) |

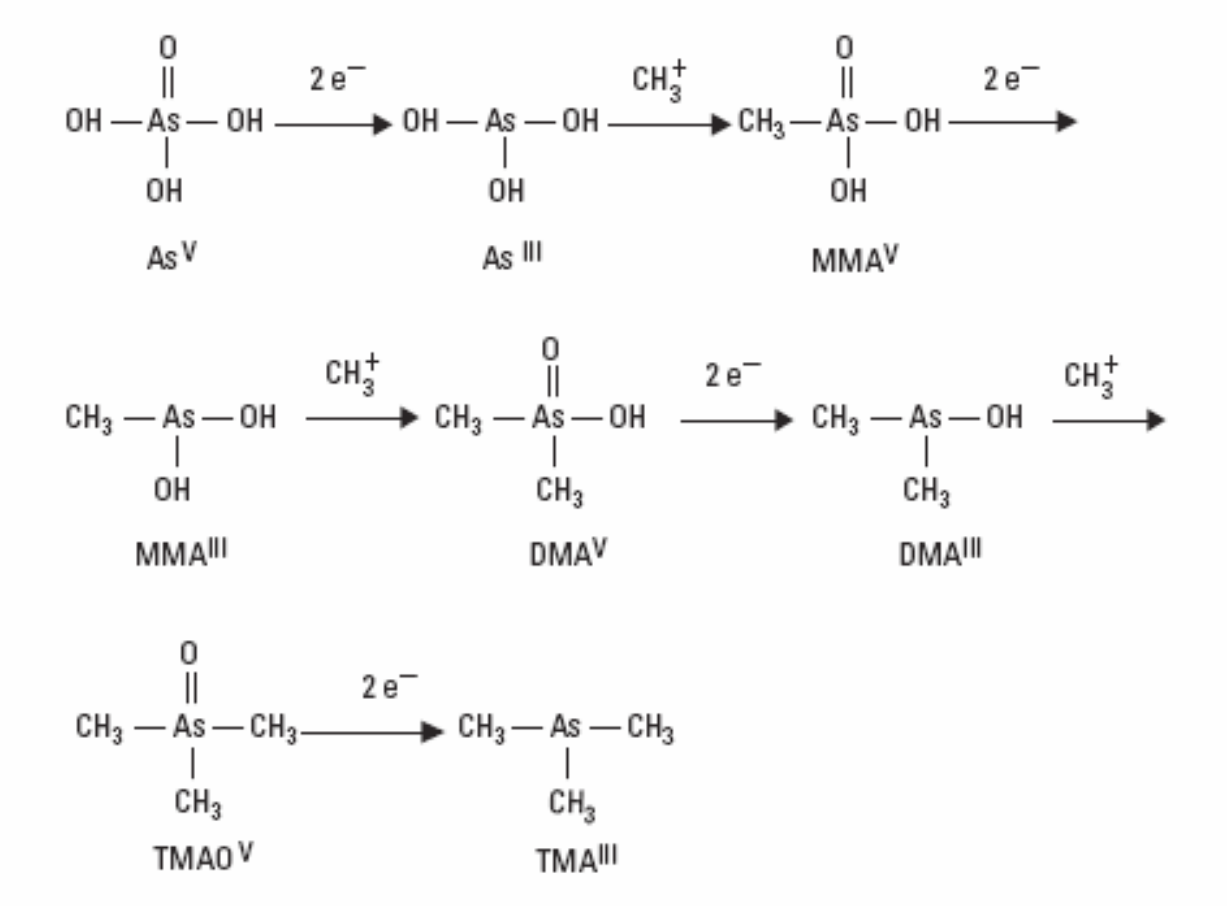



**Fig. 1- 4:** Biomethylation of inorganic arsenic (Challenger, 1945, Le et al., 2004).

### 1.1.7.1 Arsenic Metabolism in Mammals

Arsenic metabolism is characterized in many species by two main types of reactions: (1) reduction of pentavalent to trivalent arsenic, and (2) oxidative methylation reactions. In this reaction, trivalent forms of arsenic are sequentially methylated to form mono-, di- and trimethylated products using *S*-adenosyl methionine (SAM) as the methyl donor and glutathione (GSH) as an essential co-factor (Fig. 1-5) Reduction of pentavalent to trivalent arsenic species is required for methylation of arsenic. Arsenate reduction is known to occur non-enzymatically under conditions of low oxygen tension (i.e. an anaerobic environment such as exists in the gut) or over time at pH 2 or lower (Vahter and Envall, 1983). There are qualitative and quantitative interspecies differences in methylation to the extent that some species do not appear to methylate arsenic at all (Vahter, 1999).

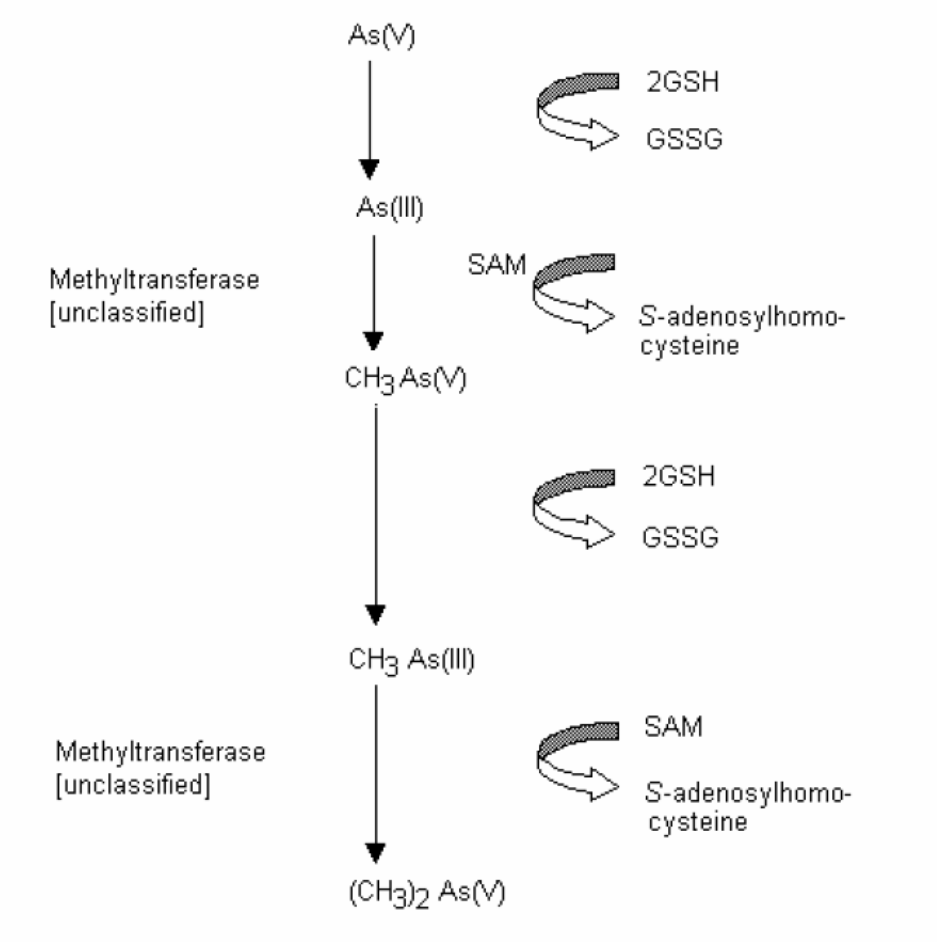



**Fig. 1- 5:** Arsenic methylation in mammals. Trimethylated forms are produced in small amounts, if animals or humans are administrated DMA (World Health Organisation, 2001).

The ubiquitous cellular tripeptide GSH is able to reduce arsenate to arsenite in both aqueous systems and in intact erythrocytes. Interestingly, bacteria have the capability to enzymatically reduce inorganic arsenate to arsenite. Vahter and Envall (1983) demonstrated in vivo reduction of arsenate to arsenite before methylation. Arsenic methylation activity is localized in the cytosol and appears to occur sequentially and mainly in the liver. Both in vivo and in vitro studies have demonstrated that SAM and GSH are essential co-factors in enzymatic arsenic methylation (Buchet and Lauwerys, 1985; Styblo et al., 1996).

Methylation is an equally important mechanism for expediting the excretion of both arsenate and arsenite from the body. Although the liver may have the greatest overall arsenite methylation capacity, extrahepatic metabolism may also be significant. This would be particularly the case for routes of exposure such as inhalation, where there is opportunity for first-pass metabolism in the lung.

On the basis of case reports in the medical literature, it has been theorized that prolonged exposure to arsenic can result in the development of tolerance. This hypothesized tolerance could in theory be a result of increased excretion due to enhanced methylation, or an increase in some other excretory mechanism. The meat of terrestrial animals destined for human consumption was reported to contain arsenic in the sub mg As/kg dry mass range. Exceptions were meat of swine (up to 6.3 mg As/kg) and poultry (up to 5.5 mg As/kg) (Leonard, 1991). These higher arsenic concentrations result from phenylarsonic acids added to swine and poultry feeds to enhance weight and feed efficiency (Nriagu and Azcue, 1990).

### 1.1.7.2 Arsenic Metabolism in Humans

Controlled ingestion studies indicate that both arsenate and arsenite are extensively methylated in humans, as is also observed in laboratory animals. DMA is the principle methylated metabolite excreted in human urine. A difference between humans and laboratory animals is that MA is excreted in the urine of humans to a greater extent. The biological basis for this difference is unknown, but it is consistent with the large interspecies differences observed in arsenic methylation among experimental animals. It is also noteworthy that the proportion of MA excreted in human urine is highly variable. Humans acutely intoxicated by high doses of inorganic arsenic show a marked delay in the urinary excretion of DMA (Foa et al., 1984).

In the case of exposure to arsenic via drinking-water the methylation of arsenic seems to be relatively unaffected by the dose. Results from in vitro studies using human hepatocytes suggested that the delay in urinary excretion of DMA might occur because the high tissue concentration of arsenite inhibits or saturates the methyltransferase catalysing the second methylation step (Styblo et al., 1999). Inorganic arsenic metabolism is known to be affected by liver disease in humans. In patients with other non-hepatic disease, arsenic methylation was unaffected.

The median arsenic concentration in organs and body fluids of unexposed humans was reported to be between 0.02 and 0.06 mg As/kg (Leonard, 1991). Higher concentrations may be found in muscle, lung, femur, skin, teeth, nails, and especially hair (Leonard, 1991), which can contain from a few to several hundred µg As/kg (Wolfsperger et al., 1994). Blood and urine arsenic concentrations of unexposed humans are usually about 10 µg As/l (Iyengar and Woittlez, 1988).

## 1.2 Methods for the Determination of Arsenic

Several analytical methods for the determination of total arsenic concentrations are currently available. Several detectors for the determination of total arsenic and their detection limits are listed in Table 1-3.

**Table 1- 3:** Methods for the determination of total arsenic concentrations (adapted from National Research Council of Canada, 1999).

| Method | Detection limit | |
|---|---|---|
| | Absolute | Concentration |
| **Hydride generation** | | |
| Atomic fluorescence spectrometry | | 20 ng/L |
| Graphite furnace AAS | 0.2 ng | |
| DC – plasma spectrometry | 0.4 µg | 4 µg/L |
| ICP emission spectrometry | 2 ng | 20 ng/L |
| ICP-MS | 10 pg | 0.1 ng/L |
| **Spectroscopic** | | |
| Flame atomic absorption spectrometry | | 1 mg/L |
| Graphite furnace AAS | | 1 µg/L |
| DCP or ICP-AES | | 10 µg/L |
| ICP-MS | | 0.05 µg/L |
| **Electrochemical** | | |
| Differential pulse polarography | 20 ng | 1 µg/L |
| Anodic stripping voltammetry | 6 pg | 0.3 ng/L |

Abbreviations: AAS, atomic absorption spectrometry; DC, direct current; ICP-MS, inductively coupled plasma-mass spectrometry; DCP, direct current plasma; AES, atomic emission spectrometry.

Most methods for the determination of As require the transformation from the solid into the liquid state and also the total dissolution of all arsenic containing species in the sample. Two mineralisation techniques are available. Either the samples can be mineralised via dry ashing with inorganic oxidants, or via wet ashing with nitric acid. Microwave induced heating for wet digestion procedures have gained significant importance during the last years as an effective method of sample preparation (Lamble and Hill, 1998). Benefits of these methods are reduced digestion times, decrease of risks of contamination as well as of losses of analyte, together with the requirement of lower amounts of sample and reagents. Microwave-assisted digestion can be performed in open or closed systems. The latter have the advantage that elevated pressures can be used to achieve the temperatures necessary for digestion with low boiling point acids, such as nitric acid.

Apart from these techniques, also electrochemical methods (differential pulse polarography, anodic stripping voltammetry) and colorimetric methods can be employed for the determination of arsenic.

A hydride generation step can be employed prior to analysis to lower detection limits for the determination of arsenic. Methods for the determination of arsenic in peat applied in this work are described in the following sections.

### 1.2.1 Hydride Generation Technique

The hydride generation technique (HG) can only be used for the determination of the hydride forming elements arsenic, bismuth, germanium, lead, antimony, selenium, tin, and tellurium. Mercury is reduced to its elemental form. The purge gas separates the hydrides from the liquid sample leading to significant lower detection limit, as the analyte is completely introduced into the gaseous state.

Sodium tetrahydroborate ($NaBH_4$) in acidic medium is generally employed for hydride generation. The tetrahydroborate decomposition is complete within a few microseconds and the resulting hydrogen reduces the analyte to hydride:

$$BH_4^- + 3\ H_2O + H^+ \rightarrow H_3BO_3 + 8\ H$$

$$6\ H + AsO_3^{3-} + 3\ H^+ \rightarrow AsH_3\uparrow + 3\ H_2O$$

The acid concentration, the formation of other volatile species, the oxidation state of the elements, as well as the $NaBH_4$ concentration influence hydride generation. Spectral and chemical interferences are general encountered in hydride generation. Chemical interferences appear either by prohibition or limitation of the formation of the volatile hydrides, or by compound formation after hydride generation. Generally the alkali and alkaline earth elements do not interfere. The transition elements and heavy metals, such as nickel, cobalt, copper, platinum, and palladium are preferentially reduced and suppress hydride formation (Agilent Technologies, 2000).

Hydrides can either be directly transported to the detection unit or they can be trapped in a collection device until the evolution is completed and then be transported to a detection unit (Fig. 1-6). Three direct transfer methods are employed: continuous flow (CF), flow injection (FI) and batch mode (Dedina and Tsalev, 1995). Continuous flow hydride generation is the most popular mode of hydride generation.

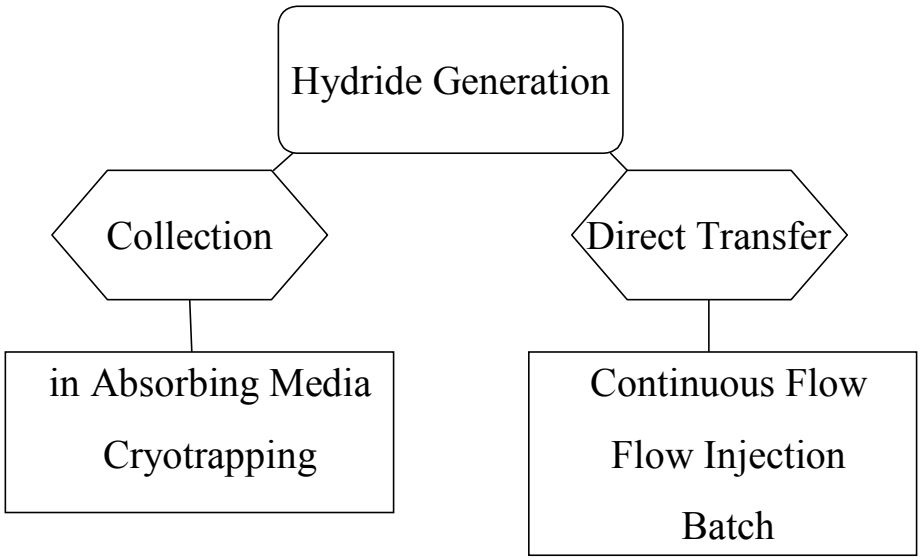



**Figure 1-6:** Methods for hydride generation (Dedina and Tsalev, 1995).

Hydride generation can be used for the separation of arsenic species when it is combined with a liquid nitrogen trap. All arsines are collected in the trap and can be separated by distillation.

Arsenous acid, arsenic acid, MA, DMA, and TMAO can be reduced in acidic solution by $NaBH_4$ to the corresponding arsines $AsH_3$, $CH_3AsH_2$, $(CH_3)_2AsH$, and $(CH_3)_3As$. Recently, Schmeisser et al. (2004) report that arsenosugars, major arsenic species in marine organisms also produce volatile analytes by the hydride generation (HG) method.

Arsenobetaine, arsenocholine, and the tetramethylarsonium cation cannot be reduced to volatile hydrides without further treatment.

Various detection systems, such as atomic absorption spectrometer (AAS), atomic emission spectrometer (AES), atomic fluorescence spectrometer (AFS), inductively coupled plasma mass spectrometer (ICP-MS), and inductively coupled plasma atomic emission spectrometer (ICP-AES) can be combined with the hydride generation technique.

#### 1.2.1.1 Hydride Generation-Atomic Absorption Spectrometry (HG-AAS)

In atomic absorption spectrometry (AAS) the gaseous atoms of an element are excited by the appropriate light emitted from a hollow cathode lamp. To generate gaseous atoms it is necessary to supply energy. For breaking the chemical bonds between atoms in molecules energy is necessary. For this purpose atomisers such as flames or electro-thermal heating are used. Atomic absorption spectrometry is a common technique for quantitative determination of trace elements. With the flame technique (FAAS) dissolved or liquid samples are sprayed into a flame, in which the atomisation of the analyte takes place. Flame atomic absorption spectrometry (FAAS) suffers from flame interferences and high detection limits (Table 1-3).

Electro-thermal techniques (ETV-AAS, ET-AAS, or GF-AAS) enable the atomisation of dissolved, liquid, and solid samples and are generally among the most sensitive atomic spectroscopic methods.

HG-AAS is probably the most widely used method for the determination of arsenic in various matrices. Most of the reported errors in the determination of arsenic by HG-AAS with $NaBH_4$ can be attributed to variation in the production of the hydride and its transport into the atomizer. The addition of a solution of L-cysteine to a sample before hydride generation eliminates interference by a number of transition metals, and improves responses of arsine generated from MMA and DMA in the presence of arsenite and arsenate (Le et al., 1994). HG-AAS has been used for arsenic speciation of inorganic arsenic and its urinary metabolites, MA and DMA via cold-trapping. Hasegawa et al. (1994) published the first report of trivalent methyl arsenicals ($MA^{III}$ and $DMA^{III}$), being found and measured in natural waters. They were separated from the pentavalent species by solvent extraction and determined by HG-AAS after cold trapping and chromatographic separations.

The main disadvantage of atomic spectrometry is the small linear range of the calibration curves and difficulties to make multi-element determinations.

Selected peat samples from the Outokumpu (Out) core were analysed for As using HG-AAS.

#### 1.2.1.2 Hydride Generation-Atomic Fluorescence Spectrometry (HG-AFS)

Atomic fluorescence (AF) is the optical emission from gas-phase atoms that have been excited to higher energy levels by absorption of energy. The absorption of this energy causes an electron of the atom to move to an orbital that is further away from the nucleus. If the electron returns to the same orbital from which it was excited, the wavelength of emission is the same as the wavelength of excitation. If the electron falls into a different orbital than that from which it was excited, the wavelength of emission is different.

The main advantage of fluorescence detection compared to absorption measurements is the greater sensitivity achievable because the fluorescence signal has a very low background.

Disadvantages of hydride generation-atomic fluorescence spectrometry (HG-AFS) are the small linear range of calibration curves. Moreover HG-AFS can only be used for the determination of the hydride forming elements and no multi-element determination is possible.

Selected peat samples from the Outokumpu core were analysed for As using HG-AFS.

### 1.2.2 Instrumental Neutron Activation Analysis (INAA)

Multi-element determinations with low detection limits are possible with instrumental neutron activation analysis (INAA). Samples are irradiated with neutrons, which cause the formation of radioactive species. The intensity of the radiation emitted by the radioactive isotopes is measured. Disadvantages of instrumental neutron activation technique are the high amounts of sample needed, the dependence on the activation source as well as the handling of radioactive material and the problem of radioactive waste.

In the Harjavalta core As, Sb, and Sc concentrations were determined using instrumental neutron activation analysis (INAA, ACTLABS, Activation Laboratories Ltd., Ancaster, ON,

Canada) in order to avoid contamination of the ICP-SF-MS instrument due to the high element concentrations expected in this core.

## 1.2.3 Inductively Coupled Plasma - Sector Field - Mass Spectrometry (ICP-SF-MS)

### 1.2.3.1 Introduction

Inductively coupled plasma - sector field - mass spectrometry (ICP - SF - MS) allows the simultaneous detection of almost all elements of the periodic table. The main advantage of this method is the low detection limit. ICP - SF - MS allows direct analysis of certain elements that cannot be handled by conventional ICP - QMS (inductively coupled plasma - quadrupole mass spectrometry).

The difference lies in the construction of the mass analyser that separates isotopes/elements of different mass. In ICP-SF-MS, magnetic and electrostatic sectors are used instead of the so-called quadrupole which has a corresponding function in ICP - QMS. A sector field instrument can separate ions with much smaller differences in mass, compared to a quadrupole instrument. The technique is therefore often called high resolution ICP - MS (HR - ICP - MS). Its higher resolution makes it possible to separate the analyte signal from spectral interferences. For elements not affected by such interferences, ICP - SF - MS can be used at low resolution, which makes it possible to achieve significantly lower detection limits than by ICP - QMS.

ICP - SF - MS technique combines high temperature argon plasma (6000 to 8000°K) as a highly efficient ion source with magnetic and electrostatic sectors. The plasma is generated in a quartz torch. Solutions of samples are introduced into the plasma via a nebuliser as a fine aerosol. When the aerosol reaches the plasma the sample gets completely volatilised, atomised, and ionised under atmospheric pressure. This process produces a cloud of positively charged ions. The sample ions are transferred into a mass spectrometer containing the magnetic and electrostatic sectors. The ions are detected by a secondary electron multiplier. For quantitative analysis the count rate obtained for a certain ion is proportional to its concentration.

### 1.2.3.2 Nebuliser and Spray Chamber

Solutions of samples are introduced into the plasma via a nebuliser as a fine aerosol. Liquid samples can either be transported via self aspirating, or a peristaltic pump can be used to transport the solution to the nebuliser. The main task of a nebuliser is to produce aerosol droplets of < 10 μm diameter. Concentric (e.g. Meinhard® nebulisers) and cross flow (e.g. Babington) nebulisers are usually used for the ICP – MS technique. Other types of nebulisers such as ultrasonic, microconcentric, microflow (flow rates of: 20, 50, 100, 400 μl $min^{-1}$) and the hydraulic high-pressure nebuliser can also be applied.

Pneumatic nebulisers produce aerosols with a broad distribution of droplet diameters up to 100 μm. To remove large droplets from the gas stream and deliver it to waste, a spray chamber is placed after a nebuliser. This improves signal stability. The aerosol enters the spray chamber where it undergoes changes in direction. The large droplets can not follow these changes in direction and run to waste. The spray chamber ensures that only droplets that are small enough to remain in the gas flow are carried to the plasma. With most pneumatic nebulisers this means a loss of 99% of the sample solution (Jarvis et al., 1992).

### 1.2.3.3 Inductively Coupled Plasma

The fine argon/sample aerosol from the nebuliser is fed (via an injector) into the center region of the plasma. When the aerosol reaches the plasma, the sample gets completely volatilised, atomised, and ionised under atmospheric pressure. This process produces a cloud of positively charged ions.

The inductively coupled plasma (ICP) is an electrodeless discharge in a gas at atmospheric pressure (Jarvis et al., 1992). Argon is commonly used because it is relative easy ionised, has a large mass, and therefore it has good impulse transfer properties. The plasma is generated in the quarz torch. This torch consists of three concentric quartz tubes. To prevent the torch from melting, the outer tube of the torch carries the cooling gas that has a much higher velocity compared to the auxiliary gas and the sample gas in the center of the torch. It cools the torch and shapes the plasma towards the tip of the torch (ELEMENT2 Hardware Manual).

The plasma is maintained by energy coupled to it from a radio frequency field, usually 27.12 or 40.68 MHz (Fisher and Hill, 1999), which is generated by a cooled copper coil

placed around the torch (Fig. 1-7). A spark from a Tesla coil, which provides free electrons to couple with the magnetic field, ignites the plasma. Temperatures in the plasma range from 6000 to 8000 K.

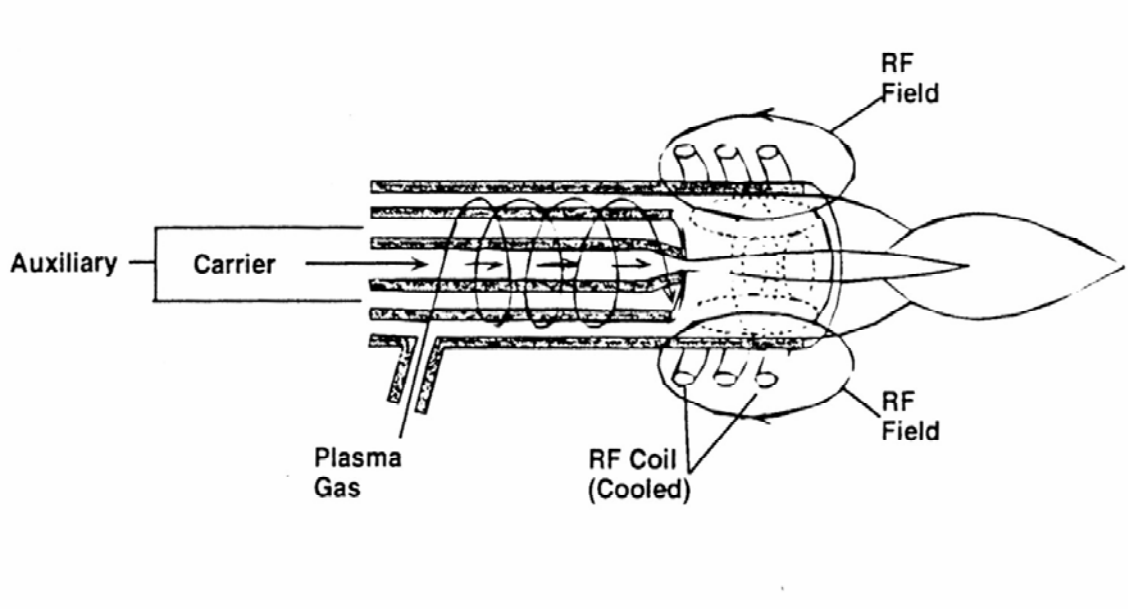



**Fig. 1-7:** Schematic diagram of ICP torch and the induced magnetic field (Hewlett Packard, 1996).

### 1.2.3.4 Interface

The sample ions are transferred into a vacuum system containing magnetic and electrostatic sectors. Extracting ions from the plasma into the vacuum system is critical. The Interface system contains the sample cone, the skimmer cone and the gate valve. The ions enter a region evacuated by a mechanical pump through the orifice (~1 mm) of a cooled cone (sample cone). Then the ions pass through a second orifice, called the skimmer orifice. The gate valve operates with argon gas and separates the interface and the analyser section. At the back of the skimmer cone a vacuum of about $10^{-6}$ mbar is built by two turbo molecular pumps.

### 1.2.3.5 Lens System

In the analyzer housing the ions get attracted and accelerated by the potential of the extraction lens and the following transfer optics, shaped and focused to the entrance slit. The transfer lens system (Fig. 1-8) is used to: extract the ions from the particle stream, which enters the analyzer section through the orifices of the cones with very high velocity; to focus and to correct the direction of the beam onto the target (entrance slit); to accelerate the ions to the full speed (with 8 kV); and to shape the beam into a flat shape to make him fit through the entrance slit (ELEMENT2 Hardware Manual, 2002). The ions are now shooting with the desired speed through the focus point (entrance slit) and start to diverge again slightly. In order to have the ion beam under control during the travel path through the magnetic field and the electric field the system controls the rotation of the beam and focuses again to the next focus point (ELEMENT2 Hardware Manual, 2002).

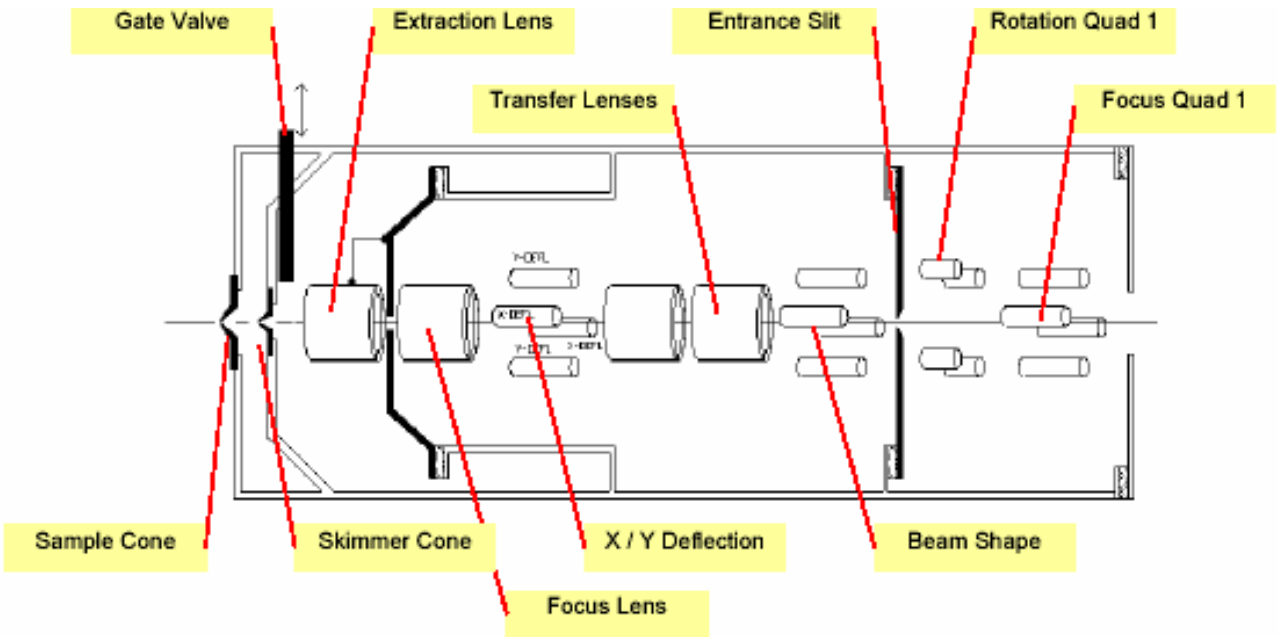



**Fig. 1-8:** Schematic diagram of the lens system (ELEMENT2 Hardware Manual, 2002).

At the next step two quadrupoles (Focus quad 1 and Rotation quad 1) correct the focus and the beam rotation to align the beam. A quadrupole consists of four metal rods parallel to and equidistant from the axis (Jarvis et al., 1992). Opposite rods are connected together and have

RF and DC voltages applied to them. For one pair the DC voltage is positive while for the other pair it is negative. On each pair the RF voltages have the same amplitude but they are opposite in sign. The velocities of ions that enter the quadrupole are dependent on their energy and mass. By varying the RF and DC voltages the rods act as a mass filter. Only ions of a certain m/z ratio have stable oscillatory paths through the rods and will emerge from the quadrupole on the other end. Other ions will be unstable and collide with the rods.

### 1.2.3.6 Magnetic Sector, Electrostatic Sector, and Detector

The beam passes the magnetic sector for mass separation, and the electrostatic sector (ESA) for energy separation and energy focusing.

The magnetic field (Fig. 1-9) bends the ions depending on their mass. Components of the magnet sector unit are: the laminated magnet with the integrated field probe and the flight tube which is on high voltage (8000 volts, ELEMENT2 Hardware Manual, 2002).

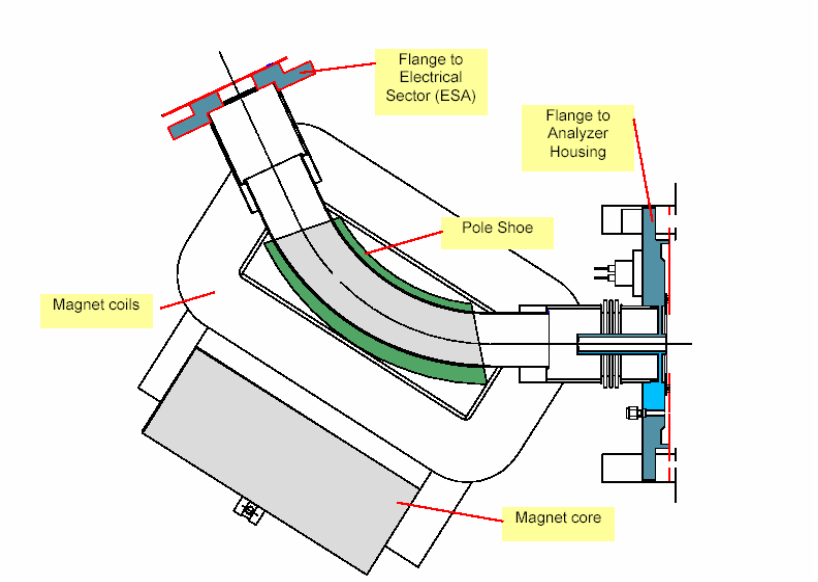



**Figure 1-9:** Schematic diagram of the magnetic sector (ELEMENT2 Hardware Manual, 2002).

Behind the magnetic sector the ion beam passes an intermediate slit. The electrostatic analyzer (ESA, Fig. 1-10) is located in the ESA housing. The ion beam passes the electrostatic field for energy focusing. The ESA is mainly a condenser, providing the

electrical field between the poles. The electrical field bends and focuses the ions in respect to their energy (ELEMENT2 Hardware Manual, 2002).

At the next step again two quadrupoles (Focus quad 2 and Rotation quad 2) correct the focus and the beam rotation to align the beam to the exit slit. Directly behind the exit slit a deflection device directs the beam to the conversion dynode. The width of the exit slit corresponds to the width of the entrance slit. Both widths are set for the different resolution values (low resolution mode: $m/\Delta m \sim 300$, medium resolution mode: $m/\Delta m \sim 4000$, high resolution mode: $m/\Delta m \sim 10000$). The ion detection behind the exit slit is realized by a conversion dynode and a secondary electron multiplier (SEM). Ions pass the exit slit and hit the conversion electrode. Secondary electrons are released from the surface of the conversion dynode, which are attracted and multiplied by the secondary electron multiplier (SEM).

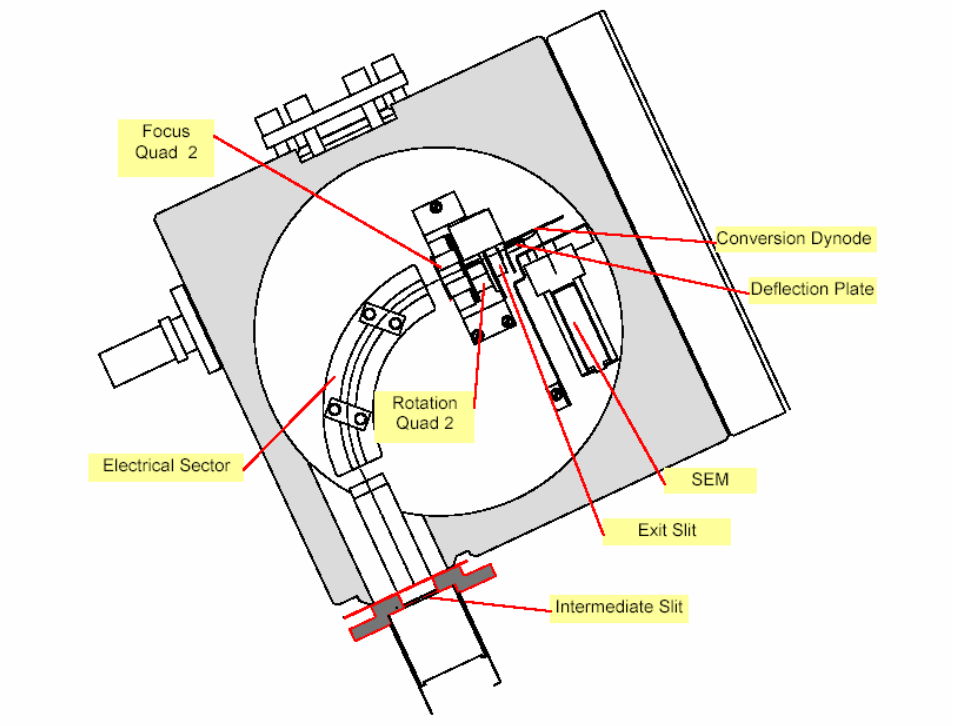



**Fig. 1-10:** Schematic diagram of the electricostatic analyser (ELEMENT2 Hardware Manual, 2002).

### 1.2.3.7 Interferences

For quantitative analysis the count rate obtained for a certain ion is proportional to its concentration. Interferences in ICP-SF-MS can be of spectroscopic or non spectroscopic nature (Jarvis et al., 1992). Spectroscopic interferences result from signals of oxides ($MO^+$), doubly charged ions ($M^{2+}$), hydroxides ($MOH^+$), argides, isobaric overlaps, and of molecules with the same ratio of mass and charge such as the element of interest. Non-spectroscopic interferences are either physical effects which result of the solids present in a solution or analyte suppression or enhancement effects which result from influences of matrix elements in the sample on the yield of formed ions (Jarvis et al., 1992).

Two peat cores, Hietajärvi (Hie) and Outokumpu (section 2.4), were measured using ICP - SF - MS for the following elements: Cd, Sn, Mo, Sc, V, Cr, Co, Ni, Cu, Zn, As (In was used as internal standard).

## 1.2.4 X-Ray Fluorescence Spectrometry (XRF)

An electron can be ejected from its atomic orbital by the absorption of a light wave (photon) of sufficient energy. When an inner orbital electron is ejected from an atom, an electron from a higher energy level orbital will be transferred to the lower energy level orbital. During this transition a photon may be emitted from the atom. This fluorescent light is called the characteristic X-ray of the element.

The energy of the emitted photon will be equal to the difference in energies between the two orbitals occupied by the electron making the transition. Because the energy difference between two specific orbital shells, in a given element, is always the same (i.e. characteristic of a particular element), the photon emitted when an electron moves between these two levels, will always have the same energy. Therefore, it is possible to determine the identity of that element. By determining the energy of the X-ray peaks in a sample's spectrum, and by calculating the count rate of the various elemental peaks, it is possible to qualitatively establish the elemental composition of the samples and to quantitatively measure the concentration of these elements.

XRF Spectrometry is a multi-elemental technique. It has the advantage of using small samples (1 g or less) and being a non-destructive technique. However, high amounts of lead present in the sample interfere with the determination of arsenic.

All three peat cores (section 2.4) were measured by Dr. Andriy Cheburkin using XRF Spectrometry for the following elements: Harjavalta (HAR): K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Pb. Outokumpu (Out): Al, Si, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Pb, As, Se, Br, Rb, Sr, Y, Zr, Ga. Hietajärvi (Hie): K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Pb.

## 1.3 Methods for the Determination of Arsenic Species

With the knowledge about the albeit different toxicities of the various arsenic species as well as with the development of powerful hyphenated techniques for the identification and quantification of arsenic species, arsenic speciation has gained importance and is nowadays accepted as the only tool to estimate the toxicity of arsenic containing material. For the identification and quantification of arsenic species several techniques are available (Fig. 1-11). In all cases the arsenic species need to be separated first.

Information of arsenic species in samples can be obtained by hydride generation, liquid-chromatography, gas-chromatography, high performance liquid-chromatography (HPLC) and capillary electrophoresis. Hydride generation can be used for the separation of arsenic species when it is combined with a liquid nitrogen trap.

For the separation of arsenic species in liquid environmental and biological samples, ion-exchange chromatography is widely used. The combination of chromatographic methods with different element-specific detectors allows nowadays separation and identification of arsenic species with detection limits in the sub µg As/L range.

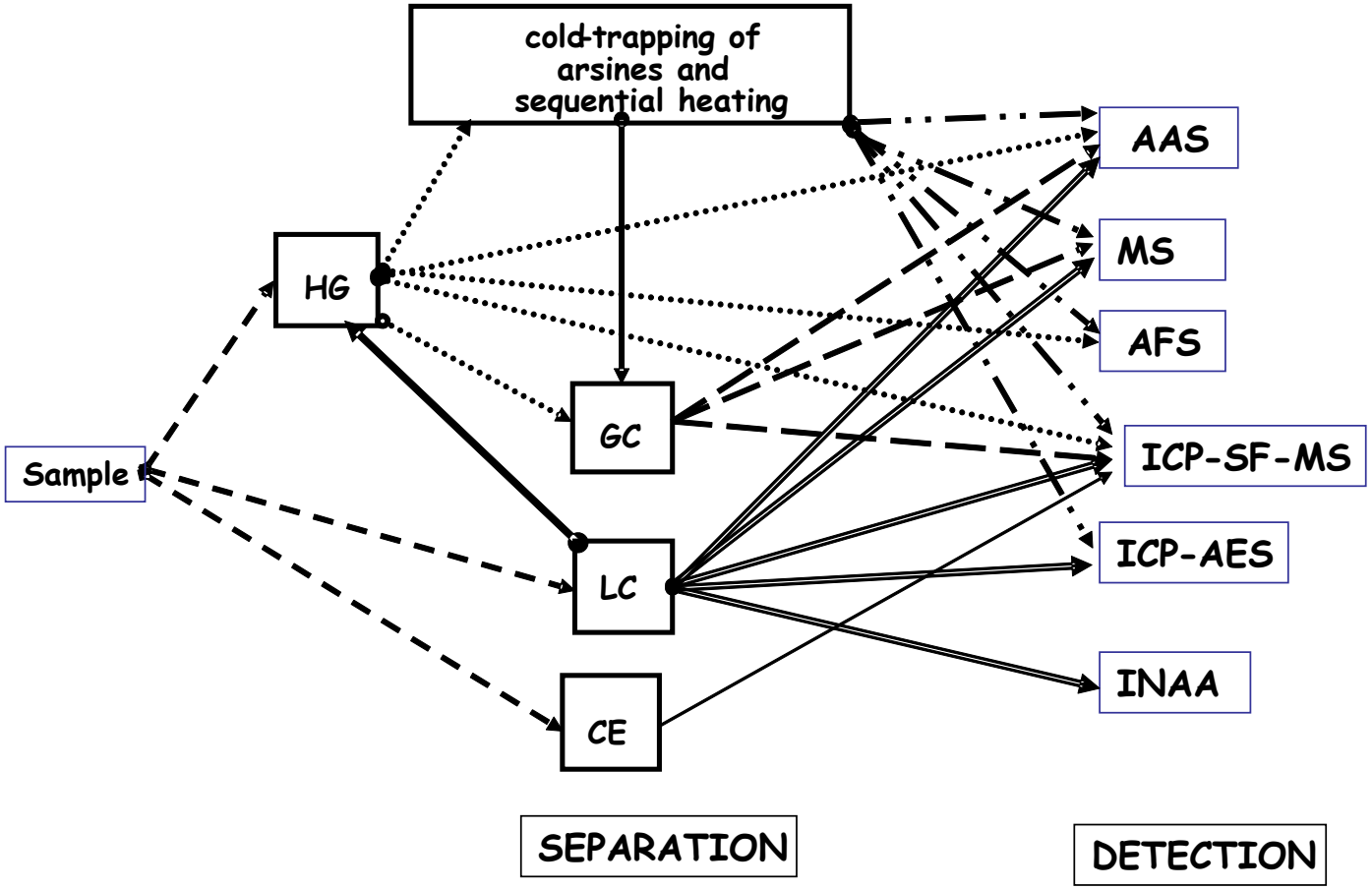



**Fig. 1-11:** Methods for the identification and quantification of arsenic species (adapted from Frank, 2001). (Abbreviations: HG Hydride Generation; GC Gas Chromatography; LC Liquid Chromatography; CE Capillary Electrophoresis; AAS Atomic Absorption Spectrometry; MS Mass Spectrometry; AFS Atomic Fluorescence Spectrometry; ICP-SF-MS Inductively Coupled Plasma-Sector Field-Mass Spectrometry; ICP-AES Inductively Coupled Plasma - Atomic Emission Spectrometry; INAA Instrumental Neutron Activation Analysis)

### 1.3.1 Extraction of Arsenic Species

Arsenic species should be extracted without decomposition or chemical conversion. Since it is currently not possible to separate all known arsenic species within one step, a combination of separation methods must be used for the determination of all arsenic species. Common extractants for arsenic species in biological material are methanol, water, methanol/water mixtures, and phosphoric acid.

The use of methanol/water mixtures or methanol as the extractant has the advantage, that methanol extracts fewer non-arsenical species and that it can easily be removed by evaporation. Arsenobetaine, for example is soluble in both, water and methanol. Therefore extraction efficiencies of > 90% were commonly obtained for the exraction of arsenic species from marine animals, rich in arsenobetaine. However, methanol is known to be a poor solvent for the extraction of inorganic arsenicals (Edmons et al., 1994). Moreover, the extraction of non-polar arsenicals (arsenolipides) using methanol, which might extract some non-polar arsenic, and subsequent evaporation of methanol prior to analysis, would lead to a loss of these arsenolipides (Francesconi and Kuehnelt, 2004).

Nearly all of the naturally-occurring arsenic species identified so far are polar and very water soluble. Therefore water might be the best general solvent for extracting arsenic species, provided it can penetrate the sample matrix (Francesconi and Kuehnelt, 2004).

Additionally Tukai et al. (2002), who examined extraction efficiencies of three types of marine algae, found varying optimal methanol percentages, depending on the type of alga.

However, as some terrestrial plants do not readily give up their arsenic to water or methanol/water mixtures, thus the use of other extractants, such as aqueous trifluoroacetic acid were investigated (> 80% of As extracted, Abedin et al., 2002; Heitkemper et al., 2001). Also an aqueous phosphoric acid solution, which was thought to assist breakage of native As-S bonds, improved extraction efficiency for arsenic from plant materials (Bohari et al.,2002).

The main extraction methods are: mixing/shaking, sonication, and pressurised extraction systems, such as microwave-assisted heating in closed chambers (Francesconi and Kuehnelt, 2004).

## 1.3.2 High Performance Liquid Chromatography (HPLC)

High-performance liquid chromatography (HPLC) is a powerful separation method which requires only small amounts of sample and which can easily be connected to most detection systems. When HPLC is combined with HG and an inductively coupled plasma - mass spectrometer as element - specific detector a further decrease of detection limits can be obtained.

HPLC allows a rapid separation of substances with high selectivity under mild conditions. A schematic diagram of an HPLC system is shown in Figure 1-12.

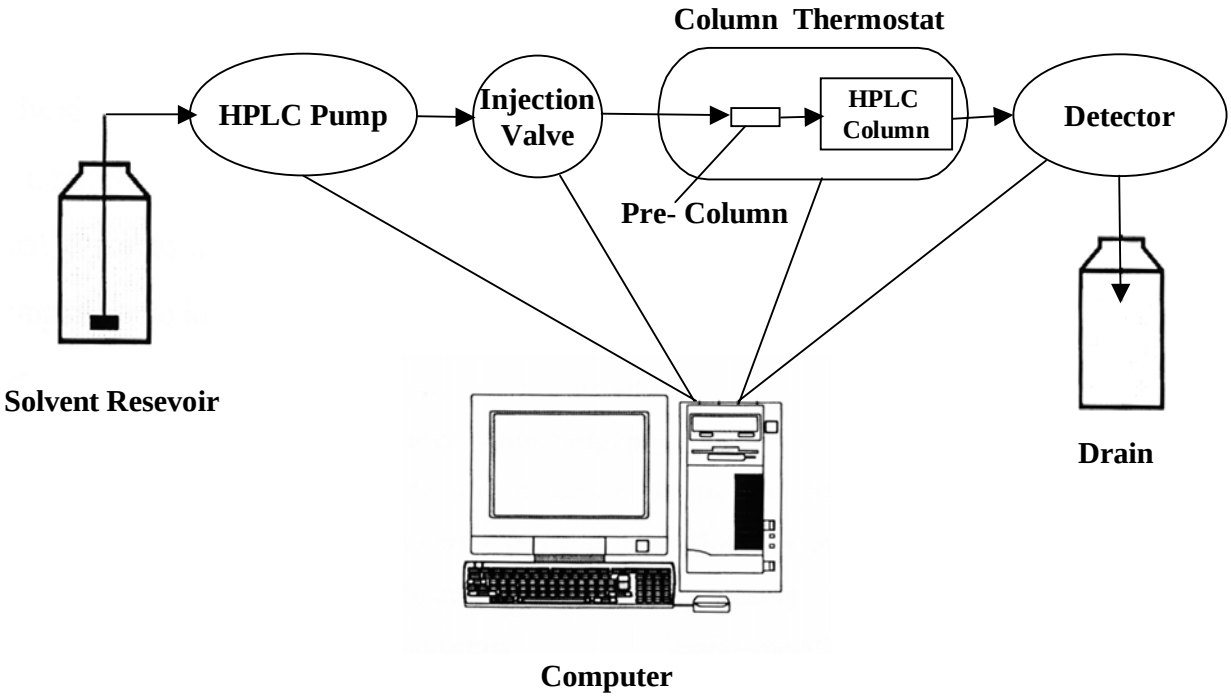



**Figure 1-12:** Schematic diagram of an HPLC system (Frank, 2001).

An HPLC pump transports the mobile phase constantly from the solvent reservoir through the system against a pressure up to several 100 bar without pulsation (Boecker, 1997). A pump can either work as a constant flow or a constant pressure pump. Constant flows are necessary

for a good reproducibility of retention times and peak areas. Constant flow pumps are commonly used nowadays.

HPLC columns are commonly made of stainless steel (Lindsay, 1992). A pre-column protects the analytical column. This pre-column is filled with the same stationary phase as the analytical column. The stationary phase, mainly silica or polymer stationary phases modified with charged functional groups in ion-exchange chromatography, is tightly packed into the column. In ion-exchange HPLC charged species are separated because of their different interaction with the charged functional groups of the stationary phase (Frank, 2001).

The sample injection can be performed manually or automatically (auto sampler). The injected volume should be highly reproducible. Injection systems most commonly used are valves, where the volume of the sample loop defines the injection volume.

Detectors, which should provide low background noise, low detection limits and no baseline drift, can be universal (sensing everything in the sample) or selective (sensing only certain components). Selective detectors can either be molecule or element specific detectors (Frank, 2001). In this work an ICP-SF-MS was used as element - specific detector for the determination of arsenic species.

# 1.4 Peat Bogs as Archives of Atmospheric Element Deposition

## 1.4.1 Introduction

One of the basic concepts of environmental geochemistry is that of the natural chemical cycle or geochemical cycle of an element. Because of increasing population and industrialization, human activity is now the dominant process affecting the global biogeochemical cycling of many elements, especially some of the trace metals.

One way to quantify the pre-anthropogenic fluxes of atmospheric trace elements is to study and interpret environmental archives. These may preserve not only the chronological record of atmospheric fluxes of trace elements as they may have occurred prior to industrialisation, but also contemporary fluxes which are needed for comparison.

Examples of such archives include polar snow and ice, marine and lacustrine sediments, annual bands of marine corals and tree rings, and organic-rich sediments from peatlands such as bogs, fens, and swamps. Each of these archives has its own inherent advantages and disadvantages: they are very different with respect to accessibility, time span, accumulation rates (and therefore temporal resolution), and ability to preserve various records of environmental change. Of these, alpine and polar snow and ice, lake sediments, and peat bogs have been studied most intensively (Livett, 1988). Geological archives have been particularly successful with respect to Pb, a metal whose global biogeochemical cycle has been more intensively influenced by human activities, and for a longer period of time, than any other trace element (Hutchinson, 1987).

Ombrotrophic peat bogs are hydrologically isolated from the influence of ground and surface waters, and only fed by atmospheric deposition. Ombrotrophic peat bogs are increasingly being found to function as meaningful archives of recent as well as ancient atmospheric metal deposition (Livett, 1988; Hutchinson, 1987; Shotyk et al., 1998; Shotyk, 1996; Weiss et al., 1998).

## 1.4.2 Classification of Wetlands

Wetlands cover approximately 4% of the earth´s toal land area and 30% of the land area of Finland (Shotyk, 1988).

In general, two different types of wetlands can be distinguished: mineral wetlands with peat accumulation less than 40 cm, and organic wetlands (peatlands) that are defined as soils with peat accumulation greater than 40 cm in depth (National Wetlands Working Group, 1988). According to this classification fens and bogs are peatlands, whereas swamps and marshes may either be mineral wetlands or peatlands. Several different types of wetlands can be distinguished (Table 1-4).

**Table 1- 4:** Types of wetlands (adapted from Shotyk, 1992 and Charman, 2002).

| Types of wetlands | Properties |
|---|---|
| Mire | All ecosystems described in English as swamp, bog, fen, moor, muskeg and peatland but often used synonymously with peatlands. |
| Peatland | Any ecosystem where in excess of 30-40 cm of peat has formed. Includes some wetlands but also organic soils where aquatic processes may not be operating (e.g.drained or afforested peatlands). |
| Swamp | Treed wetland and peatland. Subjected to periodic or regular flooding. Vegetation: cover of deciduous or coniferous trees, scrubs, herbs and mosses. |
| Fen | Meadow-like peatlands. Vegetation: sedges, grasses, reeds, brown mosses, and shrubs. |
| Marsh | Wetlands and peatlands, often associated with open water, subjected to periodic or regular inundation with standing or slowly moving water. Vegetation: emergent sedges, grasses, rushes, reeds, aquatic plants in the zones of open water. |
| Bog | A mire which receives water solely from rain and/or snow falling onto its surface. They are dominated by *Sphagnum* mosses, but ericaceous shrubs, sedges and herbs also are common. |

Minerotrophic wetlands receive their mineral nutrition from flooding surface waters, groundwaters or both.

In contrast ombrothrophic ("rain-fed") peatlands that are termed as bogs or peat bogs are wetlands that receive all their inputs from the atmosphere and are therefore not affected by groundwater or surface water runoff from other areas. Ombrotrophic "raised" bogs have a convex, domed structure which raises the upper part of the peat above the level of the local groundwater table (Fig. 1-13). The plants growing on the surface of bogs (mainly *Sphagnum* mosses) receive their mineral nutrition solely from atmospheric deposition. Bogs are usually treeless (Fig. 1-13), and trees which are present are frequently stunted and distorted (Shotyk, 1988).

*Sphagnum* mosses have large water-holding and cation exchange capacities, thus peat often contains more than 95% water by weight. The water remains in the bog due to a combination of capillary effects (*Sphagnum* mosses have hollow, tubular stems which encourage capillary action) and the low hydraulic conductivity of the main mass of peat, the catotelm (anoxic part of the bog) (Roos-Barraclough, 2002). Therefore, neither groundwater nor runoff from other areas can reach this raised, ombrotrophic part of the bog.

These mires are especially common in areas of high atmospheric humidity (Shotyk, 1988). A ring of minerotrophic peat, often known as the "lagg", can surround the dome of ombrotrophic peat (Fig. 1-13).

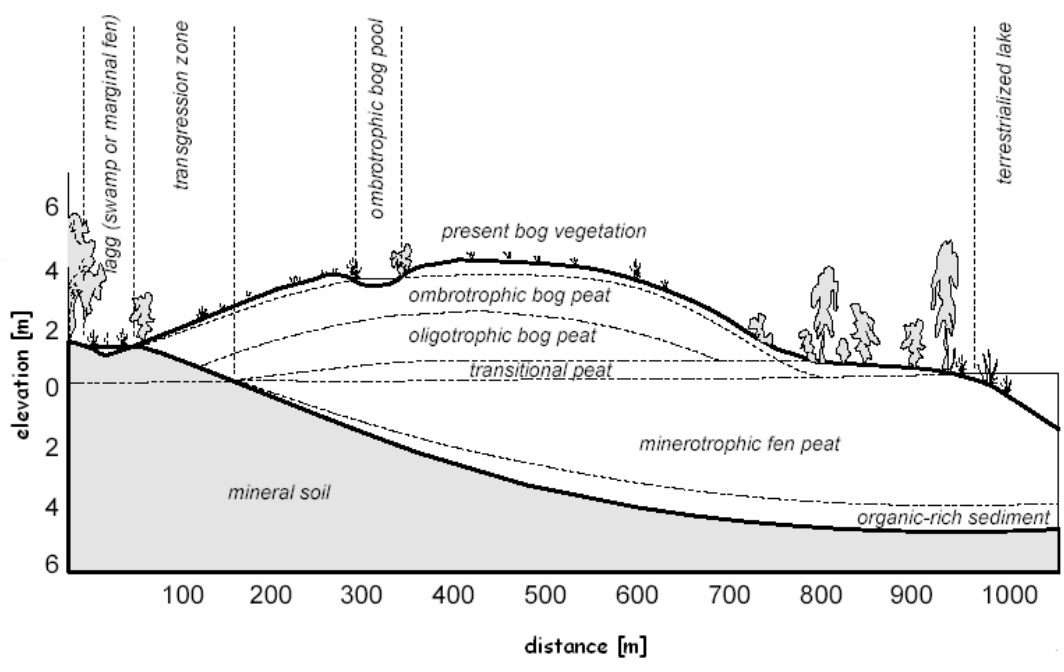



**Fig. 1-13:** Schematic diagram of an ombrotrophic bog (adapted from Souci, 1938).

### 1.4.3 Development of Peat Bogs

Typical peats contain over 75% organic matter and may be almost entirely organic. Peat formation is favoured in areas of low temperatures, an excess of precipitation over evapotranspiration and slight runoff. Wetlands in which peat has accumulated are widespread in formerly glaciated regions of northern Eurasia, the northern United States and Canada. Peat forms on waterlogged grounds. Therefore suitable geological conditions are also required for the formation of a peatland to occur. The sediment or rock underlying the peat must be relatively impermeable to water.

Mires can form either by infilling a former lake or estuary basin by limnic sediments and aquatic vegetation and microorganisms, often gyttja (terrestrialisation; progressive filling of a lake basin by limnic, telmatic and eventually terrestric vegetation) or by waterlogging of terrestrial soils via rising ground water to the surface (paludification), that may occur when precipitation or evaporation changes, in cool regions of imperfectly drained soils with an excess of precipitation or in poorly drained soils with high water tables (Shotyk,1992).

The formation of raised bogs normally begins when the mire occupies a topographic depression and is well supplied with nutrient rich water (Fig. 1-14, 1). When the plants growing around the edges die, they sink and accumulated at the bottom of the lake or the wet hollow (Fig. 1-14, 2). After hundreds of years the dead plants have filled the entire lake or hollow and transformed it into either a fen (in case of a wet hollow) (Fig. 1-14, 3), or a marsh (in case of a lake). Ombrotrophic peat develops when the peat accumulating in fens become isolated from the groundwater. When the roots of plants lose contact with the groundwater, as mineral soils beneath the thick peat are so deep that plant roots cannot reach this source of nutrition: their only source of nutrients is from rainwater and the atmosphere. New types of plants, such as *Sphagnum* mosses colonise the surface of the mire and as they die transforme the fen into a bog. In cases of climate change during peat formation (dry period) trees may colonise the bog (Fig. 1-14, 4). The peat continues to grow in thickness and forms a raised bog (Fig. 1-14, 5), so that in the case of a depression a fen-bog transition and in the case of a lake a marsh-fen-bog transition occurs. Thus, bogs which are ombrotrophic at the surface are normally underlain by fen peat and sometimes aquatic sediments (Fig 1-13).

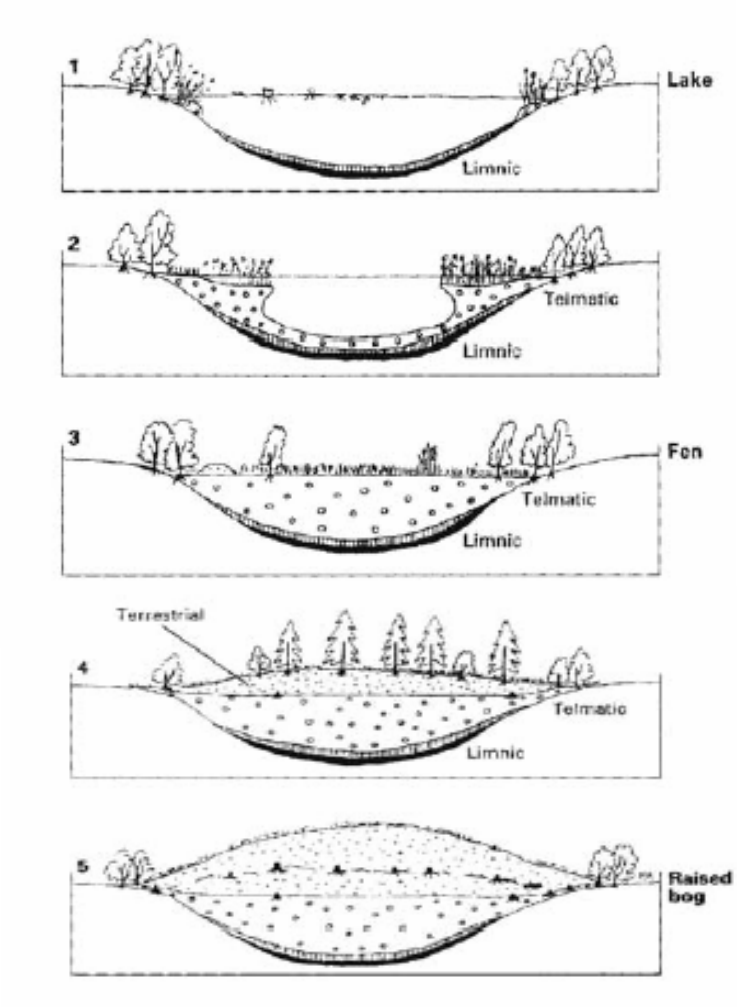



**Fig. 1-14:** Schematic diagram of peat bog development (Lowe and Walker, 1991).

## 1.4.4 Distinguishing Ombrotrophic from Minerotrophic Bogs

A typical peat bog can be divided into the surface layer (acrotelm), an active oxic layer, where plant decay occurs rapidly, and the deepest layer (catotelm), an anoxic layer, where plant decay occurs very slowly. Due to the limiting environmental conditions in bogs, namely limited available oxygen for plant growth and the lack of essential nutrients including nitrogen, phosphorus and potassium as well as the acidic soil, bogs can limit the growth and survival of many plant species. Thus, the specific plant species growing on peat can help to distinguish ombrotrophic from minerotrophic peat.

Typical plant species found in ombrotrophic peat sites are for example *Sphagnum magellanicum*, *Sphagnum fuscum* and *Sphagnum capillifolium*. These plant species can easily be distinguished in the field from typical fen species, such as *Carex nigra* and *Schoenus nigricans* (Charman, 2002). However, this method fails when peat bogs grow for example on oceanic sites, where the atmosphere provides sufficient nutrition and high precipitation. In other words: when the quantity of nutrients deposited on the bog surface increases, typical fen species can also grow on ombrotrophic sites. Therefore the surface vegetation alone is no reliable indicator of the trophic status of the underlying peat profile. As ombrotrophic peat layers generally overlie minerotrophic peats, it is essential to determine the thickness of the ombrotrophic layer and the level of fen-bog transition.

The thickness as well as the level of fen-bog transition can be determined by studying plant macrofossils using optical microscopy. This reveals which sections of the peat column were ombrotrophic at their time of growth. To determine whether the peat has also remained rain-fed after its formation, chemical analysis of the peat and the peat pore waters are essential to identify ombrotrophic peat. These chemical parameters include the pH, the concentrations of major elements (Ca, Mg, Al, Si), the dominant mineral fraction in the peat ash, the chemistry of the main elements in the pore waters ($Cl^-$, $Mg^{2+}$, $Ca^{2+}$), their ratios to one another ($Ca^{2+}/Cl^-$) and their comparison with local rainwater values.

In ombrotrophic bogs the pH is ~ 3-5 and constant with depth. In the ombrotrophic zone, pH is mainly controlled by the release of organic acids, mainly humic substances, whereas the pH in minerotrophic peats increases with depth and is controlled by bicarbonate equilibria (Steinmann and Shotyk, 1997). Moreover, *Sphagnum* mosses have developed high cation exchange capacities, mainly due to the limited nutrients. Cation exchange involves the removal of cations from solution and their replacement with hydrogen ions. The release of hydrogen ions and the (more important) release of organic acids through decay, leads to the low pH in ombrotrophic bogs.

Comparison of the Ca/Mg molar ratio of the solid peat with local rainwater values show, that ombrotrophic peats have Ca/Mg values comparable to rainwater, whereas peats which exceed this value have an additional, non -atmospheric source of Ca and are therefore minerotrophic (Weiss et al., 1997).

Ombrotrophic peats generally contain less mineral material than minerotrophic peats and the amount of mineral material matter does not increase significantly with depth. The amount of ash in the peat can be expressed as sum of $SiO_2$, $Al_2O_3$, $TiO_2$, $Fe_2O_3$, CaO, MgO,

and $SO_2$. In ombrotrophic peats $SiO_2$ and $Al_2O_3$ dominate (ash content up to ~2%), whereas in minerotrophic peats (ash content ~ 10%) CaO dominates (Weiss et al., 1997).

In ombrotrophic pore waters the concentrations of $Mg^{2+}$, $Cl^-$, $Ca^{2+}$, and the ratio of $Ca^{2+}/Cl^-$ are constant with depth and comparable to rainwater values or even below, whereas in contrast pore waters from minerotrophic sites show increasing $Cl^-$, $Mg^{2+}$ and $Ca^{2+}$ concentrations with depth (mixing between the pore waters and groundwater), exceeding rainwater values. Thus the cation charge balance in ombrotrophic peat pore waters is dominated by $H^+$ and $NH_4^+$, whereas in minerotrophic peat it is dominated by $Ca^{2+}$. Most common criteria for the interpretation of the ombrotrophic character of a peat bog are summarised in Table 1-5.

**Table 1- 5:** Characteristics of ombrotrophic and minerotrophic peat bogs.

| **Properties** | **Ombrotrophic** | **Minerotrophic** |
|---|---|---|
| Plant species | *Sphagnum* | *Carex* |
| pH | 3-5, constant with depth | 4-6, increases with depth |
| Ca/Mg molar ratio in solid peat | comparable to rainwater value | exceeds rainwater values |
| Ash concentration | $SiO_2$, $Al_2O_3$ dominant | CaO dominant |
| Concentration of $Mg^{2+}$, $Cl^-$, $Ca^{2+}$ in pore waters | constant with depth, comparable to rain water values | increase with depth, exceed rainwater values |

Other possible tools for distinguishing ombrotrophic from minerotrophic peats include for example the determination of the isotopic composition ($^{18}O$, $^{16}O$, $^{37}Cl/^{35}Cl$) of the ombrotrophic bog pore water that should resemble rainwater (and should therefore significantly differ from groundwaters) (Shotyk, 1994).

### 1.4.5 Peat Bogs as Archives

One of the most significant questions regarding the use of peat bogs as archives of atmospheric metal deposition has been the possible importance of post-depositional migration of metals (Coleman, 1985; Livett, 1988; Urban et al., 1990; Shotyk, 1996). Peat bog waters are naturally acidic, and organic rich (~ 50 mg/l DOC), and may vary between oxic and anoxic depending on the depth of the water table which fluctuates seasonally. Thus, there is considerable opportunity for a variety of chemical and biochemical transformations of metals which could liberate them from the solid phase and facilitate their removal by diffusive or advective flow, or gaseous volatilization. However, there is a growing body of evidence which indicates that lead and mercury, at least, are effectively immobile in peat profiles, and that ombrotrophic bogs are capable of preserving the changing rates of atmospheric Pb (Vile et al., 1995, 1999; Shotyk et al., 1996, 1997a, b; Farmer et al., 1997; MacKenzie et al., 1997, 1998; Shotyk et al., 1998; Weiss et al., 1999a, b; Shotyk et al., 2001) and Hg (Jensen and Jensen, 1991; Norton et al., 1997; Benoit et al. 1994; Benoit et al., 1998; Martinez-Cortizas et al., 1999) deposition. The mechanisms by which Pb, Hg and other metals are retained by the peat are currently unknown.

One hypothesis is, that metallic cations with strong affinities for organic ligands ($Cu^{2+}$, $Pb^{2+}$) become fixed to the solid phase which prevents them from migrating (in fluid flow or by diffusion). Therefore the metal bearing particles would have to dissolve first in the acidic waters so that the metals can then become adsorbed. This mechanism can not explain why metals existing predominantly in anionic form under the typical Eh and pH conditions of ombrotrophic peat bog waters, such as As and Sb, seem also well preserved in peat bogs. Thus a mechanism which can explain the retention of both metallic cations as well as some metallic anions needs to be invoked.

One other possible approach is the hypotheses, that atmospheric metal particles become coated by organic molecules (e.g. humic acids) upon their deposition, and that these organic molecules form protective coatings preventing the particles from dissolving. If this hypothesis is correct, the metals in the peat bog would be mainly in the form of particulates.

The mechanisms by which trace elements are retained by peat are poorly understood and deserve further study.

## 1.4.6 Peatlands in Finland

Peatlands cover ~ 515,000 km$^2$ of Europe, with the most extensive areas found in the north, particularly in Finland, Sweden, Norway and Russia. The cool and wet climate of these countries provides ideal conditions for peat formation.

Finland has a geological mire area of 5.1 million hectares, which is estimated to contain a total of 69 billion cubic metres of peat in situ. The exploitable mire area amounts to 1.2 million hectares, which contains 30 billion cubic metres of peat. Most of this is decomposed peat that can be used for energy generation, while the rest is poorly decomposed *sphagnum* peat that can be used as a substrate for horticulture. The energy content of the exploitable peat reserves is equivalent to 1100 million tonnes of oil or two thirds of the energy content of the known oil reserves of Norway. Lapland and northern Ostrobothnia are the Finnish regions with the largest mire area (Geological Survey of Finland GTK, 2003). An overview of peatlands surveyed by the GTK (Geological Survey of Finland GTK, 2004) is given in Figure 1-15.

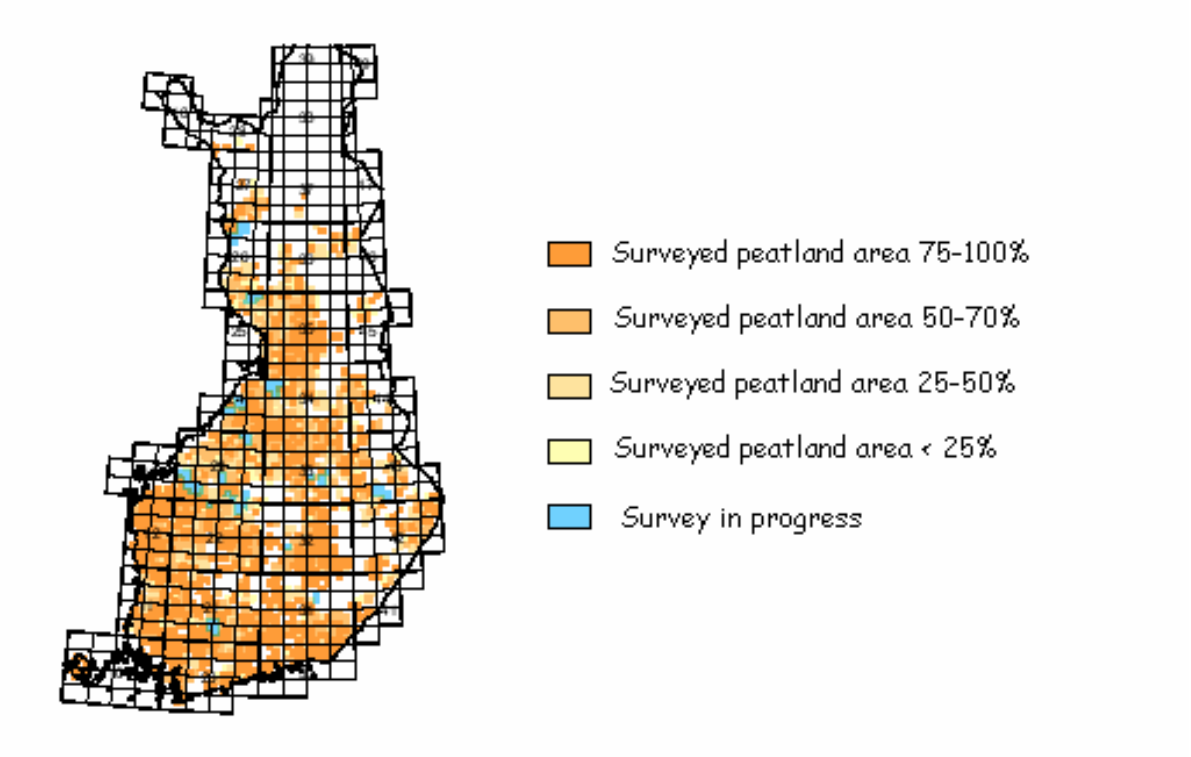



**Fig. 1-15:** Peatland research in Finland (adapted from Geological Survey of Finland GTK, 2004).

## 1.5 Aims of the Work

• To develop accurate, sensitive, and robust analytical procedures for the direct determination of arsenic (As) in nitric acid digests of peat samples using inductively coupled plasma - sector field - mass spectrometry (ICP - SF - MS), hydride generation - atomic absorption spectrometry (HG - AAS) as well as hydride generation - atomic fluorescence spectrometry (HG - AFS).

• To compare the chronology of atmospheric As accumulation in age-dated peat cores from ombrotrophic bogs with historical records of industrialisation. To do this, cores were selected from three bogs in Finland: Harjavalta, near a Cu-Ni smelter, Outokumpu near the famous Cu-Ni mine, and Hietajaervi, a low background site and to elucidate whether or not ombrotrophic peats preserve the changing rates of atmospheric As deposition.

• As an independent check on the retention of As by the peat cores, As was also determined in the porewaters. To do this, an APEX sample introduction system was coupled to an ICP – SF - MS. The ability of the APEX sample introduction to cope with $(^{40}Ar^{35}Cl)^{+}$ interferences on $^{75}As$ in order to determine the very low total As concentrations in pore waters was investigated. With this sample introduction system it was possible to determine total As concentrations in pore waters in the low resolution mode of the ICP - SF - MS.

• To prepare an "internal peat reference material" to quantify losses of As due to sample handling (oven drying at 105°C compared to freeze-drying and most important to fresh peat samples).

• As a further check on the preservation of As by the peat cores, As was extracted using water and the predominant As species determined using HPLC - ICP - SF - MS. The main objective here was to determine the yields of As from peat in solutions resembling rainwater and pore waters. A second objective was to identify possible transformations of As in the oxic and anoxic peat layers and to discuss possible mechanisms for the preservation of this species in peat bogs.

# 2 Experimental

## 2.1 General Reagents

**Ammonia Solution:** $NH_3$, 25%, Suprapur®, Merck.

**Ammonium Dihydrogen Phosphate :**$NH_4H_2PO_4$, p.a., Merck.

**Arsenate Stock Standard Solution (1000 mg As/L):** As(V), Tritisol®, Merck.

**Arsenite Stock Standard Solution (1000 mg As/L):** As(III), Atomic Spectroscopy Standard Solution Fluka, Fluka, Buchs, Switzerland.

**Arsenobetaine**: $(CH_3)_3As^+CH_2COOH\ Br^-$ gift from Prof. Kevin Francesconi, Karl-Franzens University of Austria, Graz, Austria.

**Ascorbic acid**: $C_6H_8O_6$, p.a., Carl Roth GmbH + Co., Karlsruhe, Germany

**Dimethylarsinic Acid:** $(CH_3)_2AsO(OH)$ gift from Prof. Kevin Francesconi, Karl-Franzens University of Austria, Graz, Austria.

**Disodium Hydrogen Arsenate Heptahydrate**: $Na_2HAsO_4 \cdot 7\ H_2O$, pa., Merck.

**Hydrochloric Acid**: HCl, 32%, analytical-reagent grade, Riedel-de Haen, Seelze, Germany.

**Hydrogen Peroxide:** $H_2O_2$, 30%, Baker analysed, J.T. Baker, Deventer, The Netherlands.

**ICP Multi-Element Standard Solution VI:** Merck 1.10580

**Indium Stock Standard Solution (1000 mg In/L):** $In(NO_3)_3 \cdot 4.5\ H_2O$ in 0.5 mol/L $HNO_3$, Merck.

**L-cysteine:** $C_3H_7NO_2S$, >99%, Fluka.

**Methanol:** $CH_3OH$, puriss. p.a., Fluka.

**Methylarsonic Acid:** $CH_3AsO(OH)_2$, gift from Prof. Kevin Francesconi, Karl-Franzens University of Austria, Graz, Austria.

**Nitric Acid:** $HNO_3$, 65%, analytical-reagent grade, Merck. The nitric acid from Merck was further purified by distillation, using a high purity quartz unit for sub-boiling of acids (MLS GmbH, Leutkirch, Germany). The sub-boiling distillation unit was operated in a clean room.

**Potassium iodide:** KI, puriss. p.a., Fluka.

**Pyridine:** $C_5H_5N$, Merck, p.a.

**Sodium Borhydride :** $NaBH_4$, analytical-reagent grade, Riedel-de Haen.

**Sodium Hydroxide:** NaOH, analytical-reagent grade, Carl Roth GmbH+Co.

**Sodium Metaarsenite:** $NaAsO_2$, p.a., Merck.

**Tetrafluoroboric acid:** $HBF_4$, ~50%, purum, Fluka.

**Water ($H_2O$):** All solutions were prepared with high purity water (specific resistivity 18.2 MΩ cm) from a MilliQ system designed for ultra trace analysis (Element, Millipore, Milford, MA, USA). The water purification system was operated in a clean room.

## 2.2 Reference Materials

**CTA-VTL-2:** Virginia Tobacco Leaves, CTA Polish Academy of Sciences.

**CTA-OTL-1:** Oriental Tobacco Leaves, CTA Polish Academy of Sciences.

**GBW 07602:** Bush Branches and Leaves, Institute of Geophysical and Geochemical Exploration, Langfang, China.

**Apple Leaves:** Reference Material 1515, NIST, National Institute of Standards and Technology, Gaithersburg, MD, USA.

**Bituminous Coal:** Standard Reference Material 1632c, NIST.

**NIMT Peat:** Peat reference material, Details of the preparation and characterization of this in-house peat reference material can be found elsewhere (Yafa et al., 2004).

**Tomato Leaves:** Standard Reference Material 1573a, NIST.

**Peach Leaves:** Standard Reference Material 1547, NIST.

**Pine Needles:** Standard Reference Material 1575, NIST.

**Peat 1:** in-house reference material. Details of the preparation and characterization of this in-house peat reference material can be found elsewhere (Krachler et al., 2001).

**Peat 2:** in-house reference material. Details of the preparation and characterization of this in-house peat reference material can be found elsewhere (Krachler et al., 2001).

**Peat 3:** in-house reference material prepared as described in section 2.6.10.

**Peat 4:** in-house reference material prepared as described in section 2.6.10.

**SLRS-4:** River Water Reference Material for Trace Metals, National Research Council of Canada, Institute for National Measurement Standards, Ottawa, Canada.

**Subbituminous Coal:** Standard Reference Material 1635, NIST.

The algal extract *Fucus serratus* prepared and identified as described elsewhere (Madsen et al., 2000), containing the four major arsenosugars: glycerol-, phosphate, sulfonate-, and the sulfate-arsenoriboses (arsenoriboses I, II, III, and IV; Fig. 1-2), was a gift from Prof. Kevin Francesconi, Karl-Franzens University of Graz, Austria.

## 2.3 General Working Solutions

### 2.3.1 General Working Solutions for the Determination of Arsenic Using HG-AAS

The carrier solution for the flow injection system was prepared from hydrochloric acid. $NaBH_4$ solutions (0.5 % m/v) were prepared daily by dissolving appropriate amounts of powdered $NaBH_4$ in 0.1% (m/v) NaOH. As(V) was reduced to As(III) with aqueous solutions containing 2 ml of a 50 g $l^{-1}$ L-cysteine solution or 2 ml of a solution containing 30% (m/v) potassium iodide (KI).

### 2.3.2 General Working Solutions for the Determination of Arsenic Using HG-AFS

The carrier solution (4.5 mol $l^{-1}$) for the flow injection system was prepared from hydrochloric acid. $NaBH_4$ solutions (1.0 % m/v) were prepared daily by dissolving appropriate amounts of powdered $NaBH_4$ in 0.04% (m/v) NaOH.

As(V) pre-reduction was tested systematically with aqueous solutions containing 4.8 g $l^{-1}$ to 12.8 g $l^{-1}$ L-cysteine (Fluka) or 0.5% (w/v) potassium iodide (KI) and 0.1% (w/v) ascorbic acid for comparison.

### 2.3.3 General Working Solutions for the Determination of Arsenic Species Using HPLC-ICP-SF-MS

Standard solutions (1000 mg As/l) of arsenous acid, arsenic acid, methylarsonic acid, dimethylarsinic acid and arsenobetaine bromide were prepared by dissolving 433.0 mg $NaAsO_2$, 1041 mg $Na_2HAsO_4 \cdot 7\ H_2O$, 466.6 mg methylarsonic acid and 460.5 mg dimethylarsinic acid and 864.2 mg arsenobetaine bromide in 0.25 l of MilliQ-water. The stock solutions were stored in a refrigerator at 4°C. Dilute solutions were prepared daily before use by diluting the stock solutions with MilliQ-water.

The mobile phase for the separations on the Hamilton PRP-X100 anion-exchange column (Hamilton, Reno, USA) was prepared in a concentration of 20 mmol/l by dissolving 2.30 g $NH_4H_2PO_4$ in ~ 0.95 l MilliQ-water and adjusting the pH to 5.6 by addition of 25% aqueous ammonia. After reaching a pH of 5.6 the solution was filled up to 1 l with MilliQ-water.

## 2.4 Origin of Samples

Three complete vertical peat cores were collected by Dr. N. Rausch from a Finnish peat bog near a former Cu/Ni mine at Outokumpu (Out) in south-eastern Finland, from Harjavalta (Har), nearby a Cu-Ni smelter and from Hietajärvi (Hie), which acts as the low background site without any significant, local anthropogenic sources.

The reference site, Hie, is located in Patvinsuo National Park, in eastern Finland (Fig. 2-1), with no agricultultural activities and roads in the vicinity.

At Har a copper smelter has been operating since 1945 and a nickel smelter since 1959 (Outokumpu Harjavlata Metals OY). The ores used for smelting until the early 1970s, were mainly domestic sulfidic minerals from the Outokumpu mine. Nowadays, ore concentrates originating from different parts of the world are used. Peat samples were taken from a peat bog located 6 km northeast of Harjavalta in the southwestern part of Finland (Fig. 2-1).

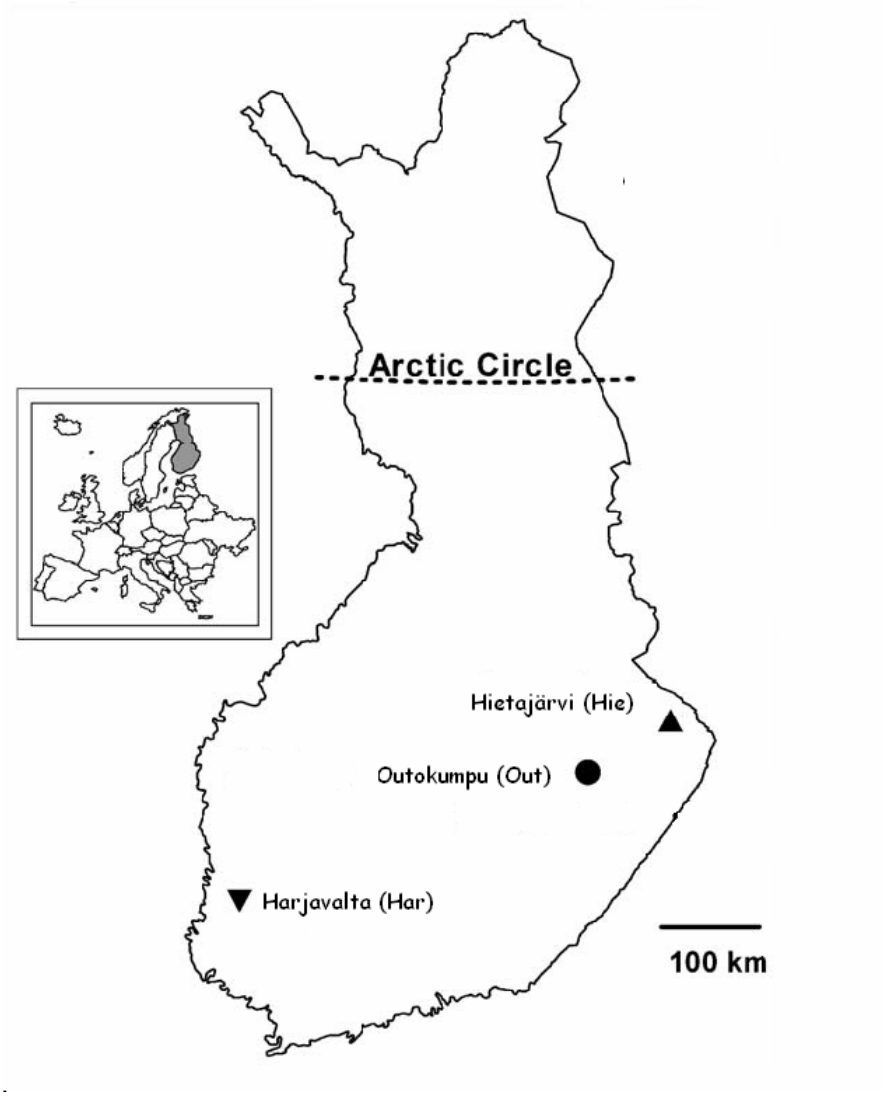



**Fig. 2-1:** Location of the Finnish peat bogs.

In 1910 the ore of Outokumpu was found and a copper factory was built in 1913. The sampling site is located in Eastern Finland, a few km SW of the city Outokumpu (Fig. 2-1). In Outokumpu a famous Cu-Ni mine operated from 1910 until 1980's and a small smelter from 1913 until 1929.

The vegetation on each bog was characterised by a sparse tree cover. Most of the ground layer in all the sites consisted of *Sphagnum* species e.g. *Sphagnum fuscum*, *Sphagnum balticum*, *Sphagnum angustifolium* or *Sphagnum magellanicum*, all of which indicate ombrotrophy. In addition, some dwarf shrubs and a few herbs such as *Carex globularis* and *Rubus chamaemorus* are found in varying amounts at each site (Ukonmaanaho et al., 2004). A detailed description of the studied peat bogs is given in Table 2-1.

**Table 2-1:** General description of the sampling sites (adapted from Ukonmaanaho et al., 2004).

| Site | Hietajärvi | Outokumpu | Harjavalta |
|---|---|---|---|
| Climatic zone | Middle boreal | Southern boreal | Southern boreal |
| Location | 63°09′N, 30°40′E | 62°40′N, 28°5′E | 61°21′N, 22°11′E |
| Annual mean temperature[a] [°C] | 1.5 | 2.3 | 4.1 |
| Annual precipitation sum[a] [mm] | 616 | 615 | 571 |
| Altidude a.s.l. [m] | 168 | 108 | 40 |
| Peat type | Cottongrass-pine bog[b] | Cottongrass-pine bog[b] | Cottongrass-pine bog[b] |
| Depth of peat [m] | > 2 | > 6[c] | > 2 |
| pH | 4.1 | 4.0 | 3.8 |
| Name of the mire complex | Patvinsuo | Viurusuo | Pyhäsuo |

[a] for period 1950-1999, estimated using the method described by Ojansuu and Henttonen, 1983
[b] Laine and Vasander, 1996
[c] Leino and Saarelainen, 1990

The samples were taken in the central part of the bog where it is strongly domed and has the greatest peat accumulation. The peat was sampled using a Wardenaar peat profile sampler (Wardenaar, 1987) to remove a monolith 15*15*100 cm that was subsequently cut frozen into 1 cm slices for further analysis. All peat samples were milled in an ultracentrifugal mill (Retsch, Haan, Germany) equipped with a titanium sieve and rotor (detailed peat sample preparation procedures are described in section 2.6.1).

Pore waters (volume: 10 ml) from all three sites were collected by Dr. N. Rausch from specific depths using a pre-cleaned, homemade pore water extraction device constructed from plexiglass (Rausch et al., 2005). Pore water preparation procedures are described in sections 2.6.2.

## 2.5 Instrumentation

### 2.5.1 ultraCLAVE II

The digestion of the samples was performed with a MLS-ultraClave II microwave digestion system (Fig. 2-2).

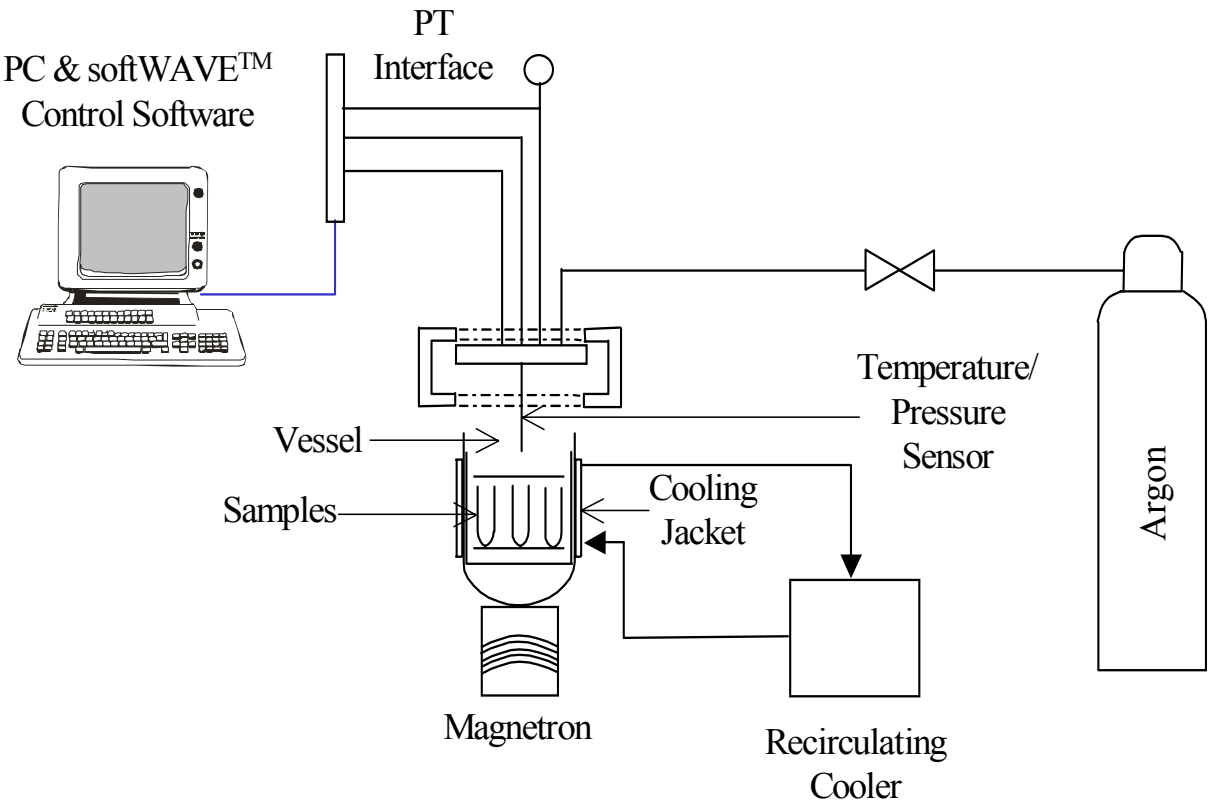



**Fig. 2-2:** Schematic diagram of the MLS-ultraCLAVE II (Frank, 2001).

With this instrument it is possible to digest 40 samples simultaneously. In contrast to a conventional microwave, the ultraCLAVE II consists of a high grade steel pressure vessel with a volume of 4.2 litres and a maximum tolerable pressure of 200 bar that provides more

complete digestion solutions (in comparison to conventional digestion systems) for the determination of elements in peat.

The pressure vessel is enclosed with a PTFE/TFM-insert (polytetrafluoroethylen/ tetrafluorometoxil), in order to protect the high grade steel pressure vessel and for thermic isolation.

#### 2.5.1.1 Instrumental Settings for the Digestion of Peat Samples, Reference Materials, and Extracts

Aliquots (~ 200 mg) of the powdered peat samples and plant reference materials or 5 ml of water or phosphoric acid extracts were dissolved in 20 ml PTFE digestion vessels with the microwave digestion program given in Table 2-2.

When the temperature program was finished and the temperature was < 70°C, the pressure was released at a rate of 7 bar/min. When the whole pressure was released, the clamps were opened and the reaction vessel was opened. The mounting was removed from the microwave system. After removing the caps, the digestion solutions were quantitatively transferred into 15 ml-Falcon® tubes.

**Table 2-2:** Microwave digestion program for peat samples.

| Step | Time [min] | Temperature [°C] |
|---|---|---|
| 1 | 9 | 60 (ramped) |
| 2 | 25 | 125 (ramped) |
| 3 | 10 | 160 (ramped) |
| 4 | 12 | 240 (ramped) |
| 5 | 20 | holding |
| 6 | 40 | cooling |

To do so, the tubes were rinsed 3 times with MilliQ-water and the solutions were also poured into the polyethylene tubes. Blank solutions were prepared by application of the entire digestion procedure to reagent solutions containing no sample.

## 2.5.2 HG-AAS

The HG-AAS setup consisted of a continuous-flow system (Hydridsystem HS 51, Analytik Jena, Jena, Germany) equipped with an autosampler (AS52S, Analytik Jena) coupled to an atomic absorption spectrometer (AAS vario® 6, Analytik Jena). The spectrometer was equipped with an As super hollow cathode lamp (S-HCL; Phototron Pty. Ltd., Victoria, Australia) and a super lamp power supply (Phototron Pty. Ltd.).

### 2.5.2.1 Instrumental Settings for the Determination of As Using HG-AAS

For the determination of As by HG-AAS, gaseous hydrides were generated using $NaBH_4$ (0.5%, m/v) solution (stabilized with 0.1% m/v NaOH) and 7 mol $l^{-1}$ HCl as carrier solution. The $NaBH_4$ and HCl flow rates were set to 2.2 ml $min^{-1}$ (Table 2-3). The resulting mixture was transferred into the gas-liquid separator from where the gaseous hydrides were transported to the electrically heated quartz tube atomizer of the AAS. A boosted super hollow cathode lamp (S-HCL) for As was used throughout the experiments.

**Table 2-3:** Optimized operating conditions for HG-AAS.

| | |
|---|---|
| *Hydride generation* | |
| Pre-reduction solution (L-cysteine) | 10 g $l^{-1}$ |
| $NaBH_4$ solution concentration | 0.5% m/v, stabilized with 0.1% m/v NaOH |
| $NaBH_4$ and HCl solution flow rate | 2.2 ml $min^{-1}$ |
| *Atomic absorption spectrometer* | |
| Instrument | AAS ®vario 6 (Analytik Jena, Jena, Germany) |
| Wavelength | 193.7 nm |
| Slit width | 0.2 nm |
| Quartz tube atomizer temperature | 940 °C |
| Lamp primary current | 18 mA |
| Lamp boost current | 22 mA |
| Signal recording mode | Peak area |

When the performance of the HG-AAS measurements deteriorated, the quartz tube was conditioned by soaking in concentrated hydrofluoric acid for 10 minutes. The quartz tube was subsequently rinsed 3-times with high purity water and allowed to dry at room temperature. Prior to any further determinations of As the HG-AAS was checked for optimum signal intensity and stability by measuring a 2 μg $l^{-1}$ As(III) standard solution.

### 2.5.3 HG-AFS

For As analysis, a continuous flow hydride generation-atomic fluorescence spectrometer (Fig. 2-3, Millenium Excalibur, PS Analytical Ltd., Orpington, Kent, England) equipped with an arsenic boosted- discharge hollow cathode lamp (BDHCL) was used.

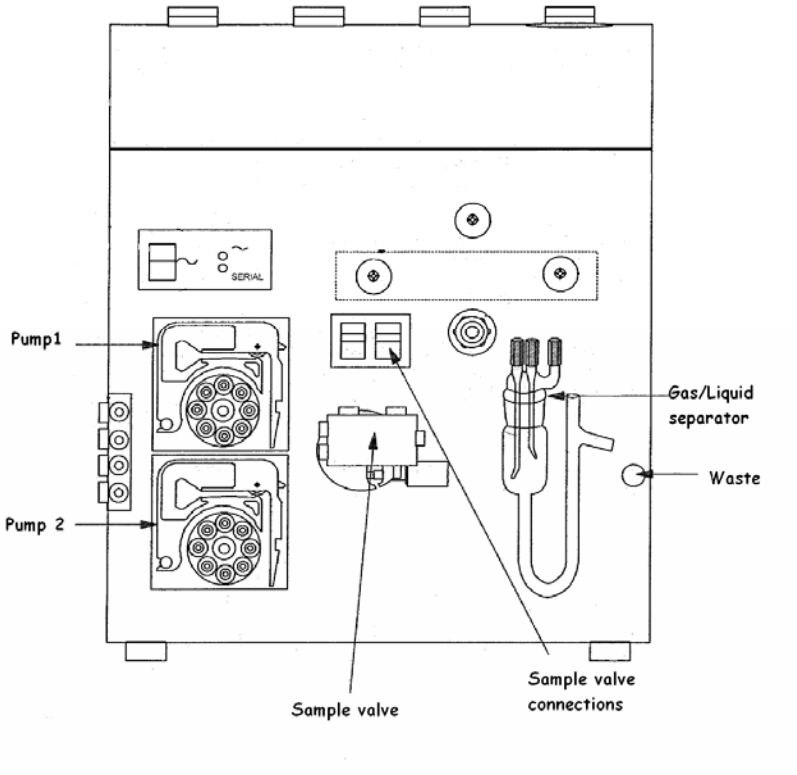



**Fig. 2- 3 :** Schematic diagram of the Millenium Excalibur (adapted from Millenium Excalibur User Manual, 2000).

### 2.5.3.1 Instrumental Settings for the Determination of Arsenic Using HG-AFS

As fluorescence was monitored at a wavelength of 197.3 nm. The lamp primary current was set to 27.5 mA, the lamp boost current to 34.9 mA. $NaBH_4$ and HCl solution flow rates were 4.5 and 9 ml $min^{-1}$, respectively. The integration time was set to 40 s and signals were recorded as peak area (Table 2-4).

**Table 2-4:** Optimized operating conditions for HG-AFS.

| | |
|---|---|
| Pre-reduction solution (L-cysteine) | 12.8 g $l^{-1}$ |
| $NaBH_4$ solution concentration | 1% m/v, stabilised with 0.04% m/v NaOH |
| $NaBH_4$ solution flow rate | 4.5 ml $min^{-1}$ |
| HCl solution concentration | 4.5 mol $l^{-1}$ |
| HCl solution flow rate | 9 ml $min^{-1}$ |
| Instrument | Millenium Excalibur (PS Analytik Ltd., Orpington, Kent, England) |
| Resonance wavelength | 197.3 nm |
| Lamp primary current | 27.5 mA |
| Lamp boost current | 34.9 mA |
| Signal recording mode | Peak area |

## 2.5.4 ICP-SF-MS

The general components of this instrument were described in section 1.2.3. The inductively coupled plasma-sector field-mass spectrometer (ICP-SF-MS) (ELEMENT 2, Thermo Electron, Bremen, Germany) was equipped with a guard electrode to eliminate secondary discharge in the plasma and to enhance overall sensitivity.

For the determination of trace elements in acid digests of peat, plant, and reference materials as well as for the determination of As in digested water and phosphoric acid extracts, a micro volume autosampler (ASX 100, Cetac Technologies, Omaha, NE, USA) and

a HF resistant sample introduction kit consisting of a 100 µl PFA low flow nebulizer (MicroFlow, Elemental Scientific Inc., ESI Inc., Nebraska, USA), a PEEK cyclone spray chamber and a sapphire injector tube were employed to transport the analytes into the plasma of the ICP - SF - MS.

For the determination of As in pore waters, an Apex sample introduction system (ESI Inc.) was used. A description of the APEX sample introduction system and the instrumental settings for the determination of As in pore waters are given in sections 2.5.4.2 and 2.5.4.3.

The entire sample introduction system, including the autosampler and the plasma region of the ICP - SF - MS, was hosted in a class 100 laminar flow bench.

Before starting measurements, the ICP - SF - MS was tuned manually to give maximum count rates and low rates of oxides and doubly charged ions with respect to torch position, gas flows, and resolution. For daily mass calibration of the ICP-SF-MS, a multi element solution containing 10 mg $l^{-1}$ of each Ba, B, Co, Fe, Ga, In, K, Li, Lu, Na, Rh, Sc, Tl, U and Y was diluted with was diluted 1% $HNO_3$ to a concentration level of 1 µg $l^{-1}$. Indium at a concentration of 1 µg $l^{-1}$ was used for internal standardization of the measurements.

#### 2.5.4.1 Instrumental Settings for the Determination of Trace Elements Using ICP-SF-MS

The following elements were determined using ICP-SF-MS: Cd, Sn, Mo, Sc, V, Cr, Co, Ni, Cu, Zn, As (In was used as internal standard). The elements Cu, Co, Cd and Zn were part of another study (Rausch, 2005).

For the determination of As, the ICP-SF-MS was operated in the high resolution mode ($m/\Delta m$ ~10000) to overcome potential $(^{40}Ar^{35}Cl)^+$ interferences. Optimised operating conditions are summarised in Table 2-5.

**Table 2-5:** Optimized operating conditions for ICP-SF-MS measurements.

| | |
|---|---|
| Instrument | Element 2 (Thermo Finnigan MAT, Bremen, Germany) |
| Forward power | 1250 W |
| Cones | Nickel, sampler ∅ 1mm, skimmer ∅ 0.8 mm |
| Plasma gas | 15.9 l $min^{-1}$ |
| Nebuliser gas | Optimized to obtain maximum signal intensities |
| Auxillary gas | 0.9 l $min^{-1}$ |
| Pneumatic nebuliser | Low flow nebuliser, 100 µl $min^{-1}$ |
| Runs/Passes | 7/7 |
| Selected isotopes in the low resolution mode (m/Δm ~300) | $^{111}Cd$, $^{118}Sn$, $^{95}Mo$, $^{98}Mo$ $^{115}In$ (internal standard) |
| Selected isotopes in the medium resolution mode (m/Δm ~4000) | $^{45}Sc$, $^{51}V$, $^{52}Cr$, $^{59}Co$, $^{60}Ni$, $^{63}Cu$, $^{64}Zn$, $^{66}Zn$, $^{115}In$ (internal standard) |
| Selected isotopes in the high resolution mode (m/Δm ~10000) | $^{75}As$, $^{115}In$ (internal standard) |

#### 2.5.4.2 The Apex Sample Introduction System

Due to the low As concentrations expected in the pore waters, an Apex sample introduction system (ESI Inc.) was coupled to the ICP-SF-MS to improve sensitivity and reduce interferences. The Apex system can directly be connected to the torch injector of the ICP-SF-MS. The Apex was equipped with a microFlow nebuliser (100 µl) that transports the aerosol to a heated cyclonic spray chamber (Fig. 2-4). For the determination of As in pore waters, the spray chamber was heated to 140°C and the peltier-cooled multipass condenser was cooled to -5°C. To increase signal intensity, to improve stability, and to reduce the formation of oxide interferences, nitrogen is mixed with the sample aerosol stream in the last loop of the Peltier-cooled condenser. The exact amount of $N_2$ was optimised daily to maximise signal intensity and stability.

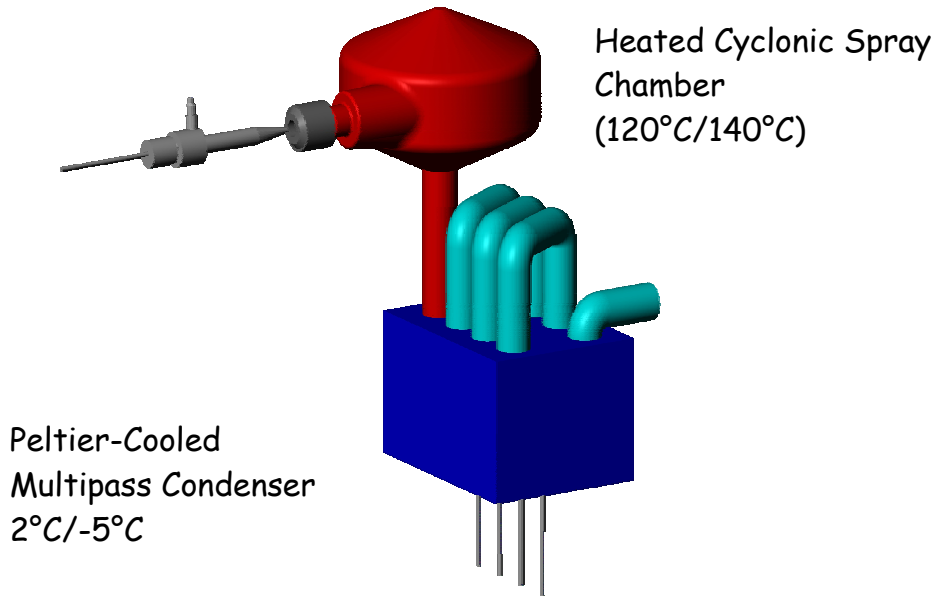



**Fig. 2- 4:** Schematic diagram of the Apex sample introduction system (adapted from Widerin, 2004).

### 2.5.4.3 Instrumental Settings for the Determination of Arsenic in Pore Waters and Water Extracts

For the determination of As in pore waters and water extracts, it was possible to operate the ICP-SF-MS in the low resolution mode (m/Δm ~300), due to the high capability of the Apex system to overcome potential $(^{40}Ar^{35}Cl)^{+}$ interferences (Fig. 3-20).

Optimised operating conditions are summarised in Table 2-6. Before each measurement session, the ICP-MS was tuned manually in order to obtain a stable and high $^{115}In$ signal and the lowest possible oxide formation rate.

For daily mass calibration of the ICP-SF-MS, a multi element solution containing 10 mg $l^{-1}$ of each Ba, B, Co, Fe, Ga, In, K, Li, Lu, Na, Rh, Sc, Tl, U and Y was diluted with 1% $HNO_3$ to a concentration of 0.1 µg $l^{-1}$. Indium at a concentration of 0.1 µg $l^{-1}$ was used for internal standardization of the measurements.

**Table 2-6:** Optimized operating conditions for the determination of As in pore waters and water extracts using the Apex sample introduction system coupled to ICP-SF-MS.

| | |
|---|---|
| Forward power | 1250 W |
| Cones | Nickel, sampler ∅ 1mm, skimmer ∅ 0.8 mm |
| Plasma gas flow rate | 15.98 l $min^{-1}$, optimised daily |
| Auxillary gas flow rate | 0.6 l $min^{-1}$, optimised daily |
| Sample gas flow rate | 0.905 l $min^{-1}$, optimised daily |
| Nebuliser gas and $N_2$ gas from Apex inlet system | Optimized daily to obtain maximum signal intensities |
| Pneumatic nebuliser | Low flow nebuliser, 100 µl $min^{-1}$ |
| Take up time | 80 s |
| Washing time between samples | 120 s with 1% $HNO_3$ |
| Selected isotopes in the low resolution mode (m/Δm ~300) | $^{75}As$, $^{115}In$ (internal standard) |
| Scan type | Electric scans over small mass ranges (E-scan) |
| Mass window, % | 75 |
| Integration window, % | 55 |
| Runs/Passes | 3/10 |

## 2.5.5 HPLC

The high performance liquid chromatographic (HPLC) system used was a Dionex GP50 gradient pump equipped with a thermostated column compartiment (TCC-100) and an autosampler (AS50) (all Dionex GmbH, Idstein, Germany).

Trigger data acquisition was performed using a 5V TTL signal. The chromatographic system was connected to the ICP-SF-MS system using a 100 mm PEEK capillary tubing (0,25 mm i.d.). The outlet of the column was directly connected to the nebulizer of the ICP-SF-MS. The CROMELEON® chromatography management system controls the entire chromatography system and allows direct instrument operation and control via the PC. A schematic diagram of the HPLC-ICP-SF-MS is displayed in Fig.2-5.

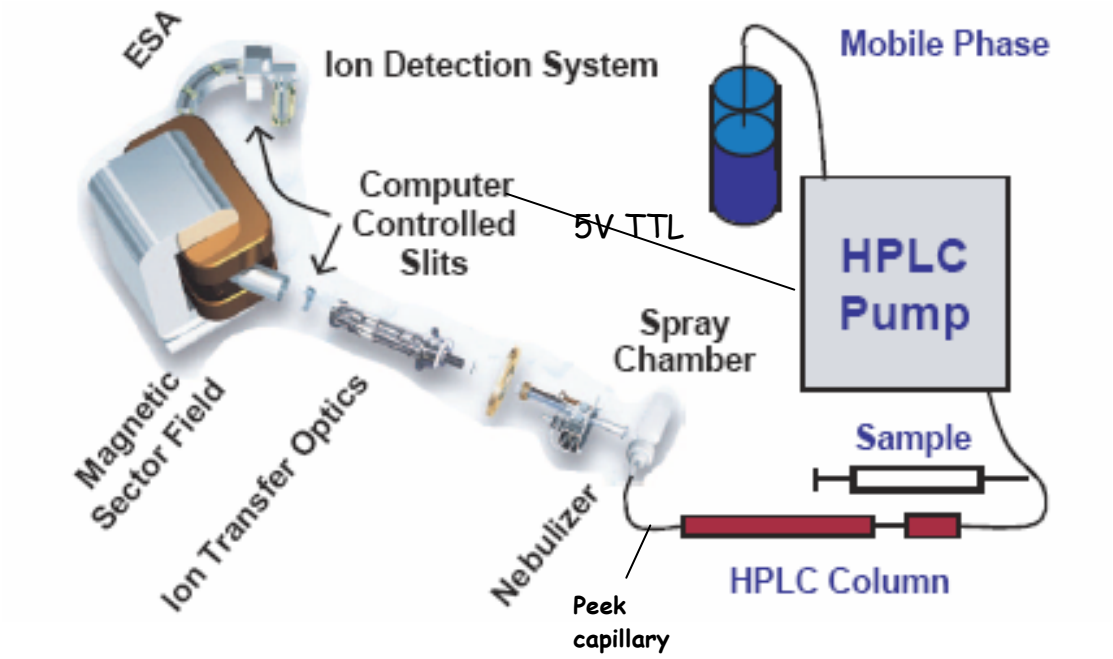



**Fig. 2-5:** Schematic diagram of the HPLC-ICP-SF-MS (adapted from Lindemann et al., 2002).

### 2.5.5.1 Instrumental Settings for the Determination of Arsenic Species Using HPLC-ICP-SF-MS

Anion-exchange chromatography was employed for the separation of arsenous acid, arsenic acid, methylarsonic acid and dimethylarsinic acid in peat. The separations were performed on a Hamilton PRP-X100 (Reno, Nevada, USA) anion-exchange column (250 mm length, 4.1 mm inner diameter, stationary phase: 10-µm styrene-divinylbenzene particles with trimethylammonium exchange-sites).

The mobile phase consisted of an aqueous 20 mM solution of $NH_4H_2PO_4$ at pH 5.6 (adjusted with 25% $NH_3$).

The sample injection volume was set to 100 µL, the flow-rate to 1.5 mL/min and the column was operated at 40°C. Optimised HPLC-ICP-SF-MS operating conditions are summarised in Tab. 2-7.

Prior to HPLC measurements the ICP-SF-MS was manually tuned with respect to torch position, gas flows, and lens voltages by monitoring indium ($^{115}In$), which was added to all mobile phases at a concentration of 1 µg/l. Recording of the chromatograms started automatically by the TTL signal from the HPLC system to the ICP-SF-MS. The chromatograms were exported and integrated with the CROMELEON® chromatography management system.

**Table 2-7.** HPLC –ICP-MS system operating conditions for the determination of arsenic species.

| | |
|---|---|
| *HPLC* | |
| Anion-exchange column | Hamilton PRP-X100 |
| Mobile phase | 20 mM $NH_4H_2PO_4$, pH 5.6 |
| Injection volume | 100 µl |
| Flow rate | 1.5 ml $min^{-1}$ |
| Temperature | 40°C |
| Analysis time | 600 s (PRP-X100) |
| *ICP-SF-MS* | |
| Forward power | 1250 W |
| Cones | Nickel, sampler ∅ 1mm, skimmer ∅ 0.8 mm |
| Plasma gas flow rate | 15.98 l $min^{-1}$, optimised daily |
| Auxillary gas flow rate | 0.6 l $min^{-1}$, optimised daily |
| Sample gas flow rate | 0.905 l $min^{-1}$, optimised daily |
| Pneumatic nebuliser | Quartz concentric, 2 ml $min^{-1}$ |
| Spray chamber | Scott type |
| Runs/Passes | 426/1 |
| Selected isotopes in the low resolution mode (m/Δm ~300) | $^{75}As$ |
| Scan type | Electric scans over small mass ranges (E-scan) |
| Mass window | 10% |
| Sample time | 150 ms |
| Samples per peak | 100 |
| Analysis time | 600 s (PRP-X100) |

## 2.6 Analytical Procedures

All sample handling in the laboratory and the preparation of all standards were performed in clean rooms under laminar flow clean air benches of class 100 to minimize the potential risk of contamination.

### 2.6.1 Preparation of Peat Samples

Details of sample collection and preparation can be found elsewhere (Givelet et al., 2004). A short overview is given in the following sections (2.6.1.1, 2.6.1.2).

#### 2.6.1.1 Slicing the Cores

The Finnish peat samples were collected using a home-made (Ti-Al-Mn alloy) Wardenaar (Wardenaar, 1987) peat profile cutter (15*15*100 cm). After extraction, the Wardenaar corer was laid horizontally on a large sheet of plastic. The cores were described visually in the field (length, colour, texture, plant remains, moisture) and photographed. The exposed surface and two sides of the cores were wrapped in polyethylene cling film (Givelet et al., 2004).

Wooden core boxes built specifically for the Wardenaar core were lined with plastic. The plastic-lined wooden core boxes were placed over the peat cores. Two people lift the bottom half of the Wardenaar corer, flip it carefully backward 180°, allowing the peat core to slide down into the box (Givelet et al., 2004). The surface of the cores is wrapped in polyethylene cling film. The core is covered with plastic, labelled and the lid attached using screws.

Cores were kept cool until they could be frozen: this was done soon as possible after collection, and kept frozen at -18 °C until they could be prepared in the laboratory.

Finnish peat cores were cut frozen in the lab into 1 cm increments using a stainless steel band saw with stainless steel blades. The width of the blade is 1 mm, so ca. 10% of each

slice is lost during cutting. The accuracy of the thickness of theses slices is better than ± 1 mm (Givelet et al., 2004).

The individual slices were subsequently placed on a polyethylene cutting board and the outer 1 cm of each slice was trimmed away using a 13 × 13 cm polyethylene plate and an acid rinsed Ti knife (Givelet et al., 2004). The outside edges were systematically discarded, as those could have been contaminated during the sampling and preparation. The cutting board and knife were rinsed with deionised water three times between each slice. Then slices were packed into labelled zip-lock plastic bags and kept frozen for storage and until further preparation.

#### 2.6.1.2 Drying and Milling

The peat samples were dried at 105 °C in acid-washed Teflon bowls to constant weight, and macerated in a centrifugal mill equipped with a Ti rotor and 0.25 mm Ti sieve (Ultra centrifugal Mill ZM 1-T, F.K. Retsch GmbH and Co., Haan, Germany). This yields a very fine, homogeneous powder with average particle size of ca. 100 μm (and Gaussian particle size distribution).

The powdered samples were manually homogenised and stored in airtight plastic beakers. The milling was carried out in a Class 100 laminar flow clean air cabinet to prevent possible contamination of the peat samples by lab dust. In the laboratory, all of the sample handling and preparation was carried out using clean laboratory techniques. Peat powder stored for longer than one year in humid conditions should be re-dried prior to analysis (Givelet et al., 2004).

### 2.6.2 Preparation of Pore Waters

Details of pore water collection and pore water preparation procedures can be found elsewhere (Rausch et al., 2005).

Briefly, the pore water samples were filtered on-site through 0.45 µm high purity filters (GD/XP, Whatman) into 15 ml-Falcon® tubes. Following US EPA Method 1669 (Telliard 1996), pore water samples were acidified with double sub boiled nitric acid to 1% (v/v) in a class 100 clean bench upon arrival in the laboratory (Rausch, 2005). After some days of storage at 4°C in the refrigerator, a precipitate of humic acids was visible in the pore water solutions (Rausch, 2005).

Krachler et al.(2004) investigated 24 trace elements (Ag, Al, Ba, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Mg, Mn, Ni, Pb, Rb, Sb, Sc, Sr, Tl, Ti, U, V, Zn) in these porewaters. Results for these elements revealed that generally the precipitate contains only a very small amount (from 2 to 4% of the total metal concentration of the filtered pore water sample). Therefore it is well justified to consider only the supernatant for analyses (Krachler et al., 2005).

### 2.6.3 Digestion Procedures for the Determination of Trace Elements

Aliquots (200 mg) of the powered reference materials or peat samples were weighed to 0.1 mg into 20 ml PTFE vessels. Nitric acid (3 ml) and 100 µl of $HBF_4$ were added to the powders and gently shaken to mix the contents. After sealing the vessels with a PTFE lid, samples were digested in a high-pressure microwave autoclave. A starting pressure of 50 bar (with Argon) was applied to the reaction chamber. Vessels were then heated in the microwave autoclave with a heating program given in section 2.5.1.1.

After cooling for approximately 40 min, the reaction chamber was opened and the clear solutions in the digestion vessels, were quantitatively transferred into 15 ml graduated polyethylene tubes and filled to 10 ml with high purity water. Blank solutions were prepared by application of the entire digestion procedure to reagent solutions containing no sample.

Prior to every sample digestion a cleaning step for the digestion vessels was employed, following the same analytical procedure applied for the digestion of the peat samples, peat and plant reference materials.

### 2.6.4 Digestion Procedures for the Determination of Arsenic

Aliquots (200 mg) of the powered reference materials or peat samples were weighed to 0.1 mg into 20 ml PTFE vessels. Nitric acid (3 ml) was added to the powders and gently shaken to mix the contents. Because the acid digests always contained small precipitates of silicates, the addition of tetrafluoroboric acid ($HBF_4$) to the acid mixture for dissolving silicates was investigated. For this purpose, 3 ml of nitric acid and 100 µl of $HBF_4$ were added into the PTFE vessels following the digestion procedure given in section 2.5.1.1.

For the digestion of water and phosphoric acid extracts for the determination of As using HG-AFS, 5 ml of the extracted solution and 3 ml of nitric acid were addet to the PTFE vessels of the microwave autoclave. The vessels were heated with the digestion program given in section 2.5.1.1.

After cooling for approximately 40 min, the reaction chamber was opened and the clear solutions in the digestion vessels, were quantitatively transferred into 15 ml graduated polyethylene tubes and filled to 10 ml with high purity water. Blank solutions were prepared by application of the entire digestion procedure to reagent solutions containing no sample.

Prior to every sample digestion a cleaning step for the digestion vessels was employed, following the same analytical procedure applied for the digestion of the peat samples, peat and plant reference materials.

## 2.6.5 Determination of Arsenic Using HG-AAS

The concentration of arsenic was determined with the HG-AAS setup described in section 2.5.2 with external calibration solutions containing 0.1; 0.5; 2.0; 5.0; 10 μg $l^{-1}$ As. Calibration solutions were prepared daily by diluting aliquots of stock standard solutions of As(III) or As(V) to the appropriate concentrations with high purity water. All calibration solutions were matched for the nitric acid concentration in the digested diluted samples.

For the determination of As by HG-AAS, an aliquot (0.5-1 ml) of the diluted digestion solution was transferred into a 10 ml volumetric tubes. The reduction efficiency of various volumes of solutions containing either 30% KI and 5% ascorbic acid or L-cysteine (50 g $l^{-1}$) was tested in detail. The pre-reductant solutions were added to the digestion solutions before filling up to 10 ml with high purity water. Final dilution factors ranged from 500 to 1000.

Solutions of digested samples containing more than 10 μg $l^{-1}$and 50 μg $l^{-1}$ As for the determination of As by HG-AAS were diluted to fit into the respective calibration ranges.

To evaluate the accuracy of the developed procedure for the determination of As using HG-AAS, several reference materials with certified As concentrations were analysed: CTA-VTL-2 and CTA-OTL-1, GBW 07602.

Additionally two in-house peat reference materials (Peat 1 and 2) with different chemical matrix characteristics (ash content, concentration of elements) were used to check accuracy of the developed analytical protocol. As an independent accuracy check of the developed HG-AAS procedure, selected peat samples from a Finnish peat bog collected near a former Cu/Ni mine at Outokumpu were analysed for As using both HG-AAS and ICP-SF-MS.

All reference materials and peat samples were used as bottled. Results for reference materials were corrected for the humidity content in the powders as determined on 200 mg aliquots of each material by an electronic moisture analyser (MA 100 H, Sartorius, Göttingen, Germany) as described in detail in section 2.6.9.

All samples and reference materials were digested twice and measurements were performed on at least two different days.

## 2.6.6 Determination of Arsenic Using HG-AFS

The concentration of arsenic was determined with the HG-AFS setup described in section 2.5.3 with external calibration solutions containing 100, 300, 500, 700, 900 ng $l^{-1}$ As. Calibration solutions were prepared daily by dilution of a 1000 mg $l^{-1}$ stock standard solution of As(V) to the appropriate concentrations with high purity water. All calibration solutions were matched for the nitric acid concentration in the digested diluted samples.

Solutions of digested samples containing more than 0.9 μg $l^{-1}$ As for the determination of As by HG-AFS were diluted to fit into the respective calibration ranges. Final dilution factors for the determination of As by HG-AFS ranged from 250 to 25,000.

As(V) pre-reduction was tested systematically with aqueous solutions containing 4.8 g $l^{-1}$ to 12.8 g $l^{-1}$ L-cysteine or 0.5% (w/v) potassium iodide (KI) and 0.1% (w/v) ascorbic acid for comparison.

To evaluate the accuracy of an already existing procedure for the determination of As using HG-AFS employing KI as pre-reductant (Chen et al., 2005) several selected peat samples (Out 10-70), three peat reference materials (NIMT Peat, Peat 1 and Peat 2) with different chemical matrix characteristics (ash content, concentration of major elements), and several certified plant reference materials (CTA-VTL-2 and CTA-OTL-1, GBW 07602, NIST 1547, NIST 1575, NIST 1515) were employed.

To evaluate the accuracy of the developed procedure for the determination of As using HG-AFS, employing L-cysteine as pre-reducing and masking agent, the reference materials GBW 07602, CTA-VTL-2, CTA-OTL-1, NIST 1547, NIST 1573a, NIST 1632c, NIST 1635, NIMT Peat and Peat 1 were analysed.

As an independent accuracy check of the developed HG-AFS procedure, selected peat samples from a Finnish peat bog collected near a former Cu/Ni mine at Outokumpu were analysed for As using both HG-AAS and ICP-SF-MS. Moreover selected water extracts were determined using both HG-AFS and ICP-SF-MS.

All reference materials and peat samples were used as bottled. Results for reference materials were corrected for the humidity content in the powders as determined on 200 mg aliquots of each material by an electronic moisture analyser (MA 100 H, Sartorius, Göttingen, Germany) as described in detail in section 2.6.9.

All samples and reference materials were digested twice and measurements were performed on at least two different days.

## 2.6.7 Determination of Trace Elements Using ICP-SF-MS

Total element concentrations of the Finnish peat samples were determined with the ICP-SF-MS setup described in section 2.5.4.1.

Calibration curves for the determination of total elements in peat were established with aqueous solutions containing 0.1, 0.5, 1.0, 5.0, 10, 20 $\mu g l^{-1}$ of ICP multi-element standard solution VI. Solutions of digested samples containing more than 50 $\mu g\ l^{-1}$, were diluted to fit into the respective calibration ranges. Final dilution factors for the determination of trace elements using ICP-SF-MS ranged from 500 to 1000. The nitric acid concentration of the prepared calibration curves was adjusted to the nitric acid concentration of the sample solutions.

To evaluate the accuracy of the procedure for the determination of trace elements using ICP-SF-MS, the certified reference materials CTA-OTL-1, GBW 07602, and the SRM 1573a were employed with every batch of samples.

All reference materials and peat samples were used as bottled. Results for reference materials were corrected for the humidity content in the powders as determined on 200 mg aliquots of each material by an electronic moisture analyser (MA 100 H, Sartorius, Göttingen, Germany) as described in detail in section 2.6.9.

All samples and reference materials were digested twice and measurements were performed on at least two different days. Indium at a concentration of 1 $\mu g\ l^{-1}$ was used for internal standardization of the measurements.

## 2.6.8 Determination of Arsenic Using ICP-SF-MS

The concentration of arsenic in digested solutions of peat samples was determined with the ICP-SF-MS setup described in section 2.5.4.1, the concentration of arsenic in pore waters and water extracts was determined with the ICP-SF-MS setup described in section 2.5.4.3.

Calibration curves for the determination of arsenic in peat were established with aqueous solutions containing 0.1; 0.5; 2.0; 5.0; 10 $\mu g\ l^{-1}$ As, calibration curves for the

determination of arsenic in pore waters and water extracts were established with aqueous solutions containing 1.0; 2.0; 5.0; 10; 20; 50; 100 ng $l^{-1}$ As.

Calibration solutions were prepared daily by diluting aliquots of stock standard solutions of As(V) to the appropriate concentrations with high purity water. All calibration solutions were matched for the nitric acid concentration in the digested diluted samples (0.1-0.3 ml for total digestions; 0.1 ml for the determination of pore waters and water extracts).

To evaluate the accuracy of the procedure for the determination of As in peat samples using ICP-SF-MS, the certified reference materials CTA-OTL-1, GBW 07602 and the SRM 1573a were employed with every batch of samples. Additionally two in-house peat reference materials (Peat 1 and 2) with different chemical matrix characteristics (ash content, concentration of elements) were used to check accuracy of the analytical protocol.

To evaluate the accuracy of the procedure for the determination of As in pore water samples using ICP-SF-MS, the certified reference materials SLRS-4, CTA-VTL-2, CTA-OTL-1 and NIMT peat were employed with every batch of samples.

Indium at a concentration of 1 µg $l^{-1}$ for the determination of As in peat samples and at a concentration of 0.1 µg $l^{-1}$ for the determination of As in pore waters, was used for internal standardization of the measurements, respectively.

All reference materials and peat samples were used as bottled. Results for reference materials were corrected for the humidity content in the powders as determined on 200 mg aliquots of each material by an electronic moisture analyser (MA 100 H, Sartorius, Göttingen, Germany) as described in detail in section 2.6.9.

All samples and reference materials were digested twice and measurements were performed on at least two different days.

## 2.6.9 Correction of Moisture Content

Results for reference materials were corrected for the moisture content in the powders as determined on 200 mg aliquots of each material by an electronic moisture analyser (MA 100 H, Sartorius, Göttingen, Germany).

The sample pans of the electronic moisture analyser were heated to 65 °C for 2 min without any sample to remove residual moisture. Sample pans were handled only with a pair

of tweezers. All measurements were performed with the maximum resolution setting of 0.1 mg on the balance of the moisture analyser. A sample mass of 0.2 g was used for the measurement, and the fully automatic mode of the moisture analyser was chosen because this easy-to-operate mode generally provided reproducible results. The moisture analysis was finished when the mass of a sample aliquot changed by less than 0.2 mg/24 s during the drying procedure. The instrument reports both the calculated moisture value as well as the time needed for analysis.

On completion of a measurement, the powder on the sample pan was removed by overturning the pan. To avoid potential errors arising from the use of a warm sample pan, two sample pans were employed alternately. After every measurement, the sample pan was gently cleaned with a soft tissue (igefa, Berlin, Germany) and conditioned as described above.

### 2.6.10 Preparation of Internal Peat Reference Materials for the Determination of Selected Elements and Arsenic

Two complete vertical peat ombrotrophic cores (total length ~ 100 cm) collected in August 1991 from PRD (Praz Rodet, Jura, Swizerland, Appleby et al., 1997) and one complete ombrotrophic core MBB (total length ~ 90cm, collected in July 2003 by Dr. Givelet at Mer Bleue Bog in the vicinity of Ottawa, Canada), were used for the preparation of the internal peat reference material.

The cores were cut frozen in a proportion of 60:40 (in order to obtain two different reference materials, one with high As concentrations from the upper 60 cm, and one with lower As concentrations from the remaining part) into 2*5 cm slides using a stainless steel band saw with stainless steel blades. The individual slices were subsequently placed on a polyethylene cutting board and the outer 1 cm of each slice was trimmed away using a 13 × 13 cm polyethylene plate and an acid rinsed Ti knife. The outside edges were systematically discarded. The frozen sub-samples of the first 60 cm of each core (~ 16 kg), as well as the frozen sub-samples of the last 40 cm of each core (~12 kg) were united to give a total of two individual, internal peat reference materials, Peat 3 and Peat 4, respectively.

The sub-samples of Peat 3 and Peat 4, respectively, were sent frozen to the the Fraunhofer Institut für Molekularbiologie und Angewandte Oekologie, Schmallenberg,

Germany where they were homogenized by cryogenic milling. The frozen, homogenised powder of each, Peat 3 and Peat 4 were kept frozen upon drying, as follows:

One part of the homogenised frozen powder of each peat reference material (Peat 3 and Peat 4, respectively) was dried at 105°C overnight as described in section 2.6.1.2 (leading to a total of two internal peat reference materials, Peat $3_{oven}$ and Peat $4_{oven}$). The other part of the homogenised frozen powder of each peat reference material (Peat 3 and Peat 4, respectively) was freeze - dried until constant weight (leading to a total of two internal peat reference materials, Peat $3_{freeze}$ and Peat $4_{freeze}$) and the third part was used directly (leading to a total of two internal peat reference materials, Peat $3_{fresh}$ and Peat $4_{fresh}$).

In this way six peat reference materials were prepared of which three (Peat $3_{oven,\ freeze,\ fresh}$) were expected to have lower As concentrations than the peat reference materials prepared from Peat 4.

For the determination of the water content, 10-30 g of the fresh samples (Peat 3 and Peat 4, respectively) was weighed to 0.1 mg into 100 ml PTFE vessels. The samples were dried at 105°C to constant weight.

The As concentrations in all of the peat reference materials (Peat $3_{oven,\ freeze,\ fresh}$, Peat $4_{oven,\ freeze,\ fresh}$) were determined using HG-AFS and ICP-SF-MS, respectively.

Additionally the following elements: S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, and Pb were determined by Dr. Andriy Cheburkin using XRF Spectrometry in the freeze dried and oven dried sub-samples of the peat reference materials (Peat $3_{oven,\ freeze}$, Peat $4_{oven,\ freeze}$).

## 2.6.11 Extraction of Arsenic

### 2.6.11.1 Water Extracts

The freeze dried or oven dried and pulverized samples (0.2 g of Peat $3_{oven,\ freeze}$, Peat $4_{oven,\ freeze}$, Nimt Peat, Out 33; Hie 18; Har 12) or 5-7 g of the fresh samples (Peat $3_{fresh}$, Peat $4_{fresh}$, Out 2, 5, 24, 33, 83, 86; Hie 2, 4, 16, 18, 53, 78, 80; Har 2,5,12,14,36,70,72) were weighed to 0.1 mg into screw-capped 50 ml-Falcon® tubes.

Water (10 ml) was added to each tube. The vials were closed, shaken, placed on a horizontally rotor (IKA HS501D, Janke + Kunkel IKA Labortechnik, Staufen, Germany), and mechanically agitated at 25°C by turning them at 100 rpm for 20 hours. After shaking the extracts were centrifuged 10 min at 4000 rpm (Heraeus, Megafuge1, Kendo Laboratory Products GmbH, Langenselbold, Germany). The supernatants were filtered through 0.20 µm cellulose ester filters (Minisart, RC 15, Sartorius, Göttingen, Germany) into 15 ml-Falcon® tubes.

For the determination of arsenic species, the supernatants were chromatographed immediately after filtration as described in section 2.6.12 with the HPLC-ICP-SF-MS setup described in section 2.5.5.1 without further dilution.

For the determination of total As concentrations in water extracts using ICP-SF-MS, samples were determined as described in section 2.6.8 without further digestion. Nitric acid (twice subboiled, 0.1 ml) was added to all extracts prior to the measurements.

For the determination of total As concentrations in water extracts using HG-AFS, samples were digested as described in section 2.6.4 and determined as described in section 2.6.6.

### 2.6.11.2 Orthophosphoric Acid Extracts

Aqueous solutions of orthophosphoric acid ($H_3PO_4$) at a concentration of 2 M served as extractant. (0.2 g of Peat $3_{oven,\ freeze}$, Peat $4_{oven,\ freeze}$, Nimt Peat) or 5-7 g of the fresh samples (Peat $3_{fresh}$, Peat $4_{fresh}$) were weighed to 0.1 mg into were weighed to 0.1 mg into screw-capped 50 ml-Falcon® tubes.

$H_3PO_4$ (2 M, 10 ml) was added to each tube. The vials were closed, shaken, placed on a horizontally rotor (IKA HS501D, Janke + Kunkel IKA Labortechnik, Staufen, Germany), and mechanically agitated at 25°C by turning them at 100 rpm for 20 hours. After shaking the extracts were centrifuged 10 min at 4000 rpm (Heraeus, Megafuge1, Kendo Laboratory Products GmbH, Langenselbold, Germany). The supernatants were filtered through 0.20 µm cellulose ester filters (Minisart, RC 15, Sartorius, Göttingen, Germany) into 15 ml-Falcon® tubes.

For the determination of total As concentrations in $H_3PO_4$ extracts using HG-AFS, samples were prepared as described in section 2.6.4 and determined as described in section 2.6.6.

## 2.6.12 Determination of Arsenic Species Using HPLC-ICP-SF-MS

The mobile phase (20 mM $NH_4H_2PO_4$, pH 5.6.) and the arsenic stock standard solutions were prepared as described in section 2.3.3.

The stock solutions of the arsenic species were appropriately diluted with high purity water to obtain calibration solutions of arsenous acid, arsenic acid, methylarsonic acid, dimethylarsinic acid, containing 0.5; 1; 2; 5; 7; and 10 $\mu gl^{-1}$ As, each. These calibration solutions were prepared daily.

Aliquots (1.5 ml) of the filtered water extracts were chromatographed on the Hamilton PRP-X100 anion-exchange column as described in section 2.5.5.1 without further dilution.

Prior to each measurement, the column was equilibrated with the mobile phase at a flow of 1.5 ml/min for at least 30 minutes.

### 2.6.12.1 Spiking Experiments

To ascertain the presence of the different As species in selected water extracts, aliquots of the water extracts (1.5 ml) were spiked with 7.5, 15, and 30 µl of a solution containing 100 $\mu gl^{-1}$ of arsenous acid, arsenic acid, methylarsonic acid, and dimethylarsinic acid, each. Arsenobetaine at a concentration of 1 $mgl^{-1}$ was spiked with 7.5 µl of a solution containing 100 $\mu gl^{-1}$ of arsenous acid, arsenic acid, methylarsonic acid, and dimethylarsinic acid, each to ascertain the chromatographic behaviour of AB on the Hamilton PRP-X100 anion-exchange column.

The algal extract *Fucus serratus* was prepared as described elsewhere (Madsen et al., 2000). Aliquots of the water extracts were spiked with this algal extract (0.1 ml) to check the possible presence of the four major arsenosugars: glycerol-, phosphate, sulfonate-, sulfate-arsenoriboses (arsenoriboses I, II, III, and IV; Fig. 1-2) within the peat samples.

### 2.6.13 Age Dating Using $^{210}Pb$ and $^{14}C$

Data were provided by Dr.G. Le Roux and Dr. A. K. Cheburkin (University of Heidelberg) Details of the age dating can be found elsewhere (Rausch, 2005).

Briefly, $^{210}Pb$ was measured directly in dried peat samples from the upper layers by using low background gamma spectroscopy (GCW 4028, HPGE, Canberra). Assuming a constant net flux of atmospheric $^{210}Pb$ at the accumulating peat surface, the ages of the topmost peat layers were calculated using the CRS model by Dr.G. Le Roux as described previously (Appleby et al., 1997).

Selected plant macrofossils of Sphagnum moss from deeper peat layers were dated using $^{14}C$ (atmospheric bomb pulse curve measured using Acclerator Mass Spectrometry, AMS) by decay counting (Rausch, 2005). Macrofossils were identified using optical microscopy, carefully removed, prepared using a standard procedure for plant material (Shore et al. 1995) and then age dated ($^{14}C$) using accelerator mass spectrometry (AMS) at the ETH Zürich. The conventional (calibrated) radiocarbon age dates were provided by D. G. Bonani (ETH Zürich).

### 2.6.14 Peat Decomposition and Peat Density

The humification data were provided by H. Wild (University of Heidelberg). Peat decomposition was determined on percentage light absorption of NaOH extracts of peat samples (Blackford and Chambers, 1993). Powdered peat samples (0.02 g) were extracted at approx. 90°C (1 hour) using 10 ml of 8% NaOH solution. The solution was made up to 20 ml with deionised water, shaken and filtered through filter papers (Schleicher & Schuell). Samples were diluted (1:1) using deionised water directly before colorimetric measurements using a UV-VIS spectrometer ($\lambda$=550 nm). Details are found elsewhere (Blackford and Chambers 1993).

Peat density data were provided by Dr. N. Rausch (University of Heidelberg). Peat density was calculated after determining the thickness (measured to an accuracy of 0.1 mm) of an individual bulk density plug. Three single plugs with defined area were then dried at 105°C to constant weight and the dry mass was recorded with a precision of 1 mg.

### 2.6.15 pH Measurements

The pH was measured by Dr. N. Rausch (University of Heidelberg) on fresh, unfiltered pore water samples immediately after the collection using a pH electrode (Inlab 412, Ingold, Switzerland).

### 2.6.16 Determination of Elements Using XRF Spectrometry and INAA

All three peat cores (section 2.4) were measured by Dr. Andriy Cheburkin using XRF Spectrometry for the following elements: Harjavalta (HAR): K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Pb. Outokumpu (Out): Al, Si, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Pb, As, Se, Br, Rb, Sr, Y, Zr, Ga. Hietajärvi (Hie): K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Pb.

Determination of element concentrations with the exception of Ti, Ca and Cl concentrations in powdered peat samples were performed using a X-ray fluorescence analyser (XRF) optimized for transition elements (EMMA) as described elsewhere (Cheburkin and Shotyk 1996).

The TITAN XRF analyser (Cheburkin and Shotyk 2005) optimized for Ti, was used for the determination of Ti, Ca and Cl concentrations.

In the Harjavalta core As, Sb, and Sc concentrations were determined using instrumental neutron activation analysis (INAA, ACTLABS, Activation Laboratories Ltd.,

Ancaster, ON, Canada) in order to avoid contamination of the ICP-SF-MS instrument due to the high element concentrations expected in this core.

# 3 Results and Discussion

## 3.1 Method Development for the Direct Determination of Arsenic in Acid Digests of Plant and Peat Samples Using HG-AAS and ICP-SF-MS

The main goal of this study was the development of a straightforward analytical procedure for the direct accurate and precise determination of As in digests of peat and plant samples using HG-AAS. In contrast to previous studies, an analytical procedure was developed and optimised to allow the direct determination of As in digests of plant and peat samples containing ~ 3% (v/v) $HNO_3$. This new approach avoids potential contamination of sample and standard solutions by addition of reagents which otherwise would be added to the digests in large quantities to overcome interferences of volatile nitrogen oxides ($N_xO_y$). The approach presented here also avoids the need to evaporate the digests to dryness to remove $N_xO_y$ from the analyte solutions which could otherwise lead to loss of the analyte. This study clearly demonstrates that L-cysteine can be used successfully to reduce interferences arising from nitric acid. The results obtained using HG-AAS were confirmed independently using ICP - SF - MS.

### 3.1.1 Introduction

A new analytical procedure for the reliable and direct determination of arsenic (As) in nitric acid digests of ombrothropic peat samples (as described in section 2.6.4) in the low ng $l^{-1}$ range has been developed based on hydride generation-atomic absorption spectrometry (HG-AAS, sections 2.3.1; 2.5.2). Several instrumental parameters of the HG-AAS system such as gas flow rate, pump speed and current of the S-HCL were investigated. The reduction reaction

conditions of the HG-AAS system were optimized in order to obtain the best accuracy and sensitivity.

The parameters evaluated in this study included: (a) pump speed and Ar gas flow; (b) lamp current and slit width; (c) quartz tube atomizer temperature; (d) concentration of HCl; (e) concentration of $NaBH_4$; (f) time dependence of the pre-reduction step; (g) pre-reduction conditions for $AsH_3$ generation using different amounts of KI/ascorbic acid or L-cysteine.

The pre-reduction capabilities of KI/ascorbic acid and of L-cysteine in nitric acid digests of peat and plant samples for the conversion of As(V) to As(III) were tested systematically. Using KI/ascorbic acid as pre-reductant, the accuracy and precision were poor when digests of complex matrices, such as peat were analysed for As by HG-AAS. However, 10 g $l^{-1}$ L-cysteine was successfully employed as pre-reductant in diluted nitric acid digests (~ 3% v/v) of peat samples prior to hydride generation of As with 0.5% (m/v) of $NaBH_4$ and 7 mol $l^{-1}$ HCl.

The analytical procedure was critically evaluated by analysing several certified plant reference materials (section 2.6.5), two in-house peat reference materials (section 2.6.5) and by the determination of As in diluted digests of peat samples with ICP-SF-MS (sections 2.5.4.1; 2.6.8). The results for the determination of As in various peat and plant materials showed excellent agreement with the reference values.

The method detection limits for the determination of As by the optimized HG-AAS procedure and by ICP-SF-MS were 23 ng $g^{-1}$ and 1.4 ng $g^{-1}$ in solid peat, respectively. The newly developed analytical procedure was applied to the determination of As in selected peat samples. Results for As in these peat samples obtained by the developed HG-AAS procedure and the optimized procedure for the determination of As with ICP-SF-MS highly correlated ($R^2 = 0.993$, n = 12).

### 3.1.2 Optimisation of HG-AAS Parameters

The following chemical and physical parameters were optimized to achieve the best analytical performance of the HG-AAS system for the reliable quantification of As in plant and peat samples.

To obtain a stable and robust analytical signal, the quartz tube atomizer and the lamp were allowed to warm up for at least 45 minutes before starting a measurement sequence.

Additionally, the response of the HG-AAS system to a 2 µg $l^{-1}$ As(III) standard solution was determined each day before starting measurements. Although the relative standard deviations (RSDs) of a 2 µg $l^{-1}$ As(III) standard solution were comparably low for both measurements modes (≤ 1%), evaluating peak heights resulted in about 30 times lower signal intensity compared to results obtained using peak area. Therefore, peak area was used throughout all experiments for quantifying instrumental response.

All instrumental parameters were optimized using As(III) and As(V) standard solutions, respectively, containing 2 µg As $l^{-1}$ each. The As(V) standard solution was used to assess instrumental capability for the more straightforward direct determination of As(V) in the acid digests solution, compared to the determination of As(III) by reduction of As(V) with different reduction media.

#### 3.1.2.1 Pump Speed and Gas Flow

The pump speed and the gas flow rates are important parameters, because they control the speed of the HG and transport the volatile hydrides to the quartz tube atomizer. The reagents used for the optimization of both pump speed and gas flow, were 7 mol $l^{-1}$ HCl and 0.5% $NaBH_4$ solutions. As all reagents in the HG-AAS system employed are transported by only one pump, it is not possible to optimize these parameters independently.

When the pump speed was increased, the signal intensities of As(III) and As(V) also increased (Fig. 3-1 A) but the background signal did not significantly rise. Although a higher pump speed could probably have further increased signal intensities, it could not be employed due to instrumental limits. Therefore the maximum pump speed of 2.2 ml $min^{-1}$ was used

Argon is needed as carrier gas to transport the formed hydrides to the atomizer. The gas flow settings in the employed HG-AAS instrument can only be increased in 6 l $h^{-1}$ increments up to a maximum gas flow rate of 18 l $h^{-1}$. When the gas flow rate was increased from 6 to 12 l $h^{-1}$ the signal intensities for the As(III) and As(V) standard solution significantly decreased. The signal intensities further decreased when the gas flow was set to 18 l $h^{-1}$ (Fig. 3-1 B). Consequently, a gas flow rate of 6 l $h^{-1}$ was used for all further investigations.

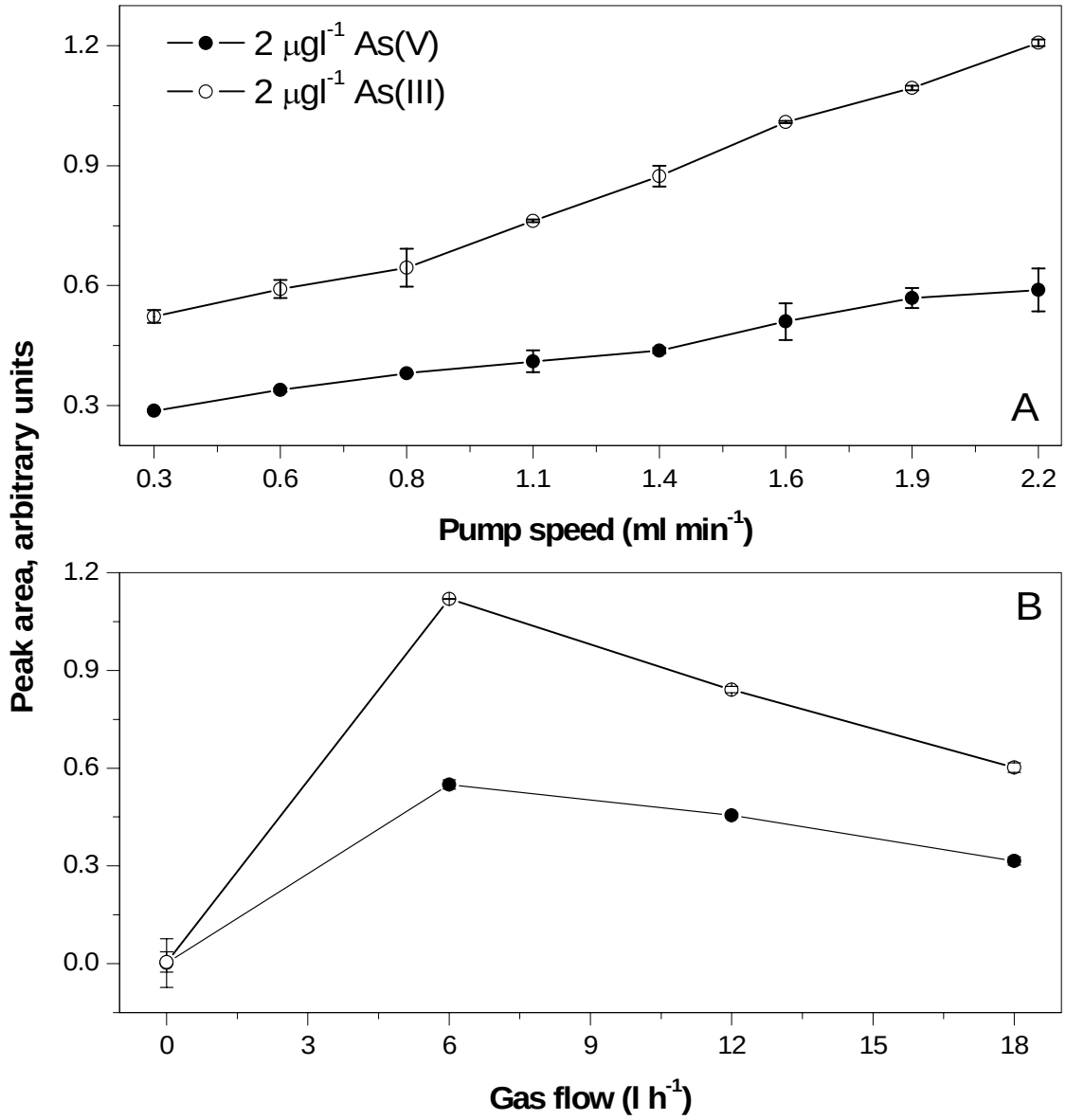



**Fig. 3-1**: Influence of pump speed (A) and gas flow rate (B) on signal intensities of a 2 μg $l^{-1}$ As(III) and a 2 μg $l^{-1}$ As(V) standard solution. Hydride generation was performed using 0.5% $NaBH_4$ and 7 mol $l^{-1}$ HCl.

### 3.1.2.2 Lamp Current and Slit Width

To obtain highest signal intensities, also the lamp current and slit width of the HG-AAS system were optimized. The AAS was equipped with an As super lamp and a super lamp power supply. Maximum signal intensity for As(III) and As(V) standard solution was observed when a lamp current of 18 mA was applied. Upon further increase of the lamp current signals decreased.

The super lamp power supply was optimized prior to the measurements to obtain highest signal intensities. A boost current of 22 mA was found to provide highest signal intensities. Additionally the four available slit widths of 0.2, 0.5, 0.8, and 1.2 nm of the monochromator were tested for the best performance of the instrument. Changing the slit width from 0.2 to 1.2 nm, the signal for As(III) and As(V) decreased by about 25%. Therefore a lamp current of 18 mA and a slit with of 0.2 nm were employed for all further investigations.

### 3.1.2.3 Quartz Tube Atomiser Temperature

Increasing the temperature of the quartz tube atomizer from 860 to 999°C had no noteworthy influence on the As response. The signal response for 2 μg $l^{-1}$ As(III) and a 2 μg $l^{-1}$ As(V) standard solution, however, slightly increased with increasing quartz tube atomizer temperature up to a maximum of about 940°C. When the quartz tube temperature was further increased the signals intensities slightly decreased. Therefore a quartz tube atomizer temperature of 940°C was used for all further investigations.

### 3.1.2.4 HCl and $NaBH_4$ Concentrations

The HCl and $NaBH_4$ concentrations are important parameters because they largely influence the HG efficiency.

The concentration of HCl, acting as a carrier solution, was investigated within the range of 4-10 mol $l^{-1}$ to obtain highest signal intensities for As(III) and As(V) standard solutions, respectively. As shown in Fig. 3-2 A, the instrumental response of the two standard solutions is different. The signal for As(III) standard solutions reached a maximum at a HCl

concentration of 7 mol $l^{-1}$ and then decreased, whereas the signal for As(V) solutions increased with increasing HCl concentration up to a maximum of 10 mol $l^{-1}$. The blank values, however, did not increase with increasing acid concentration.

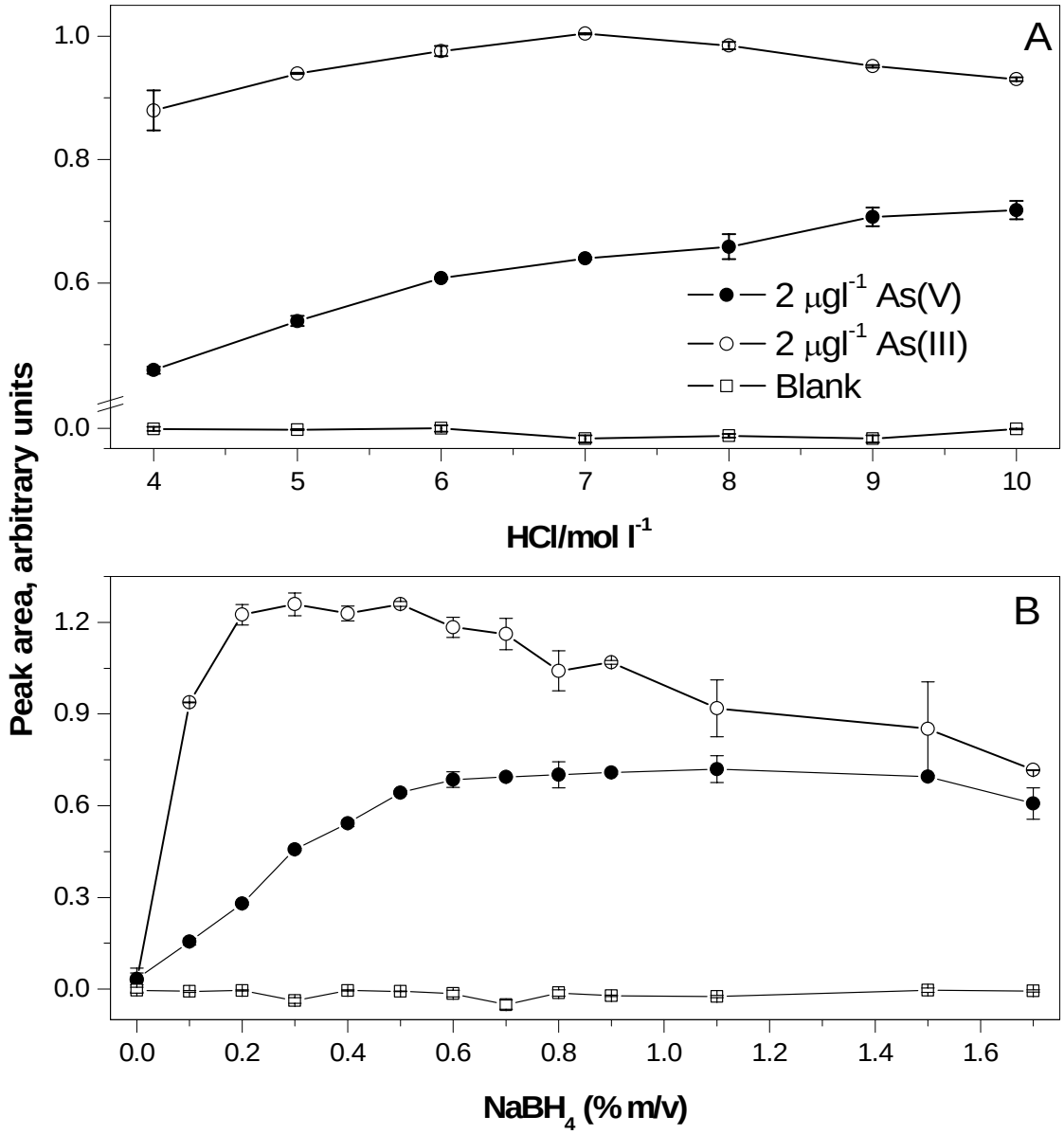



**Fig. 3-2:** Influence of $NaBH_4$ and HCl concentrations on hydride generation reaction.
(A) Influence of HCl on As(V) and As(III) standard solution;
(B) Influence of $NaBH_4$ on a 2 µg $l^{-1}$ As(V) and a 2 µg $l^{-1}$ As(III) standard solution.

As the present work focused on a rapid method for the sensitive determination of As in acid digests of peat samples, and because As in the reduced solutions is present only as As(III), a HCl concentration of 7 mol $l^{-1}$ was chosen for all further investigations.

Optimisation of $NaBH_4$ concentration was carried out between 0.1 to 1.7% using the optimized HCl concentration of 7 mol $l^{-1}$. Again As(III) and As(V) standard solutions behaved differently. For As(III), the signal intensity increased up to a concentration of 0.5% $NaBH_4$ and then significantly decreased, whereas the signal intensities for As(V) reached a maximum at concentrations between 0.6-1.5% $NaBH_4$ as shown in Fig. 3-2 B. Again the intensity of the background signal only varied marginally when the $NaBH_4$ concentration was increased. Although the optimum concentration plateau for As(III) standard solutions ranged from 0.2 to 0.5% $NaBH_4$, low amounts of $NaBH_4$ (0.2 to 0.4%) led to instable peak shapes. Therefore, a $NaBH_4$ concentration of 0.5%, providing high signal intensity and best reproducibility, was used for all further investigations.

### 3.1.3 Pre-reduction of As(V) to As(III)

Although the direct determination of As(V) is desirable, its determination suffers from high detection limits. Additionally the accuracy and precision for the direct determination of As(V) by HG-AAS in selected acid digests of plant and peat materials was about 20-40% lower compared to the target values.

As the direct determination of As(V) failed, quantitative pre-reduction of As(V) (which is the dominant As species under oxidizing conditions, characteristic of the digestion solution) to As(III) is necessary to obtain accurate results and optimum sensitivity. Moreover, the pre-reduction of the standard solutions containing the same acid concentrations, is necessary to obtain the correct calibration results.

The most popular pre-reductant is potassium iodide (KI) in combination with ascorbic acid, with the latter preventing the oxidation of iodide by air. Chen et al. (1992), however have clearly demonstrated the advantages of L-cysteine over KI as a pre-reducing agent, i.e. L-cysteine reduces chemical interferences from transition elements and other hydride forming elements (with the exception of Se and Te) and allows a quantitative pre-reduction of As(V) to As(III). Moreover several authors have reported on the successful use of L-Cysteine as

complexing and masking agent. Welz and Sucmanova (1993) for example report an about 10 times higher tolerance limit for the determination of arsenic in copper and steel compared to the reduction step with potassium iodide. Additionally L-Cysteine has also been shown to improve the hydride formation when measurements are made in the presence of metals such as iron (II), nickel(II), cobalt(II), manganese(II) and copper(II) (Howard and Salou, 1996) and palladium (Brindle et al., 1992).

In this study the pre-reduction efficiency of both KI in ascorbic acid and L-cysteine was compared.

#### 3.1.3.1 Pre-reduction with KI and Ascorbic Acid

Peat is a difficult-to-digest matrix because it consists not only of organic, plant-derived polymeric material, but also includes an inorganic fraction predominantly derived from atmospheric soil dust. The variable concentrations of matrix elements, such as Na, K, Mg, Ca and Fe (Krachler et al., 2002), may lead to severe matrix effects during the determination of As by HG-AAS.

Various concentrations of KI (15 to 180 g $l^{-1}$) stabilized with ascorbic acid (5% w/v) were tested for their potential to quantitatively reduce As(V) to As(III). Varying amounts of the pre-reduction solution were added to 1 ml of the digested solution and filled up to 10 ml with water. The pre-reduction time for the different amounts of KI/ascorbic acid was also investigated. With increasing amounts of KI/ascorbic acid, the reduction time decreased. The reduction of As(V) to As(III) was quantitative in 15 min when 60 g $l^{-1}$ KI/ascorbic acid was used.

In Fig. 3-3, the As intensities of a 2 µg $l^{-1}$ As(V) standard solution are displayed along with the digested certified reference material GBW 07602 Bush Branches and Leaves. Clearly, the behaviour of an acidified As(V) standard solution and the digestion solution of the certified reference material respond similarly to the additions of KI/ascorbic acid. Signal intensities increased with increasing amounts of KI/ascorbic acid added, and reached a maximum at a KI/ascorbic acid concentration of about 120 g $l^{-1}$. As shown in Fig. 3-3, a KI concentration of 60 g $l^{-1}$ is sufficient for the quantitative pre-reduction of As(V). Upon further addition of KI, signal intensities only marginally increased and varied within their measurement uncertainties whereas the signal intensities for the blank solutions also

increased. Therefore a KI/ascorbic acid concentration of 60 g $l^{-1}$ was used for all further investigations.

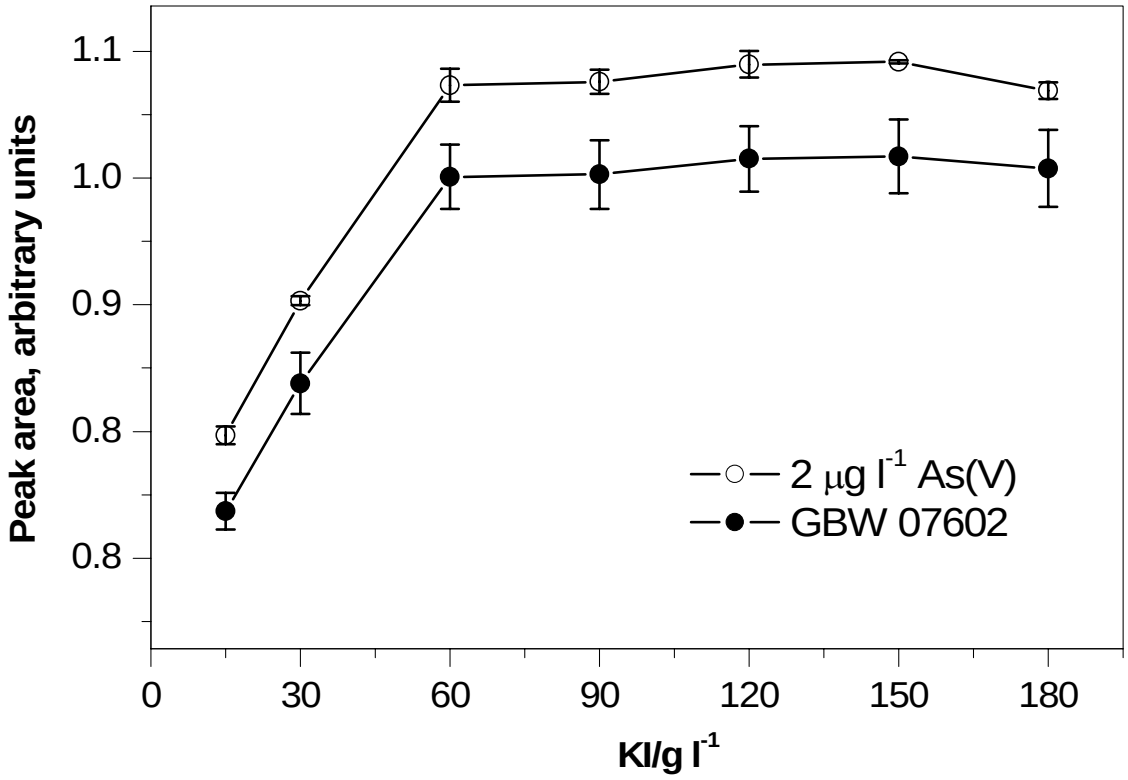



**Fig. 3-3:** Influence of KI on As pre-reduction. The influence of different concentrations of KI/ascorbic acid on the reduction effiency of a 2 µg $l^{-1}$ As(V) standard solution as well as of a diluted digest of the certified reference material GBW 07602 Bush Branches and Leaves.

Table 3-1 summarises the results for the determination of As in certified reference materials as well as two in-house peat reference materials using the optimized KI/ascorbic acid concentration. The experimentally established As values for the certified reference materials GBW 07602 Bush Branches and Leaves and CTA-OTL-1 Oriental Tobacco Leaves were in excellent agreement with the certified values (Table 3-1). The As values for the certified reference material CTA-VTL-2 Virginia Tobacco Leaves, however, were in the lower certified concentration range and the results for the two in-house peat reference materials were unacceptably low. It is important to note here that increasing the amount of KI added to the digests did not further increase the As concentration determined in these latter reference materials.

**Table 3-1.** Concentrations and standard deviations (ng $g^{-1}$ dry mass) of As in certified plant reference materials and in-house peat reference materials as determined by HG-AAS employing different amounts of KI/ascorbic acid or L-cysteine and by ICP-SF-MS.

| Reference material | Certified | HG-AAS, pre-reduction with | | | | | | | | ICP-SF-MS | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 60 g $l^{-1}$ KI | N[b] | 2.5 g $l^{-1}$ L-cysteine | N[b] | 5 g $l^{-1}$ L-cysteine | N[b] | 10 g $l^{-1}$ L-cysteine | N[b] | | N[b] |
| GBW 07602 | 950 ± 80 | 931 ± 30 | 4 | 934 ± 35 | 4 | 930 ± 23 | 5 | 946 ± 26 | 5 | 980 ± 25 | 4 |
| CTA-OTL-1 | 539 ± 60 | 554 ± 19 | 4 | 574 ± 19 | 4 | 634 ± 47 | 5 | 556 ± 16 | 5 | 558 ± 6 | 6 |
| Peat 1 | 9820 ± 370[a] | 7780 ± 400 | 6 | 7000 ± 90 | 4 | 9120 ± 900 | 4 | 10020 ± 280 | 4 | 9800 ± 260 | 6 |
| Peat 2 | 470 ± 20[a] | 234 ± 6 | 4 | 279 ± 7 | 4 | 439 ± 35 | 5 | 477 ± 40 | 5 | 475 ± 9 | 4 |
| CTA-VTL-2 | 969 ± 72 | 857 ± 43 | 4 | 996 ± 26 | 4 | 989 ± 21 | 4 | 982 ± 23 | 4 | -[c] | |
| NIST 1573a | 112 ± 4 | -[c] | | -[c] | | -[c] | | -[c] | | 111 ± 5 | 6 |

[a] Information values obtained using HG-AAS (Krachler et al., 2002)
[b] Number of sub-samples analysed
[c] Not investigated

Although several authors report on the successful use of KI as pre-reductant, most of these studies were carried out either in $H_2SO_4$, HCl or in digestion solutions that have been evaporated to dryness to remove the acids before the addition of the pre-reductant solution (Krachler et al., 2001; Krachler et al., 2002; Munoz et al., 1999). To overcome interferences caused by nitric acid, reagents such as e.g. sulfamic acid, urea, benzoic acid, and hydroxylamine hydrochloride have been evaluated. Flores et al., for example, tested sulfamic acid to minimize interferences of volatile nitrogen oxides and to produce good recoveries and reproducible results (Flores et al., 2001). Additionally, it is commonly known that the transition metals interfere with the determination of hydride forming elements when the HG technique is used (Welz and Melcher, 1984).

To further elucidate the cause of the low recoveries for the in-house peat reference materials, these samples were digested with 3 ml $HNO_3$ plus 0.1 ml $HBF_4$ to destroy siliceous matter present in peat: any As hosted in the silicates would be liberated by the $HBF_4$ thereby resulting in higher As concentrations. The addition of $HBF_4$, however, did not improve the As yields of the peat samples (Peat 1: 6940 ± 210 ng $g^{-1}$, Peat 2: 235 ± 5 ng $g^{-1}$). These findings are consistent with earlier studies (Krachler et al., 2001) showing that As yield, in peat are not improved by adding either HF or $HBF_4$ to the digestion mixture. The implication of these findings is that As supplied to ombrotrophic peat by atmospheric deposition is mainly not in the silicate fraction.

The detrimental effect of HF during the determination of As and Sb by HG-AAS using KI/ascorbic acid as the pre-reductant was previously reported by Krachler et al. (2001), while Chen et al. (2003) did not observe a diminishing effect by $HBF_4$ for the determination of Sb by HG-AFS, but they find that HF depressed the fluorescence signal.

The presence of HF or $HBF_4$ in the analyte solution may negatively affect the performance of the quartz tube atomizer. Additionally, the carry over of reaction mixtures containing transition metals could produce atomization interferences due to contamination of the inner quartz surface in HG coupled with a heated quartz tube atomizer and atomic absorption spectrometry (Ulivio et al., 2001).

As shown in Table 3-1, 60 g $l^{-1}$ KI/ascorbic acid can quantitatively reduce As in acid digests of simple matrices, such as selected plant materials. However, complete pre-reduction fails if more complex matrices, such as peat are digested.

### 3.1.3.2 Pre-reduction with L-cysteine

Firstly the pre-reduction time of different amounts of L-cysteine on a 2 μg $l^{-1}$ As(V) standard solution was checked. The time required for the quantitative reduction of As(V) to As(III) decreases with increasing amounts of L-cysteine. While the pre-reduction of As(V) by 2.5 g $l^{-1}$ L-cysteine was not completed within 2 hours, the reaction of As(V) with 10 g $l^{-1}$ L-cysteine was almost spontaneous. Although higher amounts of L-cysteine can significantly shorten the pre-reduction time, the signal intensities largely decrease with increasing amounts of L-cysteine (Fig. 3-4). A series of L-cysteine solutions with different concentrations (0-15 g $l^{-1}$) was tested in order to find the appropriate amount of L-cysteine for the quantitative pre-reduction of As(V) to As(III).

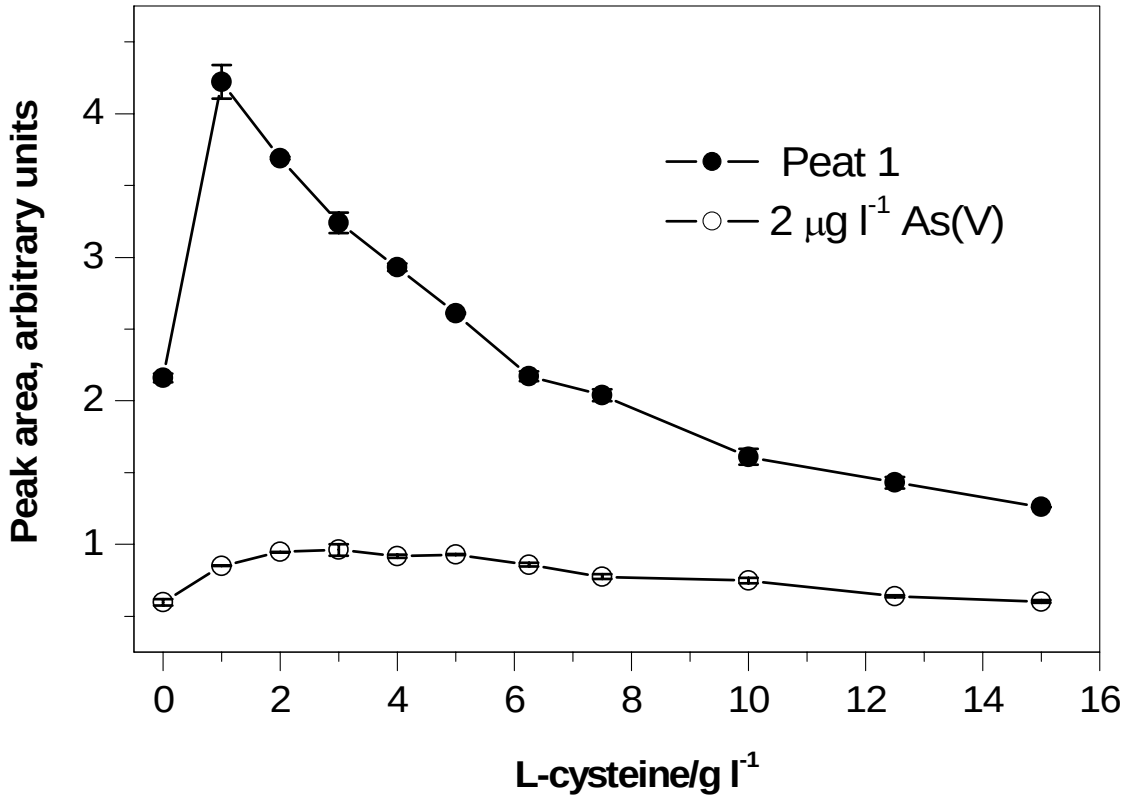



**Fig. 3-4:** Influence of L-cysteine on As pre-reduction. The influence of different concentrations of L-cysteine on the reduction effiency of a 2 μg $l^{-1}$ As(V) standard solution as well as of an diluted digested solution of an in-house peat reference material.

Figure 3-4 highlights the influence of the As signal on different amounts of L-cysteine in a nitric acid matched 2 µg $l^{-1}$ As(V) standard solution and a digested peat sample.

These results clearly indicate that the optimum pre-reduction conditions for As in nitric acid containing standard solutions largely differ from the optimum pre-reduction conditions in real sample digests. The signal intensities in the selected peat sample have a maximum at a L-cysteine concentration of about 1 g $l^{-1}$, while the optimum for the standard solution reaches a plateau at concentrations ranging between 2 to 8 g $l^{-1}$ L-cysteine.

As mentioned above, several approaches to minimize the detrimental effect of nitric acid have already been reported. Moreover, different HG systems can not be directly compared to each other not only due to different sample introduction systems (collecting, direct transfer) but also to different hydride transfer systems (continuous flow, batch mode, etc.) and different system designs.

Generally the HG system employed in this study requires a relatively high amount of HCl. As the instrumental response for a given amount of As in digests of peat samples is different to that in the acid matched standard solutions, these results can not be compared to each other. Rigby and Brindle (1999) have already reported on the importance of matrix matching to obtain calibration curves with comparable sensitivity, when they investigated As, Sb, Bi, Ge, Sn, Se and Te in a zinc sulphate solution by ICP-OES. Also Overduin and Brindle (2001) who investigated the use of L-cysteine and L-histidine for the determination of As in high purity Cu by HG-ICP-OES pointed out that matrix matching is necessary to obtain accurate results. Because of the variation in relative abundance of the matrix components present in peat, adequate matrix matching of the standard solutions is challenging. Therefore several different concentrations of the pre-reductant solution were tested for their potential to overcome matrix interferences and to produce reliable and accurate results for As in digested peat samples.

Although lower concentrations of L-cysteine provide higher sensitivity (Fig. 3-4), the accuracy and reproducibility of the results was poor in peat samples. In Table 3-1 the results for digestion solutions of several reference materials and the two in-house peat reference materials which have been treated with different amounts of L-cysteine (2.5, 5, 10 g $l^{-1}$), are shown. The different L-cysteine concentrations used for plant samples did not influence the accuracy and precision of the results (Table 3-1). Using 2.5 g $l^{-1}$ L-cysteine, the concentrations obtained for the two in house peat reference materials were significantly too low. Accurate and precise results for the peat samples were only obtained with a L-cysteine concentration of 10 g $l^{-1}$ (Table 3-1).

These results indicate that adequate accuracy and precision for the determination of As in digests of peat samples using HG-AAS can only be obtained using a L-cysteine concentration of 10 g $l^{-1}$.

### 3.1.4 Analytical Characteristics of the Developed Procedure

The analytical characteristics of the developed HG-AAS procedures as well as for the adopted ICP-SF-MS protocol are summarised in Table 3-2. The solution detection limit obtained for HG-AAS in this study, is comparable to the detection limits reported in the literature (0.037 µg $l^{-1}$) (Näkki et al.,2001), although it should be noted that all optimizations in this study were carried out using only aqueous solution. As mentioned above, different HG systems can not be compared to each other due to different instrumental capabilities. Therefore all parameters influencing the sensitivity (HCl and $NaBH_4$ concentrations, lamp current, pre-reduction agent, etc.) have to be optimized for each particular instrument and can not be directly applied from other studies. This is the first systematic optimization of the HG-AAS instrument used in this study.

**Table 3-2.** Analytical characteristics of the developed procedures.

| | HG-AAS (KI/ascorbic acid) | HG-AAS (L-cysteine) | ICP-SF-MS |
|---|---|---|---|
| Solution detection limit [a] | 0.038 µg $l^{-1}$ | 0.045 µg $l^{-1}$ | 0.003 µg $l^{-1}$ |
| Solution quantification limit [b] | 0.125 µg $l^{-1}$ | 0.151 µg $l^{-1}$ | 0.009 µg $l^{-1}$ |
| Procedure detection limit [c] | 19 ng $g^{-1}$ | 23 ng $g^{-1}$ | 1.4 ng $g^{-1}$ |
| Procedure quantification limit [d] | 63 ng $g^{-1}$ | 75 ng $g^{-1}$ | 4.7 ng $g^{-1}$ |
| Reproducibility 2 µg As $l^{-1}$ (%, n=6) | < 2.5 | < 2.5 | < 3.0 |
| Reproducibility 5 µg As $l^{-1}$ (%, n=6) | < 1.3 | < 1.3 | < 1.5 |

[a] Concentration corresponding to 3 standard deviations of the blank; [b] Concentration corresponding to 10 standard deviations of the blank; [c] Concentration corresponding to 3 standard deviations of the blank related to a sample mass of 200 mg; [d] Concentration corresponding to 10 standard deviations of blank related to a sample mass of 200 mg.

The solution detection limit was calculated as the concentration corresponding to three times the standard deviation (3 σ) of 10 blank solutions, and the solution quantification limit was based on ten times the corresponding standard deviation (10 σ).

Procedure detection and quantification limits, respectively, were calculated by multiplying the solution detection or quantification limits by the dilution factor (500). The precision expressed as relative standard deviation (RSD) was assessed by analyzing standard solutions containing 2 and 5 μg $l^{-1}$ As (n=6) each for the determination of As by HG-AAS and ICP-SF-MS, respectively.

Calibration curves were linear from 0 to at least 30 μg $l^{-1}$ for the determination of As by HG-AAS and from 0 to at least 500 μg $l^{-1}$ for the determination of As by ICP-SF-MS. Correlation coefficients for the calibration curves were always better than 0.998.

### 3.1.5 Results for Ancient Peat Samples

As already mentioned, peat samples from diverse geographic regions largely vary with respect to the chemical composition of the matrix. Peat cores collected at different places show significant differences in the amount of organic and siliceous matrix, ash content as well as concentrations of marine-derived elements, e.g. continental peat cores may contain abundant sea salt elements (Na, Cl, etc.).

To check the robustness of the developed analytical procedures, selected ombrotrophic peat samples collected from a former Cu/Ni mine in south-eastern Finland were analysed by the two analytical procedures developed in this work. Concentrations of As determined by HG-AAS in these selected Finish peat samples compared well with the values obtained by ICP-SF-MS (Fig. 3-5). Thus it is obvious that both analytical approaches produce accurate results. The precision for both methods for the determination of As in real samples was ≤ 4% for the ICP-SF-MS and HG-AAS measurements, respectively. The HG-AAS procedure developed here provides excellent detection limits which seem to be adequate for virtually all peat types, and is much less expensive to operate than ICP-SF-MS.

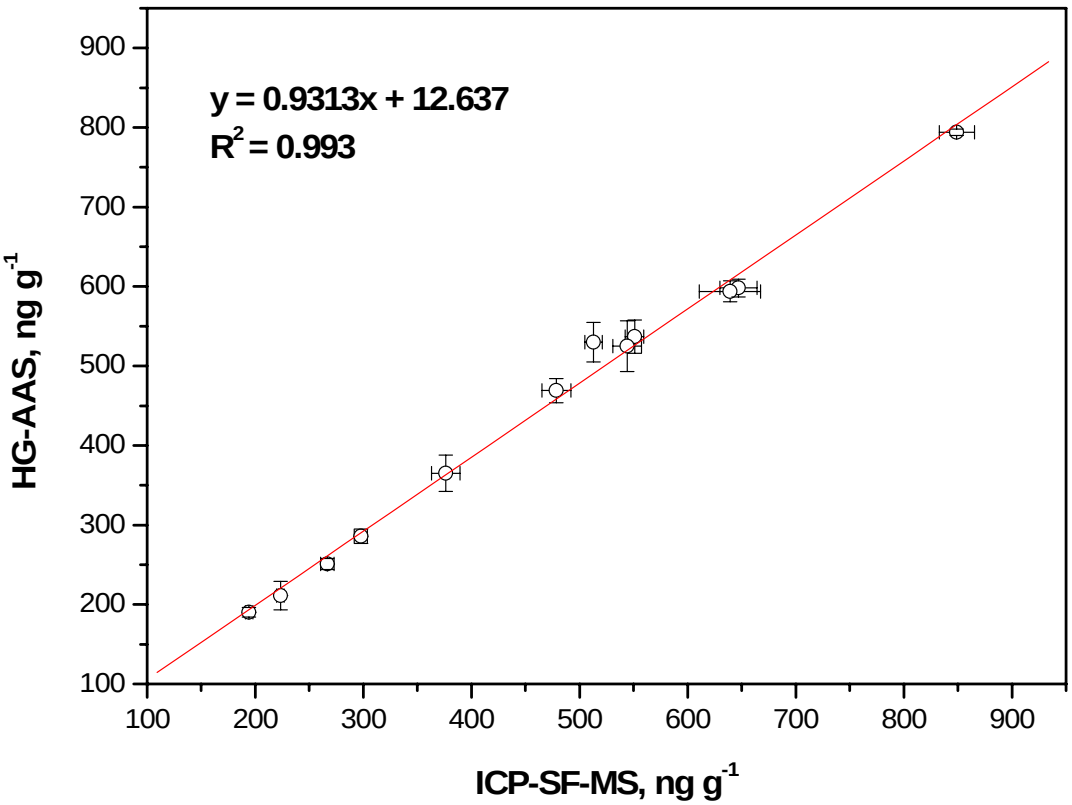



**Fig. 3-5:** Correlation for the As concentrations in the Finnish peat bogs as determined by HG-AAS and ICP-SF-MS.

## 3.1.6 *Conclusion*

Work was undertaken to develop and optimize a rapid, sensitive and reliable analytical method for the determination of As in peat samples using HG-AAS, and to compare the developed HG-AAS protocol with the optimized procedure for the determination of As by ICP-SF-MS. The developed HG-AAS procedure, which is based on continuous hydride generation-atomic absorption spectrometry, proved to be an excellent method for the reliable determination of As concentrations in the digests down to the low ng $l^{-1}$ level. The experimental conditions for $AsH_3$ generation were carefully optimized allowing reproducible and reliable routine analysis. Additional experiments showed that microwave digestion using $HNO_3$ is suitable and effective

for dissolving plant and peat materials when As has to be determined, and that the use of $HBF_4$ or HF is unnecessary. In many studies, $HNO_3$ in the digestion solution is either evaporated after digesting to eliminate the oxidising power of this reagent which might otherwise interfere with the reduction procedure of As, or the addition of acids, e.g. sulfamic acid, is needed. In the present study, however, these time consuming procedures could be avoided altogether. Moreover the addition of reagents can be avoided which might otherwise lead to increased blank signals or might contaminate the sample solution, hampering the determination of As at low concentrations.

The newly developed analytical procedures will be applied to the determination of As in age-dated peat samples to shed more light on the geochemical cycle of this environmentally important element.

## 3.2 Method Development for the Direct Determination of Arsenic in Acid Digests of Plant and Peat Samples Using HG-AFS

The aim of this work was to develop an accurate, sensitive, robust, rapid, straightforward, and low cost analytical method for the direct determination of As in acid digests of peat samples containing ~0.6% $HNO_3$. The time consuming evaporation of $HNO_3$ in the acid digests was avoided resulting in shorter analysis time and reduced risk of contamination. The potential of L-cysteine and KI as pre-reductant was critically evaluated.

### 3.2.1 Introduction

An accurate, sensitive, and robust analytical procedure for the direct determination of arsenic (As) in nitric acid digests of peat samples (section 2.6.4) using hydride generation-atomic fluorescence spectrometry (HG-AFS, sections 2.3.2; 2.5.3) has been developed. Although there already exists a method for the determination of As in plant, coal and sediment materials employing KI as pre-reductant (Chen et al., 2005), this method can not be applied to the determination of As in peat because it largely underestimates the actual As concentrations in peat samples.

Here, the pre-reduction capabilities of KI and L-cysteine in nitric acid digests of peat and plant samples were tested systematically revealing that only L-cysteine (12.8 g $l^{-1}$) provided accurate results for peat samples.

The newly developed analytical procedure was successfully applied to the determination of As in several peat reference materials as well as certified environmental reference materials (section 2.6.6) yielding excellent agreement between found and certified values. The LOD of 4 ng $l^{-1}$ and the precision of < 3% for peat samples, allowed the reliable quantification of As in all investigated peat samples. Results for As in selected peat samples obtained using the new HG-AFS procedure were confirmed in-house using ICP-SF-MS and HG-AAS.

### 3.2.2 Pre-reduction of As(V) to As(III)

The optimised method for the determination of As in environmental and geological specimens using HG-AFS, previously developed by our group, for the reliable determination of As in environmental and geological specimens using HG-AFS (Chen et al., 2005) was evaluated for its applicability for the determination of As in peat samples.

The results presented in Table 3-3 demonstrate the accuracy and precision for the determination of As in various reference materials of the developed method using KI and ascorbic acid as pre-reductant. However, when As in peat has to be determined, KI can not be employed as pre-reductant, leading to significantly lower As concentrations.

**Table 3-3.** Concentrations (mean ± standard deviation; ng $g^{-1}$ dry mass) of As in various reference materials and selected peat samples (Out 10-71) as determined using HG-AFS employing 0.5% (m/v) KI and 0.1% (m/v) ascorbic acid as well as ICP-SF-MS.

| Sample name | Certified | HG-AFS | N[a] | ICP-SF-MS | N[a] |
|---|---|---|---|---|---|
| GBW 07602 | 950 ± 80 | 900 ± 40 | 5 | 980 ± 25 | 4 |
| CTA-OTL-1 | 539 ± 60 | 480 ± 10 | 4 | 558 ± 6 | 5 |
| CTA-VTL-2 | 969 ± 72 | 960 ± 40 | 12 | -[b] | |
| NIST 1575 | 210 ± 40 | 232 ± 7 | 8 | -[b] | |
| NIST 1515 | 38 ± 7 | 44 ± 1 | 4 | -[b] | |
| SRM 1547 | 60 ± 18 | 65 ± 2 | 3 | -[b] | |
| NIMT Peat | 2440 ± 550[c] | 1640 ± 70 | 20 | -[b] | |
| Peat 1 | - | 6670 ± 350 | 4 | 9800 ± 260 | 6 |
| Peat 2 | - | 291 ± 20 | 5 | 475 ± 9 | 4 |
| Out 10 | - | 158 ± 27 | 4 | 647 ± 17 | 4 |
| Out 12 | - | 256 ± 11 | 3 | 849 ± 16 | 4 |
| Out 13 | - | 208 ± 16 | 3 | 1033 ± 42 | 4 |
| Out 40 | - | 237 ± 6 | 4 | 1007 ± 23 | 3 |
| Out 71 | - | 169 ± 4 | 3 | 286 ± 13 | 4 |
| Peat $4_{oven}$ | - | 215 ± 9 | 8 | 332 ± 9 | 3 |
| Peat $4_{freeze}$ | - | 223 ± 8 | 13 | 313 ± 7 | 4 |

[a] Number of sub-samples analysed
[b] Not investigated
[c] Information value (Yafa et al., 2004)

However, when As in peat has to be determined, KI can not be employed as pre-reductant, leading to significantly lower As concentrations (Table 3-3). Moreover, increasing KI concentrations up to 15% (m/v) did not improve the values. Thus the use of potassium iodide for pre-reduction is not applicable for the accurate determination of As in peat samples.

To overcome the drawbacks of using KI, the pre-reduction and interference reducing capabilities of a series of L-cysteine solutions with concentrations of 4.8 – 12.8 g $l^{-1}$ were investigated systematically. It is important to note here, that all investigated concentrations of L-cysteine gave consistent As concentrations for certified plant reference materials. In other words, using L-cysteine as pre-reductant, the As values found were always within the certified range, independent of the employed L-cysteine concentration (Fig. 3-6).

The situation for peat samples, however, was different. L-cysteine concentrations of up to 11.2 g $l^{-1}$ yielded neither accurate nor precise As results for any of the peat samples, and were significantly too low. Further increasing L-cysteine concentrations to 12.8 g $l^{-1}$ provided both, accurate and precise As results for peat samples. Addition of higher concentrations of L-cysteine to the analyte solutions did not further improve the results but rather decreased the sensitivity. The improvements achieved using L-cysteine as pre-reductant are most likely due to the complexation capability of L-cysteine for interfering elements (transition and heavy metals, as well as other hydride forming elements), that are present in peat at comparatively high and variable concentrations.

Another potential source of the low As yields, the presence of siliceous matter, was also investigated. To this end, 0.1 ml of $HBF_4$ was added to 3 ml $HNO_3$ prior to digestion to destroy siliceous matter, otherwise always present in the digestion solutions. When $HBF_4$ was present in the digestion solution, the recorded As fluorescence signal for the digestion blank increased with increasing concentrations of L-cysteine up to a concentration of ~1.9 µg $l^{-1}$ As (12.8 g $l^{-1}$ L-cysteine) when $HBF_4$ was present in the digestion solution (Fig. 3-7). This high background probably resulted from As release from the glass of the gas/liquid separator: when these blank solutions were determined for As using ICP-SF-MS, distinctly lower blank levels were established. However, the ultimate reason for the high blank signals using $HBF_4$ with the HG-AFS procedure was not further elucidated in this study, as the silicate fraction was found to contribute insignificantly to the As inventory of the peat samples.

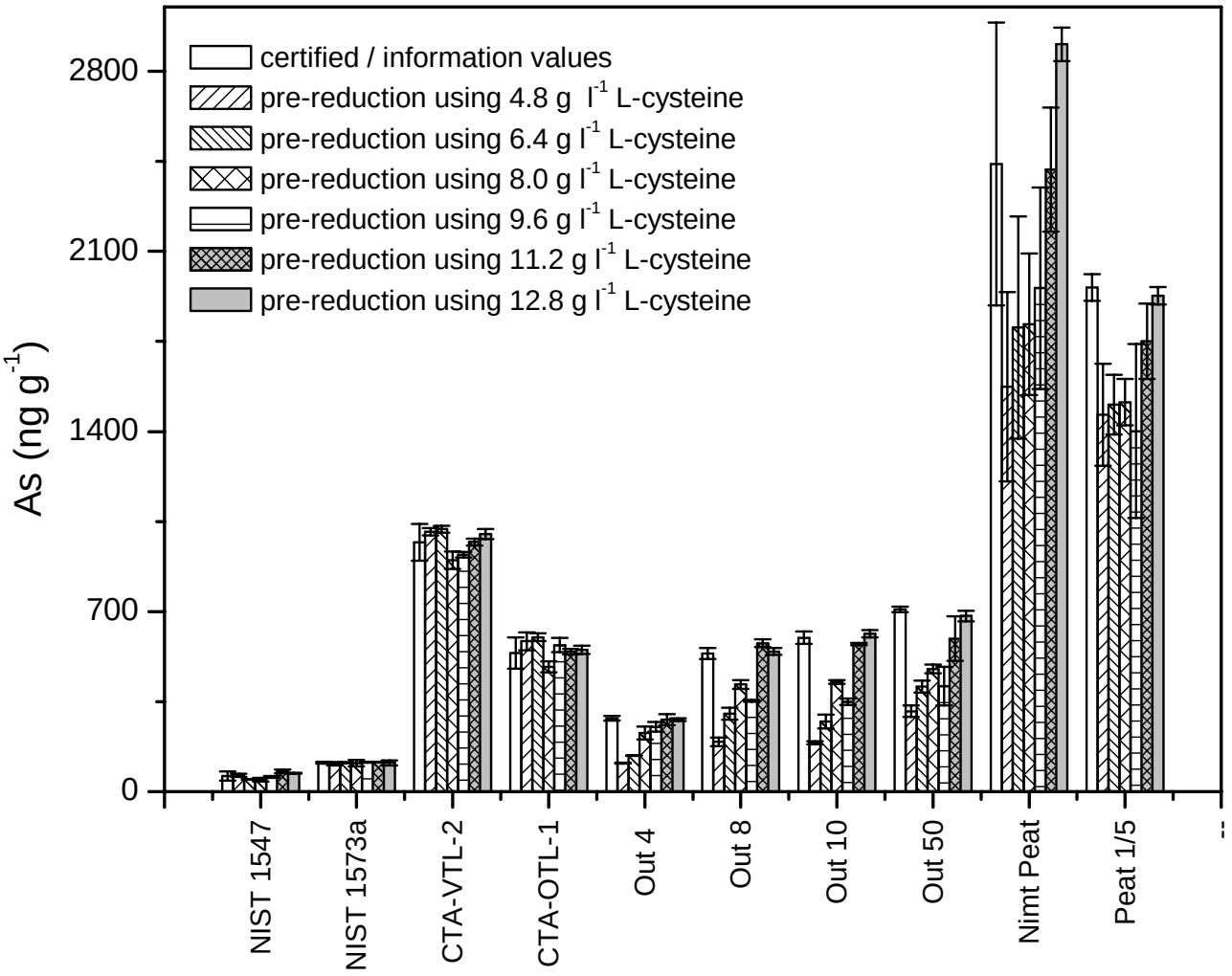



**Fig. 3-6:** Results for the determination of As in various environmental reference materials as well as four selected peat samples using different amounts of L-cysteine as pre-reductant. Information values for Out 4, Out 8, Out 10 were determined in-house using HG-AAS. Information values for Peat 1 and Out 50 were determined in-house using ICP-SF-MS. For convenience, the concentration values for Peat 1 have been divided by a factor of five. Mean and standard deviations are results of at least two independent digests measured at least on two different days.

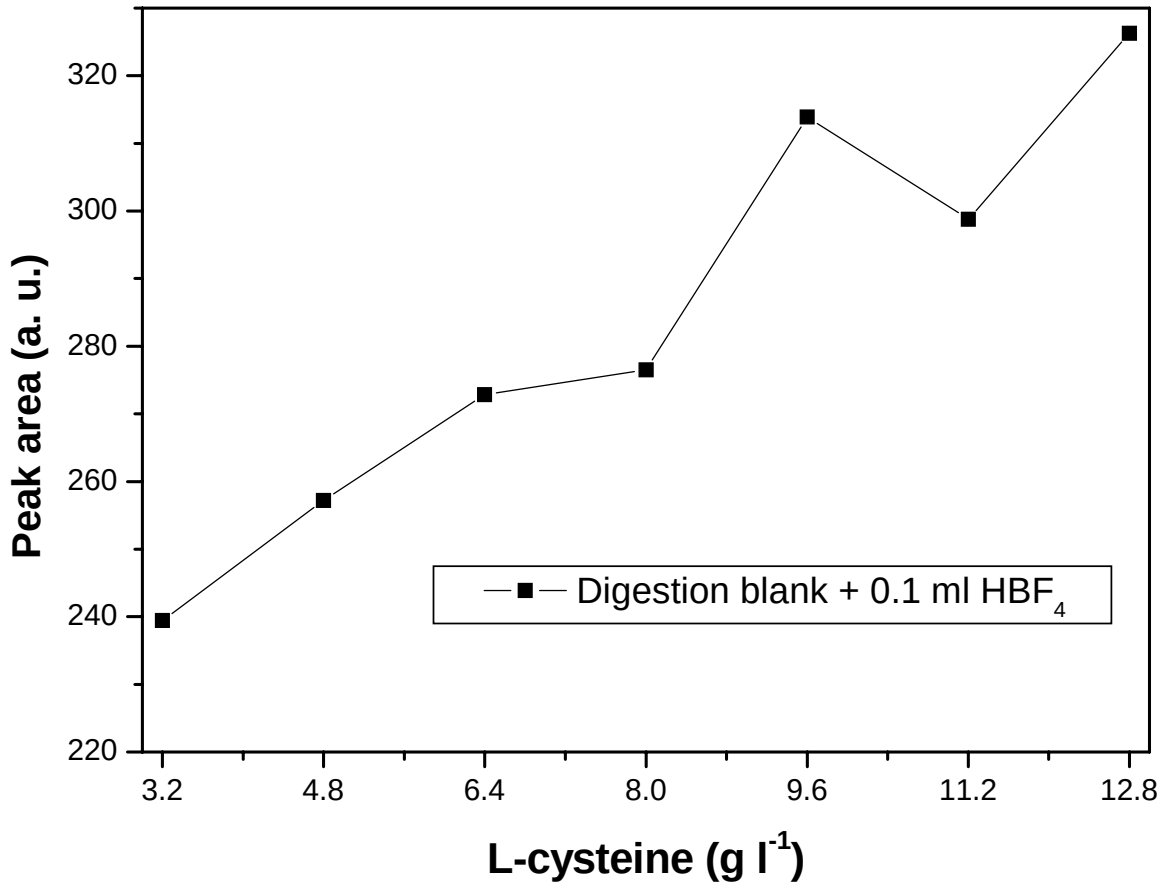



**Fig. 3-7:** Influence of the L-cysteine concentration on the digestion blank (3 ml $HNO_3$ + 0.1 ml $HBF_4$).

### 3.2.3 Quality Control and Analytical Characteristics of the Developed Procedure

Employing the developed HG-AFS procedure for the determination of As, several certified plant reference materials as well as two peat reference materials (NIMT Peat, Peat a) were investigated. As shown in Table 3-4 the As concentrations found were always in excellent agreement with the certified or information values.

**Table 3-4:** Concentrations (mean ± standard deviation; ng $g^{-1}$ dry mass) of As in various reference materials as determined using HG-AFS employing 12.8 g $l^{-1}$ of L-cysteine (N ≥ 3).

| Material | Sample name | Certified | Found |
|---|---|---|---|
| Plant | GBW 07602 | 950 ± 80 | 990 ± 20 |
| | CTA-OTL-1 | 539 ± 60 | 550 ± 20 |
| | CTA-VTL-2 | 969 ± 72 | 1000 ± 20 |
| | NIST 1547 | 60 ± 18 | 57 ± 3 |
| | NIST 1573a | 112 ± 4 | 112 ± 10 |
| Coal | NIST 1632c | 6160 ± 270 | 6000 ± 130 |
| | NIST 1635 | 420 ± 150 | 439 ± 9 |
| Peat | NIMT Peat | 2440 ± 550 [a] | 2910 ± 70 |
| | Peat 1 | 9800 ± 260 [b] | 9640 ± 170 |

[a] Information value (Yafa et al., 2004)
[b] Information values obtained in-house using ICP-SF-MS operated at m/Δm ~ 10,000

The solution detection limit was calculated as the concentration corresponding to three times the standard deviation (3 σ) of 10 independently prepared blank solutions. The solution quantification limit was based on 10-times of the standard deviation (10 σ). Procedure detection and quantification limits were calculated by multiplying the solution detection limits by the dilution factor (sample mass 200 mg dissolved in 50 ml solution). The sensitivity was calculated from the slope of the calibration curve and the precision expressed as relative standard deviation (RSD) was assessed by analysing a solution containing 50 ng $l^{-1}$ or 100 ng $l^{-1}$ As (n=6). Calibration curves had correlation coefficients always > 0.999 and were linear from 0 to at least 900 ng $l^{-1}$. The major analytical characteristics of the developed procedure are summarised in Table 3-5.

**Table 3-5.** Analytical characteristics of the developed digestion/HG-AFS procedure.

| | |
|---|---|
| Solution detection limit [a] | 4 ng $l^{-1}$ |
| Solution quantification limit [b] | 14 ng $l^{-1}$ |
| Procedure detection limit [c] | 1.0 ng $g^{-1}$ |
| Procedure quantification limit [d] | 3.5 ng $g^{-1}$ |
| Reproducibility 50 ng As $l^{-1}$ (n=6) | < 2.0% |
| Reproducibility 100 ng As $l^{-1}$ (n=6) | < 1.0% |
| Sensitivity [e] | 9.52 |

[a] Concentration corresponding to 3 standard deviations of the blank; [b] Concentration corresponding to 10 standard deviations of the blank; [c] Concentration corresponding to 3 standard deviations of the blank related to a sample mass of 200 mg; [d] Concentration corresponding to 10 standard deviations of blank related to a sample mass of 200 mg. [e] Peak area per ng As $l^{-1}$.

### 3.2.4 Results for Peat Samples

The well established HG-AAS procedure for the reliable determination of As concentrations in peat samples, previously developed, suffers from relatively high procedure quantification limits (75 ng $g^{-1}$, Frank et al., 2005). Therefore it was necessary to develop a more sensitive, low cost procedure for the determination of As concentrations in uncontaminated, pre-anthropogenic peat samples. Employing the new HG-AFS procedure, the method quantification limit of 3.5 ng $g^{-1}$ allowed the reliable determination of As in all investigated peat samples, including samples thousands of years old which pre-date anthropogenic metal emissions. The method quantification limit obtained using HG-AFS (3.5 ng $g^{-1}$) is comparable to that of ICP-SF-MS (4.7 ng $g^{-1}$, Frank, 2005), but at a fraction of the cost.

To evaluate the robustness of the developed procedure, selected ombrotrophic peat samples were analysed using the developed HG-AFS procedure, as well as using ICP-SF-MS and HG-AAS: The HG-AFS As concentrations in these peat samples are in excellent agreement with the As values obtained using HG-AAS and ICP-SF-MS (Fig. 3-8 A+B).

The developed analytical procedure will be applied to the determination of As in uncontaminated, pre-anthropogenic peat samples, helping to establish “natural background” As concentrations as well as past and present As fluxes.

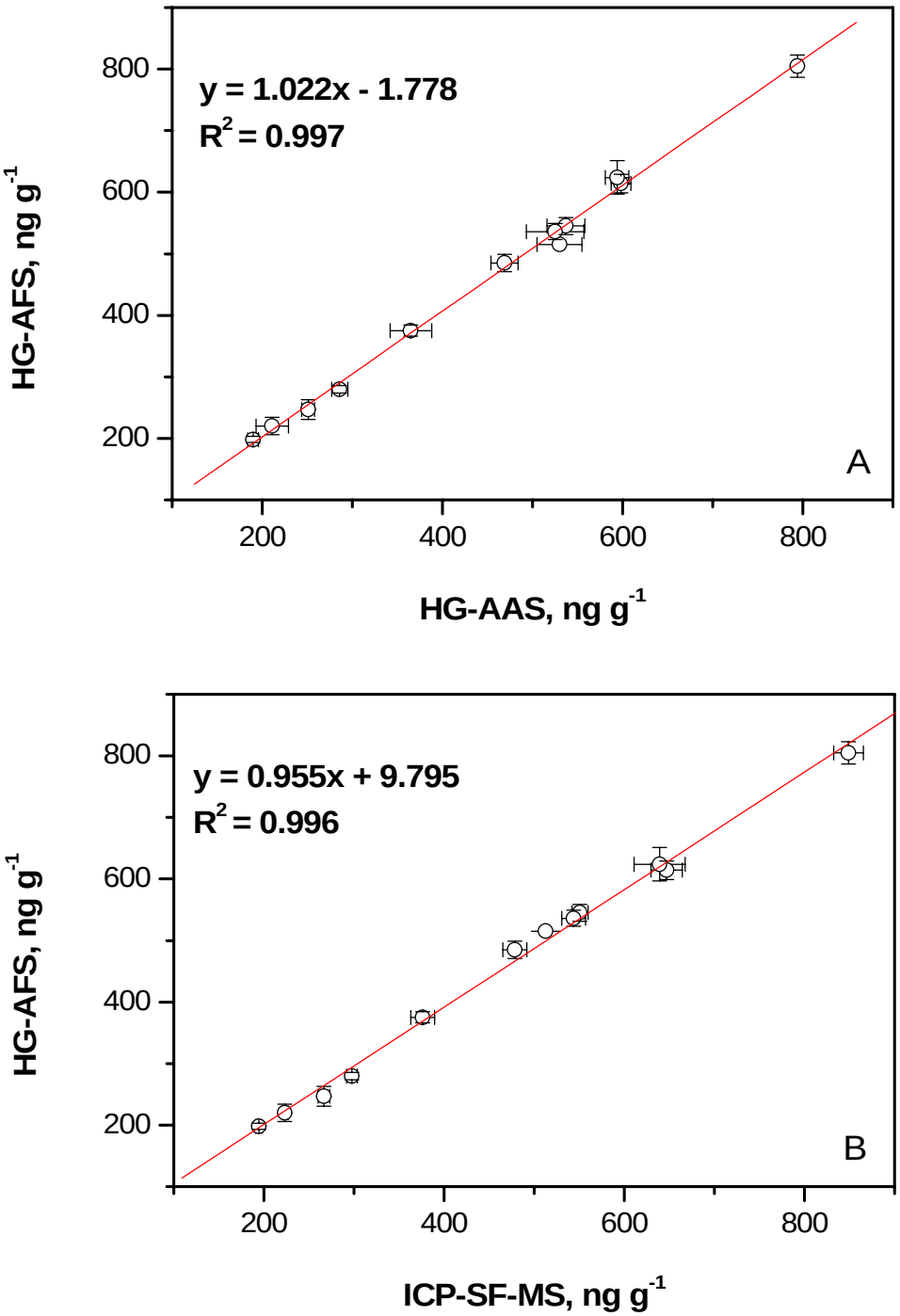



**Fig. 3-8:** Correlation of As concentrations in selected Finnish peat samples as determined using (A) HG-AFS and HG-AAS and (B) HG-AFS and ICP-SF-MS.

# 3.3 Natural and Anthropogenic Atmospheric Arsenic Accumulation in Ombrotrophic Peat Bogs from Finland

The main goal of this study was to reconstruct the changing rates of atmospheric As deposition using peat cores from three bogs in Finland: Harjavalta, near a Cu-Ni smelter, Outokumpu near the famous Cu-Ni mine, and Hietajaervi, a low background site. To evaluate how faithful atmospheric As has been preserved in the peat cores, the chronology of accumulation (obtained using $^{210}Pb$ and $^{14}C$) was compared with the historical records of smelting and mining at Harjavalta and Outokumpu, respectively. The "natural background" concentrations and accumulation rates were determined by measuring As concentrations in deeper peat layers dating from pre-industrial times. Bromine is used as a reference element, as it also derived from atmospheric inputs, is thought to be efficiently retained by the bog, and has no significant anthropogenic source.

## 3.3.1 Introduction

To date, there is no published record of the changing rates of atmospheric As deposition since industrialisation, for two reasons. First, until fairly recently the analytical methods employed to measure As concentrations in environmental archives were not sufficiently sensitive to determine the "natural background" As concentrations in samples dating from pre-anthropogenic times. This problem has recently been solved for peat (Frank et al., 2005; Krachler et al., 2002). Second, at least in the case of ombrotrophic peat bogs, it is not yet clear the extent to which these acidic, anoxic, organic-rich archives preserve the changing rates of atmospheric As deposition. The main goal of this study is to address the latter issue.

This is the first detailed record of atmospheric arsenic deposition in ombrotrophic peat bogs. Arsenic has been determined in two peat bogs using ICP - SF - MS in the high resolution mode after acid dissolution of peat samples in a microwave autoclave. Peat cores from Finnish bogs at three sites have been selected for the study: Harjavalta (Har), nearby a Cu-Ni smelter and Outokumpu (Out), near a famous Cu-Ni mine, both which have been impacted by

atmospheric emissions from metal mining and refining, and a peat bog at Hietajärvi (Hie) which is remote from industrial activity.

Whereas the As chronologies of the Out and Hie core are similar, the As chronology of the Har core is different, due to the smelter: the As inventories for the last hundred years for Hie and Out are comparable (0.159 and 0.162 mg/m$^2$/yr) whereas the As inventory for the Har core (0.618 mg/m$^2$/yr) is about 4 times higher.

Additionally accumulation rates for the last 100 years have been calculated which agree well with the mining history. At Hie and Out the maximum accumulation rates are ~350 µg/m$^2$/yr, respectively. In contrast the maximum accumulation rate for the Har core is ~750 µg/m$^2$/yr. Moreover maximum As concentrations in all three cores date from ~1950, despite different depths.

Comparison of anthropogenic and natural As and Pb concentrations show that anthropogenic As and Pb decrease from ~1000 AD onwards (coal burning), respectively, and confirm the theory that As is, as Pb, well preserved within the peat profiles. The Finnish profiles have received As exclusively from the atmosphere.

### 3.3.2 Quality Control

Three complete vertical peat cores were collected from a Finnish peat bog (section 2.4) and prepared as described in section 2.6.1.

Digestion of the powdered peat samples and plant reference materials was performed as described in section 2.5.1.1 and determined for As and Sc using ICP-SF-MS as described in section 2.5.4.1.

Bromine and lead concentrations in all three cores were analysed using the EMMA XRF spectrometer (section 2.6.16). The EMMA XRF spectrometer was calibrated and checked for accuracy and precision as described elsewhere (Cheburkin et al., 1996; Cheburkin et al., 1999).

In the Harjavalta core As and Sc concentrations were determined using instrumental neutron activation analysis (INAA, section 2.6.16.)

Quality control was performed as described in sections 2.6.7 and 2.6.8. The data summarised in Table 3-6 highlight the excellent agreement between experimentally established and certified elemental concentrations in both certified standard reference materials as well as the two in-house peat reference materials.

**Table 3-6.** Concentrations and standard deviations (ng $g^{-1}$ dry mass) of As and Sc in certified plant reference materials and in-house peat reference materials as determined by ICP - SF - MS.

| Reference material | Certified As | ICP - SF- MS | N[b] | Certified Sc | ICP- SF- MS | N[b] |
|---|---|---|---|---|---|---|
| GBW 07602 | 950 ± 80 | 980 ± 25 | 4 | 310 ± 20 | 328 ± 10 | 9 |
| CTA-OTL-1 | 539 ± 60 | 558 ± 6 | 6 | 380[c] | 446 ± 5 | 8 |
| Peat 1 | 9640 ± 170[a] | 9800 ± 260 | 6 | - | - | |
| Peat 2 | 470 ± 20[a] | 475 ± 9 | 4 | - | - | |
| NIST 1573a | 112 ± 4 | 111 ± 5 | 6 | - | - | |

[a] Information values obtained in-house using HG-AFS (Frank, 2005)
[b] Number of sub-samples analysed
[c] Information value
- Not certified

### 3.3.3 Peat Decomposition, Peat Density and Age Dating

The peat cores are poorly decomposed in the upper layers, as determined on percent light absorption of NaOH. However, highest As concentrations are found in these layers. Therefore the variations in element concentration can not be explained by the decomposition of the peat (Fig. 3-9 A). Additionally the peat density shows a similar trend as the peat decomposition especially for the Out core (Fig. 3-9 B). Therefore peat density compensates for variations in the degree of humification.

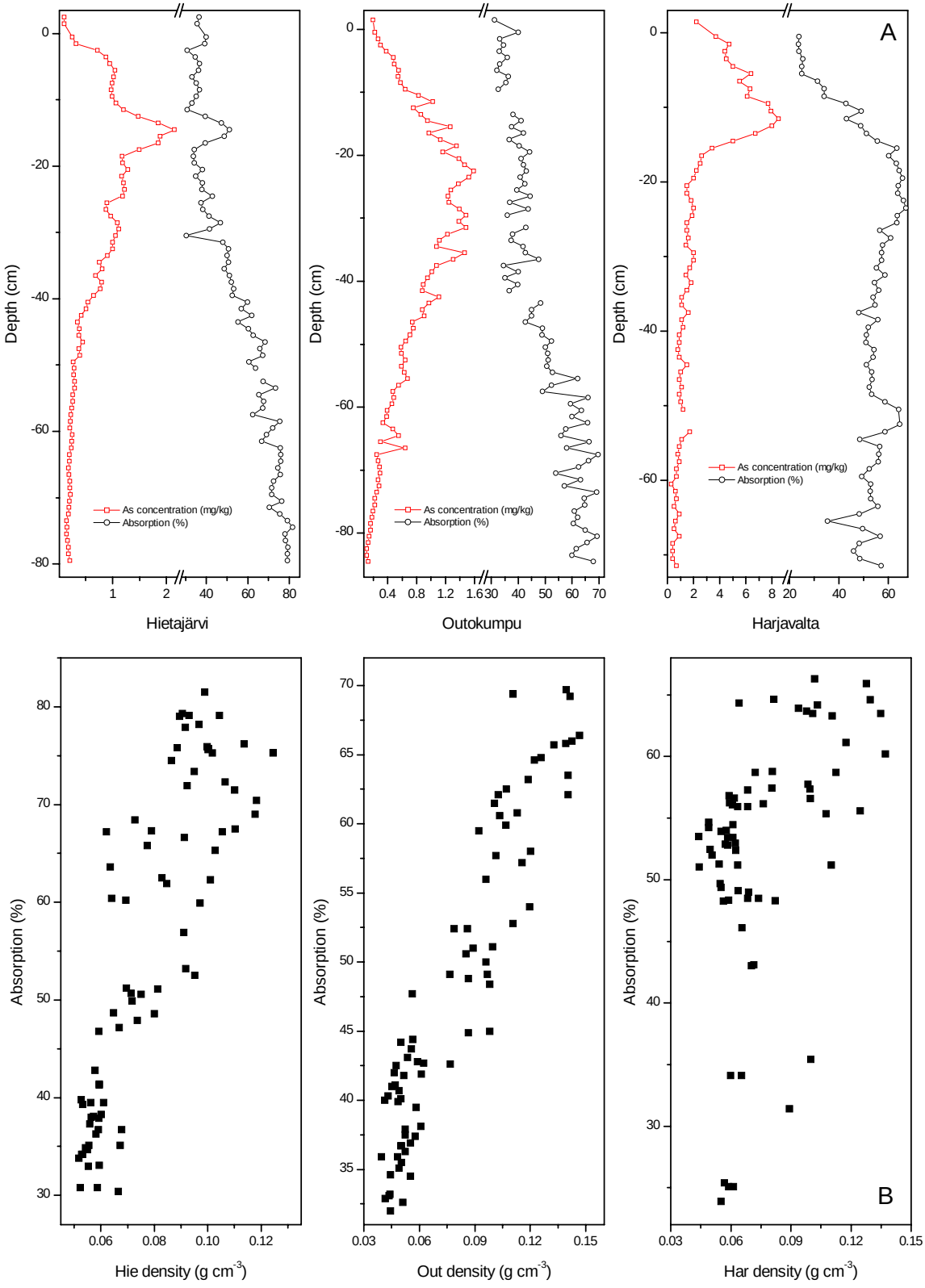



**Fig. 3-9:** Absorption (A) and density (B) in the three Finnish peat bogs (Out: Outokumpu, Hie: Hietajärvi, Har: Harjavalta).

Age dates were performed as described in section 2.6.13. Detailed information about the age dating and ages can be found elsewhere (Rausch, 2005).

Briefly, good agreement between the age dating models was found in the Out and Hie core. At Har, the $^{14}C$ b. p. c. dates do not constrain the $^{210}Pb$ ages due to sub-sampling difficulties regarding this core. Additionally the mathematical error for the $^{210}Pb$ ages (until ~ 1900 AD) is higher for the Har core (± 6 to 75 years) than in the Out (± 3 to 30 years) and the Hie (± 1 to 8 years) due to greater variation in density and lower $^{210}Pb$ activities in this core for the reasons mentioned above.

### 3.3.4 Seeking for an Appropriate Reference Element for Arsenic

The total element concentrations alone do not necessarily provide a direct reflection of changes in the atmospheric element inputs. This might have a significant effect on the element concentration profiles. However, the maximum As concentrations in all three cores date from the same period of time, despite different depths [1931 ± 41 AD (Har), 1942 ± 14 AD (Out) and 1953 ± 3 AD (Hie)] (Fig. 3-10; 3-11).

#### 3.3.4.1 Scandium

In Figure 3-10 the concentration profiles of arsenic and scandium in the three peat cores are plotted next to the As/Sc ratio. Sc appears to behave most conservatively of all of the lithogenic elements (such as Al, Ti, Zr, etc), and is widely distributed in all silicate minerals which means it is least subject to chemical and physical fractionation during crustal weathering. Thus the Sc concentration profile (Fig. 3-10) may be viewed as a surrogate for the abundance of atmospheric soil dust in the peat core as described in detail elsewhere (Shotyk et al., 2001).

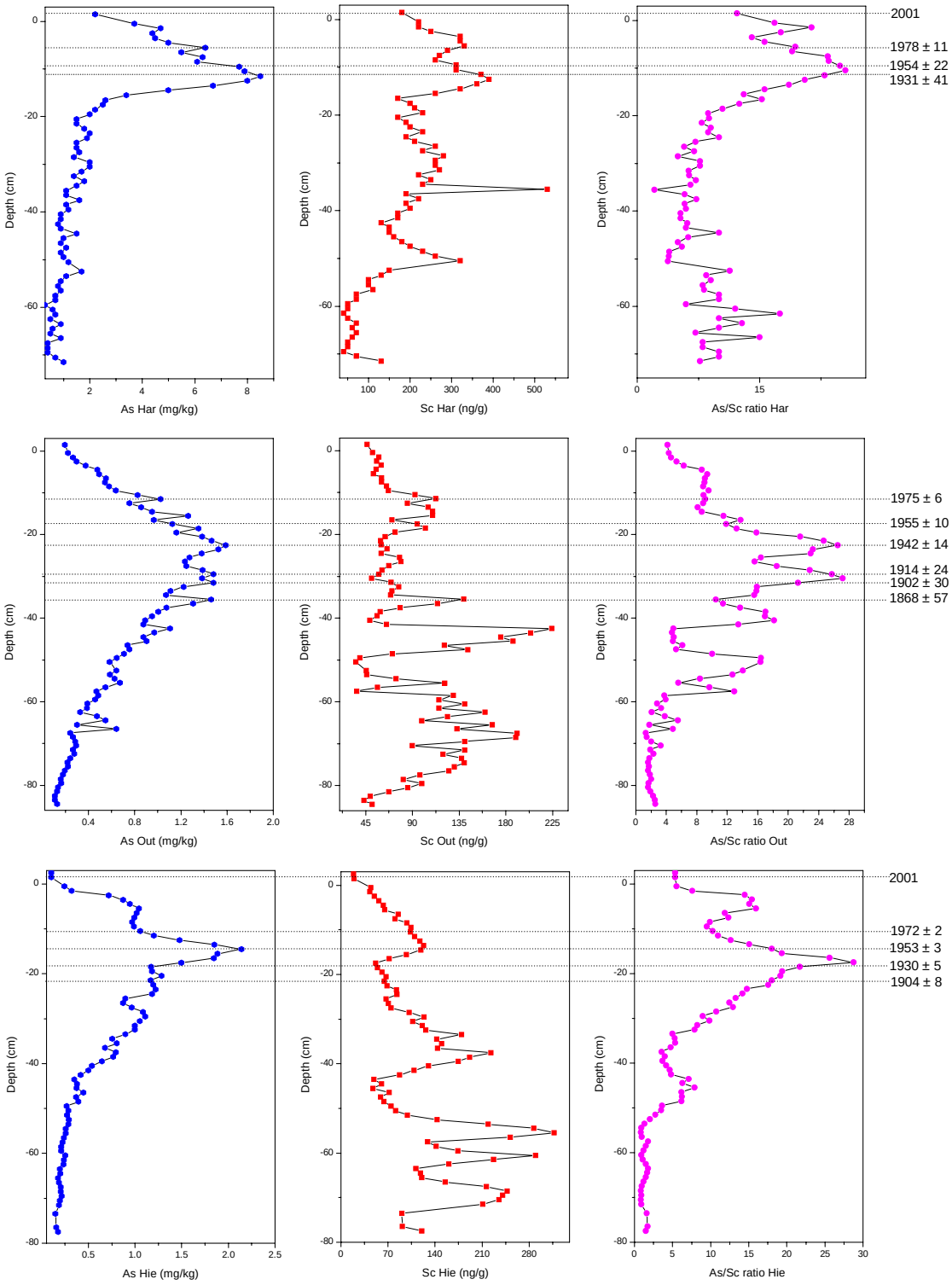



**Fig. 3-10:** As and Sc concentrations as well as As/Sc ratio in the three peat cores. (Out: Outokumpu, Hie: Hietajärvi, Har: Harjavalta).

### 3.3.4.2 Bromine

Bromine has been used as a reference element for mercury in peat, because the correlation observed between Hg and Br indicates either that the biogeochemical cycles of these two elements are similar, that they are linked to one another, or both. Also, both can be microbially methylated to form volatile organic species which have short atmospheric lifetimes (Roos-Barraclough et al., 2002). In contrast to Sc, Br is primarily supplied to the bog by precipitation (Görres and Frenzel, 1993). This might be also true for arsenic. The majority of Br supplied to the bog ultimately derived from marine aerosols. The oceans supply the atmosphere with Br from acidified sea salt aerosols and through biogenic emissions of reactive organic Br species. These species (e.g. $CHBr_2Cl$, $CHBr_2Cl_2$, $CH_2BrCl$) dissociate by photolysis and reaction with $OH^-$. The resulting Br atoms react with ozone ($O_3$) to form Br oxide radicals (BrO•). There are, however, also terrestrial sources of atmospheric Br such as the release of volatile methyl bromide ($CH_3Br$) during litter decay due to the halogen-methylating ability of wood-rotting fungi (Lee-Taylor and Holland, 2000), biomass burning (Andreae et al., 1996) and abiotic oxidation of organic matter (Keppler et al., 2000).

In Figure 3-10, the As and Sc concentration profiles are plotted next to the As/Sc concentration profile. It can easily be seen that the Sc concentration profile does not reflect the As concentration profile. The Sc concentrations are highly variable especially in the deepest parts of the bog, and show great variations in abundance of this element (Har: ~10 - 500 ng $g^{-1}$, Out ~ 45 - 225 ng $g^{-1}$, Hie ~ 40 - 290 ng $g^{-1}$), in contrast to As. Moreover the As/Sc ratio does not reflect the As concentration, as for example the Har core shows As/Sc ratio of app. 15 even in deeper layers (Fig. 3-10).

Thus, the Sc concentration profiles do not reflect the As concentration profiles within a peat core and it seems that Br is a better reference element for As. In Figure 3-11 the As and Br concentration together with the As/Br ratios are displayed. Also the Br concentrations show variations, but in a smaller relative concentration range (Har ~ 15 - 60 mg $kg^{-1}$, Out ~ 4 – 20 mg $kg^{-1}$, and Har 15 – 60 mg $kg^{-1}$). Moreover the As/Br ratios do reflect the As concentration profiles: In general the As/Br ratio at Out and Hie look quite similar, showing a broad peak up to a depth of about -60 cm. The Har profile looks different. It shows a rather sharp peak at the very top to a depth of about -20 cm (Fig. 3-11).

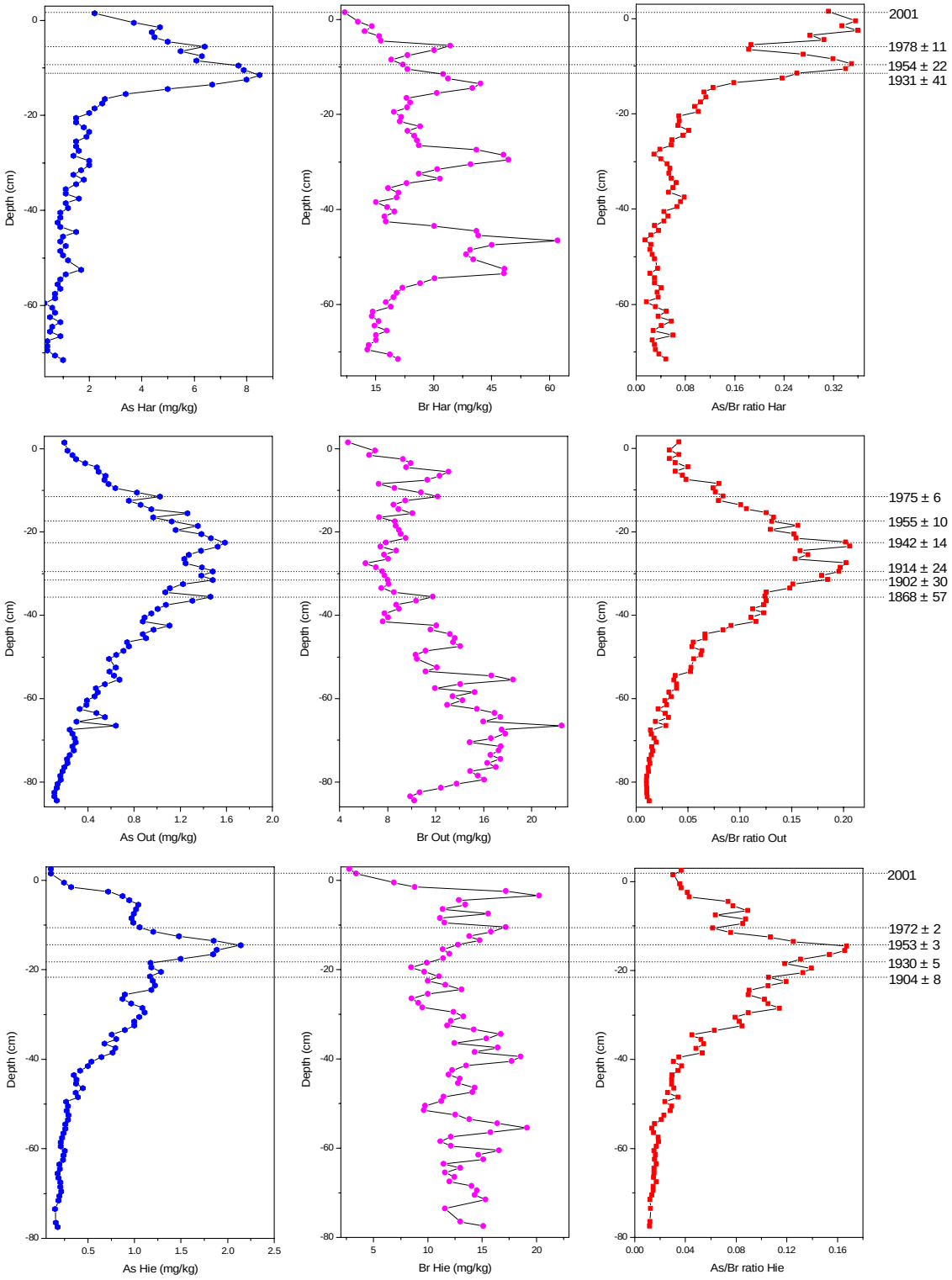



**Fig. 3-11:** As and Br concentrations as well as As/Br ratios of the three peat cores (Out: Outokumpu, Hie: Hietajärvi, Har: Harjavalta).

It is important to note here, that the "background" ratio of As to Br at Hietajärvi (0.015 ± 0.002, n=26, 778-986 AD, Fig. 3-11) and Outokumpu (0.013 ± 0.003, n=16, 1017-1192 AD, Fig. 3-11) are in the same range, whereas the "background" ratio of As to Br at Harjavalta is about three times higher (0.038 ± 0.013, n=13, 1156-1282 AD, Fig. 3-11) (n corresponds to the number of sub-samples).

For comparison with peat cores from other regions, the "background" ratio of As to Br at Hie and Out is also the "background" value for peat samples dating from 6,000 to 9,000 years old from the bog at Etang de la Gruère (EGR) in Switzerland (0.014 ± 0.005).

Thus it is likely to assume that As, as Br was also supplied to the peat cores exclusively from the atmosphere, preliminary by precipitation, that therefore As as Br is independent from atmospheric soil dust, and that thus Br is the better reference element for As.

### 3.3.5 Enrichment Factors for As Relative to Background Values

The Enrichment Factors (EF) of As relative to background values were calculated as

$$EF_{(As)} = ([As]/[Br]_{peat} / ([As]/[Br])_{peat,\ natural\ background}$$

where [As] refers to the total concentration of As measured in the peat samples (mg/kg) and [Br] to the total concentration of Br. Instead of using crustal abundances as the point of reference to calculate As enrichments, an alternative approach is to determine the natural, "backround" metal concentrations in pre-anthropogenic aerosols using ancient peat samples (Shotyk et al., 1998). Not only does this approach completely avoid the problem of natural enrichment of trace elements in soil-derived aerosols, relative to crustal abundance, but it allows this fractionation process to be quantified and explained by comparing the pre-anthropogenic values from peat samples with the corresponding values in the Earth`s Crust (Shotyk et al., 2002). By using a natural background for As/Br (0.014) a realistic EF can be calculated.

The calculated enrichment factors for As are displayed in Fig. 3-12. The peat cores at Hietajärvi and Outokumpu are enriched in As by 12 to 15 times, respectively, with remarkably similar chronologies (Fig. 3-12).

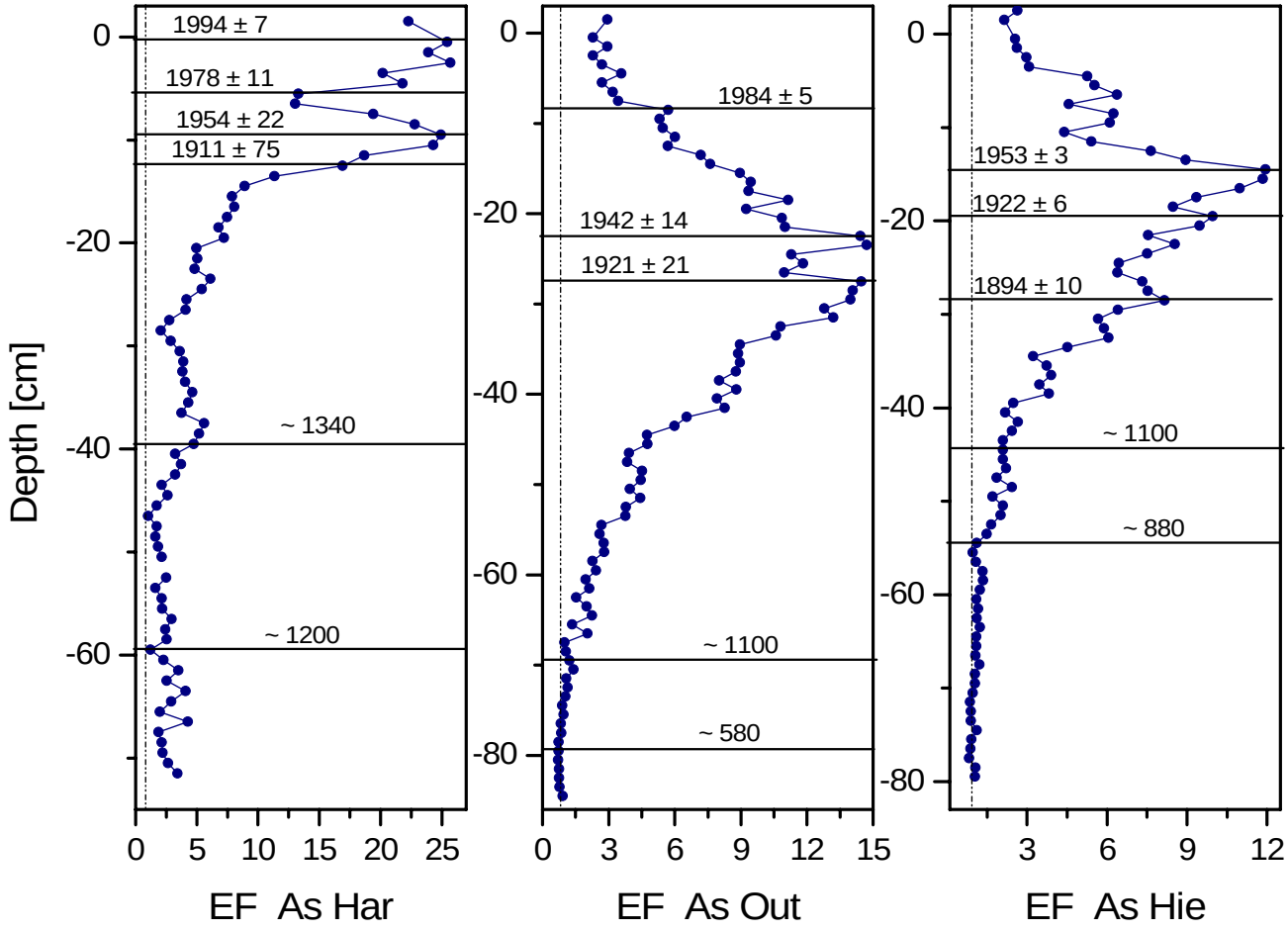



**Fig. 3-12:** Temporal variation in EF (normalised to "natural background" values as described in the text) for As in the three cores. The solid vertical line (EF=1) represents values which are neither significantly enriched nor depleted.

At Outokumpu the maximum EF for As is found at an age of 1938 ± 15 AD (CRS model) with pronounced peaks at 1921 ± 21 AD and 1942 ± 14 AD (CRS model). After 1921 ± 21 AD the EF for As decreases and reaches a minimum at app. 1100 AD ($^{14}$C age dating). At Hietajärvi the As EF is lower, showing a maximum (11.95) at 1953 ± 3 AD (CRS model). Going deeper,

to older peat layers, the EF for As decreases, reaching its constant value at app. 880 AD ($^{14}C$ age dating). In contrast, the maximum As enrichment at Harjavalta is 26 times (1989 ± 8 AD, CRS model, Fig. 3-12), with a pronounced peak at 1954 ± 22 AD (CRS model), relative to the background As/Br ratio: this core shows a different As chronology. Two pronounced peaks in the uppermost layers of the Har peat profile in contrast to one broad peak in the Out and Hie peat profile, respectively. As mentioned above the age dates are not very accurate for this core. However, it seems that the Har core displays the same chronology as the Out and Hie core, until the beginning of the smelting.

### 3.3.6 Calculation of Accumulation Rates for Arsenic

Accumulation rates ($\mu g\ m^2\ yr^{-1}$) for arsenic were calculated to estimate the atmospheric fluxes as follows:

$$AR_{(As)} = 10 \times [As] \times \delta \times GR$$

where [As] refers to the total As concentration ($ng\ g^{-1}$), $\delta$ to the bulk density of the peat ($g\ cm^{-3}$) and GR to the growth rate ($cm\ yr^{-1}$).

Growth rates were determined using ages calculated for each layer by the age-depth relationship of each core. This calculation takes into account both changes in peat accumulation rates due to differences in surface growth rates and in compaction due to differing degrees of peat decomposition. Calculated accumulation rates for arsenic in the three Finnish peat cores are shown in Fig. 3-13. The Hie accumulation rates look quite similar to the Out accumulation rates, showing pronounced peaks at ~1940-1960. Whereas accumulation rates for the Hie core increase from app. 1940, the accumulation rates for Out show an additionally pronounced peak between app. 1900-1920. Additionally both cores show a pronounced peak between 1980 - 2000. The As accumulation rates for the Har core also shows pronounced peaks at app. 1900-1920, as well as app. 1920-1960 and app. 1980-1990. Slight variations in the rates of atmospheric arsenic accumulation for the cores may be due to variations in bulk density within individual peat slices.

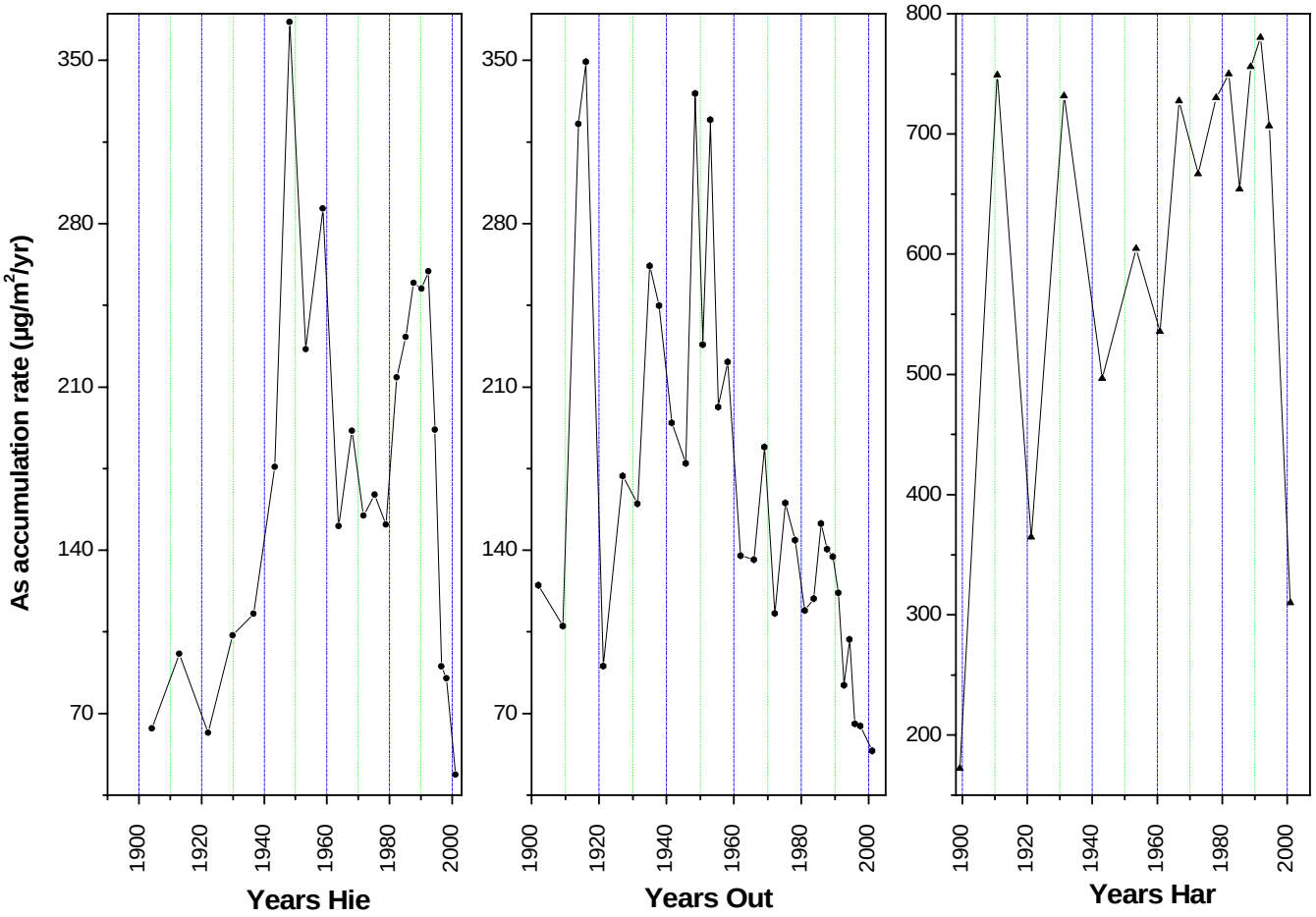



**Fig. 3 -13:** Arsenic accumulation rates in the three Finnish peat bogs.

## 3.3.7 Inventory

Inventories for As were calculated for the last ~ 100 years for all three peat cores. The inventories for Out and Hie were 0.162 mg/m$^2$/yr and 0.159 mg/m$^2$/yr, respectively. The As inventory calculated for Har was 0.617 mg/m$^2$/yr, which is about 4 times higher. The calculated As inventory for the Out core for the last ~ 1500 years was 0.027 mg/m$^2$/yr, for Hie (~ last 2650 years) 0.013 mg/m$^2$/yr and for Har (last ~ 350 years) 0.341 mg/m$^2$/yr. Therefore the Out inventory (for the whole core) is app. 2 times the Hie inventory, and the Har inventory is app. 20 times the Hie and 13 times the Out inventory.

### 3.3.8 Calculation of Natural and Excess As and Pb in the Peat Profiles Using either Br or Sc

To elucidate to which extent the anthropogenic contribution is predominant for As in the peat cores, and because the "background" Pb/Sc ratio of ombrogenic peats provides the Pb/Sc ratio for atmospheric soil dust derived from the weathering of crustal rocks (Shotyk et al., 1998), As and Pb from natural sources have been calculated using Br (for As) and Sc (for Pb) concentrations (ng/g) and a background As/Br ratio (0.010, see text for explanation) or Pb/Sc (4) ratio as:

$$[As]_{natural} = [Br]_{sample} \times ([As]/[Br])_{background}$$

and

$$[Pb]_{natural} = [Sc]_{sample} \times ([Pb]/[Sc])_{background}$$

which allows the concentrations of anthropogenic As or Pb to be calculated as:

$$[M]_{anthropogenic} = [M]_{total} - [M]_{natural}$$

where [M] refers to either As or Pb, respectively.

When the natural background ratio of Hie (0.015 ± 0.002) or Out (0.013 ± 0.003) was used for the calculation of the natural As input, negative results occurred. This means that the natural As input is overestimated or in other words: there is an anthropogenic As input also in the deepest samples of the remote site at Hietajärvi. Therefore the calculation of natural As was

modified. When the As/Br ratio was assumed to be 0.010, no more negative results occurred. The calculation of natural and anthropogenic As was performed using this assumed As/Br ratio. It is important to note here, that this assumed value did not significantly change the anthropogenic As input.

## 3.3.9 Interpretation of the $As_{ex}$ and $Pb_{ex}$ Profiles

### 3.3.9.1 Harjavalta

At Har a copper smelter has been operating since 1945 and a nickel smelter since 1959 (Outokumpu Harjavlata Metals OY). The ores used for smelting until the early 1970s, were mainly domestic sulfidic minerals from the Outokumpu mine. Nowadays, ore concentrates originating from different parts of the world are used. Heavy metals and arsenic are emitted as components of fugitive dust release. The smelter company started monitoring of emissions in 1985 (Table 3-7). Arsenic monitoring was started in 1993. During the past few years, dust emissions have been drastically decreased by changes in process technology and the installation of new filters. The slag produced during smelting is stored in land basins at the plant site. The Cu slag is pumped into the tailing area as slug and the Ni slag is piled in heaps and landscaped. The emissions from the smelter have severely affected the forest vegetation in the immediate vicinity of the stack.

**Table 3-7.** Emissions from Harjavalta smelters in tonnes per year during 1985-1999. Arsenic monitoring started in 1993 (data from Outokumpu Harjavalta Metals Oy).

| Year | Dust | Pb | As |
|---|---|---|---|
| 1985 | 1100 | 55 | - |
| 1986 | 1200 | 60 | - |
| 1987 | 1800 | 94 | - |
| 1988 | 1000 | 48 | - |
| 1989 | 1000 | 70 | - |
| 1990 | 960 | 80 | - |
| 1991 | 640 | 45 | - |
| 1992 | 280 | 9 | - |

| Year | Dust | Pb | As |
|---|---|---|---|
| 1993 | 250 | 6 | 11.0 |
| 1994 | 190 | 3 | 5.0 |
| 1995 | 70 | 0.5 | 0.2 |
| 1996 | 195 | 1.9 | 4.2 |
| 1997 | 360 | 4 | 10.0 |
| 1998 | 132 | 2.4 | 10.1 |
| 1999 | 48 | 1.0 | 1.8 |
| 2000 | 36 | 0.2 | 0.8 |
| 2001 | 50 | 0.7 | 1.6 |

The beginning of anthropogenic vs. natural As in this core could not be calculated, as the oldest age for this core dates only from ~ 1100 AD. As shown in Fig. 3-14, this core is not old enough to calculate the beginning of anthropogenic As.

Anthropogenic As and Pb concentrations increase from ~ 1770 AD (Fig. 3-14) onwards and reach their maximum at 1931 ± 41 AD (As), and 1954 ± 22 AD and 1978 ± 11 AD (Pb). After 1954 ± 22 AD the As and Pb significantly decrease. Although the smelting started in 1945 AD in this area, the profiles pre-date the true beginning of the smelting. As mentioned before, the age dates for this core are uncertain. Therefore the anthropogenic As and Pb input reflects the general trends and is only controlled by the smelting activities in this area until 1931 ± 41. Elevated As concentration predating this date may be due to the agricultural areas located close to the Harjavlata site and the possible application of As-containing agrochemicals in this area (Kauranne and Sillanpää, 1992).

#### 3.3.9.2 Outokumpu

In 1910 the ore of Outokumpu was found and a copper factory was built in 1913. The smelting plant worked inefficiently and even 40% of copper was left in waste. In 1918 a railway was built from Outokumpu mine to the lake Juojärvi to improve transport conditions. In this year, also the first train left Outokumpu. A new mine shaft and a large concentration mill was built in 1926-1928 and the old copper factory was closed in 1929. Mökkivaara mine shaft was built in 1939. Keretti mine shaft and the Keretti concentrating mill were built in 1954. In 1965 a new ore deposit was found at Vunonos, 6 km to the NE from the Outokumpu mine. The building of the Vuonos mine was started in 1970, a bit later also Keretti was renewed (Kuisma, 1985).

The Pb profile shows pronounced peaks at 1975 ± 6 AD, 1962 ± 9 AD and 1886 ± 41 AD (Fig. 3-14). Pb is increasing from ~ 1914 AD, shows its highest concentration at app. 1975 ± 6 AD and after that decreases. Therefore it seems that the anthropogenic Pb reflects the general trends of the mining history.

Arsenic tells a different story. The broad As peak shows several pronounced As concentrations. However as for the other cores, the maximum As concentration dates from app. 1942 ± 14 AD (Fig. 3-14, 3pt. median As total). From app. 1914 ± 24 AD, the mining history seems to be reflected by anthropogenic As input. However, there are pronounced peaks even before 1914 ± 24 AD. Interestingly also the Pb concentrations are pronounced between 1500 AD and 1868 AD (Fig. 3-14). Therefore there must have been another source of anthropogenic input during this time, as it can not be explained due to the mining history. Actually the As and Pb concentrations increased from app. 1100 AD until 1942 ± 14 AD (As) and 1975 ± 6 AD (Pb) and then decrease. Therefore it seems, that the bog at Out does not provide accurate background concentrations even before the Outokumpu ore was found. Whether the anthropogenic As and Pb input before the discovery of the Outokumpu ore is due to the burning of fossil fuels can not be explained here. Anthropogenic As input in this core started from app. 1000 AD onwards most likely due to coal burning (149:144 ng $g^{-1}$; As nat:As anthrop.).

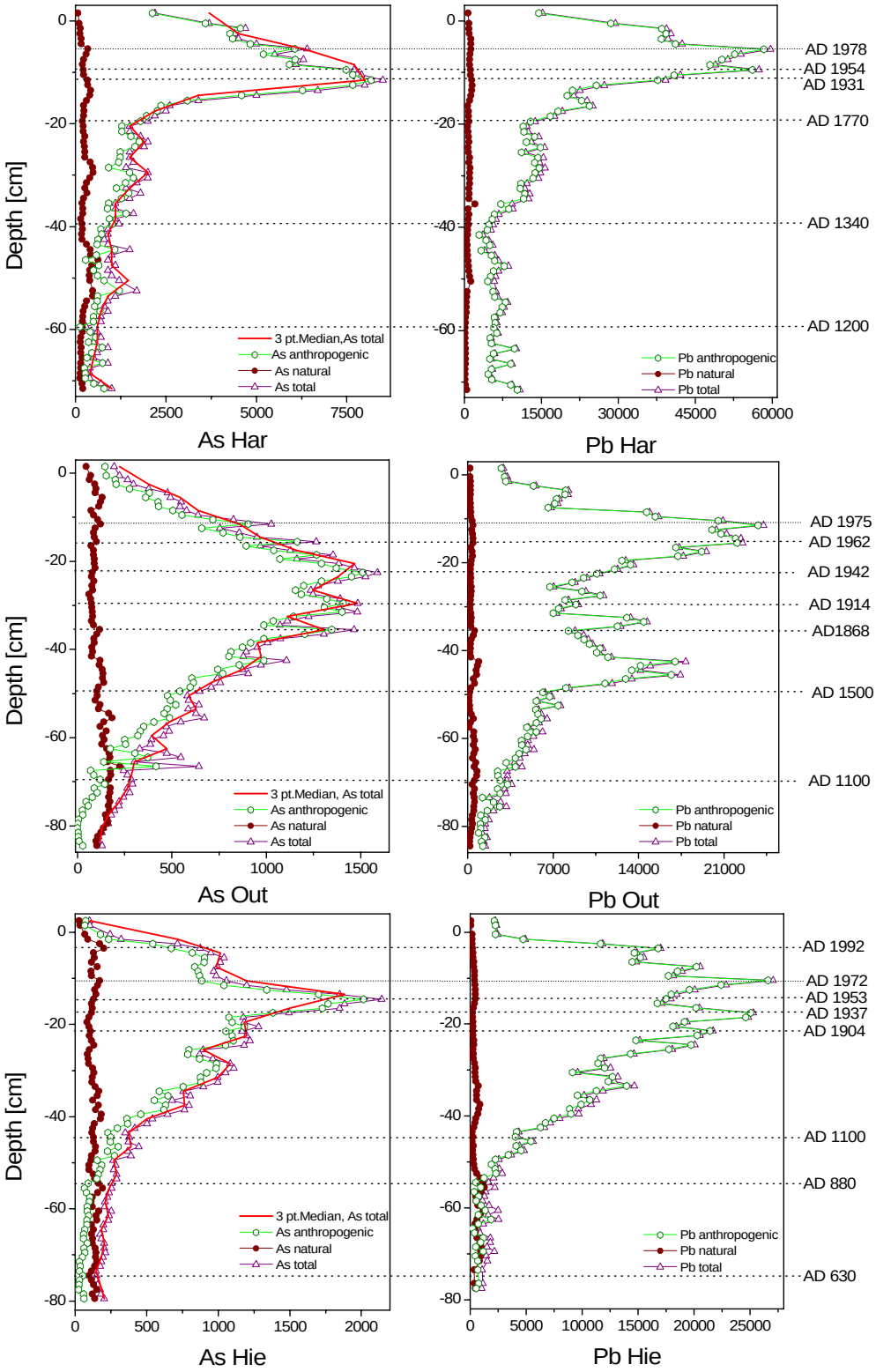



**Fig. 3-14:** Total, anthropogenic and natural As and Pb in the Har, Out and Hie core, respectively.

### 3.3.9.3 Hietajärvi

The reference site, Hie, is located in Patvinsuo National Park, in eastern Finland, with no agricultultural activities and roads in the vicinity. As for the Har core, arsenic follows Pb trends in this core. Interestingly, the maximum anthropogenic As (1953 ± 3 AD) and Pb (1972 ± 2 AD) is higher than in the Out core (Fig. 3-14). The As and the Pb concentrations increase from ~ 1100 AD, respectively. After 1953 ± 3 AD (As) and 1972 ± 2 AD they decrease. As the monitoring of annual bulk deposition only started in 1990 in the vicinity of the coring site, the interpretation of the data is uncertain. Anthropogenic As in this core started from app. ~ 1000 AD (112:156 ng $g^{-1}$; As nat:As anthrop.)

It is commonly known, that anthropogenic arsenic is released as a by-product of mining, metal refining processes, the burning of fossil fuels and agricultural use (Azcue and Nriagu, 1994; Nriagu and Pacyna, 1988). Possible trace metal sources in this area might include: settlement, forest fires, paper and pulp production. However, as Pb is known to be immobile in peat and as the arsenic follows the Pb, it is most likely that also As in well preserved in this profile.

## 3.3.10 Fate of Arsenic in Peat Bogs

There is a growing body of information suggesting that Pb is immobile in ombrothrophic peat (Shotyk et al., 2005, and references cited therein). Taking Pb to represent an immobile element in peat, the coincidence of As and Pb concentration peaks suggest, that As is also well retained within the peat profile. Bromine is an useful reference element for As because it is also supplied to the peat only by atmosphere, and because the ratio of As/Br is constant in peat dating from pre-industrial times. Moreover, the inventories for Out and Hie for the last 100 years are in the same range (0.162 mg/$m^2$/yr and 0.159 mg/$m^2$/yr, respectively) and anthropogenic As in the Out and Hie core started roughly at the same period of time (at app. 1000 AD onwards).

### 3.3.11 Conclusion

This is the first detailed record of atmospheric As deposition. The Finnish profiles have received As and Pb exclusively from the atmosphere. This finding is consistent with several studies describing Pb accumulation in ombrotrophic peat. The data presented here also argue that As is well retained in the peat profile.

The As concentration profiles reflect the mining history of the three cores, the same is true for Pb. Taking Br as an reference element for As, anthropogenic and natural As concentrations were calculated. Results demonstrate that anthropogenic As and Pb started roughly at the same period of time in the Out and Hie core, most likely due to coal burning. Additionally As inventories for the Out and Hie core are in the same range. Taken together, these findings strongly suggest that As is preserved within the peat profiles. To further elucidate these findings pore waters as well as predominant As species within the peat profiles were determined.

### 3.3.12 Additional Information

Some additional information is given in the following pages.

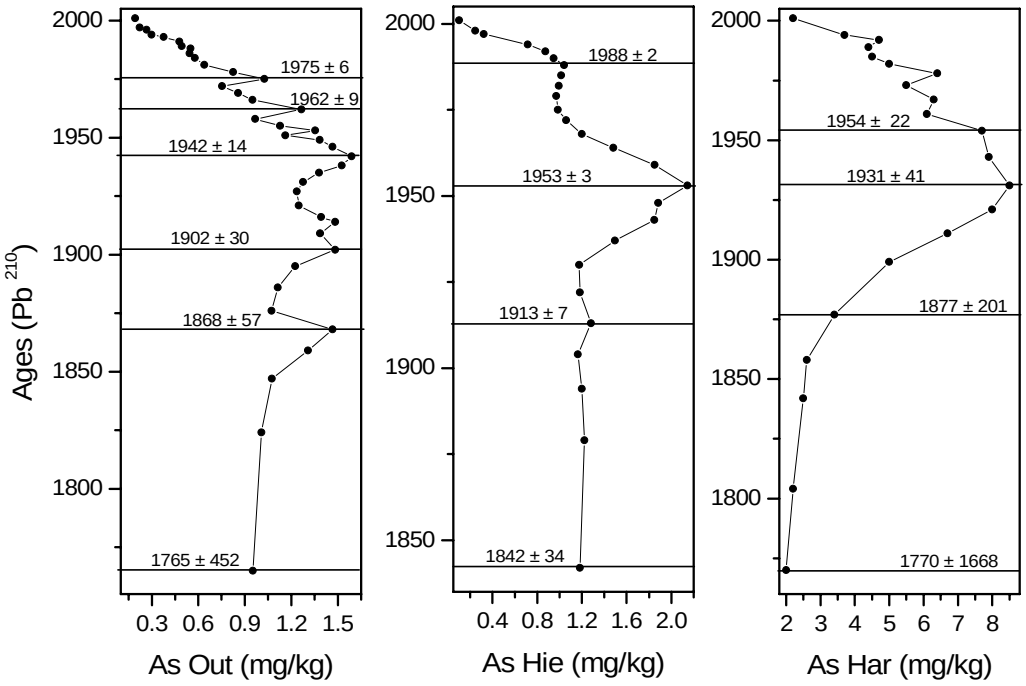



**Fig. 3-15:** Total As concentrations in the uppermost layers of the Finnish peat samples.

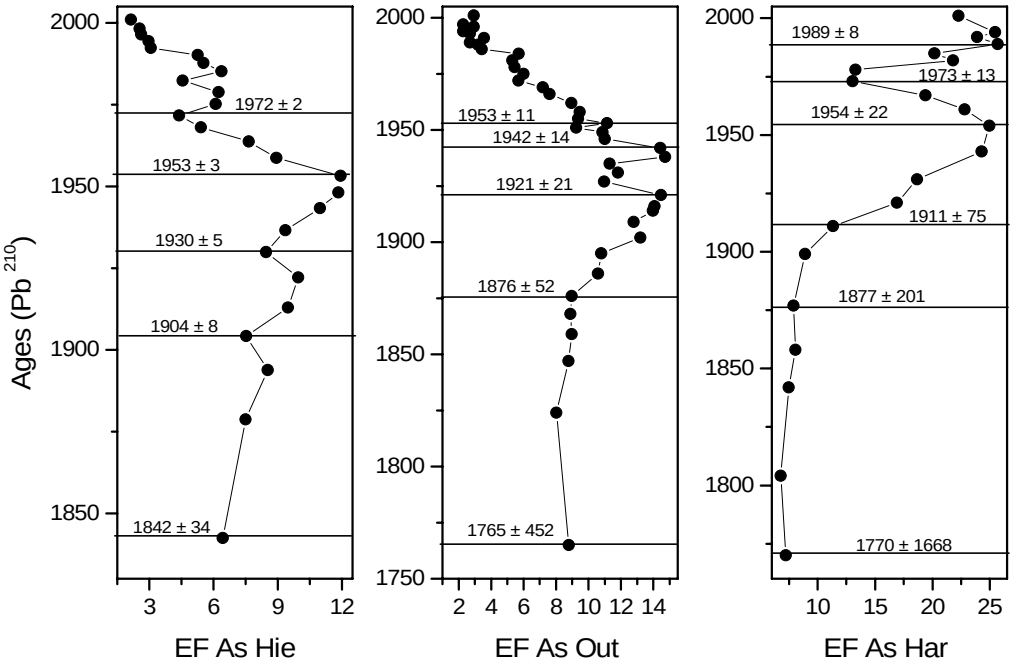



**Fig. 3-16:** As EF in the uppermost layers of the Finnish peat samples.

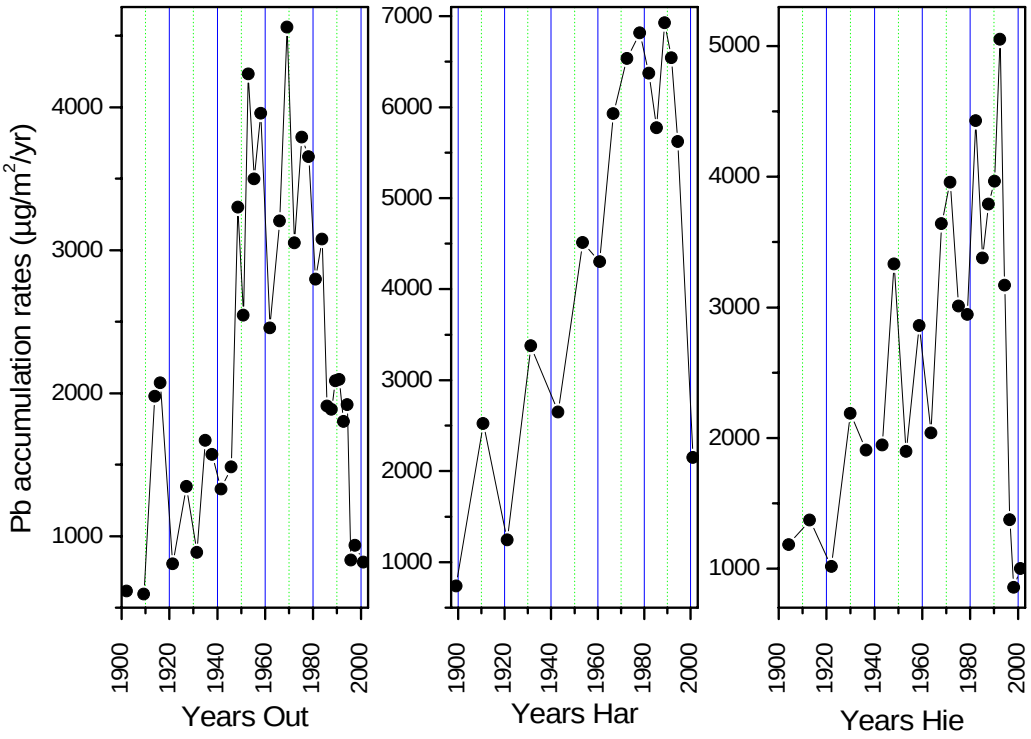



**Fig. 3-17:** Pb accumulation rates in the uppermost layers of the Finnish peat samples.

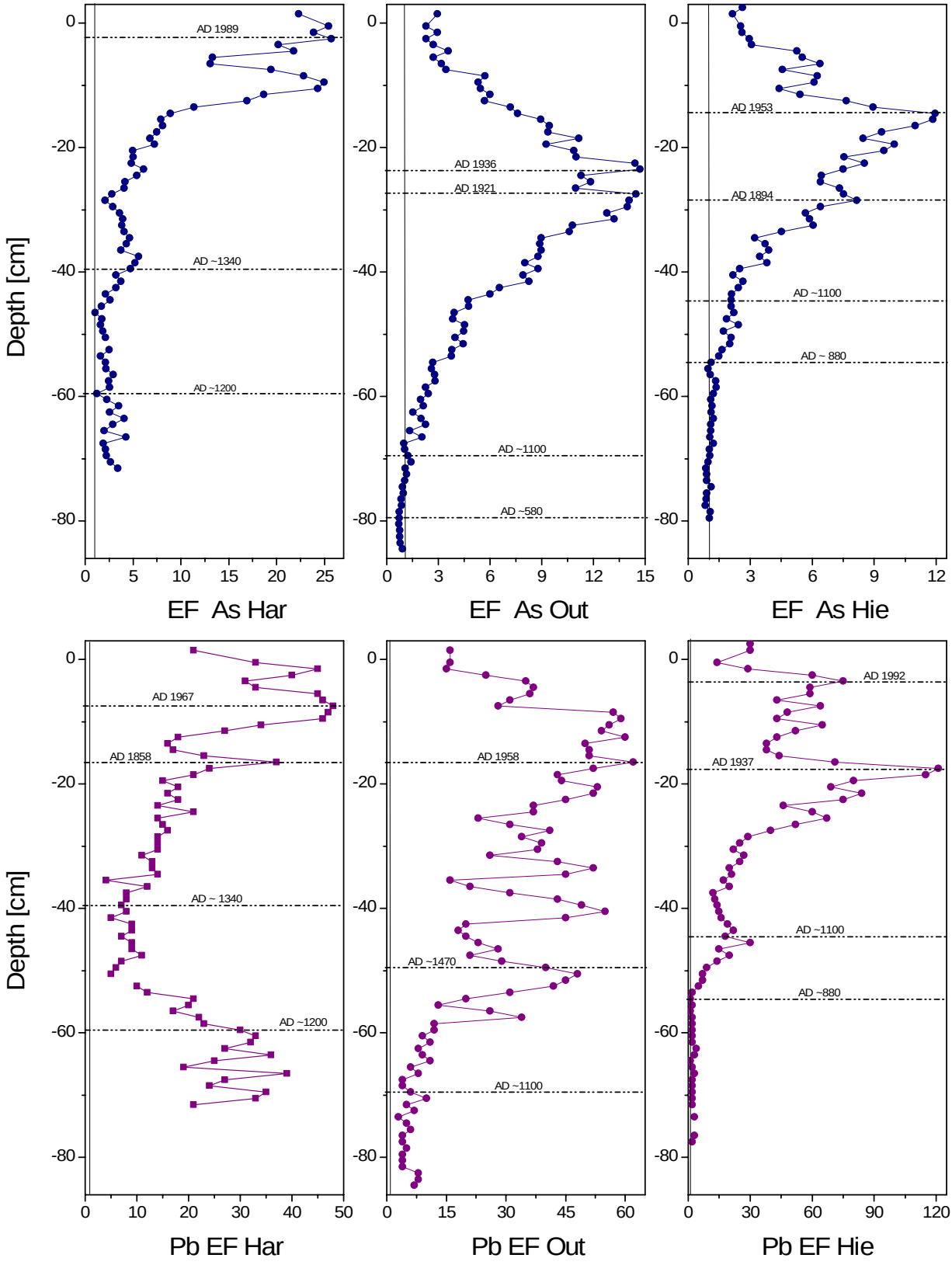



**Fig. 3-18:** Comparison of As EF and Pb EF in the Finnish peat samples.

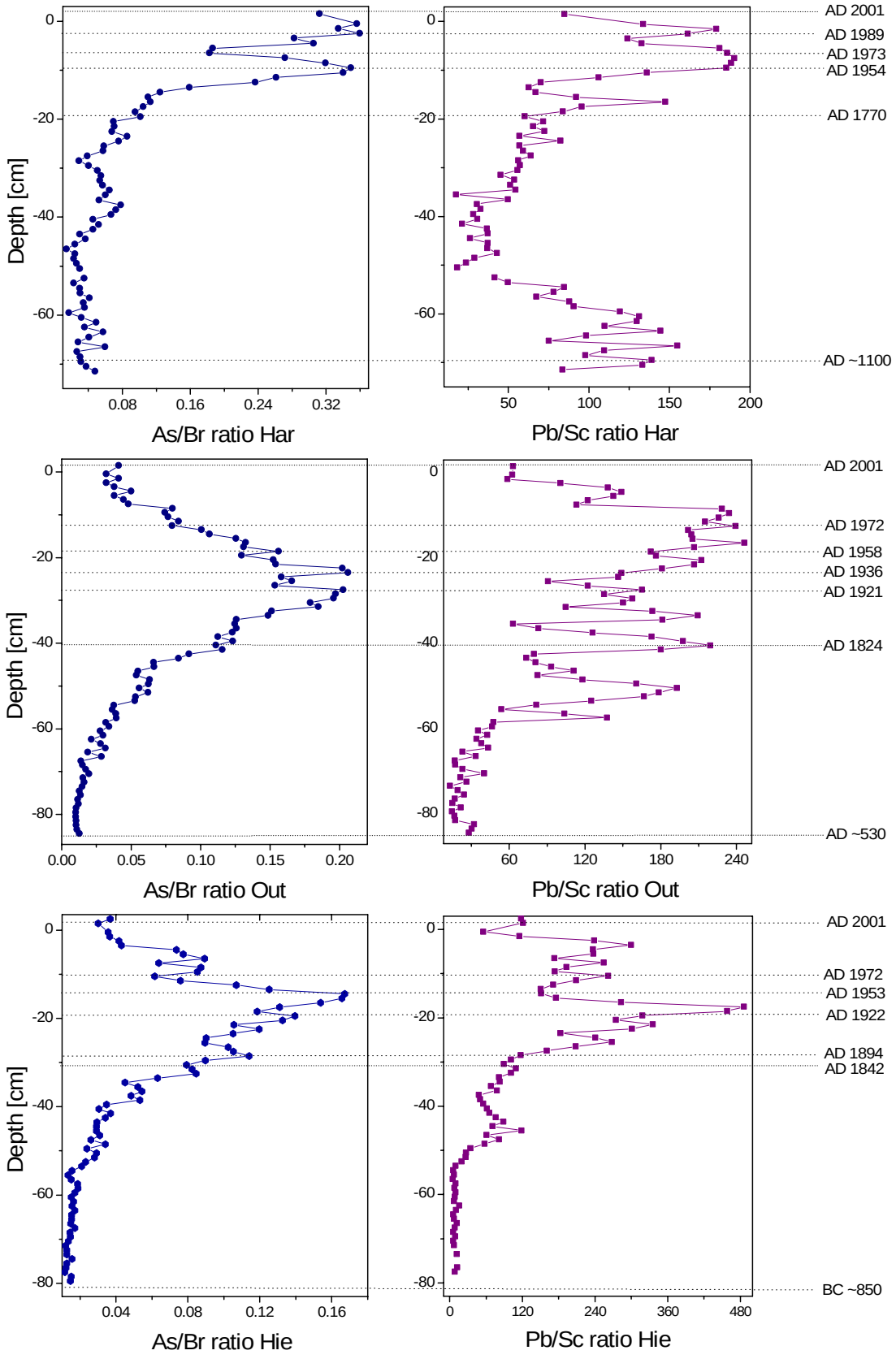



**Fig. 3-19:** Comparison of As/Br and Pb/Sc ratios in the Finnish peat bogs.

# 3.4 Determination of Arsenic in Pore Waters from Ombrotrophic Peat Bogs in Finland

The main goal of this study was the accurate, and precise determination of total As concentrations in pore water samples using the Apex sample introduction system coupled to ICP-SF-MS that was operated in the low resolution mode to enhance sensitivity, and either to confirm the hypothesis that As is well preserved within peat bogs, or to determine the extent of As mobility within these bogs.

## 3.4.1 Introduction

The chemical composition of the pore waters is a sensitive indicator of the release of trace metals from atmospheric particles to the pore fluids, and the potential of these metals to migrate subsequent to their deposition. The aim of this study was to evaluate the use of pore waters as a sensitive indicator of the release of As from atmospheric particles to the pore fluids, as well as the potential of As to migrate subsequent to its deposition.

Arsenic trace metal concentrations in pore waters are typically below the parts per billion levels; therefore determination of As concentrations in pore waters is challenging. To overcome the decrease in sensitivity of the ICP-SF-MS when As is determined in the high resolution mode ($m/\Delta m$ ~10000), the Apex sample introduction system was critically evaluated for its applicability to the determination of total As concentrations in small volumes of humic-rich pore water samples from peat bogs using clean room facilities. With this sample introduction system it was possible to operate the ICP-SF-MS in the low resolution mode ($m/\Delta m$ ~300) to enhance sensitivity. The capability of the Apex system to overcome potential $(^{40}Ar^{35}Cl)^+$ interferences was critically evaluated. Moreover analysis time was significantly reduced, when As was determined in the low resolution mode.

Pore water samples were taken form ombrotrophic peat bogs in Finland (section 2.4) and prepared as described in section 2.6.2.

Pore waters were determined using ICP-SF-MS as described in section 2.5.4.3. Where possible (limited volume of pore waters remaining), all pore water samples were determined in triplicate.

The developed analytical procedure was successfully applied to the determination of As in pore water samples, in extracts of selected peat samples (section 2.6.11.1), as well as certified environmental reference materials (section 2.6.8), yielding excellent agreement between found and certified values.

The solution detection limit and the solution quantification limit for the determination of As using the Apex sample introduction system coupled to ICP-SF-MS were 2.0 ng $l^{-1}$ and 4.0 ng $l^{-1}$, respectively.

At the Har site, the As concentrations of the pore waters ranged from 2.93 μg $l^{-1}$ to 4.37 μg $l^{-1}$. At Hie the As concentrations of the pore waters were significantly lower, ranging from 0.28 μg $l^{-1}$ to 0.43 μg $l^{-1}$. Interestingly pore waters from the Out site had As concentrations below the As concentrations in pore waters from the Hie site, with values ranging from 0.12 μg $l^{-1}$ to 0.38 μg $l^{-1}$.

### 3.4.2 Quality Control and Analytical Characteristics of the Developed Procedure

Employing the developed procedure (Apex sample introduction system coupled to ICP-SF-MS) for the determination of As in pore waters and in extracts (section 2.5.4.3), two certified plant reference materials, one peat reference materials (NIMT Peat), and one certified water reference material were investigated (section 2.6.8). As shown in Table 3-8 the found As concentrations were always in excellent agreement with the certified or information values.

Quality control was performed as described in section 2.6.8. The data summarised in Table 3-8 highlight the excellent agreement between experimentally established and certified elemental concentrations in both, certified standard reference materials as well as the peat reference material.

**Table 3-8:** Concentrations (mean ± standard deviation; ng $g^{-1}$ dry mass) of As in various reference materials as determined using the Apex sample introduction system coupled to ICP-SF-MS.

| Material | Sample name | Certified | Found | N[b] |
|---|---|---|---|---|
| Plant | CTA-OTL-1 | 539 ± 60 | 587 ± 1 | 3 |
| | CTA-VTL-2 | 969 ± 72 | 930 ± 20 | 3 |
| Water | SLRS-4 | 0.680 ± 0.060 | 0.717 ± 0.013 | 6 |
| Peat | NIMT Peat | 2440 ± 550 [a] | 2580 ± 30 | 3 |

[a] Information value (Yafa et al., 2004)
[b] Number of sub-samples analysed

The solution detection limit was calculated as concentration corresponding to three times the standard deviation (3 σ) of 10 independently prepared blank solutions. The solution quantification limit was based on six times of the standard deviation (6 σ).

The sensitivity was calculated from the slope of the calibration curve and the precision expressed as relative standard deviation (RSD) was assessed by analysing a solution containing 5 ng $l^{-1}$ or 10 ng $l^{-1}$ As (n=6). Calibration curves had correlation coefficients always > 0.999 and were linear from 0 to at least 20 µg $l^{-1}$. The major analytical characteristics of the developed procedure are summarised in Table 3-9.

**Table 3-9.** Analytical characteristics of the developed procedure.

| | |
|---|---|
| Solution detection limit [a] | 2.0 ng $l^{-1}$ |
| Solution quantification limit [b] | 4.0 ng $l^{-1}$ |
| Reproducibility 5 ng As $l^{-1}$ (n=6) | < 0.9% |
| Reproducibility 10 ng As $l^{-1}$ (n=6) | < 0.5% |
| Sensitivity [c] | ~ 100 cps |

[a] Concentration corresponding to 3 standard deviations of the blank; [b] Concentration corresponding to 6 standard deviations of the blank; [c] Counts per ng As $l^{-1}$.

### 3.4.3 Can the Apex Sample Introduction System Overcome $(^{40}Ar^{35}Cl)^+$ Interferences?

Spectroscopic interferences in ICP-MS result from signals of oxides ($MO^+$), doubly charged ions ($M^{2+}$), hydroxides ($MOH^+$), argides, and of molecules with the same ratio of mass and charge such as the element of interest. The presence of $(^{40}Ar^{35}Cl)^+$ ions strongly hampers the determination of $^{75}As$. These interferences can be eliminated by the use of ICP - SF - MS instruments that are operated in the high resolution mode ($m/\Delta m \sim 10000$). However the use of the high resolution mode decreases sensitivity.

Therefore the Apex sample introduction system was critically evaluated for its applicability to overcome $(^{40}Ar^{35}Cl)^+$ interferences. As pore water samples and extracts were expected to contain low As concentrations (low µg $l^{-1}$ to ng $l^{-1}$ range) the determination of As in pore waters and extracts in the low resolution mode was desirable.

For the evaluation of the Apex sample introduction system, a solution containing 50 ng $l^{-1}$ As with various $Cl^-$ concentrations (0-100 mg $l^{-1}$) was prepared and analysed with the Apex sample introduction system coupled to ICP – SF – MS that was operated in the low resolution mode. Blank solutions were prepared without addition of 50 ng $l^{-1}$ As. Indium ($^{115}In$) was used as internal standard element to correct for potential matrix effects and drifts of sensitivity. All solutions were matched for the nitric acid concentration in the prepared pore water samples.

In Figure 3-20, results for the determination of 50 ng $l^{-1}$ As in the presence of various $Cl^-$ concentrations (0-100 mg $l^{-1}$) are displayed. It can clearly be seen that the Apex sample introduction system is capable to overcome $(^{40}Ar^{35}Cl)^+$ in the low resolution mode, even when As has to be determined at very low concentrations (50 ng $l^{-1}$), up to a $Cl^-$ concentration as high as 6 mg $l^{-1}$.

As continental pore waters from ombrotrophic peat bogs from Switzerland typically contain 0.3 mg $l^{-1}$ $Cl^-$ (Steinmann and Shotyk, 1997), the Apex sample introduction system is more than capable to overcome the potential resulting $(^{40}Ar^{35}Cl)^+$ interferences. Moreover $Cl^-$ concentrations up to 6 mg $l^{-1}$ do not hamper the determination of As, even when present at a concentration of 50 ng $l^{-1}$.

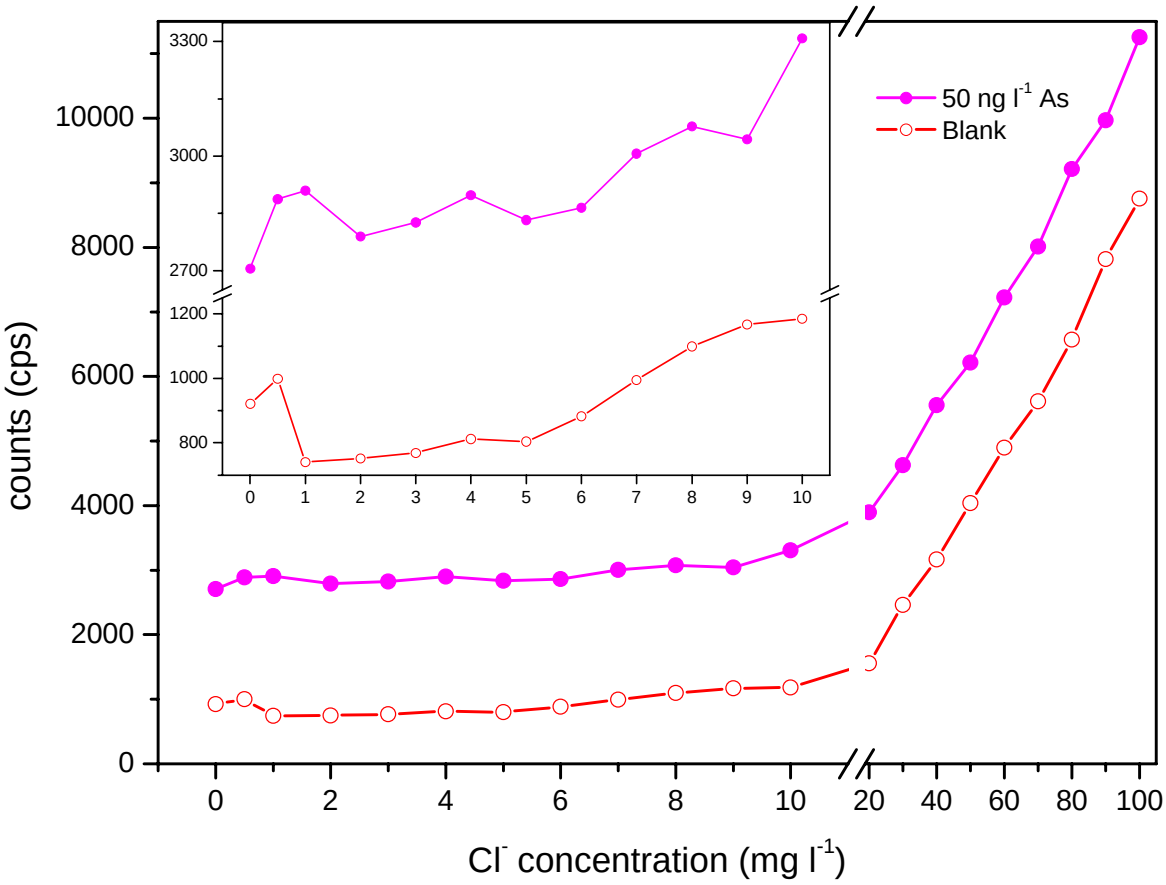



**Fig. 3-20:** Determination of 50 ng $l^{-1}$ As in the presence of various (0-100 mg $l^{-1}$) $Cl^-$ concentrations.

## 3.4.4 Determination of As Concentrations in Pore Waters from Finland and Comparison with As Concentrations from Solid Peat

Results for the determination of As in the Finish pore waters are displayed in Fig. 3-21.

### 3.4.4.1 Hariavalta

The concentration profile of arsenic in the Harjavalta core (Figs. 3-10; 3-11) shows a pronounced peak in between the first 20 cm of the peat profile. Above 40 cm the concentrations of arsenic do not show any more significant variations. The maximum arsenic concentration in the Har profile is 8.5 mg/kg at a depth of -11.5 cm corresponding to an age of 1931 AD (CRS model). The maximum As concentration in the Har pore waters is 4.37 $\mu g\ l^{-1}$ (Fig. 3-21). Therefore at the Har site app. 0.05% of the total As were found in the pore waters.

### 3.4.4.2 Outokumpu

In contrast to Harjavalta, the Outokumpu concentration profile of As shows a broad peak from the top of the peat profile to a depth of about -60 cm. The maximum As concentration (1588 ng/g) at a depth of -22.5 cm (Figs. 3-10; 3-11), corresponds to an age of 1945 AD (CRS model). The maximum As concentration in the pore waters from the Out site is 0.38 $\mu g\ l^{-1}$ (Fig. 3-21), that accounts only 0.02% of the maximum total As concentration in the solid peat form Out. At Har, pore waters are enriched ~ 2.5 times compared to the pore waters from the Out site. In contrast, the maximum As concentration of solid peat at the Out site is approximately 5 times lower than the maximum As concentration in the Har peat profile. At the Out site, pore water concentrations increase to a depth of app. -50 cm and then decrease. The same is true for the As concentrations in solid peat at this site, that show a pronounced peak up to a depth of app. -60 cm and then decrease (Figs. 3-10; 3-11).

### 3.4.4.3 Hietajärvi

Hietajärvi, the low background site in eastern Finland, with no agriculture or roads nearby and no point sources of heavy metal air pollution within tens of kilometres, shows a pronounced As peak in a depth of -14.5 cm corresponding to an age of 1953 AD (CRS model, Figs. 3-10; 3-11). Interestingly the maximum As concentration (2140 ng/g) is higher than the maximum As concentration in the Out peat profile. The same is true for the As concentrations in the pore waters at the Hie site. The maximum As concentration in the pore waters is 0.43 µg $l^{-1}$ (Fig. 3-21). This accounts to ~ 0.02% of the maximum As concentration in solid peat and is equal to the Out core.

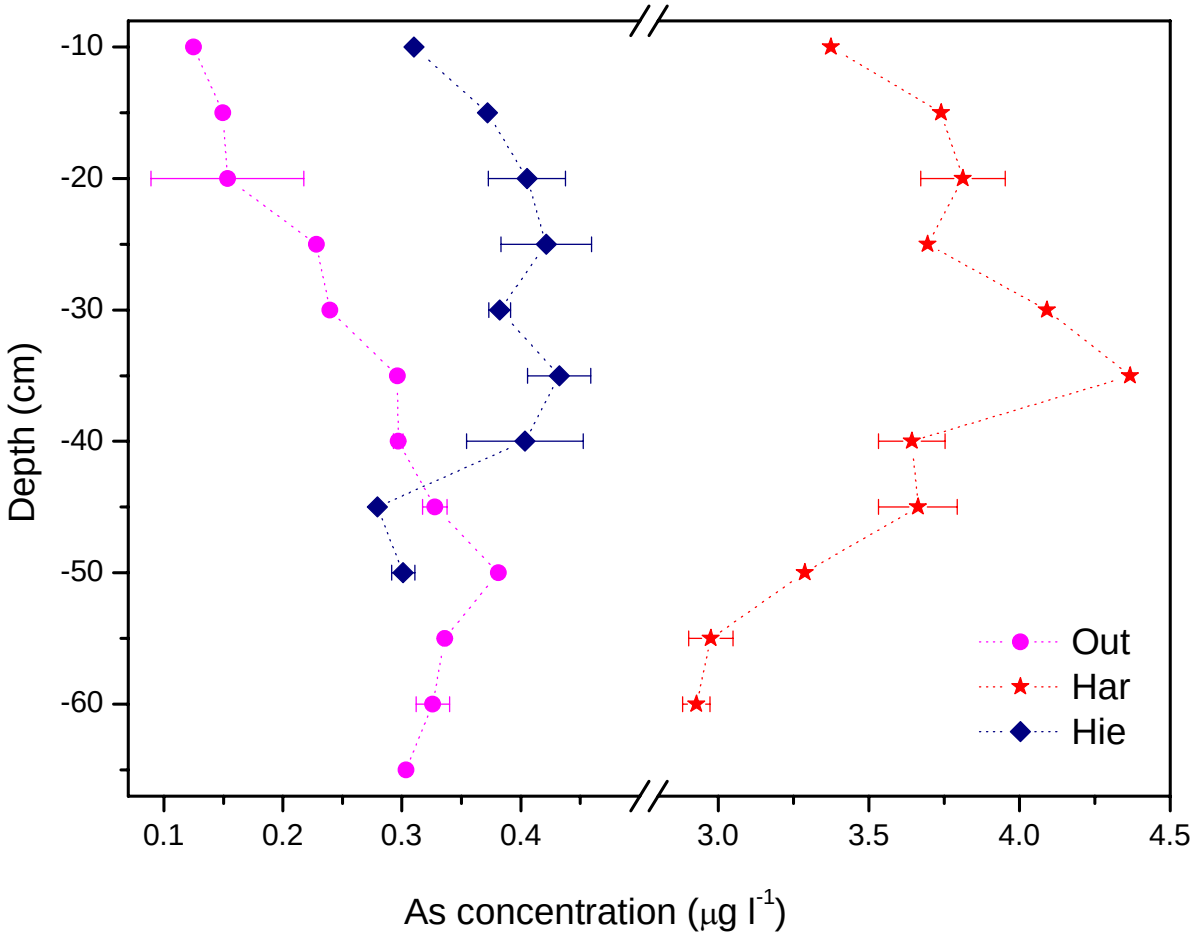



**Fig. 3-21:** As concentrations in the Finish pore waters in correlation with depth.

As for solid peat, the concentration profile of As in the pore waters of Hie looks similar to the Out concentration profile, whereas the Har concentration profiles of the pore waters and solid peat, respectively, look different. At Out and Hie only ~ 0.02% of the total As concentrations were found in the pore waters. In contrast the As concentrations found in pore waters in the Har site were enriched by 2.5 times for both, the Hie and the Out site, respectively.

### 3.4.5 Conclusion

Pore water concentrations at the Out and Hie site look similar. Only ~ 0.2% of the maximum As concentrations from solid peat could be found in the pore waters of both Hie and Out, respectively. As for solid peat, the Har site tells a different story. Maximum As concentrations in solid peat at the Har site are enriched ~ 5 times. Maximum As concentrations in the pore waters are enriched ~ 2.5 times.

Taken together, the low As concentrations found in the pore waters, the similarity of the As chronologies of the Out and Hie core in the pore waters and in solid peat, respectively, together with the different As chronology of the Har core in both pore waters and solid peat, respectively, the data confirm the hypothesis that As is well preserved within the peat profiles and that the Finnish profiles have received As exclusively from the atmosphere.

# 3.5 Correlation of Arsenic Concentrations in the Finish Peat Bogs with the Concentrations of Calcium, Magnesium, and Iron

Arsenic is known to be sorbed (as arsenite and arsenate) by hydroxides (hydrated oxides) of aluminum, iron(III), and manganese. The main goal of this study was to provide information about the association of arsenic with these elements in ombrotrophic peat bogs. Data for Mn, Fe, Ca and S were provided by Dr. Andriy Cheburkin using XRF Spectrometry.

## 3.5.1 Introduction

The most common minerals with arsenic as major component are arsenopyrite (FeAsS), arsenic sulfides ($As_2S_3$ orpiment; $As_4S_4$ realgar), and arsenates (for instance, (Fe, Al)($AsO_4$) • 2 $H_2O$ scorodite). Most commercially mined sulfidic ores (Cu-sulfide, pyrite) contain arsenic as a minor component. When As is derived to the peat bogs from these minerals, peat bogs may contain grains of such arsenic minerals.

Dissolution of these minerals will generally occur only in strongly acidic and strongly oxidizing acids, such as concentrated nitric acid and aqua regia. Weathering of the arsenic minerals will generate arsenic trioxide, the anhydride of arsenous acid $H_3AsO_3$, and in the presence of water arsenous acid. Arsenous acid will be oxidized under aerobic conditions by atmospheric oxygen to arsenate (degree of protonation depending on the pH).

Arsenic acid, an acid with deprotonation constants about equal to those of phosphoric acid, will form rather insoluble salts with cations abundant in solutions (Kuehnelt, 2000). Such arsenates could be $Ca_3(AsO_4)_2$, $FeAsO_4$, $AlAsO_4$, and $Mn_3(AsO_4)_2$ (Kuehnelt, 2000). These arsenates are soluble in strongly acidic solution, because the high concentration of hydronium ion causes protonation of the $AsO_4^{3-}$ ion to $HAsO_4^{2-}$, $H_2AsO_4^{-}$, and $H_3AsO_4$ and reduces the

concentration of $AsO_4^{3-}$. Consequently, peat bogs will release arsenate ions into an aqueous solution when treated with a strong acid.

Arsenite and arsenate are known to be sorbed by surface-rich hydroxides (hydrated oxides) of aluminum, iron(III), and manganese (O'Neill, 1999; Bhumbla and Keefer, 1994). Arsenic bound in this manner will be released into solution, when the hydroxides are dissolved by addition of strong acids or by addition of a reducing agent [for $Fe(OH)_3$]. Neutral, weakly acidic, or weakly alkaline water will not bring sorbed arsenate or arsenate present as calcium, iron, or aluminum salt into solution.

## 3.5.2 Harjavalta

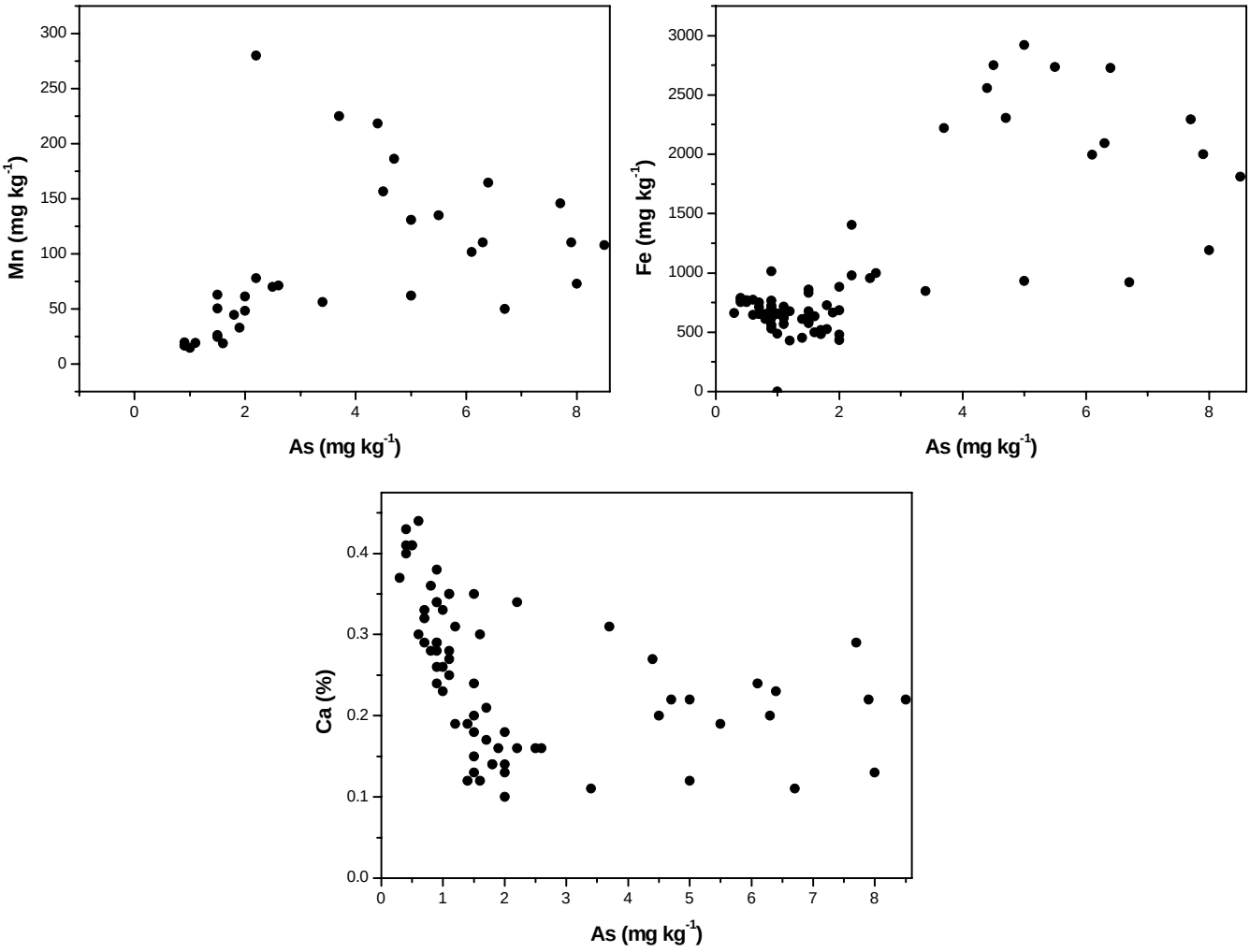



**Fig. 3-22:** Correlation of As concentrations with the concentrations of Mn, Fe and Ca in the Harjavalta peat core.

The correlation of the total arsenic concentrations with the concentrations of Mn, Fe, and Ca were compared in the Finish peat bogs. No correlation of the arsenic concentration with the concentrations of these elements was observed at the Har site. Results for the correlation of As concentrations with Ca, Fe and Mn concentrations are displayed in Fig. 3-22.

### 3.5.3 Outokumpu

The correlation of the total arsenic concentrations with the concentrations of Ca, Mn, Fe and S were compared in the Out core.

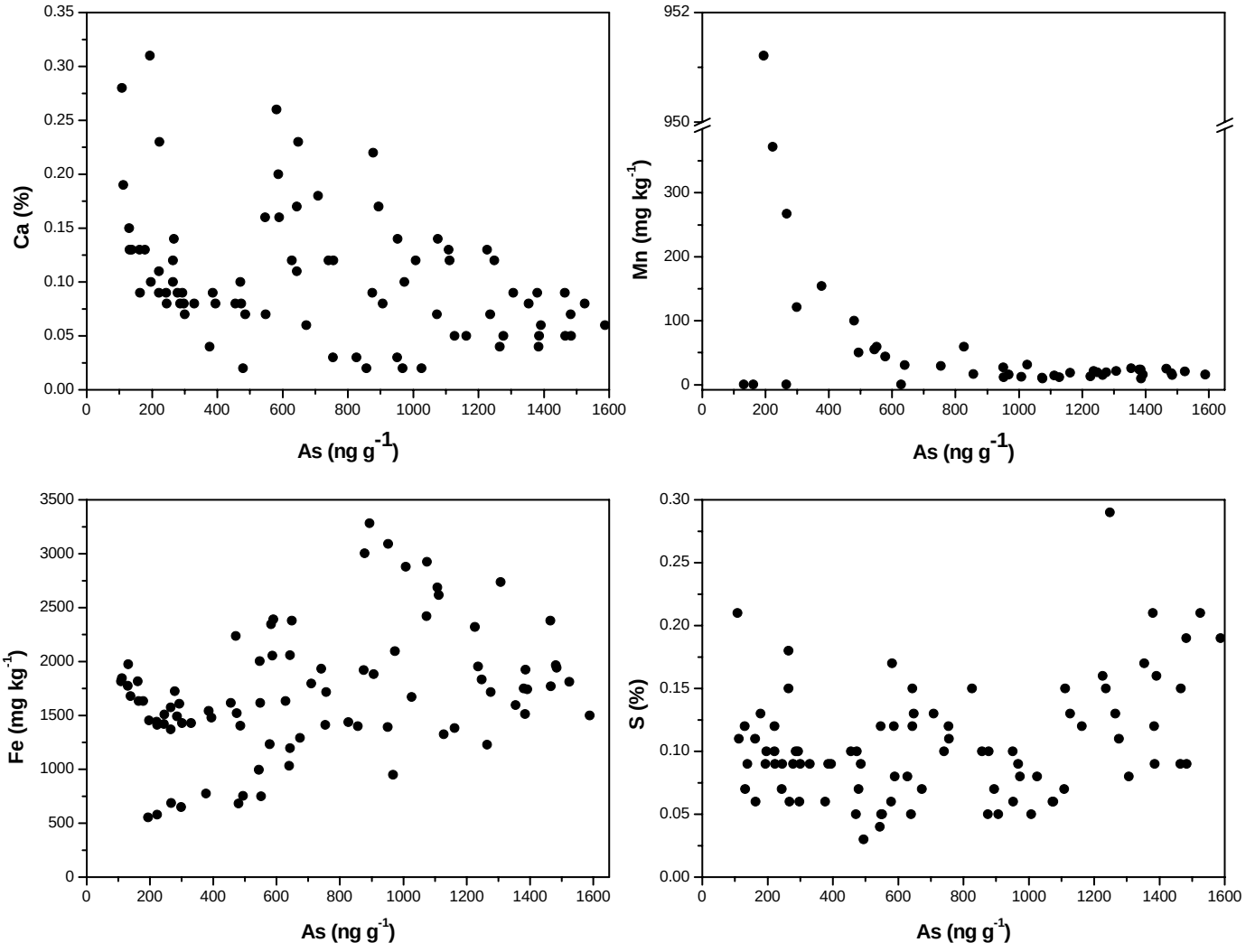



**Fig. 3-23:** Correlation of As concentrations with the concentrations of Ca, Mn, Fe and S in the Outokumpu peat core.

No correlation of the arsenic concentrations with the concentrations of these elements was observed. Results for the correlation of As concentrations with Ca, Fe and Mn and S concentrations are displayed in Fig. 3-23.

### 3.5.4 Hietajärvi

The correlation of the total arsenic concentrations with the concentrations of Ca, Mn, and Fe were compared in the Hie core (Fig. 3-24).

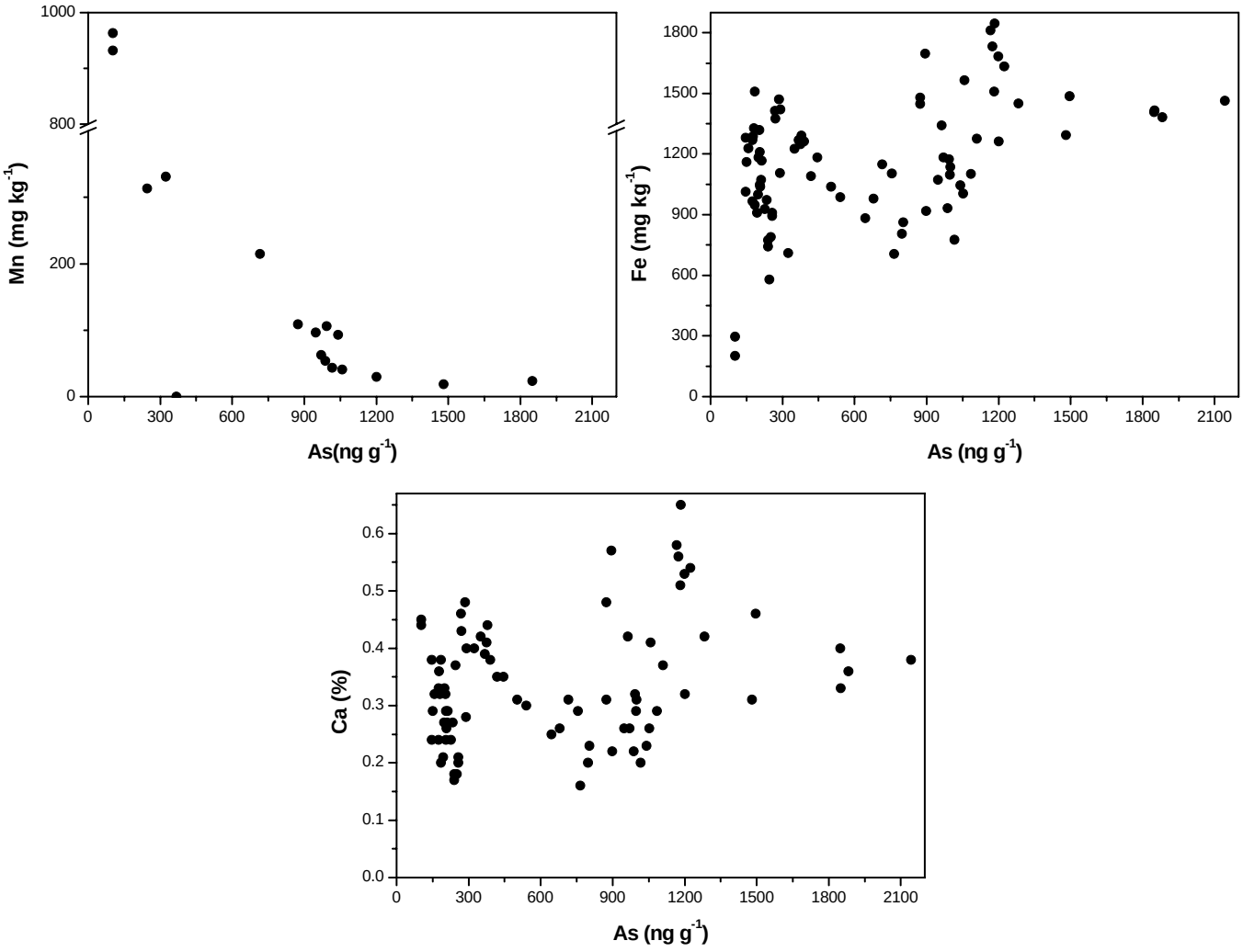



**Fig. 3-24:** Correlation of As concentrations with the concentrations of Mn, Fe and Ca in the Hietajärvi peat core.

No correlation of the arsenic concentrations with the concentrations of these elements was observed.

### 3.5.5 Conclusion

As mentioned above, arsenite and arsenate are known to be sorbed by hydroxides (hydrated oxides) of aluminum, iron(III), and manganese. Therefore, the results indicate that the major part of the arsenic species is not bound to the mineral phase of the peat bogs. The above results together with the missing correlation of the arsenic concentrations with the concentration of aluminum and iron indicate that the arsenic acid is not located in the mineral particles. These findings further confirm the hypothesis that the Finnish profiles have received As exclusively from the atmosphere.

# 3.6 Determination of Selected Elements and Arsenic in the Internal Peat Reference Materials

The aim of this work was to prepare "internal peat reference materials" to quantify losses of As due to sample handling (oven drying at 105°C as described in section 2.6.1.2 compared to freeze drying and most important to fresh peat samples).

## 3.6.1 Introduction

The preservation of the native element and As concentrations during the entire sample pre-treatment procedure (sampling, drying, milling, extraction, etc.) is of utmost importance to allow to draw meaningful conclusions from the obtained results. Therefore internal reference materials are needed to evaluate potential loss of selected elements and As during the peat sample preparation procedure (oven drying at 105°C).

## 3.6.2 Quality Control

The preparation of the internal peat reference materials is described in section 2.6.10. Arsenic concentrations in these materials were determined using ICP-SF-MS and HG-AFS as described in sections 2.6.6; 2.6.8 with the instrumental settings described in sections 2.5.3 and 2.5.4.1. Quality control was performed as described in sections 2.6.6 and 2.6.8 (see Table 3-4; Tables 3-1 and 3-6 for details). Determinations of S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, and Pb were performed by Dr. Andriy Cheburkin using XRF Spectrometry. The quality control schemes using XRF Spectrometry can be found elsewhere (Cheburkin and Shotyk, 1996; Cheburkin and Shotyk, 2005).

### 3.6.3 Determination of Selected Elements Using XRF Spectrometry

In Table 3-10 results for the determination of selected elements in the internal peat reference material using XRF Spectrometry are displayed.

**Table 3-10.** Determination of Elements using XRF Spectrometry [mg $kg^{-1}$].

| Element | LOD | Peat $3_{oven}$ | Peat $3_{freeze}$ | Average | Peat $4_{oven}$ | Peat $4_{freeze}$ | Average |
|---|---|---|---|---|---|---|---|
| S | 150 | 1891 | 1473 | 1680 ± 300 | 1098 | 1069 | 1080 ± 20 |
| Cl | 100 | 631 | 692 | 660 ± 40 | 917 | 1228 | 1070 ± 220 |
| K | 15 | 691 | 519 | 600 ± 120 | 229 | 201 | 215 ± 20 |
| Ca | 10 | 2576 | 2234 | 2410 ± 200 | 2034 | 2214 | 2120 ± 130 |
| Ti | 1.5 | 396.9 | 252.9 | 330 ± 100 | 145.0 | 120.6 | 133 ± 17 |
| Cr | 1.0 | 6.5 | 4.5 | 5 ± 1 | 2.8 | 2.1 | 2.4 ± 0.5 |
| Mn | 0.9 | 17.8 | 16.3 | 17 ± 1 | 9.8 | 9.6 | 9.7 ± 0.1 |
| Fe | 5 | 1720 | 1877 | 1800 ± 100 | 508 | 625 | 567 ± 83 |
| Ni | 2.5 | 7.7 | 3.2 | 5 ± 3 | 1.4 | 2.9 | 2 ± 1 |
| Cu | 2 | 6.1 | 4.4 | 5 ± 1 | 2.4 | 6.0 | 4 ± 2 |
| Zn | 1.5 | 31.7 | 34.5 | 33 ± 2 | 7.0 | 10.3 | 9 ± 2 |
| As | 1 | 4.4 | 3.7 | 4 ± 1 | < 1 | < 1 | |
| Se | 0.6 | < 0.6 | < 0.6 | | < 0.6 | < 0.6 | |
| Br | 0.6 | 43.5 | 46.8 | 45 ± 2 | 59.8 | 64.2 | 62 ± 3 |
| Rb | 0.7 | 3.3 | 3.6 | 3.5 ± 0.2 | 0.9 | 1.4 | 1.2 ± 0.3 |
| Sr | 1 | 18.1 | 15.4 | 17 ± 2 | 14.8 | 15.3 | 15.1 ± 0.3 |
| Zr | 2 | 13 | 9.2 | 11 ± 3 | 2.9 | 2.4 | 2.6 ± 0.4 |
| Pb | 0.6 | 29 | 22.1 | 26 ± 5 | 1.6 | 1.7 | 1.65 ± 0.01 |

Results are consistent in oven and freeze dried peat and vary only within the analytical uncertainty of the XRF Spectrometry method. Therefore our peat preparation procedure (oven drying at 105°C) does not lead to any loss of the elements listed in Table 3-10.

### 3.6.4 Determination of Water Content

To calculate the native As concentration within the internal peat reference materials, firstly the water contents of Peat $3_{fresh}$ and Peat $4_{fresh}$ were determined. For this purpose, varying amounts (10-25 g) of Peat $3_{fresh}$ and Peat $4_{fresh}$, respectively, were weighed to 0.1 mg into PTFE vessels and dried at 105°C to constant weight. Results for the determination of the water content of Peat $3_{fresh}$ and Peat $4_{fresh}$ are displayed in Table 3-11.

**Table 3-11.** Water content of the internal peat reference materials.

| Sample | Average [% $H_2O$] | N[a] |
|---|---|---|
| Peat $3_{fresh}$ | 91.8 ± 0.1 | 7 |
| Peat $4_{fresh}$ | 90 ± 1 | 7 |

[a] Number of sub-samples analysed

### 3.6.5 Determination of Total As Concentrations Using ICP-SF-MS and HG-AFS

As concentrations in the peat samples were determined using ICP-SF-MS and HG-AFS. In Fig. 3-25 results for the determination of As in these peat materials are displayed. A possible loss of As during the drying procedures (freeze drying, oven drying) was not observed. In Table 3-12 results for the determination of As in fresh, freeze dried and oven dried materials are displayed

(see also Fig. 3-25). As concentrations from fresh samples were calculated using the water content as described in section 3.6.4.

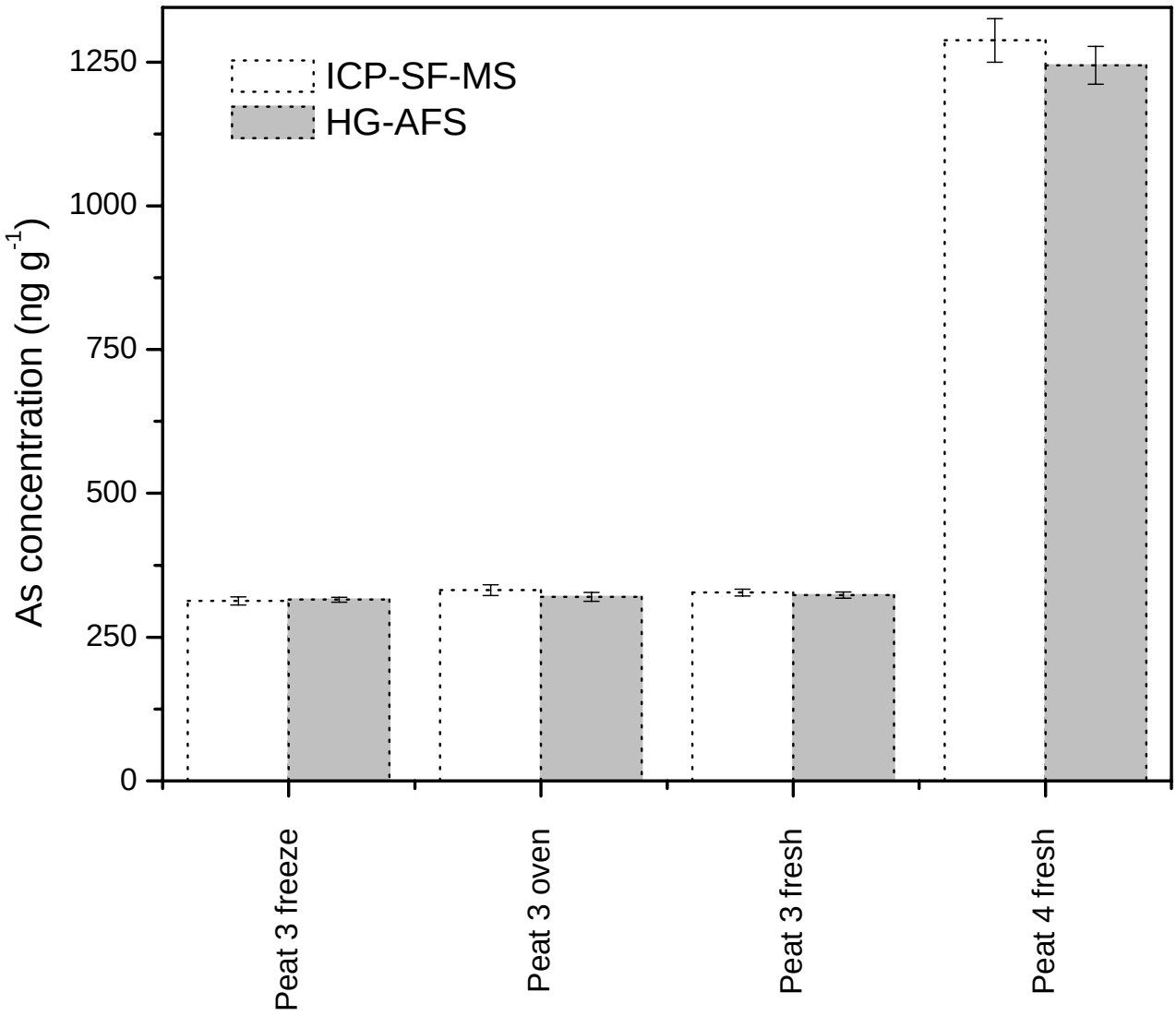



**Fig. 3-25:** Results for the determination of As concentrations within the internal peat reference materials using ICP-SF-MS and HG-AFS. Results for $Peat3_{fresh}$ and $Peat4_{fresh}$ were calculated using water contents (section 3.6.4).

It is obvious (Fig. 3-25, Table 3-12) that both methods lead to nearly identical results. The As concentrations show no significant variations and vary only within the analytical uncertainties of these methods.

**Table 3-12.** Results for the determination of As within the internal peat reference materials

| | ICP-SF-MS [ng $g^{-1}$] | HG-AFS [ng $g^{-1}$] | Overall average [ng $g^{-1}$] |
|---|---|---|---|
| Peat $3_{oven}$ | -[a] | 1290 ± 30 | 1270 ± 20 |
| Peat $3_{freeze}$ | -[a] | 1260 ± 60 | |
| Peat $3_{fresh}$ | 134 ± 4 | 130 ± 4 | |
| Peat $3_{fresh}$ (calculated)[b] | 1290 ± 40 | 1240 ± 30 | |
| Peat $4_{oven}$ | 332 ± 9 | 320 ± 8 | 322 ± 7 |
| Peat $4_{freeze}$ | 313 ± 7 | 315 ± 4 | |
| Peat $4_{fresh}$ | 26.9 ± 0.5 | 26.5 ± 0.5 | |
| Peat $4_{fresh}$ (calculated)[b] | 328 ± 6 | 323 ± 6 | |

[a] not investigated

[b] calculated using the water content as described in section 3.6.4

## 3.6.6 Conclusion

No loss of total element and As concentrations was observed when peat samples were oven or freeze dried, respectively, compared to fresh samples. Investigated total As concentrations for both HG-AFS and ICP-SF-MS measurement were in excellent agreement.

# 3.7 Extraction of As

The aim of this work was to mimic the leaching ability of the natural pore fluids of the peat which are derived exclusively from rainwater and therefore to remove as little of arsenic as possible, using only high purity water as the leachate.

## 3.7.1 Introduction

Traditional sediment fractionation schemes which seek to maximise the amount of metal which can be removed from the solid phase were developed at a time when trace metals could be measured using relatively insensitive methods such as flame and graphite furnace AAS (ppm to ppb concentration range).

Here, an effort was made to take advantage of the extreme sensitivity offered by the detecting power of the ICP – SF - MS (ppt to ppq concentration range), and to remove as little of the As as possible, using only high purity water as the leachate. The strategy being developed is to mimic the leaching ability of the natural pore fluids of the peat which are derived exclusively from rainwater to provide insight into the binding mechanism and fate of As in peat.

Selected peat samples which had already been well characterised and age dated, were extracted with water as described in section 2.6.11.1.

To assess the extraction yield for arsenic, total As concentrations were determined using ICP-SF-MS (section 3.3), HG-AAS (section 3.1) and HG-AFS (section 3.2). Similarly, concentrations of As in the extraction solutions were determined using ICP-SF-MS coupled to the Apex sample introduction system, as described in section 2.5.4.3 and HG-AFS (section 2.5.3).

Based on the total As concentrations in the peat samples, the efficiency of the water extraction procedure was calculated, which should be a regular part of any quality control scheme.

### 3.7.2 Extraction of As from the Internal Peat Reference Materials

The internal peat reference materials were extracted using high purity water as described in section 2.6.11.1 and 2 M orthophosphoric acid as described in section 2.6.11.2. Samples were extracted using mechanical agitation. Extracts were determined for total As concentrations using the Apex sample introduction system coupled to ICP-SF-MS as described in section 2.5.4.3.

Quality control as well as further information about the determination of As concentrations with this setup are described in section 3.4. Results for the determination of total As concentrations within these extracts are displayed in Fig. 3-26. Based on the total elemental concentrations in the peat samples, the efficiency of the water and orthophosphoric acid extraction procedures were calculated (Table 3-13).

**Table 3-13:** Concentrations of As in the water and orthophosphoric extracts as determined using ICP-SF-MS and HG-AFS (water extracts), and HG-AFS ($H_3PO_4$ extracts), respectively.

| | Water | | 2 M $H_3PO_4$ | |
|---|---|---|---|---|
| | Average [ng $g^{-1}$] | Extraction yield [%] | HG-AFS [ng $g^{-1}$] | Extraction yield [%] |
| Peat $3_{oven}$ | 288 ± 9 | 18 | 424 ± 13 | 33 |
| Peat $3_{freeze}$ | 78.07 ± 0.07 | 10 | 214 ± 6 | 17 |
| Peat $3_{fresh}$ | 5.19 ±0.06 | | 14.5 ± 0.6 | |
| Peat $3_{fresh}$ [a] | 49.8 ± 0.6 | 4 | 140 ± 4 | 11 |
| Peat $4_{oven}$ | 59 ± 5 | 23 | 152 ± 5 | 47 |
| Peat $4_{freeze}$ | 32 ± 1 | 6 | 62 ± 3 | 19 |
| Peat $4_{fresh}$ | 2.3 ± 0.2 | | 7.31 ± 0.05 | |
| Peat $4_{fresh}$ [a] | 28 ± 2 | 9 | 89 ± 3 | 28 |
| NIMT Peat | 287 ± 7 | 12 | 552 ± 18 | 23 |

[a] calculated using the water content as described in section 3.6.4

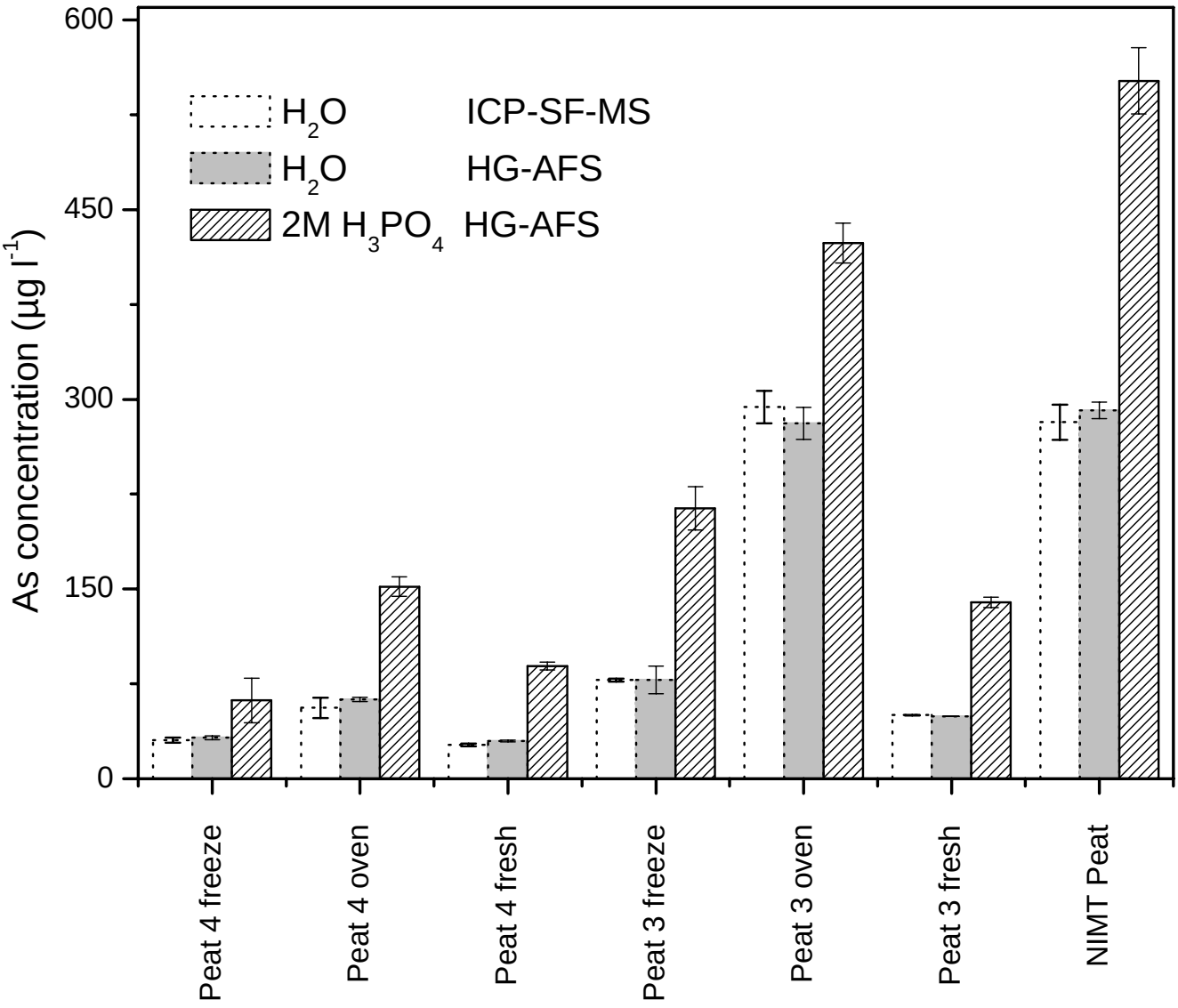



**Fig. 3-26:** Results for the determination of total As concentrations in water and orthophosphoric extracts of the internal peat reference materials and for NIMT peat as determined using ICP-SF-MS and HG-AFS. Results for $Peat3_{fresh}$ and $Peat4_{fresh}$ were calculated using water contents (section 3.6.4).

Mechanical agitation is known to provide better extraction yields in comparison to sonication (Kuehnelt, 2000). The reason could be caused by the longer agitation time and/or by the better mixing by rotation. Better mixing of extractant and sample might favour the interchange of species between the two media. Moreover sonication can lead to self-heating of the samples, which could disturb the thermodynamically equilibrium. The longer time dependence using mechanical agitation is negligible, as samples were extracted over night.

2 M orthophosphoric acid was also chosen as extractant as it is known to extract more arsenic than formic acid or methanol/water mixtures from soil samples, and to provide a quick check if the extraction efficiency increases when orthophosphoric acid is chosen. Additionally, methanol, is a poor solvent for extracting inorganic arsenicals, and hence is not suitable for samples containing such species (Francesconi and Kuehnelt, 2004).

However, the main goal of this study was to mimic the leaching ability of the natural pore fluids. Additionally, nearly all the naturally occurring arsenic species identified so far are polar and very water-soluble and they would mostly favour water over methanol as an extraction solvent. This is particularly true for the arsenosugars, some of which are very polar. For these reasons, the best general solvent for extracting arsenic species is probably water, provided it can penetrate the sample matrix. Even reported methods using methanol, which might extract some non-polar arsenic, include a step to remove the methanol and redissolve the residue in water prior to analysis. Non-polar arsenicals would be "lost" at this stage (Francesconi and Kuehnelt, 2004).

As shown in Fig. 3-26, results for the determination of As in water extracts using ICP-SF-MS and HG-AFS are in excellent agreement.

When samples were extracted using high purity water, about 10-20% of the As were extracted (Table 3-13). The extraction yields for fresh and freeze dried samples were low (Peat $3_{fresh}$, Peat $3_{freeze}$: 4, 10%; Peat $4_{fresh}$, Peat $4_{freeze}$: 9, 6%, see Table 3-13) whereas the extraction yields for oven dried samples were significantly higher (Peat $3_{oven}$: 23%; Peat $4_{oven}$: 18%). The reason for the higher extraction yields from oven dried samples might be, that the drying process at 105°C, a quite drastic treatment, leads to changes of the sample matrix (formation of agglomerates, the disruption of cells and break up of tissues that should give better access to the extractants, speciation changes in the course of the preparation treatments). Thus the extractant can better penetrate the matrix and therefore higher extraction yields are achieved.

When the internal peat reference materials were extracted with 2M orthophosphoric acid, 10-50% of the total arsenic was transferred from the solid into solution. Therefore, a 1.5-3 times better extraction of arsenic is reached with 2M orthophosphoric acid in comparison with

water as extractant. Hence 2M $H_3PO_4$ appears more efficient than water for the extraction of As probably due to the ability of the acids to break some of the S–As bonds.

### 3.7.3 Extraction of As from Ombrotrophic Peat Bogs from Finland

Fresh and oven dried Finnish peat samples were extracted using only high purity water as described in section 2.6.11.1. Results for the extraction of As concentrations as well as extraction efficiencies are given in Table 3-14. Total As concentrations for Out 2 and Out 5 are average values as determined using HG-AAS, HG-AFS and ICP-SF-MS, respectively (see sections 3 .1, 3.2, for details). As concentrations in the other Out samples (Out 24 - 86, Table 3-14) as well as in the Hie samples were determined using ICP-SF-MS (see section 3.3 for details). As concentrations in the Har core were determined using INAA.

Extracts were determined for total As concentrations using the Apex sample introduction system coupled to ICP-SF-MS as described in section 2.5.4.3. Quality control as well as further information about the determination of As concentrations with this setup are described in section 3.4. Water contents were determined as described in section 2.6.14. The high standard deviations for the determination of As in extracts of some peat samples are due to inhomogenities within these samples, as these high standard deviations were not observed when extracts of the internal peat reference materials were determined using HG-AFS and the Apex ICP-SF-MS setup (Table 3-13). Unfortunately it was not possible to provide cryogenic milling to the investigated samples, due to the high costs associated with this sample preparation procedure. Therefore frozen samples were only homogenised mechanically before extraction. However, as shown in Table 3-14 cryogenic milling would be desirable.

Extraction yields from oven dried samples (Out 33, Hie 18, Har 12) were higher than extraction yields from fresh samples. This finding is consistent with the extraction yield of the fresh, freeze dried and oven dried internal peat reference materials (possible explanations are given in section 3.7.2).

**Table 3-14:** Concentrations of As and extraction efficiencies in the water extracts of selected Finnish peat samples (see text for details).

| | | Total As[a] [ng $g^{-1}$] | As extracted [ng $g^{-1}$] | Water content[b] [%] | Extraction yield [%] |
|---|---|---|---|---|---|
| Outokumpu | Out $2_{fresh}$ | 218 ± 6 | 0.6 ± 0.1 | 94.3 ± 0.5 | 4.6 |
| | Out 5 $_{fresh}$ | 372 ± 6 | 0.5 ± 0.1 | 94.2 ± 0.4 | 2.5 |
| | Out 24 $_{fresh}$ | 1590 ± 40 | 1.0 ± 0.1 | 93.5 ± 0.4 | 0.9 |
| | Out 33 $_{fresh}$ | 1480 ± 40 | 1.32 ± 0.04 | 93 ± 1 | 1.3 |
| | Out 33 $_{oven}$ | 1480 ± 40 | 145 ± 23 | | 10 |
| | Out 83 $_{fresh}$ | 130 ± 5 | 0.40 ± 0.03 | 87.5 ± 0.9 | 2.5 |
| | Out 86 $_{fresh}$ | 131 ± 3 | 0.50 ± 0.05 | 88.4 ± 0.3 | 3.6 |
| Hietajärvi | Hie $2_{fresh}$ | 250 ± 20 | 0.83 ± 0.01 | 93.3 ± 0.8 | 5.0 |
| | Hie 4 $_{fresh}$ | 720 ± 20 | 1.03 ± 0.02 | 92 ± 1 | 1.9 |
| | Hie 16 $_{fresh}$ | 2140 ± 50 | 1.2 ± 0.2 | 91.4 ± 0.9 | 0.7 |
| | Hie 18 $_{fresh}$ | 1850 ± 30 | 1.0 ± 0.1 | 92.5 ± 0.5 | 0.7 |
| | Hie 18 $_{oven}$ | 1850 ± 30 | 23 ± 2 | | 1.2 |
| | Hie 53 $_{fresh}$ | 271 ± 6 | 0.54 ± 0.04 | 91.8 ± 0.6 | 2.6 |
| | Hie 78 $_{fresh}$ | 158 ± 8 | 0.31 ± 0.01 | 88.8 ± 0.5 | 1.8 |
| | Hie 80 $_{fresh}$ | 181 ± 6 | 0.43 ± 0.11 | 89.6 ± 0.6 | 2.2 |
| Harjavalta | Har 2 $_{fresh}$ | 3700 | 9 ± 2 | 92.9 ± 0.7 | 3 |
| | Har 5 $_{fresh}$ | 4500 | 14 ± 4 | 90.98 ± 0.04 | 4 |
| | Har 12 $_{fresh}$ | 7900 | 43 ± 6 | 92.5 ± 0.03 | 7 |
| | Har 12 $_{oven}$ | 7900 | 1740 ± 80 | | 22 |
| | Har 14 $_{fresh}$ | 8000 | 86 ± 7 | 91 ± 2 | 12 |
| | Har 36 $_{fresh}$ | 1500 | 2.7 ± 0.8 | 92.4 ± 0.8 | 2.4 |
| | Har 70 $_{fresh}$ | 400 | 2.6 ± 0.5 | 92 ± 2 | 8 |
| | Har 72 $_{fresh}$ | 700 | 2.4 ± 0.4 | 92 ± 4 | 4.1 |

[a] Total As concentrations for the Outokumpu and Hietajärvi samples were determined using ICP-SF-MS. Total As concentrations for the Harjavalta core were determined using INAA.

[b] The water content was determined as described in section 2.6.14.

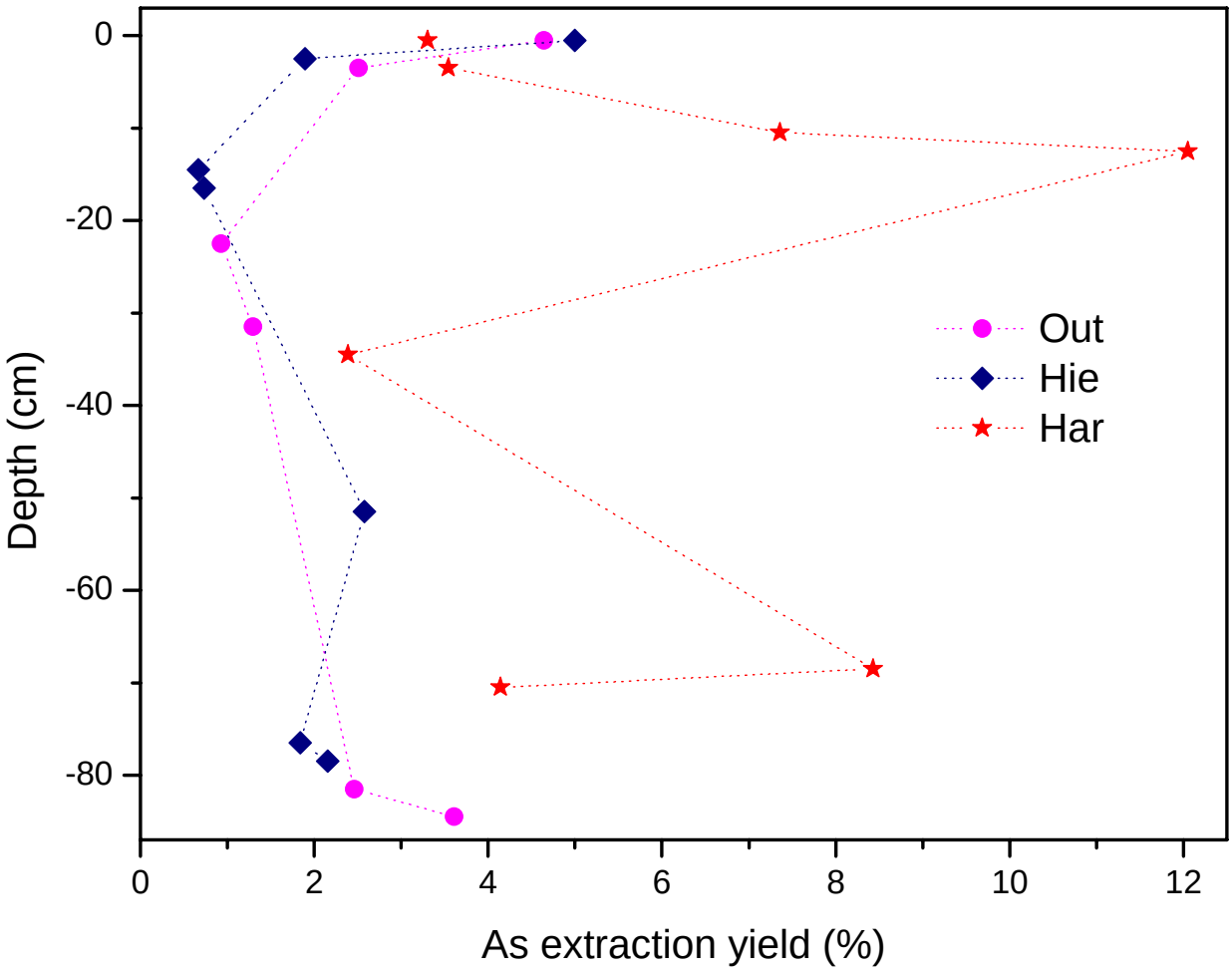



**Fig. 3-27:** As extraction yield of water extracts from selected fresh Finish peat samples as determined using ICP-SF-MS in combination with the Apex sample introduction system in correlation with depth (see text for explanation).

### 3.7.4 Conclusion

As for solid peat (section 3-3) once again, the Outokumpu and the Hietajärvi core look similar and provide similar extraction yields, whereas extraction yields for the Harjavalta core differ. This fact together with the low extraction yields from fresh samples further consolidates the findings that arsenic is well retained within the peat samples.

# 3.8 Determination of Arsenic Species Using HPLC-ICP-SF-MS

The aim of the speciation of As from water extracts (the reason for using only high purity water as extractant is given in section 3.7) of the peat cores was to show which As species are predominant in the peat column, if their distribution changes with the depth and how the species may be preserved. To gain more information about the geochemical cycle of As, it is imperative to find out which are the dominant As species in the peat cores, how their abundance changes in the oxic and anoxic peat layers, and to discuss possible mechanisms for the preservation of this As species in the peat bogs.

## 3.8.1 Introduction

To understand the fate of arsenic, it is essential to quantify not only the total concentrations, but also the concentrations of individual species of As.

The separation of all available arsenic species that may be cationic, anionic, or uncharged depending on the pH of the mobile phase is not possible on a cation-exchange, on an anion-exchange, or a reversed-phase column. On an anion-exchange column the cationic and uncharged species leave the column largely unseparated with or close to the solvent front. The anionic and uncharged species suffer a similar fate on a cation-exchange column. On a reversed-phase column only species with a charge opposite to the charge of the ion-pairing reagent will be separated. Consequently, a solution containing several arsenic species must be chromatographed on more than one column for the identification of all arsenic species.

A universal extractant for all arsenic species does not exist. Extractants should be "fitted" at least to the organic arsenic species, to the acid-soluble arsenates, and to the acid-insoluble arsenides and arsenic sulfides (Kuehnelt, 2000). Arsenic species should be extracted without decomposition or chemical conversion.

High-performance liquid chromatography (HPLC) is a powerful separation method which requires only small amounts of sample and can easily be connected to most detection systems.

In this work anion-exchange chromatography was employed for the separation of the arsenic species. On the Hamilton PRP-X100 column arsenous acid, arsenic acid, methylarsonic acid, and dimethylarsinic acid can be separated. Arsenobetaine has almost the same retention time as arsenous acid. Tetramethylarsonium iodide and arsenocholine, species that are cationic irrespective of pH, leave the column with the solvent front. Arsenous acid can only be determined in the absence of the cationic arsenic species arsenobetaine, trimethylarsine oxide, arsenocholine, and the tetramethylarsonium cation whose signals would overlap the signal for arsenous acid.

#### 3.8.1.1 Investigated Arsenic Species

Since there exist several different arsenic species for most of the arsenic species, this species should be named differently.

For the discussion of arsenic species investigated in this work only one name will be employed for each arsenic compound in the following sections (Table 3-15). Arsenous acid, arsenic acid, and methylarsonic acid can be neutral or anionic, dimethylarsinic acid cationic, neutral, or anionic, arsenobetaine cationic or zwitterionic depending on the pH (Frank, 2001). The following names will be used for the arsenic species:

**Table 3-15**. Names and abbreviations of the arsenic species.

| Name | Species | Abbreviation |
|---|---|---|
| Arsenous acid | for $H_3AsO_3$ and its anions | As(III) |
| Arsenic acid | for $H_3AsO_4$ and its anions | As(V) |
| Methylarsonic acid | for $CH_3AsO_3H_2$ and its anions | MA |
| Dimethylarsinic acid | for $(CH_3)_2AsO_2H$, its cation and its anion | DMA |
| Arsenobetaine | for $(CH_3)_3As^+CH_2COO^-$ and its cation | AB |

### 3.8.1.2 Acid Dissociation Constants of Arsenic Species

The acid dissociation constant, $K_a$, is the equilibrium constant for a dissociation reaction. For the generic acid dissociation reaction with water

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

the acid dissociation equilibrium constant is the mathematical product of the equilibrium concentrations of the products of this reaction divided by the equilibrium concentration of the original acid.
The $K_a$ value is defined by the following equitation:

$$K_a = \frac{[H_3O^+]\cdot[A^-]}{[HA]}$$

The degree of dissociation of most arsenic species is strongly influenced by the pH. Exceptions are the permanent cations arsenocholine and the tetramethylarsonium cation. The degree of ionisation at a specific pH depends on the $pK_a$ values of the compound. The $pK_a$ value, which is defined by the following equitation, is the negative decadic logarithm of the $K_a$ value.

$$pK_a = - \log K_a$$

The $pK_a$ values of the investigated arsenic species are given in Table 3-16.

**Table 3-16:** $pK_a$ values of arsenic species (adapted from Frank, 2001; Kuehnelt, 2000).

| Compound | Species | pKa |
|---|---|---|
| *anionic:* | | |
| Arsenous Acid | $H_3AsO_3 \leftrightarrow H_2AsO_3^- + H^+$ | 9.2 |
| | $H_2AsO_3^- \leftrightarrow HAsO_3^{2-} + H^+$ | 13.5 |
| | $HAsO_3^{2-} \leftrightarrow AsO_3^{3-} + H^+$ | 14.0 |
| Arsenic Acid | $H_3AsO_4 \leftrightarrow H_2AsO_4^- + H^+$ | 2.3 |
| | $H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+$ | 6.7 |
| | $HAsO_4^{2-} \leftrightarrow AsO_4^{3-} + H^+$ | 11.6 |
| MA | $CH_3AsO_3H_2 \leftrightarrow CH_3AsO_3H^- + H^+$ | 3.6 |
| | $CH_3AsO_3H^- \leftrightarrow CH_3AsO_3^{2-} + H^+$ | 8.2 |
| DMA | $(CH_3)_2As^+O_2H_2 \leftrightarrow (CH_3)_2AsO_2H + H^+$ | 1.3 |
| | $(CH_3)_2AsO_2H \leftrightarrow (CH_3)_2AsO_2^- + H^+$ | 6.2 |
| *cationic:* | | |
| AB | $(CH_3)_3As^+CH_2COOH \leftrightarrow (CH_3)_3As^+CH_2COO^- + H^+$ | 2.2 |

Species distribution diagrams (percentage of the different species plotted versus the pH) are useful to obtain information about the species present in solution at a certain pH value. Fig. 3-28 shows the species distribution diagrams of arsenous acid, arsenic acid, methylarsonic acid, dimethylarsinic acid, and arsenobetaine at pH values from 0 to 14.

Arsenous acid, arsenic acid, methylarsonic acid and dimethylarsinic acid will deprotonate with increasing pH and become negatively charged.

Arsenous acid is present as the undissociated acid in acidic solutions and in solutions not exceeding pH 8.

Arsenic acid has three acidic protons with corresponding $pK_a$ values of 2.3, 6.7 and 11.6. The major species in solution at the pH range of the Finish peat bogs (pH ~ 3.4 - 4.1) is $H_2AsO_4^-$, but also the undissociated acid is present (Fig. 3-28). At this pH value, methylarsonic acid appears as nearly aequimolar mixture of $CH_3AsO_3H^-$ and $CH_3AsO_3H_2$ (Figure 3-28). Dimethylarsinic acid is mainly uncharged at the pH of the Finish peat bogs. Arsenobetaine is mainly present as $(CH_3)_3As^+CH_2COO^-$ with an abated contribution of $(CH_3)_3As^+CH_2COOH$. Above pH 4.2 it is zwitterionic [$(CH_3)_3As^+CH_2COO^-$].

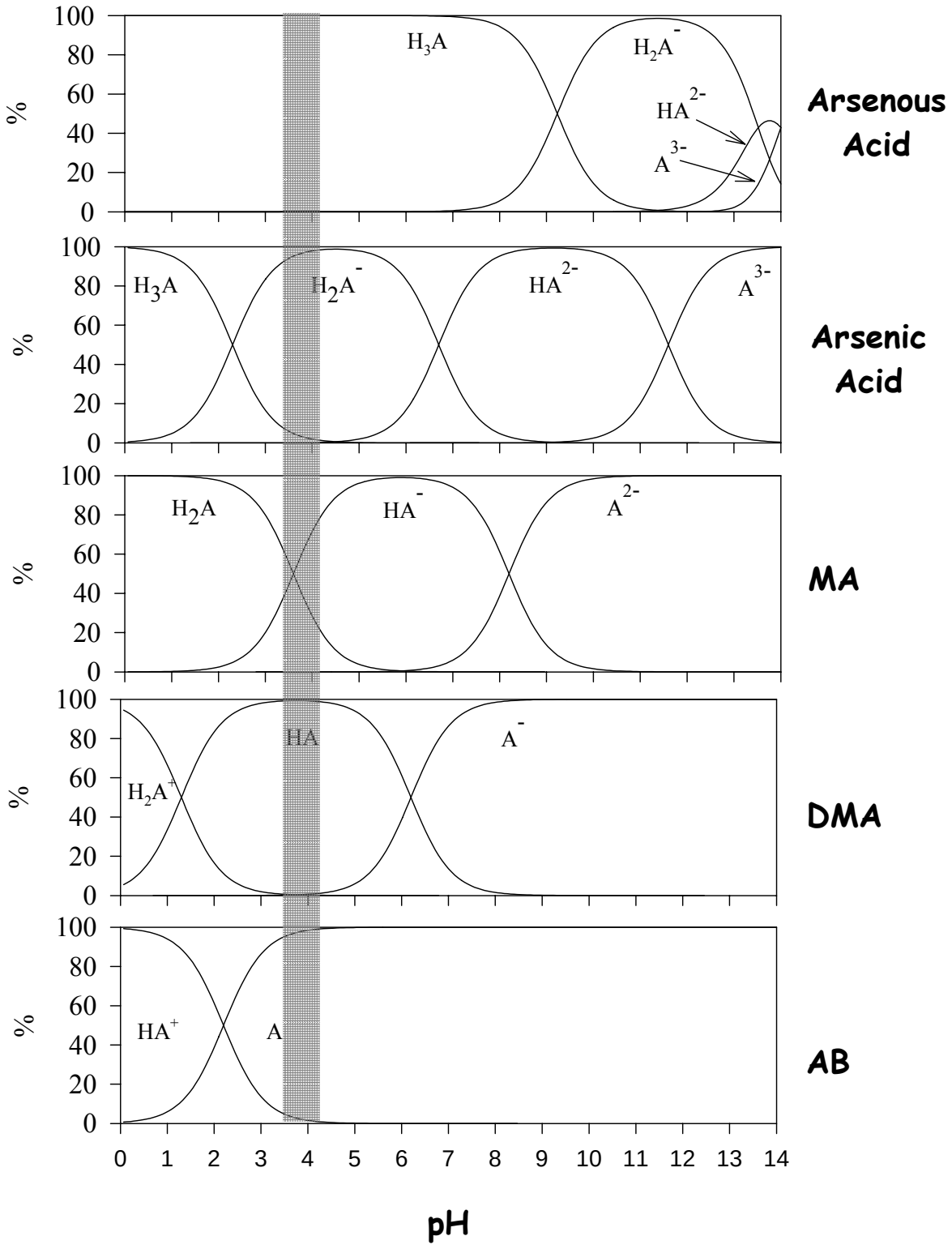



**Fig. 3-28:** Species distribution diagrams of arsenous acid, arsenic acid, MA, DMA and AB in the pH-range from 0 to 14 (the shaded pH range represents the ph values of the Finish peat bogs, adaptet from Kuehnelt, 2000; Frank, 2001).

### 3.8.1.3 Apparent Charge

The apparent charge ($Z_a$) is very useful to describe the charge of a compound at a certain pH. The apparent charge is defined by eqn. IX.

$$Z_a = \frac{\sum_{i=1}^{n} z_i [A_i]}{\sum_{i=1}^{n} [A_i]}$$

$z_i$: charge of species $A_i$

$[A_i]$: concentration of species $A_i$

n: number of species

The apparent charge of a compound is the average charge, which one molecule of this compound has, if the distribution of the different species of this compound in solution is considered.

In Fig. 3-29 the apparent charge of the arsenic species is plotted versus the pH. So the average charge of a compound at a certain pH can be easily estimated.

At a pH value of ~ 1 for arsenous acid, arsenic acid, and methylarsonic acid, and at a pH level of ~ 2.6 for methylarsonic acid, the four arsenic species are present in solution as neutral, fully protonated molecules. With increasing pH, they will deprotonate and thus get negatively charged (Frank, 2001).

Arsenous acid is present as neutral $H_3AsO_3$ and therefore uncharged at the pH value of the Finish peat bogs (Figure 3-29). Dimethylarsinic acid and arsenobetaine are also uncharged at these pH values. Arsenic acid and methylarsonic acid have apparent charges of ~1.0 and ~0.5 to ~0.7, respectively, at these pH values (Figure 3-29).

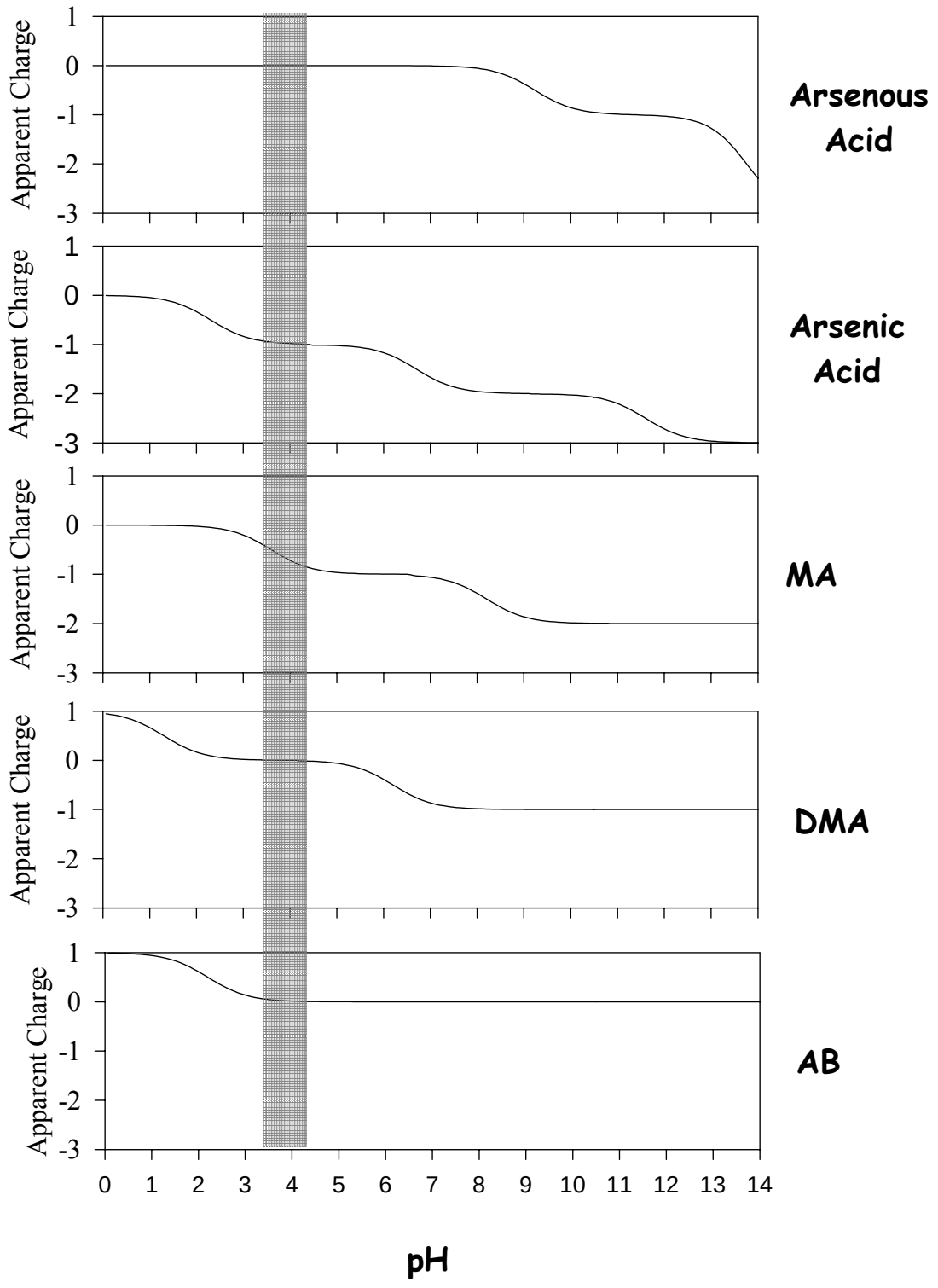



**Fig. 3-29:** Apparent charges of arsenous acid, arsenic acid, MA, DMA and AB (the shaded pH range represents the ph values of the Finish peat bogs, adaptet from Kuehnelt, 2000; Frank, 2001).

### 3.8.1.4 Chromatographic Behaviour of the Arsenic Species on the PRP-X100 Anion Exchange Column

In ion-exchange chromatography charged species in the sample are separated because of their different interaction with the charged functional groups of the stationary phase (Frank, 2001). A Hamilton PRP-X100 anion-exchange column was used for the separation of the arsenic species.

The polymeric packing of the Hamilton PRP-X100 anion-exchange column (25 cm x 4.1 mm i.d., 10-µm styrene-divinylbenzene particles with trimethylammonium exchange-sites) is stable from pH 1 to 13. The outlet of the PRP-X-100 anion-exchange column was directly connected to the ICP-SF-MS (section 2.5.5) A 20 mM aqueous solution of $NH_4H_2PO_4$ at pH 5.6 was employed as mobile phase (section 2.6.12).

Arsenous acid is present as neutral $H_3AsO_3$ and therefore uncharged at the pH value of 5.6. Therefore the retention time for arsenous acid is independent of the nature of the mobile phase at the investigated pH value and of the concentration of the buffer solution. However, weak, unknown interactions are reported (Gailer, 1996).

Under these conditions, arsenobetaine has almost the same retention time as arsenous acid. Tetramethylarsonium iodide and arsenocholine, species that are cationic irrespective of pH, leave the column with the solvent front. Arsenous acid can only be determined in the absence of arsenobetaine whose signals would overlap the signal for arsenous acid.

Dimethylarsinic acid is mainly uncharged at pH 5.6 but as also $(CH_3)_2AsO_2^-$ is present, thus interaction of the anion with the ammonium groups on the stationary phase will lead to an increase of the retention time.

Methylarsonic acid, principally present as the monoanion at pH 5.6 has an apparent charge of –1.0. As the phosphate mobile phase at pH 5.6 is present as $H_2PO_4^-$ with a small contribution of the species $HPO_4^{2-}$, a competition for the positively charged groups at the surface of the stationary phase between the doubly charged phosphate species, which has a higher affinity, and the monoanion will lead to a shorter retention time than expected (Frank, 2001). Arsenic acid, which is mainly present as $H_2AsO_4^-$ with a small contribution of $HAsO_4^{2-}$ at the investigated pH value will also compete with the dihydrogen - and hydrogenphosphate anions as mentioned above, which will also result in decrease of the retention time (Frank, 2001).

### 3.8.2 Determination of Arsenic Species in the Internal Peat Reference Materials and in Selected Peat Samples from Finland Using HPLC-ICP-SF-MS

Standard mixtures of the arsenic species were chromatographed with 20 mM aqueous solution of $NH_4H_2PO_4$ at pH 5.6 (Fig.3-30) as mobile phase. Arsenous acid, dimethylarsinic acid, methylarsonic acid, the phosphate-arsenoribose, arsenic acid, the sulfonate-arsenoribose, and the sulfate-arsenoribose can be separated with an aqueous 20 mM ammonium phosphate solution at pH 5.6 and a column temperature of 40°C (Raber et al., 2000). Under these conditions arsenocholine, the tetramethylarsonium cation, and trimethylarsine oxide, elute at the solvent front. Arsenous acid, arsenobetaine, and glycerol-ribose migrate almost with the solvent front and are not separated from each other under these conditions (Raber et al., 2000).

The peat samples were extracted as described in section 2.6.11.1 and determined as described in detail in section 2.6.12. In Fig. 3-30, chromatograms of standard solutions containing arsenous acid, arsenic acid, dimethylarsinic acid and methylarsonic acid at concentrations of 0.5, 1.0, 2.0, 5.0, 7.0 and 10 µg As $l^{-1}$ each are shown. The elution order was arsenous acid < dimethylarsinic acid < methylarsonic acid < arsenic acid.

The arsenic species were quantified with external calibration curves containing 0.5, 1.0, 2.0, 5.0, 7.0, and 10 µg As $l^{-1}$ each (Fig. 3-31). Generally, all arsenic species should have the same signal intensity, when an ICP-MS is used as detector. This assumption is valid in most cases. However, when different chromatographic systems are employed, arsenous acid, methylarsonic acid, and dimethylarsinic acid can suffer from signal depression (Falk and Emons, 2000). Such depression effects can be recognized, when mixtures of standard arsenic species are injected. Arsenic species suffering from signal depression on a certain chromatographic system can only be quantified with calibration curves of the particular compound. Arsenic species not suffering from this phenomenon can be quantified also with calibration curves established with other arsenic species (Fig. 3-31).

The water extracts of the Finnish peat bogs and the internal peat reference materials were subjected to anion-exchange HPLC-ICP-SF-MS. Standard solutions of seven arsenic species (arsenous acid, arsenic acid, methylarsonic acid, dimethylarsinic acid, glycerol-, phosphate-, sulfate-, sulfonate-arsenoriboses) were chromatographed to identify and quantify

the arsenic species in the extracts. No glycerol-, phosphate-, sulfonate-, or sulfate-arsenoribose was detected in any of the peat samples (Fig. 3-32).

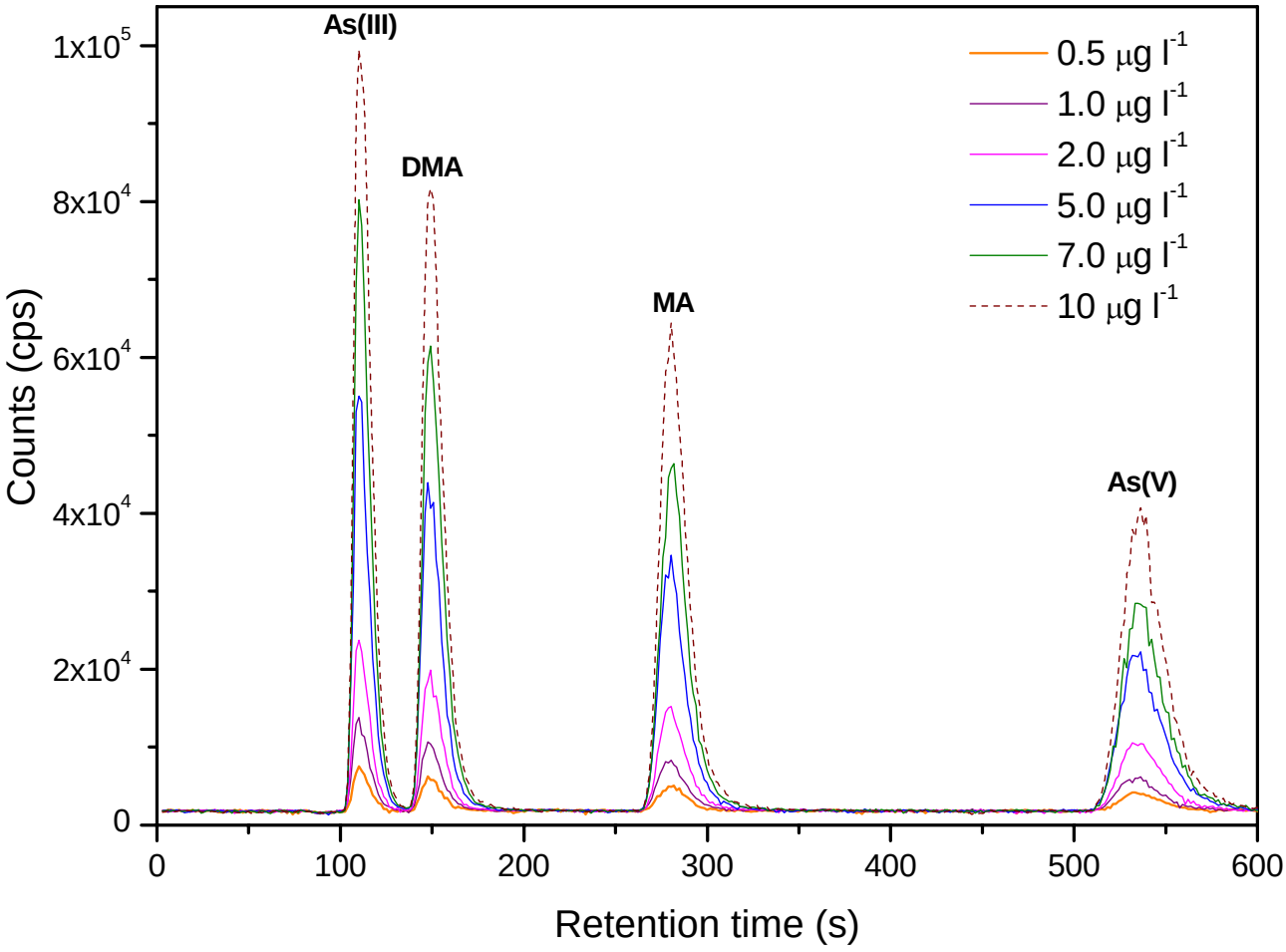



**Fig. 3-30:** Chromatograms of standard solutions containing arsenous acid, arsenic acid, dimethylarsinic acid and methylarsonic acid (Hamilton PRP-X100 anion-exchange column at 40°C, aqueous 20 mM NH4H2PO4 solution at pH 5.6, 100 µL injected, flow rate of 1.5 ml min-[1]) coupled to an ICP-SF-MS as element specific detector).

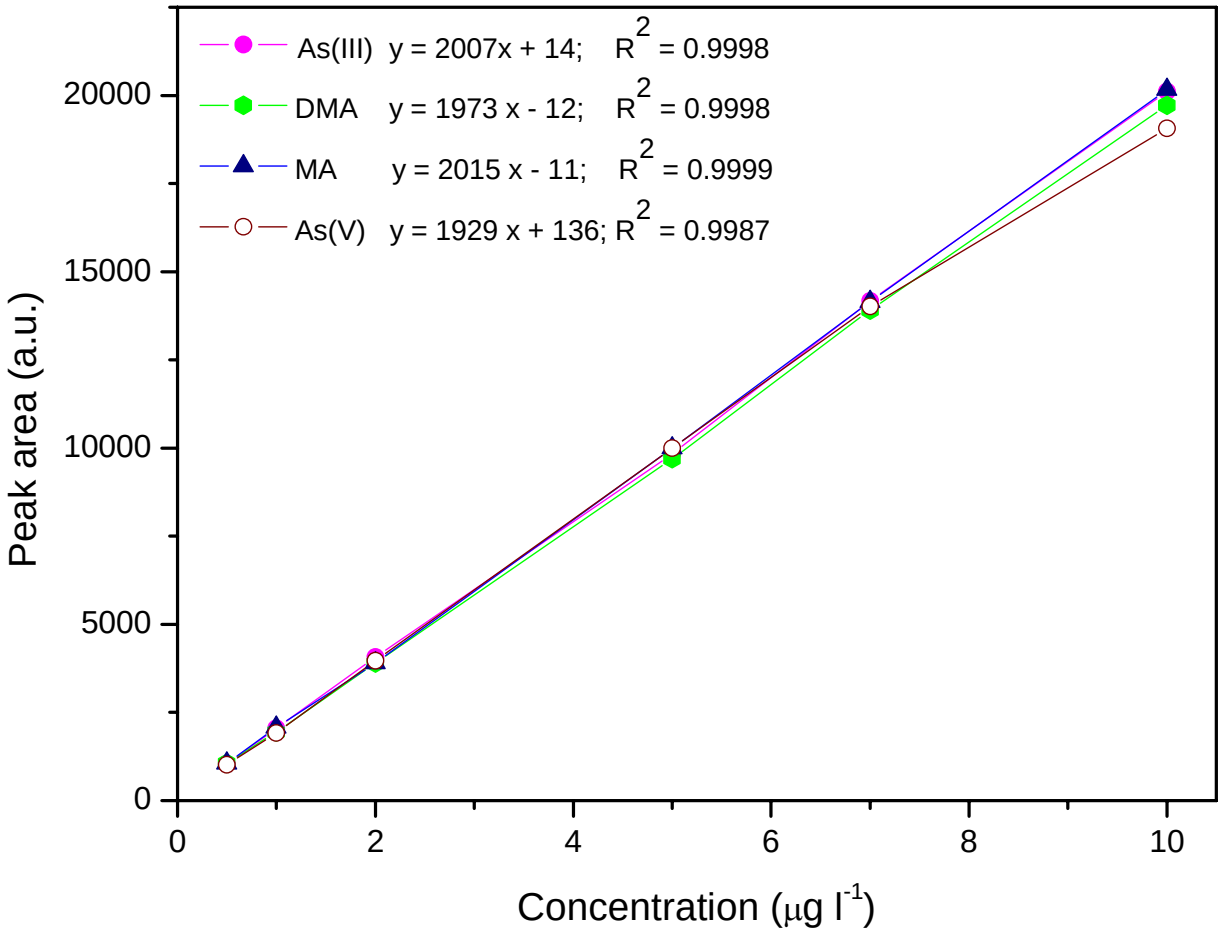



**Fig. 3-31:** Calibration curves of 0.5, 1.0, 2.0, 5.0, 7.0, 10 µg As $l^{-1}$ each, obtained after their chromatographic separation in distilled water on a Hamilton PRP-X100 anion-exchange column (mobile phase 20 mM $NH_4H_2PO_4$ solution at pH 5.6, 100 µL injected, flow rate of 1.5 ml $min^{-1}$, coupled to an ICP-SF-MS as element specific detector).

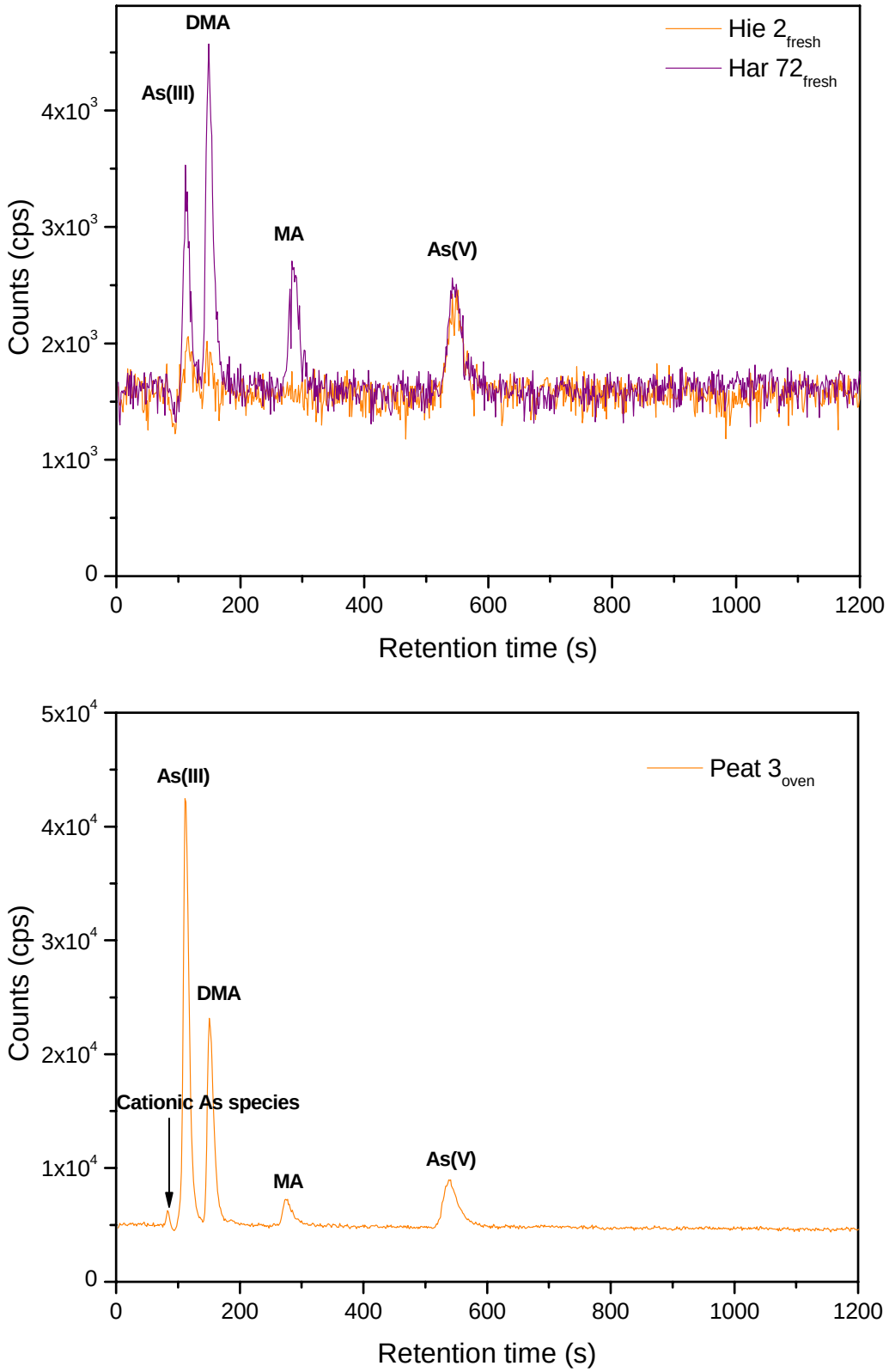



**Fig. 3-32:** Chromatograms of Hie $2_{fresh}$, Har $72_{fresh}$ and Peat $3_{oven}$ (Hamilton PRP-X100 anion-exchange column, aqueous 20 mM $NH_4H_2PO_4$ solution at pH 5.6, 100 µL injected, flow rate of 1.5 ml $min^{-1}$) coupled to an ICP-SF-MS as element specific detector.

### 3.8.2.1 Spiking Experiments

To ascertain the presence of the arsenic species, aliquots of the water extracts (1.5 ml) of selected peat samples (Har $12_{fresh}$, Out $33_{oven}$) were spiked with 7.5, 15, and 30 µl of a solution containing 100 $\mu g l^{-1}$ of arsenous acid, arsenic acid, methylarsonic acid, and dimethylarsinic acid, each (Fig. 3-33).

Although corresponding retention times and especially spiking experiments are a strong hint for the identity of the compound to be determined with a standard compound, they are no absolute proof. However, coincidences observed regarding the retention times of the various arsenic species (Fig. 3-33) increased the certainty of the identification.

The detection limits (3 sigma blank calculated from 5 replicate injections of a 0.5 µg As $l^{-1}$ standard solution) of the HPLC-ICP-SF-MS method as determined in the low resolution mode ($m/\Delta m \sim 300$) were 0.010 µg As $l^{-1}$ for arsenous acid, 0.060 µg As $l^{-1}$ for dimethylarsinic acid, 0.010 µg As $l^{-1}$ for methylarsonic acid and 0.031 µg $l^{-1}$ for arsenic acid (Table 3-17).

**Table 3-17:** Detection limits, relative standard deviations, and reproducibility of the HPLC-ICP-SF-MS determinations (reproducibility calculated from 2 replicate injections of Peat $3_{freeze}$).

| Species | DL [µg $l^{-1}$ As] * | | |
|---|---|---|---|
| As(III) | 0.010 | | |
| DMA | 0.060 | | |
| MA | 0.010 | | |
| As(V) | 0.031 | | |
| Peat $3_{freeze}$ | Area (first Injection) | Area (second Injection) | RSD [%] |
| As(III) | 334.5 | 334.6 | 0.01 |
| DMA | 272.7 | 275.4 | 0.68 |
| MA | 152.8 | 152.9 | 0.10 |
| As(V) | 348.1 | 357.4 | 1.83 |

* 3σ was calculated from a 0.5 µg As/L standard solution

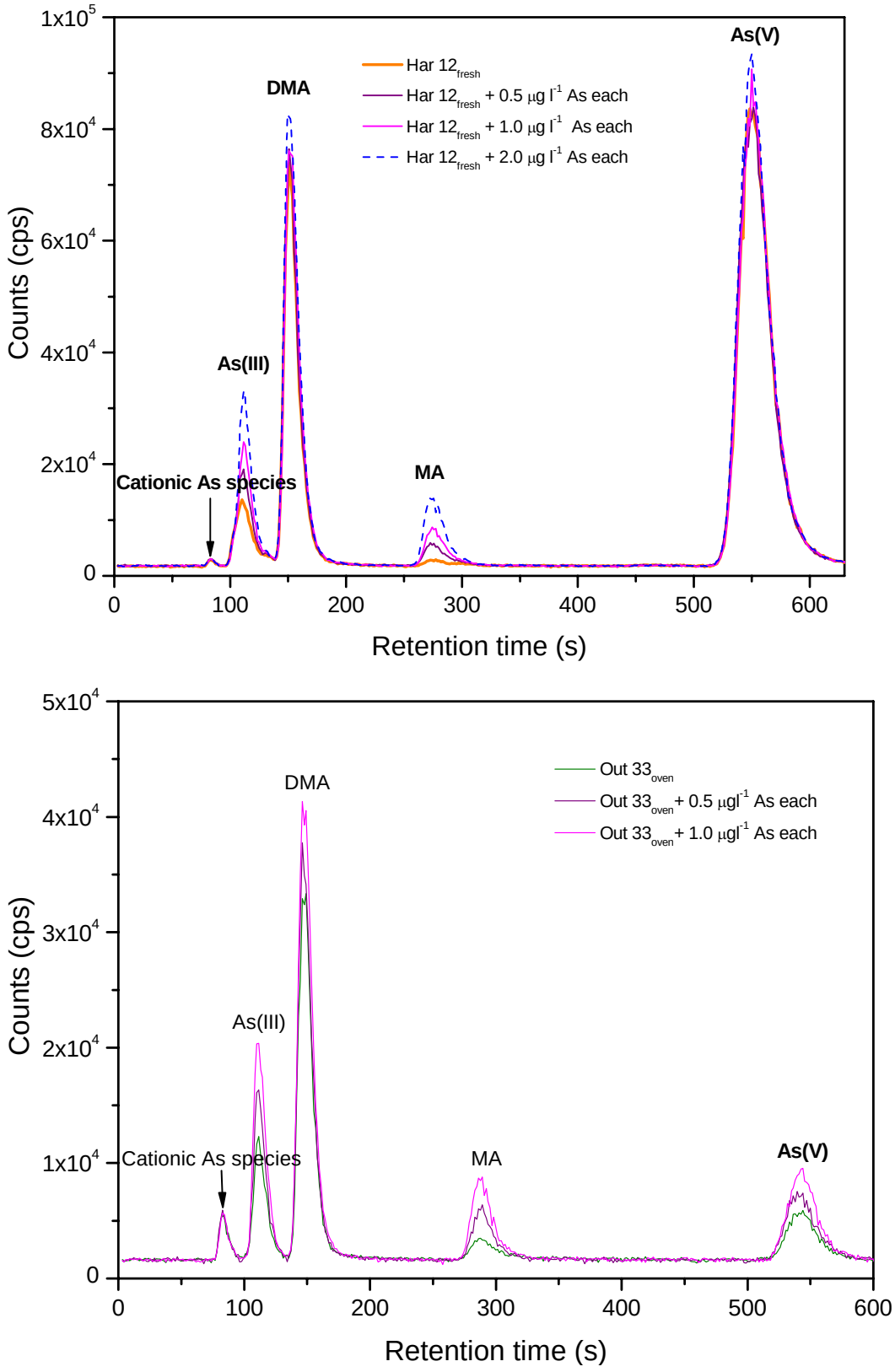



**Fig 3-33:** Water extracts (1.5 ml) of selected peat samples (Har $12_{fresh}$, Out $33_{oven}$) spiked with 7.5, 15, and 30 µl of a solution containing 100 $\mu g l^{-1}$ of arsenous acid, arsenic acid, methylarsonic acid, and dimethylarsinic acid, each.

### 3.8.2.2 Arsenic Species in the Internal Reference Materials and in the Finnish Peat Samples

The results of the HPLC-ICP-SF-MS determinations of the arsenic species in the water extracts of the Finnish peat samples and the internal peat reference materials are summarised in Table 3-18 (HPLC conditions: Hamilton PRP-X100 anion-exchange column, aqueous 20 mM $NH_4H_2PO_4$ solution at pH 5.6, 100 µL injected, flow rate of 1.5 ml $min^{-1}$).

At least two water extracts were prepared for each sample. Generally, the concentrations of arsenous acid, arsenic acid, MA and DMA obtained for the two extracts were in good agreement (in case there were high standard deviations, these are due to inhomogenities within the peat samples).

A small front peak is present in the chromatograms of the water extracts of most peat samples and in the water extracts of all of the prepared internal peat reference materials (Fig. 3-32, Fig. 3-33, Fig. 3-34, and Fig. 3-35) which can be attributed to the presence of cationic arsenic species. The presence of these cationic arsenic species is also responsible that the sum of the concentration of the arsenic species in some peat samples is lower, than the total arsenic concentrations of the water extracts (e.g. Har $12_{oven}$, Table 3-18). However, the sum of the four anionic arsenic species in most peat samples is in reasonable agreement with the total arsenic concentrations of the water extracts (Table 3-18).

Whereas lower concentrations of arsenic are most likely due to undetected arsenic species on a certain chromatographic system, higher concentrations of arsenic found with the external calibration can be attributed to the influence of organic species on the arsenic signal. The ICP-SF-MS signal for elements with first ionization energies between 9 and 11 eV (arsenic 9.81 eV) are enhanced, if organic species are present in the solution (Allain et al., 1991). When arsenic species are extracted, organic species might be co-extracted and therefore cause erroneously high concentrations for arsenic. Contrary, constituents of the matrix co-eluting with arsenic species, can depress the signals for these species (Kuehnelt, 2000).

Quantifications could become impossible without deconvolution of signals, when species with neighbouring signals are present in vastly different amounts. Under these conditions the signals of the species present in small amounts could merge with the signal of the major compound. Fortunately, the signals for the four arsenic species are separated from each other in the chromatograms obtained for all peat samples (Fig. 3-32, Fig. 3-33, Fig. 3-34, and Fig. 3-35).

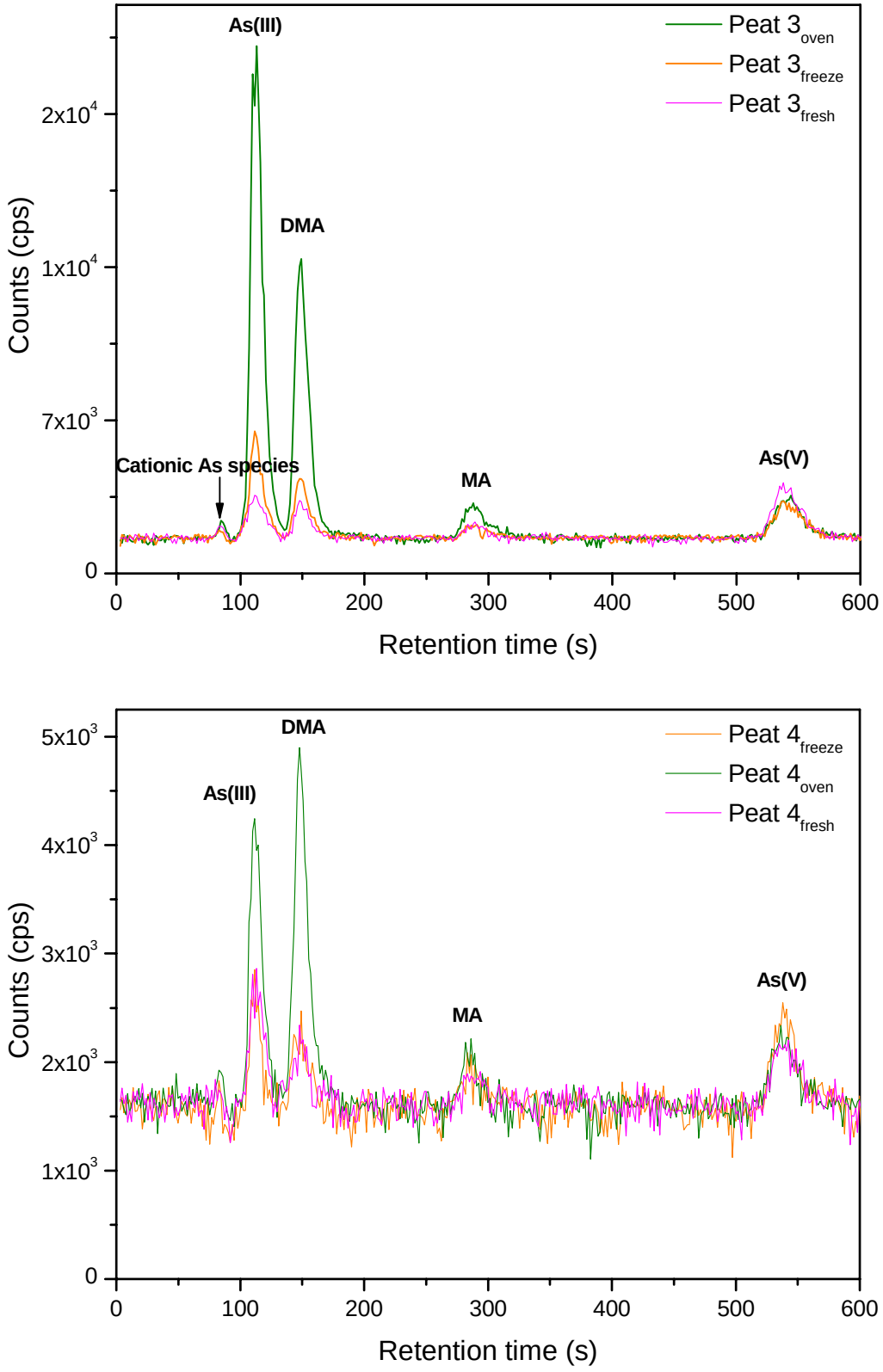



**Fig. 3-34:** Chromatograms of Peat $3_{freeze,\ oven,\ fresh}$ and Peat $4_{freeze,\ oven,\ fresh}$ (Hamilton PRP-X100 anion-exchange column at 40°C, aqueous 20 mM $NH_4H_2PO_4$ solution at pH 5.6, 100 µL injected, flow rate of 1.5 ml $min^{-1}$) coupled to an ICP-SF-MS as element specific detector).

**Table 3-18:** Concentrations of arsenic species from at least two extractions with water in selected Finnish peat samples as well as in the internal peat reference materials as determined by HPLC-ICP-SF-MS (see text for details).

| | As(III) [ng $g^{-1}$] | DMA [ng $g^{-1}$] | MA [ng $g^{-1}$] | As(V) [ng $g^{-1}$] | Sum of species [ng $g^{-1}$] | As extracted[a] [ng $g^{-1}$] |
|---|---|---|---|---|---|---|
| Out $2_{fresh}$ | - | - | - | 0.490 ± 0.002 | 0.5 | 0.6 ± 0.1 |
| Out $5_{fresh}$ | - | - | - | 0.270 ± 0.004 | 0.3 | 0.5 ± 0.1 |
| Out $24_{fresh}$ | 0.023 ± 0.001 | 0.646 ± 0.009 | | 0.35 ± 0.02 | 1 | 1.0 ± 0.1 |
| Out $33_{fresh}$ | 0.20 ± 0.02 | 0.63 ± 0.07 | 0.08 ± 0.02 | 0.47 ± 0.08 | 1.38 | 1.32 ± 0.04 |
| Out $33_{oven}$ | 24.48 ± 0.08 | 93.83 ± 0.04 | 6.417 ± 0.003 | 19.4 ± 0.6 | 144 | 145 ± 23 |
| Out $83_{fresh}$ | 0.09 ± 0.03 | - | - | 0.25 ± 0.02 | 0.34 | 0.40 ± 0.03 |
| Out $86_{fresh}$ | 0.04 ± 0.02 | - | - | 0.178 ± 0.003 | 0.22 | 0.50 ± 0.05 |
| Hie $2_{fresh}$ | 0.16 ± 0.05 | 0.14 ± 0.09 | - | 0.33 ± 0.05 | 0.63 | 0.83 ± 0.01 |
| Hie $4_{fresh}$ | 0.152 ± 0.07 | 0.13 ± 0.02 | - | 0.191 ± 0.007 | 0.47 | 1.03 ± 0.02 |
| Hie $16_{fresh}$ | 0.23 ± 0.02 | 0.5 ± 0.1 | 0.07 ± 0.01 | 0.37 ± 0.02 | 1.1 | 1.2 ± 0.2 |
| Hie $18_{fresh}$ | 0.151 ± 0.003 | 0.43 ± 0.01 | 0.0472 ± 0.0004 | 0.31 ± 0.03 | 0.9 | 1.0 ± 0.1 |
| Hie $18_{oven}$ | 3.6 ± 0.4 | 4.5 ± 0.7 | 1.23 ± 0.03 | 7.5 ± 0.4 | 17 | 23 ± 2 |
| Hie $53_{fresh}$ | 0.07 ± 0.02 | - | - | 0.198 ± 0.008 | 0.27 | 0.54 ± 0.04 |
| Hie $78_{fresh}$ | 0.087 ± 0.005 | - | - | 0.21 ± 0.03 | 0.30 | 0.31 ± 0.01 |
| Hie $80_{fresh}$ | 0.117 ± 0.009 | - | - | 0.18 ± 0.05 | 0.3 | 0.43 ± 0.11 |

| | As(III) [ng $g^{-1}$] | DMA [ng $g^{-1}$] | MA [ng $g^{-1}$] | As(V) [ng $g^{-1}$] | Sum of species [ng $g^{-1}$] | As extracted[a] [ng $g^{-1}$] |
|---|---|---|---|---|---|---|
| Har 2 $_{fresh}$ | 1.3 ± 0.1 | 0.61 ± 0.09 | 0.14 ± 0.08 | 1.24 ± 0.05 | 3 | 9 ± 2 |
| Har 5 $_{fresh}$ | 1.530 ± 0.001 | 1.1 ± 0.2 | 0.11 ± 0.04 | 6.225 ± 0.008 | 9 | 14 ± 4 |
| Har 12 $_{fresh}$ | 1.92 ± 0.05 | 14 ± 4 | 0.12 ± 0.01 | 30 ± 1 | 46 | 43 ± 6 |
| Har 12 $_{oven}$ | 620 ± 10 | 565 ± 3 | 12 ± 3 | 515.35 ± 0.02 | 1717 | 1740 ± 80 |
| Har 14 $_{fresh}$ | 45 ± 3 | 30 ± 5 | 1.9 ± 0.7 | 12 ± 2 | 89 | 86 ± 7 |
| Har 36 $_{fresh}$ | 0.56 ± 0.05 | 0.89 ± 0.02 | 0.76 ± 0.01 | 0.208 ± 0.001 | 2.4 | 2.7 ± 0.8 |
| Har 70 $_{fresh}$ | 0.46 ± 0.04 | 0.48 ± 0.05 | 0.11 ± 0.01 | 0.42 ± 0.07 | 1.5 | 2.6 ± 0.5 |
| Har 72 $_{fresh}$ | 0.4 ± 0.2 | 0.85 ± 0.07 | 0.36 ± 0.02 | 0.42 ± 0.01 | 2.1 | 2.4 ± 0.4 |
| Peat 3$_{oven}$ | 127 ± 4 | 75 ± 2 | 13.15 ± 0.09 | 24.1 ± 0.4 | 240 | 288 ± 9 |
| Peat 3$_{freeze}$ | 32.2 ± 0.1 | 15.85 ± 0.01 | 7 ± 1 | 20.17 ± 0.08 | 76 | 78.07 ± 0.07 |
| Peat 3$_{fresh}$ | 0.75 ± 0.08 | 0.65 ± 0.01 | 0.42 ± 0.02 | 1.66 ± 0.01 | 3 | 5.19 ± 0.06 |
| Peat 4$_{oven}$ | 17.08 ± 0.03 | 21.3 ± 0.3 | 4.3 ± 0.4 | 12.3 ± 0.1 | 55 | 59 ± 5 |
| Peat 4$_{freeze}$ | 9.63 ± 0.05 | 8.475 ± 0.007 | 2.430 ± 0.008 | 10.7 ± 0.1 | 31 | 32 ± 1 |
| Peat 4$_{fresh}$ | 0.607 ± 0.001 | 0.3257 ± 0.0001 | 0.136 ± 0.005 | 1.236 ± 0.004 | 2.3 | 2.3 ± 0.2 |
| NIMT Peat | 55 ± 7 | 34.3 ± 0.3 | 30.4 ± 0.9 | 91 ± 5 | 211 | 287 ± 7 |

[a] Total As concentrations in the extracts were determined using the Apex sample introduction system coupled to ICP-SF-MS (section 3.7.2, Table 3-13, and section 3.7.3, Table 3-14).

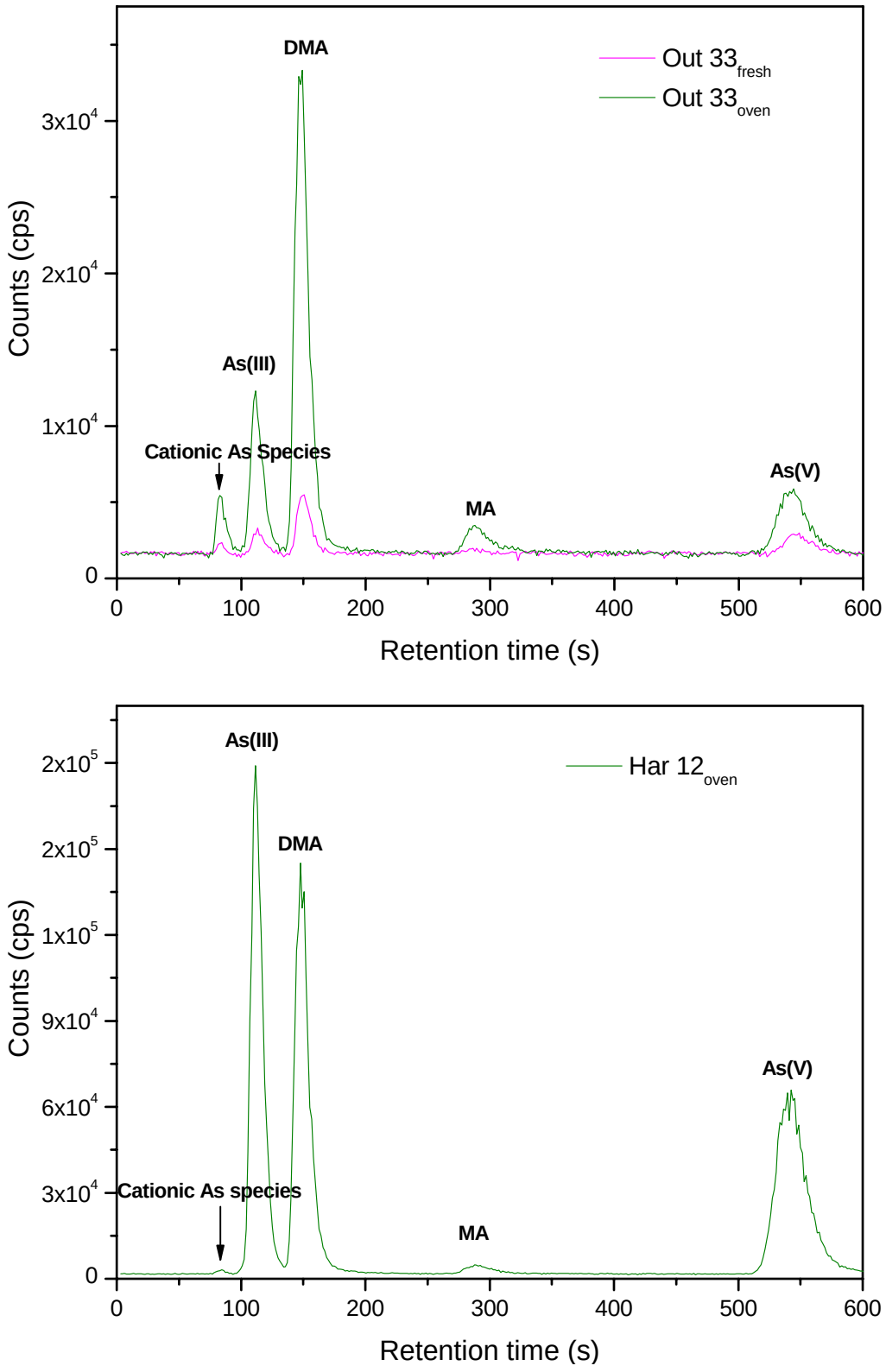



**Fig. 3-35:** Chromatograms of Out $33_{oven,\ fresh}$ and Har $12_{oven}$ (Hamilton PRP-X100 anion-exchange column at 40°C, aqueous 20 mM $NH_4H_2PO_4$ solution at pH 5.6, 100 µL injected, flow rate of 1.5 ml $min^{-1}$) coupled to an ICP-SF-MS as element specific detector).

All water extracts from fresh Finnish peat samples contained arsenic acid (Table 3-18) in the concentration range from 0.1 to 0.5 ng $g^{-1}$ (Out, Hie) and 1 to 12 ng $g^{-1}$ (Har), with one single exception that contained 30 ± 1 ng $g^{-1}$ (Har $12_{fresh}$).

Arsenous acid was present in all fresh Finnish peat samples in concentrations of 0.02 to 4 ng $g^{-1}$ with the exception of Out $2_{fresh}$ and Out $5_{fresh}$, that contained no arsenic acid. The concentration of arsenic acid in Har $14_{fresh}$ (45 ± 3) was significantly higher than the found arsenic acid concentration in the other peat samples from Finland.

Dimethylarsinic acid was present at concentrations of 0.21 to 0.6 ng $g^{-1}$ in the Out and Hie samples, whereas in the Har samples concentrations for dimethylarsinic acid varied from 0.5 to 30 ng $g^{-1}$.

Methylarsonic acid was only detected in one fresh peat sample form the Out core, and only in two fresh peat samples from the Hie core, whereas it was present in all fresh peat samples from the Har core (Table 3-18). These findings are consistent with data reported in the literature: extraction efficiencies and therefore results for As species may change even for different samples of the same organism (Francesconi and Kuehnelt, 2004). The differences between the arsenic species in related plants may be caused by the fact that the plants developed different mechanisms of dealing with arsenic concentrations and/or due to the presence of different species or population of microorganisms. It is also possible that arsenic species present in low concentrations in a certain peat sample are just below the detection limits.

Arsenous acid and methylarsonic acid contributed to 31%, 31% and 7.8%, 7.8% to the sum of the found As species (55 ng $g^{-1}$ for Peat $4_{oven}$; 31 ng $g^{-1}$ for Peat $4_{freeze}$) in Peat $4_{oven}$ and Peat $4_{freeze}$, respectively. In Peat $4_{oven}$ the DMA contributed to 39% and As(V) to 22% to the sum of the found As species, whereas DMA and MA in Peat $4_{freeze}$ contributed to 14% and 54%, respectively. In Peat $4_{fresh}$, As(III), and DMA contributions to the sum of the As species (2.3 ng $g^{-1}$) were lower (26%, 14%, respectively) than in Peat $4_{freeze,oven}$ whereas the As(V) contribution (54%) was significantly higher.

The contribution of As(III), MA, DMA and As(V) in Peat $3_{oven,\ freeze,\ fresh}$ to the sum of the As species was highly variable (53%, 42%, 25% As(III); 31%, 21%, 22% DMA; 5%, 9%, 14% MA; and 22%, 35% and 53% As(V) for Peat $3_{oven,\ freeze,\ fresh}$ respectively.

The effects of light on the stability of As(III) and As(V) in pure water was investigated by Bednar (Bednar et al., 2002). As(V) and As(III) remained unchanged for at least 24 h under both light or dark conditions. After four days, As(V) had been totally converted to As(III)

probably microbially mediated. As the extractants were chromatographed immediately after their extraction, interconversion within the extracts is unlikely.

Dissolution of arsenic species will occur, only when the extractant will penetrate to the components in biota that contain the arsenic species. The extracellular solutions should be accessible to the extractant without difficulty after destruction of the tissues. Consequently, for a quantitative transfer of the arsenic species present in the extracellular and intracellular aqueous solutions, only a break up of the tissue and rupture of the cells is required. Freeze-drying and oven drying before extraction will force the cells to rupture, leading to different extraction yields and therefore also to different contributions of the As species to the extraction yields.

#### 3.8.2.3 Outokumpu

Arsenous acid was present in four of the six investigated water extracts from fresh samples in concentrations of 0.04 to 0.2 ng $g^{-1}$. No arsenous acid was present in the uppermost samples. The sum of As species for these samples is in good agreement with the total extracted As concentrations and varies only within the analytical uncertainties.

DMA is not present in the uppermost and deepest layers of the Out samples, but DMA concentrations in Out $24_{fresh}$ and Out $33_{fresh}$ corresponding to depths of -22.5 and -31.5 cm are higher than the As(III), and As(V) concentrations in these particular samples (Fig. 3-36). MA was only detected in one sample (Out $33_{fresh}$, corresponding to a depth of -31.5 cm, Fig. 3-36).

As(V) was detected in all Out samples, with highest concentrations at the surface and lowest concentrations in the deepest sample. These findings suggest that As is introduced to the peat surface at the Out site mainly as As(V). In deeper samples, the presence of DMA and MA reveals the activity of microorganisms. In deeper layers, the As transformation is stopped, either because the microorganisms transformating As died and/or due to the limited oxygen available. It is also possible that these arsenic species present are just below the detection limits, but more unlikely regarding the fact that the sum of determined arsenic species and the total As concentrations in the water extracts are in good agreement.

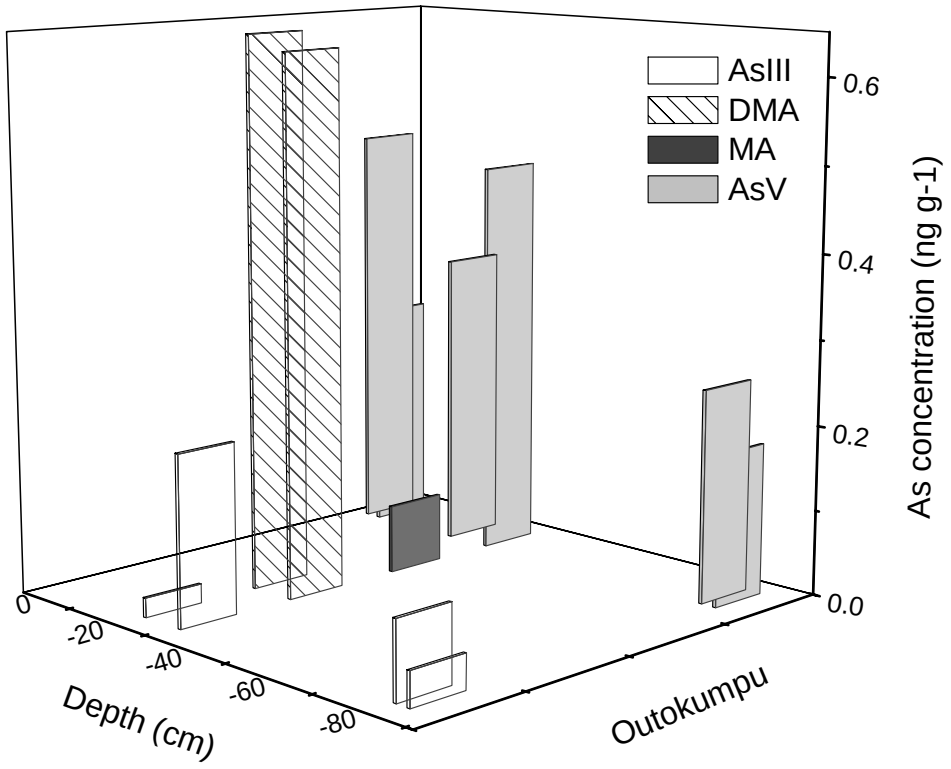



**Fig. 3-36:** Distribution of As species as determined using HPLC-ICP-SF-MS in the Out core in correlation with depth.

### 3.8.2.4 Hietajärvi

Arsenous acid and arsenic acid were present within all investigated Hie samples. As shown in Fig. 3-36, concentrations for As(III) are highest in the uppermost layers and then decrease.

DMA was detected in the uppermost peat samples up to a depth of - 16.5 cm (Hie $18_{fresh}$). As for the Out core, concentrations for DMA for Hie $16_{fresh}$ (-14.5 cm) and Hie $18_{fresh}$ (-16.5 cm) were higher than the concentrations of the other species in these particular samples.

MA was only detected in two samples (Hie $16_{fresh}$ (-14.5 cm) and Hie $18_{fresh}$ (- 16.5 cm)) at very low concentrations ($0.07 \pm 0.01$ and $0.0472 \pm 0.0004$ ng $g^{-1}$, respectively).

As(V) was detected in all Hie samples, with highest concentrations at the surface and lowest concentrations in the deepest sample.

As for solid peat and for pore waters also the distribution of the arsenic species in the Hie and Out core are similar: DMA and MA are not present in the deepest layers of both cores. MA is only present at very low concentrations in both cores.

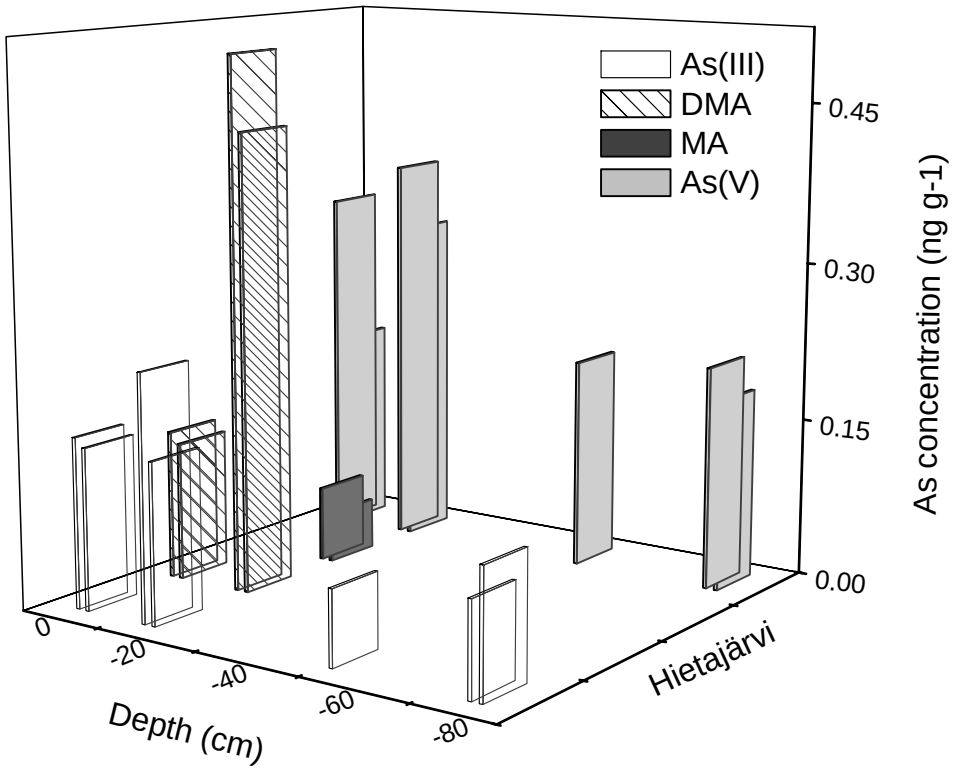



**Fig. 3-37:** Distribution of As species as determined using HPLC-ICP-SF-MS in the Hie core in correlation with depth.

Additionally concentrations for arsenous acid and arsenic acid are low in the deepest layers (Fig. 3-36, Fig. 3-37).

### 3.8.2.5 Harjavalta

In the Har core, arsenous acid, dimethylarsinic acid, methylarsonic acid and arsenic acid were present in all investigated samples. The concentrations of all investigated arsenic species increases from the uppermost layers, reaches a maximum at a depth of - 12.5 cm (Har $14_{fresh}$) with the exception of As(V) that reaches its maximum at a depth of - 10.5 cm (Har $12_{fresh}$) and then decreases.

In contrast to the Out and Hie samples, MA and DMA was detected in all investigated Har samples. Additionally, as mentioned in section 3.8.2.2, a front peak, attributed to cationic arsenic species was present in all of the investigated Har samples.

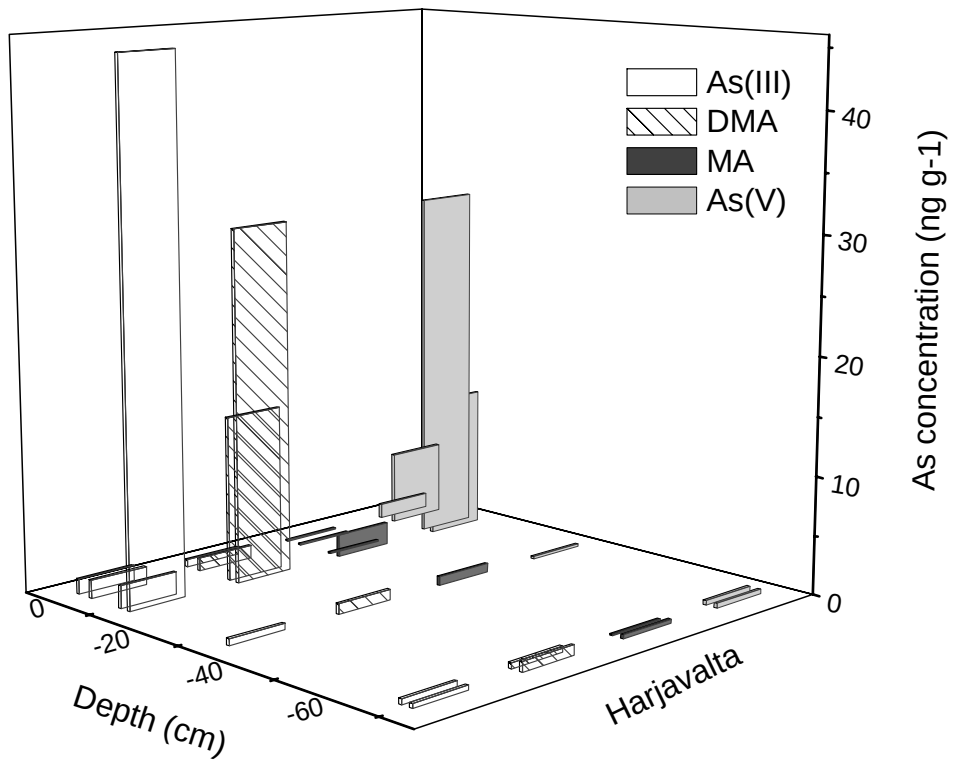


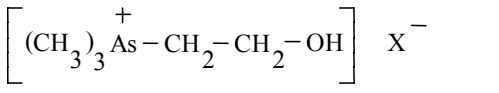

**Fig. 3-38:** Distribution of As species as determined using HPLC-ICP-SF-MS in the Har core in correlation with depth.

The presence of all of the investigated arsenic species in all Har samples, irrespective from depth, may be due to the fact that the Har core is generally less decomposed than the Hie and the Out core. Therefore more oxygen might be available for microorganisms to survive and/or to continue biotransformation of As, also in deep layers of this core. Moreover plant species and/or microorganisms may have developed unique strategies to cope the high As burden (up to 8000 mg $kg^{-1}$ As) deriving from the smelter located in the vicinity of this bog.

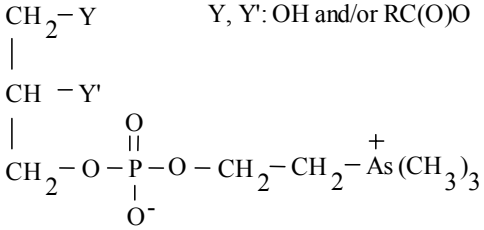
### 3.8.2.6 Possible Mechanisms for As Retention in Ombrotrophic Peat Bogs

Dissolution of the arsenic species from extracts only occurs when an extractant is able to penetrate to the components in biota. The extracellular solutions should be accessible to the extractant without difficulty, whereas the intracellular solutions will come into contact with an extractant only when the membrane is ruptured. Removal of all water will force the cells to rupture. Grinding of the dry material to a fine powder will aid the break up of the biological structures. An extractant should now have easy access to the arsenic species and the extraction should be quantitative.

However, our results indicate, that the arsenic species are only dissolved to relatively small amounts in extra - and intracellular water and could therefore be bonded to insoluble constituents of cells. Hardly anything is known with certainty about such insoluble species. Arsenocholine (Fig. 3-40), the 2-hydroxyethyltrimethylarsonium cation is easily soluble in aqueous systems.



(I)




(II)

**Fig. 3-40**: Structures of arsenocholine (I) and arsenolecithins (II) (Kuehnelt, 2000).

When arsenocholine is bound via an ester-oxygen atom to the phosphorus atom in phosphatitic acid, the resulting arsenic-containing phospholipid, the arsenic-analogue of a lecithin (arsenolecithin) (Irgolic et al., 1977; Bottino et al., 1978), will not be soluble in water and minimally in methanol (Kuehnelt, 2000). Arsenolecithins could be incorporated into cell membranes. Arsenoriboses could be bound to cell surfaces as many other simple and complex carbohydrates are. Other arsenic species (arsenous acid, arsenic acid, methylarsonic acid, dimethylarsinic acid) could be bonded to biopolymers, such as proteins containing amino acids with thiol groups. Reactions of trivalent arsenic species with thiol groups of enzymes are postulated to be the cause of arsenic toxicity. Pentavalent arsenic species can be reduced in vivo to trivalent species (Vather and Envall, 1983), which in turn will react with thiols. The As-S species formed in these reactions are expected to be stable towards hydrolysis and especially stable, when a five-membered heterocycle with the S-As-S group is obtained (Kuehnelt, 2000). Among the arsenic species likely to be present in biota, arsenic-containing sugars (dimethylribosylarsine oxides) and arsenic-containing, fully acylated or partially hydrolized phospholipids (II) could also be present. Moreover the arsenic species could be preserved due to reaction of their functional groups in the following ways.

Arsenous acid is neutral at the pH of the Finnish peat bogs (between pH 3.4 and pH 4.1, Fig. 3-28). No ionic interactions can occur. However, our results indicate that arsenous acid is preserved within ombrotrophic peat bogs. Therefore, other interactions must be responsible for this behaviour. Since arsenous acid contains no alkyl groups, hydrophobic interactions can be excluded. However, the presence of three OH-groups allows the formation of hydrogen bonds. The preservation of arsenous acid might also be explained by these hydrogen bonds.

At pH 3.4 ~15% of arsenic acid are present as uncharged arsenic acid (Fig. 3-28) and ~85% have a charge of –1 resulting in an apparent charge of –0.9 (Fig. 3-29). At a pH of 4.1, $H_2AsO_4^-$ becomes dominant and the apparent charge drops to –1. Thus, arsenic acid could additionally be preserved in the peat due to ionic interaction with cations present in peat, or by the formation of hydrogen bonds.

At pH 3.4 ~60% of methylarsonic acid are uncharged (Fig. 3-28). The percentage of uncharged methylarsonic acid drops to ~25% at pH 4.0 and the negatively charged species becomes dominant. The apparent charge decreases from –0.1 to –0.7 in this pH range (Fig. 3-29). The negatively charged species of methylarsonic acid may form an ion pair with the cations present in peat.

At pH 3.4 DMA is present as uncharged dimethylarsinic acid. This species can interact hydrophobically and form hydrogen bonds. Above pH 4.0 negatively charged $(CH_3)_2AsO_2^-$ ions

are present (Fig. 3-28). They may form ion pairs with cations present in the peat. Additionally, two methyl groups are present, which could interact hydrophobically.

At pH 3.4 and above this pH, arsenobetaine is zwitterionic $(CH_3)_3As^+CH_2COO^-$ and has an apparent charge of 0 (Fig. 3-29). Ion pair formation might be responsible for the preservation of arsenobetaine. In addition to ionic interactions, hydrophobic interactions as well as the formation of hydrogen bonds can also force the preservation of arsenobetaine in peat.

The apparent charge of trimethylarsine oxide decreases from +0.3 [~30% $(CH_3)_3As^+OH$] to 0.1 [90% $(CH_3)_3AsO$], in the pH range of 3.4 to 4.1. Above pH 5.0 trimethylarsine oxide should be neutral (Kuehnelt, 2000). Ionic interactions between the positively charged TMAO molecules and negatively charged groups within the peat might be responsible for the preservation of arsenocholine. Hydrophobic interactions as well as hydrogen bonds can also occur and further increase the preservation. Another possible reason for the preservation of TMAO within peat bogs may be the following interaction (adapted from Kuehnelt, 2000):

However, whether the mechanism postulated above is additionally responsible for the preservation of TMAO within peat bogs cannot be predicted and should be investigated in future work.

Arsenocholine (Fig. 1-2) is a cation irrespective of the pH. Ionic interactions between the positively charged arsenocholine molecules and negatively charged groups within the peat might be responsible for the preservation of arsenocholine. Hydrophobic interactions as well as hydrogen bonds could also occur and further increase the preservation.

The tetramethylarsonium cation (Fig. 1-2) is a cation irrespective of the pH. It shows the same behavior as arsenocholine, within the pH from 3.4 to 4.1.

The apparent charge of arsenocholine and the tetramethylarsonium cation is the same and the same mechanisms should be responsible for the preservation of these two arsenic species. However, the structures of the two species are different (Fig. 1-2). The tetramethylarsonium cation is a tetraedric molecule carrying four $CH_3$ moieties around the

arsenic atom and smaller than arsenocholine, in which one $CH_3$ group is replaced by a $CH_2CH_2OH$ moiety. Therefore, the tetramethylarsonium cation can interact more efficiently and should be better preserved than arsenocholine.

The phosphate-ribose, the sulfonate-ribose, and the sulphate-ribose have one acidic hydrogen atom in the molecule. These riboses should be deprotonated from pH 3.8 to 9.0 (Raber et al., 2000). Thus, ion pair formation, hydrophobically interaction and the formation of hydrogen bonds may occur. The glycerol-ribose should be neutral at the pH of the Finnish peat bogs. However, experiments predict that the dimethylarsinoyl moiety can be protonated at low pH values (pH <5.0, Raber et al., 2000). Phospholipids can be zwitterionic or cationic (Kuehnelt, 2000).

## 3.9 Conclusion and Further Prospects

To date, there is no published record of the changing rates of atmospheric As deposition since industrialisation, for two reasons. First, because of the difficulties associated with the determination of this element at low concentrations in complex matrices. This hampers the determination of the "natural background" As concentrations in samples dating from pre-anthropogenic times. Second, in the case of ombrotrophic peat bogs, it is not yet clear the extent to which these acidic, anoxic, organic-rich archives preserve the changing rates of atmospheric As deposition. The main goal of this study is to address the latter issue.

To do so, there is a real need to develop accurate and sensitive analytical procedures with low detection limits for the determination of As in peat. In this work, several new analytical procedures for the reliable and direct determination of As in nitric acid digests of ombrotrophic peat samples at low ng $l^{-1}$ concentrations were developed (HG-AAS, HG-AFS, ICP-SF-MS). Prior to HG-AAS, HG-AFS and ICP-SF-MS samples were digested with nitric acid in a high-pressure microwave autoclave at 240°C. Additionally the necessity to add tetrafluoroboric acid ($HBF_4$) to the digests to destroy siliceous matter in which As might be hosted, was evaluated. The pre-reduction capabilities of KI/ascorbic acid and L-cysteine for the conversion of As(V) to As(III) using HG-AAS and HG-AFS were critically evaluated. Using KI/ascorbic acid as pre-reductant, the accuracy and precision were poor. Therefore L-cysteine was successfully employed as pre-reductant prior to HG of As. $HBF_4$ was found to interfere with the HG techniques but can be avoided, as As is not hosted in the silicate fraction of the

peat samples. The analytical procedures were critically evaluated by analysing several certified plant and peat reference materials. The newly developed procedures were applied to the determination of As in selected peat samples. Results for As in these peat samples highly correlated underpinning the accuracy of all adopted analytical protocols (HG-AAS, HG-AFS, ICP-SF-MS).

The changing rates of atmospheric As deposition have been reconstructed using peat cores from three bogs in Finland. Whereas the As chronologies for two cores (Out, Hie) are similar, the As chronology of the third core (Har) is different, due to a smelter located in its vicinity. Additionally the As inventories for the last hundred years for Hie and Out are equal whereas the As inventory for the Har core is about 4 times higher. Moreover, accumulation rates agree well with the mining history. Also maximum As concentrations in all three cores date from the same time, despite different depths, suggesting fixation of As in peat.

To confirm the hypothesis that As is well preserved within peat bogs, or to determine the extent of As mobility within these bogs, total As concentrations in pore water samples from the Finish peat bogs were additionally determined using ICP-SF-MS. As for solid peat, pore water concentrations at the Out and Hie site are similar. Only ~ 0.2% of the maximum As concentrations from solid peat could be found in the pore waters of both Hie and Out, respectively. As for solid peat, the Har site tells a different story with maximum As concentrations enriched ~ 2.5 times in comparison to the Out and Hie sites.

To quantify losses of As due to sample handling, internal peat reference materials were prepared. The total As concentrations within these peat reference materials were determined using ICP-SF-MS and HG-AFS. No loss of As concentrations was observed when peat samples were oven or freeze dried, respectively, compared to fresh samples. Investigated total As concentrations for both HG-AFS and ICP-SF-MS measurements were in excellent agreement.

To mimic the leaching ability of the natural pore fluids of the peat which are derived exclusively from rainwater, As was extracted from the Finnish peat bogs using water and the predominant As species were determined using anion-exchange HPLC-ICP-SF-MS. Once again, the Out and the Hie core provided similar extraction yields (0.7-10%), whereas extraction yields for the Har core were higher (3-22%). All water extracts from fresh Finnish peat samples contained arsenic acid with significantly higher concentration ranges found in the Har core. Arsenous acid was present in all fresh Finnish peat samples with two exceptions of the Out core that contained no arsenic acid. Dimethylarsinic acid was the predominant organoarsenic species and present at concentrations of 0.21 to 0.6 ng $g^{-1}$ in the Out and Hie samples, whereas in the Har samples concentrations were higher. Methylarsonic acid was only

detected in one fresh peat sample form the Out core, and only in two fresh peat samples from the Hie core, whereas it was present in all fresh peat samples from the Har core. The identified arsenic species have low molecular masses and have in their molecules functional groups (onium centers, hydroxyl groups, doubly bonded oxygen atoms) that should provide solubility in polar solvents such as water. The low extraction yields of As species from fresh peat bogs together with the low As concentrations in the pore waters indicate, that the arsenic species may react with functional groups of the organic species making up the plant material and thus becoming preserved. Our results further indicate that many of these arsenic species will not be extractable into aqueous solvents (e.g. no arsenoriboses were detected in any of the peat samples).

Arsenoriboses could be bound to cell surfaces. Arsenolecithins could be incorporated into cell membranes. Arsenous acid, arsenic acid, MA and DMA could be bonded to biopolymers, such as proteins containing amino acids with thiol groups.

Optimization of the extraction of the arsenic species is desirable. The more of the total arsenic is extracted from a material the more information about the whole spectrum of arsenic species present is obtained. Thus, extractants other than aqueous solutions must be chosen or hydrolytic reactions must cleave the bonds holding the arsenic species to the biopolymer and release the arsenic species. Therefore, extraction of arsenic species from peat bogs has to be optimized with respect to the matrix. Since no common extractants for all arsenic species in all different kinds of samples exist, this point will still be one of the main research areas in future. Additionally identification of the predominant cationic As species within peat samples is necessary to elucidate the arsenic metabolism in the terrestrial environment, specially when organisms are stressed by high arsenic concentrations in their environment as it is the case at Harjavalta.

For comparison with the peat cores from Finland, peat cores from other regions could provide an independent assessment of the behaviour and fate of As, and help elucidate the hypothesis that As is preserved in the peat column. This could most conveniently be addressed by comparing the chronology of As accumulation in peat profiles from regions where the historical record of anthropogenic emissions is known, as it is true in the case of Outokumpu and Harjavalta. This point is of utmost importance and will not only help to improve our knowledge about the biochemical pathway of arsenic in the environment but will also shade more light into the geochemical cycle of this element.

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**Erklärung gem. § 8 (3) b) und c) der Promotionsordnung der Naturwissenschaftlich-Mathematischen Gesamtfakultät der Ruprecht-Karls-Universität Heidelberg**

Ich erkläre hiermit, dass ich die vorgelegte Dissertation selbst verfasst und mich keiner anderen als der von mir ausdrücklich bezeichneten Quellen und Hilfen bedient habe.

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Jutta Frank