

Forsmark site investigation

Chemical characterisation of deposits and biota

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

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Abstract

In order to characterise deposits and biota with respect to chemical composition in the Forsmark area a number of different samples were analysed for elements with ICP. In total 114 samples from terrestrial and limnic environments were analysed. Besides the content of the macro-nutrients carbon, nitrogen and phosphorus, 61 other elements were determined in the samples.

Sammanfattning

För att kemiskt karakterisera avlagringar och biota i Forsmarksområdet analyserades ett antal olika prover på grundämnena med hjälp av ICP. Totalt analyserades 114 prover från terrestra och limniska miljöer. Förutom innehållet av kol, kväve och fosfor analyserades proverna på 61 andra grundämnena.

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1 Introduction

This document reports the data gained by the activities “Analyses of elements and isotopes in deposits and terrestrial vegetation” and “Analyses of elements and isotopes in biota samples”, which are two of the activities performed within the site investigation at Forsmark. The work was carried out in accordance with activity plans AP PF 400-05-061 and AP PF 400-05-099. In Table 1-1 controlling documents for performing this activity are listed. Activity plans are SKB’s internal controlling documents.

In order to characterise both deposits and biota with respect to the chemical composition, a number of different samples from the Forsmark area were analysed for elements. The initial intention was also that some specific isotopes should be determined on the same samples but this was never accomplished. Isotopes will instead be determined on other samples and reported in another report.

The samples were taken from terrestrial and limnic environments. A chemical characterisation of the marine environment in Forsmark has been performed and will be presented in /Kumblad and Bradshaw 2006/. Most of the analysed samples had been collected during other activities within the site investigation, whereas some samples were collected specifically for this investigation. A description of the samples is available in Chapter 3 whereas the equipment used and the procedures for the analyses are described in Chapters 4 and 5. The analyses were performed during the time period August 2005–March 2006.

The original results are stored in the primary data base (SICADA) and are traceable by the activity plan numbers (AP PF 400-05-061 and AP PF 400-05-099).

Table 1-1. Controlling documents for the performance of the activity.

Activity plan	Number	Version
Analyses of elements and isotopes in deposits and terrestrial vegetation	AP PF 400-05-061	1.0
Analyses of elements and isotopes in biota samples	AP PF 400-05-099	1.0

2 Objective and scope

Chemical analyses of elements were performed on samples of deposits and biota. The purpose was to generate information which will be used in different models of the surface (eco)systems at Forsmark. The information may also be used in an EIA (Environmental Impact Assessment) for a future repository for spent nuclear fuel.

The elements determined are shown in Table 2-1.

Table 2-1. Determined elements.

Oxides (in deposits except peat)	Unit	Elements (in non-deposit samples)	Unit
Al ₂ O ₃	%	Al	mg/kg dw
CaO	%	Ca	mg/kg dw
Fe ₂ O ₃	%	Fe	mg/kg dw
K ₂ O	%	K	mg/kg dw
MgO	%	Mg	mg/kg dw
MnO	%	Mn	mg/kg dw
Na ₂ O	%	Na	mg/kg dw
P ₂ O ₅	%	P	mg/kg dw
SiO ₂	%	Si	mg/kg dw
TiO ₂	%	Ti	mg/kg dw
Sum oxides	%		
LOI (Loss on ignition)	%		
In all samples			
Elements	Unit	Macroelements¹	Unit
Ag	mg/kg dw	Total carbon ²	mg/kg dw
As	mg/kg dw	Total organic carbon ²	mg/kg dw
B	mg/kg dw	Total nitrogen	mg/kg dw
Ba	mg/kg dw	Total organic nitrogen	mg/kg dw
Be	mg/kg dw	Phosphate (PO ₄)	mg/kg dw
Br	mg/kg dw		
Cd	mg/kg dw		
Ce	mg/kg dw		
Cl	mg/kg dw		
Co	mg/kg dw		
Cr	mg/kg dw		
Cs	mg/kg dw		
Cu	mg/kg dw		
Dy	mg/kg dw		
Er	mg/kg dw		
Eu	mg/kg dw		
Ga	mg/kg dw		
Gd	mg/kg dw		
Hf	mg/kg dw		
Hg	mg/kg dw		
Ho	mg/kg dw		

I	mg/kg dw
La	mg/kg dw
Li	mg/kg dw
Lu	mg/kg dw
Mo	mg/kg dw
Nb	mg/kg dw
Nd	mg/kg dw
Ni	mg/kg dw
Pb	mg/kg dw
Pr	mg/kg dw
Rb	mg/kg dw
S	mg/kg dw
Sb	mg/kg dw
Sc	mg/kg dw
Se	mg/kg dw
Sm	mg/kg dw
Sn	mg/kg dw
Sr	mg/kg dw
Ta	mg/kg dw
Tb	mg/kg dw
Th	mg/kg dw
Tl	mg/kg dw
Tm	mg/kg dw
U	mg/kg dw
V	mg/kg dw
W	mg/kg dw
Y	mg/kg dw
Yb	mg/kg dw
Zn	mg/kg dw
Zr	mg/kg dw
Dry substance (105°C)	%
Ash substance (550°C) ³	%

¹ In some cases the amount of sample material has been restricted. If enough sample for performing all analyses was not available, elements were prioritised before macroelements. If some, but not all, macroelements could be determined, carbon was prioritised before nitrogen and nitrogen before phosphorus.

² For biota samples it was assumed that all carbon and nitrogen are part of organic matter, and therefore only organic or total carbon/nitrogen are reported for most of these samples (except for terrestrial and limnic flora). Phosphate was generally measured only for organic parts of deposits; in biota samples phosphorus was determined instead.

³ Only for a few samples (algal mat in lake and soil samples from one site). Ash substance was determined for organic samples.

3 Samples

The first batch of samples sent to Analytica AB for analyses were those included in activity plan AP PF 400-05-061 (deposits and terrestrial vegetation). The deposits were sampled earlier according to activity plans AP PF 400-02-46, AP PF 400-02-49 and AP PF 400-04-117 (sediments in lakes and shallow bays), AP PF 400-02-12 (quaternary deposits), AP PF 400-03-062 and AP PF 400-05-134 (peat and wetlands). The terrestrial vegetation, including roots, as well as the uppermost soil layers had been sampled according to AP PF 400-04-109. The samples are listed and further described in Table 3-1. The sites where these samples have been collected are shown in Figure 3-1.

The second batch of samples sent for analyses were those included in AP PF 400-05-099 (aquatic vegetation, terrestrial and aquatic fauna). The limnic vegetation was sampled earlier according to activity plan AP PF 400-04-063, whereas the bottom fauna (mussels) were collected specifically for this purpose in late autumn 2005. The fish samples were collected earlier according to AP PF 400-03-057. All limnic samples were considered to represent the lake where they were sampled and have been given the lake area code (see Table 3-1).

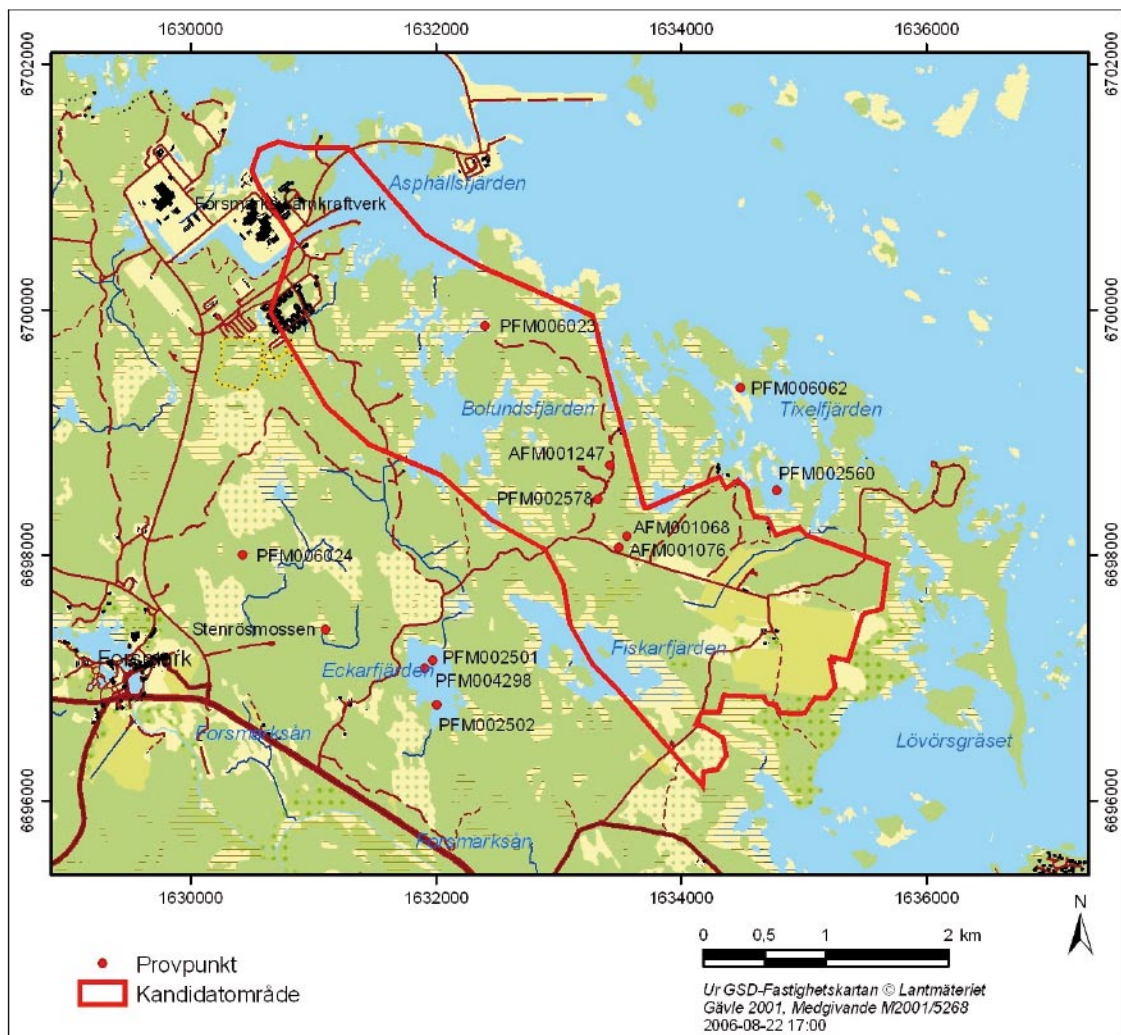


Figure 3-1. Sites where sediment, peat, wetland, soil and terrestrial vegetation samples were collected.

Table 3-1. Sample description. When more than one replicate of the same sample were analysed, that is denoted (repl), otherwise more than one sample means different levels in the same core (sediment, peat, soil), different size and/or location (roots, moose) or different species (limnic vegetation, small rodents).

	Sampling site	Number and description of samples	Sample state before analysis
Deposits			
Sediment	Eckarfjärden		
	PFM002502	1 (algal mat)	Freeze-dried
	PFM002501	2 (upper sediment)	Cooled
	PFM004298	7 (deeper sediment)	Freeze-dried
	Tixelfjärden		
	PFM002560	2 (upper sediment)	Frozen
Peat/wetland	PFM006062	5 (deeper sediment)	Cooled
	Puttan		Frozen
	PFM006023	4	
Soil	Rönningarna		
	PFM006024	6	
	Spruce wetland		Frozen
	AFM001076	6	
	Mesic spruce forest		
	AFM001068	6	
	Spruce forest on thin soil		
	AFM001247	6	
	moraine		
	PFM002578 (deeper soil in the whole area)	1	
Terrestrial environment			
Roots (spruce)	Spruce wetland		
	AFM001076	3 (root Ø < 1 mm in humus layer; 2,5 cm-, root Ø > 2 mm in whole humus layer, root Ø > 2 mm in mineral soil layer; 0–20 cm)	Dried
	Mesic spruce forest		
AFM001068	2 (root Ø < 1 mm in mineral soil layer; 0–10 cm, root Ø > 2 mm in mineral soil layer; 0–20 cm)		
Vegetation (above ground)	Spruce forest on thin soil		
	AFM001247	3 (root Ø < 1 mm in humus layer; 2,5 cm-, root Ø > 2 mm in whole humus layer, root Ø > 2 mm in mineral soil layer; 0–20 cm)	
	Spruce wetland		Frozen
AFM001076	5 (<i>Picea abies</i> (green shoots and wood), <i>Fraxinus excelsior</i> (small bushes), <i>Rubus saxatilis</i> , moss)		
	Mesic spruce forest		
	AFM001068	5 (<i>Picea abies</i> (green shoots and wood), <i>Vaccinium myrtillus</i> , <i>Rubus saxatilis</i> , <i>Rhytidiadelphus triquetrus</i>)	
	Spruce forest on thin soil		
AFM001247	5 (<i>Picea abies</i> (green shoots and wood), <i>Vaccinium myrtillus</i> , <i>Melampyrum sylvaticum</i> , <i>Hylocomium splendens</i>)		
Moose	Forsmark area	5	Frozen
	AFM000100, AFM001272 (Björnbo), AFM001273 (Vamsta)		

	Sampling site	Number and description of samples	Sample state before analysis		
Small rodents	Forest		Frozen		
	PFM007322 ¹	2 (yellow-necked mouse, bank vole)			
	AFM001289 ²	1 (bank vole autumn)			
	PFM007325 ³	1 (bank vole spring)			
	AFM001290 ⁴	1 (yellow-necked mouse autumn)			
	Ditch				
	PFM007323 ⁵	3 repl/1 (water vole spring/autumn)			
	PFM007324 ⁶	3 repl (water vole autumn)			
	Shrews				
	AFM001291 ⁷	1			
Fox	Forsmark area		Frozen		
	AFM000100	1			
Limnic environment					
Fish	Bolundsfjärden	Bentivorous fish: ruffe 1 repl. ⁸ tench 3 repl Piscivorous fish: pike 1 repl	Frozen		
	AFM000050				
	Eckarfjärden			Planktivorous fish: small roach 1 repl ⁹ Bentivorous fish: tench 3 repl Piscivorous fish: pike 2 repl	
	AFM000010				
	Fiskarfjärden	Planktivorous fish: small roach 1 repl ¹⁰ Bentivorous fish: tench 3 repl Piscivorous fish: pike 1 repl ¹¹			
	AFM000051				
	Chara	Bolundsfjärden		3 repl (<i>Chara tomentosa</i>)	Dried
		AFM000050			
		1 repl (<i>Chara tomentosa</i>)			
Fiskarfjärden					
AFM000051					
Bottom fauna (mussel)	Bolundsfjärden	3 repl (<i>Anodonta</i>) ¹²	Frozen		
	AFM000050				

¹ 8 and 10 individuals from site J5 in Figure 4-5a in SKB report P-04-04.

² 12 individuals from three different sites are represented by this idcode (site D8, F2 and L7 in Figure 4-5a in SKB report P-04-04).

³ 11 individuals from site J8 in Figure 4-5a in SKB report P-04-04.

⁴ 10 individuals from two different sites are represented by this idcode (L10 and L7 in Figure 4-5a in SKB report P-04-04).

⁵ 6, 6, 6 and 8 individuals from site D10 in Figure 4-5a in SKB report P-04-04.

⁶ 5, 8 and 8 individuals from site D4 in Figure 4-5a in SKB report P-04-04.

⁷ 30 individuals from all sampling sites (for map see Figure 4-5a in SKB report P-04-04).

⁸ 6 individuals.

⁹ 18 individuals.

¹⁰ 16 individuals.

¹¹ 5 individuals.

¹² 2 individuals.

The terrestrial fauna was sampled according to AP PF 400-03-035 (small rodents) whereas samples of moose and fox were provided by local hunters. For all fauna, muscle tissues were prepared and analysed. The samples are listed and further described in Table 3-1.

In order to gain enough sample matter for the small rodents, individuals were pooled together as one sample. In some cases all individuals in a sample were caught at the same site, but more often the samples contain individuals from more than one site, see Table 3-1 for more details.

4 Equipment

4.1 Description of equipment

The analyses were performed by ICP-AES, ICP-SFMS, ICP-QMS and AFS. In all techniques except AFS a plasma formed by argon gas was used.

ICP-AES stands for optical emission spectrometry with an inductively coupled plasma. The plasma flows through a radiofrequency field where it is kept in a state of partial ionisation, i.e. the gas consists partly of electrically charged particles. This allows it to reach very high temperatures of up to 10,000°C. At high temperature, most elements emit light of characteristic wavelengths, which can be measured and used to determine their concentrations.

In ICP-QMS (quadrupole mass spectrometry) and ICP-SFMS (sector field mass spectrometry) the plasma is of the same type as in ICP-AES, but it is used to convert elements to ions which are then separated by mass in a mass spectrometer. This allows the different elements in a sample (and their natural isotopes) to be separated and their concentrations determined.

Atomic fluorescence (AFS) has been used for the determination of Se. This technique uses photon emission from atoms as in ICP-AES, although excitation is not achieved thermally, but by light of a wavelength characteristic of the element. This light is absorbed by the atom and subsequently re-emitted to generate the analytical response.

5 Execution

5.1 General

The samples were collected by SKB and the sample preparations and elemental analyses were performed by Analytica AB. Macroelements were determined by a subcontractor, GBA (Gesellschaft für Bioanalytik, Hamburg).

The collected samples are of different types such as soil, sediment and biological material.

5.2 Preparations

Several digestion methods suitable for different types of samples have been used. Table 5-1 shows an overview of the analysis packages.

Description of the analysis packages:

MG1

- The sample was dried at 50°C. For the elements As, Cd, Hg, Cu and S, the sample was leached with 7 M nitric acid (HNO₃) in a closed Teflon vessel in a microwave oven. Concentrations have been reported on a dry weight (105°C) basis. For Br, Cl and I, the sample was leached in high purified water. The other elements were determined after fusion with lithium metaborate followed by dissolution in diluted nitric acid.

MG3

- The sample was dried at 50°C. For the elements As, Cd, Hg, Cu and S, the sample was leached in nitric acid (HNO₃)/hydrogen peroxide (H₂O₂) in a closed Teflon vessel in a microwave oven. Concentrations have been reported on a dry weight (105°C) basis. For Br, Cl and I, the sample was leached in high purified water. The other elements were determined after ashing at 550°C followed by fusion with lithium metaborate and dissolution in diluted nitric acid.

M4

- The sample was dried in 50°C and then leached with nitric acid (HNO₃) and a small amount of hydrofluoric acid (HF) in a closed Teflon vessel in a microwave oven.

Table 5-1. Overview of analysis packages.

Type of sample	Analysis package	Macroelements
Soil, sediment	MG1, M7	TOC, C-tot, N-tot, N-org., PO ₄
Organic soil	MG3, M7	TOC, C-tot, N-tot, N-org., PO ₄
Biological material (plant)	M4	C-tot, N-tot, N-org., PO ₄
Biological material (animal)	M4F	C-tot*, N-tot*

* For some of the biological animal samples, triplicate analyses were performed.

M4F

- The sample was freeze dried and then leached with nitric acid (HNO₃) and a small amount of hydrofluoric acid (HF) in a closed Teflon vessel in a microwave oven.

M7

- Sample was digested using hydrofluoric acid (HF)/ perchloric acid (HClO₄)/nitric acid (HNO₃) on a hot plate.

Macroelements

- Total carbon and total organic carbon (TOC), were carried out according to standard method DIN ISO 10694, Soil quality – Determination of organic and total carbon after dry combustion (elementary analysis).
- Total nitrogen and organic nitrogen, were carried out according to standard method DIN ISO 11261, Soil quality – Determination of total nitrogen – Modified Kjeldahl method.
- Phosphate (PO₄) was determined with standard method DIN EN ISO 15681-2, Water quality – Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) – Part 2: Method by continuous flow analysis (CFA). This method is used after the sample has been extracted in calcium-lactate.

5.3 Execution of analysis

The instruments were optimised and calibrated at the start of each working day. Calibration consisted of running a sequence of synthetic blanks, sample preparation blanks, quality control samples (certified reference materials) prepared in parallel with the unknowns, and standard solutions. The calibration sequence was repeated after every 10–15 sample measurements. For measurements by ICP-AES and ICP-SFMS, the internal standard technique was employed to allow correction for instrumental drift and non-spectral interference effects during the analyses.

5.4 Data handling/post processing

SICADA orders were registered under three different order numbers in the LIMS (Laboratory Information Management System). Data from LIMS were extracted to Excel-files with the laboratory standard program LMM (LabMasterMail). Using a special macro for SICADA, information was extracted from the Excel-files to the SICADA template, then the templates were saved with names corresponding to the order numbers. The macro-file constituted a database that translated the element code to SICADA element code. After the SICADA templates were delivered to SKB the activity leader included some information concerning the different samples, e.g. comments on how many individuals were used in pooled samples and information about extra samples used.

5.5 Nonconformities

A somewhat poorer access to material than expected led to fewer samples of deposits and terrestrial vegetation than planned (according to AP PF 400-05-061).

For all animal samples, muscles were prepared and analysed. In order to investigate how the element composition deviated in fish muscle compared to the whole fish, it was planned to do the same analyses on muscle as well as on whole pike. Unfortunately this could not be performed as it was impossible to disintegrate the whole fish without using a metal mill which would have contaminated the sample. Instead, muscle has been analysed for both of these two samples.

6 Results

The original results are stored in the primary data base (SICADA) and these will be used for further interpretation. The data are traceable in SICADA by the activity Plan numbers (AP PF 400-05-061 and AP PF 400-05-099). The whole data set is presented in Appendix 1.

References

Kumblad L, Bradshaw C, 2006. Stoichiometry of biota, water and sediment in Tixelfjärden, Baltic Sea. SKB report in progress. Svensk Kärnbränslehantering AB.

Results of chemical analyses

