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## Oskarshamn site investigation

## **Precipitation at Simpevarp 2004**

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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 author and do not necessarily coincide with those of the client.

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## Abstract

Sampling and analysis of precipitation was performed throughout 2004 at an open field site at Äspö. The purpose of this activity was to measure chemical compounds in the precipitation within the site investigation area at Oskarshamn.

The precipitation was collected in samplers placed two to ten metres apart in an area with a diameter of approximately 25 metres. The samplers were emptied weekly and volume was measured. Water from six of the periods was sent for full analysis (positive and negative ions, alkalinity, pH, conductivity and isotopes) to different laboratories. Water from the rest of the weeks were only analysed for negative ions, alkalinity, pH and conductivity if precipitation had occurred.

The concentrations of different ions varied between the different measuring periods. Calculations of ion balances showed rather great imbalances in many of the samples (more than 10% relative error). This imbalance was so large that there must be an error either in the analysis or in the handling of the samples.

The weighted average concentration of some of the ions and of pH was compared with results from three national monitoring stations for depositions in south east Sweden. The comparison shows that the concentration of ions was generally higher at Äspö. The average of pH was similar though. The main reason for higher concentration of ions is probably that the Äspö station is situated very close to the sea with a greater influx of sea salt. A corrected average of SO<sub>4</sub>-S (which excludes the part of sulphur that originates from sea salt) at Äspö was also more similar to the other stations in south east Sweden.

The hydrogen isotope ratio of deuterium varied with the lowest ratio in winter. As expected these ratios correlated well with the ratios of <sup>18</sup>O and the linear relation corresponds well with the "Global Meteoric Water Line". The ratios of tritium varied with a small tendency for lower values in late autumn and in winter periods.

Two types of nonconformities have occurred. The first is that sampling was not performed during three periods in 2004 (2004-01-01 to 2004-01-19, 2004-07-05 to 2004-08-02 and 2004-12-20 to 2004-12-31). The second type of nonconformity was that some analysis was not performed on every occasion. On several occasions HCO<sub>3</sub> was not analysed because of very low pH. Likewise conductivity was not analysed on two occasions in the autumn of 2004.

## Sammanfattning

Provtagning och analys av regnvatten från Äspö har utförts under 2004. Syftet med undersökningarna var att mäta regnvattnets kemiska sammansättning inom området för platsundersökningen i Oskarshamn.

Regnvatten samlades in i behållare som slumpmässigt placerats inom ett område med en diameter på ca 25 m. Behållarna tömdes och volymen mättes regelbundet varje vecka. Vatten från sex av perioderna analyserades på samtliga parametrar (positiva och negativa joner, alkalinitet, pH, konduktivitet samt isotoper). Vatten från övriga veckor analyserades endast på negativa joner, alkalinitet, pH och konduktivitet om det fanns vatten tillräckligt för analys.

Koncentrationen av olika joner varierade mycket mellan olika provtagningsperioder. Beräkningar av jonbalanserna visade på relativt stora avvikelser (mer än 10 % relativt fel) i många av proverna. Skillnaderna var så stora att ett fel måste föreligga, antingen vid analyserna eller vid hanteringen av proverna.

Viktade medelvärden av några av de undersökta jonerna samt av pH jämfördes med resultat från stationer i det nationella nederbördskemiska nätet som ligger i sydöstra Sverige. Jämförelsen visar att halten av joner generellt var högre vid Äspö. Medelvärdet av pH var dock relativt lika. Den huvudsakliga orsaken till skillnaden i jonkoncentration är sannolikt närheten till havet. Ett beräknat korrigerat värde för SO<sub>4</sub>-S (som utesluter svavel som härrör från havet) var också mer likt resultaten från de andra stationerna i sydöstra Sverige.

Väteisotopen deuterium varierade mellan provtagningstillfällena med den lägsta kvoten under vintern. Som förväntat var kvoterna av deuterium väl korrelerade med kvoterna av <sup>18</sup>O. Även kvoterna av tritium varierade mellan provtillfällena med en svag tendens till lägre värden under senhösten och vintern.

Två typer av avvikelser från vad som planerats har förekommit under året. Den första är att provtagning inte genomfördes under tre perioder (2004-01-01 to 2004-01-19, 2004-07-05 to 2004-08-02 and 2004-12-20 to 2004-12-31). Den andra är att inte alla planerade parametrar har analyserats vid varje provtillfälle. Vid flera tillfällen analyserades inte HCO<sub>3</sub> på grund av för lågt pH. Konduktivitet analyserades inte heller vid två tillfällen under 2004.

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## 1 Introduction

This document reports the results gained by the sampling and analysis of precipitation during 2004, which is one of the activities performed within the site investigation at Oskarshamn. The work was carried out in accordance with activity plan AP PS 400-04-011. In Table 1-1 controlling documents for performing this activity are listed. Both activity plan and method descriptions are SKB's internal controlling documents.

The aim of the activity was to measure chemical substances in the precipitation (rain and snow). These data will be a part of the data needed to describe the circulation of water and water transported substances in the investigation area. The sampling was performed from January to December of 2004 at the site PSM002170 at Äspö (Figure 1-1). All data generated was stored in the database SICADA. The data is traceable by the activity plan number.



*Figure 1-1.* Site for sampling of precipitation at the island of Äspö. Coordinates for the site is N 6368188.887; E 1551081.634 (RT90/RHB70). The elevation is 6.165 m.

Table 1-1.	Controlling	documents	for the	performance	of the activity
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Activity plan	Number	Version
Platsundersökning Oskarshamn. Nederbörds- provtagning 2004.	AP PS 400-04-011	1.0
Method descriptions	Number	Version
Metodbeskrivning för provtagning och analys av nederbörd.	SKB MD 423.003	1.0

## 2 Objective and scope

The purpose of this activity was to measure the bulk deposition, i.e. chemical compounds in the precipitation, within the site investigation area. The method used was designed to measure precipitation in an open field and in undisturbed conditions. Samples for analysis were to be taken once every week provided enough water was present. After the sampling of water the samplers was completely emptied.

The measurements and analysis performed aimed also to give results of high quality from an undisturbed site. To ensure high quality the samples were transported to the laboratories as fast as possible. Calculations of the ion balance in each sample were later a mean to prove high quality of the samples. According to the method description (SKB MD 423.003, internal document) the relative error in the ion balance should be less than 10%.

The parameters measured in the samples are presented in Table 4-1.

### 3 Equipment

Fourteen samplers were placed in the open field site approximately half a metre above the ground (Figure 3-1). Exact locations with coordinates are given in Table 3-1. The samplers were placed two to ten metres apart in an area with a diameter of approximately 25 metres. The total volume caught in the samplers in each sampling period was treated as one sample to ensure that enough water was caught for all analysis planned.

In summer the samplers were cans with funnels with a diameter of 15.5 cm. In winter buckets with a diameter of 21 cm were used. The cans and the bucket could hold a maximum volume of five litres. Plastic bags made of polyethene were used inside the cans or buckets to prevent contamination. A new plastic bag was used for every measuring period. When emptying the samplers a graduated glass was used to measure the volumes in the samplers. One or two five litres plastic container was then used to transport the sample to the laboratory were the sample was divided into smaller bottles before they were delivered to the different analysing laboratories. When the sample was divided into smaller bottles the water for some analysis were filtrated with a syringe through a 0.45  $\mu$ m sterile-R single use filter. All handling of the samples was performed with protective plastic gloves.



*Figure 3-1.* The samplers used in summer at the site for sampling of precipitation at the island of *Äspö*.

ID code	Northing (m)	Easting (m)
PSM002164	6368190.379	1551095.219
PSM002165	6368190.772	1551092.651
PSM002166	6368191.406	1551089.403
PSM002167	6368189.112	1551087.298
PSM002168	6368186.288	1551085.978
PSM002169	6368186.333	1551083.621
PSM002170	6368188.887	1551081.634
PSM002171	6368191.387	1551082.044
PSM002172	6368192.608	1551081.786
PSM002173	6368194.691	1551080.047
PSM002174	6368197.498	1551078.972
PSM002175	6368198.224	1551081.681
PSM002176	6368198.204	1551086.452
PSM002177	Not measured	Not measured

 Table 3-1. Locations with coordinates for the individual samplers (RT90/RHB70).

## 4 Execution

#### 4.1 Preparations

To prevent contamination and avoid extensive algal growth plastic bags made of polyethene were used inside the samplers. New plastic bags were used for each measuring period.

#### 4.2 Execution of field work

The precipitation was collected in samplers placed in an open field at Äspö (Figure 1-1, Figure 3-1). The samplers were emptied regularly each week and if the precipitation had been large enough water was stored and later sent for analysis at different laboratories (Table 4-1). The total volume gathered from the samplers was measured with a graduated glass. In winter if the samplers contained snow or ice the volume was measured on a scale.

Approximately 20% of the sample from each week was assembled to a general sample. The general sample was stored in a refrigerator and samples from each week were added for six months before analysis. The general sample of the last six month period were not analysed when this report was written. These data will be evaluated in the year 2005 report.

In each week the rest of the sample was saved as a "point sample". If the volume of the "point sample" was larger than one litre, but smaller then 3.2 litre, half of the sample was delivered to the Äspö laboratory for "quick analysis". The rest of the sample was stored in a refrigerator marked with date, week and volume until a decision was taken on which analysis to perform or if analysis should be performed at all. If the "point sample was larger than 3.2 litre then 500 ml of the sample was marked with an SKB-number and delivered to the Äspö laboratory for "quick analysis". The rest of the sample was marked with the same SKB-number and stored in a refrigerator until analysis was performed. If the volume of the "point sample" was smaller than one litre the sample was stored in the same manner as other "point samples" but no sample was delivered to the Äspö laboratory for "quick analysis".

From week 26 the routine was changed slightly. Instead of a demand for 3.2 litre for a full "point sample" the demand was changed to 2.7 litre. This was due to a change in the tritium analysis which only needed a sample of 500 ml instead of 1,000 ml.

When decision had been taken on which "point samples" to analyse the bottles were marked with SKB-numbers and sent to the laboratories. During the year six "point samples" were analysed. Analyses were also performed on the general sample from the period of 2004-01-01 to 2004-06-30. This sample was only analysed for <sup>2</sup>H (deuterium), <sup>3</sup>H (tritium) and <sup>18</sup>O.

Notes on the handling of the samples were kept in a diary.

See Table 4-1 for the different kind of samples and SKB-numbers.

The analysis performed follow chemistry class 3 (MD 450.001 SKB's internal controlling document) (Table 5-1). The method used is described in detail in MD 423.003, SKB internal document.

The handling of the samples prior to analysis with type of bottles, filtration, acidification, filling instructions and the laboratories used are shown in Table 4-2 (MD 423.003, SKB internal document). In addition two archive samples of 250 ml and two archive samples of 100 ml was taken out and stored by SKB. The 250 ml archive samples where filtrated in a Pall filter (0.45  $\mu$ m) and the 100 ml samples were filtrated with a syringe and acidified with 1% HNO<sub>3</sub> prior to storage.

Three different ways of delivery to the laboratories were chosen. The samples for Äspö laboratory were delivered directly. To Analytica the samples were sent by postal service. The samples for IFE in Norway and EIL in Canada were sent by DHL delivery service.

Sample period	Sample no	Type of sample and analyses
2004-01-19–2004-01-26	7085	Anions, pH, conductivity and HCO <sub>3</sub> -
2004-01-26-2004-02-02	7107	Anions, pH, conductivity and HCO₃⁻
2004-01-19–2004-01-02	7339	7085 and 7107 combined. Only main components, D, Tr and 18O
2004-02-02-2004-02-09	7110	Anions, pH, conductivity and $HCO_3^-$ . Main components stored at the Äspö laboratory
2004-02-16-2004-02-24	7152	Anions, pH, conductivity and HCO <sub>3</sub> <sup>-</sup> . Main components stored at the Äspö laboratory
2004-03-01-2004-03-09	7154	Anions, pH, conductivity and HCO <sub>3</sub> <sup>-</sup> . Main components stored at the Äspö laboratory
2004-03-15-2004-03-22	7203	Anions, pH, conductivity and HCO₃ <sup>−</sup> . Main components stored at the Äspö laboratory
2004-03-22-2004-03-29	7255	Anions, pH, conductivity and HCO <sub>3</sub> <sup>-</sup> . Main components stored at the Äspö laboratory
2004-03-29–2004-04-05	7260	Anions, pH, conductivity and $HCO_3^-$ . Main components stored at the Äspö laboratory
2004-04-05–2004-04-13	7261	Complete sample. Anions, pH, conductivity, HCO₃⁻, main components, D, Tr and 18O
2004-04-19–2004-04-26	7301	Anions, pH, conductivity and $HCO_3^-$ . Main components stored at the Äspö laboratory
2004-05-03-2004-05-10	7348	Anions, pH, conductivity and $HCO_3^-$ . Main components stored at the Äspö laboratory
2004-05-10–2004-05-17	7385	Anions, pH, conductivity and HCO <sub>3</sub> <sup>-</sup> . Main components stored at the Äspö laboratory
2004-05-24-2004-06-01	7422	Anions, pH, conductivity and $HCO_3^-$ . Main components stored at the Äspö laboratory
2004-06-07-2004-06-14	7499	Anions, pH, conductivity and HCO <sub>3</sub> <sup>-</sup> . Main components stored at the Äspö laboratory
2004-06-14-2004-06-21	7506	Anions, pH, conductivity and $HCO_3^-$ . Main components stored at the Äspö laboratory
2004-06-21–2004-06-28	7562	Complete sample. Anions, pH, conductivity, HCO₃⁻, main components, D, Tr and 18O
2004-01-01–2004-06-30	7564	General sample. Only D, Tr and 18O
2004-01-01–2004-06-30	7565	Control sample of 7564. D, Tr and 18O stored at the Äspö laboratory
2004-08-02-2004-08-09	7631	Anions, pH, conductivity and $HCO_3^-$ . Main components stored at the Äspö laboratory
2004-08-16–2004-08-23	7674	Anions, pH, conductivity and $HCO_3^-$ . Main components stored at the Äspö laboratory
2004-08-23–2004-08-30	7715	Complete sample. Anions, pH, conductivity, HCO₃⁻, main components, D, Tr and 18O

Table 4-1. Explanations of the different kind of samples and SKB-numbers. (The complete samples and the general sample are highlighted).

Sample period	Sample no	Type of sample and analyses
2004-08-23–2004-08-30	7863	Control sample of 7715. Main components, D, Tr and 18O stored at the Äspö laboratory
2004-08-30–2004-09-06	7723	Anions, pH, conductivity and $HCO_3^-$ . Main components, D, Tr and 18O stored at the Äspö laboratory
2007-09-27–2004-10-04	7858	Anions, pH, conductivity and $\text{HCO}_3$ . Main components stored at the Äspö laboratory
2004-10-04–2004-10-11	7860	Anions, pH, conductivity and $\text{HCO}_{3^-}$ . Main components stored at the Äspö laboratory
2004-10-11–2004-10-18	7862	Anions, pH, conductivity and $\text{HCO}_{3^-}$ . Main components stored at the Äspö laboratory
2004-10-18–2004-10-25	7864	Complete sample. Anions, pH, conductivity, HCO₃⁻, main components, D, Tr and 18O
2004-11-02–2004-11-10	7903	Anions, pH, conductivity and $\text{HCO}_3^{-}.$ Main components stored at the Äspö laboratory
2004-11-10–2004-11 16	7904	Anions, pH, conductivity and $\text{HCO}_3^$ Main components stored at the Äspö laboratory
2004-11-16-2004-11-22	7945	Anions, pH, conductivity and $\text{HCO}_3^$ Main components stored at the Äspö laboratory
2004-11-22–2004-11-29	7956	Complete sample. Anions, pH, conductivity, HCO₃⁻, main components, D, Tr and 18O
2004-11-29–2004-12-06	7965	Anions, pH, conductivity and $\text{HCO}_3^$ Main components stored at the Äspö laboratory
2004-12-13–2004-12-20	7981	Anions, pH, conductivity and $\text{HCO}_{3}\Bar{-}.$ Main components stored at the Äspö laboratory

Table 4-2. Analysed components, treatments of samples and analysing laboratory.

Components	Bottle/volume	Preparation of sample	Laboratory
pH, Conductivity, HCO <sub>3</sub>	150 ml	-	Äspö laboratory
Cl, Br, SO <sub>4</sub> , F, Si	100 ml	filtration 0.45 µm	Äspö laboratory
Density	250 ml	-	Äspö laboratory
Ca, Fe, K, Mg, Na, S (SO₄-S meas), Si, Li, Mn, Sr	50 ml, acid rinsed	filtration 0.45 $\mu$ m/acidification 1% HNO <sub>3</sub>	Analytica
³Н	1,000 ml/500 ml	dried bottle, flow over twice	Environmental Isotope Lab at the University of Waterloo, Canada
<sup>2</sup> H, <sup>18</sup> O	100 ml	flow over twice	Institutute for Energy Technology, Norway

#### 4.3 Data handling and calculations

After analysis data has continuously been reported from the laboratories. As a routine a first preliminary control of the data quality was performed before storing them in the database SICADA. Data for this evaluation was delivered from SICADA 2005-05-25.

The precipitation (P) during the sampling periods was calculated from the collected average volume (V) and the area of the samplers (A). P (mm) =  $10 \times V$  (ml)/A (cm<sup>2</sup>).

The concentration of SO<sub>4</sub>-S (calc) in the precipitation was calculated as the atomic proportion of SO<sub>4</sub> ([SO<sub>4</sub>-S] = [SO<sub>4</sub>]/96×32).

A part of the SO<sub>4</sub>-S originates from sea salt which makes it difficult to compare the concentrations of SO<sub>4</sub>-S from different sites at different distances from the sea. A corrected value which excludes the part that originate from sea salt was calculated from the concentration of Na ([SO<sub>4</sub>-S<sub>corr</sub>] = [SO<sub>4</sub>-S] – 0.0837×[Na]) (concentrations in mg/l).

To compare with results from other sites in south east Sweden weighted averages was calculated on some of the ions and pH. The calculations were made from the formula  $X_m = \sum (c_i \times m_i) / \sum (m_i)$  were c is the concentration during a period and m is the precipitation during the same period.

#### 4.4 Nonconformities

Two types of nonconformities have occurred. The first is that sampling was not performed during three periods in 2004 (2004-01-01 to 2004-01-19, 2004-07-05 to 2004-08-02 and 2004-12-20 to 2004-12-31).

The second type of nonconformity was that some analysis was not performed on every occasion. On several occasions HCO<sub>3</sub> was not analysed because of very low pH. Likewise conductivity was not analysed on two occasions in the autumn of 2004.

### 5 Results

All data gained are stored in the primary data base SICADA. The data is traceable in SICADA and GIS by the Activity Plan number (AP PS 400-04-011). These data will later be used for further interpretation and modelling. Here the results are presented in a more general way.

Precipitation was measured in 42 sampling periods during 2004. The average volume collected per sampler during this period was 198 ml (Table 5-1). The mean calculated precipitation per sampling period was 7.5 mm. The total measured precipitation of the year was 324 mm. This is certainly an underestimation of the true total precipitation since measurements weren't performed during three periods of the year.

# Table 5-1. Sampling periods and measured volumes of water in the samplers and calculated precipitation during the periods when measurements were performed.

Sample period	Total volume (ml)	Average volume per sampler (ml)	Sampler diameter (cm)	Sampler area (cm²)	Precipitation (mm)
2004-01-01-2004-01-19	no measurements				
2004-01-19–2004-01-26	3,200	246	21.0	346.4	7.1
2004-01-19–2004-02-02					
2004-01-26-2004-02-02	5,000	385	21.0	346.4	11.1
2004-02-02-2004-02-09	2,480	191	21.0	346.4	5.5
2004-02-09-2004-02-16	0	0	21.0	346.4	0.0
2004-02-16-2004-02-24	2,400	185	21.0	346.4	5.3
2004-02-24-2004-03-01	150	12	21.0	346.4	0.3
2004-03-01-2004-03-09	1,370	105	21.0	346.4	3.0
2004-03-09-2004-03-15	600	46	21.0	346.4	1.3
2004-03-15-2004-03-22	5,400	415	21.0	346.4	12.0
2004-03-22-2004-03-29	2,280	175	21.0	346.4	5.1
2004-03-29-2004-04-05	1,360	105	21.0	346.4	3.0
2004-04-05-2004-04-13	7,140	549	21.0	346.4	15.9
2004-04-13-2004-04-19	0	0	21.0	346.4	0.0
2004-04-19–2004-04-26	1,565	120	21.0	346.4	3.5
2004-04-26-2004-05-03	0	0	21.0	346.4	0.0
2004-05-03-2004-05-10	1,970	152	21.0	346.4	4.4
2004-05-10-2004-05-17	3,620	278	21.0	346.4	8.0
2004-05-17–2004-05-24	1,195	92	21.0	346.4	2.7
2004-05-24-2004-06-01	1,925	148	21.0	346.4	4.3
2004-06-01-2004-06-07	0	0	15.5	188.7	0.0
2004-06-07-2004-06-14	2,770	198	15.5	188.7	10.5
2004-06-14-2004-06-21	2,345	168	15.5	188.7	8.9
2004-06-21-2004-06-28	3,420	244	15.5	188.7	12.9
2004-06-28-2004-07-05	860	61	15.5	188.7	3.3
2004-07-05-2004-08-02	no measurements				

Sample period	Total volume (ml)	Average volume per sampler (ml)	Sampler diameter (cm)	Sampler area (cm²)	Precipitation (mm)
2004-08-02-2004-08-09	1,940	139	15.5	188.7	7.3
2004-08-09–2004-08-16	0	0	15.5	188.7	0.0
2004-08-16–2004-08-23	2,560	183	15.5	188.7	9.7
2004-08-23-2004-08-30	6,040	431	15.5	188.7	22.9
2004-08-30–2004-09-06	3,275	234	15.5	188.7	12.4
2004-09-06–2004-09-13	0	0	15.5	188.7	0.0
2004-09-13–2004-09-20	1,130	81	15.5	188.7	4.3
2004-09-20–2004-09-27	1,070	76	15.5	188.7	4.1
2007-09-27–2004-10-04	1,325	95	15.5	188.7	5.0
2004-10-04–2004-10-11	3,750	268	15.5	188.7	14.2
2004-10-11–2004-10-18	4,660	333	15.5	188.7	17.6
2004-10-18–2004-10-25	6,790	485	15.5	188.7	25.7
2004-10-25–2004-11-02	0	0	15.5	188.7	0.0
2004-11-02–2004-11-10	4,310	308	21.0	346.4	8.9
2004-11-10–2004-11 16	1,280	91	21.0	346.4	2.6
2004-11-16–2004-11-22	3,870	276	21.0	346.4	8.0
2004-11-22–2004-11-29	21,200	1,514	21.0	346.4	43.7
2004-11-29–2004-12-06	2,785	199	21.0	346.4	5.7
2004-12-06–2004-12-13	0	0			
2004-12-13–2004-12-20	1,900	136	21.0	346.4	3.9
2004-12-20–2004-12-31	no measurements				
Average		198			7.5
Standard deviation		247			8.3

Samples were sent for full analysis on six occasions. The concentrations of different ions varied much between the different measuring periods (Table 5-2). On at least three occasions the concentrations of the positive ions far exceeded the concentrations of the negative ions. This imbalance is large and there must be an error either in the analysis or in the handling of the samples. To test the quality of the samples the relative error in the ion balance was calculated (Table 5-3). These calculations show rather great imbalances (more than 10% relative error) in many of the samples). The reason for this is hard to interpret, partly because two major ions (NO<sub>3</sub> and NH<sub>4</sub>) hasn't been analysed. In a nearby station for measurement of precipitation (Norra Kvill in the municipality of Vimmerby) the average concentrations of NO<sub>3</sub> and NH<sub>4</sub> was 0.22 mg/l and 0.22 mg/l in 2004 (www.ivl.se). If the relation between NO<sub>3</sub> and NH<sub>4</sub> is similar at the Äspö site the imbalance would be similar. Therefore the lack of results on NO<sub>3</sub> and NH<sub>4</sub> is not a probable explanation to the imbalance.

Table 5-2. Measured concentrations of ions and some other components during the measuring periods when full analyses were performed. (There is one measured and one calculated  $SO_4$ -S value for the samples).

Sample period	Sample number	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Fe (mg/l)	Mn (mg/l)	Li (mg/l)	Si (mg/l)	Sr (mg/l)
2004-01-19-2004-02-02	7339*/7085**	1.9*	<0.40*	0.6*	0.1*	0.022*	0.01*	<0.004*	0.0*	0.01*
2004-04-05-2004-04-13	7261	8.1	<0.40	2.6	0.1	0.032	0.01	<0.004	0.0	0.06
2004-06-21-2004-06-28	7562	0.4	0.52	0.4	0.1	0.036	0.01	<0.004	0.0	0.00
2004-08-23-2004-08-30	7715	2.8	0.93	1.8	0.2	0.078	0.03	<0.004	0.0	0.04
2004-10-18-2004-10-25	7864	0.8	0.48	0.2	0.1	0.061	0.04	<0.004	0.0	0.00
2004-11-22-2004-11-29	7956	1.0	<0.40	0.1	0.1	<0.020	0.01	<0.004	0.0	0.00

Sample period	Sample number	SO₄-S meas. (mg/l)	Cl (mg/l)	SO₄ (mg/l)	SO₄-S calc. (mg/l)	SO₄-S <sub>korr</sub> calc. (mg/l)	Br (mg/l)	F (mg/l)	HCO₃ (mg/l)
2004-01-19-2004-02-02	7339*/7085**	0.35*	2.0**	1.98**	0.660**	0.501**	<0.20**	<0.20**	0**
2004-04-05-2004-04-13	7261	1.28	0.9	2.15	0.717	0.039	<0.20	0.68	
2004-06-21-2004-06-28	7562	0.47	0.4	0.84	0.280	0.247	<0.20	<0.20	
2004-08-23-2004-08-30	7715	0.74	2.3	1.53	0.510	0.276	<0.20	<0.20	
2004-10-18-2004-10-25	7864	0.44	1.2	1.13	0.377	0.310	<0.20	<0.20	
2004-11-22-2004-11-29	7956	0.27	1.6	0.74	0.247	0.163	<0.20	<0.20	

\* Analyses performed on sample 7339. \*\* Analyses performed on sample 7085.

Table 5-3.	Calculated relative err	ors of the ion	balance in the	samples from t	he different
measuring	j periods.			-	

Sample period	Sample number	lon balance relative error (%)
2004-01-19–2004-02-02	7339/7085*	11.8
2004-04-05-2004-04-13	7261	66.1
2004-06-21–2004-06-28	7562	35.4
2004-08-23–2004-08-30	7715	41.8
2004-10-18–2004-10-25	7864	9.0
2004-11-22–2004-11-29	7956	7.0

\* Cations performed on sample 7339, anions performed on sample 7085.

Also pH and conductivity varied much between the different measuring periods (Table 5-4). Some periods differ with slightly higher pH and conductivity. Perhaps some of the variation can be explained by influx of sea water spray in to one or more of the sampling containers. The measurements of the density was, as can be expected, quite stable (Table 5-4).

To compare some of the results with national monitoring stations for depositions in south east Sweden weighted averages was calculated of some of the ions and of pH (see Chapter 4.3). Three stations situated in the counties of Kalmar, Kronoberg and Blekinge were chosen and the results as weighted averages from 2004 were taken from the Swedish environmental program for air and precipitation financed by SEPA (Swedish Environmental Protection Board) (data can be obtained from www.ivl.se). The data from 2004 was also compared to the data obtained at the Äspö site during 2002 to 2003 /Ericsson 2004/. The comparison shows that the concentration of ions is generally higher at Äspö (Table 5-5).

Station	CI (mg/l)	SO₄-S <sub>korr</sub> (mg/l)	Na (mg/l)	Ca (mg/l)	K (mg/l)	Mg (mg/l)	pH (mg/l)
Äspö 2004	1.50	0.25	2.13	0.78	0.51	0.12	4.75
Äspö 2002 to 2003	1.64	0.50	2.05	0.74	0.78	0.16	5.09
N Kvill	0.36	0.26	0.28	0.11	0.10	0.05	4.89
Aneboda	1.27	0.35	0.87	0.14	0.09	0.12	4.69
Sännen	1.04	0.59	0.68	0.24	0.34	0.11	4.72

# Table 5-5. Volume weighted averages of some major ions and pH in Äspö and in some other stations in south east Sweden 2004.

# Table 5-4. Measured values of pH. Conductivity and density during periods when analysis were performed.

Sample period	Sample number	рН	Conductivity (mS/m)	Density (g/ml)
2004-01-19-2004-01-26	7085	5.03	3.1	
2004-01-26-2004-02-02	7107	4.06	5.5	
2004-02-02–2004-02-09	7110	4.50	2.7	
2004-02-16-2004-02-24	7152	4.75	1.2	
2004-03-01-2004-03-09	7154	4.30	3.4	
2004-03-15-2004-03-22	7203	4.90	1.6	
2004-03-22–2004-03-29	7255	4.57	2.1	
2004-03-29–2004-04-05	7260	4.97	3.6	
2004-04-05-2004-04-13	7261	4.52	5.4	
2004-04-19–2004-04-26	7301	4.64	5.3	
2004-05-03–2004-05-10	7348	5.82	5.3	
2004-05-10–2004-05-17	7385	4.98	1.3	
2004-05-24–2004-06-01	7422	4.62	3.8	
2004-06-07–2004-06-14	7499	5.11	2.2	
2004-06-14–2004-06-21	7506	5.11	1.9	
2004-06-21-2004-06-28	7562	4.54	4.9	
2004-08-02-2004-08-09	7631	4.25	2.0	
2004-08-16-2004-08-23	7674	5.16	3.4	
2004-08-23-2004-08-30	7715	4.81	2.5	0.9960
2004-08-30-2004-09-06	7723	4.95	2.5	0.9961
2007-09-27–2004-10-04	7858	4.42	5.7	
2004-10-04–2004-10-11	7860	4.86	4.2	0.9964
2004-10-11–2004-10-18	7862	4.88	3.1	0.9962
2004-10-18–2004-10-25	7864	4.72	2.2	0.9962
2004-11-02–2004-11-10	7903	4.92	6.5	
2004-11-10–2004-11 16	7904	5.13		
2004-11-16–2004-11-22	7945	4.96	3.3	0.9969
2004-11-22–2004-11-29	7956	4.75	1.9	
2004-11-29–2004-12-06	7965	4.21		
2004-12-13–2004-12-20	7981	5.13		
Average		4.79	3.36	0.9963
Standard deviation		0.36	1.51	0.0003

The average of pH has varied but this years average value was similar to the other sites in south east Sweden. The main reason for higher concentration of ions at the Äspö site is probably that Äspö is situated very close to the sea with a greater influx of sea salt. The corrected average of  $SO_4$ - $S_{korr}$  (which excludes the part of sulphur that originates from sea salt) at Äspö was also more similar to the other stations in south east Sweden 2004 (Table 5-5).

The hydrogen isotope ratio of deuterium (dD) varied with the lowest ratio in winter (Table 5-6). These ratios correlated well with the ratios of <sup>18</sup>O (Figure 5-1). The linear relation corresponds reasonable well with the "Global Meteoric Water Line" (dD =  $8 \times {}^{18}O+10$ ) which is based on precipitation data from locations around the globe /Craig 1961/. The ratios of tritium (<sup>3</sup>H) varied with a small tendency for lower values in late autumn and in winter.

Sample period	Sample number	dD (‰ VSMOW)	³H (TU)	<sup>18</sup> O (‰ VSMOW)
2004-01-19-2004-02-02	7339	-124.6	9.10	-16.90
2004-04-05-2004-04-13	7261	-62.7	11.90	-6.60
2004-06-21-2004-06-28	7562	-65.9	18.80	-8.90
2004-08-23-2004-08-30	7715	-55.5	13.50	-8.70
2004-10-18-2004-10-25	7864	-75.1	10.50	-10.80
2004-11-22–2004-11-29	7956	-95.9	14.40	-13.90
Average		-80.0	13.03	-101.97
Standard deviation		25.9	3.42	3.80
2004-01-01-2004-06-30	7564	-76.2	12.70	-9.60

# Table 5-6. Isotope data obtained during the measuring periods. The last sample is the general sample gathered during the period 2005-01-01 to 2005-06-30.



**Figure 5-1.** The relationship between the ratios of deuterium (dD) and  ${}^{18}O$  at the  $\ddot{A}$ spö site in 2004. The green square is the data from the general sample gathered during the period 2005-01-01 to 2005-06-30.

## 6 References

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