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## **Oskarshamn site investigation**

# Sampling and chemical analysis of precipitation 2007

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February 2009

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*Keywords:* Precipitation, Major ions, Isotopes, Conductivity, pH and alkalinity, Simpevarp, Sweden, AP PS 400-07-039.

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.

Data in SKB's database can be changed for different reasons. Minor changes in SKB's database will not necessarily result in a revised report. Data revisions may also be presented as supplements, available at www.skb.se.

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## Abstract

Sampling and analysis of precipitation was performed from May to December 2007 in a small forest clearing at Äspö. The purpose of this activity was to monitor chemical compounds in the precipitation within the site investigation area at Oskarshamn.

The precipitation was collected in samplers placed two to ten meters apart in an area with a diameter of approximately 15 meter. The samplers were emptied weekly and the water volume was measured. Water from five of the weekly periods was sent for full analysis (anions and main components, alkalinity, pH, conductivity and isotopes) to different laboratories. Water from the rest of the periods were analysed for anions, alkalinity, pH and conductivity if precipitation had occurred. General samples composed of water from each week in each quarter of a year was analysed for isotopes.

The concentrations of different ions varied between the different measuring periods. Calculations of ion balances showed a great imbalance in two of the samples (more than 10% relative error). This imbalance was so large that there might be an error either in the analysis or in the handling of the samples. Another explanation might be that the concentrations of many of the ions were close to or below the detection limits which could cause calculation errors.

The weighted average concentration of some of the ions and of pH was compared with results from two national monitoring stations for depositions in south east Sweden. The comparison shows that the concentrations of ions were 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  $SO_4$ -S (which excludes the part of sulphur that originates from sea salt) at Äspö was more similar to the other stations in south east Sweden.

The hydrogen isotope ratio of  $\delta^2$ H (deuterium) varied with a small tendency of lowest ratio in winter. As expected these ratios correlated well with the ratios of  $\delta^{18}$ O (oxygen-18) and the linear relation corresponds reasonably well with the "Global Meteoric Water Line". The ratios of <sup>3</sup>H (tritium) varied with a small tendency for lower values in the autumn.

One nonconformity with the activity plan has occurred. The analysis of HCO<sub>3</sub> was not performed on every occasion, due to low pH values.

## Sammanfattning

Provtagning och analys av regnvatten från Äspö har utförts från maj till december 2007. Syftet med undersökningarna var att monitera 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 15 m. Behållarna tömdes och volymen mättes regelbundet varje vecka. Vatten från fem av veckoperioderna analyserades på samtliga parametrar (anjoner och huvudkomponenter, alkalinitet, pH, konduktivitet samt isotoper). Vatten från övriga veckor analyserades på anjoner, alkalinitet, pH och konduktivitet om det fanns vatten tillräckligt för analys. Kvartalsvisa samlingsprover med vatten från varje vecka analyserades också på isotoper.

Koncentrationen av olika joner varierade mycket mellan olika provtagningsperioder. Beräkningar av jonbalanserna visade på relativt stora avvikelser (mer än 10 % relativt fel) i två av proverna. Skillnaderna var så stora att ett fel kan föreligga, antingen vid analyserna eller vid hanteringen av proverna. En annan förklaring kan vara att koncentrationen av många av jonerna var under eller nära detektionsgränsen vilket kan orsaka fel i beräkningarna.

Viktade medelvärden av några av de undersökta jonerna samt av pH jämfördes med resultat från stationer i sydöstra Sverige som ingår i det nationella nederbördskemiska nätet. Jämförelsen visar att halten av joner generellt var högre vid Äspö. Medelvärdena av pH var dock relativt lika. Den huvudsakliga orsaken till skillnaden i jonkoncentration är sannolikt närheten till havet. Ett beräknat korrigerat värde för  $SO_4$ -S (som utesluter svavel som härrör från havet) var också mer likt resultaten från de andra stationerna i sydöstra Sverige.

Väteisotopen  $\delta^2 H$  (deuterium) varierade mellan provtagningstillfällena med den lägsta kvoten under vintern. Som förväntat var kvoterna av  $\delta^2 H$  väl korrelerade med kvoterna av  $\delta^{18}O$  (syre-18). Även kvoterna av <sup>3</sup>H (tritium) varierade mellan provtillfällena med en svag tendens till lägre värden under hösten.

En avvikelse från vad som planerats har förekommit under året. HCO<sub>3</sub> analyserades inte vid flera tillfällen på grund av för låga pH-värden.

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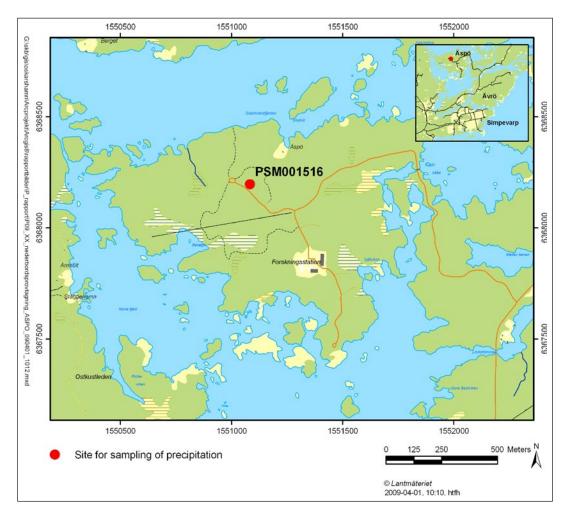
## 1 Introduction

This document reports the results gained by the sampling and analysis of precipitation during 2007, 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 400-07-039. 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 May to December of 2007 at the site PSM001516 at Äspö (Figure 1-1). All data generated was stored in the database SICADA. The data is traceable by the activity plan number.

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

Activity plan Nederbördsprovtagning och analyser 2006 (monitering)	<b>Number</b> AP PS 400-07-039	Version 1.0	
Method descriptions	Number	Version	
Metodbeskrivning för provtagning och analys av nederbörd	SKB MD 423.003	2.0	



*Figure 1-1.* Site for sampling of precipitation (PSM001516) at the island of Äspö. Coordinates for the site is N 6368196; E 1551083 (RT90/RHB70). The elevation is 5.89 m.

## 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 is 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 to give results of high quality from an undisturbed site. 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

Five samplers were placed in a forest clearing approximately two meter above the ground (Figure 3-2). Exact location with coordinates for the different samplers is given in Table 3-1. The samplers were placed two to ten meters apart in an area with a diameter of approximately 15 meter. 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. The number of functional samplers at the site was five.

In the summer season the "NILU Precipitation Collector" was used. This is essentially a can with a funnel with a diameter of 20 cm (Figure 3-1). In winter the "NILU Particulate Fallout Collector", essentially a bucket, with a diameter of 20 cm were used (Figure 3-2). The can and the bucket could hold a maximum volume of 2.5 litres and 12.5 litres respectively. The samplers were emptied weekly into one or two five litres plastic container that was used to transport the mixed sample to the laboratory. At the laboratory a graduated glass was used to measure the total volumes of water in the sample. Later the sample was divided into smaller bottles before delivery to the different analysing laboratories. When the sample was divided into smaller bottles the water for analysis of main components were filtrated with a membrane filter (0.45  $\mu$ m).

Table 3-1. Location of PSM001516 with coordinates for the individual samplers (RT90/RHB70).

Northing (m)	Easting (m)
6368197.483	1551079.054
6368194.742	1551080.070
6368195.975	1551082.957
6368192.689	1551081.771
6368192.513	1551087.517
	6368197.483 6368194.742 6368195.975 6368192.689



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



Figure 3-2. The sampler used in winter at the site for sampling of precipitation at the island of Äspö.

## 4 Execution

#### 4.1 General

The precipitation was collected in samplers placed two to ten meters apart in an area with a diameter of approximately 15 meter. The samplers were emptied weekly and the water volume was measured. Water from five of the weekly periods was sent for full analysis (anions and main components, alkalinity, pH, conductivity and isotopes) to different laboratories. Water from the rest of the periods were analysed for anions, alkalinity, pH and conductivity if enough precipitation had occurred. The work was performed in accordance to the method description "Metodbeskrivning för provtagning och analys av nederbörd, SKB MD 423 003".

#### 4.2 Execution of field work, week 19 to week 32

The precipitation was collected in samplers placed in a small forest clearing at Äspö (Figure 1-1, 3-1 and 3-2). The samplers were emptied regularly each week and if the precipitation had been large enough some of the water was stored and later sent to different laboratories for analysis (Table 4-1). The total volume gathered from the samplers was measured with a graduated glass. If the samplers contained snow or ice the volume was measured at the laboratory with a graduated glass after melting. Notes on the handling of the samples were kept in a diary.

Approximately 20% of the sample from each week was assembled to a so called "general sample". The general sample was stored in a refrigerator and samples from each week were added for six months before the sample was sent for analysis.

In each week the rest of the sample was saved as a so called "point sample". If the volume of the "point sample" was larger than one litre, but smaller than 2.7 litres the sample was marked with a SKB number. Half of the sample was delivered to the Äspö laboratory for "quick analysis" (conductivity, pH, Cl, SO<sub>4</sub>, Br, and F). The rest of the sample was, according to the priority order (Table 4-5), filled into smaller bottles and 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 2.7 litres 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 divided into smaller bottles, marked with the same SKB-number and stored in a refrigerator until a decision was taken on which analysis to perform or if analysis should be performed at all.

If the volume of the "point sample" was smaller than one litre the sample was discarded.

When decisions were taken on which "point samples" to analyse the bottles were sent to the laboratories for analysis of main components and  $\delta^2$ H, <sup>3</sup>H and  $\delta^{18}$ O. During the period one "point sample", denominated as a complete sample, was analysed. This sample contained more than 2.7 litres. Analysis of  $\delta^2$ H, <sup>3</sup>H and  $\delta^{18}$ O was also performed on one general sample. Volumes from different weeks in the general sample are presented in Table 4-2.

See Table 4-1, 4-2, 4-3 and 4-4 for information on analysis, volumes and SKB-numbers in different kind of samples.

Sample period	Sample number	Type of sample and analyses
2007-05-30 – 2007-06-07	11915	Anions, pH, conductivity and HCO₃⁻
2007-06-13 – 2007-06-20	11936	Complete sample. Anions, pH, conductivity, HCO₃⁻, main components, ठ²H, ³H and ठ¹⁰O
2007-06-20 – 2007-06-27	11969	Anions, pH, conductivity and HCO <sub>3</sub> ⁻
2007-06-27 – 2007-07-04	11994	Anions, pH, conductivity and HCO <sub>3</sub> <sup>−</sup>
2007-05-04 – 2007-07-04	11995	General sample. $\delta^2$ H, $^3$ H and $\delta^{18}$ O
2007-07-04 – 2007-07-12	15000	Anions, pH, conductivity and HCO <sub>3</sub> <sup>−</sup>
2007-07-12 – 2007-07-23	15012	Anions, pH, conductivity and HCO <sub>3</sub> <sup>−</sup>
2007-07-23 – 2007-08-01	15030	Anions, pH, conductivity and HCO <sub>3</sub> <sup>−</sup>
2007-08-09 – 2007-08-15	15054	Anions, pH, conductivity and HCO₃⁻
2007-08-15 – 2007-08-22	15080	Anions, pH, conductivity and HCO₃⁻
2007-08-22 – 2007-08-29	15100	Anions, pH, conductivity and HCO₃⁻
2007-08-29 – 2007-09-06	15109	Complete sample. Anions, pH, conductivity, HCO <sub>3</sub> -, main components, δ²H, ³H and δ¹®O
2007-09-06 – 2007-09-12	15110	Anions, pH, conductivity and HCO <sub>3</sub> <sup>−</sup>
2007-09-18 – 2007-09-26	15125	Anions, pH, conductivity and HCO₃ <sup>−</sup>
2007-09-26 – 2007-10-03	15126	Anions, pH, conductivity and HCO₃⁻
2007-07-04 – 2007-10-03	15129	General sample. $\delta^2$ H, $^3$ H and $\delta^{18}$ O
2007-10-10 – 2007-10-17	15147	Anions, pH, conductivity and HCO <sub>3</sub> <sup>-</sup>
2007-10-17 – 2007-10-23	15152	Anions, pH, conductivity and HCO <sub>3</sub> <sup>−</sup>
2007-10-23 – 2007-10-31	15167	Complete sample. Anions, pH, conductivity, HCO <sub>3</sub> -, main components, δ²H, ³H and δ¹ <sup>s</sup> O
2007-10-31 – 2007-11-07	15170	Anions, pH, conductivity and HCO <sub>3</sub> <sup>−</sup>
2007-11-07 – 2007-11-14	15197	Complete sample. Anions, pH, conductivity, HCO <sub>3</sub> -, main components, $\delta^2$ H, <sup>3</sup> H and $\delta^{18}$ O
2007-11-14 – 2007-11-21	15212	Anions, pH, conductivity and HCO₃⁻
2007-11-21 – 2007-11-29	15217	Anions, pH, conductivity and HCO₃⁻
2007-11-29 – 2007-12-04	15226	Anions, pH, conductivity and HCO₃⁻
2007-12-04 – 2007-12-12	15227	Complete sample. Anions, pH, conductivity, HCO <sub>3</sub> -, main components, δ²H, ³H and δ¹ <sup>8</sup> O
2007-10-03 – 2007-12-19	15279	General sample. $\delta^2$ H, <sup>3</sup> H and $\delta^{18}$ O

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

# Table 4-2. Volumes from different sampling weeks in the general sample from the period 2007-05-04 to 2007-07-04.

Sample date	Sample number	Volume (ml)	Volume (%)	Comments
2007-05-10	_	246	5.3	no point sample for analysis
2007-05-16	_	226	4.9	no point sample for analysis
2007-05-23	_	188	4.1	no point sample for analysis
2007-05-30	_	44	1.0	no point sample for analysis
2007-06-07	11915	410	8.9	
2007-06-13	_	0	0.0	no point sample for analysis
2007-06-20	11936	543	11.8	
2007-06-27	11969	1,912	41.4	
2007-07-04	11994	1,046	22.7	

Sample date	Sample number	Volume (ml)	Volume (%)	Comments
2007-07-12	15000	1,364	26.8	
2007-07-23	15012	513	10.1	
2007-08-01	15030	450	8.9	
2007-08-09	_	166	3.3	no point sample for analysis
2007-08-15	15054	256	5.0	
2007-08-22	15080	278	5.5	
2007-08-29	15100	158	3.1	
2007-09-06	15109	872	17.2	
2007-09-12	15110	377	7.4	
2007-09-18	_	48	0.9	no point sample for analysis
2007-09-26	15125	322	6.3	
2007-10-03	15126	279.2	5.5	

 Table 4-3. Volumes from different sampling weeks in the general sample from the period

 2007-07-04 to 2007-10-03.

Table 4-4. Volumes from different sampling weeks in the general sample from the period
2007-10-03 to 2007-12-19.

Sample date	Sample number	Volume (ml)	Volume (%)	Comments
2007-10-10	_	0	0.0	no point sample for analysis
2007-10-17	15147	169	5.0	
2007-10-23	15152	121	3.6	
2007-10-31	15167	552	16.3	
2007-11-07	15170	417	12.3	
2007-11-14	15197	556.4	16.4	
2007-11-21	15212	120.4	3.5	
2007-11-29	15217	143.2	4.2	
2007-12-04	15226	682	20.1	
2007-12-12	15227	634	18.7	
2007-12-19	_	0	0.0	no point sample for analysis

#### 4.3 Execution of field work, week 32 to week 51

The execution after week 32 was essentially the same as before and differed mostly on which amount of water that was necessary for point samples. The text below is therefore almost identical to the text in the previous section.

The precipitation was collected in samplers placed in a small forest clearing at Äspö (Figure 1-1, 3-1 and 3-2). The samplers were emptied regularly each week and if the precipitation had been large enough water was stored and later sent to different laboratories for analysis (Table 4-1). The total volume gathered from the samplers was measured with a graduated glass. If the samplers contained snow or ice the volume was measured at the laboratory with a graduated glass after melting. Notes on the handling of the samples were kept in a diary.

Approximately 20% of the sample from each week was assembled to a so called "general sample". The general sample was stored in a refrigerator and samples from each week were added for three months before the sample was sent for analysis. Care was taken to minimize the volume of air in the storage container by using a succession of larger containers as the sample volume grew.

In each week the rest of the sample was saved as a so called "point sample". If the volume of the "point sample" was larger than 250 ml, but smaller than 2.2 litres the sample was marked with a SKB number. Bottles for "quick analysis" were immediately delivered to the Äspö laboratory (conductivity, pH, Cl, SO<sub>4</sub>, Br, and F). The rest of the sample was, according to the priority order (Table 4-5), filled into smaller bottles and 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. When the bottle for analysis of tritium was filled it was overflowed one to three times depending on the amount of water available.

If the "point sample" was larger than 2.2 litres then 2x250 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, according to the priority order (Table 4-5), filled into smaller bottles and 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. When the bottle for analysis of tritium was filled it was overflowed three times.

If the volume of the "point sample" was smaller than 250 ml litre the sample was discarded.

When decisions were taken on which "point samples" to analyse the bottles were sent to the laboratories for analysis of main components and  $\delta^2$ H, <sup>3</sup>H and  $\delta^{18}$ O. During the period four "point sample", denominated as a complete sample, was analysed. All of these contained more than 2.7 litres. Analysis of  $\delta^2$ H, <sup>3</sup>H and  $\delta^{18}$ O was also performed on two general samples. Volumes from different weeks in the general sample are presented in Table 4-3 and 4-4. See Table 4-1, 4-2, 4-3 and 4-4 for information on analysis, volumes and SKB-numbers in different kind of samples.

#### 4.4 Handling of samples before analysis

The analysis performed follow chemistry class 3. The method used is described in detail in MD 423.003, SKB internal document.

The handling of the samples prior to analysis with priority order, type of bottles, filtration, acidification, filling instructions and the laboratories used are shown in Table 4-5. In addition two archive samples of 250 ml was taken out and stored by SKB. The 250 ml archive samples where filtrated in a Pall filter (0.45  $\mu$ m) prior to storage.

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

Components	Priority	Bottle/volume	Preparation of sample	Laboratory
pH, Conductivity, HCO₃	1	250 ml	-	Äspö laboratory
Cl, Br, SO <sub>4</sub> , F	1	250 ml	filtration-(in connection with analysis)	Äspö laboratory
Ca, Fe, K, Mg, Na, S, Si, Li, Mn, Sr	4	100 ml, acid rinsed	filtration membrane filter/ acidification 1% HNO <sub>3</sub>	Analytica
<sup>3</sup> H	3	500 ml	dried bottle, flow over at least once	Environmental Isotope Lab at the University of Waterloo, Canada
<sup>2</sup> H, <sup>18</sup> O	2	100 ml	-	Institutute for Energy Technology, Norway
Archive samples	5	2 × 250 ml	filtration with pallfilter	-

Table 4-5. Analysed components, priority, treatments of samples and analysing laboratory.

#### 4.5 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 2009-02-10.

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

The concentration of SO<sub>4</sub>-S in the precipitation was calculated as the atomic proportion of SO<sub>4</sub>  $([SO_4-S] = [SO_4]/96 \times 32).$ 

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 ( $[SO_4-S_{corr}] = [SO_4-S] - 0.0837 \times [Na]$ ) (concentrations in mg/l).

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

#### 4.6 Nonconformities

The analysis of HCO<sub>3</sub> was not performed on every occasion, due to very low pH.

### 5 Results

All data gained were stored in the primary data base SICADA. The data is traceable in SICADA by the Activity Plan number (AP PS 400-05-027). Only data in databases are accepted for further interpretation and modelling. The data presented in this report are regarded as copies of the original data. Data in the databases may be revised, if needed. Such revisions will not necessarily result in a revision of the P-report, although the normal procedure is that major revisions entail a revision of the P-report. Minor revisions are normally presented as supplements, available at www.skb.se.

Precipitation was measured in 32 sampling periods during 2007. The average volume collected per sampler during this period was 409 ml (Table 5-1). The mean calculated precipitation per sampling period was 13.0 mm. The total measured precipitation from the beginning of May to late December was 416.8 mm. This is probably an underestimation of the true total precipitation during this period due to evaporation from the samplers.

The complete results from the analysis are presented in the Appendix at the end of this report. The results from the five occasions when full analysis were performed are also presented in Table 5-2, 5-4, 5-5, and 5-6. The concentrations of different ions varied much between the different measuring periods (Table 5-2 and Appendix). On two occasions the concentrations of cations far exceeded the concentrations of the anions. The imbalance was large and there might 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 for this report (Table 5-3). These calculations show rather great imbalances (more than 10% relative error) in two of the five samples. The reason for this is difficult to interpret. It cannot be explained by the lack of analysis of two major ions, NO<sub>3</sub> and NH<sub>4</sub>. In a nearby station for measurement of precipitation (Norra Kvill in the municipality of Vimmerby) the average concentrations of NO<sub>3</sub>-N and NH<sub>4</sub>-N was 0.24 mg/l and 0.19 mg/l in 2007 (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 unaltered. For one of the samples (sample number 15109) there might be another explanation though, the concentration of many of the ions was close to or below the detection limits which could have caused calculation errors.

Also pH and conductivity varied between the different measuring periods (Table 5-4 and Appendix). Some periods differ with markedly higher conductivity. Influx of sea water spray might be an explanation but there was no corresponding increase of the concentrations of chloride or sulphate in these periods (Appendix).

To compare some of the results with those from national stations for monitoring deposition in south east Sweden, weighted averages was calculated on some of the ions and on pH (see Chapter 4.4). Two stations situated in the counties of Kalmar and Kronoberg were chosen and the results as weighted averages from 2004, 2005, 2006 and 2007 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 results from 2007 was also compared to the data obtained at the Äspö site during 2002 to 2007 /Ericsson 2004, Ericsson 2005, Ericsson and Engdahl 2007, Ericsson and Engdahl 2008/. The comparison shows that the concentration of ions is generally higher at Äspö (Table 5-5). The average of pH has varied at the Äspö site with slightly higher values than the other sites in south east Sweden. The main reason for higher concentration of ions at the Äspö site is probably because the site is situated very close to the sea with a greater influx of sea salt. The average of SO<sub>4</sub>-S<sub>korr</sub> (which excludes the part of sulphate that originates from sea salt) at Äspö has also been more similar to the other stations in south east Sweden (Table 5-5).

The hydrogen isotope ratio of  $\delta^2$ H varied with an indication of lower ratios in winter (Table 5-6 and Appendix). These ratios correlated well with the ratios of  $\delta^{18}$ O (Figure 5-1). The linear relation corresponds reasonable well with the "Global Meteoric Water Line" ( $\delta^2$ H = 8 × <sup>18</sup>O + 10) which is based on precipitation data from locations around the globe /Craig 1961/. The ratios of <sup>3</sup>H varied with a small tendency for lower values in the autumn.

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)
2007-05-04 - 2007-05-10	1,230	246	20	314.2	7.8
2007-05-10 - 2007-05-16	1,130	226	20	314.2	7.2
2007-05-16 - 2007-05-23	940	188	20	314.2	6.0
2007-05-23 – 2007-05-30	220	44.0	20	314.2	1.4
2007-05-30 – 2007-06-07	2,050	410	20	314.2	13.1
2007-06-07 - 2007-06-13	0	0	20	314.2	0
2007-06-13 – 2007-06-20	2,715	543	20	314.2	17.3
2007-06-20 – 2007-06-27	9,560	1912	20	314.2	60.9
2007-06-27 - 2007-07-04	5,230	1046	20	314.2	33.3
2007-07-04 - 2007-07-12	6,820	1364	20	314.2	43.4
2007-07-12 - 2007-07-23	2,565	513	20	314.2	16.3
2007-07-23 – 2007-08-01	2,250	450	20	314.2	14.3
2007-08-01 – 2007-08-09	830	166	20	314.2	5.3
2007-08-09 – 2007-08-15	1,280	256	20	314.2	8.1
2007-08-15 – 2007-08-22	1,390	278	20	314.2	8.8
2007-08-22 – 2007-08-29	790	158	20	314.2	5.0
2007-08-29 – 2007-09-06	4,360	872	20	314.2	27.8
2007-09-06 – 2007-09-12	1,885	377	20	314.2	12.0
2007-09-12 – 2007-09-18	240	48.0	20	314.2	1.5
2007-09-18 – 2007-09-26	1,610	322	20	314.2	10.2
2007-09-26 – 2007-10-03	1,396	279	20	314.2	8.9
2007-10-03 – 2007-10-10	0	0	20	314.2	0
2007-10-10 – 2007-10-17	845	169	20	314.2	5.4
2007-10-17 – 2007-10-23	605	121	20	314.2	3.9
2007-10-23 – 2007-10-31	2,760	552	20	314.2	17.6
2007-10-31 – 2007-11-07	2,085	417	20	314.2	13.3
2007-11-07 – 2007-11-14	2,782	556	20	314.2	17.7
2007-11-14 – 2007-11-21	602	120	20	314.2	3.8
2007-11-21 – 2007-11-29	716	143	20	314.2	4.6
2007-11-29 – 2007-12-04	3,410	682	20	314.2	21.7
2007-12-04 – 2007-12-12	3,170	634	20	314.2	20.2
2007-12-12 – 2007-12-19	0	0	20	314.2	0
Average		409			13.0
Standard deviation		415			13.2

Table 5-2. Measured concentrations of ions and some other components during the measuring periods when full analyses were performed on point samples. (There is one measured and one calculated  $SO_4$ -S value for the samples, the calculated  $SO_4$ -S was calculated from  $SO_4$ , see Chapter 4.4).

Sample period	Sample number	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Fe (mg/l)	Mn (mg/l)
2007-06-13 - 2007-06-20	11936	3.90	0.51	0.84	1.04	0.022	0.00855
2007-08-29 - 2007-09-06	15109	< 0.5	< 1	< 0.2	< 0.5	0.018	0.00240
2007-10-23 – 2007-10-31	15167	< 0.1	< 0.4	0.20	< 0.09	< 0.02	0.00824
2007-11-07 – 2007-11-14	15197	0.83	< 0.4	0.62	0.11	< 0.02	0.00320
2007-12-04 – 2007-12-12	15227	0.62	< 0.4	0.63	0.11	0.032	0.00307
Sample period	Sample number	Li (mg/l)	Si (mg/l)	Sr (mg/l)	SO₄-S meas. (mg/l)	Cl (mg/l)	SO₄ (mg/l)
2007-06-13 – 2007-06-20	11936	< 0.004	0.05	0.011	0.54	0.34	1.38
2007-08-29 – 2007-09-06	15109	< 0.05	< 0.5	< 0.001	0.10	0.38	0.32
2007-10-23 – 2007-10-31	15167	< 0.004	< 0.03	< 0.002	< 0.2	0.45	0.39
2007-11-07 – 2007-11-14	15197	< 0.004	< 0.03	0.002	0.59	0.94	1.77
2007-12-04 – 2007-12-12	15227	< 0.004	< 0.03	0.002	0.63	0.84	1.88
Sample period	Sample number	SO₄-S calc. (mg/l)	SO₄-S <sub>korr</sub> calc. (mg/l)	Br (mg/l)	F (mg/l)	HCO₃ (mg/l)	
2007-06-13 – 2007-06-20	11936	0.46	0.13	< 0.2	< 0.2		
2007-08-29 – 2007-09-06	15109	0.11	0.06	< 0.2	< 0.2		
2007-10-23 – 2007-10-31	15167	0.13	0.12	< 0.2	< 0.2	< 0.3	
2007-11-07 – 2007-11-14	15197	0.59	0.52	< 0.2	< 0.2	< 0.3	
2007-12-04 - 2007-12-12	15227	0.63	0.57	< 0.2	< 0.2		

Table 5-3. Calculated relative errors of the ion balance in the samples from the different measuring periods.

Sample period	Sample number	lon balance relative error (%)
2007-06-13 - 2007-06-20	11936	68.8
2007-08-29 - 2007-09-06	15109	67.0
2007-10-23 – 2007-10-31	15167	-6.7
2007-11-07 – 2007-11-14	15197	5.9
2007-12-04 - 2007-12-12	15227	9.5

Sample period	Sample number	рН	Conductivity (mS/m)
2007-05-30 - 2007-06-07	11915	5.23	2.0
2007-06-13 - 2007-06-20	11936	4.68	1.1
2007-06-20 - 2007-06-27	11969	4.99	8.2
2007-06-27 - 2007-07-04	11994	4.89	1.0
2007-07-04 - 2007-07-12	15000	4.81	37.7
2007-07-12 - 2007-07-23	15012	5.12	0.9
2007-07-23 - 2007-08-01	15030	4.86	3.9
2007-08-09 - 2007-08-15	15054	5.02	0.9
2007-08-15 - 2007-08-22	15080	4.85	1.7
2007-08-22 - 2007-08-29	15100	3.80	1.6
2007-08-29 - 2007-09-06	15109	4.15	0.5
2007-09-06 - 2007-09-12	15110	3.81	0.6
2007-09-18 - 2007-09-26	15125	4.24	11.2
2007-09-26 - 2007-10-03	15126	3.83	2.9
2007-10-10 - 2007-10-17	15147	5.31	0.8
2007-10-17 - 2007-10-23	15152	5.35	0.6
2007-10-23 - 2007-10-31	15167	5.32	0.8
2007-10-31 - 2007-11-07	15170	5.31	1.9
2007-11-07 - 2007-11-14	15197	5.37	1.5
2007-11-14 - 2007-11-21	15212	4.29	3.3
2007-11-21 - 2007-11-29	15217	4.53	2.2
2007-11-29 - 2007-12-04	15226	4.61	1.6
2007-12-04 - 2007-12-12	15227	4.71	11.7
Average		4.74	4.3
Standard deviation		0.51	8.0

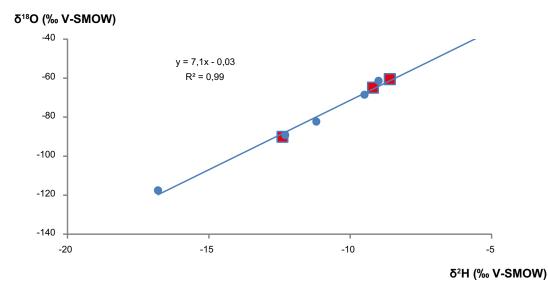
Table 5-4. Measured values of pH and conductivity during periods when analysis were performed.

# Table 5-5. Volume weighted averages of some major ions and pH in Äspö and in some other stations in south east Sweden 2004, 2005, 2006 and 2007.

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 2007	0.57	0.27	1.10	0.47	0.58	0.37	4.77
Äspö 2006	0.66	0.36	1.33	0.38	0.88	0.27	4.97
Äspö 2005	0.99	0.41	0.74	0.37	0.59	0.15	4.66
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 2007	0.50	0.26	0.32	0.15	0.07	0.06	4.89
N Kvill 2006	0.42	0.32	0.27	0.19	0.21	0.07	4.88
N Kvill 2005	0.50	0.26	0.33	0.15	0.09	0.05	4.77
N Kvill 2004	0.36	0.26	0.28	0.11	0.10	0.05	4.89
Aneboda 2007	2.68	0.39	1.65	0.20	0.11	0.20	4.80
Aneboda 2006	1.00	0.37	0.65	0.13	0.16	0.09	4.71
Aneboda 2005	0.69	0.38	0.44	0.14	0.11	0.06	4.69
Aneboda 2004	1.27	0.35	0.87	0.14	0.09	0.12	4.69

Table 5-6. Isotope data obtained during the measuring periods. The last samples are the general samples gathered during the period 2007-05-04 to 2007-07-04, 2007-07-04 to 2007-10-03 and 2007-10-03 to 2007-12-19.

Sample period	Sample number	δ²Η (‰ V-SMOW)	³H (TU)	δ <sup>18</sup> Ο (‰ V-SMOW)
2007-06-13 - 2007-06-20	11936	-68.5	11.6	-9.5
2007-08-29 - 2007-09-06	15109	-61.4	9.6	-9
2007-10-23 – 2007-10-31	15167	-82.3	7.2	-11.2
2007-11-07 – 2007-11-14	15197	-117.6	11.3	-16.8
2007-12-04 – 2007-12-12	15227	-89.3	10.8	-12.3
Average		-83.8	10.1	-11.8
Standard deviation		21.9	1.8	3.1
Sample period	Sample number	δ²H (‰ V-SMOW)	³H (TU)	δ¹ଃΟ (‰ V-SMOW)
2007-05-04 - 2007-07-04	11995	-64.9	12.40	-9.20
2007-07-04 – 2007-10-03	15129	-60.5	11.80	-8.60
2007-10-03 – 2007-12-19	15279	-90.1	9.10	-12.40



**Figure 5-1.** The relationship between the ratios of  $\delta^2 H$  and  $\delta^{18}O$  at the Äspö site in 2007. The red square is the data from the general samples.

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## Primary results

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)
2007-05-30 - 2007-06-07	11915									
2007-06-13 - 2007-06-20	11936	3.9	0.51	0.8	1.04	0.0224	0.00855	< 0.004	0.05	0.011
2007-06-20 - 2007-06-27	11969									
2007-06-27 - 2007-07-04	11994									
2007-07-04 - 2007-07-12	15000									
2007-07-12 - 2007-07-23	15012									
2007-07-23 - 2007-08-01	15030									
2007-08-09 - 2007-08-15	15054									
2007-08-15 - 2007-08-22	15080									
2007-08-22 - 2007-08-29	15100									
2007-08-29 - 2007-09-06	15109	< 0.5	< 1	< 0.2	< 0.5	0.0180	0.00240	< 0.05	< 0.5	< 0.001
2007-09-06 - 2007-09-12	15110									
2007-09-18 - 2007-09-26	15125									
2007-09-26 - 2007-10-03	15126									
2007-10-10 - 2007-10-17	15147									
2007-10-17 - 2007-10-23	15152									
2007-10-23 - 2007-10-31	15167	< 0.1	< 0.4	0.2	< 0.09	< 0.02	0.00824	< 0.004	< 0.03	< 0.002
2007-10-31 - 2007-11-07	15170									
2007-11-07 - 2007-11-14	15197	0.8	< 0.4	0.6	0.11	< 0.02	0.00320	< 0.004	< 0.03	0.002
2007-11-14 - 2007-11-21	15212									
2007-11-21 - 2007-11-29	15217									
2007-11-29 - 2007-12-04	15226									
2007-12-04 - 2007-12-12	15227	0.6	< 0.4	0.6	0.11	0.0318	0.00307	< 0.004	< 0.03	0.002

Sample period	Sample number	SO4-S meas. (mg/l)	CI (mg/l)	SO4 (mg/l)	Br (mg/l)	F (mg/l)	HCO3 (mg/l)	рН	Conductivity (mS/m)
2007-05-30 - 2007-06-07	11915		0.4	1.81	< 0.2	< 0.2	< 0.3	5.23	2.0
2007-06-13 - 2007-06-20	11936	0.54	0.3	1.38	< 0.2	< 0.2		4.68	1.1
2007-06-20 – 2007-06-27	11969		0.3	1.03	< 0.2	< 0.2	0.57	4.99	8.2
2007-06-27 – 2007-07-04	11994		0.4	0.69	< 0.2	< 0.2		4.89	1.0
2007-07-04 – 2007-07-12	15000		0.3	0.65	< 0.2	< 0.2		4.81	37.7
2007-07-12 – 2007-07-23	15012		0.7	0.89	< 0.2	< 0.2	1.99	5.12	0.9
2007-07-23 – 2007-08-01	15030		0.5	0.84	< 0.2	< 0.2		4.86	3.9
2007-08-09 – 2007-08-15	15054		0.3	1.06	< 0.2	< 0.2	1.42	5.02	0.9
2007-08-15 – 2007-08-22	15080		0.9	2.02	< 0.2	< 0.2		4.85	1.7
2007-08-22 – 2007-08-29	15100		1.2	2.31	< 0.2	< 0.2		3.80	1.6
2007-08-29 – 2007-09-06	15109	0.10	0.4	0.32	< 0.2	< 0.2		4.15	0.5
2007-09-06 – 2007-09-12	15110		0.5	0.49	< 0.2	< 0.2		3.81	0.6
2007-09-18 – 2007-09-26	15125		0.5	< 0.2	< 0.2	< 0.2		4.24	11.2
2007-09-26 – 2007-10-03	15126		1.1	4.20	< 0.2	< 0.2		3.83	2.9
2007-10-10 – 2007-10-17	15147		0.8	0.47	< 0.2	< 0.2	< 0.3	5.31	0.8
2007-10-17 – 2007-10-23	15152		0.5	0.41	< 0.2	< 0.2	< 0.3	5.35	0.6
2007-10-23 – 2007-10-31	15167	< 0.2	0.4	0.39	< 0.2	< 0.2	< 0.3	5.32	0.8
2007-10-31 – 2007-11-07	15170		0.5	0.28	< 0.2	< 0.2	< 0.3	5.31	1.9
2007-11-07 – 2007-11-14	15197	0.59	0.9	1.77	< 0.2	< 0.2	< 0.3	5.37	1.5
2007-11-14 – 2007-11-21	15212		0.8	2.39	< 0.2	< 0.2		4.29	3.3
2007-11-21 – 2007-11-29	15217		0.6	1.57	< 0.2	< 0.2		4.53	2.2
2007-11-29 – 2007-12-04	15226		0.7	0.73	< 0.2	< 0.2		4.61	1.6
2007-12-04 – 2007-12-12	15227	0.63	0.8	1.88	< 0.2	< 0.2		4.71	11.7

Sample period	Sample number	δ2H (‰ V-SMOW)	3H (TU)	δ18O (‰ V-SMOW)
2007-05-30 - 2007-06-07	11915			
2007-06-13 - 2007-06-20	11936	-68.5	11.60	-9.50
2007-06-20 - 2007-06-27	11969			
2007-06-27 - 2007-07-04	11994			
2007-07-04 - 2007-07-12	15000			
2007-07-12 - 2007-07-23	15012			
2007-07-23 - 2007-08-01	15030			
2007-08-09 - 2007-08-15	15054			
2007-08-15 - 2007-08-22	15080			
2007-08-22 - 2007-08-29	15100			
2007-08-29 - 2007-09-06	15109	-61.4	9.60	-9.00
2007-09-06 - 2007-09-12	15110			
2007-09-18 - 2007-09-26	15125			
2007-09-26 - 2007-10-03	15126			
2007-10-10 - 2007-10-17	15147			
2007-10-17 - 2007-10-23	15152			
2007-10-23 - 2007-10-31	15167	-82.3	7.20	-11.20
2007-10-31 - 2007-11-07	15170			
2007-11-07 - 2007-11-14	15197	-117.6	11.30	-16.80
2007-11-14 - 2007-11-21	15212			
2007-11-21 - 2007-11-29	15217			
2007-11-29 - 2007-12-04	15226			
2007-12-04 - 2007-12-12	15227	-89.3	10.80	-12.30
Sample period	Sample number	δ2H (‰ V-SMOW)	3H (TU)	δ18O (‰ V-SMOW)
2007-05-04 - 2007-07-04	11995	-64.9	12.40	-9.20
2007-07-04 - 2007-10-03	15129	-60.5	11.80	-8.60
2007-10-03 - 2007-12-19	15279	-90.1	9.10	-12.40