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Forsmark site investigation

Sampling and analysis of precipitation, years 2002 to 2005

Daniel Nilsson, Geosigma

June 2005

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Keywords: AP PF 400-02-41, AP PF 400-04-089, Precipitation, Water sampling, Chemical analysis, Major constituents, Environmental isotopes.

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 in Forsmark were performed from November 2002 to May 2005. Ten specially made samplers were used and they were first placed near drill site DS1. Since the traffic on an adjacent road increased, a new place for the samplers was selected in order to avoid the risk of contamination by dust from the road. The samplers were generally emptied once a month and if the water volume was large enough, samples were sent to different laboratories for analyses.

The precipitation analyses included the major constituents Na, K, Ca, Mg, Al, Fe, NH_4^+ , Br^- , Cl^- , SO_4^{2-} , NO_3^- and HCO_3^- as well as measurements of pH and electric conductivity. Further, the stable isotopes deuterium and syre-18 and the radioisotope tritium were determined.

The analytical results obtained are reasonable/consistent with a few exceptions where the charge balance errors are quite high. The yearly average concentrations are comparable with those from sampling stations within the Swedish national monitoring programme for precipitation during the same time period.

Sammanfattning

Provtagning och analys av nederbörd i Forsmark genomfördes mellan november 2002 och maj 2005. Tio specialtillverkade provuppsamlare användes och placerades inledningsvis nära borrhållplats BP1. När fordonstrafiken på den närbelägna vägen ökade, valdes en ny placering för provuppsamlarna för att undvika kontaminering av vägdam. Normalt tömdes provbehållarna en gång per månad och om vattenvolymen var tillräcklig, skickades prov till de anlitate laboratorerna.

Analyserna av nederbörd inkluderade huvudkomponenterna Na, K, Ca, Mg, Al, Fe, NH_4^+ , Br^- , Cl^- , SO_4^{2-} , NO_3^- och HCO_3^- samt mätningar av pH and elektrisk konduktivitet. Vidare analyserades de stabila isotoperna deuterium and syre-18 samt radioisotopen tritium.

Analysresultaten är rimliga/konsistenta med ett fåtal undantag där felen i jonbalansen är väl höga. Årsmedelvärdena av de olika koncentrationerna är jämförbara med dem från nederbördsstationer inom det Svenska nationella programmet för nederbörd under samma tidsperiod.

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1 Introduction

This document reports the analytical results gained from sampling of precipitation, which is one of the activities performed within the site investigation at Forsmark /1/. The work was carried out in accordance with activity plans AP PF 400-02-41 and AP PF 400-04-089. In Table 1-1 controlling documents for performing this activity are listed. Both activity plans and method description are SKB's internal controlling documents. Precipitation was collected at the sampler location PFM002457 and later on at PFM002564. The positions of these samplers are shown in Figure 1-1.

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

Activity plan	Number	Version
Provtagning och analys av nederbörd	AP PF 400-02-41	1.0
Provtagning och analys av nederbörd 2004	AP PF 400-04-089	1.0
Method descriptions	Number	Version
Provtagning och analys av nederbörd	SKB MD 423.003	1.0

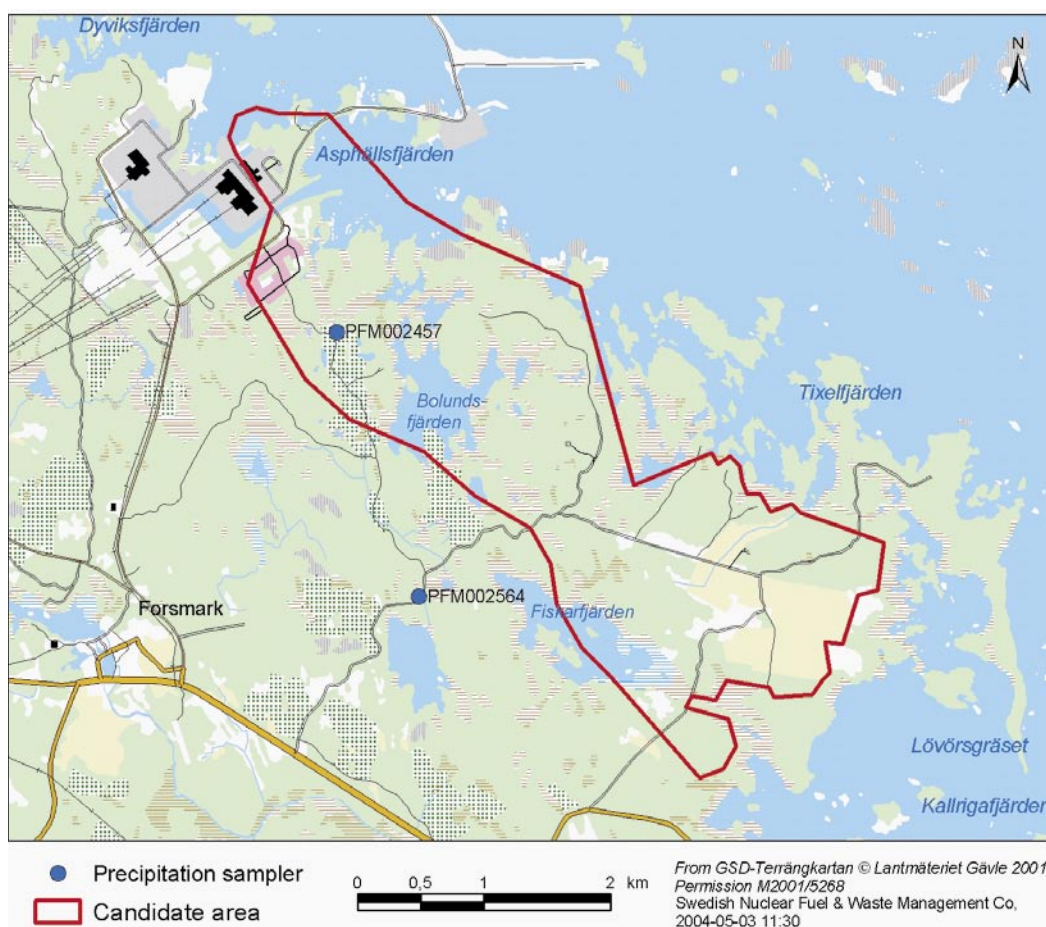


Figure 1-1. The investigation area at Forsmark (approximately the area inside the black square) including the candidate area selected for more detailed investigations. The locations of the samplers for precipitation, PFM002457 and PFM002564, are marked with blue circles.

2 Objective and scope

Sampling and analysis of precipitation are conducted in order to obtain chemical information on today's precipitation in Forsmark. The information is useful in contexts as:

- Understanding of groundwater formation and hydrogeological conditions at the site.
- Limiting conditions for chemical modelling purposes.
- Chemical composition of precipitation that may be used as reference water in mixing calculations.

Sampling and analyses of precipitation are mainly performed according to SKB class 3 /1/. However, aluminium, iron, DOC and some nutrient salts are also included in the analytical protocol.

3 Equipment

The samplers for precipitation were delivered by IVL (Institutet för vatten och luftvård) and consist of a summer and a winter equipment. The summer equipment contains ten equal aluminium foiled 5 L bottles with a funnel on top. A strainer is mounted inside the funnel to prevent larger particles or objects (insects, leaves etc) to enter the bottle. The summer equipment is shown in Figures 3-1 and 3-2.

The winter equipment also contains ten units and is similar to the summer equipment apart from a plastic thin walled tube from the funnel to an upper thick walled tube. The winter equipment is presented in Figure 3-3.

Each piece of equipment is mounted on a stand.



Figure 3-1. The ten samplers are placed within an area of 3x3 m in an open and undisturbed environment (PFM002564).



Figure 3-2. Precipitation sampler used in summer time.



Figure 3-3. Precipitation sampler used in winter time.

4 Performance

4.1 Sampling

4.1.1 Summer

The sampler bottles are removed every month and the content is pooled together to one sample. A thin-walled plastic bag is placed in each one of the ten bottles to avoid the necessity of cleaning the bottles and to prevent contamination of the water samples. The bag is replaced after each sampling.

4.1.2 Winter

All the ten sampler units are removed from their stands once a month and the plastic tubes are sealed. The samplers are brought indoors to let the snow melt into the bottles. After melting, the procedure is the same as for the summer samples.

4.2 Sample treatment and chemical analysis

Each sample is divided into different sub samples and sent to a number laboratories for analysis, see Table 4-1.

Table 4-1. Type of analysis of sub-samples and performing laboratories.

Sub sample volume	Components	Laboratory
Ca 150 mL	HCO ₃ , pH, EC	Forsmark (analyses on the site)
100 mL*	Na, K, Ca, Mg, Al, Fe	Analytica (every 5:th sampling occasion)
500 mL	Cl, Br, SO ₄ , DOC, Na, K, Ca, Mg, Al, Fe, NO ₃ , P _{tot} , Kjeldahl nitrogen	IVL
100 mL**	DOC	Paavo Ristola (every 5:th sampling occasion)
500 mL	³ H	University of Waterloo
100 mL	² H, ¹⁸ O	IFE
100 mL	³⁷ Cl	University of Waterloo
2 x 100 mL*	Archive	
2 x 100 mL**	Archive	

* Filtered 0.45 µm, 1% HNO₃

** Filtered 0.45 µm

4.3 Data handling

The following routines for quality control and data management are generally applied for hydrochemical analysis data, independently of sampling method or sampling object.

Several components are determined by more than one method and/or laboratory. Moreover, duplicate analyses by an independent laboratory are performed as a standard procedure on each fifth or tenth collected sample.

All analytical results are stored in the SICADA database. The applied hierarchy path “Hydrochemistry/Hydrochemical investigation/Analyses/Water in the database” contains two types of tables, raw data tables and primary data tables (final data tables).

Data on *basic water analyses* are inserted into raw data tables for further evaluation. The evaluation results in a final reduced data set for each sample. These data sets are compiled in a primary data table named “water_composition”. The evaluation is based on:

- Comparison of the results from different laboratories and/or methods. The analyses are repeated if a large disparity is noted (generally more than 10%).
- Calculation of charge balance errors. Relative errors within $\pm 5\%$ are considered acceptable (in surface waters $\pm 10\%$).

$$rel.error(\%) = 100 \times \frac{\sum cation(equivalents) - \sum anions(equivalents)}{\sum cation(equivalents) + \sum anion(equivalents)}$$

- General expert judgement of plausibility based on earlier results and experiences.

All results from *special analyses of trace metals, isotopes and precipitation data* are inserted directly into primary data tables. In those cases where the analyses are repeated or performed by more than one laboratory, a “best choice” notation will indicate those results which are considered most reliable. An overview of the data management is given in Figure 4-1.

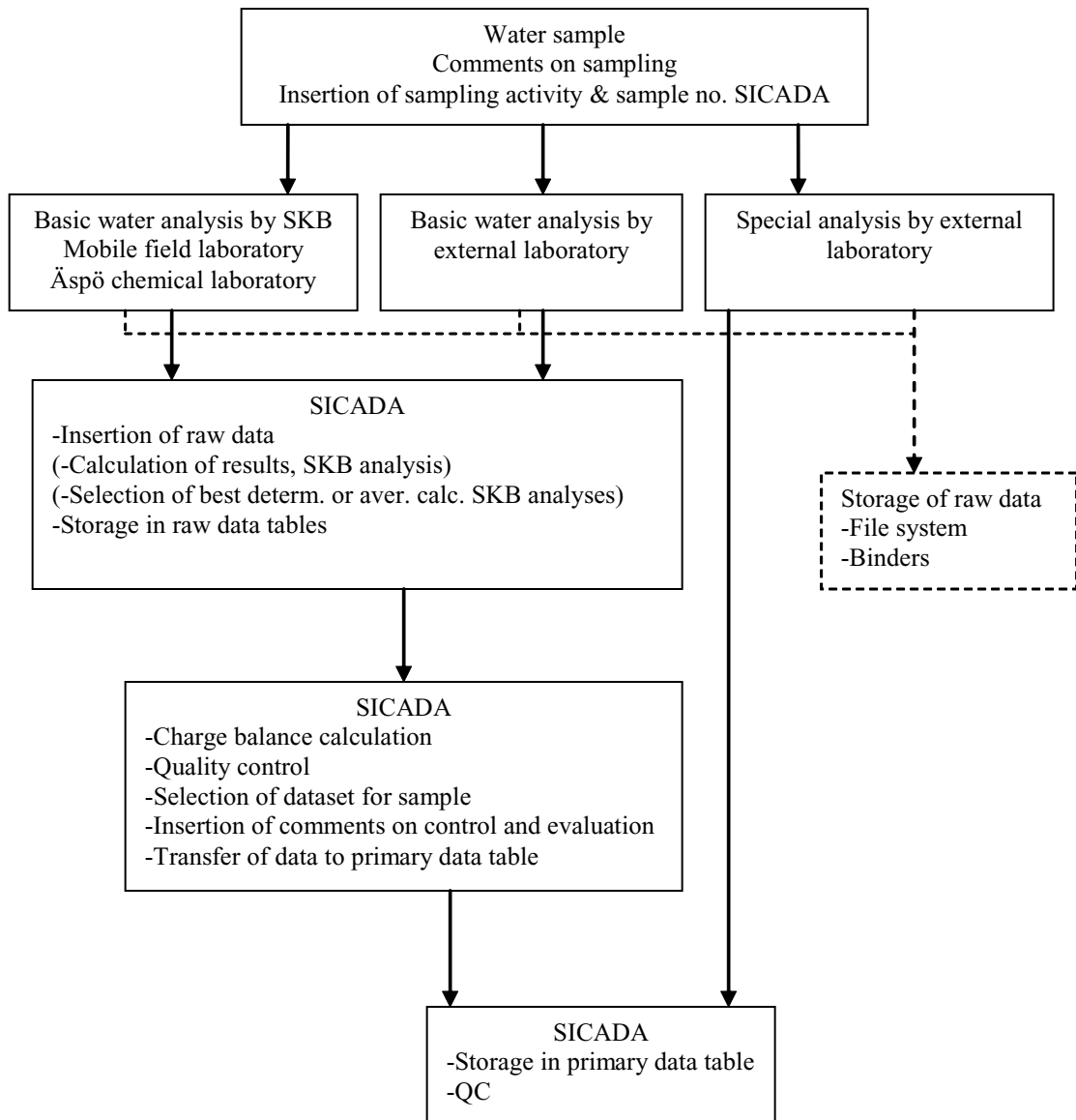


Figure 4-1. Overview of data management for hydrochemical data.

4.4 Nonconformities

The first sampler location at PFM002457 was later found to be unsuitable due to the adjacent road and more frequent traffic to drill site DS1. The samplers were moved (2003-09-15) to the more distant and undisturbed location PFM002564.

The chloride concentrations in the samples were too low for ^{37}Cl determinations.

5 Results and discussion

5.1 General

An ambition was to collect the precipitation samples close in time after rain- or snowfalls. Figure 5-1 shows the sampling occasions in relation to the amount of precipitation.

The results from the sampling activity in Forsmark may be compared with results from the stations sampled within the national monitoring program in Sweden. In Figures 5-2 and 5-3, the chemical compositions of the precipitation in four selected stations /2/ are compared to precipitation in Forsmark. The locations of these stations are shown in Figure 5-4. From the diagrams it could be noticed that the concentrations are similar. However, sodium and chloride ions show slightly higher values in Forsmark, Sannen and Tyresta. This may be explained by their coastal positions and the influence of sea spray.

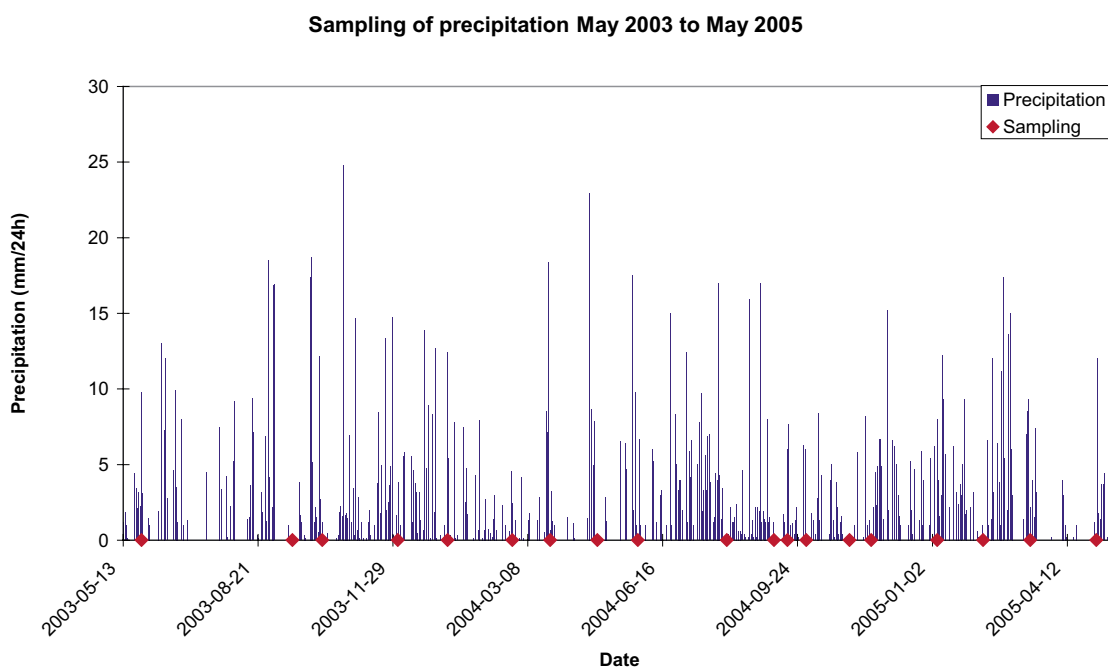


Figure 5-1. Sampling occasions in relation to amount of precipitation.

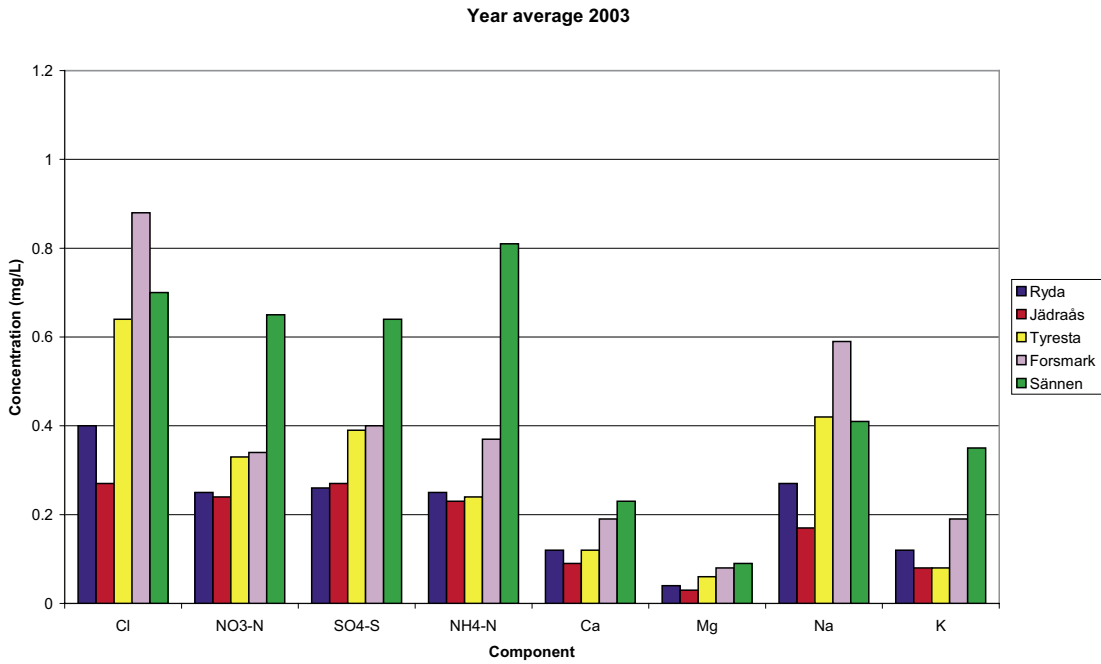


Figure 5-2. Comparison of precipitation data between four sampling stations within the national monitoring program for precipitation and the Forsmark site, year 2003.

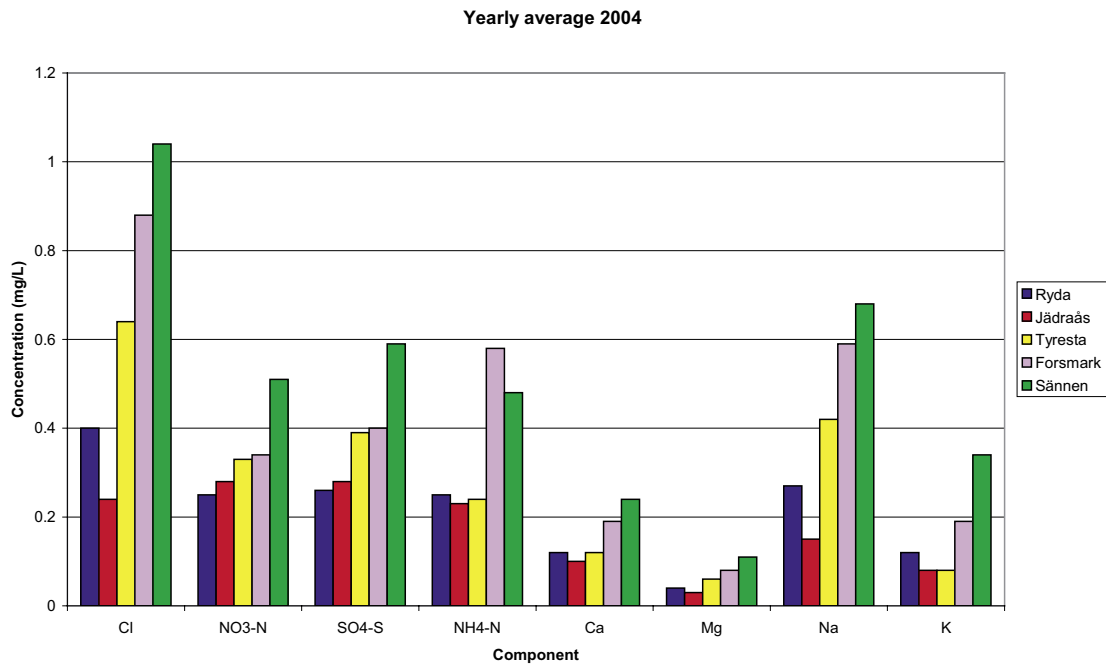


Figure 5-3. Comparison of precipitation data between four sampling stations within the national monitoring program for precipitation and the Forsmark site, year 2004.

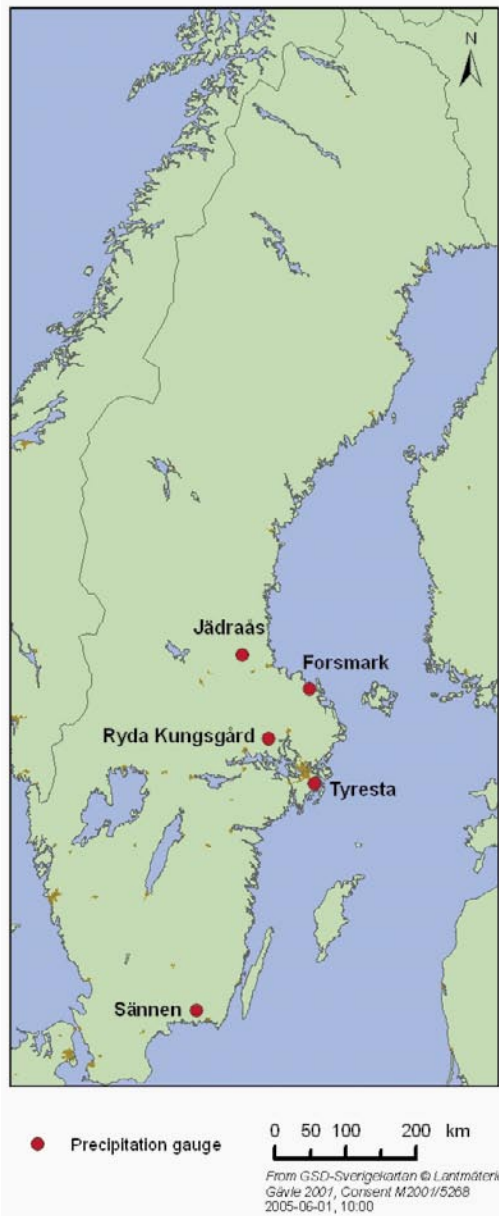


Figure 5-4. The locations of the sampling stations for precipitation used for comparison in Figures 5-2 and 5-3.

5.2 Basic water analysis

The basic water analysis includes the major components Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{2+} , H_2PO_4^- , Br^- , Cl^- , SO_4^{2-} , NO_3^- and HCO_3^- . Furthermore, batch measurements of pH and electric conductivity are included. The basic water analysis data are compiled in Appendix 1.

Calculation of the relative charge balance error gives an indication of the quality and uncertainty of the data on the major constituents. Normally, for surface waters a relative charge balance error within $\pm 10\%$ is considered acceptable. However, the ion concentrations in precipitation are much lower than in the most dilute surface waters. Many constituents show concentrations close to the reporting limit and analytical errors have a large effect on the charge balance. Some Forsmark samples also demonstrate large relative errors, see Figure 5-5. In samples 8500, 8501 and 8602, the ammonium content seems to be abnormally high by a factor 3. Sample 8647 exhibits an extremely high aluminium concentration, by a factor 30 in comparison to the other samples.

Another quality check of the precipitation data is to calculate and compare TDS (Total Dissolved Salts) from analytical results and from electric conductivity ($\text{TDS} \approx \text{EC}/0.47$), see Figure 5-6. The agreement may be regarded as satisfactory considering the very dilute waters.

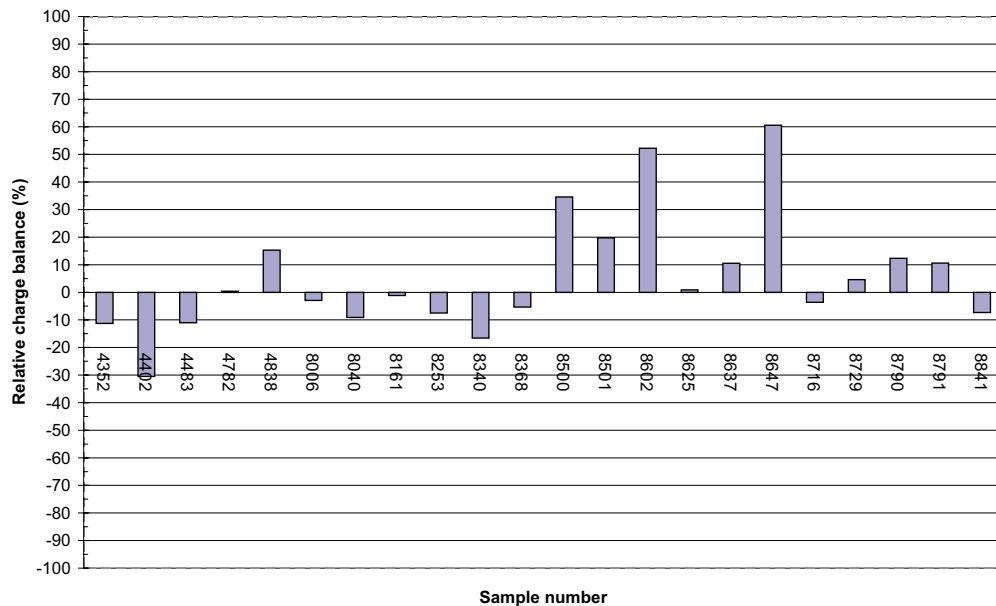


Figure 5-5. Calculated relative charge balance errors for the different precipitation samples.

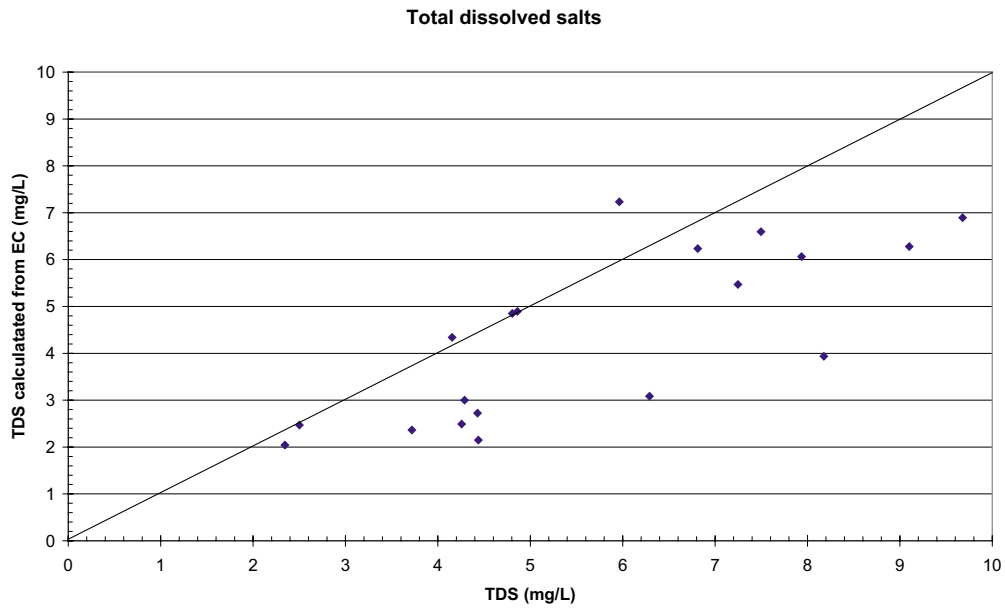


Figure 5-6. Comparison of TDS (Total Dissolved Salts) calculated from analytical results and estimated from electric conductivity.

5.3 Isotopes

The isotope determinations include the stable isotopes δD and $\delta^{18}O$ as well as the radioisotope Tr. The available isotope data are compiled in Appendix 2.

A plot of $\delta^{18}O$ (‰VSMOW(Vienna standard mean ocean water)) versus δD (‰VSMOW) corresponds well with the “Global meteoric water line” based on precipitation data from around the world /3/, see Figure 5-7. This indicates that the isotope data on precipitation are reasonable.

The variation of Tritium over the year indicates higher amounts in the summer periods and dips in the winter, Figure 5-8.

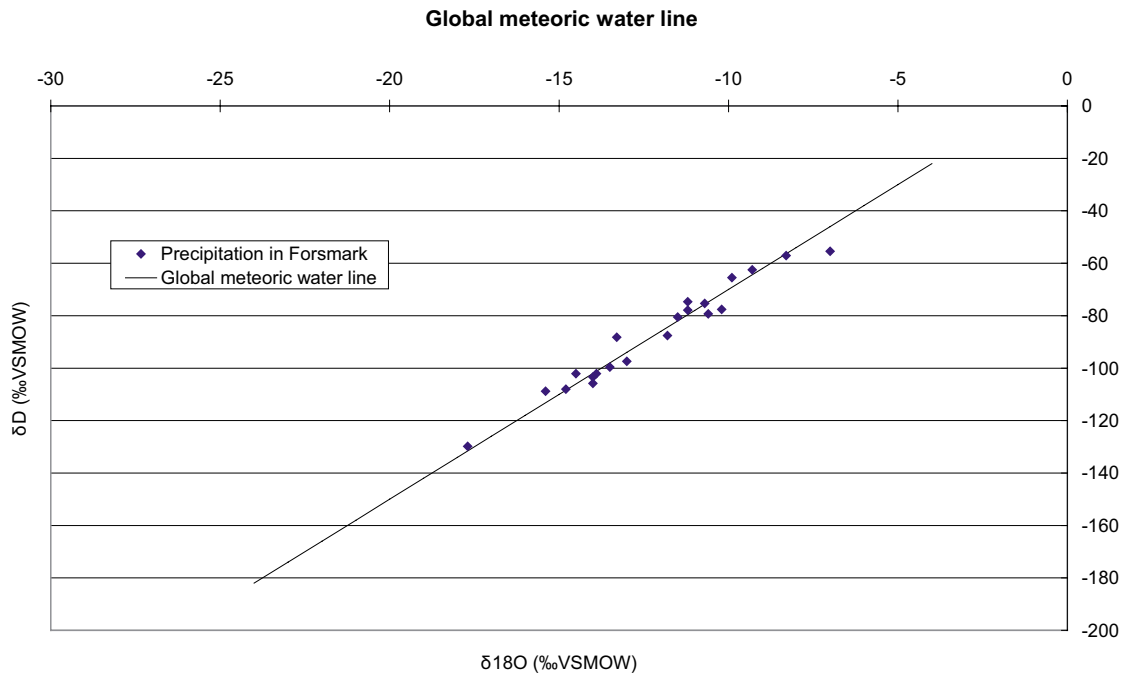


Figure 5-7. $\delta^{18}O$ plotted versus δD in comparison with the “global meteoric water line”.

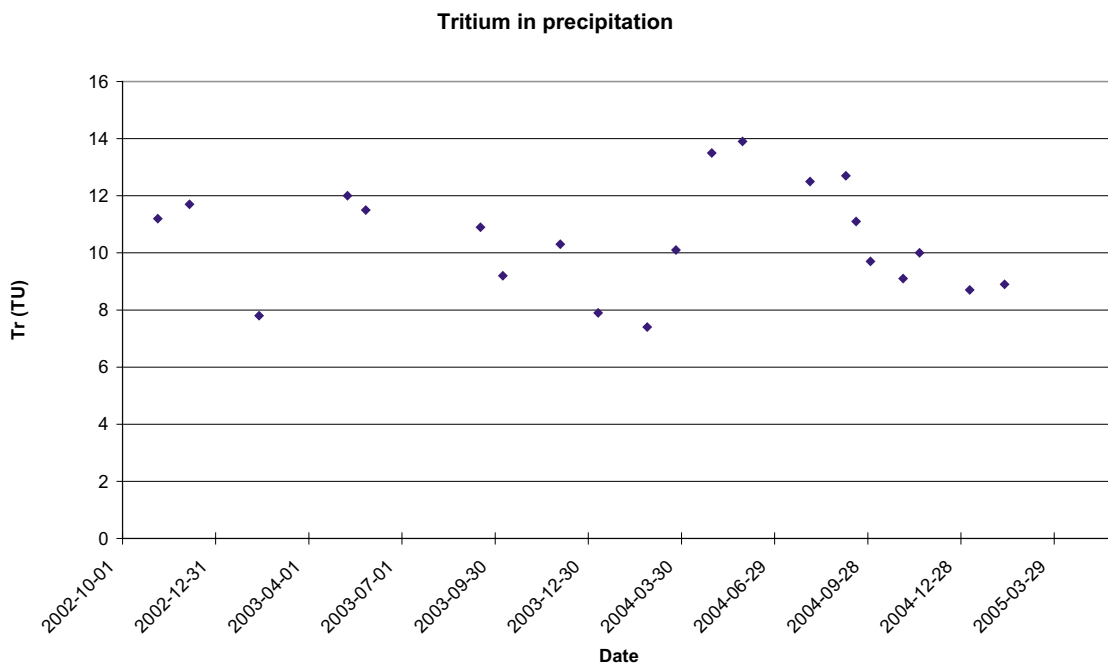


Figure 5-8. The variation of Tritium in the precipitation during the sampling period.

References

- /1/ **SKB, 2001.** Site investigations. Investigation methods and general execution programme. SKB TR-01-29. Svensk kärnbränslehantering AB.
- /2/ **IVL Svenska miljöinstitutet AB.** Website:
[http://www.ivl.se/db/plsql/dvsnedar\\$b1.actionquery?p_ar=2002](http://www.ivl.se/db/plsql/dvsnedar$b1.actionquery?p_ar=2002), 2005-06-03.
- /3/ **Craig H, 1961.** Isotopic variations in meteoric waters. Science133, 1702–1703.

Water composition

Compilation June 2005.

Idcode	Date	Sample no.	Charge balance %	Al mg/L	Br mg/L	Ca mg/L	Cl mg/L	EC mS/m	Fe mg/L	HCO ₃ mg/L	K mg/L	NH ₄ -N mg/L	Mg mg/L	Na mg/L	NO ₃ -N mg/L
PFM002457	2002-11-04	4352	-11.3	<0.015	<0.005	0.17	0.753		0.017	<1	0.08	0.3	0.061	0.55	0.359
PFM002457	2002-12-05	4402	-30.5	<0.015	<0.005	0.09	0.694		<0.015	<1	0.16	<0.15	0.046	0.42	0.372
PFM002457	2003-02-11	4483	-11.0	0.026	<0.005	0.26	1.128		0.29	<1	0.07	0.31	0.083	0.69	0.595
PFM002457	2003-05-08	4782	0.4	0.046	<0.005	0.51	0.504	3.4	<0.015	<1	0.06	0.33	0.076	0.51	0.479
PFM002457	2003-05-26	4838	15.3	0.15	<0.005	0.83	0.419	1.85	<0.015	<1	0.35	0.77	0.08	0.26	0.722
PFM002457	2003-09-15	8006	-3.0	<0.015	<0.005	0.48	2.88	1.45	<0.015	<1	<0.05	0.17	0.17	1.1	0.044
PFM002564	2003-10-07	8040	-9.1	<0.015	<0.005	0.15	0.96	2.3	<0.015	<1	0.12	0.25	0.088	0.57	0.35
PFM002564	2003-12-02	8161	-1.2	<0.015	<0.005	0.17	0.54	2.04	<0.015	<1	0.09	0.38	0.066	0.31	0.32
PFM002564	2004-01-08	8253	-7.5	<0.015	<0.005	0.09	0.92	1.11	<0.015	<1	0.07	0.2	0.063	0.52	0.26
PFM002564	2004-02-25	8340	-16.6	0.043	<0.005	0.07	0.86	2.57	0.025	<1	0.17	0.41	0.094	0.62	0.8
PFM002564	2004-03-24	8368	-5.3	0.038	<0.005	0.31	1.5	2.85	0.023	<1	0.1	0.41	0.14	1	0.59
PFM002564	2004-04-28	8500	34.6	0.025	<0.005	0.36	0.42	3.1	<0.015	<1	0.67	1.5	0.072	0.36	0.33
PFM002564	2004-05-28	8501	19.7	0.018	<0.005	0.46	0.38	2.93	<0.015	<1	0.16	1.1	0.084	0.31	0.37
PFM002564	2004-08-02	8602	52.3	0.023	<0.005	0.08	0.3	1.01	<0.015	<1	0.35	1.4	0.02	0.22	0.14
PFM002564	2004-09-06	8625	0.9	0.021	<0.005	0.12	0.359	1.16	<0.015	<1	0.09	0.16	0.044	0.25	0.166
PFM002564	2004-09-16	8637	10.6	0.073	<0.005	0.24	3.059	2.95	<0.015	<1	0.26	0.43	0.246	2.02	0.351
PFM002564	2004-09-30	8647	60.6	1.176	<0.005	0.07	0.495	1.17	<0.015	<1	0.1	0.28	0.045	0.35	0.248
PFM002564	2004-11-01	8716	-3.6	0.05	<0.005	0.13	0.882	2.28	<0.015	<1	0.09	0.31	0.073	0.57	0.327
PFM002564	2004-11-17	8729	4.6	<0.015	<0.005	0.13	0.48	0.96	<0.015	<1	0.07	0.14	0.042	0.32	0.144
PFM002564	2005-01-05	8790	12.4	<0.06	<0.2	0.23	0.615	1.41	<0.02	<1	<0.4	*	<0.09	0.54	0.265
PFM002564	2005-02-08	8791	10.6	<0.06	<0.2	0.19	0.61	1.28	<0.02	<1	<0.4	*	<0.09	0.56	0.297
PFM002564	2005-03-15	8841	-7.3	<0.06	0.01	0.29	1.88	3.24	0.022	<1	<0.4	*	0.148	1.17	0.628
PFM002564	2005-05-03	8892	-11.4	<0.06	0.06	0.76	1.275	2.47	0.020	<1	<0.4	*	0.115	0.67	0.763

*Not analysed

Compilation June 2005.

Idcode	Date	Sample no.	P_{tot} mg/L	pH	DOC mg/L	SO₄-S mg/L
PFM002457	2002-11-04	4352	0.003	4.81	2.3	0.5
PFM002457	2002-12-05	4402	<0.002	4.42	1.3	0.555
PFM002457	2003-02-11	4483	<0.002	4.45	1.9	0.549
PFM002457	2003-05-08	4782	<0.002	4.88	2.7	0.566
PFM002457	2003-05-26	4838	0.019	5.59	3.3	0.631
PFM002457	2003-09-15	8006	0.002	6.89	2.6	0.38
PFM002564	2003-10-07	8040	0.005	4.89	0.9	0.36
PFM002564	2003-12-02	8161	<0.002	4.78	0.9	0.35
PFM002564	2004-01-08	8253	0.002	5.1	0.6	0.21
PFM002564	2004-02-25	8340	0.008	4.83	2.9	0.43
PFM002564	2004-03-24	8368	<0.002	4.32	3.4	0.56
PFM002564	2004-04-28	8500	0.11	5.21	3.1	0.73
PFM002564	2004-05-28	8501	0.075	5.35	2.9	0.78
PFM002564	2004-08-02	8602	0.11	6.81	2	0.34
PFM002564	2004-09-06	8625	<0.002	4.91	1.9	0.223
PFM002564	2004-09-16	8637	0.004	5.39	1.1	0.363
PFM002564	2004-09-30	8647	0.016	4.86	0.9	0.184
PFM002564	2004-11-01	8716	0.1	4.62	1	0.386
PFM002564	2004-11-17	8729	0.002	5.15	0.8	0.156
PFM002564	2005-01-05	8790	0.007	4.87	2.2	0.258
PFM002564	2005-02-08	8791	0.008	4.84	1.1	0.258
PFM002564	2005-03-15	8841	0.01	4.42	2.9	0.783
PFM002564	2005-05-03	8892	0.024	4.71	5.5	0.679

Isotopes

Compilation June 2005.

Idcode	Date	Sample no.	²H (‰ VSMOW)	³H (TU)	¹⁸O (‰ VSMOW)
PFM002457	2002-11-04	4352	-88.2	11.2	-13.3
PFM002457	2002-12-05	4402	-102.1	11.7	-14.5
PFM002457	2003-02-11	4483	-129.8	7.8	-17.7
PFM002457	2003-05-08	4782	-97.4	12.0	-13.0
PFM002457	2003-05-26	4838	-55.4	11.5	-7.0
PFM002457	2003-09-15	8006	-75.3	10.9	-10.7
PFM002564	2003-10-07	8040	-74.7	9.2	-11.2
PFM002564	2003-12-02	8161	-102.1	10.3	-13.9
PFM002564	2004-01-08	8253	-108.0	7.9	-14.8
PFM002564	2004-02-25	8340	-108.8	7.4	-15.4
PFM002564	2004-03-24	8368	-99.6	10.1	-13.5
PFM002564	2004-04-28	8500	-80.5	13.5	-11.5
PFM002564	2004-05-28	8501	-77.9	13.9	-11.2
PFM002564	2004-08-02	8602	-77.6	12.5	-10.2
PFM002564	2004-09-06	8625	-79.3	12.7	-10.6
PFM002564	2004-09-16	8637	-62.5	11.1	-9.3
PFM002564	2004-09-30	8647	-57.1	9.7	-8.3
PFM002564	2004-11-01	8716	-65.5	9.1	-9.9
PFM002564	2004-11-17	8729	-87.6	10.0	-11.8
PFM002564	2005-01-05	8790	-105.8	8.7	-14.0
PFM002564	2005-02-08	8791	-103.4	8.9	-14.0
PFM002564	2005-03-15	8841	-102.9	*	-15.1
PFM002564	2005-05-03	8892	*	*	*

*Will be reported later