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**Tekijät ovat vastuussa julkaisun sisällöstä, eikä siihen voida
vedota vesihallituksen virallisena kannanottona.**

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COMPARABILITY OF RESULTS FROM DEPOSITION SAMPLES

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A comparison was made of deposition measurements performed in Sodankylä, northern Finland during one year by the Finnish Meteorological Institute, the Finnish Water Research Institute and the Department of Meteorology, University of Stockholm. The results for strong acids, sulfates, nitrates and ammonia, and also the values for pH and conductivity corresponded rather well, but the deposition results for chloride, alkali and alkali earth metals showed larger differences. Possible reasons for the differences are discussed.

Index words: Air quality, deposition, sampling device.

1. INTRODUCTION

Deposition samples are used in attempts to monitor air quality and to estimate the airborne load on the land and water. To obtain an overall picture from the results for several countries, it is essential to ensure that the methods used in the different countries are comparable. For example, this is important when Swedish and Finnish data are combined in estimating the load of pollutants on the Baltic.

Over the years, many research institutes have gathered and analysed deposition samples for various purposes, using different deposit gauges. Since, for instance, the form of

the gauge is known to have a significant influence on the volume of the monthly sample, doubt attaches to the comparability of deposition samples collected with different types of gauges.

The present study was undertaken to compare equipment used regularly to collect precipitation for chemical analyses by the Finnish Meteorological Institute, the Finnish Water Research Institute and the Department of Meteorology, University of Stockholm. The study was made during the period 1.7.1980 to 30.6.1981 at Sodankylä in northern Finland. The samples were sent from the gauges to the respective laboratories, just as they are in routine operation in the networks.

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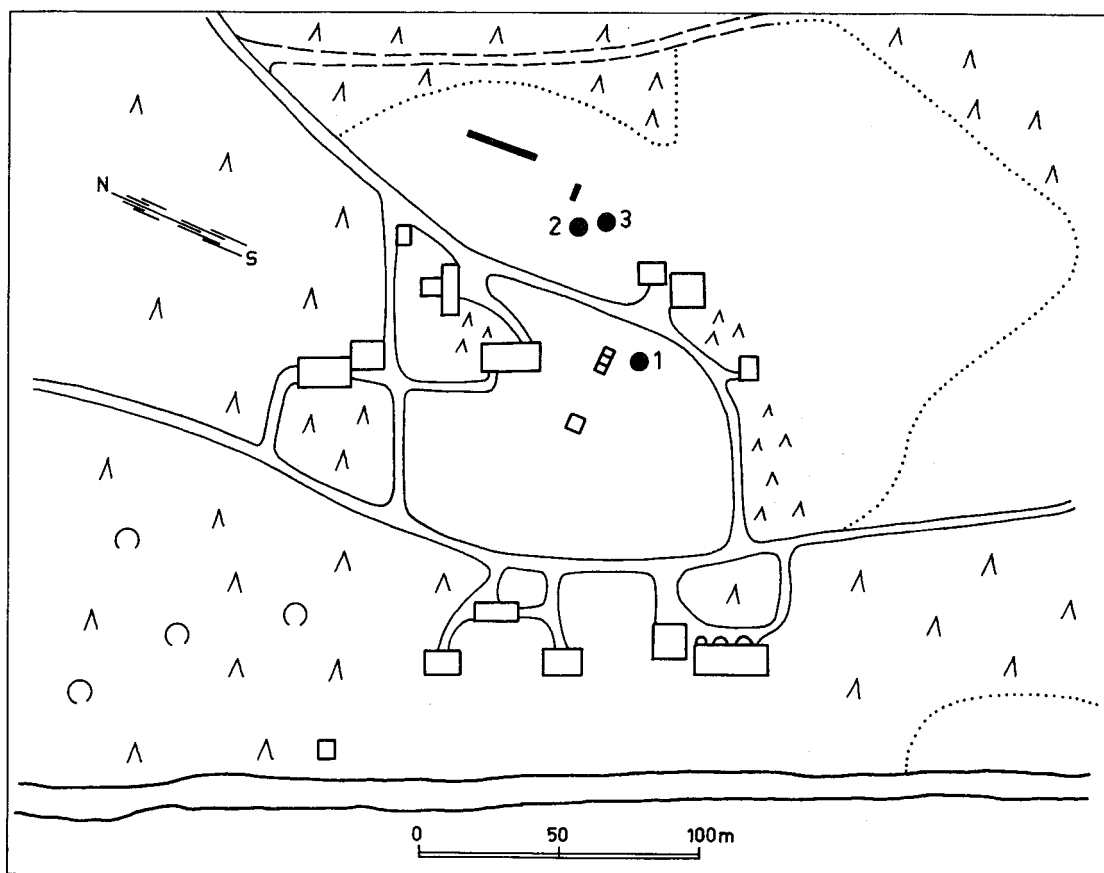


Fig. 1. Map of the Sodankylä station. Sampling devices, 1. Finnish Meteorological Institute, 2. Water Research Institute and 3. Department of Meteorology, University of Stockholm.

2. MATERIAL

2.1. Description of the Sodankylä station

This observatory of the Finnish Meteorological Institute is situated about 6 km south-southeast of Sodankylä village. It is surrounded by fairly sparse pine forest on level ground. The low buildings at the station are heated with light oil, the total annual consumption being about 100 tons. There is no traffic worth mentioning on the gravel roads in the immediate neighbourhood of the station (Kulmala et al. 1982).

Fig. 1 shows the location of the buildings and roads at the station, the type of terrain and the location of the sampling devices in the area.

2.2 Sampling

Each institute sent standard sampling equipment each month to the station. The staff at the observatory changed the sampling vessels as instructed and checked the running of the equipment.

The sampler of the Finnish Meteorological Institute (FMI) divides the wet deposition (rain or snow) from the deposition settling during dry periods. The sampler consists of two cylindrical polyethylene vessels (diameter 200 mm), conforming to the Finnish standard SFS 3865 (Suomen Standardisoimisliitto, 1978). The lid, regulated by a rain sensor, always covers one of the vessels, depending on the weather. The equipment is shown in Fig.

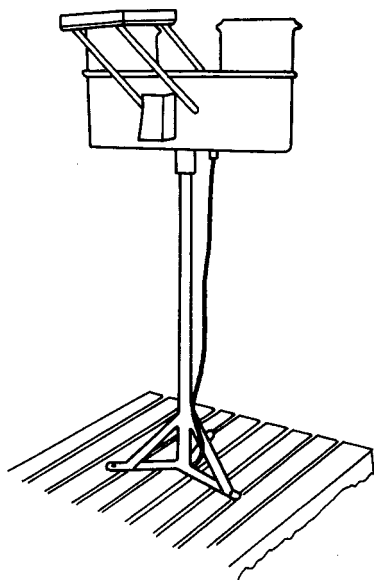


Fig. 2. Sampler for dry and wet deposition (FMI).

2. The upper edges of the vessels are about 1.5 m above the ground. A net on the lid and other horizontal surfaces prevents splashing into the open vessel (Kulmala et al. 1982).

At the end of the month the staff at the station poured the collected wet precipitation into a transport bottle, covered the dry deposition vessel with a tight lid and sent them to the laboratory. Clean sampling vessels were sent to the station each month.

The Water Research Institute (WRI) uses the sampler shown in Fig. 3. The device consists of two separate polyethylene parts: a funnel and a sampling vessel. The section joining them has a teflon plate with holes, which prevents insects, conifer needles and other litter from entering the sampling vessel. Saw teeth have been cut in the upper edge of the funnel, to prevent birds from sitting on the edge, but a separate bird ring has not been used. The diameter of the funnel is 210 mm. The water collected by this size of funnel in a month is usually sufficient for analysis.

The upper part of the sampling device was located about 2 m above the ground. The sampling vessel was replaced at the end of the month with a clean vessel sent from the laboratory and at the same time the funnel was rinsed with distilled water (Järvinen and Haapala 1980).

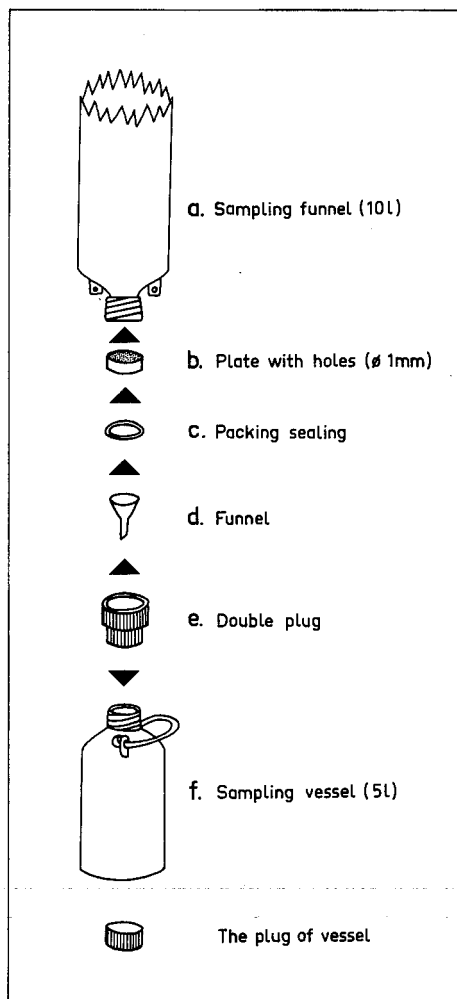
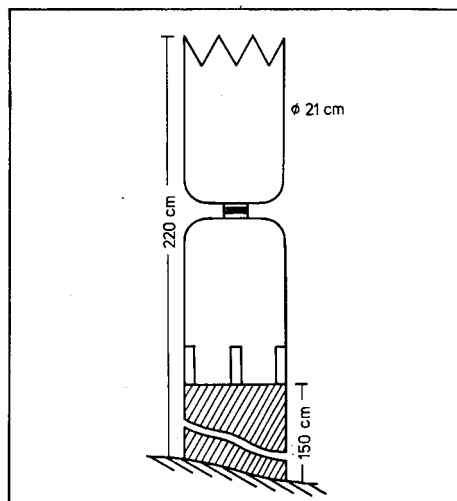


Fig. 3. Sampling equipment (WRI).

kept at room temperature. In the laboratories they were kept in refrigerators until analysed.

2.3 Analytical methods

The wet and dry deposition samples were analysed separately at FMI. The dry deposition was dissolved in deionized water before analysis. The analytical methods were as follows:

- pH was measured potentiometrically and the conductivity conductometrically
- Strong acids (H^+) were determined by automatic, coulometric titration according to Gran.
- Chlorides were determined as the hexachloroferrate (III) complex with Fe (II) perchlorate
- Sulfates were analysed by the automatic Thorin method.
- Ammonia nitrogen was analysed by the indophenolblue method.
- Nitrate nitrogen was determined by the automatic cadmium copper reduction method.
- Sodium, potassium, calcium and magnesium were determined by flame atomic absorption. Addition of lanthanum chloride was used in the calcium and magnesium determinations, and rubidium addition was used in the sodium and potassium determinations.

The methods used at WRI were mostly the same as above, the differences being as follows:

- Chlorides were analysed with an automatic analyzer using mercurycyanate and ferriammoniumsulfate.
- Sodium addition was used in the determination of potassium by flame absorption.

The analytical methods used, except the chloride method of FMI, have been described in detail in a separate report (Vesihallitus 1981).

The methods used at MISU were the same as those of FMI, with the following exceptions:

- Strong acid was titrated manually (to pH 5.6).
- Chlorides were analysed with an automatic analyzer using mercurycyanate and ferriammoniumsulfate (same as WRI).
- Sodium and potassium were determined by flame emission (no addition).

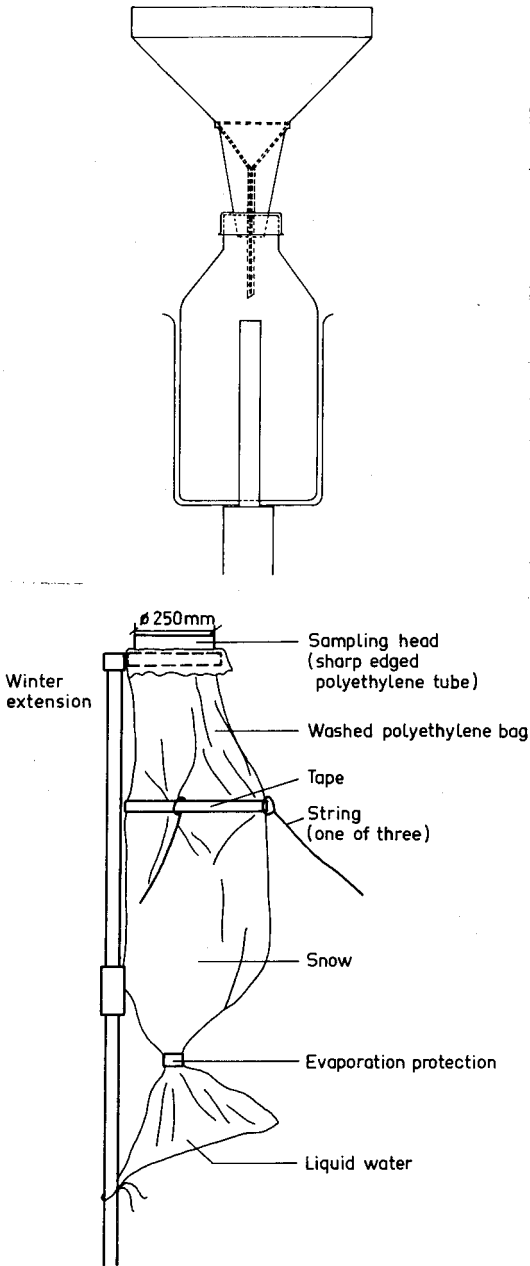


Fig. 4. Sampling equipment (MISU). A: summer. B: winter.

Fig. 4 shows a sketch of the sampling equipment of the Department of Meteorology, University of Stockholm (MISU).

It took about one week to transport all the samples from the sampling station to the laboratories. During this time the samples were

— Calcium and magnesium were determined by flame atomic absorption after addition of lanthanum and hydrochlorid acid.

3. RESULTS

The concentrations in the deposition samples were multiplied by the standard amount of precipitation, to obtain deposition per unit area. The concentrations in the dry deposition samples of FMI were multiplied by the volume of extraction water used. The total deposition is the sum of the dry and wet deposition for each substance.

Fig. 5 gives the official monthly precipitation values during the observation period at the Sodankylä observatory, which were used to calculate the deposition.

The monthly deposition of different substances is presented in figures 6...16. The figures show the medians of the monthly values and the results of the two parallel samplers from MISU. The results from the equipment labelled MISU 1 were used in calculating the median.

The pH values are presented in pH units and the conductivity as microsiemens per cm. As the pH and conductivity of the dry deposition samples of FMI are dependent on the volume of extraction water used, only the results of the wet deposition samples are presented. Thus these results cannot be compared directly with the results of the other institutes.

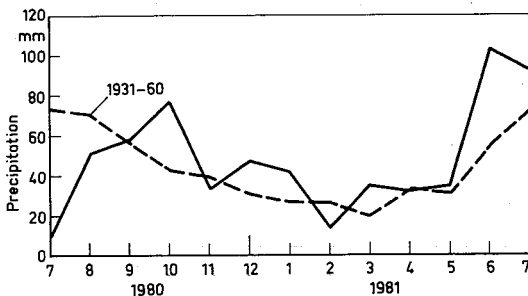


Fig. 5. The precipitation at the Sodankylä observatory during the period 1980...1981 and the mean precipitation during 1931...1960 (Ilmatieteen laitos, 1980...1981).

4. DISCUSSION

The efficiency with which the different sampling devices collected precipitation is shown in table 1. The efficiency was computed as percentage of the precipitation measured by the standard Finnish precipitation gauge (Helimäki and Tammelin 1973). The efficiency was usually below 100 % and varied considerably.

Fig. 17 shows the sampling efficiency of the devices as a function of the amount of precipitation. The efficiency of the WRI sampler is high (even above 100 %) during the summer months (May...September) and poor (average 55 %) in the winter (October...April). The collection efficiency of the MISU samplers seems to increase with the precipitation. The FMI sampler gives satisfactory sampling results more frequently (80...100 %). In order to increase the comparability of deposition data, it is recommended that the standard amount of precipitation is used in calculations.

Many factors influence the sampling efficiency. Comparison of the samplers suggests that the most important are the aerodynamic factors around the sampling devices, and also, to some extent, evaporation or condensation in the sampling vessel, the volume of water remaining in the vessels after emptying and accumulation of snow in the vessel (Førland ja Joranger 1980). Differences in efficiency are probably chiefly due to differences in the construction of the samplers which alter the

Table 1. Percentage sampling efficiency. FMI=Finnish Meteorological Institute, WRI=Water Research Institute and MISU=Department of Meteorology, University of Stockholm. (x sampler in action only half a month, result multiplied by 2).

Month	Standard precipitation mm	Sampling efficiency %		
		FMI	WRI	MISU
1980/7	7.7		83	78
8	50.7	97	117	57
9	57.7	96	115	87
10	76.8	72	98	82
11	33.0	87	63	
12	46.6	96	62	79
1981/1	41.2	94	60	73
2	12.5	99	52	56
3	34.6	49x	44	72
4	31.5	84	80	79
5	33.8	40	99	68
6	104.1	79	107	94
7	92.4	91	114	91

effect of the wind on the sampling vessels.

The wind affects the accumulation in the vessels of both drops of rain and air-borne particles, thus causing differences in the composition of the samples. Use of the official precipitation records in calculating deposition values can reduce differences caused by variation in sampling efficiency. There is, however, the risk that the results will be too high, especially in the summer, since evaporation concentrates the sample.

The observation period was somewhat rainier than the normal climatological period 1931...1960. The total precipitation exceeded the mean value by 8 % (Ilmatieteen laitos 1980...1981). Fig. 5 shows the monthly deviations. The first month of the observation period was exceptionally dry, the precipitation being only one tenth of the usual.

In spite of the rather great differences in the construction of the samplers, the results for H^+ , S_{SO_4} , N_{NO_3} and N_{NH_4} agreed fairly well (Figs. 7, 9, 10 and 11 and Table 2). The total deposition for the months when the samplers were in operation is given in Table 2. The pH values and conductivity results also agreed well, when the collection principles were the same (Figs. 6 and 8). The differences in the deposition values for chloride (Fig. 12) were larger and especially large variation could be seen in the values for alkali and alkali earth metals (Figs. 13...16). The calcium values from WRI were high in comparison with the others.

As in Table 2, the sum of the monthly values is generally used in calculating yearly deposition. Sometimes the monthly median is used instead, because this eliminates the effect of exceptionally large or small monthly depositions. However, the use of the monthly median

involves a risk of underestimating yearly deposition, because it does not take account of the real annual variation in the deposition of some substances. For example, the deposition of sulfate is clearly higher in the summer (Fig. 9).

In order to estimate how much of the variability between the results is due to the chemical analyses, an intercalibration study was performed during summer 1982. Five precipi-

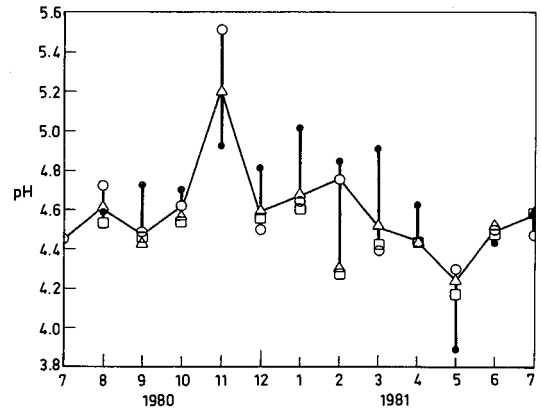


Fig. 6. Monthly values of pH.

Legend:

- Finnish Meteorological Institute (FMI)
- Water Research Institute (WRI)
- △ Department of Meteorology, (MISU 1)
- University of Stockholm (MISU 2)
- ∧ median of depositions collected by three gauges.

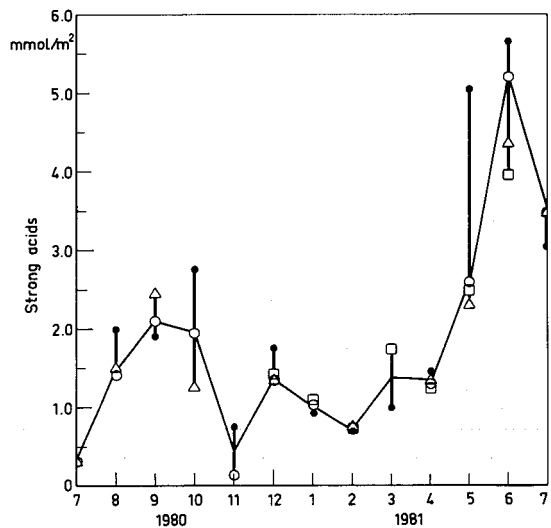


Fig. 7. Deposition of strong acids.

Table 2. Total deposition in the observation periods at Sodankylä station during 1980...1981. Depositions have been computed by using standard precipitation.

Variable	Observation periods (months)	Deposition			
		FMI	WRI	MISU	
H^+	mmol/m ²	9	24.63	20.60	19.26
S_{SO_4}	mg/m ²	12	448	462	386
N_{NO_3}	mg/m ²	11	119	118	92
N_{NH_4}	mg/m ²	11	121	101	103
Cl	mg/m ²	11	166	140	90
Na	mg/m ²	10	169	89	46
K	mg/m ²	8	79.5	36.2	14.5
Ca	mg/m ²	10	98	418	46
Mg	mg/m ²	7	11.1	29.2	5.9

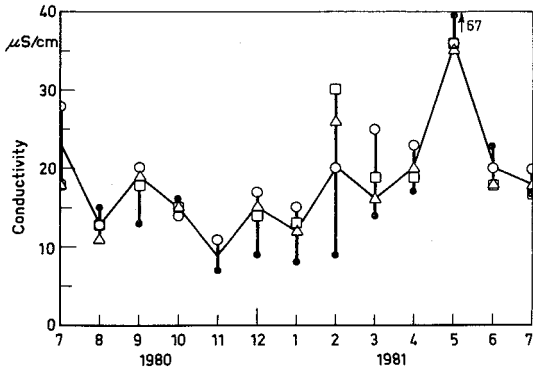


Fig. 8. Monthly values of conductivity.

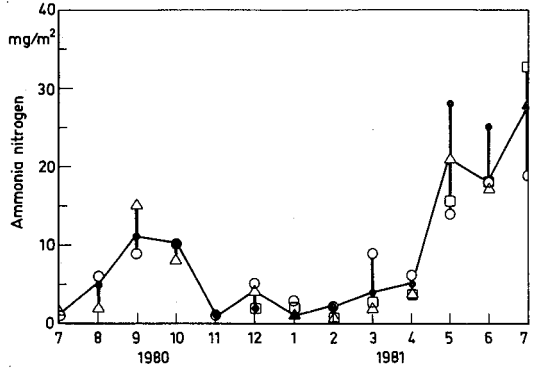


Fig. 11. Deposition of ammonia nitrogen.

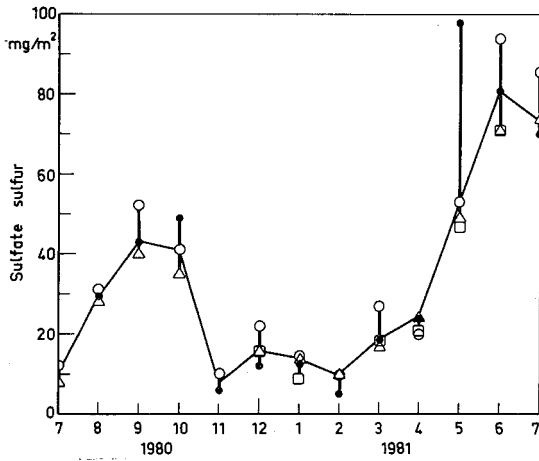


Fig. 9. Deposition of sulfate sulfur.

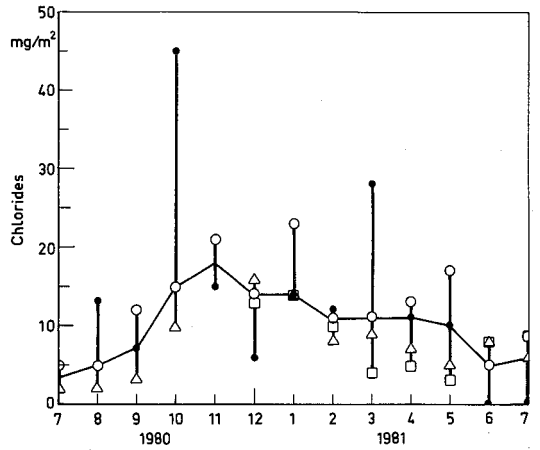


Fig. 12. Deposition of chlorides.

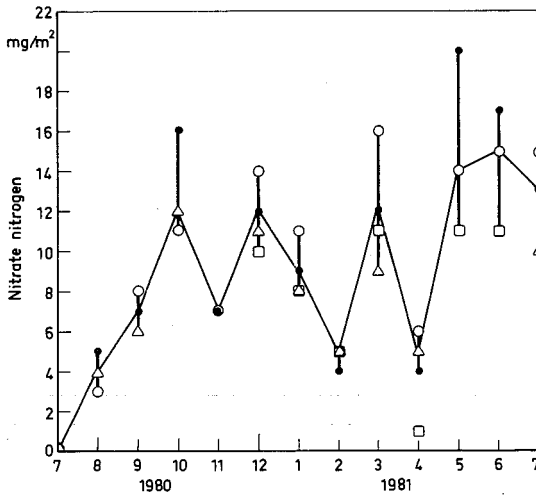


Fig. 10. Deposition of nitrate nitrogen.

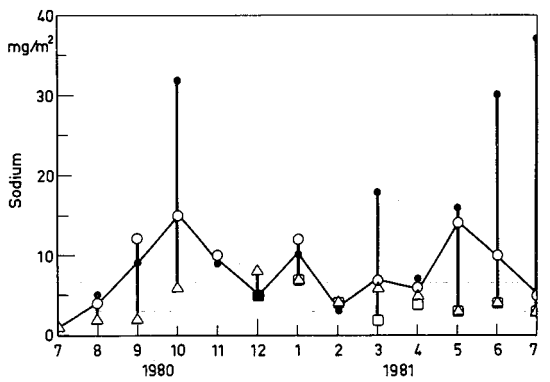


Fig. 13. Deposition of sodium.

Table 3. Intercalibration analyses for alkali and alkali earth metals in rain water, July 1982. FMI=Finnish Meteorological Institute, WRI=Water Research Institute and MISU=Department of Meteorology, University of Stockholm.

Sample	Sodium, mg/l		Potassium, mg/l	
	FMI	WRI	FMI	WRI
A	0.40	0.45	1.02	0.70
B	0.14	0.21	0.15	0.15
C	0.36	0.42	0.36	0.32
D	0.05	0.16	0.06	0.08
E	0.19	0.20	0.19	0.15

Sample	Calcium, mg/l			Magnesium, mg/l		
	FMI	WRI	MISU	FMI	WRI	MISU
A	1.40	2.18	2.44	0.34	0.37	0.36
B	0.43	0.84	0.80	0.11	0.14	0.12
C	0.34	0.74	0.77	0.12	0.14	0.12
D	0.00	0.20	0.22	0.02	0.03	0.02
E	0.16	0.50	0.44	0.05	0.08	0.06

tation samples were analysed in all three laboratories. The results are shown in Table 3. The values for sodium, potassium and magnesium agreed fairly well, but the comparability of the calcium results can still be improved. The intercalibration for calcium was repeated later at FMI and WRI, with fairly good results.

As expected, the results obtained with two deposit gauges of the same kind agreed better than the results obtained with samplers of different types (Figs. 6...16). MISU had two similar samplers at the observation station and the differences in their results are presented in Table 4. It can be seen that the differences are greatest for the same variables as before: chloride, alkali and alkali earth metals. One reason for this might be poor reliability of the analysis, because the concentrations are often near the detection limit of the methods used. MISU most often had the lowest deposition va-

Table 4. Differences between results for parallel deposition samples (MISU).

Variable	Observation periods (months)	Difference (%) between results of parallel samples (MISU)
pH	11	0.7
H ⁺	6	1.5
γ_{25}	12	3.1
S _{SO4}	6	4.7
N _{NO3}	8	7.9
N _{NH4}	8	1.3
Cl	5	10
Na	8	20
K	8	32
Ca	3	21
Mg	3	24

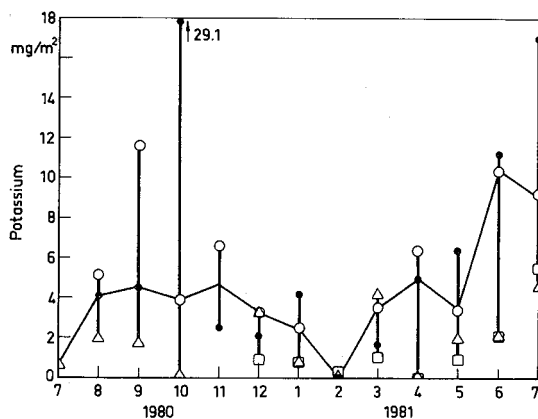


Fig. 14. Deposition of potassium.

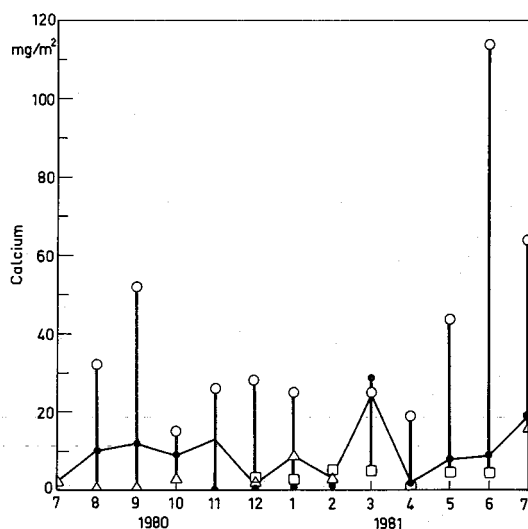


Fig. 15. Deposition of calcium.

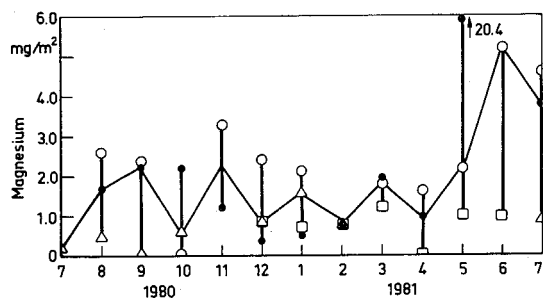


Fig. 16. Deposition of magnesium.

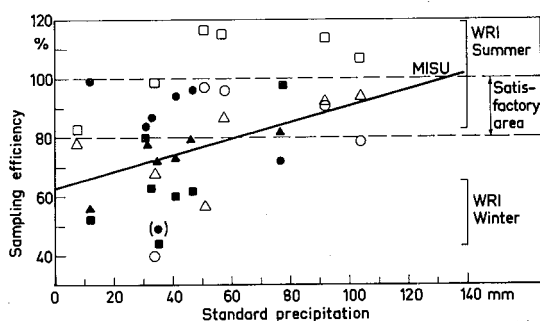


Fig. 17. The sampling efficiency of the three different collecting devices as a function of the precipitation. Legends:

	Summer	Winter
FMI	○	●
FRI	□	■
MISU	△	▲

lues for these substances. Only three pairs of values were available for alkali earth metals, which makes this result rather uncertain.

The intercalibration of the sampling equipment shows that the monthly values for some substances differ greatly from both the normal level and from the results obtained with the other samplers. Possible factors explaining the differences are contamination of the sample, analytical errors and differences in the efficiency with which the devices sample precipitation and settle particles, especially the latter. During the period without snow, dust from the ground may be transported by the wind and settle to a varying extent in the different vessel types. The air-borne particles are quite heterogeneous and the proportions of fine and coarse particles vary greatly between vessels indicating differences in sampling efficiency.

5. CONCLUSIONS

During the years 1980...1981 a comparison was made of the deposition samplers used by the Finnish Meteorological Institute, the Water Research Institute and the Department of Meteorology, University of Stockholm at the Sodankylä observation station. The Department of Meteorology, University of Stockholm, had two similar devices at the station. Each institute analysed the monthly samples, using its normal methods. The yearly deposition values obtained with the different types of equipment agreed well in the case of strong acids, sulfates, nitrates and ammonia and also in that of pH and conductivity. Greater differences occurred in the values for the individual months.

Quite marked differences were found in the values for chloride and especially for alkali and alkali earth metals. The concentrations of these ions are usually low and contamination, for instance by soil, can have a considerable effect.

LOPPUTIIVISTELMÄ

Laskeumatutkimuksissa on käytössä erilaisia näytteiden keruulaitteita. Tästä syystä on tarpeellista selvittää tulosten vertailukelpoisuutta mm. arvioitaessa suomalaisten ja ruotsalaisten tietojen perusteella Itämereen ja sen lahtiin ilman kautta laskeutuvaa kuormaa. Suoritetulla tutkimuksella haluttiin selvittää erilaisten keräinten aiheuttamaa vaikutusta laskeumatuloksiin. Tutkimus suoritettiin 1.7.1980...30.6.1981 Sodankylän meteorologisella havaintoasemalla ja siihen osallistui Ilmatieteenlaitos, Vesientutkimuslaitos ja Tukholman yliopiston Meteorologian osasto. Kukin laitos käytti omissa seuranta tutkimuksissa normaalisti käytössä olevia keräys- ja analysointimenetelmiään.

Tutkimustulokset on esitetty kuvissa 6...16. Yhteenvetona voidaan todeta, että huolimatta keräinten varsin suurista rakenteellisista eroista olivat yhteisten havaintojak-

sojen laskeumasummat vahvoille hapoille, sulfaattirikille sekä nitraatti- ja ammoniumtyypelle hyvin vertailukelpoisia. Myös sähkönjohtavuus- ja pH-tulokset olivat vertailukelpoisia, kun näytteen keruu tapahtui samalla periaatteella. Eroja vertailtavissa laskeumasuureissa havaittiin kloridissa ja erityisesti alkali- ja maa-alkalimetallien laskeumatuloksissa. Viimeksimainittujen aineiden pitoisuudet laskeumanäytteissä olivat kuitenkin lähellä totemisrajoja, jolloin mittaustarkkuus on huono.

Laitteiden keräystehokkuudet verrattuna suomalaisen sademittarin sadantaan vaihtelivat melkoisesti. Paras keruutehokkuus oli Ilmatieteen laitoksen keräimellä (80...100 %). Tulosten laskemisessa käytettiin kaikille laitteille standardisademittarin arvoja. Tämä käytäntö paransi tulosten vertailukelpoisuutta.

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