

BALTIC SEA ENVIRONMENT PROCEEDINGS

No. 41

INTERCALIBRATIONS AND INTERCOMPARISONS OF MEASUREMENT METHODS FOR AIRBORNE POLLUTANTS



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OF MEASUREMENT METHODS
FOR AIRBORNE POLLUTANTS

BALTIC MARINE ENVIRONMENT PROTECTION COMMISSION

– HELSINKI COMMISSION –

1992

This publication has been technically edited by the host country
of the intercalibrations, Sweden

For bibliographic purposes this document should be cited as:
HELCOM, 1992
Intercalibrations and Intercomparisons of Measurement Methods
for Airborne Pollutants,
Balt. Sea Environ. Proc. No. 41

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ISSN 0357-2994
Helsinki - Government Printing Centre

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PREFACE

Two intercalibrations, the first on analytical methods for the determination of trace metals, nitrate and ammonium in atmospheric precipitation and the second on the intercomparison of precipitation collectors for nitrate and ammonium, were arranged in the framework of the Helsinki Commission in 1986 and 1987-1988, respectively. The Group of Experts on Airborne Pollution of the Baltic Sea Area (EC EGAP) of the Baltic Marine Environment Protection Commission - Helsinki Commission - has decided on a programme of intercalibration and intercomparison exercises. Both stages of the exercise were organized by Sweden.

This publication contains the results of the first and second stage of the inter-calibrations. The outcome of the first stage of the inter-calibration - Report on the Intercalibration of Analytical Methods for the Determination of Trace Metals, Nitrate and Ammonium in Atmospheric Precipitation - has been prepared and edited for the purpose of the Helsinki Commission by Dr. Howard B. Ross from Sweden, and the report on the second stage of the inter-calibration - Intercomparison of Precipitation Collectors for Chemical Analysis - has been prepared and edited by Dr. Hans Areskoug and Dr. Lennart Granat, both from Sweden. The editors of this publication are responsible for the text.

REPORT ON THE INTERCALIBRATION OF ANALYTICAL METHODS FOR THE DETERMINATION OF TRACE METALS, NITRATE AND AMMONIUM IN ATMOSPHERIC PRECIPITATION WITHIN THE FRAMEWORK OF THE BALTIC MARINE ENVIRONMENT PROTECTION COMMISSION - HELSINKI COMMISSION -

Howard B. Ross
Department of Meteorology
University of Stockholm
Arrhenius Laboratory
S-106 91 Stockholm
Sweden

BACKGROUND AND INTRODUCTION

In February, 1986, the Department of Meteorology, University of Stockholm (MISU), within the auspices of the Baltic Marine Environment Protection Commission - Helsinki Commission (HELCOM) - organized an intercalibration of analytic methods for the determination of trace metals, nitrate and ammonium in atmospheric precipitation. The Group of Experts on Airborne Pollution of the Baltic Sea Area (EGAP), within HELCOM, thought this intercalibration was essential before any joint projects could be started on determining the atmospheric fluxes of these substances to the Baltic. It was also decided to emphasize the trace metal portion of this intercalibration because not all of the laboratories did such analyses routinely. In addition, sample contamination is a much greater problem for trace metals than for ammonium and nitrate.

Today there is much discussion on the sources, and ways of reducing pollution to the Baltic. It is thought that the atmosphere, via wet deposition, is the major source of such toxic metals as Cd, As, Pb and Hg (Rodhe et al., 1980). It is, therefore, important that all countries bordering the Baltic have the capability of accurately determining trace metals concentrations in atmospheric precipitation. However, the chemical analysis is difficult because samples can easily be contaminated. One of the greatest sources of contamination is the sample bottle. Many bottles have appreciable amounts of metals on their walls, relative to concentrations in precipitation, which readily dissolve into solution. To avoid such contamination bottles are washed in strong acids. Conventional polyethylene (CPE) and teflon (PTFE) bottles are usually chosen for storing low level metal solutions because they are the least contaminating after acid washing (Moody and Lindström, 1977).

A second problem is that metal concentrations can alter during storage. This is mostly due to the adsorption of metals on to the walls of the container and is sometimes referred to as the "container wall effect". Surface adsorption is a function of the storage time, the container material, the metals and its concentration. This effect is easily avoided by acidifying the samples to a pH of 1 or 2 with nitric acid. For example, Chan et al. (1983) observed that Fe, Cu, Zn and Al adsorption ranged between 26-47% in CPE bottles. Mild acid leaching (pH = 1) desorbed the metals.

The container wall effect and contamination from surface desorption are thus related. If the bottles are not acid washed, but the samples are acidified, the samples can be contaminated because all of the metals from the walls will desorb. This is exemplified by **Figure I**. Cu concentrations in rainwater collected and stored in acid washed collectors are much lower than concentrations in rain collected and stored in water washed equipment. The excess Cu in the "untreated samples" is from the walls of the container which desorbed into solution after it had been acidified to a pH = 1. In contrast, acid washing the bottles, but not acidifying the samples, will reduce trace metal concentrations. Haraldsson and Magnusson (1983) found that rain collected in acid washed equipment, had Fe concentrations of 22 $\mu\text{g l}^{-1}$. When the sample was acidified to a pH of 1, Fe concentrations increased to 29 $\mu\text{g l}^{-1}$. Therefore, for accurate determination of trace metals in precipitation it is essential to acid wash the bottles and to acidify the sample to pH = 1.

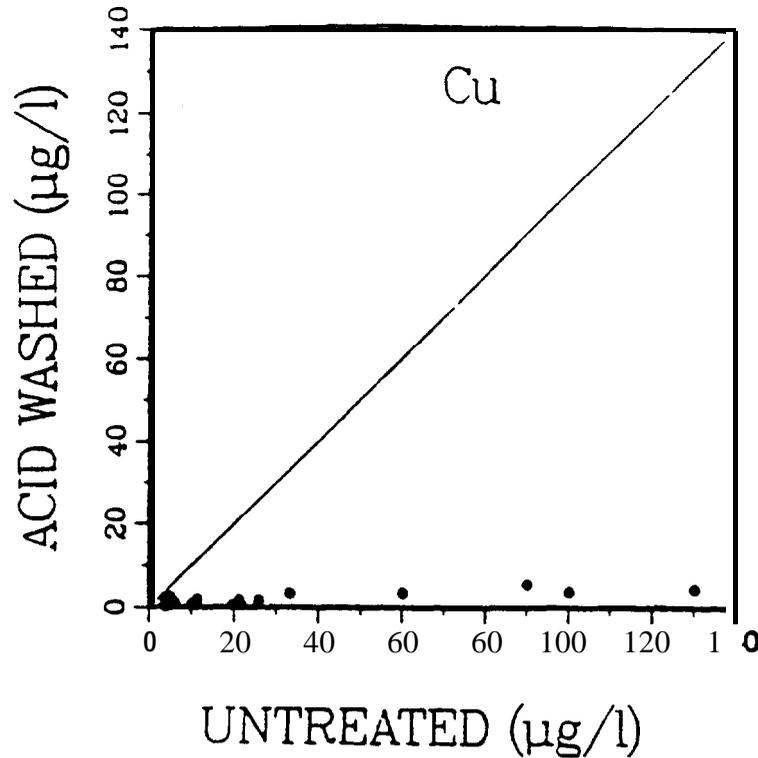


Figure 1. Cu concentration in atmospheric precipitation collected in acid washed collectors vs. concentrations in precipitation from untreated collectors. Collection and subsequent sample handling were the same for both types of samples. (source: Ross, 1986)

TRACE METAL INTERCALIBRATION

The intercalibration was designed to test if the laboratories could determine trace metal concentrations accurately. Minimum participation required the analysis of Pb, Cu and Zn. Other metals determined on an optional basis were Cd, Fe and Mn. To test how well sample bottles were cleaned, each laboratory sent 6 bottles to MISU. The bottles had been washed by the laboratory using their normal cleaning procedures. 5 of the bottles were used for intercalibration samples, while one remained at MISU for further testing.

The intercalibration consisted of the analysis of three sets of duplicate samples which contained:

SAMPLES 1 and 2: filtered ground snow from north-central Sweden. Concentrations were very low. The purpose was to see if the various laboratories had good enough detection limits.

SAMPLES 3 and 6: known synthetic standards. The purpose of these samples was to see how well analyses were performed, and if the bottles influenced sample concentrations. Sample 3 was in the laboratory's own bottle while sample 6 was in a bottle acid washed at MISU.

SAMPLES 4 and 5: ground snow samples from south-central Sweden. These samples were filtered. Concentrations in these samples are typical in precipitation from southern Sweden and other countries around the Baltic.

The intercalibration samples were sent to 8 laboratories in April, 1986 of which 6 presented results, see **Tables 1-6**. The gravimetric values of the synthetic samples (samples 3 and 6) are given under MISU. Due to a mistake sample 3 was not the same as sample 6 for LAB-5. Gravimetric concentrations for LAB-5's sample 3 are given in parenthesis. The values for samples 1 and 4 for MISU are the concentrations found in samples analyzed by laboratory personnel unaware of their identity.

The results indicate that LAB-8 contaminated their samples with respect to Cd and Zn. Evidence points to the sample bottle as being a major source of contamination, because Cd concentrations in sample 6 (a synthetic standard in a bottle acid washed at MISU) was accurately determined. In addition, it appears that LAB-1 inaccurately determined Fe concentrations. This is probably due to the chemical analyses because both the synthetic standards and ground snow samples were significantly higher than the values reported by the other laboratories. It also appears that LAB-7 has lower values for Zn. Since the laboratory acidified their samples, a guess is that the low values are due to the subtraction of an erroneously high blank value.

All of the laboratories, except LAB-2, used atomic absorption techniques for the determinations. LAB-2 used X-ray fluorescence (XRF). The results from this technique agree very well with the results obtained by using MISU graphite furnace atomic absorption spectroscopy (GFAAS). XRF is a multi-element technique providing information on many more elements, however, it can not be used for the determination of Cd.

The large spread in the data for ground snow samples from southern Sweden (samples 4 and 5) is probably due to soil and organic matter, because these samples were not filtered. In contrast, the spread in data for northern Sweden is much smaller. These results indicate that the sampling sites for any eventual projects around the Baltic must be carefully chosen to avoid soil and organic debris, or that "wet only" precipitation samplers be used. Such samplers, presently being used for the collection of precipitation for major ion analysis, are inappropriate for trace metals studies because they can contaminate samples.

A synthetic standard (pH = 1) was poured in one bottle from each laboratory. Since the standard was acidic, any metals on the wall of the bottles would be desorbed. Therefore, the bottle's influence on trace metals concentrations could be determined. Results from this experiment are given in **Table 7**. The only bottles that contaminated the test solution were the bottles from LAB-3 (for Cu and Fe) and LAB-8 (for Cd and Fe). It should be noted that the sort of bottle used by LAB-3 can greatly contaminate samples just for Cu (Ross, 1984; 1986).

AMMONIUM AND NITRATE INTERCALIBRATION

For the nitrate and ammonium intercalibration 4 samples were sent out to 10 laboratories. The samples contained the following:

SAMPLE A: rainwater from southern Sweden

SAMPLE B: 7 parts SAMPLE A and 3 parts distilled water

SAMPLE C: 9 parts SAMPLE A and 1 part distilled water

SAMPLE D: a synthetic standard

7 of 10 laboratories returned values. The results from this intercalibration are in *Table 8*. All of the laboratories did well in the ammonium determination. It would appear that the LAB-2 laboratory obtained somewhat higher values (10%) than the rest. For nitrate only one laboratory was able to analyze correctly sample 3. All of the other laboratories reported somewhat higher values.

CLOSING COMMENTS

The major problem with this intercalibration was an initial lack of information to the participating laboratories. The intercalibration started too quickly, without the participants knowing what the goals and the intentions were. Thus, there was some confusion at the EGAP Neubrandenburg (GDR) Meeting in May 1986. Another problem was that participation from the various laboratories was sometimes sporadic. In the future, participation will need to be improved.

With regard to the trace metal intercalibration it is apparent that more work is needed. A first step would be to standardize the analytical methodologies. Secondly, a workshop on analytical techniques for the determination of trace metals in precipitation would be useful. The programme should include methods for sample collection and procedures to reduce sample contamination inside the laboratory. Such a workshop could perhaps be coordinated and jointly organized with the EMEP and/or ATMOS programmes.

With regard to ammonium and nitrate it would appear that each of the laboratories can accurately determine their concentrations. Therefore, it is recommended to proceed with the second stage of the intercalibration, the intercomparison of collection equipment without hesitation.

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LABORATORIES PARTICIPATING IN THE HELCOM INTERCALIBRATION**DENMARK**

Miljøstyrelsens
Luftfureningslaboratorium
Forsøgsanlaeg Riss
DK-4000 ROSKILDE

FINLAND

Finnish Meteorological Institute
Air Quality Department
Sahaajankatu 22 E
SF-008 10 HELSINKI

National Board of Waters
Water Research Institute
Kylkaarekatu 10
SF-00550 HELSINKI

GERMAN DEMOCRATIC REPUBLIC

Meteorologisches Observatorium
des Meteorologischen Dienstes der DDR
Wahnsdorf
Altwahnsdorf 12
DDR-8 122 RADEBEUL 5

Meteorologischer Dienst DDR
Michendorfer Chaussee 23
DDR-1500 POTSDAM

FEDERAL REPUBLIC OF GERMANY

Institut für Meereskunde an der
Universität Kiel
D-2300 KIEL 1

Umweltbundesamt
Pilotstation Frankfurt
Postfach 67
D-6050 OFFENBACH

POLAND

Institute of Meteorology and Water Management
Ul. Podlesna 61
WARSZAWA

SWEDEN

Department of Meteorology
University of Stockholm
Arrhenius Laboratory
S- 106 9 1 STOCKHOLM

Swedish Environmental Protection Board
Air Chemistry Laboratory
Studsvik
S-611 82 NYKÖPING

USSR

State Committee for Hydrometeorology
and Natural Environmental Protection
Institute of Applied Geophysics
Glebovskaya 20 B
MOSCOW 107 258

TABLE 1: Cd ($\mu\text{g l}^{-1}$)

SAMPLE	1	2	3	4	5	6
LAB-1	0.2	0.2	0.4	<0.1	0.3	0.4
LAB-2						
LAB-3						
LAB-4						
LAB-5	0.03	0.03	0.23	0.40	0.05	0.34
			(0.2)*			
LAB-6	0.07	0.02	0.12	0.02	0.08	0.21
LAB-7	<0.1	<0.1	0.42	0.12	<0.1	0.42
LAB-8	2.1	1.7	5.7	1.1	2.6	0.4
MISU	0.016		0.4*	0.037		0.4*
	0.018			0.042		
	0.013			0.023		
	0.017					

* Gravimetric value

Samples 1 and 2: ground snow north-central Sweden

Samples 3 and 6: synthetic standards (samples 1-5 in the laboratories own bottles, sample 6 in bottles washed at MISU)

Samples 4 and 5: ground snow south-central Sweden

TABLE 2: Cu ($\mu\text{g l}^{-1}$)

SAMPLE	1	2	3	4	5	6
LAB-1	<1	<1	<1	<1	<1	<1
LAB-2	1.4	0.63	1.7	0.72	0.50	1.6
LAB-3						
LAB-4						
LAB-5	0.5	0.4	0.6	0.8	0.3	1.1
			(0.6)*			
LAB-6	0.60	0.20	0.30	0.20	0.30	0.60
LAB-7	<1	<1	1.4	<1	<1	1.4
LAB-S	0.21	0.45	1.21	0.24	0.31	0.90
MISU	0.30		1.2*	1.17		1.2*
	0.32			1.23		
	0.26			0.27		
	0.26					

* Gravimetric value

Samples 1 and 2: ground snow north-central Sweden

Samples 3 and 6: synthetic standards (samples 1-5 in the laboratories own bottles, sample 6 in bottles washed at MISU)

Samples 4 and 5: ground snow south-central Sweden

TABLE 3: Fe ($\mu\text{g l}^{-1}$)

SAMPLE	1	2	3	4	5	6
LAB- 1	130	16.5	106	208	212	138
LAB-2	6.1	4.7	58	67	32	35
LAB-3						
LAB-4						
LAB-5						
LAB-6						
LAB-7						
LAB-8	2.6	7.8	45.0	5.4	6.1	35.3
MISU	4.14		40''	52.4		40*
	3.14			55.7		
	3.56			15.2		
	2.92					

* Gravimetric value

Samples 1 and 2: ground snow north-central Sweden

Samples 3 and 6: synthetic standards (samples 1-5 in the laboratories own bottles, sample 6 in bottles washed at MISU)

Samples 4 and 5: ground snow south-central Sweden

TABLE 4: Mn ($\mu\text{g l}^{-1}$)

SAMPLE	1	2	3	4	5	6
LAB- 1	4.7	4.9	4.2	4.7	3.6	4.3
LAB-2	5.0	3.9	4.3	4.0	3.0	4.5
LAB-3						
LAB-4						
LAB-5						
LAB-6						
LAB-7	2.5	2.5	2.5	2.0	2.0	2.5
LAB-8	3.1	3.0	3.8	2.5	2.8	3.5
MISU	3.56		4.0*	4.36		4.0*
	3.70			4.89		
	3.42			3.17		
	3.56					

* Gravimetric value

Samples 1 and 2: ground snow north-central Sweden

Samples 3 and 6: synthetic standards (samples 1-5 in the laboratories own bottles, sample 6 in bottles washed at MISU)

Samples 4 and 5: ground snow south-central Sweden

TABLE 5: Pb ($\mu\text{g l}^{-1}$)

SAMPLE	1	2	3	4	5	6
LAB- 1	0.3	0.6	6.9	1.2	1.4	6.9
LAB-2	0.80	0.56	7.1	1.8	1.2	7.4
LAB-3						
LAB-4						
LAB-5	1.3	2.3	3.6	4.7	2.1	a.4
		(4.0)*				
LAB-6	0.80	0.60	2.60	0.90	1.80	2.20
LAB-7	1.4	< 1.0	8.5	2.1	1.9	9.0
LAB-8	0.14	0.41	6.03	0.12	0.29	5.63
MISU	0.60		8.0*	7.38		8.0*
	0.51			7.22		
	0.51			2.03		
	0.58					

* Gravimetric value

Samples 1 and 2: ground snow north-central Sweden

Samples 3 and 6: synthetic standards (samples 1-5 in the laboratories own bottles, sample 6 in bottles washed at MISU)

Samples 4 and 5: ground snow south-central Sweden

TABLE 6: Zn ($\mu\text{g l}^{-1}$)

SAMPLE	1	2	3	4	5	6
LAB-1						
LAB-2	5.4	3.9	9.0	6.6	5.0	9.9
LAB-3						
LAB-4						
LAB-5	3.5	3.9	3.4	7.6	7.0	7.5
		(4.0)*				
LAB-6						
LAB-7	1	< 1	5	3	3	7
LAB-8	> 100					
MISU	2.86		8.0*	8.12		8.0''
	3.87			8.92		
	2.60			4.92		
	2.78					

* Gravimetric value

Samples 1 and 2: ground snow north-central Sweden

Samples 3 and 6: synthetic standards (samples 1-5 in the laboratories own bottles, sample 6 in bottles washed at MISU)

Samples 4 and 5: ground snow south-central Sweden

TABLE 7: (units: $\mu\text{g l}^{-1}$)

SAMPLE	Cd	cu	Fe	Mn	Pb	Zn
LAB-1	0.193	0.66	19.6	1.99	3.72	3.5
LAB-2	0.198	0.65	18.9	1.97	3.87	3.4
LAB-3	0.198	2.57	29.8	2.09	4.24	3.8
LAB-4	0.189	0.63	18.2	1.98	3.84	3.43
LAB-5	0.197	0.67	19.3	2.09	4.09	3.5
LAB-6	0.161	0.50	16.5	1.64	3.27	2.90
LAB-7	0.191	0.67	18.8	1.99	3.88	3.4
LAB-S	> 0.60	0.79	26.8	2.16	4.08	3.57
MISU*	0.200	0.60	20	2.0	4.0	4.0

* Gravimetric value

TABLE 8.

SAMPLE	NO ₃ ⁻ - N (mg l ⁻¹)				NH ₄ ⁺ - N (mg l ⁻¹)			
	A	B	C	D	A	B	C	D
LAB-1	0.49	0.35	0.47	0.52	0.56	0.38	0.58	0.62
LAB-2								
LAB-3	0.57	0.42	0.61	0.62	0.48	0.32	0.44	0.53
LAB-4								
LAB-5	0.50	0.36	0.54	0.56	0.51	0.36	0.45	0.57
LAB-6	0.57	0.57	0.56	0.59	0.57	0.35	0.49	0.61
LAB-7	0.52	0.36	0.56	0.57	0.49	0.33	0.44	0.55
LAB-8								
LAB-9	0.54	0.38	0.59	0.61	0.53	0.34	0.46	0.58
LAB-10								
MISU	0.52 0.53	0.38 0.38	0.56 0.56	0.56 0.56 0.57				
				0.56*			0.56*	
Dilution factor	1	0.7 (.37)	0.9 (.47)		1	0.7 (.36)	0.9 (.46)	
mean	0.52	0.37	0.55		0.51		0.35	0.47
s.d.	0.03	0.02	.04		0.03		0.02	0.6

* Gravimetric value

INTERCOMPARISON OF PRECIPITATION COLLECTORS FOR CHEMICAL ANALYSIS, HELCOM INTERCALIBRATION - SECOND STAGE, Aspvreten, Sweden, 1987-1988.

Lennart Granat, Department of Meteorology, Stockholm University, S-106 91 Stockholm, Sweden.

Hans Areskoug, Swedish Environmental Protection Agency, Air Research Division, S-611 82 Nyköping, Sweden

Mads Hovmand, National Environmental Research Institute, Fredriksborgsvej 399, DK-4000 Roskilde, Denmark.

Myk Devenish, Warren Spring Laboratory, Gunnels Wood Road, Stevenage, Hertfordshire SG 1 2BX, United Kingdom.

Bemd Schneider', GKSS-Research Centre, Max-Planck **Straße**, D-2054 Geesthacht, Germany.

Elke Bieber, Umweltbundesamt, Pilotstation Frankfurt Frankfurter **Straße** 135, D-6050 Offenbach, Germany."

W. Marquardt, Institut für Energetik, Umweltzentrum, Torgauer **Straße** 114, 7024 Leipzig, Germany.

Anni Reissell, Finnish Meteorological Institute, Air Quality Department, Sahaajankatu 22E, SF 00810 Helsinki, Finland.

Olli Järvinen, National Board of Waters and the Environment, Research Laboratory, P.O.Box. 250, SF 00101 Helsinki, Finland.

Jan-Erik Hanssen, Norwegian Institute for Air Research, P.O.Box. 64, N-2001 Lillestrom, Norway.

Karin Sjöberg, Swedish Environmental Research Institute, Box 47086, S-402 58 Göteborg, Sweden.

* Present address: Institut für Meereskunde an der Universität Kiel, **Düsternbrooker** Weg 20, D-2300 Kiel 1
 † The German Democratic Republic until the German unification by 3 October 1990

1. INTRODUCTION

Within the framework of the Baltic Marine Environment Protection Commission - Helsinki Commission (HELCOM), the deposition of some harmful substances to the Baltic Sea Area are estimated on the basis of data from coastal monitoring stations.

The HELCOM monitoring programme on airborne pollution is focused on nitrogen compounds (nitrate and ammonium) and some trace metals (lead, copper, zinc and cadmium) in precipitation.

Besides from the uncertainty to interpolate results from coastal stations to the open sea, a reliable deposition estimate demands monitoring data of high quality. The location of the monitoring stations, the sampling and analytical techniques used are aspects to consider.

The Expert Group on Airborne Pollution (EGAP) within HELCOM has decided on a programme of intercalibration and intercomparison exercises to assure the data quality.

As a first stage, an intercomparison of analytical techniques for ammonium, nitrate and the trace metals was arranged in 1986 between laboratories reporting to HELCOM. The results were quite satisfactory for ammonium and nitrogen, but poor for the trace metals. (See the first report in this document).

As regards nitrate and ammonium, EGAP decided to perform the second stage of the quality assurance programme, the intercomparison of sampling equipment and sampling procedures used by the laboratories that participates in the monitoring programme. The results of the intercomparison is presented in this report.

A basic aim for the intercomparison was to compare equipment and sampling procedures as they are used in normal operation (except for the effect of differences in sampling site surroundings). Each participating laboratory should therefore sample and analyze precipitation according to their normal protocol and from its own collector(s). A sampling schedule was also required by which daily, one week, two weeks and monthly sampling periods could be compared in a cost-effective way. Means to identify and consider separately any differences due to sample treatment and chemical analyses were also required.

2. METHODS

2.1 **Organization**

The intercomparison was carried out at Aspövreten, Sweden, during winter 1987 - autumn 1988 jointly by the Air Research Division of the Swedish Environmental Protection Agency (SNV) and the Department of Meteorology, Stockholm University (MISU).

2.2 Sampling site

Aspvreten, the field laboratory belonging to SNV, is located approximately 70 km south-west of Stockholm and about 2 km from the coast in a rural area covered by mixed coniferous and deciduous forest with some meadows. An overview of the sampling site with the collectors is given in Figure 1.

2.3 Participating laboratories and equipment

Invitation to participants was sent out by HELCOM. In response to an interest from the Paris Commission (PARCOM) and the European Monitoring and Evaluation Programme (EMEP) an invitation was also extended to laboratories participating in these projects.

Eleven laboratories from the UK, the former GDR, FRG, Norway, Denmark, Finland and Sweden participated, see Table 1 and Appendix 1. Thus, most of the laboratories providing precipitation chemistry data to HELCOM were represented.

Nine bulk and eight wet-only collectors were compared. The design of each collector is shown in Figure 2. A reference for amount of precipitation was obtained from a standard precipitation collector as used by the Swedish Meteorological and Hydrological Office (SMHI). It is basically a cylindrical collector with a wind screen, see Figure 2. During the summer an evaporation shield is inserted at about half the height of the collector. The amount of collected precipitation was measured every day.

2.4 Components

Of the major components in precipitation, ammonium and nitrate are those of most interest with regard to deposition to the Baltic and they were the key elements in the study. In addition, participating laboratories were encouraged to analyze and report, on a voluntary basis, as many as possible of the other major parameters in precipitation (sulphate, chloride, sodium, potassium, magnesium, calcium, pH, acidity, and conductivity) and phosphorus.

2.5 Sampling period

Duration of sampling periods were one day, one week, two weeks or four weeks as shown in Table 1. Monthly sampling periods, used by some participants in their normal monitoring, were slightly adjusted during this experiment to fit with the four weeks sampling.

The intercomparison started in December 1987, continued through February 1988 in the case of daily or one week sampling and through May 1988 in the case of two or four week sampling periods. A similar schedule was employed for the summer period June through August 1988 with continuation through October for two and four week sampling.

Each collected sample was analyzed except those from collector 9, where daily samples were analyzed only from January and July. During the remaining periods the daily samples were analyzed as four week composite samples.

2.6 Conditions during the intercomparison

Precipitation amount and weighted mean concentrations for all collectors and each of the “months” (actually four week periods) are given in Figure 3.

The winter 1987/88 was unusually mild, the amount of precipitation was large in January and February (which is unusual in this part of Sweden) and fell both as snow and rain. With regard to sampling efficiency the conditions were thus probably more favourable than usual for this region and even more so when compared to more northerly locations. Concentration was generally low in December while a maximum in January and February for most of the anthropogenic components is earlier than usual.

Summer conditions were quite normal. However, the precipitation amount in July was larger than normal.

The seasonal variation of calcium is not typical for the region - usually it is quite similar to that for SO₂ and NH₃, (Granat 1990).

Table 2 gives typical concentrations at Aspvreten of some reactive gases and particulate material that may contribute to dry deposition (and the difference between wet only and bulk collectors).

2.7 Quality control of laboratory performance

In order to account for possible deviation in the final results due to sample treatment and chemical analyses the following measures were taken.

A synthetic rainwater sample with known concentrations of the major components was made up and distributed to the laboratories. This solution should always be analyzed together with samples from the intercomparison and provide an internal reference for this particular investigation. (It does, however, not have the status of a general purpose reference standard).

Four samples of synthetic rain were prepared by the EMEP Chemical Coordination Centre (EMEP-CCC) and sent to all laboratories. The concentration of these samples were unknown to the participants. These samples are referred to as “EMEP samples” below.

A large amount of rainwater was collected approximately once every week during the winter period of the intercomparison (eight samples) and an aliquot was sent to each laboratory. These samples are referred to as “split samples” below.

2.8 Analytical methods

A summary of the analytical methods used by the participating laboratories is given in Appendix 2.

3. RESULTS

3.1 Data

All data on precipitation amount and concentrations from the field samples and quality control samples reported by the participants are given in Appendix 3 as well as the precipitation amount measured by the reference precipitation collector.

All eleven laboratories reported data on precipitation amount, SO₂, NO_x, and NH₃; ten reported on pH, Cl, Mg, Na, Ca and K; nine reported on conductivity. However, only two laboratories measured strong acid (a few reported on H⁺ + calculated from pH-values). Therefore, the strong acid data has not been evaluated below. No laboratory reported data on phosphorus.

3.2 Laboratory performance

A comparison of laboratory performance is based on the four EMEP samples and the eight split samples. All these samples were treated as a group and since the exact composition of the split samples are not known the results from each laboratory and component are compared with the median value obtained from all the laboratories.

Table 3 shows how the median value compares with the theoretically calculated value for the EMEP samples. The agreement is very good except for a few cases and the median is probably a valid reference also for the split samples. Cl is, however, high by about 1-5%, pH is high by 0.01-0.03 units and conductivity by about 3 @/cm. The pH error is typically in the range found if the pH instrument is calibrated with ordinary buffers and no correction is applied for the lower ionic strength in real samples.

Data from the EMEP and split samples were plotted versus the median value for all compounds and laboratories (103 graphs) for a subjective inspection. Figure 4 highlight both a "normal" case and how specific deviations are reflected in calculated statistical variables. A regression line of the type $y = kx + 1$ was fitted to the data. It was forced to pass through origin ($1=0$) except in a few cases where a systematic bias was obvious. A limited number of the data points were regarded as outliers from a subjective interpretation of the graphs and were removed before calculation of the regression line as they might obscure further comparisons. The number of outliers was maximum two per component or eight per laboratory. It might be added that the number of outliers is not a suitable measure of a laboratories analytical performance since this number depends also on the precision. The statistical results are given in Table 4.

Those cases where the slope of the regression line deviated more than 5% from unity, the correlation coefficient was less than 0.89 and/or there was an off-set were inspected in more detail.

The following observations were made in particular:

Sulfate analyses from Laboratory 3 showed a slope well above unity (1.09) and an offset of +0.43 mg S/l, obviously of a systematic nature. This error was also seen in the results from the internal reference (see above) and was corrected after the winter measurements.

Laboratory 4 showed systematically high H^+ concentration (low pH) with a slope of about 1.26 obviously of a systematic nature. Comparison with ion balance calculations indicates that these results are indeed too high.

Laboratory 5 showed a minor but systematic offset for magnesium (-0.01 mg/l).

Laboratory 6 showed a significant and quite substantial offset in particular for calcium (+0.2 mg/l) but also for Na and Mg (+0.1 and +0.013 mg/l respectively).

Laboratory 7 showed systematically low H^+ concentration (high pH) with a slope of about 0.82 obviously of a systematic nature. (The difference was later shown to be caused addition of KCl to the samples before the pH-measurements. The addition increased the pH-value 0.12 units).

Laboratory 11 showed a rather large deviation from unity in the slope for NO_3^- , Na, Mg, Cl and K, but the deviation was not systematic or the performance was changing with time.

The systematic deviations described above were used to correct data before some results from the individual collectors were compared. In the following it is clearly printed out when data have been corrected and when nothing is mentioned, data are uncorrected.

The effect of systematic analytical errors (deviations) compared with that from using different collectors and sampling procedures is seen in Figure 5. The spread in analytical results is in general substantially lower than the spread between the results from sampling. However, in a few cases analytical errors were comparable in magnitude to (or exceeded) differences between collectors. The difference between collectors is however reduced when a correction for analytical errors is applied. The conclusion is that systematic analytical differences between laboratories is often small but not unimportant compared to differences obtained by using different collector types. A regular quality control during analysis is therefore advisable.

3.3 Evaluation of field data

With regard to the possible or intended use of rain chemistry data, we need to know the deviation (error) in concentration/deposition both from a single event (in this case daily samples) and as contribution to long-term mean values (ie from four week samples), reflecting seasonal and yearly averages. This will be considered in the evaluation below.

A rather detailed inspection of differences between daily samples is first made since this is thought to give an insight in the performance of individual collectors and thus give some explanation of differences obtained with longer integration times.

Precipitation amount weighted mean values are also calculated for all sampling periods up to six months to permit a direct comparison between all collectors with different sampling periods. **In several cases we also found it relevant to distinguish between summer and winter period.**

3.3.1 Precipitation amount from daily sampling

The standard gauge used by the Swedish Meteorological Service (SMHI) is taken as a reference without correction for sampling errors. During winter a typical correction would probably be of the order of **10-15 %**. (Eriksson, 1983)

In Figure 6 the amount of precipitation from each daily collector is compared with that from the reference collector for summer and winter separately. Collection efficiency (defined as the ratio between the amount from a collector and the amount from the reference collector) is given in Figure 7 as a function of amount from the reference collector. Collection efficiency for each collector is also summarized in the form of “Notched Box and Whisker Plots”, Figure 8, which in one picture shows several important statistical properties.

The scatter between collectors is larger and collection efficiency lower in winter compared to summer. For the individual collectors we note:

Collector 1 is low by 50% in winter, good agreement in summer.

Collector 9 has a large scatter in winter, high by about 20% in summer.

Collector 10 gave low values by about 10% in winter but same as the reference collector in summer.

Collector 11 was low by 15 % in winter and by 10% plus 0.3 mm in summer.

Collector 16 is low and highly variable in winter (low by about 30% or more) and low by 5% and 0.3 mm in summer.

Collector 18 is low by about 25 % in winter, (daily sampling only in December), no data in summer.

Collector 20 is high by 10% in summer, no data in winter.

In summer collector 10 and 1 show the best performance. The scatter is, however, rather small for most collectors, while the median value varies a little bit more than expected. A probable explanation for some of the deviations (ie the high values of no 9) could be that the area used for calculation is not the same as the effective sampling area. Low values can in some cases be due to the lid opening mechanism and reduced sampling efficiency due to a large collector volume that causes wind disturbance. However, the latter is probably marginal in summer conditions. It could also be seen that several low values in winter from collector 9 are compensated by several high values which gives a seemingly better mean for the whole period. In winter collector 10 and 11 show the smallest scatter and the smallest decrease in collection efficiency. Although the collectors are of the same type (during winter) there is a small but significant difference between them which has not been explained. The

reason for the low collection efficiency for collector 1 in winter was probably a provisional and too high heating which caused evaporation (this was later corrected).

3.3.2 Chemical data from daily sampling

In the case of concentration data we do not have a well established reference and we will try different means to compare data both in terms of relative deviation (from daily median) and in absolute terms of the type “all against all”. Figure 9 shows the scatter in relative deviation (from daily median) for five components. Relative deviation from the daily median as a function of precipitation amount and concentration is shown for the whole period in Figure 10 and separated between winter and summer in Figure 11. Note that Figures 10 and 11 do not exactly tell the contribution to the long-term average because the simultaneous variation of precipitation and concentration is not considered here. A comparison of concentration values (rather than relative ones) is given in Figure 12 where each collector is compared with (almost) all the other collectors for NO_x, NH₃, and Ca. Deviations in concentrations during days with a small amount of precipitation will have a rather small influence on the overall weighted concentration mean. This contribution is better seen if deposition is compared, see Figure 13 where deposition values are calculated using precipitation amount from the reference collector (since we want to compare only the effect of difference in concentration data).

The relative deviation in concentration ranges from about $\pm 10\%$ (25-75 percentile) for nitrate to about $\pm 25\%$ for Ca as seen in Figure 9. It increases with decreasing amount of precipitation and to a smaller extent with decreasing concentration, see Figure 10. The scatter is somewhat larger during winter (Figure 11), but the difference between summer and winter is not as pronounced as with precipitation amount.

The following differences and similarities between collectors were observed (Figures 12 and 13):

We note a striking agreement between collector 10 and 11 for NO_x, NH₃, and Ca (and for the other components not shown in the graphs). Both collectors are of the NILU-type but collector 11 has the cylindrical (winter) type both summer and winter. Due to the good agreement it is likely (but not proven) that samples from these two collectors represent collected rain water and are rather unaffected by disturbances at the sampling site. We have used them as a provisional reference when comparing the other collectors.

During summer the agreement between the two bulk collectors 10 and 11 and each of the collectors 1, 9 and 16 is good in the case of nitrate and ammonium. In the case of concentration of calcium the scatter is much larger (Figure 12c), but is reduced when deposition is compared (Figure 13b).

During winter NH₃ and Ca concentrations in essentially all samples from collector 1 are about 30% or more higher than from collectors 10 and 11 and with some substantially higher. On average NH₃ and Ca concentration is 80-100% higher, see Figures 12b and 12c. Deposition of NH₃ and Ca to collector 1 is on average about 40% higher (Ca: Figure 13b; NH₃, not shown). The deviation for nitrate was smaller. Concentration was on average about 30% higher than in samples from collectors 10 and 11 (Figure 12a), deposition about 10% higher (Figure 13a). The lower difference for

the deposition data is due to a better agreement at high precipitation amounts. The bad agreement at low precipitation amounts is probably due to the provisional heating (see 3.3.1) which caused evaporation (and increased concentration). This does, however, not explain the lower deviation for NO, unless one does not assume some gaseous loss.

For collector 9 the deviation is large and apparently random for both concentration and deposition data during winter, although the scatter is reduced for deposition of NO_x.

For collector 16 a relatively good agreement with collectors 10 and 11 in winter is found for NO_x, although somewhat high. In the case of NH₃, systematically higher concentrations (40-50%) were found. Ca shows a large and apparently random scatter, which is somewhat smaller for deposition data, but with some very high values.

There is no indication (from daily sampling) that the wet-only collectors were superior over the bulk collectors (10 and 11) in excluding excessive amount of soil dust or other material that might occasionally deposit in the collectors or in protecting from deposition of gaseous sulfur and nitrogen compounds.

3.3.3 Long-term concentration averages and precipitation amount

3.3.3.1 Calculations

When calculating long-term mean values from shorter sampling periods, a missing precipitation amount value from a collector due to e.g. leaks during transport or overflow during sampling was replaced with data from the reference gauge corrected according to the average collection efficiency (separate for winter and summer) for the particular collector. A missing concentration value (in general from daily collectors) due to too small volume for a complete analysis was not replaced. This corresponds to normal monitoring, when no assumptions based on results from other collectors can be done. However, in a few cases when concentration and amount data were missing due to other reasons (e.g. malfunctioning collector or samples lost during transport), concentration value from a collector was replaced with the median value for that time period from the other collectors. The median was corrected for any systematic analytical deviation in accordance with split and EMEP samples for that particular collector/laboratory. The missing precipitation amount was calculated as described above. When calculating the weekly values used in Figure 14, a missing data (amount or concentration) was replaced with a mean value which was not corrected. Concentrations reported as less than the detection limit were replaced with a value equal to 50% of the detection limit reported by the concerned laboratory.

The long-term weighted mean concentration may be different if precipitation amount is taken from the particular collector or from the reference collector.

As seen in Table 5 the use of amount data from the reference collector give higher concentrations in winter, especially for collectors with low collection efficiency and short sampling periods (ie collector no 1, 2, 16 and 17). The reason is probably a poor collection efficiency in connection with light snow when the concentration often is above average (Adams et al, 1986). The difference is from 10 to 25 % for the four collectors mentioned depending on component and about 5 % for daily sampling with collectors no 10 and 11.

During summer the collection efficiency does not decrease in the same way and for longer sampling periods (both winter and summer) the effect is not readily seen, although it may be inherently present.

In the case of daily sampling, the use of precipitation amount from a standard meteorological gauge will therefore give higher (and better) weighted mean concentrations. However, this procedure can not fully compensate a poor collection efficiency; a collector with high collection efficiency is always recommended. For longer sampling periods no improvement is obtained when using amount from a standard gauge to calculate weighted mean concentrations. In order to simulate the normal data treatment procedure it seems more relevant to compare weighted mean concentrations from precipitation amount in own collector (since a reference collector is not normally used **onsite**).

Some peculiarities were also found. Laboratory 5 (collector 11) reported concentration data even when precipitation amount was small while Laboratory 4 (collector 10) reported concentration data only when the amount was larger than about 0.4 mm. Since concentration is often higher than average in events with very little precipitation some bias could obviously be introduced in the latter case. To evaluate the magnitude of the bias a weighted mean concentration was calculated both with all available data and with data only from cases when data was available from both collectors. The result is shown in Table 6. The missing concentration data lower the mean value for SO_x and NO_x, by about 7 and 10% respectively.

3.3.3.2 Weekly samples

Weighted mean values were calculated from daily samples as outlined above and compared with weekly samples. A few cases are shown in Figure 14. The scatter has decreased compared to daily values (Figures 12 and 13) which is perhaps not surprising. However, the weekly samples seem to give a similar scatter and thus smaller than obtained from daily collection. There is thus some indication of a smoothing procedure taking place also during the collection period and not only by numerical averaging of daily data.

For the major components such as nitrate, there are very few outliers revealing quite distinctly possible systematic deviations between collectors (and analysis).

In the case of calcium (which shows the largest variability) there is a substantial scatter with occasionally very high or low values. From a qualitative inspection the scatter appears to be larger in the winter than in the summer contrary to what was expected with regard to higher calcium concentrations during the summer (during this study) and the possibility of locally emitted dust affecting the results.

3.3.3.3 Comparison of all collectors - based on seasonal and yearly averages

An overview of the variation of monthly mean concentrations and collected precipitation amount can be seen in Figure 3.

The relative performance of individual collectors for six components during conditions ranging from winter to summer is shown in Figure 15 as the ratio between the weighted mean value for each four week period for a particular collector and the median of all collectors for the same period.

Weighted means calculated for the winter, summer and winter + summer period are given in Table 7.

The relative concentration does not vary much between individual months for some collectors while others deviate substantially. Higher than average ratios were found from collectors 1,9,16 and 20 during December and January for one or several of the components sulphate, nitrate and ammonium. This deviation cannot be easily explained by poor collection efficiency alone.

Components contained in coarse particles, ie Ca, does not lead to high ratios during summer which is probably a consequence of a rather modest local dust emission during summer. The test area is therefore not particularly discriminating between different design of collectors with regard to sensitivity to dust fall collection. High ratios for Ca were on the other hand found for some collectors (1, 9, 16, 18 and 20) during winter.

To further facilitate comparison between collectors, ratios between data from one collector and the mean of all collectors for the whole period (summer+winter) were calculated. (This mean value has no other function than as a temporary reference point.) Collectors were then ordered according to increasing concentration of the major components and the ratios are shown in Figure 16 for some important components.

It is interesting to note that this order is about the same for all the major components. We can then roughly divide the collectors into three groups with regard to concentration for the major components. For collector 10 we may increase values by 7 to 10% to correct for the effect from not analyzing samples with little precipitation as discussed above.

- 1) Slightly below mean value (0.9): Collector 10 (daily collection, bulk collector), 5 (four-week, wet-only), 6 (four-week, wet-only), 2 (weekly, wet-only). It could be noted that all three of these wet-only collectors are of the same design.
- 2) Around mean value (0.97): 17 (weekly, bulk), 11 (daily, bulk), 14 and 15 (two-week, bulk), 16 (daily, wet-only), 3 (four-week, bulk) and 12 (four-week, bulk).
- 3) Above average for several components and with larger differences for individual components: 9 (daily composite, wet-only), 1 (daily, wet-only), 18 (weekly, bulk).

It is an open question which collector(s) in this array that gives the best measure of concentration in precipitation. On one hand we would look for collectors with lowest concentration of stable components - which do not decrease in concentration due to chemical (evaporation, sorption) or biological processes - such as calcium and sulfate because this indicates small contribution from other sources than precipitation. On the other hand we have seen that too low concentration values can be found if collection efficiency is poor. This can be due to design and, of course, a less than perfect lid operation in case of wet only collector.

A good agreement between an open collector (with better than average collection efficiency) and several wet only collectors as in group 1 above may indicate a "true" value. There are, however several collectors of different design (group 2 above) which shows good agreement which may also indicate a "true" value. With the present information it seems difficult to select data either from group 1 or 2 as more representative of the true value of concentration

of the various components. The difference between the two groups is rather small considering the normal variability within a network and we can still draw some interesting and valuable conclusions about influence of collector type and design.

It is thus noteworthy that collector performance is not strongly related to instrument and manpower cost. If bulk collectors are considered, daily up to two week sampling periods seems to give similar results and with less than 10% larger values for 4 week (monthly) sampling. With regard to wet-only collectors there are obviously large differences between collectors and the design of the collector seems to be more important than the choice between bulk and wet-only collector. This conclusion is valid at station Aspvreten and many other sites in Sweden but not necessarily so in other chemical climates.

Another important result is that short sampling period or use of wet-only collector instead of bulk - which is generally considered to minimize dry deposition - seems to have larger influence on components such as sulfate and nitrate than for instance on calcium. Thus in this particular environment the dry deposition of soil derived particles seems to be less important while dry deposition of sulfate, nitrate and ammonium species has some influence (10% or less). It must be cautioned that these findings are related to the particulate environment found in Sweden. From other investigations (Granat, 1991) it appears quite likely that the influence from alkaline dust has a larger influence (and thus also on the difference between different collectors and collection protocols). Such could be found in the eastern and southern part of Europe.

It is of interest to look for indication of significant loss of ammonium (as one of the least stable of the major components - due to microbiological activity) during longer sampling periods. Comparison with daily sampling does not indicate significantly lower values from four week sampling neither in summer or in winter. This does indicate that this component is stable enough for monthly collection periods the year around - at least in this environment. In one collector (no 16) samples were stored in a refrigerated volume. Here ammonium concentration was larger than in most other collectors. The difference was however equally large in winter.

The difference between most of the collectors (highest to lowest) is less than 20% for most of the components including hydrogen ion and calcium (neglecting analytical differences). To obtain a perspective on this number and to see if it is acceptable one could compare with results from various networks:

With regard to spatial gradients over Sweden, the 20% difference corresponds to a distance of about 100 km when estimated from an average of seven years and 30 stations. (Granat, 1991). A small-scale variability (yearly averages) is of the order of 10% within 50 km but it is also well known that an improper location of a collector could give a very severe bias. Thus, the deviation in mean concentration between the collectors does by no means invalidate previously obtained results. If a correction is applied the true error will of course be smaller but the problem is that such a correction (depending on the differences between collectors) probably needs to be evaluated in different environments.

With regard to calculations of total deposition, the difficulties in estimating dry deposition contributes a much larger uncertainty. It should also be considered that even precipitation amount measured with the reference gauge needs to be corrected (probably of the order of 10%).

4. CONCLUSIONS

17 collectors were compared during three winter and three summer months at a location typical for rural conditions in central Sweden. The equipment ranged in complexity from wet-only collectors with daily sampling to bulk collectors with four-week sampling periods.

The study showed systematic differences in both collection of rainwater amount and concentration measured in collected samples and gave some results of importance for evaluation of already collected data and future measurements.

- # The difference of concentrations for the whole intercomparison period between most of the collectors (highest to lowest) is less than 20% for most of the components including hydrogen ion and calcium (neglecting analytical differences). With regard to spatial gradients over Sweden this corresponds to a distance of about 100 km when estimated from an average of seven years and 30 stations.
- # With regard to spatial distribution the deviation in mean concentration between the collectors does by no means invalidate previously obtained results.
- # With regard to time trends a change from one collector to another would, during unlucky conditions, give very substantial error and could be viewed against the large effort taken in order to reduce sulfur emissions by 30% with the expectation that deposition would be reduced by a similar amount. Here great caution is necessary.
- # With regard to estimates of deposition over the Baltic, which is essential to HELCOM, the effect of using different sampling periods and different collectors seems to introduce some error which is however small in comparison with other uncertainties such as few and unevenly distributed sampling stations (in some regions), unknown representativeness for several stations and in some cases analytical errors. It should also be remembered that collectors were tested on land while deposition over open water is also required which includes the difficult question of estimating (measuring?) precipitation amount at sea.
- # The borderline between good and less good collectors is rather between different designs than between bulk and wet only collectors as such or between short and longer sampling periods (day, one, two or four week sampling could all give nearly comparable results). A simple design and modest volume of the collector seems to promote good sampling conditions. In the particular environment that is found in large areas in Sweden bulk collectors may give a rather satisfactory result but one can also expect that there are areas where the use of wet-only collectors or bulk collectors with very short collection periods with collector cleaning in between is an advantage.

- # This study showed that systematic analytical errors could sometimes give errors comparable to the difference between collectors. Usually they are smaller but not negligible. A regular quality control of the chemical analysis seems advisable.

ACKNOWLEDGEMENTS

The assistance of E. Håkansson, I. Ohlsson, P. Rosencrantz and E. Johansson at the Air Research Division of the Swedish Environmental Protection Agency for work at Aspvreten and data handling is gratefully acknowledged.

The assistance of Vuokko Karlsson at the Finnish Meteorological Institute for preliminary work is also gratefully acknowledged.

Finally, we wish to thank all laboratory personnel at the participating institutes for their work with the numerous analysis.

Financial support for the study was obtained from the Swedish Environmental Protection Agency and Stockholm University.

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SUMMARY

Within the framework of the Baltic Marine Environment Protection Commission - Helsinki Commission (HELCOM), the deposition of some harmful substances to the Baltic Sea Area is estimated on the basis of data from coastal monitoring stations.

The HELCOM monitoring programme on airborne pollution is focused on nitrogen compounds (nitrate and ammonium) and some trace metals (lead, copper, zinc and cadmium) in precipitation.

Besides from the uncertainty to interpolate results from coastal stations to the open sea, a reliable deposition estimate demands monitoring data of high quality. The location of the monitoring stations, the sampling and analytical techniques used are aspects to consider.

The Group of Experts on Airborne Pollution of the Baltic Sea Area (EGAP) within HELCOM has stressed the importance and need of intercalibration and intercomparison exercises. EGAP decided that these exercises should be divided in two stages. In the first stage, an intercalibration of the analytical methods for nitrogen compounds and trace metals in precipitation used at the laboratories involved should be accomplished. The second stage, an intercomparison of procedures for precipitation sampling, should be carried out if and when the results of the first stage were satisfactory.

In this report, the outcome of the first and second stage of the HELCOM intercalibrations is presented.

The first stage, the intercalibration of analytical methods, was accomplished in 1986. It was organized by Sweden.

Emphasis was given to the trace metals because not all laboratories did such analyses routinely at that time.

Six samples with unknown concentrations of trace metals were distributed to eight laboratories. Five returned results. Various methods were used to test if the laboratories had control of sample contamination and if they could analyze the low concentrations normally found in precipitation. Compulsory components were lead, copper and zinc. Cadmium, iron and manganese were determined on an optional basis.

A wide spread were found in the results. Some deviating results could be explained as due to contamination from sampling bottles or inappropriate analytical methods. It is concluded that much work is needed. As a first step, standardization of analytical methodologies is proposed. A workshop on methods for sampling and analytical techniques for trace metals in precipitation would be useful. (The proposed workshop has taken place in Sweden in 1989.)

For the nitrate and ammonium intercalibration, four samples were sent out to ten laboratories. Results were obtained from six of them. The results had, as expected, a much lesser spread than the results for trace metals. It is concluded that each of the laboratories can accurately determine ammonium and nitrate.

The outcome of the first stage of the intercalibrations justified the start of the second stage for nitrate and ammonium, but not for the trace metals due to the poor results.

The second stage of the intercalibration for nitrate and ammonium, the intercomparison of precipitation collectors, was also organized by Sweden. It took place in Sweden during 1987-1988.

Most of the laboratories providing precipitation chemistry data to HELCOM participated. Furthermore, in response to an interest from the Paris Commission (PARCOM) and the European Monitoring and Evaluation Programme (EMEP), laboratories involved in these projects participated.

17 collectors from eleven laboratories from the UK., the former GDR, FRG, Norway, Denmark, Finland and Sweden were compared during three winter and three summer months at a location typical for rural conditions in central Sweden. The equipment ranged in complexity from wet-only collectors with daily sampling to bulk collectors with four-week sampling periods.

Besides from the nitrogen compounds, the other major components in precipitation were studied.

The study showed systematic differences in both collection of rainwater amount and concentration measured in collected samples and gave some results of importance for evaluation of already collected data and future measurements.

- # The difference of concentrations for the whole intercomparison period between most of the collectors (highest to lowest) is less than 20% for most of the components including hydrogen ion and calcium (neglecting analytical differences). With regard to spatial gradients over Sweden this corresponds to a distance of about 100 km when estimated from an average of seven years and 30 stations.
- # With regard to estimates of deposition over the Baltic, which is essential to HELCOM, the effect of using different sampling periods and different collectors seems to introduce some error which is however small in comparison with other uncertainties such as few and unevenly distributed sampling stations (in some regions), unknown representativeness for several stations and in some cases analytical errors. It should also be remembered that collectors were tested on land while deposition over open water is also required which includes the difficult question of estimating (measuring?) precipitation amount at sea.
- # With regard to time trends a change from one collector to another would, during unlucky conditions, give very substantial error and could be viewed against the large effort taken in order to reduce sulfur emissions by 30% with the expectation that deposition would be reduced by a similar amount. Here great caution is necessary.
- # The borderline between good and less good collectors is rather between different designs than between bulk and wet only collectors as such or between short and longer sampling periods (day, one, two or four week sampling could all give nearly comparable results). A simple design and modest volume of the collector seems to promote good sampling conditions. In the particular environment that is found in large areas in Sweden bulk collectors may give a rather satisfactory result but one can also expect that there are areas where the use of wet-only collectors or bulk collectors with very short collection periods with collector cleaning in between is an advantage.
- # This study showed that systematic analytical errors could sometimes give errors comparable to the difference between collectors. Usually they are smaller but not negligible. A regular quality control of the chemical analysis seems advisable.

Table 1. Collectors used in the intercomparison and responsible laboratories.

Lab. code	Collector code	Collector type	Length of sampling period	Remark
1	1	Wet Only	1 day	
1	2	Wet Only	1 week	
1	60	Bulk	1 day	a
2	3	Bulk	4 weeks	f
2	4	Bulk	4 weeks	f
2	5	Wet Only	4 weeks	
2	6	Wet Only	4 weeks	
3	9	Wet Only	1 day	b
4	10	Bulk	1 day	f
5	11	Bulk	1 day	
6	12	Bulk	4 weeks	
7	14	Bulk	2 weeks	
7	15	Bulk	2 weeks	
8	16	Wet Only	1 day	
8	17	Bulk	1 week	
9	18	Bulk	1 week	c
10	19	Wet Only	1 week	d
11	20	Wet Only	1 day	

- a. Reference sampler for precipitation amount.
- b. Daily sampling, but during December, February, June and August all daily samples were put together and analysed as monthly samples.
- c. Daily sampling 27 Nov. 1987 - 10 Jan. 1988.
- d. Participated only during winter period, 27 Nov. 1987 - 28 Feb. 1988.
- e. Participated from 18 Jan. 1988.
- f. Special collector for snow used in winter.

Table 2. Average concentrations of some gases and particulate matter that may contribute to dry deposition and give a difference between wet-only and bulk collectors. Based on two years measurements with denuder technique.

Component	Concentration nmol/m ³
SO ₂	27
SO ₄ ²⁻ (p)	26
HNO ₃	6
NO ₃ ⁻ (p)	16
NH ₃	8
NH ₄ ⁺ (p)	61

Table 3. Synthetic precipitation samples. Comparison of 'true' concentrations (as reported by EMEP-CCC) and median of concentrations reported by the participating laboratories.

Sample	Type	PH	so4 mg S/l	NO3 mg N/l	NH4 mg N/l	Na mg/l
G1	Median	4.13	1.57	0.95	0.51	1.56
	True	4.10	1.57	0.94	0.51	1.54
G2	Median	4.51	2.00	0.59	0.44	1.55
	True	4.50	1.99	0.58	0.44	1.54
G3	Median	4.19	1.48	0.90	0.77	1.47
	True	4.16	1.46	0.90	0.75	1.47
G4	Median	4.42	2.09	0.52	0.71	1.49
	True	4.40	2.05	0.52	0.68	1.48

Sample	Type	Mg mg/l	Ca mg/l	Cl mg/l	K+ mg/l	Cond uS/cm
G1	Median	0.22	0.36	2.44	0.59	53.0
	True	0.22	0.36	2.47	0.59	49.6
G2	Median	0.23	1.31	2.25	0.53	39.8
	True	0.23	1.33	2.28	0.53	36.6
G3	Median	0.12	0.43	2.41	0.30	49.6
	True	0.13	0.43	2.53	0.30	46.2
G4	Median	0.11	1.20	2.26	0.33	42.0
	True	0.11	1.21	2.34	0.33	39.2

Table 4. Regression analysis for control samples.

Model : $Y = kX + 1$.

Y = Concentrations of a compound in 4 synthetic (EMEP) and 8 real precipitation (split) samples reported by one laboratory.

X = The 4+8 medians of all reported concentrations of a compound.

r^2 = Correlation coefficient.

Out = The number of outliers not used in the regression analysis.

If a laboratory has not reported any data, the regression equation has been assumed to be $Y=X$. No \$-values is given in these cases.

Lab		SO ₄ -S	NO ₃ -N	NH ₄ -N	Na	Mg	Ca	CL	H+	K+	Cond
01	k	1.006	1.000	0.975	1.036	1.052	0.899	0.975	1.023	1.067	0.928
	l	0	0	0	0	0	0	0	0	0	0
	r ²	0.994	0.999	0.998	0.989	0.993	0.997	0.99;	0.997	0.99;	0.993
out											
02	k	1.002	0.979	0.999	0.972	0.958	0.958	0.982	0.961	0.917	1
	l	0	0	0	0	0	0	0	0	0	0
	r ²	0.997	0.99;	1.000	0.998	0.99;	0.999	0.99;	0.991	0.992	
out				1	1				1		
03	k	1.092	1.060	1.076	1.001	0.993	0.976	0.980	1.060	0.992	1.029
	l	0.428	0	0	0	0	0	0	0	0	0
	r ²	0.977	0.992	0.99;	0.997	0.954	0.993	0.994	0.997	0.964	0.996
out		1	1	1	2		1			1	
04	k	1.003	1.018	0.945	1.021	1.039	1.039	0.983	1.257	1.040	0.899
	l	0	0	0	0	0	0	0	0	0	0
	r ²	0.998	0.999	0.999	0.995	0.995	0.999	0.996	0.94;	0.985	0.99;
out									1		
05	k	0.974	0.988	0.895	0.976	0.925	1.037	1.000	1.006	1.009	1.001
	l	0	0	0	0	-0.01	0	0	0	0	0
	r ²	0.998	0.991	0.992	0.995	0.995	0.99;	0.99;	0.99;	0.982	0.999
out											
06	k	0.979	1.008	1.018	1.035	0.960	0.983	1.031	0.966	0.963	1.038
	l	0	0	0	0.102	0.013	0.214	0	0	0	0
	r ²	0.995	1.000	0.979	0.996	0.994	0.995	0.986	0.997	0.974	0.998
out				1	1			1			
07	k	0.989	1.047	1.028	0.969	0.972	0.934	0.960	0.815	1.016	1
	l	0	0	0	0	0	0	0	0	0	0
	r ²	0.998	0.997	0.999	0.990	0.994	0.997	0.972	0.995	0.987	
out							1		1		
08	k	0.995	0.991	0.999	0.984	0.997	0.980	1.017	1.050	0.933	1.011
	l	0	0	0	0	0	0	0	0	0	0
	r ²	1.000	1.00;	0.999	0.994	0.98;	0.99;	0.998	0.995	0.99;	0.999
out					1		1		3		
09	k	1.084	1.032	1.011	0.995	0.985	1.021	1.060	0.954	0.983	0.987
	l	0	0	0	0	0	0	0	0	0	0
	r ²	0.971	0.999	0.997	0.997	0.994	0.999	0.992	0.991	0.990	0.992
out				1				2			
10	k	0.988	0.965	1.058		1	1	0.996	1	1	1
	l	0	0	0	0	0	0	0	0	0	0
	r ²	0.996	0.999	0.994				0.994			
out											
11	k	1.021	0.829	0.982	1.078	1.123	1.007	1.128	0.978	0.881	1.000
	l	0	0	0	0	0	0	0	0	0	0
	r ²	0.860	0.970	0.987	0.987	0.964	0.974	0.772	0.997	0.858	0.999
out	2	2	1		1			2			

Table 5. Comparison of weighted mean concentrations during winter and summer period calculated either with precipitation amount from the same (own) collector or from the reference gauge.

WINTER		Sulphate mg S/l		Nitrate mg N/l		Ammonium mg N/l		H+ ueqv/l	
Coll. no.	Sampl period	Amount from		Amount from		Amount from		Amount from	
		Own	Ref	Own	Ref	Own	Ref	Own	Ref
01	D	2.09	2.43	1.01	1.15	1.23	1.40	79	88
10	D	1.31	1.35	0.83	0.85	0.67	0.70	101	105
11	D	1.37	1.44	0.91	0.96	0.66	0.68	79	82
16	D	1.63	2.20	1.05	1.29	0.93	1.23	88	96
02	1w	1.44	1.64	0.88	0.98	0.75	0.87	81	88
17	1w	1.51	1.85	0.95	1.05	0.81	0.98	92	102
14	2w	1.54	1.55	1.04	1.04	0.87	0.87	70	70
15	2w	1.53	1.57	1.02	1.04	0.86	0.89	71	73
03	4w	1.64	1.62	0.99	0.98	0.86	0.84	84	84
05	4w	1.42	1.44	0.90	0.91	0.78	0.79	78	78
06	4w	1.42	1.43	0.91	0.91	0.78	0.79	76	76

SUMMER		Sulphate mg S/l		Nitrate mg N/l		Ammonium mg N/l		H+ ueqv/l	
Coll. no.	Sampl period	Amount from		Amount from		Amount from		Amount from	
		Own	Ref	Own	Ref	Own	Ref	Own	Ref
01	D	1.09	1.04	0.42	0.41	0.61	0.59	36	36
10	D	0.88	0.88	0.38	0.38	0.52	0.52	35	35
11	D	1.03	1.05	0.41	0.42	0.59	0.59	35	36
16	D	1.05	1.06	0.42	0.43	0.61	0.62	40	39
02	1w	1.00	1.01	0.39	0.39	0.51	0.52	26	26
17	1w	1.04	1.01	0.40	0.39	0.53	0.51	31	31
14	2w	1.02	1.03	0.43	0.43	0.54	0.54	23	25
15	2w	1.02	1.03	0.42	0.43	0.57	0.57	22	23
03	4w	1.01	1.00	0.40	0.40	0.52	0.52	26	26
05	4w	0.95	0.95	0.37	0.37	0.42	0.42	31	31
06	4w	0.96	0.96	0.37	0.37	0.48	0.48	27	27

Table 6. Effect of omitting concentration data from days with small amount of precipitation. Laboratory 5 reports concentration data from virtually all precipitation events while laboratory 4 reports concentrations only when precipitation data is larger than about 0.4 mm.

A. All available data are used for calculating weighted mean values (similar to real sampling conditions). B. Weighted mean values calculated only with data from those days where concentration data were available from both collectors.

A.		Volume weighted mean concentrations			
Lab.	SO_4^{2-} mg S/l	NO; mg N/l	NH_4^+ mg N/l	Ca^{2+} mg/l	
05	1.18	0.66	0.62	0.28	
04	1.06	0.58	0.58	0.27	

B.		Volume weighted mean concentrations			
Lab.	SO_4^{2-} mg S/l	NO; mg N/l	NH_4^+ mg N/l	Ca^{2+} mg/l	
05	1.14	0.62	0.61	0.27	
04	1.09	0.60	0.60	0.28	

Table 7. Precipitation amount and volume weighted mean concentrations from all collectors in the comparison. Data are corrected for systematic analytical differences.

WINTER + SUMMER PERIOD													Rem.	
A	B	Amount mm	pH	SO ₄ -S mg/l	NO ₃ - mg/l	NH ₄ mg/l	Na mg/l	Mg mg/l	Ca mg/l	Cl mg/l	K mg/l	Cond uS/cm		
01	01	296	4.29	1.47	0.65	0.87	0.37	0.09	0.39	0.50	0.10	37.4	a	
01	02	339	4.32	1.18	0.60	0.63	0.35	0.08	0.28	0.44	0.07	33.4		
02	03	388	4.23	1.34	0.72	0.70	0.34	0.07	0.28	0.61	0.09	37.5		
02	04	369												
02	05	319	4.27	1.16	0.61	0.58	0.26	0.06	0.26	0.46	0.05	34.1		
02	06	345	4.29	1.16	0.62	0.62	0.26	0.07	0.26	0.48	0.07	32.9		
03	09	402	4.25	1.31	0.64	0.70	0.35	0.08	0.33	0.56	0.09	36.2		b
04	10	373	4.27	1.08	0.58	0.63	0.27	0.07	0.26	0.49	0.08	33.9		
05	11	337	4.25	1.23	0.66	0.69	0.31	0.08	0.27	0.59	0.08	35.0		c
	12	377	4.23	1.45	0.78	0.74	0.47	0.08	0.33	0.75	0.19	40.8		
07	14	359	4.24	1.30	0.71	0.69	0.32	0.08	0.32	0.67	0.09			
07	15	366	4.24	1.29	0.68	0.70	0.31	0.08	0.32	0.61	0.10			
08	16	301	4.25	1.29	0.69	0.74	0.29	0.08	0.31	0.83	0.09	34.0		
08	17	334	4.25	1.26	0.66	0.66	0.33	0.08	0.30	0.60	0.09	38.6		
09	18	323	4.29	1.39	0.70	0.78	0.35	0.09	0.39	0.59	0.12	40.5		
10	19													d
11	20													
01	60	392												e
Average		349	4.26	1.28	0.67	0.69	0.33	0.08	0.31	0.58	0.09	36.2	f,g	
Std(%)		9	6	9	8	10	16	10	14	18	34	7		

WINTER PERIOD													Rem.	
A	B	Amount mm	pH	SO ₄ -S mg/l	NO ₃ - mg/l	NH ₄ mg/l	Na mg/l	Mg mg/l	Ca mg/l	Cl mg/l	K mg/l	Cond uS/cm		
01	01	116	4.11	2.08	1.01	1.26	0.75	0.11	0.28	0.93	0.17	54.7	a	
01	02	147	4.10	1.43	0.88	0.77	0.50	0.06	0.14	0.73	0.09	47.7		
02	03	203	4.06	1.64	1.01	0.86	0.52	0.08	0.19	0.98	0.12	52.7		
02	04	179	4.07	1.56	0.96	0.83	0.49	0.08	0.19	0.92	0.10	51.1		
02	05	140	4.09	1.42	0.92	0.78	0.43	0.06	0.16	0.80	0.08	48.8		
02	06	153	4.10	1.42	0.93	0.78	0.44	0.08	0.16	0.82	0.08	48.0		
03	09	174	4.06	1.74	0.99	1.01	0.63	0.10	0.25	0.98	0.14	51.8		b
04	10	182	4.09	1.31	0.81	0.71	0.46	0.07	0.16	0.83	0.11	44.8		
05	11	167	4.11	1.40	0.92	0.73	0.49	0.08	0.16	0.92	0.10	46.5		c
06	12	197	4.05	1.79	1.15	0.93	0.61	0.08	0.16	1.22	0.20	51.4		
07	14	183	4.06	1.56	0.99	0.84	0.52	0.09	0.19	1.02	0.10			
07	15	181	4.06	1.55	0.97	0.84	0.50	0.08	0.18	0.99	0.10			
08	16	119	4.08	1.64	1.06	0.93	0.54	0.08	0.18	1.65	0.13	50.2		
08	17	160	4.06	1.52	0.96	0.81	0.53	0.09	0.20	0.99	0.11	51.9		
09	18	144	4.08	1.85	1.08	0.99	0.61	0.10	0.31	0.99	0.12	62.7		
10	19	81								0.89				
11	20													a
01	60	204												
Average		158	4.08	1.59	0.98	0.87	0.54	0.08	0.19	0.98	0.12	50.9		f,g
Std(%)		20	5	12	8	15	15	16	24	21	28	8		

Table 7. (continuation)

SUMM		R PERIOD											
A	B	Amount mm	pH	SO4-S mg/l	NO3- mg/l	NH4 mg/l	Na mg/l	Mg mg/l	Ca mg/l	Cl mg/l	K mg/l	Cond uS/cm	
01	01	180	4.45	1.08	0.42	0.63	0.13	0.07	0.46	0.23	0.06	26.2	
01	02	192	4.60	1.00	0.39	0.53	0.24	0.09	0.39	0.23	0.06	224	
02	03	185	4.57	1.00	0.41	0.52	0.13	0.07	0.38	0.20	0.07	20.9	
02	04	190											a
02	05	179	4.49	0.95	0.38	0.42	0.12	0.06	0.34	0.19	0.03	226	
02	06	192	4.55	0.95	0.38	0.48	0.11	0.06	0.34	0.19	0.05	20.8	
03	09	229	4.47	0.98	0.37	0.46	0.14	0.07	0.38	0.24	0.06	24.3	
04	10	192	4.56	0.87	0.37	0.55	0.11	0.07	0.37	0.16	0.06	23.7	
05	11	170	4.46	1.05	0.41	0.66	0.13	0.08	0.38	0.27	0.07	23.6	
06	12	180	4.58	1.09	0.39	0.52	0.32	0.08	0.51	0.24	0.18	29.0	
07	14	176	4.54	1.03	0.41	0.53	0.12	0.08	0.45	0.29	0.09		
07	15	185	4.56	1.04	0.40	0.56	0.12	0.08	0.46	0.24	0.10		
08	16	182	4.42	1.05	0.42	0.61	0.14	0.08	0.39	0.29	0.05	23.3	
08	17	174	4.52	1.05	0.40	0.53	0.13	0.08	0.39	0.24	0.08	26.3	
09	18	178	4.58	1.02	0.40	0.61	0.14	0.09	0.45	0.27	0.13	22.5	
10	19												d
11	20	204	4.41	0.84	0.49	0.31	0.10	0.05	0.63	0.67	0.06	25.8	
01	60	188											e
Average		187	4.51	1.00	0.40	0.53	0.15	0.07	0.42	0.26	0.08	24.0	f,g
Std(%)		7	14	7	7	16	38	15	17	44	47	9	f,g

Remarks A = Laboratory code. B = Collector code.

Std(%) = 100 * (Standard deviation/Average)

a. Data missing for two months

b. Based on estimated values for 6 January 1988 (precip. amount 25 mm).
Daily median of the other collectors used.

c. No data reported for January. January data are calculated as $Y=kX+l$,
where Y=value for collector 12, X=median of reported results
for January, k and l are regression coefficients calculated for other months
than January.

d. Did not participate during summer period.

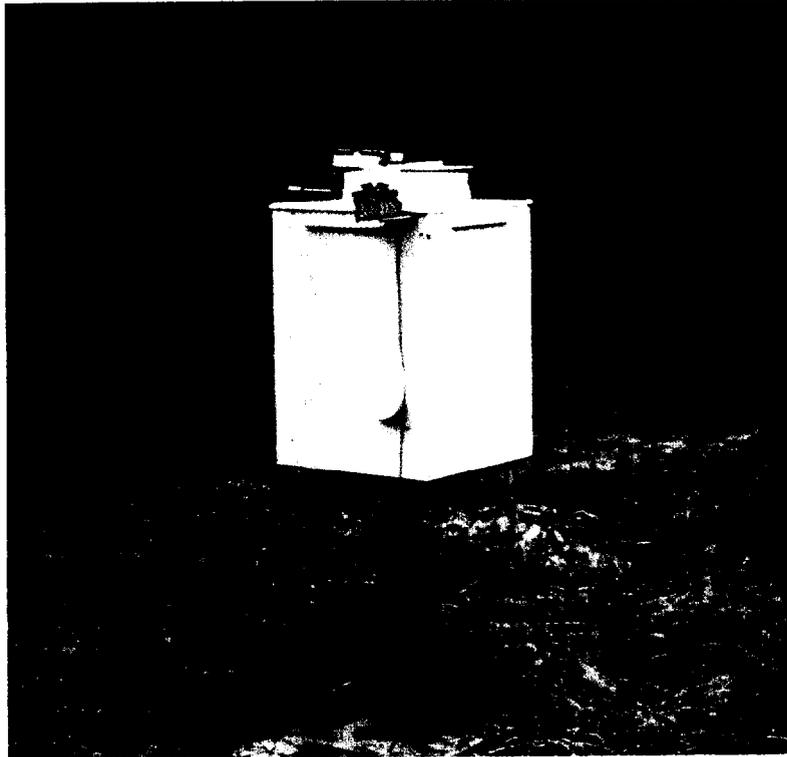
e. Reference gauge for precipitation amount.

f. **pH**. Average and std(%) calculated after transformation to H⁺-equivalents.

g. **Amount**. Data from reference gauge (collector code 60) not included in
calculations of average and standard deviation.



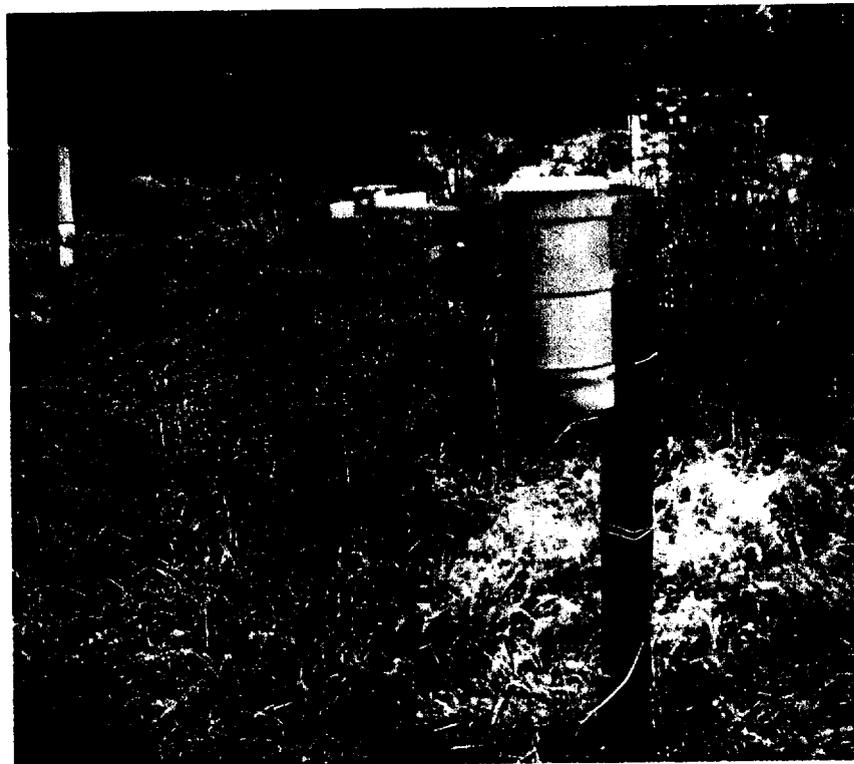
Figure 1. Sampling site with collectors. The picture is taken from the sampling platform of the field laboratory building.



Collector code no. 1

wet-only

daily sampling



Collector code no.2

wet-only

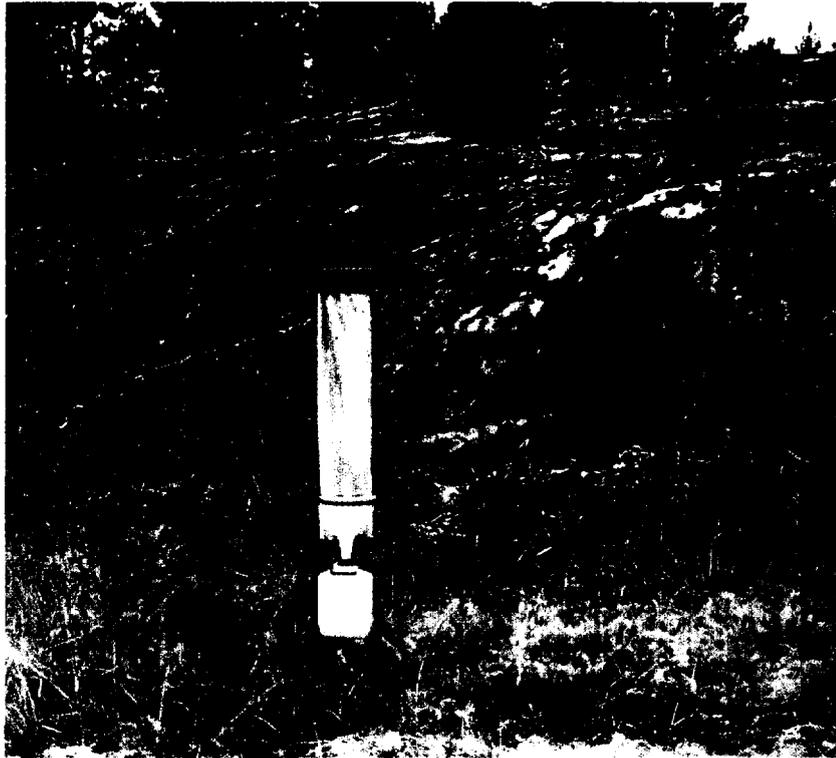
1 week sampling

Collector code no. 5 and 6

wet-only

4 week sampling

Figure 2. Collectors used during the intercomparison.



Collector code no. 3 and 4 bulk 4 week sampling winter



Collector code no. 3 and 4 bulk 4 week sampling summer

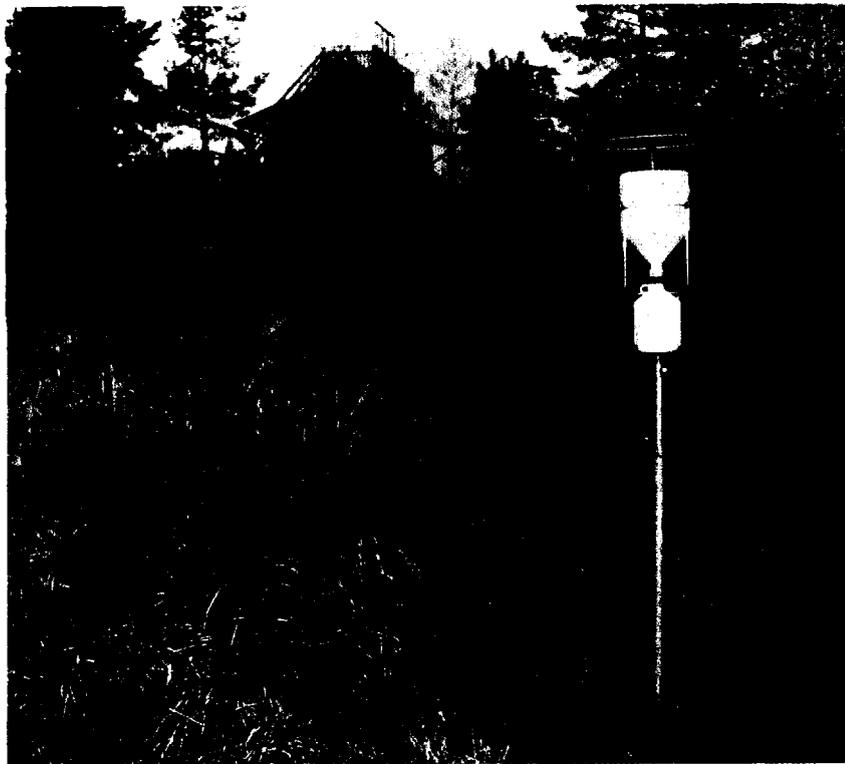
Figure 2. (continuation).



Collector code no. 9

wet-only

daily sampling



Collector code no. 10

bulk

daily sampling summer

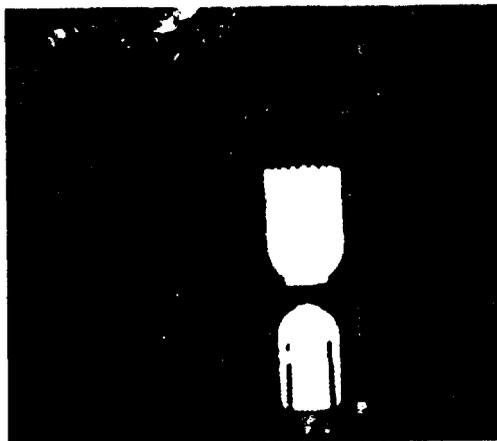
Figure 2. (continuation).



Collector code no. 10
Collector code no. 11

bulk
bulk

daily sampling winter
daily sampling all year

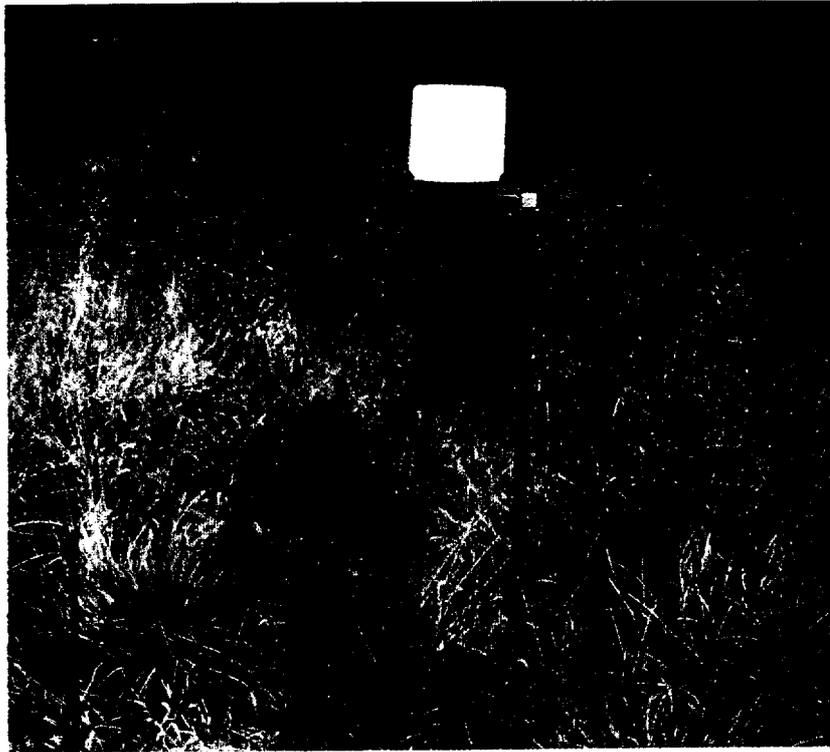


Collector code no. 12

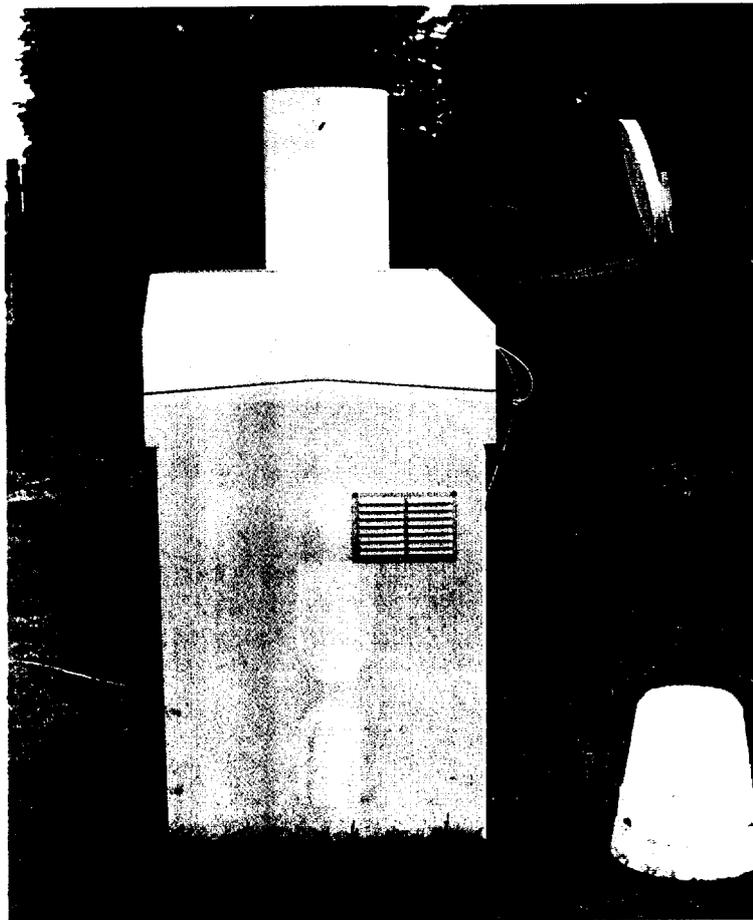
bulk

4 week sampling

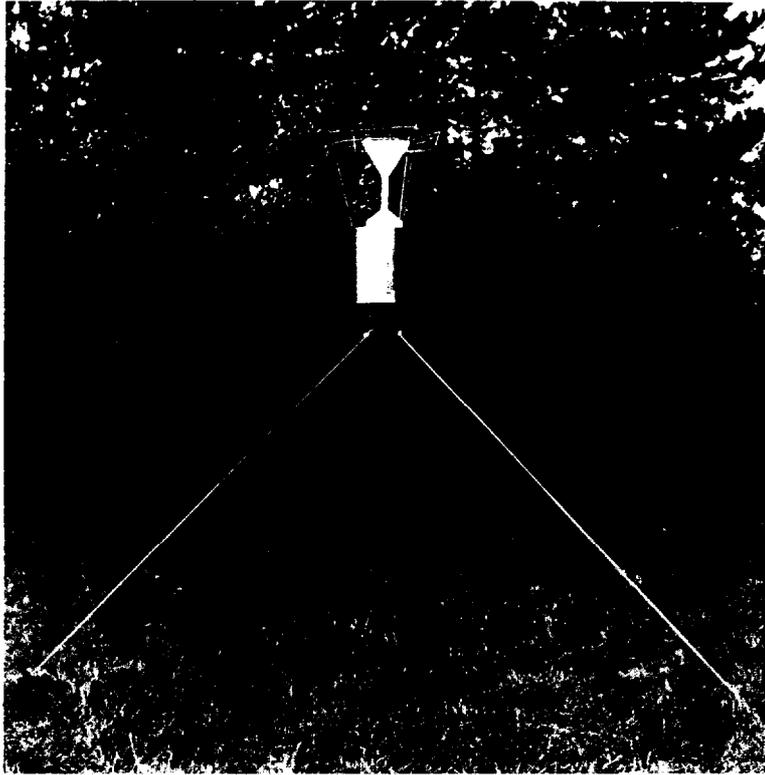
Figure 2. (continuation).



Collector code no. 14 and 15 bulk 2 week sampling



Collector code no. 16 wet-only daily sampling
Note: The collector and tipping bucket are separated by at least 10 meters during sampling



Collector code no. 17

bulk

1 week sampling



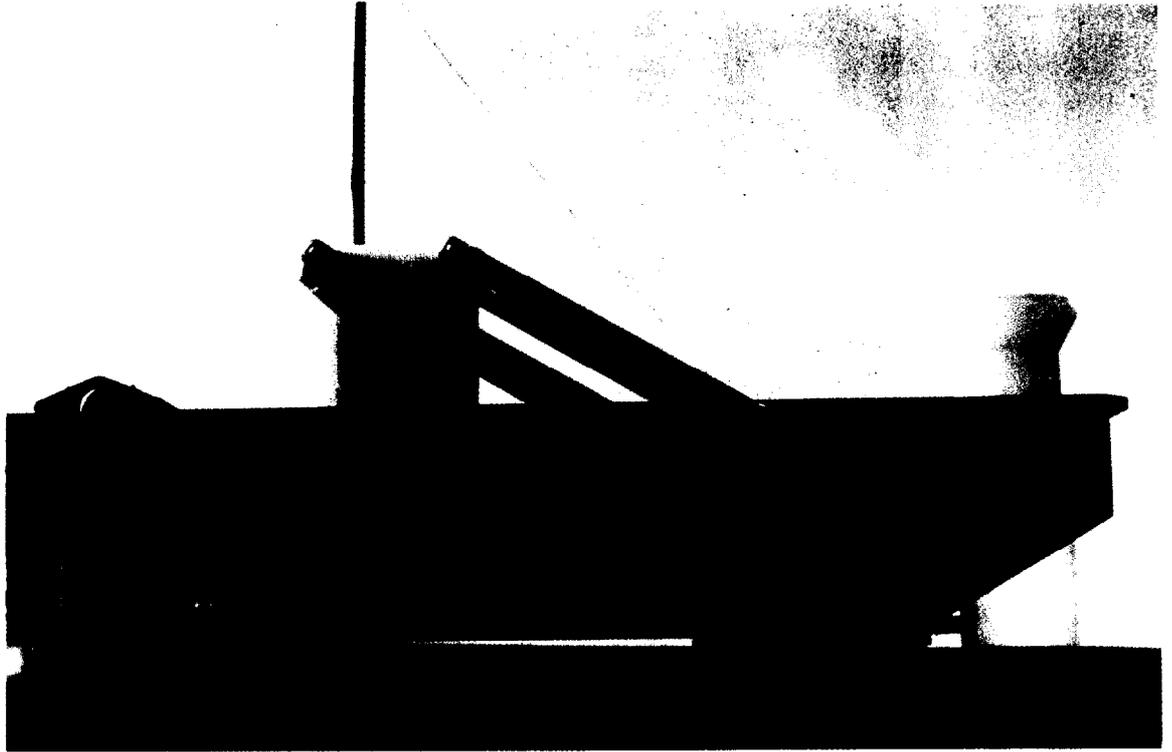
Collector code no. 18

bulk

1 week sampling*

Note: A collector of the type shown to the right were used.

* Daily sampling in December 1987.



Collector code no. 19

wet-only

1 week sampling



Collector code no. 20

wet-only

daily sampling

Figure 2. (continuation).



Collector code no. 60 bulk daily sampling
Note: Reference collector for precipitation amount

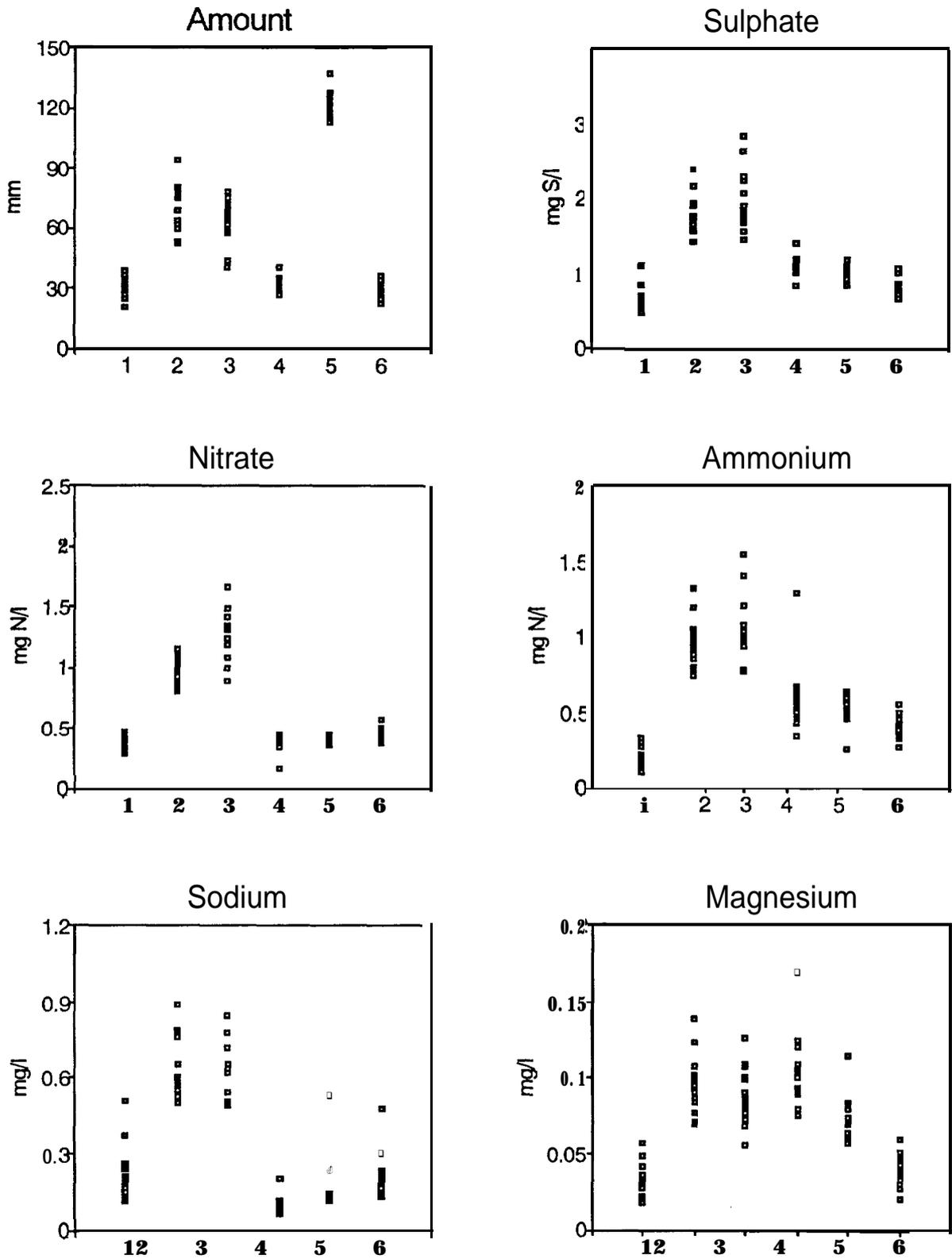


Figure 3. Monthly precipitation amount and weighted mean concentration for each month (actually four week period) from all collectors during the intercomparison. Numbers on X-axis indicates month number (1=Dec., 2=Jan., 3=Feb., 4=June, 5=July, 6=Aug.).

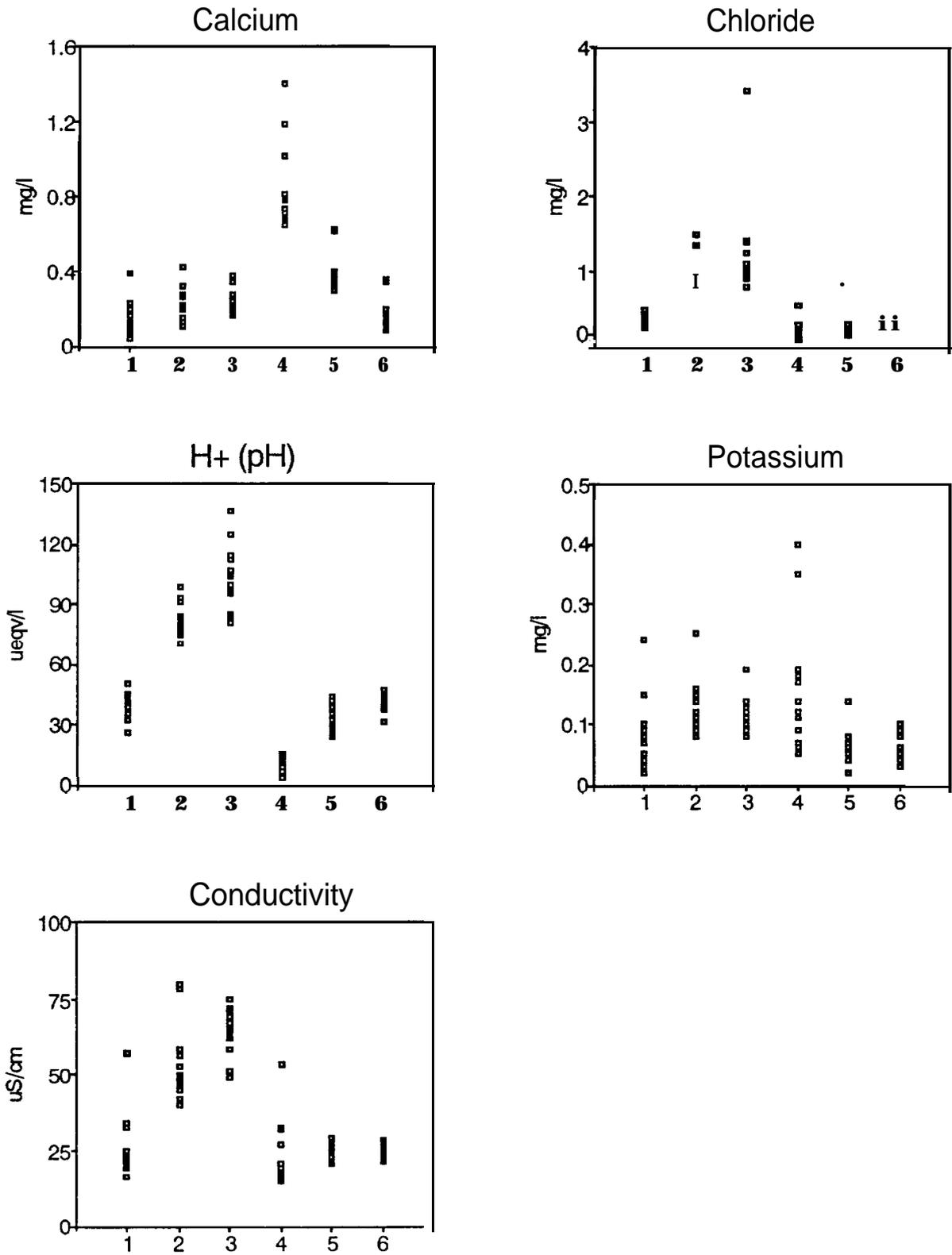


Figure 3. (continuation).

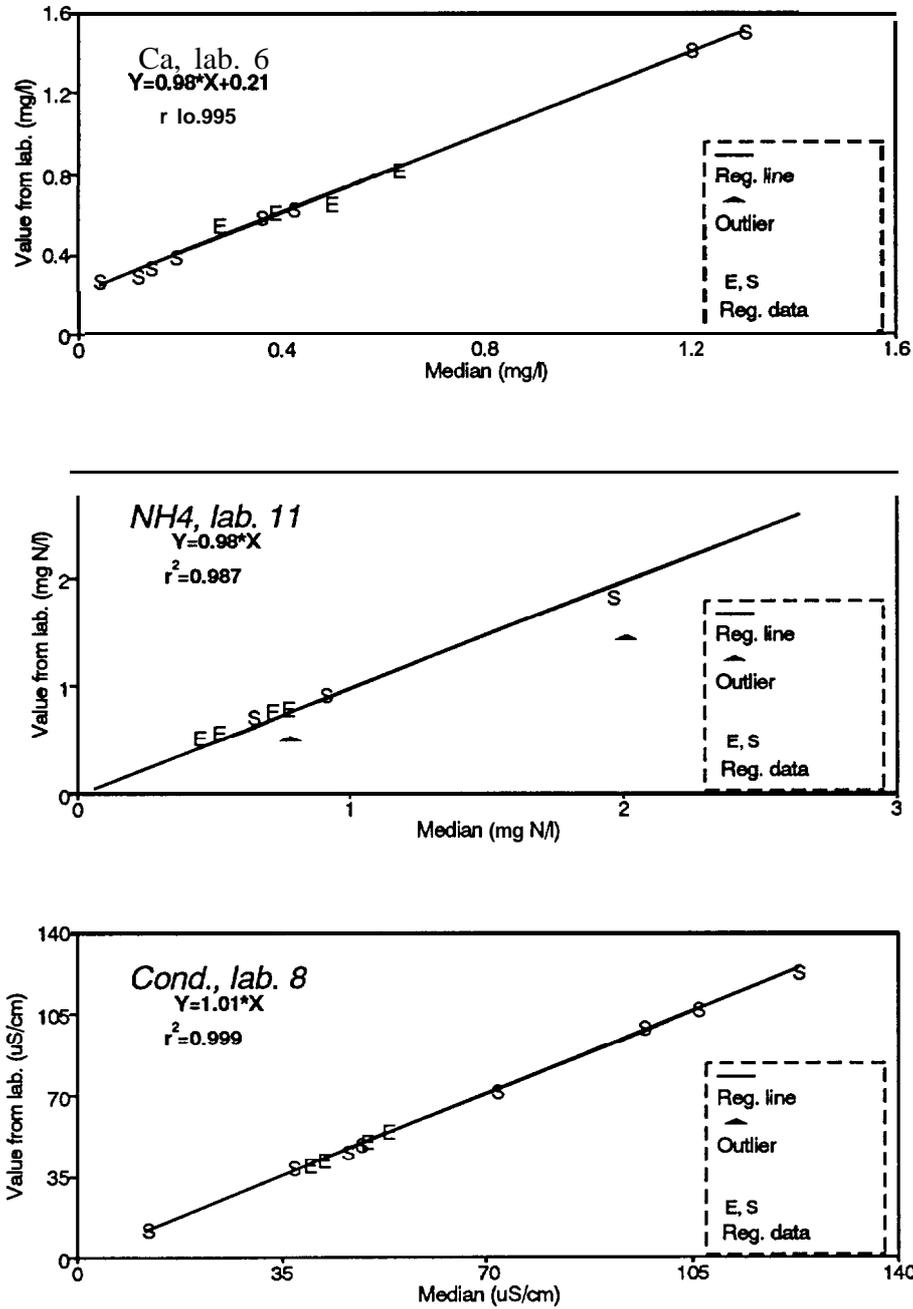


Figure 4. Example of a graphical presentation of regression analysis for EMEP (E) and split (S) samples of analysis from one laboratory vs median from **all** laboratories. More data in Table 4.

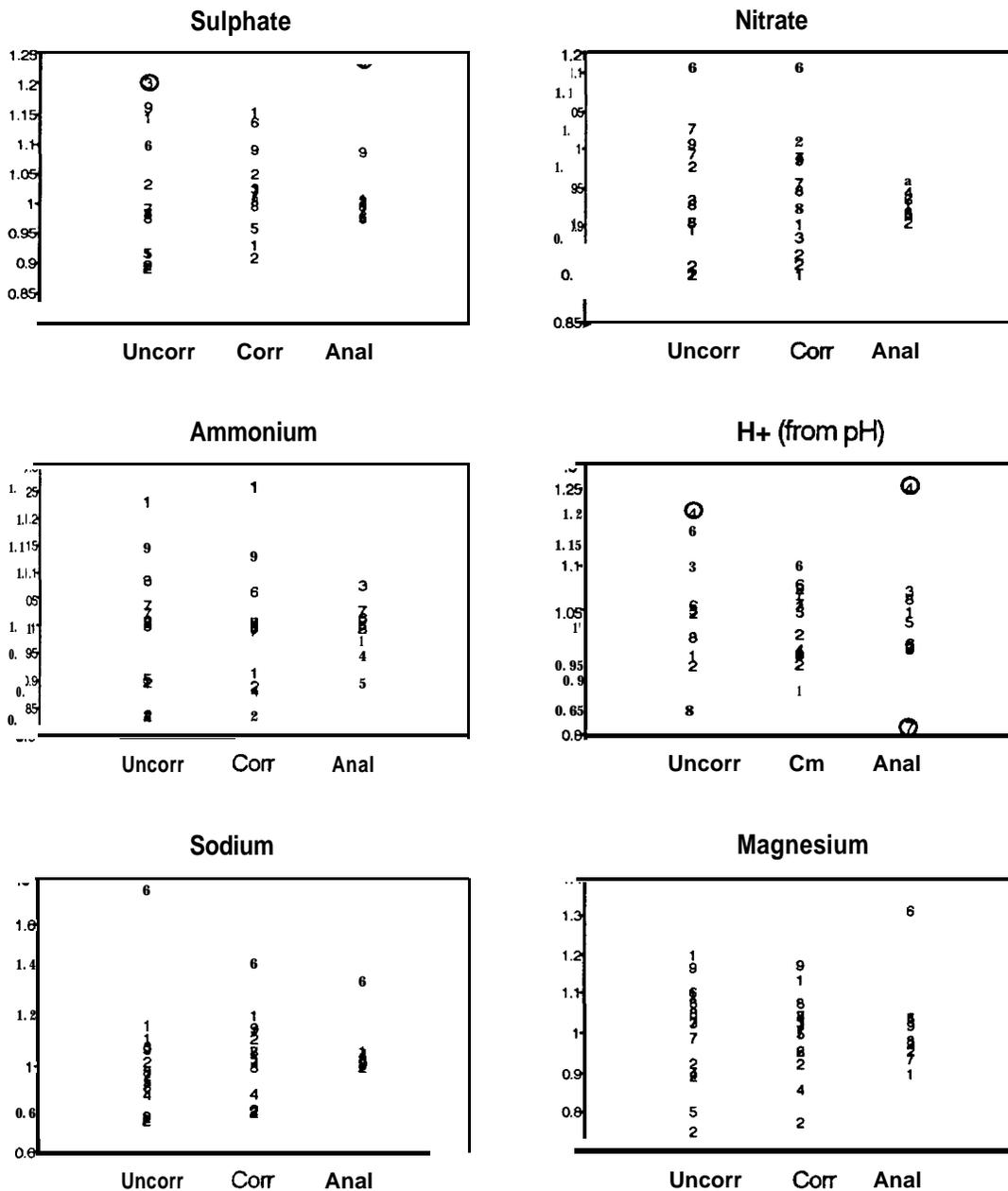


Figure 5. Influence of systematic analytical errors on volume weighted mean concentrations for the whole sampling period (winter + summer).

UNCORR is the volume weighted mean concentration (uncorrected for systematic analytical difference, see text and Table 4) for the whole intercomparison for a collector divided with the average of all uncorrected weighted mean concentrations.

CORR is calculated as UNCORR, but is based on corrected results.

ANAL is calculated as Y/X , where X is the average of all weighted corrected mean concentrations (all collectors, whole intercomparison) and Y is $kX+l$, where k and l are the regression coefficients given in Table 4.

The numbers given in the graphs are laboratory codes.

Encircled codes indicates a significant influence by systematic analytical errors.

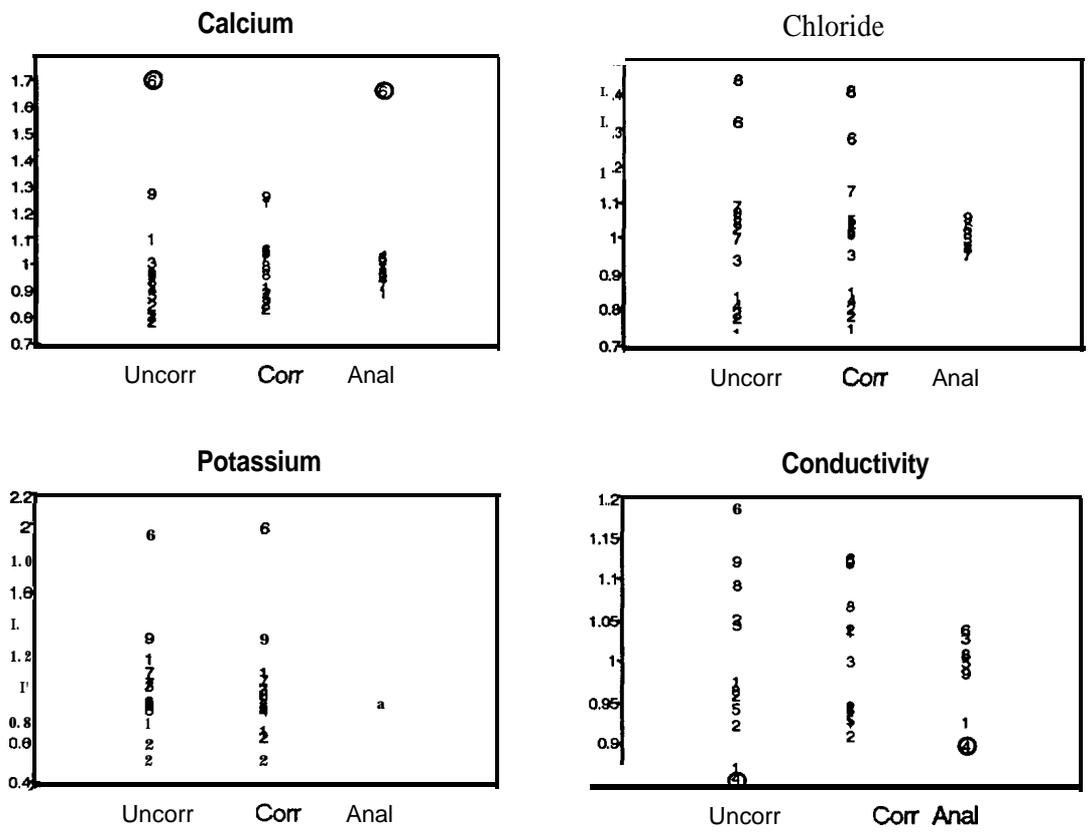


Figure 5. (continuation)

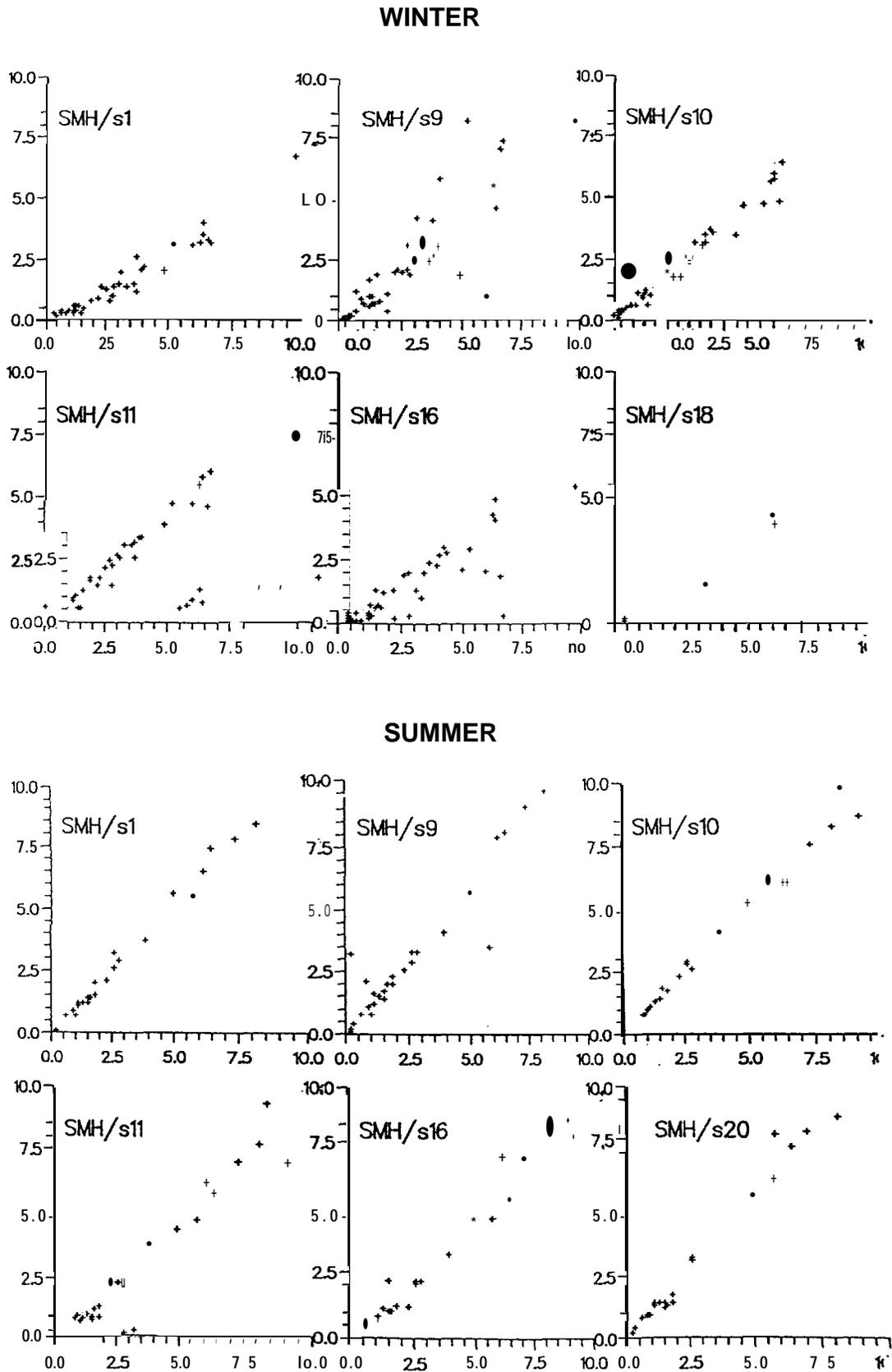


Figure 6. Comparison of daily precipitation amount from each collector (sXX) with amount from the reference (SMH) collector. Values in mm. Data from the reference collector on the x-axis. Note : Collector 18 used daily sampling only during December 1987.

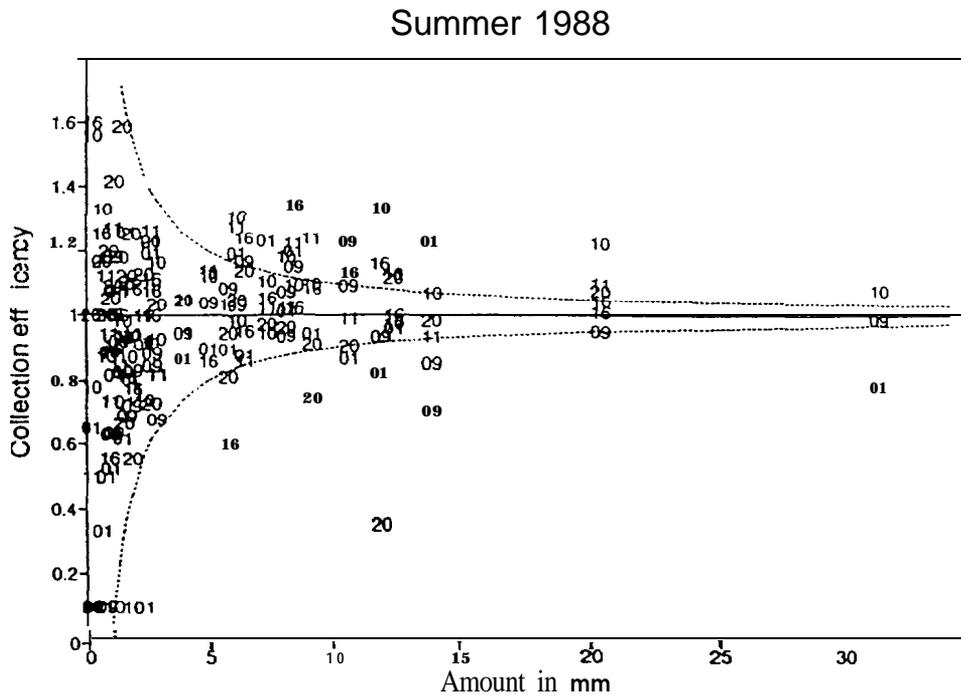
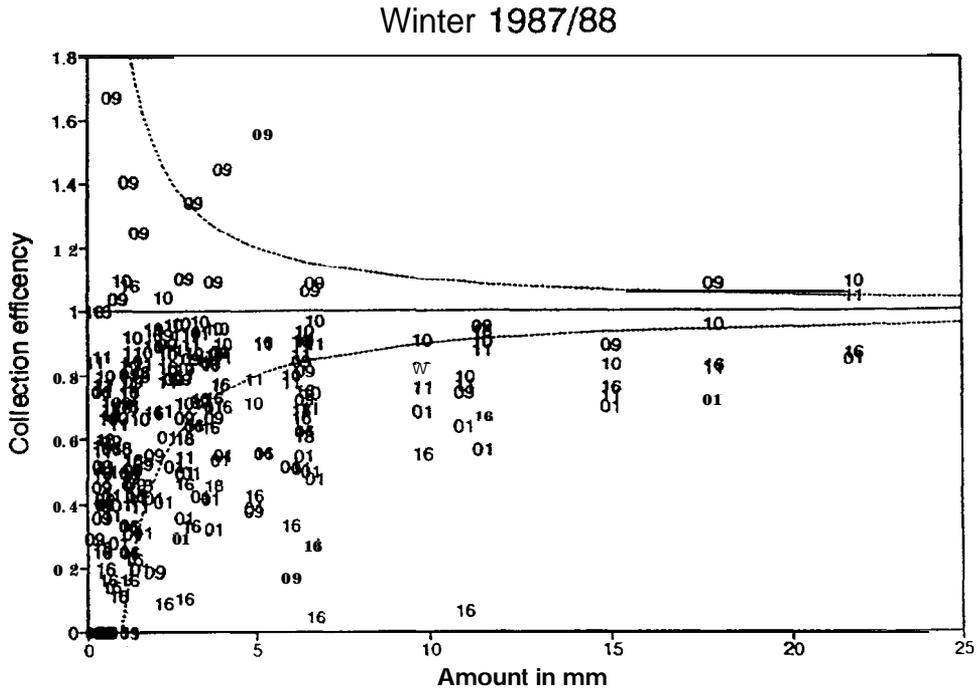


Figure 7. Collection efficiency for individual collectors versus precipitation amount (from reference gauge). Daily sampling during winter and summer. The numbers in the graphs are collector codes. The dotted lines indicates an absolute error of ± 1 mm.

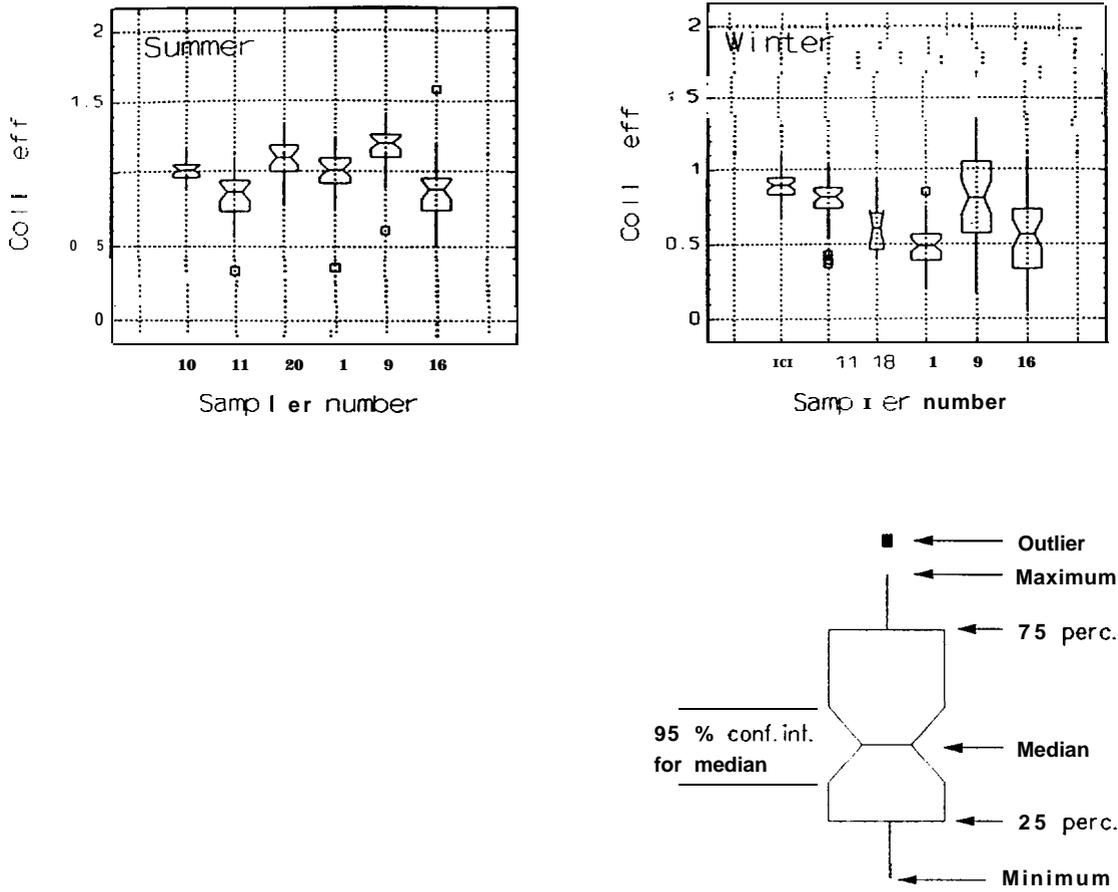


Figure 8. Notched Box and Whisker Plots for collection efficiency during daily sampling in summer and winter. An explanation of the plots is given in the separate figure. Note : Collectors 10, 11 and 18 are bulk collectors. Note : Ratios above 2 are not shown.

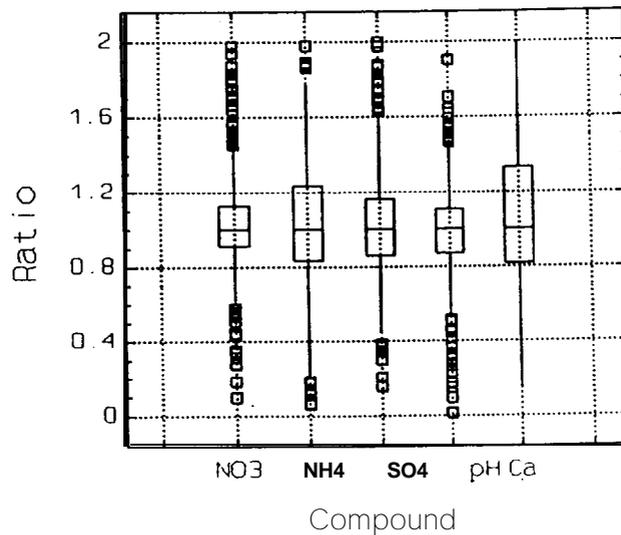


Figure 9. Box and Whisker Plots for ratios between the concentrations from all daily collectors and the daily median concentrations. Ratios above 2 are not shown. An explanation of the plots is given in Figure 8. (Note : No confidence interval, notch, for the median is given; the medians are always one in this case).

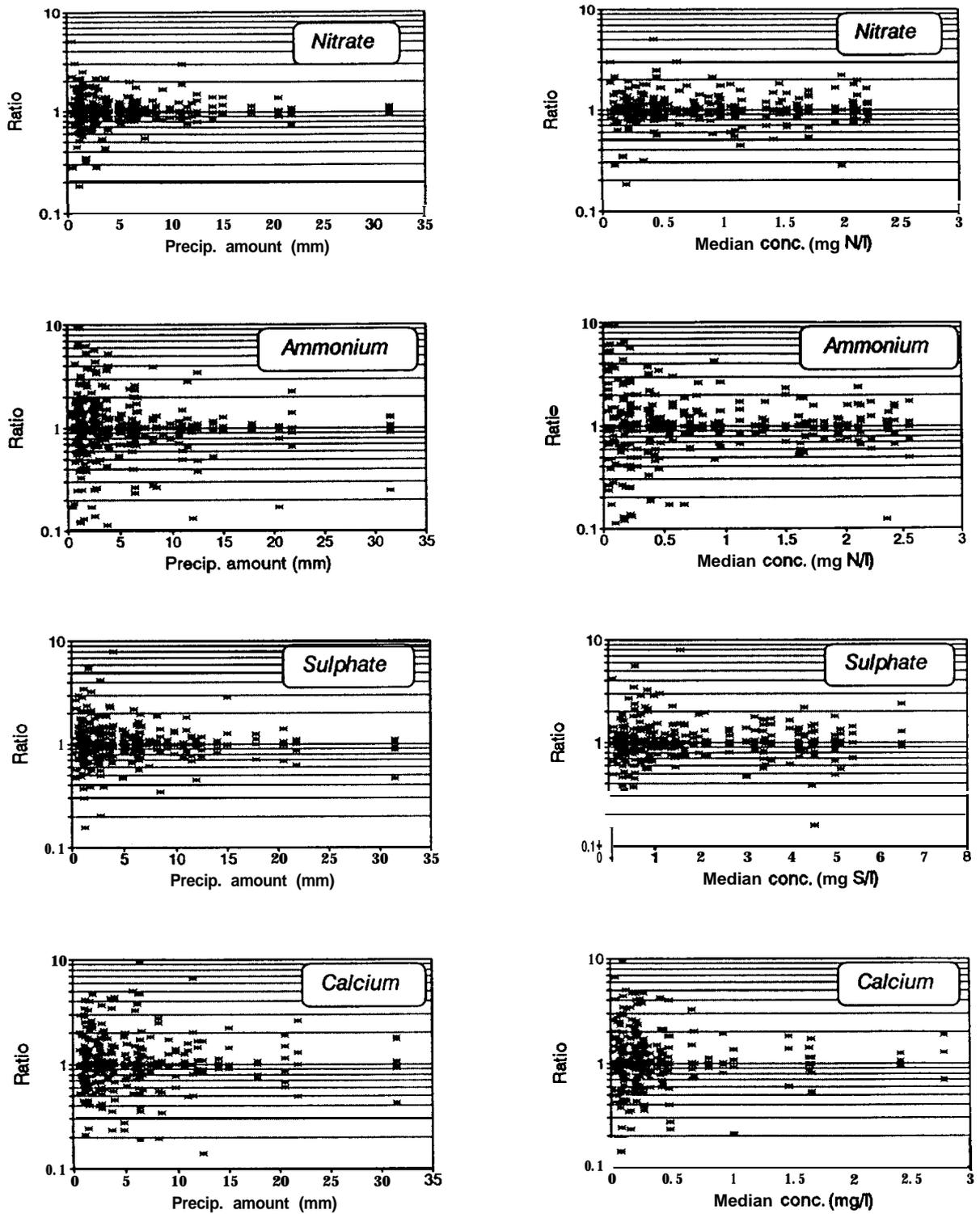


Figure 10. Ratios of daily concentrations from individual collectors and median from all collectors (during the day) as a function of precipitation amount (left column) and median concentration (right column). Based on all daily data (winter + summer).

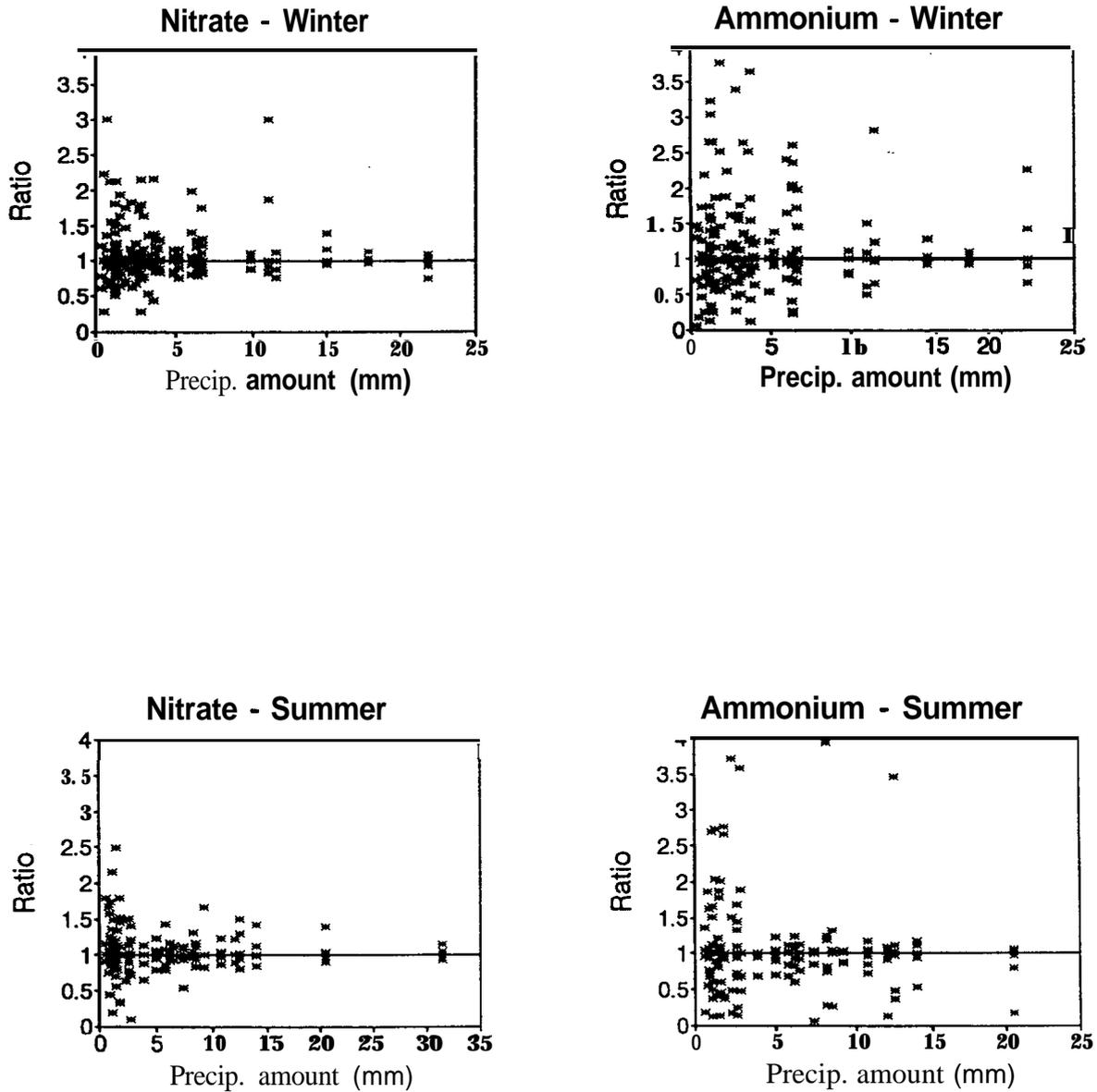


Figure 11. **Ratios** of daily concentration from individual collectors and median from all collectors (during the day) as a function of precipitation amount for NH_4 and NO_3 for winter and summer separately. (Compare Figure 10 which contained data for the whole year).

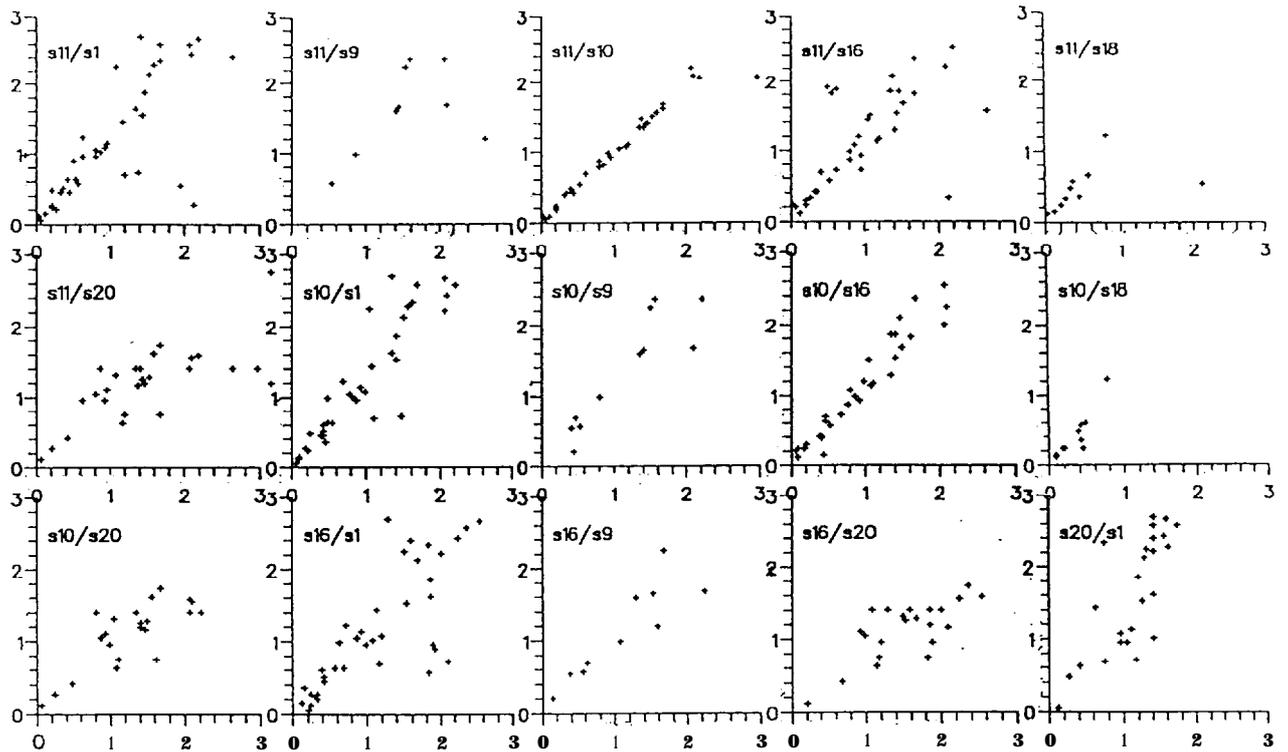
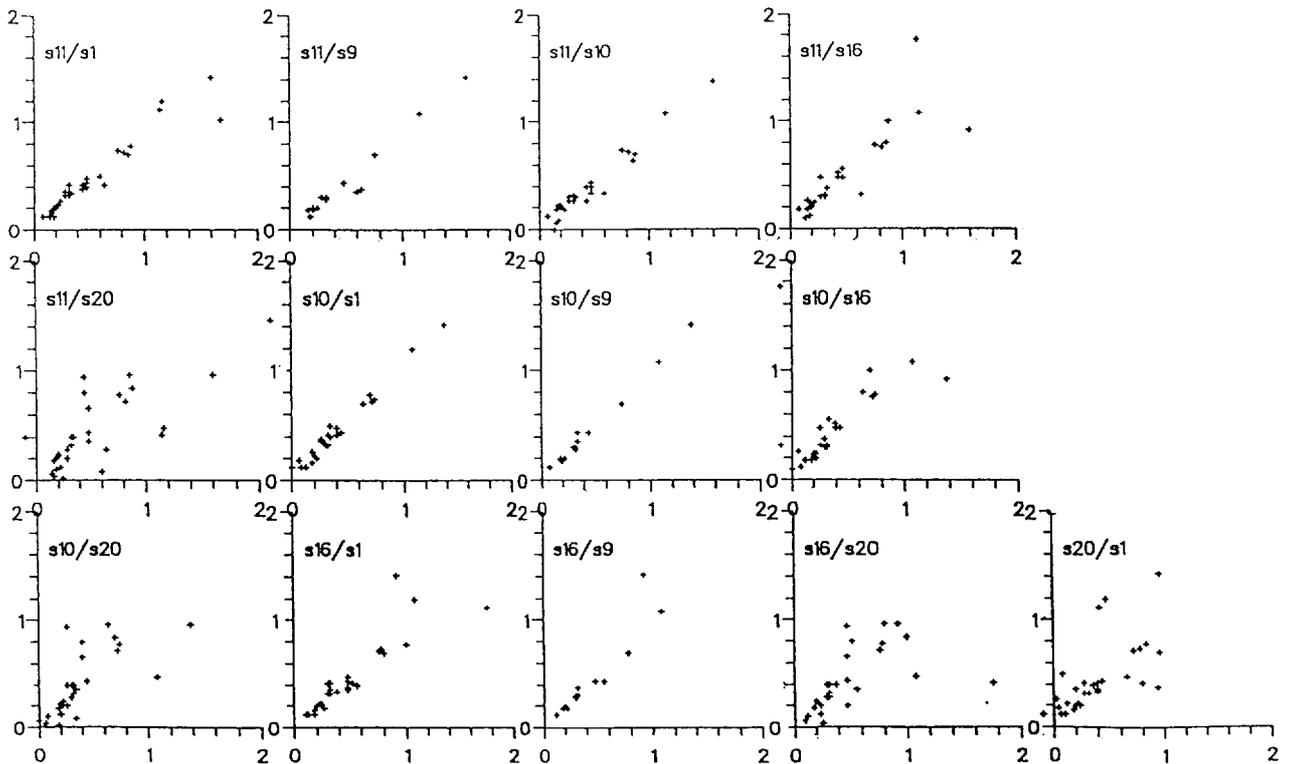
NO₃ - WINTERNO₃ - SUMMER

Figure 12 a. Comparison between concentration of NO₃ (mg NO₃-N/l) obtained from different collectors. Daily samples. Collector 10 (s10) and 11 (s11) are compared with all the others. Some other arbitrarily chosen comparisons are also shown. Collector codes are given in each graph with data from the first on the x-axis (collector 11 is on the x-axis in the first graph).

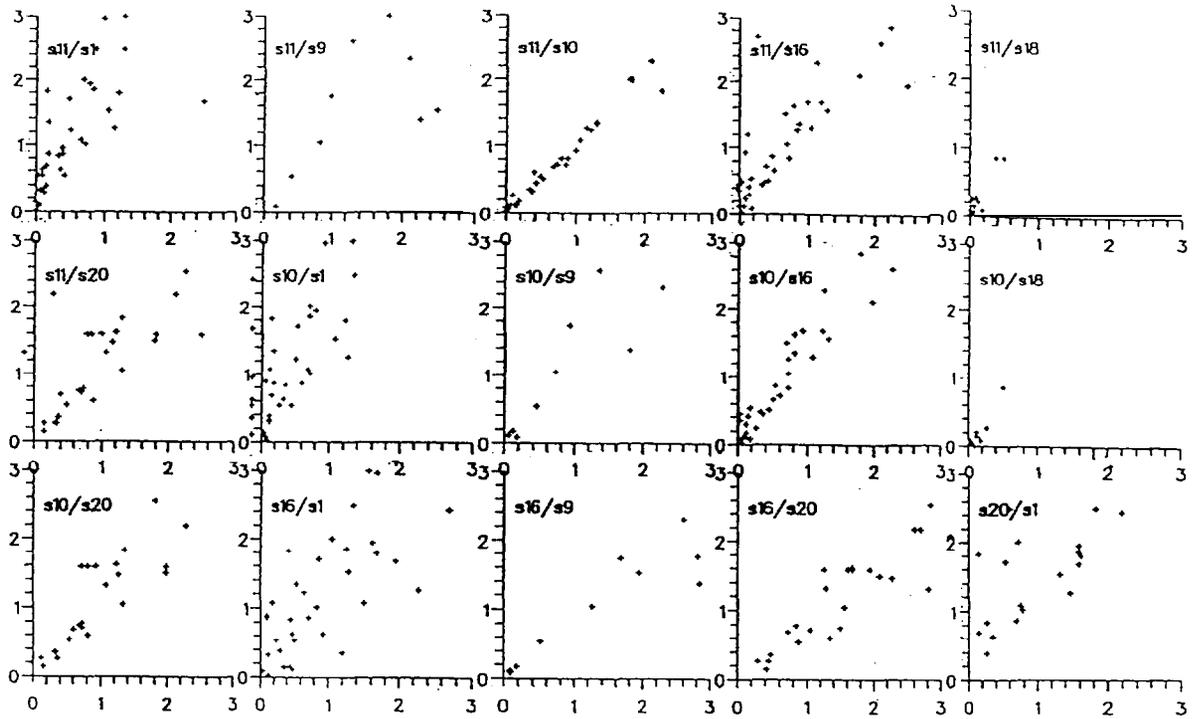
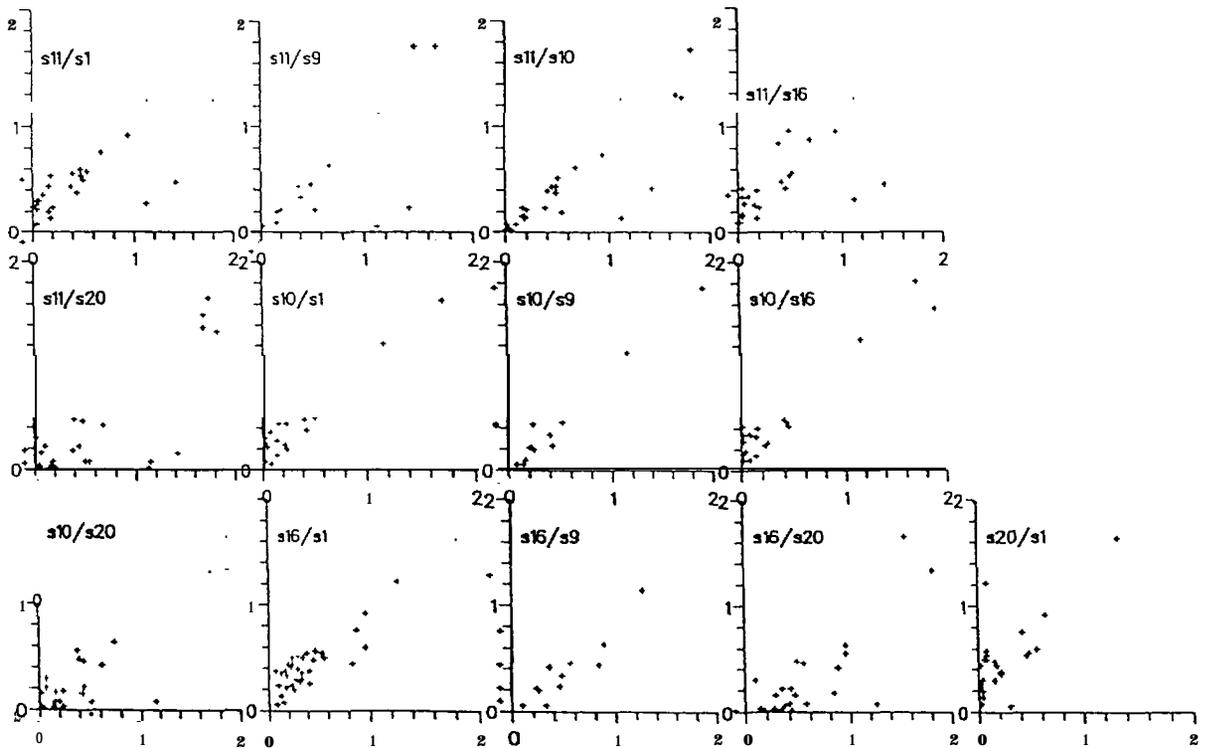
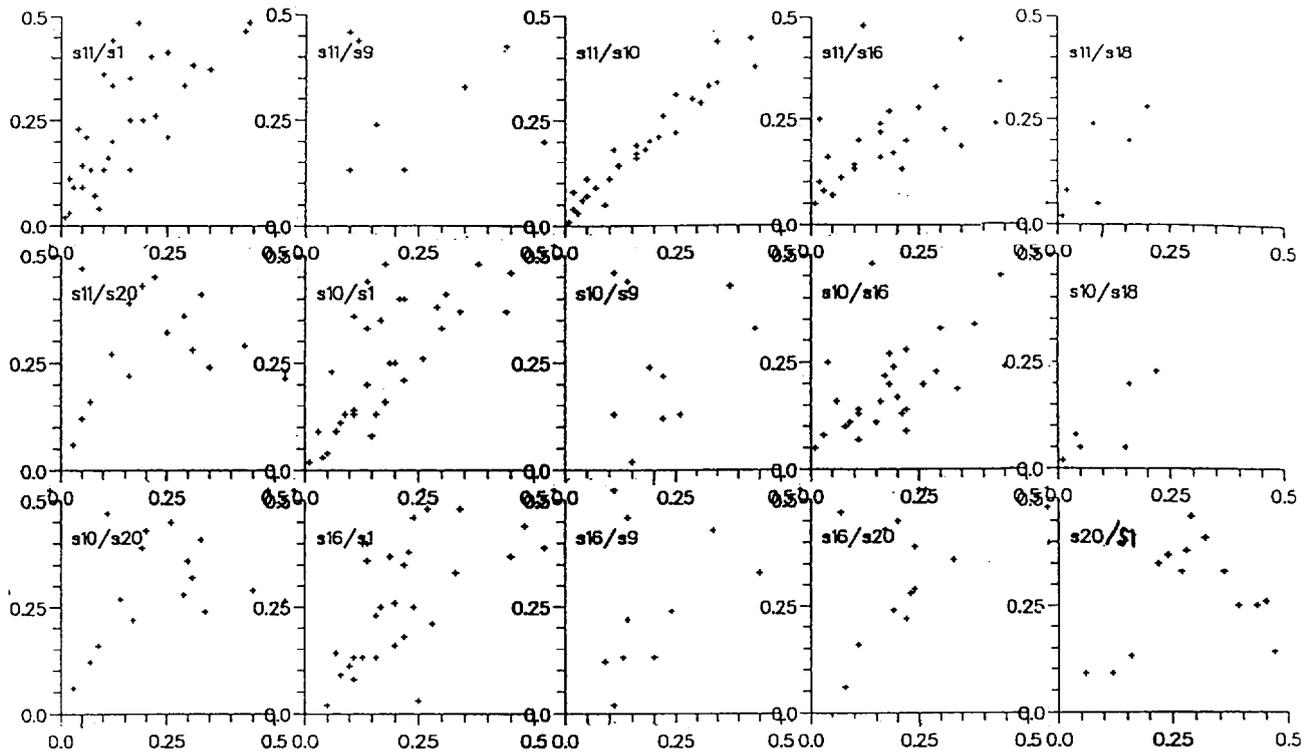
NH₄ - WINTERNH₄ - SUMMER

Figure 12 b. Comparison between concentration of NH₄ (mg NH₄-N/l) obtained from different collectors. Daily samples. Explanation, see Figure 12 a.

60
Ca - WINTER



Ca - SUMMER

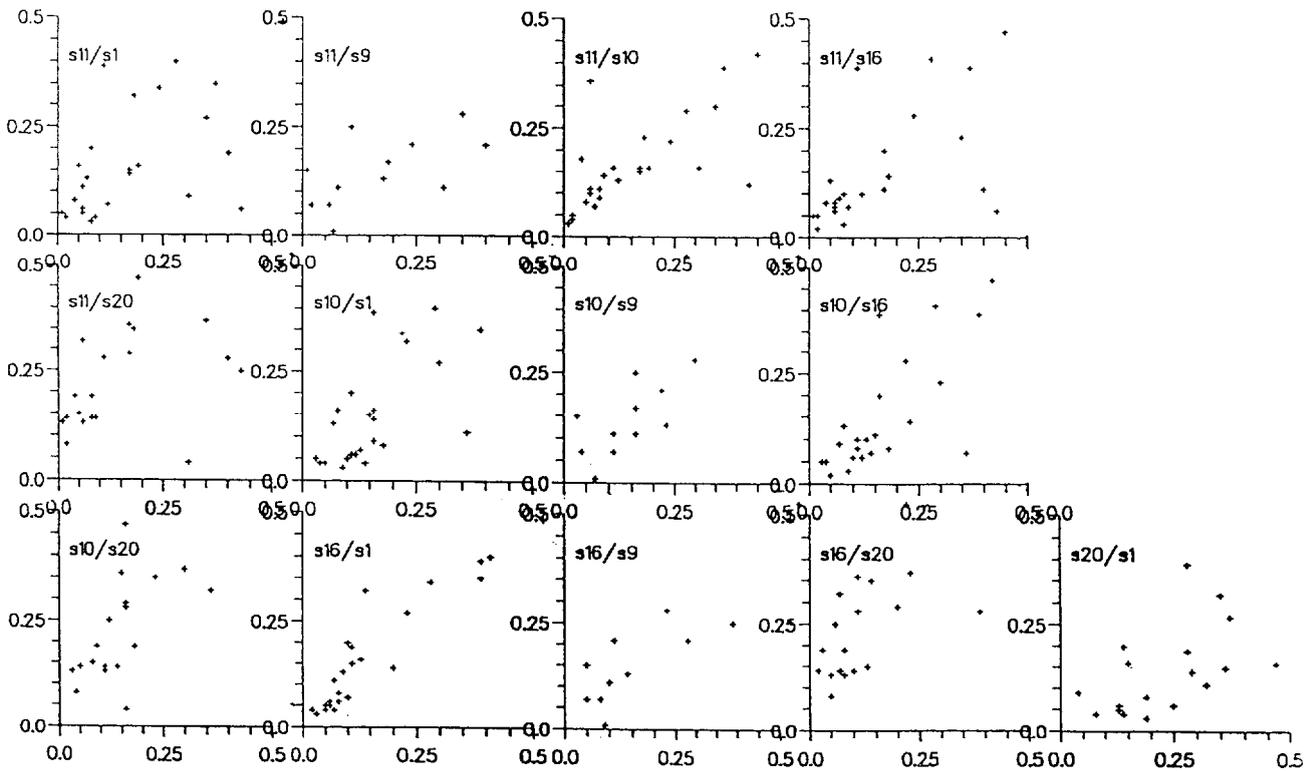


Figure 12 c. Comparison between concentration of Ca (mg Ca/l) obtained from different collectors. Daily samples. Explanation, see Figure 12 a.

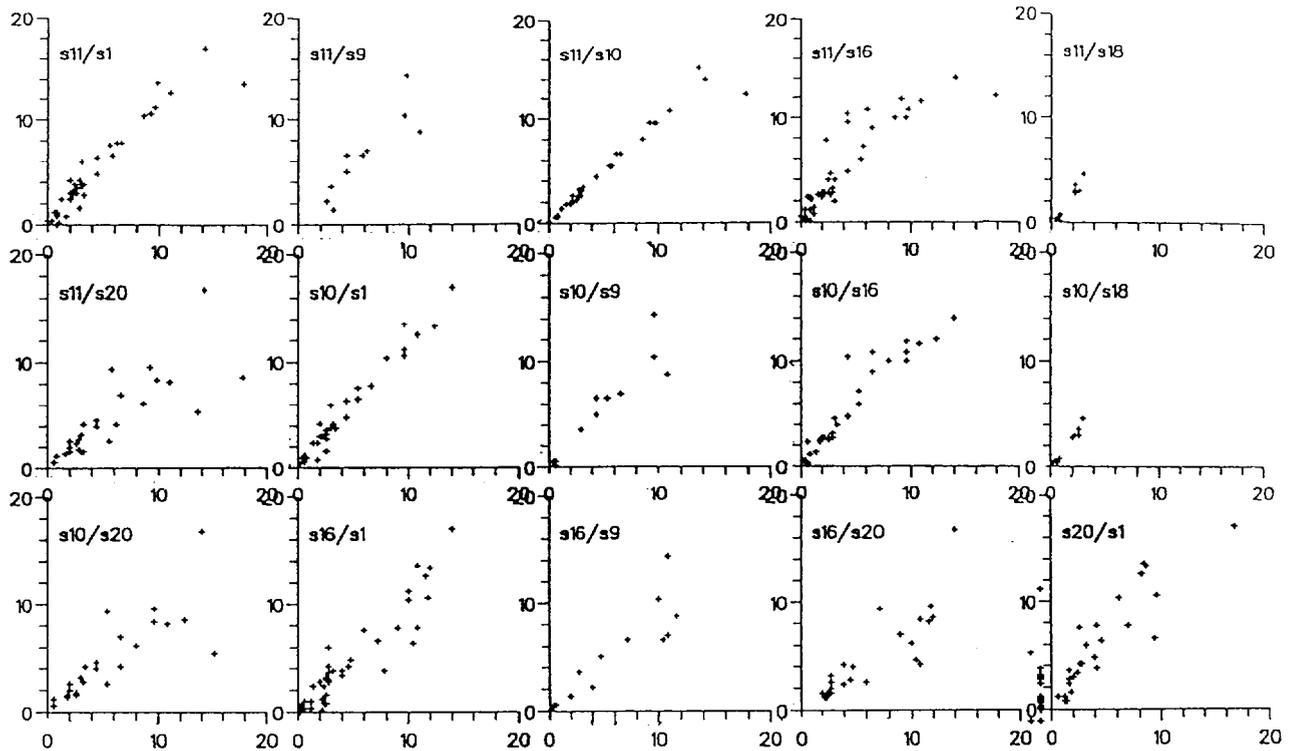
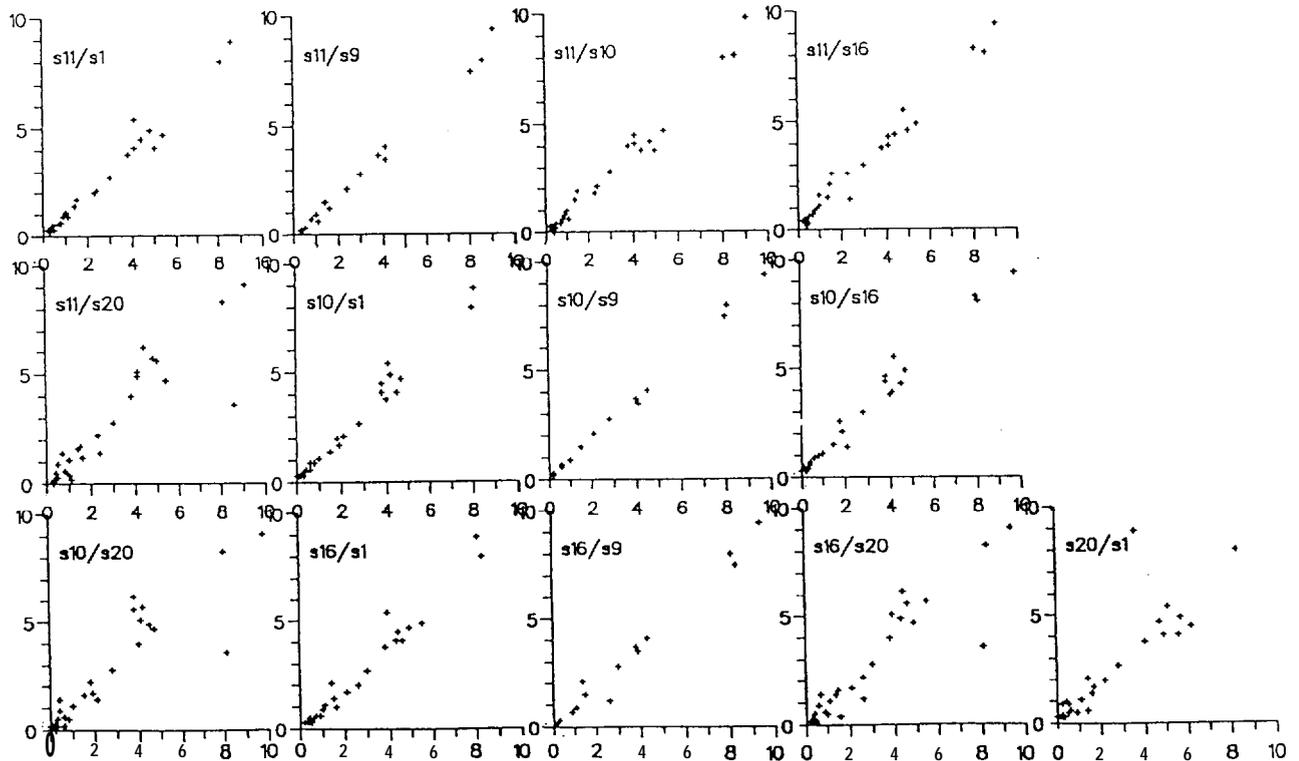
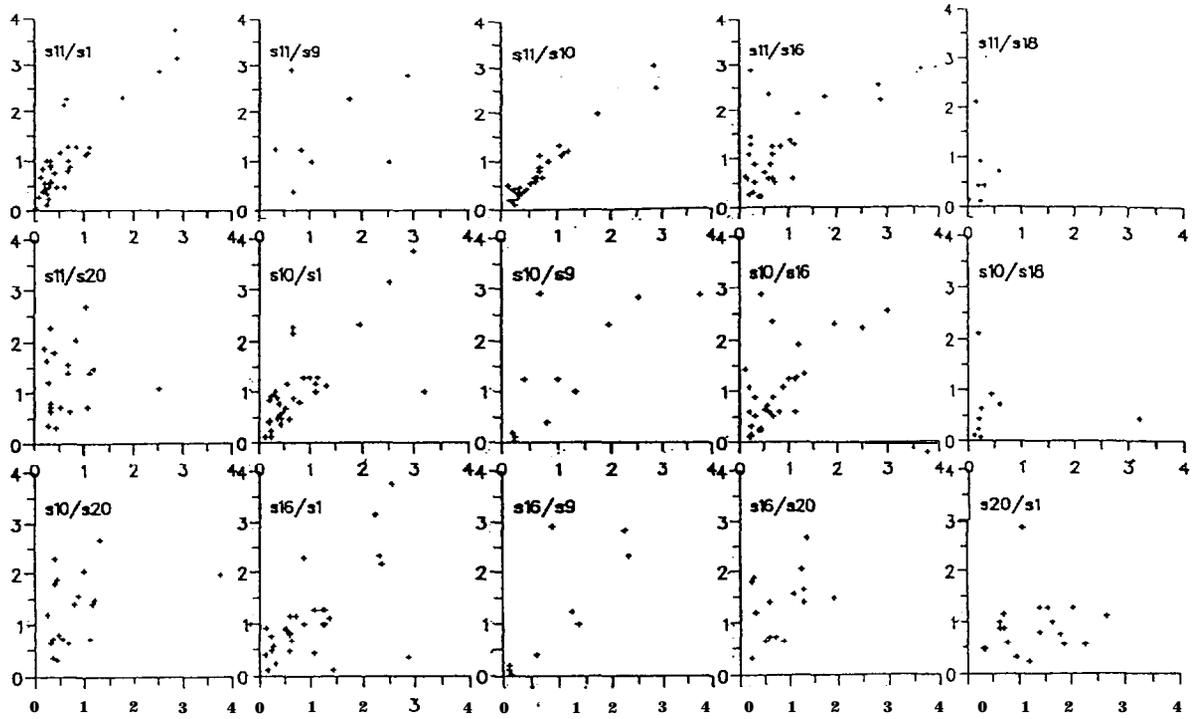
NO₃ - WINTERNO₃ - SUMMER

Figure 13 a. Comparison between deposition of NO₃ (mg NO₃-N/m²) obtained from different collectors. Daily samples. Collector 10 (s10) and 11 (s11) are compared with all the others. Some other arbitrarily chosen comparisons are also shown. Collector codes are given in each graph with data from the first on the x-axis (collector 11 is on the x-axis in the first graph). Precipitation amount from the reference collector is used when calculating the deposition values.

Ca - WINTER



Ca - SUMMER

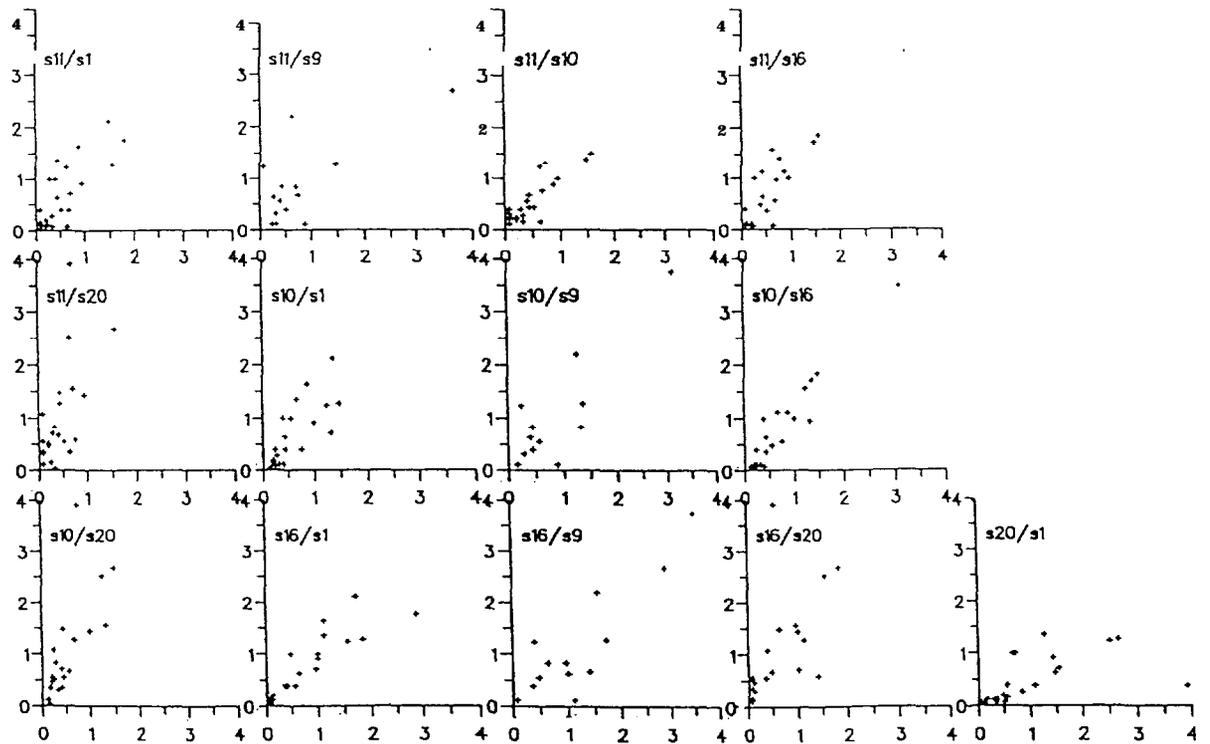


Figure 13 b. Comparison between deposition of Ca (mg Ca/m²) obtained from different collectors. Daily samoles. Explanation, see Figure 13 a.

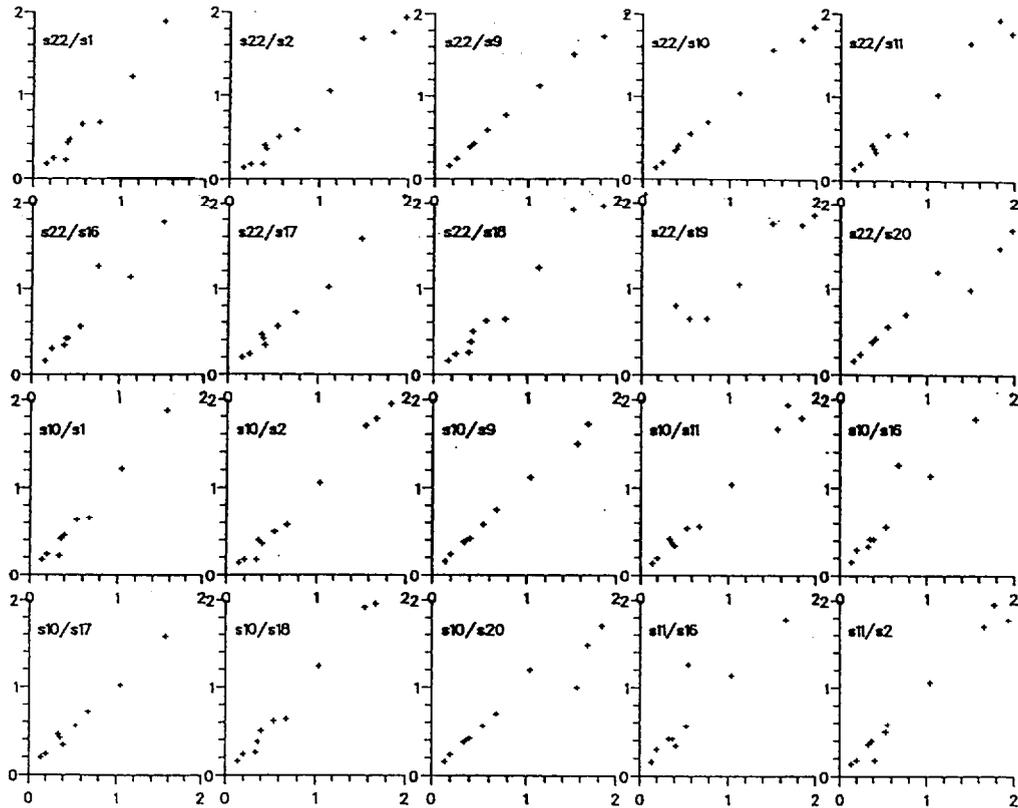
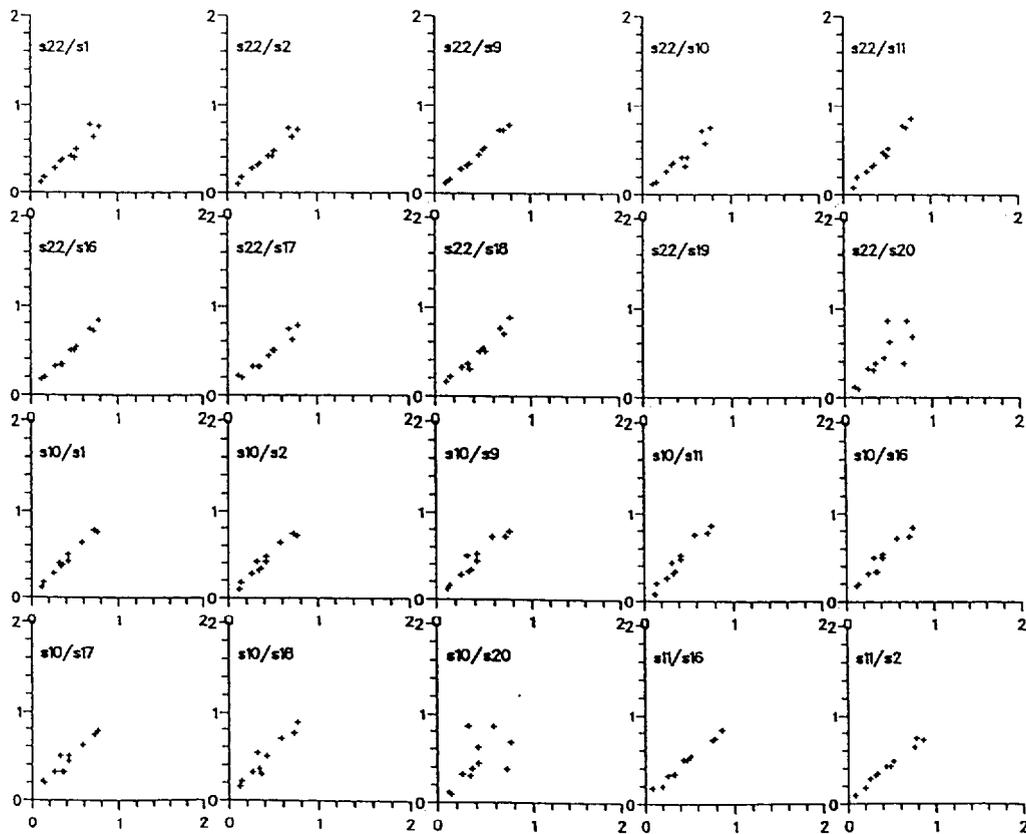
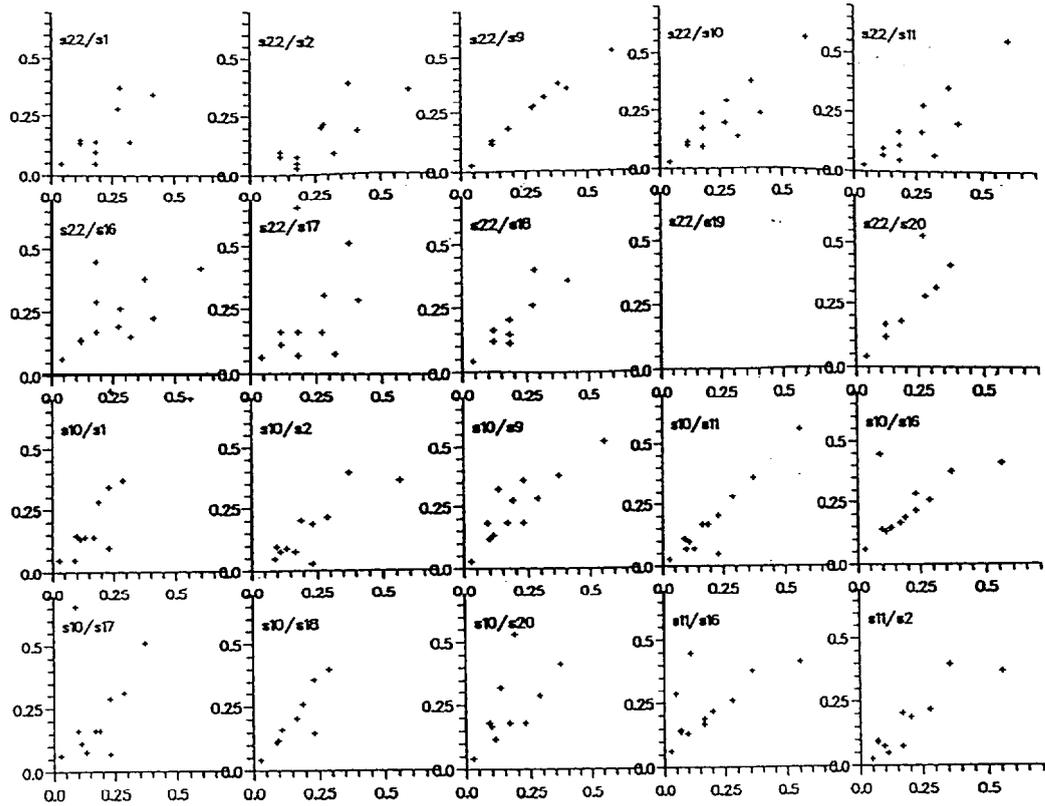
NO₃ - WINTERNO₃ - SUMMER

Figure 14 a. Comparison between concentration of NO₃ (mg NO₃-N/l) obtained from different collectors. Weekly samples either by collection or as calculated weighted means from daily collectors (own precipitation amount used). Data from individual collectors (sxx) are compared with the weekly mean (code s22) of all collectors. Some other arbitrarily chosen comparisons are also shown. Collector codes are given in each graph with data from the first on the x-axis (the weekly mean, s22, is on the x-axis in the first graph).

Ca - WINTER



Ca - SUMMER

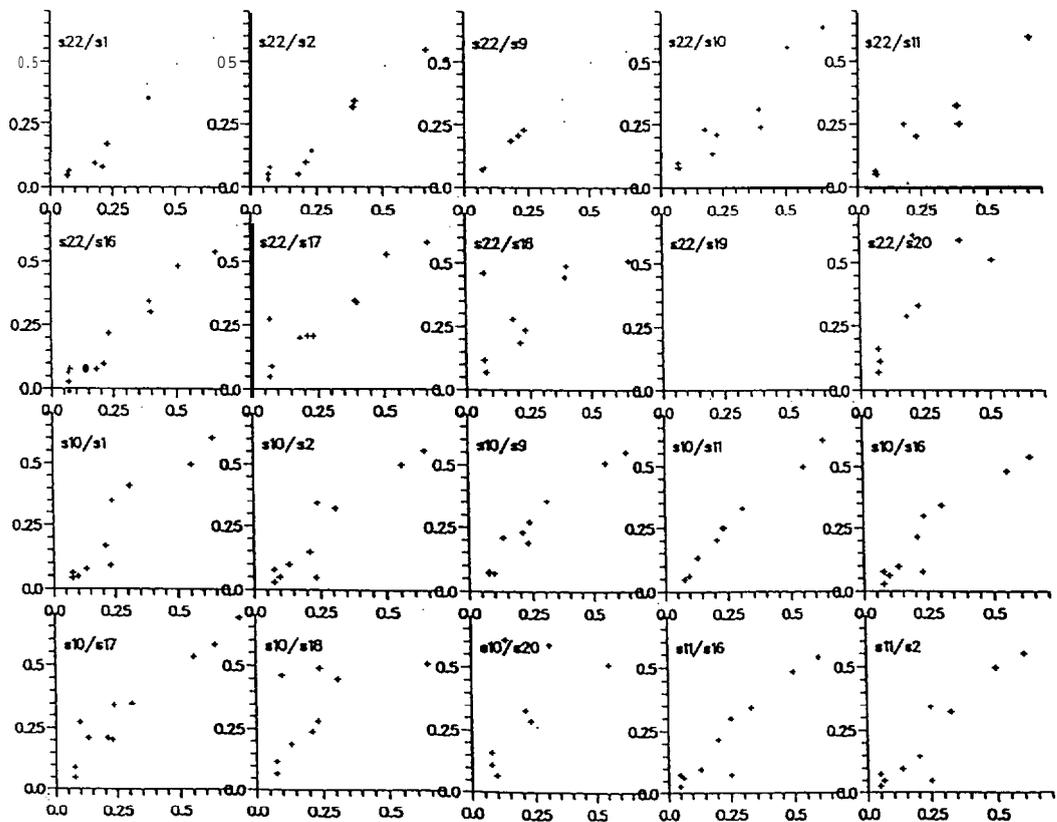


Figure 14 b. Comparison between concentration of Ca (mg Ca/l) obtained from different collectors. Weekly samples. Explanation, see Figure 14 a.

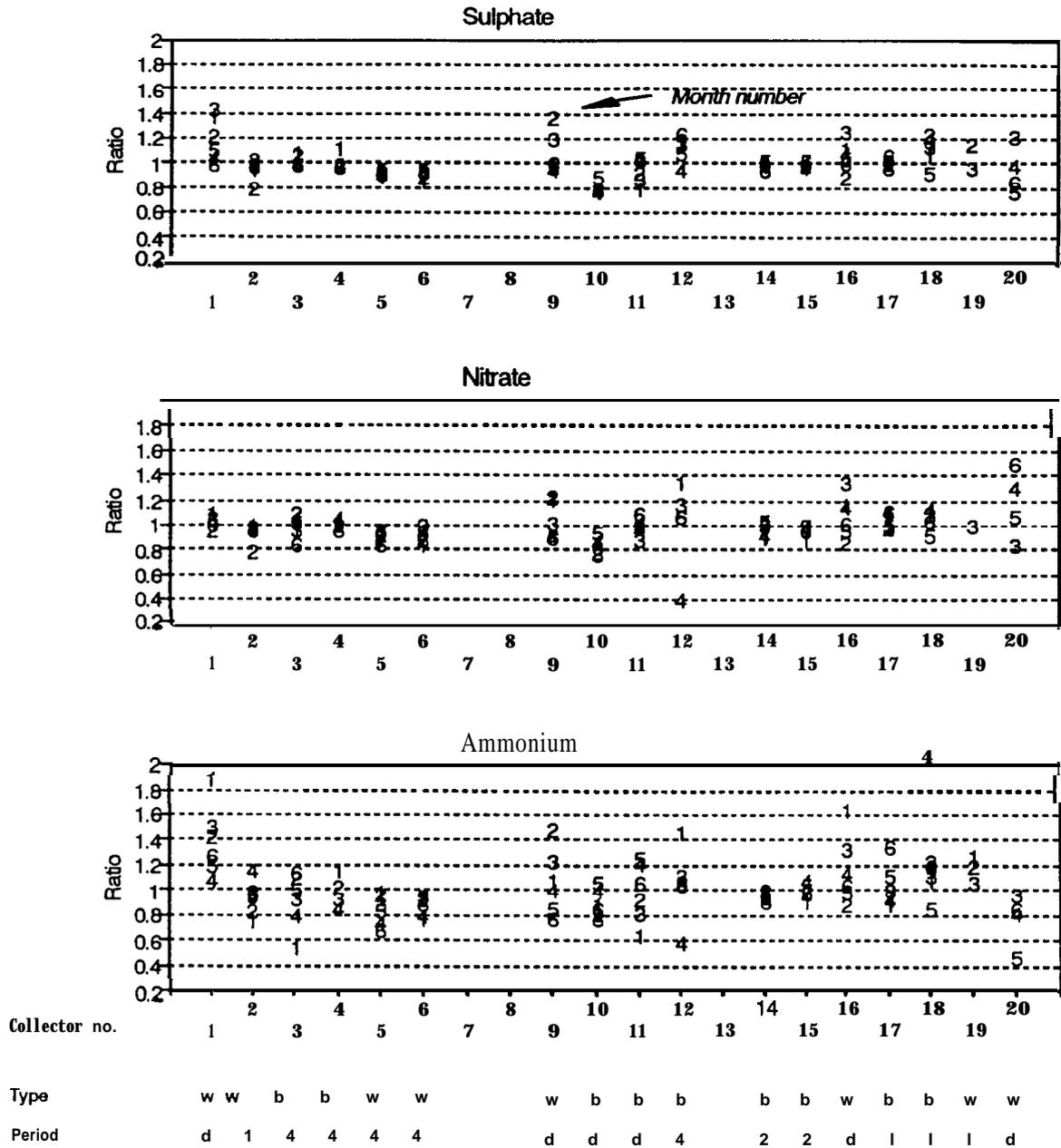


Figure 15. Overall relative performance of collectors during the intercomparison. Ratios - as 4 week weighted concentration from a collector divided with the median of all collectors for the same period - are given for six components. Numbers in the graph are months starting with **december** (Dec:1,Jan:2,Feb:3,Jun:4,Jul:5,Aug:6). Collector codes are given below the graph together with an indication of sampling period (**d**=daily;1,2 or 4 weeks) and wet-only (**w**) or bulk (**b**) collector.

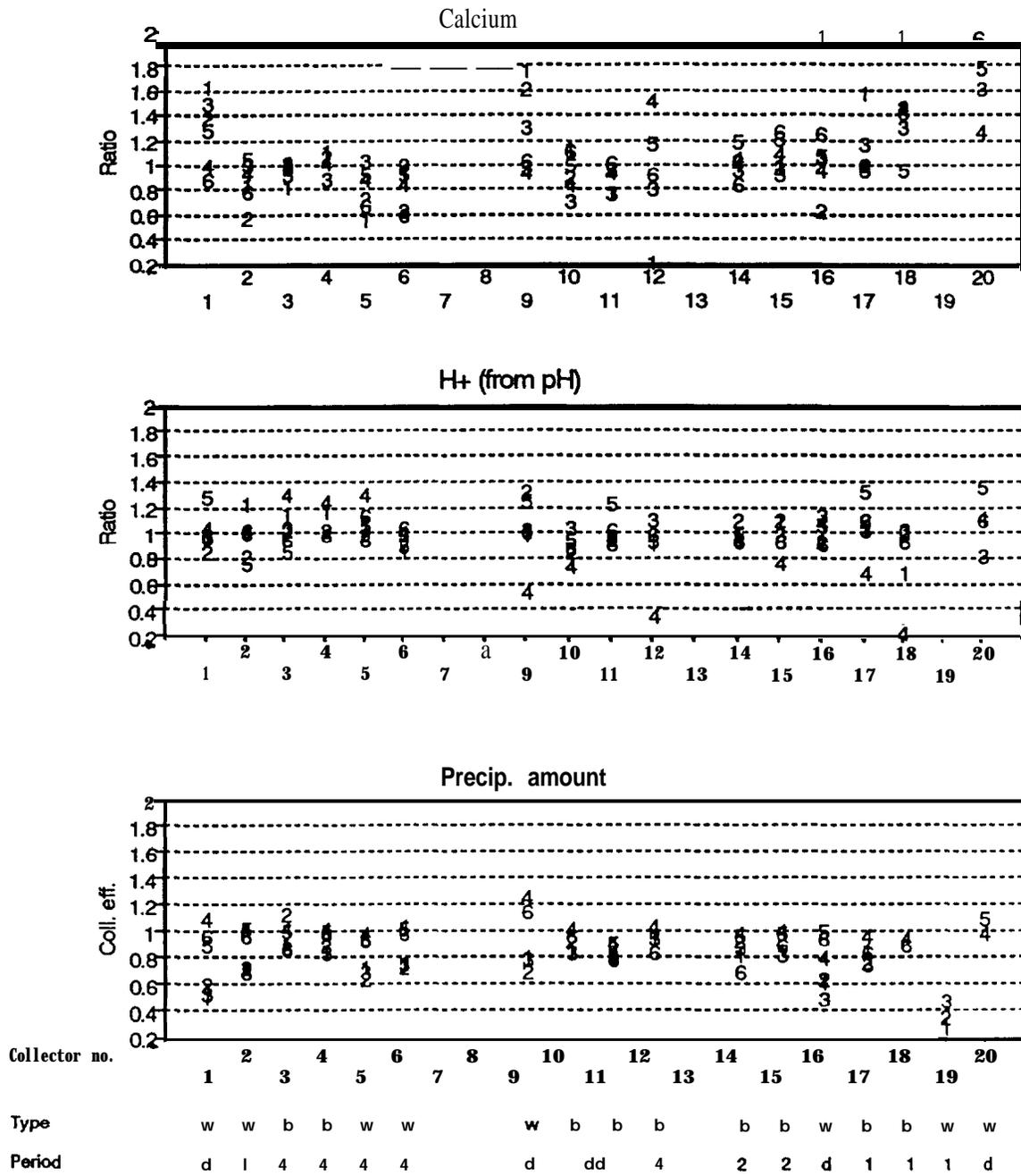


Figure 15 (continuation). Note that collection **efficiency**, see precipitation amount figure, is calculated as monthly amount collected by a sampler divided with the amount collected in the reference gauge.

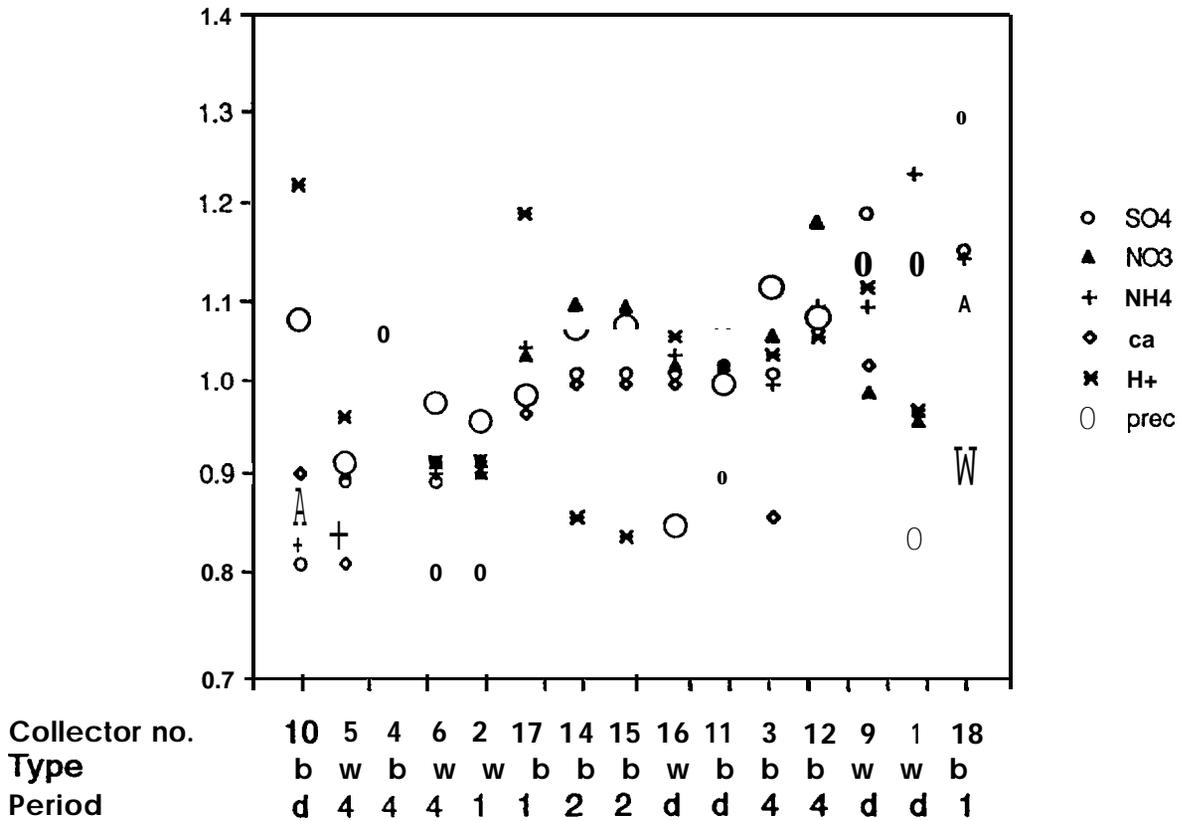


Figure 16. Relative performance of collectors with regard to precipitation amount and concentration of major components. Each symbol represents the ratio between the volume weighted mean concentration for six months and the mean value from all collectors for the same period. The collectors are arranged according to increasing concentration of the major components. Results are not corrected for systematic analytical errors. An indication of sampling period (d=daily; 1, 2 or 4 weeks) and wet-only (w) or bulk (b) collector is given below the graph.

Appendix 1.

Participating laboratories and contact persons.

Denmark

National Environmental Research Institute
Fredriksborgsvej 399
DK-4000 Roskilde
Mads Hovmand

United Kingdom

Warren Spring Laboratory
Gunnels Wood Road
Stevenage
Hertfordshire **SG1 2BX**
Myk Devenish

Germany

GKSS-Research Centre
Max-Planck Strasse
D-2054 Geesthacht
Bernd Schneider

Umweltbundesamt
Pilotstation Frankfurt
Frankfurter Strasse 135
D-6050 Offenbach [#]
Elke Bieber

Institut für Energetik
Umweltzentrum
Torgauer Strasse 114
7024 Leipzig
W. Marquardt

Finland

Finnish Meteorological Institute
Air Quality Department
Sahaajankatu 22E
SF 00810 Helsinki
Anni Reissell

National Board of Waters and the Environment
Research Laboratory
P.O.Box. 250
SF 00101 Helsinki
Olli Järvinen

Norway

Norwegian Institute for Air Research
P.O.Box. 64
N-2001 Lillestrøm
Jan-Erik Hanssen

Sweden

Swedish Environmental Research Institute
Box 47086
S-402 58 Göteborg
Karin Sjöberg

Swedish Environmental Protection Agency
Air Research Division
S-611 82 Nyköping
Hans Areskoug

Stockholm University
Department of Meteorology
S-106 91 Stockholm
Lennart Granat

[#] The German Democratic Republic until the German unification by 3 October 1990

Appendix 2.

Brief outline of analytical methods used during the intercomparison.

Lab. code	Constituent and method code								
	pH	SO4	NO3	NH4	Cl	Mg	Na	Ca	K
1	A	B	B	D	B	A	D	A	D
2	A	B	B	D	B	A	A	A	A
3	A	B	B	D	B	A	A	A	A
4	A	B	B	C	B	A	D	A	A
5	A	B	B	A	B	A	A	A	A
6	A	A	A	A	A	A	A	A	A
7	B	B	B	C	B	A	A	A	D
8	A+C	B	B	B	B	E	B	E	B
9	A	B	B	D	B	A	A	A	A
10	-	B	B	B	-	-	-	-	-
11	A	C	C	A	A	A	D	A	D

Method codes

pH	A Electrode, calibrated with buffers
	B Electrode: slight increase of ionic strength of sample
	C Electrode, calibrated with weak acid solutions
SO4	A Thorin
	B Ion chromatography (IC)
	C Nephelometry
NO3	A Griess after Cd-reduction
	B IC
	C Hydrazine reduction

NH4	A Indophenol
	B IC
	C Indophenol automatic
	D Flow Injection Analysis (FIA) Gas diffusion
Cl	A Mercury thiocyanate-iron
	B IC
Mg	A Atomic absorption (AAS)
Na	B IC
Ca	C Plasma emission spectrometry - ICP
K	D Atomic Emission (AES)
	E Plasma emission spectrometry - DCP

APPENDIX 3

Results

Table 3-1. Results from daily collectors.

A = Code for laboratory, B = Code for collector

A	B	Start	Stop	mm	pH	SO ₄ -S mgS/l	NO ₃ -N mgN/l	NH ₄ -N mgN/l	Na mg/l	Mg mg/l	Ca mg/l	Cl mg/l	H ⁺ μeq/l	K ⁺ mg/l	Cond μS/cm
1	1	11-28	11-29	3.2	4.09	1.67	0.51	0.54	0.46	0.045	0.16	0.30		0.24	42.7
3	9	11-28	11-29	5.3											
4	10	11-28	11-29	5.7	4.28	0.94	0.41	0.28	0.13	0.022	0.18	0.36		0.18	23.6
5	11	11-28	11-29	5.4	4.27	0.81	0.35	0.10	0.08	0.020	0.11	0.22	81	0.02	27.8
8	16	11-28	11-29	4.2	4.25	1.07	0.42	0.25	0.12	0.059	0.20	0.25		0.06	32.0
9	18	11-28	11-29	4.3	4.37	1.30	0.56	0.28	0.13	0.040	0.87	0.29		0.04	282.0
1	60	11-28	11-29	6.3											
1	1	11-29	11-30	4.0	4.24	0.36	0.45	0.04	0.32	0.035	0.11	0.05		0.72	24.8
3	9	11-29	11-30	5.2											
4	10	11-29	11-30	5.8	4.44	0.28	0.40	0.08	0.10	0.004	0.08	0.25		0.18	13.8
5	11	11-29	11-30	5.8	4.50	0.22	0.34	0.01	0.01	0.010	0.02	0.10	50	0.02	15.5
8	16	11-29	11-30	4.0	4.41	0.32	0.43	0.11	0.04	0.026	0.10	0.05		0.04	20.0
9	18	11-29	11-30	3.9	5.22	0.40	0.48	0.01	0.02	0.020	1.00	0.07		0.01	9.4
1	60	11-29	11-30	6.4											
3	9	11-30	12-01	0.1											
4	10	11-30	12-01	0.2											
5	11	11-30	12-01	0.2		0.26	0.02					1.11			12.4
1	60	11-30	12-01	0.2											
1	1	12-06	12-07	0.4	4.33	1.09	0.58	0.96	0.39	0.018	0.07	0.30		0.21	28.2
3	9	12-06	12-07	0.4											
4	10	12-06	12-07	0.5	4.29										29.9
5	11	12-06	12-07	0.5	4.19	1.12	0.58	0.38		0.050	0.08	0.80	99		39.1
8	16	12-06	12-07	0.1	5.00	3.34	1.84	3.92	0.68			1.18		0.31	18.0
9	18	12-06	12-07	0.5	4.52	1.14	0.67	0.86	0.24	0.040	0.24	0.44		0.05	24.8
1	60	12-06	12-07	0.7											
1	1	12-08	12-09	1.4	5.23	0.10	0.11	0.14	0.19	0.016	0.04	0.20		0.08	5.2
3	9	12-08	12-09	1.9											
4	10	12-08	12-09	2.0	5.14	0.05	0.09	0.04	0.01	0.006	0.05	0.05		0.03	3.2
5	11	12-08	12-09	1.5	5.33	0.02	0.03	0.01	0.13	0.010	0.09	0.30	8	0.20	3.7
8	16	12-08	12-09	1.3	5.81	0.42	0.23	0.44	0.26	0.051	0.51	0.44		0.06	11.0
9	18	12-08	12-09	1.7	5.15	0.12	0.12	0.02	0.06	0.010	0.05	0.13		0.02	3.8
1	60	12-08	12-09	2.8											
1	1	12-09	12-10	0.3	5.60	0.51	0.26	0.55	0.38	0.028	0.08	0.69		0.25	15.3
3	9	12-09	12-10	0.2											
4	10	12-09	12-10	0.2											
5	11	12-09	12-10	0.3	4.76	0.20	2.13	0.02				0.48	25		10.3
8	16	12-09	12-10	0.3	5.05	0.37	0.33	0.50	0.20			0.24		0.05	12.0
9	18	12-09	12-10	0.2	4.35	1.29	0.54	0.27	0.20	0.060	0.26	0.31		0.19	29.6
1	60	12-09	12-10	0.4											
1	1	12-10	12-11	0.6	4.75	0.31	0.22	0.12	0.39	0.035	0.18	0.45		0.21	11.4
3	9	12-10	12-11	0.7											
4	10	12-10	12-11	0.6											
5	11	12-10	12-11	0.6	4.52	0.39	0.26	0.04				0.79	43		17.6
8	16	12-10	12-11	0.6	4.83	0.37	0.32	0.47	0.22	0.054	0.22	0.49		0.04	14.0
9	18	12-10	12-11		4.84	0.37	0.32	0.24	0.20	0.040	0.20	0.45		0.07	11.1
1	60	12-10	12-11	1.4											
1	1	12-15	12-16	2.6	4.70	0.38	0.25	0.15	0.23	0.030	0.13	0.26		0.03	11.6
3	9	12-15	12-16	4.1											
4	10	12-15	12-16	3.5	4.51	0.31	0.20	0.04	0.03	0.016	0.16	0.20		0.02	12.6
5	11	12-15	12-16	2.6	4.71	0.27	0.20	0.01	0.09	0.020	0.16	0.28	27	0.06	10.6
8	16	12-15	12-16	2.7	4.47	0.54	0.30	0.36	0.23	0.059	0.16	0.42		0.05	21.0
9	18	12-15	12-16		4.79	0.40	0.24	0.10	0.14	0.030	0.20	0.29		0.03	10.0
1	60	12-15	12-16	3.7											
8	16	12-17	12-18	0.1	5.00	1.32	0.26	0.67	0.73			0.84			

A	B	Start	Stop	mm	pH	SO ₄ -S mgS/l	NO ₃ -N mgN/l	NH ₄ -N mgN/l	Na mg/l	Mg mg/l	Ca mg/l	Cl mg/l	H ⁺ mg/l	K ⁺ μeq/lmg/l	Cot-d μS/cm
1	1	02-27	02-28	7.0	4.47	1.17	0.07	0.40	0.26	0.040	0.09	0.32		0.06	20.9
3	9	02-27	02-28	8.2											
4	10	02-27	02-28	8.7	4.42	0.56	0.06	0.13	0.19	0.027	0.03	0.32		0.05	15.2
5	11	02-27	02-28	8.4	4.60	0.53	0.07	0.15	0.17	0.020	0.03	0.34	31	0.02	14.3
8	16	02-27	02-28	0.7	4.44	0.87	0.21	0.30	0.19	0.041	0.08	0.38		0.04	23.0
11	20	02-27	02-28			0.65	0.11	0.27	0.17	0.030	0.06	0.32			18.0
1	60	02-27	02-28	11.0											
1	1	02-28	02-29	3.2	4.10	2.46	0.64	1.07	0.82	0.108	0.09	0.98		0.15	49.5
3	9	02-28	02-29	7.3											
4	10	02-28	02-29	6.5	4.07	1.44	0.48	0.68	0.50	0.063	0.07	0.83		0.16	34.7
5	11	02-28	02-29	6.0	4.22	1.36	0.43	0.65	0.44	0.050	0.05	0.79	72	0.08	36.0
8	16	02-28	02-29	0.3	4.40	2.53	0.68	1.51	0.77			1.12			
11	20	02-28	02-29			1.69	0.43	0.75	0.85	0.080	0.12	0.98		0.04	38.8
1	60	02-28	02-29	6.7											
1	1	06-07	06-08	15.0	5.40	0.82	0.35	0.39	0.09	0.082	0.74	0.16		0.08	11.7
3	9	06-07	06-08	17.3											
4	10	06-07	06-08	13.8	5.37	0.65	0.30	0.44	0.07	0.111	0.89	0.09		0.13	12.0
5	11	06-07	06-08	11.9	5.43	0.77	0.34	0.44	0.12	0.100	0.86	0.19	0	0.21	13.5
8	16	06-07	06-08	9.9	5.18	0.85	0.39	0.42	0.10	0.112	0.79	0.32		0.07	14.0
11	20	06-07	06-08	13.1	4.93	0.74	0.41	0.22	0.06	0.070	0.79	0.14		0.06	15.8
1	60	06-07	06-08	14.0											
1	1	06-10	06-11	10.4	4.54	0.48	0.20	0.15	0.04	0.028	0.16	0.06		0.03	13.6
3	9	06-10	06-11	11.5											
4	10	06-10	06-11	9.8	4.64	0.29	0.22	0.15	0.01	0.013	0.08	0.01		0.04	11.0
5	11	06-10	06-11	9.3	4.63	0.33	0.18	0.18	0.03	0.010	0.05	0.07	36	0.04	12.7
8	16	06-10	06-11	8.7	4.60	0.40	0.25	0.15	0.04	0.031	0.13	0.03		0.02	13.0
11	20	06-10	06-11	10.2	4.99	0.12	0.20	0.04	0.01	0.010	0.15	0.08		0.01	10.6
1	60	06-10	06-11	8.5											
1	1	06-19	06-20	2.1	4.73	0.17	0.13	0.24	0.08	0.015	0.05	0.11		0.05	10.0
3	9	06-19	06-20	2.6											
4	10	06-19	06-20	2.3	4.94	0.12	0.13	0.03	0.08	0.013	0.10	0.07		0.11	5.7
5	11	06-19	06-20	2.1	4.88	0.15	0.08	0.01	0.07	0.010	0.06	0.08	17	0.05	7.0
8	16	06-19	06-20	1.7	4.82	0.17	0.19	0.10	0.08	0.017	0.06	0.10		0.07	5.0
1	60	06-19	06-20	2.3											
1	1	07-01	07-02	0.9	4.57	3.47	1.12	2.09	1.34	0.344	1.98	0.76		0.51	49.2
3	9	07-01	07-02	1.1											
4	10	07-01	07-02	0.8	4.46										44.4
5	11	07-01	07-02	0.8	4.40	3.29	1.14	1.69	0.14	0.250	2.02	0.40	56	0.29	51.4
8	16	07-01	07-02	0.5	4.33	5.99	1.77	3.27	0.22	0.522	3.20	0.65		0.26	86.0
11	20	07-01	07-02	0.9	4.43	3.71	0.42	1.51	0.14	0.160	5.12	5.74		0.31	60.0
1	60	07-01	07-02	0.9											
1	1	07-02	07-03	7.4	5.38	2.66	0.72	1.64	0.11	0.194	1.47	0.31		0.15	30.0
3	9	07-02	07-03	8.1											
4	10	07-02	07-03	6.2	5.39	2.49	0.73	1.72	0.12	0.198	1.60	0.26		0.19	29.4
5	11	07-02	07-03	5.7	5.35	3.03	0.83	1.82	0.13	0.210	1.91	0.35	2	0.19	36.0
8	16	07-02	07-03	5.6	5.39	2.74	0.76	1.83	0.11	0.217	1.60	0.29		0.10	37.0
11	20	07-02	07-03	7.6	4.80	2.68	0.72	1.35	0.18	0.160	2.09	1.30		0.14	37.2
1	60	07-02	07-03	6.5											
1	1	07-04	07-05	1.4	4.42	1.30	0.40	0.45	0.19	0.072	0.40	0.34		0.11	23.4
3	9	07-04	07-05	2.0	4.31	1.43	0.45	0.44	0.20	0.090	0.52	0.31		0.10	33.0
4	10	07-04	07-05	1.8	4.39	0.85	0.35	0.24	0.13	0.053	0.29				22.4
5	11	07-04	07-05	1.3	4.15	1.45	0.48	0.39	0.26	0.060	0.28	0.42	93	0.11	38.8
8	16	07-04	07-05	1.1	4.19	1.56	0.57	0.85	0.23	0.082	0.41	0.48		0.08	39.0
11	20	07-04	07-05	1.3	4.36	1.78	0.36	0.19	0.12	0.060	0.94	0.67		0.05	27.8
1	60	07-04	07-05	1.6											
1	1	07-06	07-07	6.5	4.38	1.24	0.44	0.77	0.13	0.044	0.34	0.25		0.07	28.2
3	9	07-06	07-07	7.9	4.32	1.26	0.45	0.64	0.12	0.030	0.21	0.23		0.05	33.0
4	10	07-06	07-07	6.4	4.37	1.10	0.45	0.63	0.10	0.037	0.22	0.16		0.05	25.8
5	11	07-06	07-07	6.1	4.32	1.17	0.48	0.68	0.12	0.030	0.24	0.25	65	0.06	30.4
8	16	07-06	07-07	7.4	4.31	1.35	0.49	0.88	0.15	0.054	0.28	0.26		0.06	32.0
11	20	07-06	07-07	8.1	4.27	1.56	0.45	0.42	0.11	0.040	1.01	0.28		0.04	35.0
1	60	07-06	07-07	6.2											

A	B	Start	Stop	mm	pH	SO ₄ -S mgS/l	NO ₃ -N mgN/l	NH ₄ -N mgN/l	Na mg/l	Mg mg/l	Ca mg/l	Cl mg/l	H ⁺ μeq/l	K ⁺ mg/l	Cond μS/cm
1	2	06-27	07-04	7.6	5.17	2.65	0.73	2.05	0.14	0.208	1.38	0.26		0.15	30.0
8	17	06-27	07-04	7.1	5.24	2.68	0.79	1.58	0.11	0.260	1.73	0.29		0.13	36.0
9	18	06-27	07-04	7.3	6.43	3.61	0.89	2.95	0.21	0.360	1.98	0.41		0.63	52.4
1	2	07-04	07-11	8.0	4.32	1.31	0.43	0.62	0.10	0.064	0.34	0.21		0.04	28.0
8	17	07-04	07-11	15.4	4.30	1.40	0.45	0.64	0.16	0.071	0.34	0.27		0.07	32.0
9	18	07-04	07-11	7.4	4.51	1.56	0.51	0.67	0.15	0.090	0.49	0.27		0.13	25.2
1	2	07-11	07-18	55.6	5.23	1.15	0.35	0.65	0.12	0.119	0.55	0.12		0.04	17.2
8	17	07-11	07-18	54.5	4.92	1.12	0.32	0.67	0.06	0.119	0.58	0.18		0.04	17.0
9	18	07-11	07-18		4.90	1.01	0.30	0.49	0.03	0.100	0.51	0.20		0.06	15.1
1	2	07-18	07-25	12.9	4.04	2.34	0.75	0.82	0.15	0.063	0.32	0.34		0.05	56.3
8	17	07-18	07-25	13.0	3.93	2.28	0.74	0.86	0.21	0.074	0.35	0.45		0.09	63.0
9	18	07-18	07-25	12.7	4.08	2.53	0.77	1.04	0.23	0.090	0.45	0.39		0.20	55.9
1	2	07-25	08-01	51.4	4.60	0.54	0.33	0.26	0.39	0.132	0.08	0.30		0.07	16.3
8	17	07-25	08-01	42.9	4.46	0.55	0.32	0.26	0.20	0.040	0.09	0.40		0.02	20.0
9	18	07-25	08-01		4.52	0.58	0.36	0.26	0.21	0.029	0.07	0.34		0.03	16.6
1	2	08-01	08-08	7.6	4.69	0.15	0.18	0.03	0.09	0.017	0.03	0.17		0.01	9.7
8	17	08-01	08-08	7.4	4.79	0.20	0.20	0.11	0.10	0.029	0.05	0.19		0.06	5.0
9	18	08-01	08-08	6.9	4.77	0.38	0.23	0.11	0.18	0.030	0.12	0.27		0.07	9.3
1	2	08-08	08-15	7.4	4.38	0.89	0.64	0.71	1.46	0.047	0.10	0.41		0.06	27.0
8	17	08-08	08-15	7.3	4.41	1.01	0.62	0.78	0.27	0.058	0.21	0.52		0.10	29.0
9	18	08-08	08-15	7.2	4.42	1.20	0.70	0.88	0.23	0.050	0.19	0.46		0.10	27.8
1	2	08-15	08-22	13.2	4.24	1.21	0.49	0.44	0.18	0.034	0.15	0.28		0.05	29.4
8	17	08-15	08-22	12.6	4.27	1.17	0.51	0.49	0.23	0.056	0.21	0.37		0.07	31.0
9	18	08-15	08-22	12.1	4.33	1.41	0.51	0.53	0.21	0.050	0.24	0.38		0.07	29.7
1	2	08-22	08-29	2.5	4.46	0.34	0.42	0.15	0.30	0.041	0.05	0.45		0.06	17.8
8	17	08-22	08-29	2.5	4.41	0.41	0.51	0.02	0.48	0.069	0.20	0.78		0.10	22.0
9	18	08-22	08-29	2.1	4.47	0.73	0.54	0.23	0.43	0.080	0.28	0.73		0.11	22.2
7	14	11-27	12-10	12.2	4.50	0.59	0.31	0.16	0.17	0.030	0.07	0.30		0.05	
7	15	11-27	12-10	13.0	4.46	0.56	0.30	0.15	0.08	0.020	0.07	0.21		0.02	
7	14	12-10	12-23	20.6	4.49	0.59	0.34	0.20	0.30	0.040	0.07	0.48		0.02	
7	15	12-10	12-23	21.0	4.45	0.59	0.34	0.18	0.27	0.040	0.07	0.47		0.11	
7	14	01-04	01-18	42.1	4.45	0.56	0.31	0.22	0.36	0.050	0.06	0.55		0.04	
7	15	01-04	01-18	44.3	4.49	0.56	0.30	0.21	0.31	0.050	0.06	0.53		0.02	
7	14	01-18	02-01	36.3	3.91	3.16	1.99	1.88	0.88	0.160	0.38	1.85		0.22	
7	15	01-18	02-01	35.4	3.89	3.20	2.01	1.93	0.90	0.160	0.37	1.82		0.22	
7	14	02-01	02-15	37.6	4.15	1.15	1.31	0.70	0.68	0.120	0.21	1.39		0.11	
7	15	02-01	02-15	33.7	4.16	1.18	1.32	0.71	0.70	0.110	0.20	1.43		0.12	
7	14	02-15	02-29	34.0	4.03	2.37	1.30	1.42	0.31	0.050	0.17	0.70		0.10	
7	15	02-15	02-29	33.3	4.00	2.39	1.32	1.46	0.31	0.050	0.16	0.67		0.09	
7	14	06-06	06-20	24.9	4.99	0.59	0.25	0.24	0.06	0.060	0.51	0.13		0.13	
7	15	06-06	06-20	25.3	5.13	0.60	0.28	0.32	0.06	0.060	0.54	0.15		0.14	
7	14	06-20	07-04	7.3	5.26	2.68	0.79	1.77	0.15	0.260	1.75	0.17		0.31	
7	15	06-20	07-04	7.2	5.15	2.71	0.79	1.79	0.15	0.260	1.80	0.21		0.33	
7	14	07-04	07-18	62.9	4.84	1.15	0.40	0.68	0.06	0.110	0.60	0.28		0.08	
7	15	07-04	07-18	64.1	4.98	1.15	0.39	0.75	0.07	0.110	0.60	0.15		0.10	
7	14	07-18	08-01	58.4	4.42	0.96	0.47	0.43	0.18	0.030	0.15	0.32		0.06	
7	15	07-18	08-01	60.2	4.41	0.96	0.46	0.42	0.18	0.030	0.16	0.31		0.06	
7	14	08-01	08-15	15.0	4.60	0.62	0.47	0.36	0.16	0.040	0.08	0.32		0.07	
7	15	08-01	08-15	14.6	4.69	0.63	0.44	0.44	0.15	0.040	0.12	0.32		0.10	
7	14	08-15	08-29	7.2	4.37	1.07	0.52	0.42	0.22	0.050	0.17	0.45		0.10	
7	15	08-15	08-29	13.9	4.37	1.04	0.48	0.39	0.21	0.050	0.21	0.36		0.08	

A	B	Start	Stop	mm	pH	SO ₄ -S mgS/l	NO ₃ -N mgN/l	NH ₄ -N mgN/l	Na mg/l	Mg mg/l	Ca mg/l	Cl mg/l	H ⁺ mg/l	K ⁺ μeq/l	Cond mg/l
2	3	11-27	12-23	36.0	4.36	0.65	0.33	0.10	0.15	0.022	0.06	0.28		0.03	25.0
2	4	11-27	12-23	34.0	4.35	0.68	0.35	0.21	0.15	0.022	0.08	0.31		0.03	25.0
2	5	11-27	12-23	29.0	4.39	0.54	0.30	0.18	0.11	0.018	0.04	0.23		0.03	22.0
2	6	11-27	12-23	30.0	4.49	0.51	0.29	0.14	0.12	0.057	0.07	0.23		0.02	19.0
3	9	11-27	12-23	32.0	4.38	1.07	0.45	0.21	0.24	0.030	0.13	0.37		0.10	23.0
6	12	11-27	12-23	38.1	4.46	0.70	0.47	0.27	0.51	0.030	0.23	0.46	40	0.15	22.8
2	3	01-04	02-01	94.2	4.08	1.89	1.08	1.05	0.65	0.102	0.21	1.21		0.15	53.0
2	4	01-04	02-01	75.1	4.08	1.76	0.99	0.98	0.59	0.090	0.22	1.10		0.11	50.0
2	5	01-04	02-01	53.2	4.10	1.64	0.92	0.92	0.50	0.071	0.15	0.95		0.09	48.0
2	6	01-04	02-01	61.4	4.13	1.58	0.88	0.88	0.50	0.087	0.13	0.90		0.09	45.0
2	3	02-01	02-29	72.5	3.98	1.82	1.19	0.99	0.51	0.076	0.20	0.98		0.09	66.0
2	4	02-01	02-29	69.7	4.00	1.79	1.18	0.98	0.51	0.076	0.18	0.97		0.09	65.0
2	5	02-01	02-29	58.1	4.02	1.66	1.18	0.94	0.49	0.068	0.21	0.92		0.08	63.0
2	6	02-01	02-29	62.0	4.00	1.71	1.23	1.00	0.50	0.081	0.20	1.01		0.08	65.0
3	9	02-01	02-29	65.1	3.94	2.83	1.35	1.40	0.64	0.100	0.27	0.99		0.14	62.0
6	12	02-01	02-29	78.6	3.95	2.07	1.48	1.20	0.78	0.090	0.38	1.40	124	0.14	69.0
2	3	02-29	03-28	25.3	3.88	3.13	1.68	1.39	0.98	0.151	0.48	1.22		0.18	93.0
2	4	02-29	03-28	16.8	3.93	2.23	1.26	0.89	0.63	0.102	0.35	1.00		0.09	75.0
2	5	02-29	03-28	13.9	3.93	2.16	1.21	0.93	0.56	0.088	0.28	1.03		0.08	75.0
2	6	02-29	03-28	18.8	4.00	1.91	1.11	0.85	0.50	0.105	0.26	0.97		0.07	65.0
6	12	02-29	03-28	21.0	3.91	2.47	1.57	1.10	1.08	0.120	0.52	1.30	147	6.28	80.0
7	14	02-29	03-28	15.7	3.97	2.23	1.44	0.93	0.70	0.100	0.44	1.13		0.08	
7	15	02-29	03-28	16.5	3.98	2.18	1.47	0.91	0.71	0.100	0.46	1.14		0.10	
2	3	03-28	04-29	30.3	4.27	1.41	0.60	0.73	0.13	0.040	0.31	0.20		0.02	38.0
2	4	03-28	04-29		4.24	1.48	0.61	0.62	0.14	0.042	0.31	0.16		0.02	40.0
2	5	03-28	04-29	26.6	4.22	1.35	0.58	0.67	0.10	0.024	0.16	0.21		0.01	40.0
2	6	03-28	04-29	23.1	4.33	1.03	0.53	0.56	0.10	0.054	0.12	0.17		0.01	31.0
6	12	03-28	04-29		4.30	1.63	0.73	0.97	0.30	0.040	0.40	0.40	59	0.12	38.7
7	14	03-28	04-29	26.3	4.89	1.45	0.65	0.84	0.15	0.040	0.35	0.29		0.04	
7	15	03-28	04-29	27.4	4.88	1.46	0.65	0.80	0.12	0.040	0.35	0.36		0.03	
2	6	04-29	05-30	12.8	4.52	0.94	0.34	0.49	0.14	0.054	0.20	0.26		0.09	25.0
6	12	04-29	05-30	8.9	5.56	1.57	0.67	0.98				0.50	8		26.0
7	14	04-29	05-30	11.9	5.05	1.24	0.46	0.66	0.16	0.150	0.82	0.30		0.27	
7	15	04-29	05-30	12.4	5.14	1.22	0.47	0.74	0.16	0.130	0.78	0.48		0.23	
2	3	06-06	07-04	33.0	4.83	1.07	0.40	0.46	0.07	0.100	0.78	0.15		0.19	17.0
2	4	06-06	07-04	33.0	4.85	1.07	0.40	0.49	0.07	0.100	0.78	0.13		0.09	17.0
2	5	06-06	07-04	32.0	4.83	1.00	0.35	0.43	0.06	0.080	0.68	0.15		0.05	18.0
2	6	06-06	07-04	34.0	4.94	1.00	0.35	0.46	0.09	0.090	0.65	0.13		0.06	16.0
3	9	06-06	07-04	40.5	5.17	1.02	0.37	0.62	0.10	0.093	0.74	0.19		0.12	18.2
6	12	06-06	07-04	33.9	5.39	1.00	0.16	0.35	0.20	0.120	1.40	0.30		0.35	53.9
2	3	07-04	08-01	125.0	4.58	1.03	0.40	0.55	0.14	0.060	0.30	0.19		0.02	21.0
2	4	07-04	08-01	126.0											
2	5	07-04	08-01	117.0	4.49	0.99	0.37	0.46	0.13	0.060	0.30	0.18		0.02	23.0
2	6	07-04	08-01	127.0	4.56	0.99	0.37	0.52	0.11	0.060	0.30	0.18		0.05	21.0
6	12	07-04	08-01	119.6	4.54	1.10	0.44	0.60	0.53	0.080	0.61	0.20	26	0.14	24.0
2	3	08-01	08-29	27.0	4.43	0.82	0.38	0.46	0.19	0.030	0.13	0.33		0.06	25.0
2	4	08-01	08-29	31.0											
2	5	08-01	08-29	30.0	4.35	0.76	0.38	0.28	0.13	0.020	0.09	0.28		0.03	26.0
2	6	08-01	08-29	31.0	4.39	0.77	0.40	0.36	0.14	0.030	0.08	0.28		0.04	25.0
3	9	08-01	08-29	36.0	4.36	0.83	0.44	0.34	0.21	0.040	0.14	0.35		0.06	27.0
6	12	08-01	08-29	26.8	4.41	1.00	0.50	0.43	0.30	0.060	0.34	0.40	42	0.10	27.0
2	3	08-29	09-26	43.0	4.52	1.31	0.58	1.06	0.45	0.100	0.32	0.83		0.17	32.0
2	4	08-29	09-26	43.0	4.79	1.31	0.58	1.10	0.45	0.130	0.36	0.92		0.42	28.0
2	5	08-29	09-26	42.0	4.27	1.12	0.51	0.47	0.35	0.050	0.20	0.71		0.05	38.0
2	6	08-29	09-26	44.0	4.31	1.14	0.53	0.59	0.37	0.060	0.20	0.73		0.06	36.0
7	14	08-29	09-26	44.7											
7	15	08-29	09-26	42.3	4.45	1.29	0.61	0.67	0.49	0.120	0.34	0.89		0.14	

A	B	Start	Stop	mn	pH	SW-S mgS/l	NO3-N mgN/l	NH4-N mgN/l	Na mg/l	Mg mg/l	Ca mg/l	CL mg/l	H+ μeq/l	K+ mg/l	Cord μS/cm
2	5	09-26	10-24	41.0	4.36	0.64	0.44	0.28	0.40	0.060	0.11	0.76		0.07	27.0
2	6	09-26	10-24	44.0	4.37	0.71	0.47	0.35	0.46	0.060	0.13	0.86		0.05	28.0
6	12	09-26	10-24	56.3	4.36	1.03	0.72	0.61	0.65	0.140	0.48	1.00	53	0.12	34.0
7	14	09-26	10-24	40.4											
7	15	09-26	10-24	42.7	4.44	0.95	0.57	0.10	0.59	0.240	0.40	1.03		0.60	

Table 3-3. Results from the analytical intercomparison.
 A = Laboratory Code; B = Sample Code.
 Real precipitation samples: B = 31-38;
 Synthetic precip. samples (EMEP): B = 41-44
 n.d. = not detected

A	B	pH	SO ₄ -S mgS/l	NO ₃ -N mgN/l	NH ₄ -N mgN/l	Na mg/l	Mg mg/l	Ca mg/l	Cl μeq/l	H+	K+	Cond μS/cm
1	31	4.63	0.24	0.15	0.07	0.27	0.018	0.06	0.18		0.03	11.8
2	31	4.64	0.32	0.16	0.05	0.13	0.014	0.14	0.22		0.04	
3	31	4.65	0.72	0.19	0.06	0.15	0.060	0.07	0.20		0.02	14.0
4	31	4.54	0.27	0.15	0.08	0.15	0.022	0.05	0.22		0.01	11.0
5	31	4.67	0.28	0.16	0.06	0.12	0.010	0.02	0.22	30	0.01	11.9
6	31	4.63	0.30	0.17		0.28	0.030	0.27	0.20		0.02	14.4
7	31	4.72	0.32	0.13	0.06	0.06	0.020	0.03	0.21		0.03	
8	31	4.62	0.34	0.18	0.06	0.15	0.022	0.04	0.24		0.02	13.0
9	31	4.69	0.35	0.14	0.05	0.12	0.020	0.04	0.24		0.01	9.4
10	31		0.44	0.16	0.01				0.33			
11	31	4.72	n.d.	0.18	n.d.	0.11	0.020	0.05	n.d.		0.01	11.8
1	32	4.17	0.91	0.61	0.46	0.66	0.079	0.13	1.04		0.10	35.4
2	32	4.20	1.06	0.62	0.45	0.59	0.078	0.15	1.13		0.06	
3	32	4.21	1.50	0.63	0.51	0.70	0.140	0.16	1.01		0.09	38.0
4	32	4.02	1.03	0.61	0.44	0.63	0.094	0.15	1.05		0.07	33.6
5	32	4.22	0.99	0.60	0.51	0.61	0.070	0.14	1.09	77	0.07	37.7
6	32	4.20	1.02	0.62		0.80	0.100	0.34	1.20		0.09	40.3
7	32	4.30	0.95	0.59	0.47	0.56	0.090	0.15	1.00		0.08	
8	32	4.19	1.04	0.61	0.48	0.63	0.096	0.14	1.16		0.14	39.0
9	32	4.26	1.02	0.62	0.46	0.57	0.080	0.14	1.16		0.06	35.0
10	32		1.07	0.58	0.40				1.16			
11	32	4.25	1.38	0.57	n.d.	0.61	0.090	0.15	1.58		0.04	35.8
1	33	3.72	3.08	2.01	1.96	0.66	0.090	0.23	1.28		0.22	98.6
2	33	3.78	3.41	2.11	2.00	1.17	0.090	0.27	1.37		0.17	
3	33	3.72	3.71	2.07	2.08	0.65	0.120	0.29	1.28		0.24	107.0
4	33	3.66	3.23	2.05	1.95	0.61	0.104	0.30	1.31		0.18	94.6
5	33	3.74	3.15	2.18	1.79	0.63	0.080	0.26	1.43	233	0.25	108.0
6	33	3.76	3.20	2.10		0.96	0.110	0.55	1.60		0.19	110.0
7	33	3.82	3.27	2.23	2.04	0.55	0.090	0.22	1.39		0.22	
8	33	3.71	3.25	2.06	2.05	0.59	0.100	0.25	1.38		0.19	107.0
9	33	3.81	3.73	2.16	2.10	0.63	0.090	0.28	1.52		0.18	101.2
10	33		3.29	1.97	2.18				1.47			
11	33	3.75	3.80	1.62	1.45	1.06	0.120	0.30	2.07		0.20	104.8
1	34	3.82	3.49	1.86	1.82	1.47	0.250	0.58	2.21		0.29	91.1
2	34	3.83	3.40	1.88	1.99	1.34	0.225	0.58	2.25		0.28	
3	34	3.82	4.30	1.95	2.15	1.36	0.250	0.65	2.26		0.35	100.0
4	34	3.77	3.50	1.93	1.85	1.30	0.233	0.63	2.26		0.24	88.4
5	34	3.83	3.27	1.87	1.82	1.26	0.210	0.67	2.14		0.28	95.9
6	34	3.72	3.30	1.86		1.50	0.240	0.82	2.50	199	0.29	103.0
7	34	3.91	3.44	2.01	2.00	1.19	0.220	0.56	2.32		0.30	
8	34	3.81	3.42	1.83	1.94	1.33	0.237	0.61	2.32		0.37	99.0
9	34	3.92	3.84	1.88	2.04	1.31	0.225	0.63	2.53		0.25	96.1
10	34		3.40	1.77	2.19				2.29			
11	34	3.85	3.31	1.48	1.82	1.42	0.240	0.66	3.14		0.22	97.2
1	35	4.12	1.14	1.03	0.65	0.62	0.089	0.19	1.09		0.09	43.6
2	35	4.23	1.09	1.00	0.63	0.59	0.080	0.19	1.09		0.10	
3	35	4.08	1.88	1.18	0.77	0.58	0.090	0.21	1.24		0.10	50.0
4	35	4.02	1.16	1.00	0.63	0.66	0.089	0.22	1.16		0.08	40.3
5	35	4.14	1.06	1.03	0.60	0.63	0.070	0.18	1.13	98	0.09	46.2
6	35	4.12	1.07	1.06		0.68	0.100	0.39	1.30		0.10	46.5
7	35	4.20	1.09	1.10	0.69	0.58	0.090	0.19	0.16		0.12	
8	35	4.08	1.12	1.03	0.66	0.60	0.094	0.17	1.18		0.08	46.0
9	35	4.16	1.15	1.10	0.63	0.61	0.080	0.19	1.21		0.10	44.9
10	35		1.06	1.01	0.63				1.14			
11	35	4.13	1.53	0.88	0.72	0.60	0.080	0.15	1.43		0.04	47.0

A	B	pH	SO4-S	NO3-N	NH4-N	Na	Mg	Ca	CL	H+	K+	Cond
			mgS/l	mgN/l	mgN/l	mg/l	mg/l	mg/l	mg/l	mg/l	μeq/lmg/l	μS/cm
1	36	3.92	1.61	1.73	0.80	1.15	0.164	0.38	1.79			0.16 68.4
2	36	3.95	1.63	1.69	0.78	1.08	0.149	0.36	1.76			0.17
3	36	3.88	0.61	0.25	0.91	1.15	0.160	0.39	0.09			0.16 76.0
4	36	3.72	1.65	1.77	0.78	1.17	0.164	0.42	1.93			0.26 63.5
5	36	3.91	1.55	1.66	0.75	1.12	0.130	0.40	1.86	146		0.15 71.3
6	36	3.95	1.63	1.75		1.26	0.160	0.61	1.80			0.19 73.0
7	36	3.99	1.59	1.84	0.84	1.11	0.160	0.34	1.96			0.21
8	36	3.88	1.61	1.71	0.80	1.12	0.172	0.39	1.87			0.15 72.0
9	36	3.97	1.70	1.83	0.76	1.12	0.150	0.38	2.11			0.16 73.1
10	36		1.50	1.69	0.75				1.77			
11	36	3.92	2.46	0.57	0.53	1.34	0.160	0.34	1.86			0.10 70.5
1	37	3.69	3.98	2.92	2.62	0.53	0.097	0.47	1.12			0.22 115.8
2	37	3.69	3.78	2.73	2.66	0.40	0.086	0.48	1.08			0.18
3	37	3.66	4.77	3.06	2.88	0.43	0.100	0.54	1.16			0.22 76.0
4	37	3.61	3.96	2.99	2.48	0.43	0.095	0.51	1.11			0.21 112.7
5	37	3.69	3.86	2.71	2.26	0.43	0.070	0.48	1.10	256		0.18 123.0
6	37	3.70	3.67	2.89		0.54	0.030	0.65	1.10			0.20 128.0
7	37	3.80	3.86	2.96	2.77	0.40	0.080	0.47	1.18			0.19
8	37	3.68	3.81	2.86	2.64	0.45	0.132	0.56	1.23			0.17 123.0
9	37	3.70	4.52	2.97	2.67	0.45	0.090	0.52	1.23			0.19 127.2
10	37		3.86	2.81	2.78				1.15			
11	37	3.69	3.54	1.23	2.58	0.45	0.100	0.40	1.56			0.12 123.0
1	38	4.10	1.92	0.61	0.91	0.42	0.052	0.11	0.56			0.14 47.7
2	38	4.11	1.84	0.58	0.88	0.41	0.046	0.12	0.63			0.22
3	38	4.08	2.68	0.63	0.93	0.68	0.060	0.13	0.60			0.09 52.0
4	38	3.90	1.88	0.62	0.83	0.40	0.057	0.11	0.56			0.13 43.2
5	38	4.06	1.81	0.58	0.82	0.31	0.040	0.11	0.53	106		0.08 47.4
6	38	4.10	1.87	0.62		0.51	0.060	0.30	0.60			0.19 49.5
7	38	4.19	1.86	0.69	0.92	0.42	0.050	0.14	0.79			0.24
8	38	4.13	1.88	0.59	0.91	0.52	0.068	0.11	0.91			0.33 49.0
9	38	4.07	1.51	0.64	0.86	0.34	0.050	0.11	0.57			0.09 48.6
10	38		1.73	0.57	0.94				0.56			
11	38	4.11	1.71	0.58	0.93	0.33	0.050	0.16	0.62			0.09 48.6
1	41	4.11	1.59	0.95	0.52	1.60	0.235	0.34	2.45			0.62 44.6
2	41	4.15	1.62	0.94	0.51	1.50	0.210	0.35	2.41			0.54 54.0
3	41	4.10	2.16	1.12	0.58	1.55	0.200	0.34	2.41			0.58 53.0
4	41	4.07	1.53	0.95	0.48	1.57	0.226	0.38	2.37			0.62 45.9
5	41	4.12	1.55	1.08	0.51	1.55	0.190	0.37	2.47	88		0.60 52.9
6	41	4.16	1.57	0.97	0.54	1.70	0.220	0.59	2.40	85		0.56 54.2
7	41	4.23	1.53	0.94	0.54	1.55	0.210	0.34	2.22			0.59
8	41	4.10	1.58	0.94	0.51	1.51	0.202	0.32	2.45			0.54 55.0
9	41	4.17	1.59	0.95	0.50	1.56	0.220	0.37	2.51			0.59 47.5
10	41		1.54	0.91	0.49				2.44			
11	41	4.17	1.54	0.83	0.59	1.64	0.260	0.37	2.50			0.74 54.0
1	42	4.50	2.08	0.62	0.44	1.59	0.243	1.16	2.17			0.56 34.4
2	42	4.52	2.02	0.58	0.43	1.51	0.220	1.26	2.19			0.47 40.0
3	42	4.48	2.59	0.69	0.49	1.54	0.210	1.24	2.15			0.49 40.0
4	42	4.46	1.96	0.59	0.42	1.65	0.238	1.36	2.18			0.59 34.6
5	42	4.52	1.98	0.59	0.44	1.51	0.200	1.38	2.28	36		0.53 39.5
6	42	4.51	2.03	0.59	0.47	1.70	0.230	1.50	2.30	35		0.48 40.6
7	42	4.59	1.91	0.59	0.47	1.54	0.220	1.24	2.04			0.53
8	42	4.50	2.01	0.58	0.44	1.52	0.218	1.26	2.25			0.49 40.0
9	42	4.56	2.00	0.60	0.44	1.55	0.230	1.35	2.28			0.53 35.9
10	42		1.97	0.57	0.43				2.26			
11	42	4.58	1.49	0.57	0.53	1.78	0.270	1.59	2.33			0.59 41.0

A	B	pH	SO ₄ -S mgS/l	NO ₃ -N mgN/l	NH ₄ -N mgN/l	Na mg/l	Mg mg/l	Ca mg/l	Cl mg/l	H ⁺ μeq/l	K ⁺ mg/l	Cond μS/cm
1	43	4.16	1.52	0.91	0.77	1.48	0.127	0.39	2.47		0.33	40.9
2	43	4.20	1.49	0.89	0.77	1.43	0.120	0.40	2.41		0.27	50.0
3	43	4.15	2.10	1.06	0.84	1.45	0.110	0.45	2.41		0.28	50.0
4	43	4.14	1.41	0.90	0.71	1.53	0.130	0.45	2.41		0.31	43.6
5	43	4.18	1.43	0.91	0.74	1.44	0.110	0.43	2.50	77	0.30	49.3
6	43	4.26	1.60	0.93	0.77	1.60	0.140	0.63	2.50	73	0.29	50.1
7	43	4.27	1.41	0.90	0.76	1.46	0.120	0.39	2.28		0.29	
a	43	4.16	1.48	0.90	0.75	1.44	0.115	0.40	2.51		0.29	50.0
9	43	4.21	1.47	0.91	0.72	1.48	0.120	0.42	2.57		0.30	46.3
10	43		1.46	0.88	0.86				2.36			
11	43	4.20	1.59	0.84	0.80	1.56	0.150	0.53	2.41		0.31	49.8
1	44	4.40	2.15	0.56	0.71	1.53	0.105	1.06	2.18		0.36	36.2
2	44	4.43	2.09	0.51	0.71	1.45	0.100	1.15	2.26		0.30	43.0
3	44	4.39	2.71	0.61	0.77	1.48	0.100	1.14	2.22		0.31	42.0
4	44	4.39	2.02	0.52	0.65	1.51	0.114	1.24	2.22		0.33	36.9
5	44	4.42	2.04	0.51	0.67	1.46	0.090	1.24	2.31	44	0.34	42.0
6	44	4.42	2.10	0.53	0.71	1.70	0.110	1.40	2.30	46	0.30	43.0
7	44	4.50	2.01	0.51	0.71	1.47	0.110	1.12	2.11		0.32	
a	44	4.40	2.08	0.52	0.69	1.46	0.100	1.19	2.32		0.32	42.0
9	44	4.45	2.09	0.54	0.66	1.49	0.110	1.22	2.36		0.33	39.8
10	44		2.06	0.51	0.65				2.26			
11	44	4.44	2.20	0.52	0.78	1.58	0.130	1.21	2.35		0.33	43.0

BALTIC SEA ENVIRONMENT PROCEEDINGS

- No. 1 JOINT ACTIVITIES OF THE BALTIC SEA STATES WITHIN THE FRAMEWORK OF THE CONVENTION ON THE PROTECTION OF THE MARINE ENVIRONMENT OF THE BALTIC SEA AREA 1974-1978
(1979)*
- No. 2 REPORT OF THE INTERIM COMMISSION (IC) TO THE BALTIC MARINE ENVIRONMENT PROTECTION COMMISSION
(1981)
- No. 3 ACTIVITIES OF THE COMMISSION 1980
- Report on the activities of the Baltic Marine Environment Protection Commission during 1980
- HELCOM Recommendations passed during 1980
(1981)
- No. 4 BALTIC MARINE ENVIRONMENT BIBLIOGRAPHY 1970-1979
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- No. 5A ASSESSMENT OF THE EFFECTS OF POLLUTION ON THE NATURAL RESOURCES OF THE BALTIC SEA, 1980
PART A-1: OVERALL CONCLUSIONS
(1981)*
- No. 5B ASSESSMENT OF THE EFFECTS OF POLLUTION ON THE NATURAL RESOURCES OF THE BALTIC SEA, 1980
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PART A-2: SUMMARY OF RESULTS
PART B: SCIENTIFIC MATERIAL
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- No. 7 ACTIVITIES OF THE COMMISSION 1981
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National Statements by the Contracting Parties on the Achievements in Implementing the **Goals**
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Helsinki University of Technology, Ship Hydrodynamics Laboratory, Otaniemi, Finland
P. Tuovinen, V. Kostilainen and A. **Hämäläinen**
(1984)
- No. 12 GUIDELINES FOR THE BALTIC MONITORING PROGRAMME FOR THE SECOND
STAGE
(1984)
- No. 13 ACTIVITIES OF THE COMMISSION 1983
- Report of the activities of the Baltic Marine Environment Protection Commission during 1983
 including the Fifth Meeting of the Commission held in Helsinki 13-16 March 1984
- HELCOM Recommendations passed during 1983 and 1984
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- No. 14 SEMINAR ON REVIEW OF PROGRESS MADE IN WATER PROTECTION MEASURES
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- No. 15 ACTIVITIES OF THE COMMISSION 1984
- Report of the activities of the Baltic Marine Environment Protection Commission during 1984
 including the Sixth Meeting of the Commission held in Helsinki 12-15 March 1985
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- No. 16 WATER BALANCE OF THE BALTIC SEA
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(1986)
- No. 17A FIRST PERIODIC ASSESSMENT OF THE STATE OF THE MARINE ENVIRONMENT OF
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17-18 November 1986, **Norrköping**, Sweden
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- No. 22 SEMINAR ON OIL POLLUTION QUESTIONS
19-20 November 1986, **Norrköping**, Sweden
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- Report on the activities of the Baltic Marine Environment Protection Commission during 1988 including the Tenth Meeting of the Commission held in Helsinki 14-17 February 1989
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- No. 32 DEPOSITION OF AIRBORNE POLLUTANTS TO THE BALTIC SEA AREA 1983-1985 AND
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