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Publisher *Taylor & Francis*

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International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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To cite this Article Slanina, J. , Möls, J. J. , Baard, J. H. , Van Der Sloot, H. A. , Van Raaphorst, J. G. and Aaman, W.(1979) 'Collection and Analysis of Rainwater; Experimental Problems and the Interpretation of Results', International Journal of Environmental Analytical Chemistry, 7: 2, 161 — 176

To link to this Article: DOI: 10.1080/03067317908071486

URL: <http://dx.doi.org/10.1080/03067317908071486>

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Collection and Analysis of Rainwater; Experimental Problems and the Interpretation of Results[†]

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(Received May 15, 1979)

Eight open and eight wet-only rain samplers, placed together on an open field near Den Helder, The Netherlands, were sampled three times a week. Greatest care in sampling and analysis procedures was taken to avoid contamination. The samples were analysed for H^+ , NH_4^+ , Na, K, Ca, Mg, Fe, Zn, Pb, Cd, Cu, Mn, Al, V, SO_4^{2-} , NO_3^- , Cl^- , Br^- and F^- by wet chemical techniques, AAS and instrumental neutron activation analysis.

For many species the difference between the results of open and wet-only samplers was negligible.

The correlation between some cations and anions was computed and indications were found for the presence of HNO_3 and $(NH_4)_2SO_4$ in the atmosphere, whereas little H_2SO_4 or NH_4NO_3 seems to be present.

It is possible to detect whether various pollutants are of continental or marine origin.

KEY WORDS: Rainwater, sampling, analysis, statistical evaluation, wet deposition, total deposition.

1. INTRODUCTION

ECN and IMOU are engaged in a research program on deposition and precipitation chemistry. Recently we published the results of a study using 21 open rain samplers closely spaced together to test small-scale variations

[†]Presented at the Ninth Annual Symposium on the Analytical Chemistry of Pollutants, Jekyll Island, Georgia, May 1979.

in the chemical compositions of rainwater.¹ These variations must be low if study of precipitation chemistry is to be useful.

In this study 11 samplers were emptied daily and 10 were sampled monthly. The standard deviation in the results of the daily and monthly samples was 3 to 6% relative and 10 to 25% relative, respectively. The following questions can be raised:

- What is the ratio between wet and total deposition in our rain samplers? This is important because it was not clear to us whether wet-only samplers must be used for precipitation chemistry. The possibility of calculating a total burden from wet or total deposition in rain samplers depends also on this ratio.
- Is it possible to detect chemical species in the atmosphere by analysing rainwater? The excellent work of D. Klockow and coworkers² makes clear that in background areas this detection is possible. They found that sulfuric acid and ammonium nitrate were present on mount “Schau-ins-land” in the Schwarzwald, F.R.G.
- To what extent is source identification feasible? For instance Pattenden and co-workers³ have drawn the conclusion from their precipitation chemistry work that the North Sea could be a source of heavy metals.

The set-up of the experiment determines whether one can obtain information on any of these questions.

A number of important conditions can be pointed out:

- 1) The chemical composition of the rain samples must be representative for the sampled rain. This seems rather obvious, but it is a difficult problem:
 - The amount of rain sampled is incorrect if the wind near the rain samplers is disturbed, so buildings, hills and trees must be at a distance of at least five times their height.
 - The wet-only samplers must open very fast on the first raindrops. The lid of the samplers should not disturb the airflow around the sampler and no rain should splash off the lid into the sampler.
 - Adsorption or introduction of substances in the rain sampler must be avoided. This is a tough problem for trace metals especially for wet-only samplers, where a lot of contaminating surface is available.
 - The contamination of the samples by algae, bacteria, insects and birds must be avoided.
- 2) The sample preparation and analysis must not introduce artefacts.
 - The concentration of trace metal elements in rain water can be very

low, e.g. cadmium 0.01 ppb, copper 0.2 ppb. So the samples are easily contaminated.

The air in laboratories is often contaminated with species such as HCl , HNO_3 and NH_3 to such a degree that appreciable quantities of these components can be introduced in rain water samples.

—Many methods used for rain water analysis were originally developed for surface water, they must be checked for their accuracy if applied to rain water.

3) The results must be correlated with meteorological data.

—The weather in the Netherlands is quite variable, so sampling periods must be short (3 days or less) otherwise the meteorological parameters will vary too much during a sampling period. The precipitation samples obtained in this period are limited. So it is necessary to employ analytical methods which can handle small samples. Generally we need less than 25 ml for the analysis of some 20 cations and anions.

We have tried to consider all these parameters in the set-up of our study.

2. SAMPLING

2.1. Open rain samplers

The open rain samplers are designed as previously described.¹

A polyethylene funnel (inner diameter 22.3 cm) is mounted on an iron tripod. 2- or 5-l polyethylene bottles are connected to the funnel by means of a screwcap.

The standard deviation in the results of heavy metal determinations at the beginning of our study indicated that the frame contaminated the rain samples. After coating the frame with metal-free paint the mean concentration and standard deviations were significantly lower.

2.2. Wet-only rain samplers

The wet-only sampler consists of an open sampler and a lid (see Figure 1). The lid is connected to a pneumatic rotator (Kuhnke). We prefer this pneumatic device because it is very strong and rugged.

The rain is detected by means of a change in electrical conductivity (see Figure 1). The detecting surface of 50 cm² consists of 1 mm yellow copper plates, isolated by 1 mm strips of C.A.F. The metal plates are heated by an electric heater of 2 watts to avoid detection of dew or fog. When

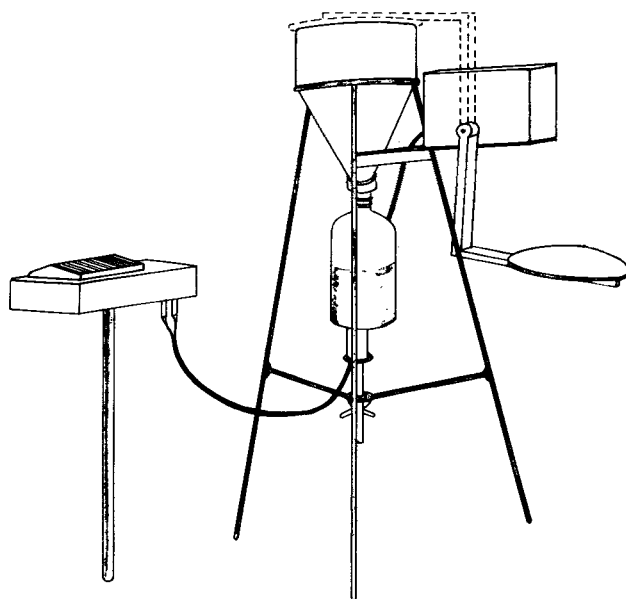


FIGURE 1 Wet-only rain collector.

activated they are heated by 8 watts to dry them quickly after the end of the rain. If the resistance between adjacent plates decreases below an adjustable value a relay actuates two valves and the sampler is opened. If the resistance increases above the critical value the lid is closed again. In the first half of the study contamination of heavy metals was detected by the high scatter of the results. The aluminium lid, the rotator house and tripod were coated with the same inert paint as used for the open rain samplers. None the less some contamination was observed for Zn, Cu and Cd. We are investigating other coating materials at the moment.

Because the lid is 40 cm below the funnel in opened position, the wind is not disturbed and no water will splash from the lid into the funnel. The combination of the large detection surface and the fast action of the rotator ensures that the cover is removed very quickly after the onset of the rain. This is important because we have found by sequential rain sampling that the concentrations of some compounds can be 50 times higher in the first 0.1 to 0.3 mm of a rain squall, compared to the concentrations found in the middle of the squall.

2.3. Siting of the samplers

It is very difficult to find a suitable area, even in Noord-Holland, where the distance to trees and buildings is sufficient and no local sources are in the vicinity. The airfield "De Kooy" of the Royal Netherlands Navy was in many respects a very suitable location.

In our previous study¹ we observed that a considerable number of "outliers" was present in the results (about 15%). We decided to employ 8 samplers of each type, as a compromise between the necessity of many data for statistical treatment and the corresponding enormous amount of analytical work.

2.4. Sampling period, sample transfer and sample preparation

2.4.1. All samplers were emptied three times a week on Monday, Wednesday and Friday. The sampling bottles were removed from the rain samplers and closed immediately.

All samplers were scrubbed with demineralized water, the water was allowed to drip out of the funnels during 10 minutes and the new weighed bottles were connected to the rain samplers.

Work in the field must be kept to a minimum to avoid contamination.

2.4.2. The sample bottles were transferred to the ECN chemical laboratory. The bottles were weighed and the sample volume was calculated. Samples less than 40 ml (aeq. to 0.1 mm rain) were discarded. The outside of the bottle was cleaned and it was brought into a clean room, where the sample was divided into three portions: 2 ml for instrumental neutron activation analysis (INAA), 18 ml for atomic absorption spectrometry (AAS) measurements and 18 ml for the determination of H^+ , NH_4^+ and the anions.

Utmost care was taken to avoid contamination of the samples. First the aliquots for the trace analyses were taken with Oxford pipettes; the tips were renewed for each sampling period, the aliquots for the bulk elements were pipetted next. Prior to use the tips of the pipettes were soaked 24 hours in dilute nitric acid.

The samples for AAS and NAA were acidified to 0.1 M HNO_3 with p.a. or ultrapure quality HNO_3 directly after dividing the samples.

All samples were analysed within 14 days after sampling.

Demiwater was sampled in the same way and analysed each fortnight to check the amount of contamination.

Initially some contamination from handling occurred in the laboratory, but during the last 27 sampling periods contamination was minimal.

3. ANALYTICAL METHODS

3.1. Anions

Fluoride and chloride were determined by means of ion selective electrodes (Ise) using standard additions techniques.

In the first half of the experiment the analyses were performed manually, in the second half by means of a dedicated computer system.⁵

Sulphate was measured nephelometrically⁶ and nitrate was determined by U.V. spectrometry at 210nm using a special active carbon filter to remove interferences⁷. Bromide and chloride were measured by means of INAA (see 3.3).

Table I gives the analytical parameters.

TABLE I
Analytical parameters of methods for anions

Anion	Method	Det. limit in ppm	Typical accuracy in % rel.	Sample volume in ml
Cl ⁻	Ise (Man)	0.3	5	0.5
Cl ⁻	Ise (Comp)	0.1	3	0.5
Cl ⁻	NAA	0.005	3	1 ^a
Br ⁻	NAA	0.001	5	1 ^a
NO ₃ ⁻	U.V. Spectr.	0.1	3	0.3
SO ₄ ²⁻	Nephel.	0.5	5	0.5
F ⁻	Ise (Man)	0.01	5	0.5
F ⁻	Ise (Comp)	0.005	3	0.5

^aSix elements are measured simultaneously in 1 ml sample by INAA.

3.2. Cations

H⁺ is measured by means of a glass electrode, using a standard addition technique (Gran's plot) either manual or under computer control.⁵ Ammonium is measured by a gas-sensing electrode. Here we employed direct measurements either manual or under computer control because this electrode is very selective in rain water samples.⁵

Na, K, Mg, Ca, Fe, Zn are measured by AAS by means of flame techniques (see Table II), Cu, Pb and Cd are measured by means of a graphite furnace (see Table III).

Either an Instrumental Laboratories or Jarrell Ash dual beam, dual monochromater system was used. The graphite furnace was a H.G.A. 74 (Perkin-Elmer).

Mn, V and Al are measured by INAA (see 3.3).

TABLE II
Determination by AAS flame

Species	Flame	Ionisation buffer	Wave length in nm	Detection limit in ppb	Range in ppm
Na	C ₂ H ₂ -air	1000 ppm Cs ⁺	589.6	<10	0-20
K	C ₂ H ₂ -air	1000 ppm Cs ⁺	766.5	<10	0-2
Mg	C ₂ H ₂ -N ₂ O	1000 ppm Cs ⁺	285.2	<10	0-2
Ca	C ₂ H ₂ -N ₂ O	1000 ppm Cs ⁺	422.7	<10	0-2
Fe	C ₂ H ₂ -air	—	213.9	10	0-2
Zn	C ₂ H ₂ -air	—	248.3	5	0-2

TABLE III

Determination by AAS graphite furnace (20 μ l injection, peak area measurement, no background correction necessary, all standards are prepared in 5 ppm Na⁺, 0.5 ppm Ca²⁺, 0.5 ppm K⁺ and 0.5 ppm Mg²⁺ as a synthetic rainwater)

Species	Wave length in nm	Range in ppb	Detection limit in ppb
Cu	324.7	0-30	0.1
Cd	228.8	0-6	0.01
Pb	283.3	0-120	0.2

Table IV gives the characteristics of the analytical methods employed for cations.

3.3. Neutron activation analysis

A special procedure was developed for the determination of six elements in ≈ 1 ml rain water by instrumental neutron activation analysis. The procedure is based on a short irradiation (2 min) at a thermal neutron flux of $5.10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ using the pneumatic rabbit system to the High Flux Reactor at Petten. Strontium is applied as an internal fluxmonitor. In short the procedure runs as follows:

1.2 ml volumes of rain water samples are transferred to polythene capsules.

- 50 μ l of a Sr(NO₃)₂ solution, containing $\approx 32 \mu\text{g}$ Sr, is added and the sample frozen.

TABLE IV
Analytical parameters of the cation determinations

Cation	Method	Detection limit in ppb	Typical accuracy in % rel.	Sample volume
Na	NAA	5	3	1 ^a
Na	AAS-flame	< 10	3	0.2
K	AAS-flame	< 10	3	0.5
Mg	AAS-flame	< 10	3	0.5
Ca	AAS-flame	< 10	3	0.5
Fe	AAS-flame	10	3	0.5
Zn	AAS-flame	5	10	0.5
Cd	AAS-furnace	0.01	10	0.2
Pb	AAS-furnace	0.2	10	0.2
Cu	AAS-furnace	0.1	10	0.2
Al	NAA	5	10	1 ^a
V	NAA	0.5	10	1 ^a
Mn	NAA	0.5	10	1 ^a

^aSix elements are measured simultaneously in 1 ml sample by INAA.

TABLE V
Nuclides measured in INAA

Element	Radionuclide	$T_{1/2}$	E_{γ} in keV
Na	²⁴ Na	15.05 h	1368
Cl	³⁸ Cl	37.3 min	1642
V	⁵⁰ V	3.75 m	1434
Mn	⁵⁶ Mn	2.57 h	846
Al	²⁸ Al	2.30 min	1778
Br	⁸⁰ Br	17.6 m	619
Sr (monitor)	^{87m} Sr	2.81 h	388

- In frozen condition three samples and two standards (1.2 ml containing Sr, Al, Na and Cl or Sn, Mn, V and Br) are irradiated simultaneously for 2 min.
- After return to the laboratory 1 ml is pipetted in test tubes for counting. With ≈ 20 minutes after irradiation samples and standards are counted.
- After ≈ 2.5 hours samples and standards are counted for 10 minutes, to eliminate interference from ²⁸Mg on the ⁵⁶Mn determination.

The spectra are read-out on magnetic tape and processed by a computer program for peak calculation and corrections for decay and pulse pile-up. The nuclides and γ -lines employed are given in Table V.

Using an additional program in a PDP-11 laboratory computer count-rates per sample are normalized against ^{87m}Sr monitor and the concentrations in the sample calculated.

Before calculation the standards are checked for deviations from previously-determined Sr normalized specific count-rates.

4. QUALITY CONTROL OF THE ANALYTICAL TECHNIQUES

The results of standards analysed by INAA and AAS or Ise methods simultaneously corresponded quite well (see Table VI).

TABLE VI
Comparison of results of different techniques (12 samples or standards)

Element	NAA/ result AAS	Result INAA/ result ISE
Na	1.02 (mean conc. 5 ppm)	0.97 (mean conc. 5 ppm)
Cl^-		
Mn	0.90 (mean conc. 5 ppb)	
Al	1.12 (mean conc. 60 ppb)	

The wet analytical and AAS methods for bulk elements were checked in rain water analyses in round robins in the Netherlands. The accuracy was better than 10%.

The AAS trace analysis methods were checked in IAEA "trace elements in water" round robins and their accuracy was better than 10% for all elements in the concentration range typical for rain water.

Ion-chromatography was employed as a reference technique for the analysis of anions, the results agreed within 6%.

Our least dependable method, the nephelometric SO_4^{2-} determination was checked regularly by Klockow's isotope dilution method.

5. RESULTS

In the beginning of the study we encountered difficulties with the wet-only samplers. The ratio between the sampled volume of wet-only and open samplers was below 0.95. The reason for this was a too long delay time

TABLE VII
Outliers of results of bulk elements

	Wet deposition	Total deposition
Total number of results for bulk elements	2400	2700
Total number of rejects	202	190
Number of rejects in case of three or more rejects per sample	124	93
Other rejects	78 (3 %)	97 (3.5 %)

before opening. Also contamination was a problem. In Tables VIII, IX and X we give the results of the last 27 sampling periods, where these problems, with exception of the Cu, Cd and Zn contamination in the wet-only samplers, were eliminated.

The mean and standard deviation of the eight results per sample period can be influenced severely by outliers, so we wanted a statistical test to eliminate them. We could not find a suitable test for outliers for this kind of experiment in literature so we decided to apply a Dixon test. Each group of eight results is tested by means of a w/s criterion (w is range, s is standard deviation) to see whether a Gaussian distribution is present. Next a Dixon test ($\alpha=0.1$) is applied.

We believe that testing for Gaussian distribution on eight results is a poor procedure, but we are trying to develop an alternative.

An indication that the results of this procedure are acceptable is given by the fact that for bulk elements half of the outliers belong to samples which gave three or more rejected results for bulk elements. These samples are clearly suspect. This leaves a number of ca 175 outliers which could be falsely rejected on a total of 5100 results of total and wet deposition measurements (see Table VII).

We decided not to tabulate all the results, but we will send them on request.

6. DISCUSSION

The first goal of our study was to measure the ratio of total and wet deposition. In Table VIII the sum of wet and total deposition of 28 periods is given. The mean concentration is derived from the deposition

TABLE VIII

Wet and total deposition, mean total and wet concentrations for 28 sample periods.

	TOTAL RAINCOLLECTORS				WET RAINCOLLECTORS			
	DEPOSITION IN 10-3 MOLEN.M-2		CONCENTRATION (IN 10-6 MOLEN.L-1)		DEPOSITION (IN 10-3 MOLEN.M-2)		CONCENTRATION (IN 10-6 MOLEN.L-1)	
	SUM	ST. DEV.	MEAN	ST. DEV.	SUM	ST. DEV.	MEAN	ST. DEV.
Rainfall	8133.	31.14			8271	40.42		
Hydrogen	11.76	.1395	61.75	.7321	12.57	.2078	64.91	1.073
Ammonium	13.32	.2214	65.53	1.089	11.95	.1918	57.81	.9278
Sodium	23.49	.1609	115.5	.7913	20.18	.2830	97.60	1.368
Potassium	.9572	.3767E-01	4.708	.1853	.7955	.1976E-01	3.847	.9555E-01
Calcium	1.952	.1237E-01	9.601	.6085E-01	1.873	.3953E-01	9.057	.1912
Magnesium	3.068	.2466E-01	15.09	.1213	3.577	.1418	17.30	.6855
Sulphate	11.00	.7387E-01	54.11	.3633	10.98	.1225	53.09	.5923
Nitrate	10.58	.5161E-01	52.01	.2538	11.05	.2266	53.46	1.096
Chloride	28.93	.2660	142.3	1.308	25.89	.4842	125.2	2.342
Fluoride	.2434	.1918E-02	1.312	.1034E-01	.2214	.2785E-02	1.168	.1469E-01
Zinc	.1078	.1616E-02	.5304	.7946E-02	.2998	.2901E-01	1.450	.1403
Lead	.1324E-01	.1300E-03	.6511E-01	.6395E-03	.1320E-01	.2343E-03	.6382E-01	.1138E-02
Cadmium	.4895E-03	.5263E-05	.2408E-02	.2588E-04	.8385E-03	.1312E-04	.4057E-02	.1510E-03
Copper	.1597E-01	.2723E-02	.7852E-01	.1339E-01	.1347E-01	.4072E-03	.6512E-01	.1969E-02
Iron	.1675	.2576E-02	.8238	.1267E-01	.1727	.3919E-02	.8352	.1895E-01
Bromine	.6117E-01	.1038E-02	.3531	.5991E-02	.5695E-01	.1087E-02	.3254	6212E-02
Manganese	.1763E-01	.1655E-03	.1018	.9552E-03	.1725E-01	.4558E-03	.9882E-01	.2604E-02
Vanadium	.8022E-02	.8352E-04	.4631E-01	.4822E-03	.7485E-02	.1477E-03	.4277E-01	.8439E-03
Aluminium	.3420	.1582E-01	1.974	.913E-01	.3175	.9993E-02	1.815	.5710E-01

X Statistical significant ($\neq 0.05$) difference between total and wet deposition.

n.s. Difference between total and wet deposition is falsified by contamination.

TABLE IX
Deposition by 8 small rains (<2.5 mm) in open- and wet-only samplers

Species	Total deposition in $10^{-3} \text{ M} \cdot \text{m}^{-2}$	Wet deposition in $10^{-3} \text{ M} \cdot \text{m}^{-2}$	Ratio wet/total deposition
H ⁺	0.85	0.98	1.15
NH ₄ ⁺	2.15	1.80	0.84
Cl ⁻	4.99	4.01	0.80
SO ₄ ²⁻	1.54	1.31	0.85
NO ₃ ⁻	1.27	1.22	0.96
Na	3.95	3.37	0.85
K	0.154	0.123	0.80
Mg	0.515	0.527	1.02
Ca	0.335	0.255	0.76
Pb	0.00166	0.00157	0.94
Mn	0.0030	0.00255	0.84
V	0.00110	0.00095	0.87
Al	0.049	0.044	0.90

TABLE X
Correlation between NH₄, H⁺, SO₄²⁻ and NO₃⁻ (some anions and cations, 25 sampling periods)

	Degrees of freedom	Correlation coefficient	Regression coefficient
Total conc.			
NH ₄ ⁺ v.s. SO ₄ ²⁻	27	0.81	1.74
NH ₄ ⁺ v.s. NO ₃ ⁻	27	0.59	1.78
H ⁺ v.s. SO ₄ ²⁻	25	0.51	1.23
H ⁺ v.s. NO ₃ ⁻	25	0.75	1.00
H ⁺ + NH ₄ ⁺ v.s. 2SO ₄ ²⁻ + NO ₃ ⁻	25	0.95	0.79
Wet conc.			
NH ₄ ⁺ v.s. SO ₄ ²⁻	27	0.72	1.59
NH ₄ ⁺ v.s. NO ₃ ⁻	27	0.56	1.99
H ⁺ v.s. SO ₄ ²⁻	25	0.49	1.36
H ⁺ v.s. NO ₃ ⁻	25	0.75	0.99
NH ₄ ⁺ + H ⁺ v.s. 2SO ₄ ²⁻ + NO ₃ ⁻	25	0.95	0.77

The critical value of the correlation coefficient is 0.45.

according to

$$\bar{c} = \frac{\sum h_p \cdot c_p}{\sum h_p}$$

\bar{c} = mean concentration over 28 periods,

h_p = mean amount of rain per square metre per period,

c_p = mean concentration per period.

The difference between total and wet deposition is statistically insignificant for sulfate, lead, iron, manganese and aluminium. A difference less than 5% was found for calcium and nitrate. Contamination problems invalidate any conclusions for Zn, Cd and Cu.

The influence of dry deposition is important in samples that represent less than 2.5 mm precipitation (see Table IX).

The amount of H^+ in the open samplers is less than in the wet-only: presumably because of dry deposition.

This confirms the conclusion of other authors⁸ that the use of wet-only samplers is a necessity in precipitation chemistry studies. This result encourages us to evaluate in the future whether the total burden on the earth surface of several important ions, e.g. NO_3^- and SO_4^{2-} , can be calculated from deposition measurements.

We applied statistics to detect inorganic compounds present in gaseous form or as aerosols in the atmosphere, which are transported by means of rain water to the surface.

Here again no suitable statistical treatment seems to be available in the literature. Up till now we have employed orthogonal regression calculation⁹ after a check for Gaussian distribution. This is not an optimal procedure, as we already indicated in Section 5, but we are investigating better methods. In Table XI the results of some correlations of major an- and cations are given. Significant correlations are found between NH_4 and SO_4 , between H^+ and NO_3^- and between $(NH_4^+ + H^+)$ and $(2SO_4^{2-} + NO_3^-)$. This indicates that HNO_3 and $(NH_4)_2SO_4$ are present in the atmosphere at Den Helder. The slope of the line gives the ratio between the correlated species, for the total rain samples. This results in $H_{1.00}NO_3$, $(NH_4)_{1.74}SO_4$ and for the wet-only samples in $H_{0.99}NO_3$, $(NH_4)_{1.5}SO_4$.

We found a correlation between Ca and Mg and sulphate also, but it is clear from the ratio of calcium and sulphate concentrations that most of the sulphate is present as ammoniumsulphate.

We have confidence in the SO_4^{2-} , NO_3^- , NH_4^+ and H^+ measurements of the first half of the experiments. If these results are included the same correlations are found (see Table XI).

The meteorological conditions change every few days in the

TABLE XI
Correlation between the concentration of some an- and cations 40
sampling periods

Correlation	Degrees of freedom	Correlation coefficient	Regression coefficient
Total conc.			
NH_4^+ v.s. SO_4^{2-}	40	0.77	1.65
NH_4^+ v.s. NO_3^-	39	0.54	1.72
H^+ v.s. SO_4^{2-}	38	0.60	1.24
H^+ v.s. NO_3^-	38	0.76	1.00
Wet conc.			
NH_4^+ v.s. SO_4^{2-}	40	0.72	1.50
NH_4^+ v.s. NO_3^-	39	0.56	1.40
H^+ v.s. SO_4^{2-}	38	0.54	1.36
H^+ v.s. NO_3^-	38	0.83	0.963

The critical value of the correlation coefficient is 0.40.

TABLE XII
Ratios of concentrations between continental and
marine rains (open samplers)

Species	Ratio cont./marine	Species	Ratio cont./marine
H^+	1.5	Cu	2.0
NH_4^+	3.3	Cd	2.0
Na	0.2	V	2.1
SO_4^{2-}	2.0	Mn	3.0
NO_3^-	2.4	Al	2.1
Cl^-	0.2	Fe	1.9
Zn	1.9		
Pb	1.8		

Netherlands. We will investigate in the next experiment whether 1 day sampling periods will result in better information. We intend to check the conclusion that HNO_3 and not H_2SO_4 is the predominant acid species in the North-western part of the Netherlands by measurements in the atmosphere.

We have divided the sampling periods in two categories: "continental rains" (associated with wind coming from the southwest, southeast, northeast) and "marine rains" (associated with wind from the north and west). The ratios of the mean concentrations of the continental and marine rains as sampled with open rain samplers are given in Table XII.

The ratios give clear indication of the origin of the different ions: H^+ , NH_4^+ , SO_4^{2-} , NO_3^- and all heavy metals come from continental sources mainly.

Sodium and chloride are of a marine origin as expected.

It is clear that ammonium in this part of the Netherlands is not produced at the coastline, as has been suggested.⁸

Furthermore, the North Sea is not a significant source of heavy metals, as is suggested by Cambray *et al.*³ This conclusion is supported by the measurements of heavy metals in air, made by Kretzschmar and co-workers.¹⁰

We will report a more thorough analysis of these results at a later time.

7. CONCLUSION

For some species the difference in results obtained by open and wet-only samplers is negligible in the north-western part of the Netherlands. The next question is whether a total burden can be calculated from the chemical composition of rain water. This depends on the difference in deposition efficiency of gases and aerosols between the open rain sampler and the surroundings and the ratio between dry and wet deposition. If the ratio found in open or wet-only samplers is very close to one (we can measure this ratio with an accuracy of ca 5%) and it can be proved that the scavenging efficiency of the sampler compared with the surroundings is in the same order of magnitude, total burdens could be calculated. The results indicate strongly that species present in the atmosphere, such as HNO_3 , and $(\text{NH}_4)_2\text{SO}_4$ can be detected if short sampling periods are employed. A rain water sampling network can be a cheap way to monitor the general situation.

Sources of different pollutants can be broadly traced if the sampling periods are comparable to the length of periods of constant meteorological conditions.

Acknowledgements

We are indebted to the Royal Netherlands Navy for allowing us to work on the air base "De Kooy" and for the assistance and help given by Navy personnel at many occasions.

We thank the Royal Netherlands Meteorological Institute (KNMI) for their help in acquiring all meteorological data.

We are indebted to Mr. H. P. Datema for the sampling, to Mrs. Bruyn-Hes, Miss L. Bergman and Messrs. F. P. Bakker, D. Börger, W. A. Lingerak, J. A. J. Peters and J. Zonderhuis for performing some 15,000 analyses and to Dr. W. L. Zijp for the helpful discussions on statistics and the review of the manuscript.

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