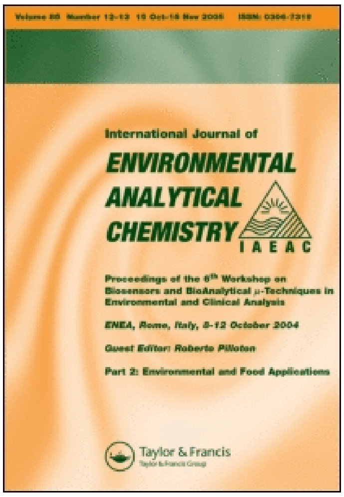


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

An Evaluation of the Chemical Composition of Precipitation Sampled with 21 Identical Collectors on a Limited Area

J. Slanina[a]; J. G. Van Raaphorst[a]; W. L. Zijp[a]; A. J. Vermeulen[b]; C. A. Roet[b]
[a] Netherlands Energy Research Foundation (ECN), [b] Provincial Waterboard of Noord-Holland,

To cite this Article Slanina, J. , Van Raaphorst, J. G. , Zijp, W. L. , Vermeulen, A. J. and Roet, C. A.(1979) 'An Evaluation of the Chemical Composition of Precipitation Sampled with 21 Identical Collectors on a Limited Area', International Journal of Environmental Analytical Chemistry, 6: 1, 67 — 81

To link to this Article: DOI: 10.1080/03067317908071160

URL: http://dx.doi.org/10.1080/03067317908071160

Intern. J. Environ. Anal. Chem., 1979, 6, pp. 67 81

Printed in Great Britain

An Evaluation of the Chemical Composition of Precipitation Sampled with 21 Identical Collectors on a Limited Area

J. SLANINA, J. G. VAN RAAPHORST and W. L. ZIJP

Netherlands Energy Research Foundation (ECN)

A. J. VERMEULEN and C. A. ROET

Provincial Waterboard of Noord-Holland

(*Received April 20, 1978*)

Twenty-one raincollectors were placed together in a flat area. From 11 collectors samples were taken on a daily basis and from 10 collectors on a monthly basis. The results of the analysis for SO_4^{2-}, Cl^-, NO_3^-, NH_4^+, Na^+, Pb^{2+} and pH of the daily samples agreed very well. The results of the monthly samples, analysed for Cl^-, Na^+, Ca^{2+}, Fe^{3+}, F^-, Pb^{2+}, Zn^{2+}, Cd^{2+}, and Cu^{2+}, were less satisfactory. Differences up to 50% are found between the results of daily and monthly samples.

KEY WORDS: Comparative study, air pollution, precipitation samples, collectors.

1. INTRODUCTION

A number of research institutes and governmental agencies are involved in research concerning the chemical composition of precipitation in The Netherlands.

The aims of these investigations differ considerably. For instance, the total amount of inorganic salts that is deposited by precipitation is of great interest for agronomists and authorities concerned with the quality of soil, surface and drinking water and the environment in general[1]. Other institutes are investigating wash-out and rain-out rates for precursors and products in plumes of power plants[2], etc. In a number of discussions between all involved groups in The Netherlands, two major problems were defined in precipitation chemistry:

1) If one measures the chemical composition of rain water by means of a collector, what is the value of these data? Will collectors placed in the same area yield the same results or are large variations possible over a short distance?

2) What is the ratio between wet and dry deposition?

The department of environmental control of Provinciale Waterstraat van Noord-Holland (the provincial Water Board of Noord-Holland), a regional agency, which is responsible for environmental protection in the province of Noord-Holland, operates an extensive network by ECN.

To determine the value of the results of this network it was decided to execute a field experiment, which would, at least partially, answer the question of the short distance variation of the chemical composition of precipitation. Such experiments have been made in the U.S.[3] but not yet in The Netherlands.

For this purpose we have placed 21 identical rain gauges in a pasture near the village of Heerhugowaard, in the province of Noord-Holland. This area, situated in the north-western part of The Netherlands, is relatively free of pointsources, the nearest heavy industry is located at a distance of 25 kilometers.

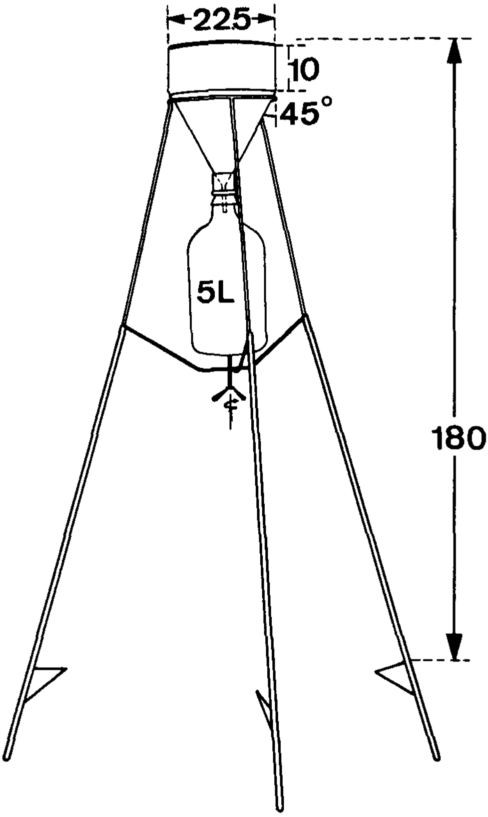
Eleven collectors were sampled daily and the precipitation samples were analyzed for sulphate, nitrate, chloride, pH, ammonium, sodium and lead. Ten collectors were sampled on a monthly basis and sodium, calcium, iron, zinc, lead, cadmium, copper, chloride and fluoride were measured.

2. PROCEDURES

2.1. Collection

The 11 precipitation collectors for daily measurements and the 10 collectors for montly samples were composed of polyethylene funnels fitted to iron tripods which were well painted to prevent contamination by rust (Figure 1). The polyethylene collecting bottle is attached by a screw cap to the funnel and supported by the tripod. Both the funnels and the collection bottles were placed in dilute nitric acid to test whether the polyethylene contained heavy metals, but no contamination was detected.

The collectors were positioned in a pasture, length 320 meters, width 75 meters. The distance between the collectors and the nearest trees was at least eight times the height of the trees (see Figure 2). Eleven collectors were emptied every day if the precipitation exceeded 0.3 mm. Ammonium, sodium, lead, pH, sulphate, nitrate and chloride were measured.



Rig for rain collection in North Holland Measures in cm.

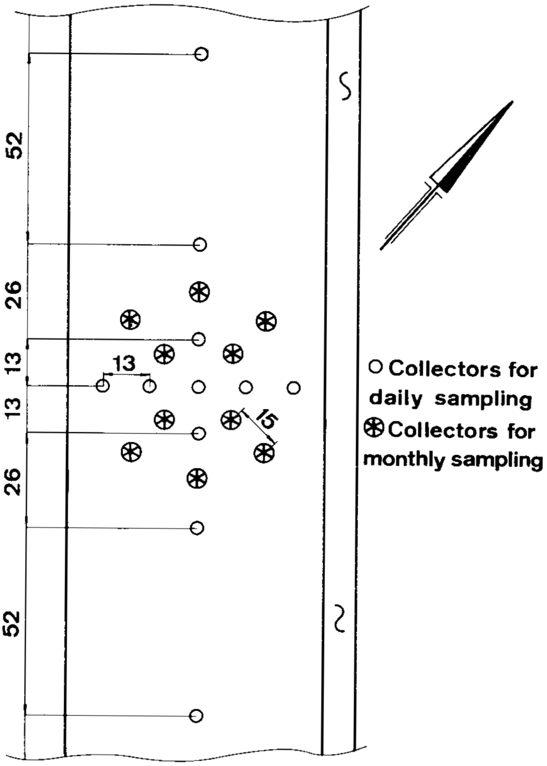
FIGURE 1

Ten collectors were sampled each month. We wanted to measure the concentration of heavy metals in the samples. So 40 ml concentrated nitric acid were added to the collection bottles before they were installed to avoid adsorption of trace constituents on the polyethylene walls and to inhibit growth of algae and bacteria. Sodium, calcium, iron, zinc, copper, cadmium, chloride and fluoride were determined.

2.2. Analytical procedures

Sodium, calcium, iron, zinc, lead, copper and cadmium are measured by atomic absorption spectrometry. The sample is acidified to 0.2 M with nitric acid and is allowed to stand for some days. Some metals, e.g. zinc and copper, require some time to dissolve completely.

This treatment is insufficient for iron. The sample is filtered through a 4 μm millipore filter and the filter plus precipitate, which contains up to 80% of all iron, is digested in a teflon bomb by means of 4 ml concentrated nitric acid at a temperature of 150°C.



POSITION OF THE COLLECTORS

FIGURE 2

Sodium, calcium, iron and zinc are measured by use of an acetylene-oxygen flame. Rain water is a very favourable matrix for A.A.S., no background correction is necessary. The analyses are performed by a dual channel dual monochromator instrument, and two elements can be measured simultaneously. The conditions of the analyses are given in Table I.

TABLE I
Analysis of Na, Ca, Fe and Zn by A.A.S.-flame

Element	Wavelength in nm	Concentration range in ppm	Precision in % rel.
Na	589.6	0.05–20	2
Ca	427.7	0.05–10	2
Fe	428.3	0.01– 2	2
Zn	219.9	0.01– 0.2	2

Lead, cadmium and copper are measured by means of a graphite furnace, lead at 283.3 nm, concentration range 0.002–0.2 ppm, cadmium at 228.8 nm, concentration range 0.1–10 ppb, copper at 324.7 nm, concentration range 1–50 ppb. The precision is typically 3–5% relative. We use simulated rain water as a standard, with sodium (5 ppm), calcium (2 ppm) and iron (0.5 ppm) added.

For the analysis of *chloride and fluoride* a chloride or fluoride ion selective electrode is used. The concentration in the sample is determined according to the method of Gran, by means of standard addition. We prefer the standard addition method to a direct measurement because of the better estimate of the total amount of chloride or fluoride available (i.e. the sum of free and complexed ions). A minimum sample of 5 ml is required, the concentration range for the chloride electrode is 1–1000 ppm, for the fluoride electrode the concentration range is 0.02–100 ppm and the precision is 2–5% in both cases.

Sulphate is measured by nephelometry. 20 μl 0.5 m HCl and 20 μl 1 m H_2O_2 are added to a sample of 4 ml, to attain $pH=1$ and to oxidise sulphite to sulphate. Solid bariumchloride (25 mg) is added and the sample is shaken vigorously. Near the surface of the crystals the Ba^{2+} concentration will be high, and very small bariumsulphate crystals are formed, which have a low deposition velocity. After 15 minutes the sample is shaken again and the formed $BaSO_4$ is measured nephelometrically at 530 nm. The concentration range is 0.5 to 50 ppm, the precision is 2–5%.

Nitrate is determined by means of a UV spectrophotometric method, developed in our laboratory[4]. A sample of 3 ml is acidified with 3 ml 0.2 M perchloric acid. The sample solution is pumped through a filter, which consists of active carbon on a carrier material (Filopur, Basel, Switzerland). Interfering organic species and suspended materials are removed and the absorbance of the nitrate ions is measured at 210 nm. The range of the method is 0.1–30 ppm, the precision is 0.6–3%.

Ammonium analyses are performed by means of an ammonia-gas-sensing electrode. A sample (5 ml) is mixed with 0.1 ml 4 M sodiumhydroxide to convert all ammonium ions to NH_3. The ammonium is determined by a calibration curve. The selectivity of the electrode and the absence of complexing agents make a standard addition procedure unnecessary. The concentration range of the method is 0.05 to 200 ppm, the precision is 1.5–7 %.

The *amount of precipitation* was measured by weighing the sample bottles before and after the sampling period.

3. APPARATUS

Atomic absorption spectrometer:	Jarrel-Ash 881, dual beam-dual monochromator system.
Graphite furnace:	Graphite furnace (HGA 74), Perkin-Elmer.
Spectrophotometers:	Zeiss PMQ II, equipped with a log-lin converter, Optilab, Sweden. Vitatron UC-II, in a fluorescence configuration.
Amplifiers:	Input impedance $<5.10^{12}\,\Omega$, with adjustable span and offset, ECN-design
Chloride electrode:	Orion 93-17, U.S.A.
Fluoride electrodes:	Orion 94-09 Orion 9609, with built-in reference electrode.
Ammonia electrodes:	Orion 95-10, and E.I.L. 8002-B, England.

4. RESULTS

Tables 2 and 3 give the results of the collectors for daily samples. In the period of the experiment precipitation exceeded 19 times 0.3 mm, and was analysed. The average value of each measured quantity of 11 collectors for one sampling period is $\bar{u}$ and $s(\bar{u})$ is the estimate of the standard deviation in the average,

$$s(\bar{u})=\sqrt{\frac{\sum_1^m (u_j-\bar{u})^2}{m(m-1)}} \qquad m=\text{number of collectors}$$

$$u_j=\text{result for collector } j$$

The results of the monthly samples are given in Table 4. $\bar{u}$ is the average value and $s(\bar{u})$ is the estimate of the standard deviation in the average of 10 collectors.

TABLE II

Results of the daily precipitation sampling of pH, SO_4^{2-}, NO_3^- and Cl^-, in ppm

	m.m. precip.		pH			SO_4^{2-}			NO_3^-			Cl^-		
Sample	$\bar{u}$	$s(\bar{u})$	$\bar{u}$	$s(\bar{u})$	Range	$\bar{u}$	$s(\bar{u})$	Range	$\bar{u}$	$s(\bar{u})$	Range	$\bar{u}$	$s(\bar{u})$	Range
1	3.93	0.04	4.64	0.02	4.58–4.71	23.05	0.58	20.4–26.4	5.31	0.14	4.8–6.5	2.10	0.29	1.2–4.6
2	0.84	0.05	4.16	0.02	4.05–4.28	9.65	0.51	7.7–10.4	5.32	0.20	4.1–6.1	6.83	0.26	3.1–5.5
3	6.74	0.05	4.42	<0.01	4.40–4.43	6.81	0.19	6.1–7.7	1.71	0.03	1.6–1.8	7.27	0.03	6.9–7.5
4	8.79	0.12	4.34	0.01	4.30–4.40	4.71	0.20	3.7–5.8	1.86	0.02	1.8–1.9	2.27	0.03	2.1–2.4
5	0.85	0.02	4.18	0.01	4.10–4.22	11.92	0.78	8.0–16.3	5.39	0.22	4.4–6.5	2.84	0.14	2.6–3.9
6	0.99	0.02	4.12	0.02	3.99–4.20	22.88	0.57	19.2–24.8	15.49	0.28	14.4–17.1	6.06	0.23	5.3–7.8
7	5.87	0.04	3.72	0.02	3.61–3.85	18.84	0.56	17.3–22.9	4.30	0.11	3.9–4.8	11.67	0.40	9.4–13.2
8	3.60	0.08	4.50	0.03	4.39–4.76	28.44	0.52	26.1–31.5	8.99	0.06	8.5–9.3	6.32	0.11	5.7–6.9
9	1.89	0.02	4.81	0.04	4.65–5.10	19.02	0.55	17.4–23.6	5.39	0.08	5.2–6.0	6.34	0.11	6.2–7.0
10	1.42	0.04	4.71	0.06	4.35–5.00	18.88	1.63	12.1–28.7	11.69	1.08	7.2–16.6	8.87	0.57	6.0–11.7
11	0.90	0.01	4.90	0.09	4.68–5.65	8.50	0.31	7.4–11.2	3.76	0.09	3.4–4.0	7.77	0.19	7.1–8.3
12	1.10	0.04	3.79	0.03	3.60–3.80	32.05	0.52	28.6–33.2	30.71	0.34	28.8–33.4	66.71	1.35	58.5–73.8
13	2.87	0.02	4.38	0.03	4.22–4.58	12.07	0.63	10.3–15.5	8.86	0.60	7.8–14.3	25.48	0.64	23.0–30.4
14	1.06	0.02	6.32	0.10	5.75–6.75	32.05	0.69	28.5–36.3	14.17	0.90	6.4–17.3	12.93	0.27	11.3–14.6
15	2.55	0.04	6.27	0.11	5.43–6.70	19.25	0.48	17.1–22.0	6.44	0.18	6.1–7.3	5.20	0.24	4.3–7.7
16	0.75	0.02	6.02	0.18	4.90–6.88	23.95	0.52	17.9–26.2	12.96	0.68	9.3–17.2	30.70	1.20	26.3–36.4
17	3.22	0.05	4.58	0.10	4.32–5.20	14.34	0.56	11.1–18.2	6.20	0.20	5.0–7.5	4.06	0.12	3.7–4.8
18	0.87	0.02	6.74	0.07	6.40–7.10	33.25	1.19	25.3–43.8	13.97	1.19	7.5–17.9	12.73	0.33	7.6–14.4
19	3.65	0.02	6.06	0.08	5.70–6.30	8.46	0.21	7.2–9.0	3.88	0.11	3.3–4.4	8.76	0.07	7.0–9.1

TABLE III

Results of the daily precipitation sampling of NH_4^+, Na^+ and Pb^{2+}

	NH_4^+ [ppm]			Na^+ [ppm]			Pb [ppb]		
Sample	$\bar{u}$	$s(\bar{u})$	Range	$\bar{u}$	$s(\bar{u})$	Range	$\bar{u}$	$s(\bar{u})$	Range
1	3.40	0.20	2.6– 4.4	0.59	0.02	0.51– 0.77	66.8	2.3	56– 82
2	6.83	0.26	5.5– 8.5	1.86	0.09	1.29– 2.12	120.3	13.1	80–235
3	2.90	0.07	2.5– 3.2	3.90	0.03	3.78– 4.05	34.5	1.0	31– 44
4	1.88	0.04	1.7– 2.1	1.16	0.01	1.12– 1.20	27.3	0.7	25– 32
5	1.58	0.15	1.5– 1.8	1.14	0.11	1.00– 1.50	118.5	6.7	83–158
6	6.39	0.15	5.6– 7.3	3.20	0.10	2.9 – 4.0	117.4	4.2	98–130
7	6.76	0.22	5.6– 7.9	1.31	0.08	1.16– 2.06	98.9	3.1	84–116
8	9.31	0.16	8.1– 9.8	3.54	0.09	3.1 – 4.0	45.6	1.1	39– 51
9	6.59	0.27	5.8– 7.8	3.04	0.04	2.05– 3.1	74.2	3.3	56– 88
10	7.08	0.69	4.4–10.7	4.22	0.31	2.6 – 5.5	60.0	3.9	43– 80
11	2.83	0.08	2.3– 3.0	3.85	0.09	3.55– 4.7	47.3	4.2	31– 81
12	13.88	0.70	10.0–17.2	27.80	0.49	26.0 –30.5	187.5	7.5	156–245
13	4.61	0.45	3.9– 7.8	12.45	0.22	11.7 –14.0	110.4	3.5	97–135
14	21.66	1.92	14.7–27.7	7.06	0.13	6.1 – 7.6	148.3	8.1	102–202
15	8.54	1.41	5.1–21.8	3.33	0.12	2.8 – 4.0	56.5	5.3	27– 80
16	5.99	0.61	4,4–11.3	19.25	0.60	17.2 –23.2	129.9	8.1	82–174
17	6.57	1.25	3.8–18.5	2.29	0.07	2.10– 2.75	55.6	2.5	47– 75
18	31.46	4.46	12.9–64.6	9.79	0.43	8.3 –12.4	173.5	10.4	102–215
19	2.94	0.21	1.9– 4.1	5.01	0.05	4.8 – 5.3	24.3	2.2	28– 45

TABLE IV

Results of monthly precipitation sampling

	mm precip.		Chloride†			Fluoride			Sodium†			Calcium†		
Sample	$\bar{u}$	$s(\bar{u})$	$\bar{u}$	$s(\bar{u})$	Range	$\bar{u}$	$s(\bar{u})$	Range	$\bar{u}$	$s(\bar{u})$	Range	$\bar{u}$	$s(\bar{u})$	Range
Feb.‡	23.22	0.55	5.85	0.89	4.3–10.0	120.3	3.50	111–133	1.95	0.02	1.9– 2.0	1.26	0.05	1.04–1.38
March	15.01	0.71	8.51	0.51	6.3–12.1	113.5	3.95	95–134	3.67	0.17	3.1– 4.6	2.52	0.17	1.92–3.5
April	6.32	0.29	11.99	0.54	9.7–12.4	110.8	5.09	94–128	10.88	0.66	8.8–16.2	4.60	0.31	3.8 –6.5
May	7.83	0.22	6.20	0.09	5.7– 6.8	171.0	2.80	162–189	4.26	0.37	3.5– 7.5	2.42	0.08	1.9 –2.8

	Lead			Iron†			Zinc			Copper			Cadmium		
Sample	$\bar{u}$	$s(\bar{u})$	Range	$\bar{u}$	$s(\bar{u})$	Range	$\bar{u}$	$s(\bar{u})$	Range	$\bar{u}$	$s(\bar{u})$	Range	$\bar{u}$	$s(\bar{u})$	Range
Feb.‡	72.17	7.03	56– 92	0.528	0.046	0.33–0.64	180.0	66.1	103–510	22.83	1.54	19–28	1.35	0.10	1.0– 1.7
March	75.20	4.62	52–118	1.66	0.088	1.35–2.29	200.9	59.2	118–730	16.10	1.67	11–25	1.21	0.11	0.7– 1.7
April	123.2	11.08	84–200	3.21	0.34	2.32-5.00	178.3	29.3	112–389	22.00	2.25	13–38	2.59	0.95	1.1–11.0
May	80.30	3.53	62–121	4.59	0.51	2.30–7.20	163.8	34.4	101–433	13.00	0.71	10–18	1.26	0.07	1.1– 1.7

†In ppm, all other elements in ppb.

‡Only six collectors were used.

5. STATISTICAL EVALUATION

The weighed average value c of each species is calculated from the average per sampling period $\bar{u}_i$, the number of sampling periods n and the average amount of precipitation per sampling period $\bar{h}_i$, according to the relation:

$$c = \frac{\sum_{i=1}^{n} \bar{h}_i \cdot \bar{u}}{\sum_{i=1}^{n} \bar{h}_i} \qquad (1)$$

The standard deviation in the average value of n sampling periods is given in formula 2 on the assumption, that no correlation exists between $\bar{u}_i$ and $\bar{h}_i$. In our case no correlation was found for all ions except one. Only lead showed a slight correlation (corr. coeff. = 0.60).

$$s^2(c) = \sum\left[\left(\frac{\delta c}{\delta \bar{h}_i}\right)^2 \cdot s^2(\bar{h}_i)\right] + \sum\left[\left(\frac{\delta c}{\delta \bar{u}_i}\right)^2 \cdot s^2(\bar{u}_i)\right] \qquad (2)$$

where

$s(c)$ = estimate of the standard deviation of C

$s(\bar{h}_i)$ = estimate of the standard deviation of $\bar{h}_i$

$s(\bar{u}_i)$ = estimate of the standard deviation of $\bar{u}_i$.

Combination of (1) and (2) results in:

$$\frac{\delta c}{\delta \bar{h}_i} = \frac{\bar{u}_i \cdot \Sigma \bar{h}_i - \Sigma(\bar{u}_i \cdot \bar{h}_i)}{(\Sigma \bar{h}_i)^2} = \frac{\bar{u}_i - c}{\Sigma \bar{h}_i} \qquad (3)$$

and

$$\frac{\delta c}{\delta \bar{u}_i} = \frac{\bar{h}_i}{\Sigma \bar{h}_i} \qquad (4)$$

$s^2(c)$ can be calculated from (2), (3) and (4):

$$s^2(c) = \frac{1}{(\Sigma \bar{h}_i)^2} \{\Sigma \bar{h}_i^2 \cdot s^2(\bar{u}_i) + \Sigma(\bar{u}_i - c)^2 \cdot s^2(\bar{h}_i)\} \qquad (5)$$

The standard deviation of one collector $s(c_j)$ for n periods can be calculated from $s(c)$:

$$s(c_j) = s(c) \cdot \sqrt{m}$$

The results are given in Table V.

TABLE V

Standard deviation in % relative of each species

	Daily samples		Monthly samples	
Species	$s(c)$, $m=11$	$s(c_j)$	$s(c)$, $m=10$	$s(c_j)$
pH	0.21	0.7		
SO_4	0.87	2.9		
NO_3	1.01	3.3		
Cl	1.01	3.3	5.80	18.3
F			1.67	5.3
NH_4	2.4	8.1		
Na	0.74	2.5	3.10	9.8
Ca			3.18	10.1
Fe			5.06	16.0
Zn			18.76	59.3
Pb	1.22	4.0	4.65	14.7
Ca			4.60	14.5
Cd			8.97	28.4

$s(c)$ = standard deviation in weighed mean value for m collectors in % rel.
$s(c_j)$ = standard deviation in weighed mean value for 1 collector in % rel.

We have applied a t-test, in which the results of all collectors are successively compared in pairs. The existence of significant differences can be verified by this method. The null hypothesis was that there is no difference between two rainsamplers. A significance level of 95% was applied, which means there is a 5% chance to reject the hypothesis when it is true.

Since not two but more collectors are compared, the results form a matrix $u(i,j)$, where i stands for results per period and j denotes the collector.

The differences in the results of the collectors are generally not constant for all periods, but proportional to the results per period (e.g. errors in the dimensions of the collectors, in the horizontal position).

So we have decided to test the hypothesis that the relative, i.e. the standardized, paired differences are zero. Here standardized differences, $d(j, k)$, are defined as differences in units of the standard deviation of all observations in the same period.

The differences, $d(j, k)$, can be expressed as:

$$d(j,k)=\frac{u(i,j)-u(i,k)}{s(u_i)} \tag{6}$$

$$k=j+1, j+2, \ldots, m \quad \text{and} \quad j=1,2,\ldots,(m-1)$$

$s(u_i)$ is the estimate of the standard deviation in u_i.

The test criterium, $t(j,k)$, that must be compared to the critical value t_0 is given in the following equation:

$$t(j,k)=\frac{\bar{d}(j,k)}{s(d)/\sqrt{n}}=\frac{\bar{d}(j,k)}{s(d_m)} \tag{7}$$

$\bar{d}(j,k)$ = the average standardized difference

$s(d)$ = the estimate of the standard deviation in the difference

$s(d_m)$ = the estimate of the standard deviation in $d(j,k)$.

Since

$$\bar{d}(j,k)=\sum_{i=1}^{n}\frac{u(i,j)-u(i,k)}{n\cdot s(u_i)}$$

one has

$$s(\bar{d})=\sqrt{\frac{\sum_{i=1}^{n}\{d(j,k)-\bar{d}(j,k)\}^2}{n(n-1)}}$$

Since the null hypothesis reads that the differences between the mean values for each pair of collectors are zero, the test statistic becomes

$$t=\frac{\bar{d}(j,k)}{\sqrt{\frac{\sum_{i=1}^{n}\{d(j,k)-\bar{d}(j,k)\}^2}{n(n-1)}}}$$

The results are given in Table VI.

Two collectors for daily samples and two collectors for monthly samples are responsible for most of the large t-values. We suspect that they were not positioned horizontally.

To obtain an indication for the presence of dry deposition, the correlation between the concentration of several species in the samples and the number of days without precipitation in the sampling period was calculated by means of the computer program Correlatio[5].

The orthogonal regression line $x\cos\rho+y\sin\rho=n$ was used.

A significance level of 95% was adopted, corresponding to a critical value $r=0.48$ for a significant correlation.

The results are given in Table VII.

TABLE VI

Frequency of $t>t_0$ for a significance level of 95% as a test for significant differences between the results of the collectors

	Monthly samples	Daily samples
Matrix	3 × 10	19 × 11
Total of t values	45	55
Degrees of freedom	2	18
$t(o)$	4.30	2.10
	frequency $t>t_0$	frequency $t>t_0$
Species		
SO_4		4
NO_3		2
Cl	1	
F	5	
NH_4		1
Na	0	1
Ca	8	
Fe	1	
Zn	7	
Pb	1	3
Cu	5	
Cd	0	
pH		27
Precipitation	7	26

TABLE VII

Correlation between concentration of various species and days without precipitation

Species	Correlation coefficient	Significant correlation
pH	0.16	–
SO_4	0.71	+
NO_3	0.51	+
Cl	0.17	–
NH_4	0.41	–
Na	0.21	–
Pb	0.25	–

6. DISCUSSION AND CONCLUSIONS

The results of the experiment allow the conclusion that the analysis of precipitation sampled from a number of collectors positioned near each other in favourable conditions, will give comparable data.

The standard deviation of the results of the daily samples exceeds barely the standard deviation of the employed analytical methods, but the standard deviation in the results of the monthly samples is much higher.

If the results of all daily samples during a month are added and compared with the data of the corresponding monthly sample, we find unexpected differences (see Table VIII).

TABLE VIII

Comparison of the results of monthly and daily samples per month

		Monthly samples		Daly samples[a]		$\frac{\bar{u}_m}{\bar{u}_d}$
Species	Month	$\bar{u}_m$	$s(\bar{u}_m)$	$\bar{u}_d$	$s(\bar{u}_d)$	
Cl	February	5.85	0.89	4.03	0.06	1.45 ± 0.22
	March	8.51	0.51	8.98	0.19	0.95 ± 0.06
	April	11.99	0.54	22.90	0.41	0.52 ± 0.03
	May	6.20	0.09	9.33	0.14	0.66 ± 0.01
Na	February	1.95	0.02	2.01	0.01	0.97 ± 0.01
	March	3.67	0.17	2.61	0.05	1.41 ± 0.07
	April	10.88	0.66	10.86	0.15	1.00 ± 0.06
	May	4.26	0.39	5.73	0.09	0.74 ± 0.07
Pb	February	72.2	7.0	47.6	0.9	1.52 ± 0.15
	March	75.2	4.6	74.0	1.5	1.02 ± 0.07
	April	123.2	11.1	108.8	2.8	1.13 ± 0.11
	May	80.3	5.5	60.7	1.9	1.32 ± 0.10

[a] $\bar{u}_d = \frac{1}{m} \cdot \sum_{1}^{m} \frac{\Sigma u_i \cdot h_i}{\Sigma h_i}$ for one month.

The conclusion seems justified that the results of monthly measurements are less trustworthy than those from daily samples, perhaps because of the influence of algae and bacteria.

The set-up of the experiment does not permit to draw definitive conclusions about the importance of dry depositions, but the lack of correlation between the number of dry days in the sampling periods and the concentration of the different species in the first sample of rain water taken after the dry days, suggests that wet deposition dominates under the conditions of the experiment. At the present, we are performing an experiment where we use collectors for total deposition and for wet deposition only, to get a better insight in the ratio of wet and dry deposition.

Literature

1. A. J. Vermeulen, *Immissie-onderzoek met behulp van regenvangers; opzet, ervaringen en resultaten*. Report of Provinciale Waterstaat van Noord-Holland (1977).
2. J. B. Luten, *Neutron activation analysis of trace elements in rainwater*. Thesis, Univ. of Utrecht, The Netherlands (1977).
3. J. N. Galloway, G. E. Likens, *Water, Air and Soil Pollution* **6,** 241 (1976).
4. J. Slanina, W. A. Lingerak and L. Bergman. *Z. Anal. Chem.* **280,** 365 (1976).
5. C. Foggi and W. L. Zijp. "Data treatment for the isotopic correlation technique." Contribution to *Safeguarding Nuclear Materials*. Proc. of an IAEA Symposium, held in Vienna, 20–24 October 1975. (IAEA, Vienna, 1976.)