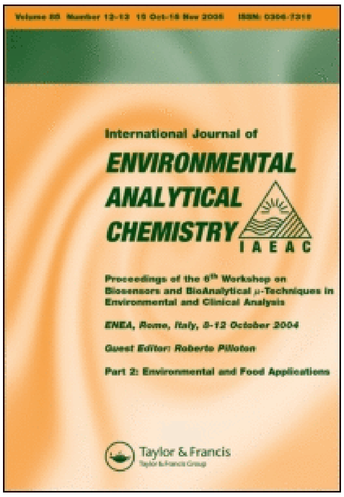

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The Stability of Precipitation Samples under Field Conditions†

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Eight wet-only samplers, placed in one location were used to sample precipitation. Subsamples were taken from the sample bottles directly after the precipitation event and at regular intervals up to a period of 2100 hours and analysed, while the samples stayed in the samplers under field conditions.

Outliers were deleted by means of conventional statistical techniques. The resulting data base was tested by means of the *F*-test for consistency and for changes in the chemical composition of precipitation samples directly after sampling or after an extended stay under field conditions. Eighty-one percent of the samples showed consistent results and no clear indication of chemical changes was found.

Regression analysis indicated that the uncertainties for samples analysed after 1 week are less than 5% generally for the bulk elements and less than 14% for the trace elements. After a period of 400 hours the uncertainties for the bulk elements increase to a level of 5–10% and 5–30% for the trace elements.

Contamination, as a result of handling the samples to obtain subsamples, seems the main cause for the increase of the concentrations which was observed.

Contamination during sample pretreatment and analysis in the laboratory is probably of minor importance.

KEY WORDS: Precipitation sampling, field conditions, contamination, sample stability, wet-only sampler.

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INTRODUCTION

The stability of precipitation samples for the period between sampling and analysis is an absolute requirement to obtain reliable data on the chemical composition of precipitation. A number of studies have been published on this issue, but these contain contradictory information.

Madsen *et al.*[1] indicated that no changes in the chemical composition of precipitation samples occur within a period of 14 days. According to Granat precipitation samples are stable, under Scandinavian conditions,[2] for at least a month.

The sample bottles of the samplers, employed in the MAP3S network[3] were cooled to a temperature of 4°C, to avoid changes in chemical composition. Mueller *et al.*[4] have reported that only instant freezing of the precipitation samples can guarantee chemical stability.

Ridder *et al.*[5] concluded that serious changes in the concentrations of nitrate and ammonium can take place in samples, collected in The Netherlands on a monthly basis.

Recent studies, in which the results obtained by weekly and event sampling have been compared for some bulk elements (H^+, NH_4^+, SO_4^{2-}, NO_3^-, Mg and Ca), have also shown contradictory results. De Pena *et al.*[6] reported lower concentrations for these bulk elements in the weekly samples. However, Sisterson *et al.*[7] have measured only lower concentrations for H^+ and NH_4^+ in the weekly samples. For NO_3^- no significant change in concentration was detected.

A study by Gnauk *et al.*[8] has also shown that the changes in concentration of some bulk elements, as H^+, NH_4^+ (and NO_3^-), increased with the storage time. Instabilities in the concentrations of sulfate and potassium (generally considered to be stable) were observed.

The results of a number of precipitation chemistry studies by ECN[9] have not indicated that instability of precipitation samples posed problems. But it is clear that even relatively small changes are of importance if trends in the chemical composition of precipitation are to be measured.

To test the stability of precipitation samples we have employed 8 identical wet-only samplers at the site of ECN. Rain-water samples were analysed directly after the precipitation event by taking a subsample from the collection bottle. The rest of the sample stayed in the collection bottle which was replaced in the sampler. More subsamples were taken after different time intervals, and the results were compared with earlier results to detect changes in the chemical composition as a function of chemical instability or contamination caused by handling the samples in the field or laboratory.

EXPERIMENTAL

Precipitation sampler

The construction of the sampler is given in Figure 1. The sampler consists of a polyethylene body, height 800 mm, with a wallthickness of 10 mm to ensure sufficient mechanical strength and thermal insulation. The sampler is opened by means of a 24 V motor. The innerside of the cover is not exposed to dry deposition, because the position of the cover is not inverted during opening or closing of the sampler.

The sampler is equipped with a controlled heating to maintain a minimum temperature of 4°C inside the sampler.

Usually, the sampler contains a sample changer with 7 positions which is actuated by a 24 V pulse, however the sample changer was not used in this experiment. All electronic parts (counters for the number of movements of the cover, timer for the total period of time during which the sampler is opened, control of the sample changer, 12 V and 24 V supplies) are placed together in a box fastened on the body of the sampler.

The sampler is designed to avoid uncertainties by contamination or by losses caused by adsorption on the walls of the funnel or collection bottle. Polyethylene is the main construction material and no metal parts are present near the funnel. A more extensive description is given in Ref. 9

The sampler fulfils two important requirements:

The large surface ($80\,cm^2$) of the detector ensures a rapid response to the onset of precipitation, so a difference of less than 1% relative in the amount of precipitation is observed if the sampler is compared with total deposition samplers equipped with the same funnel. Furthermore the cover is sufficiently distant from the funnel to avoid disturbance of the wind flow pattern near the funnel and splash off.

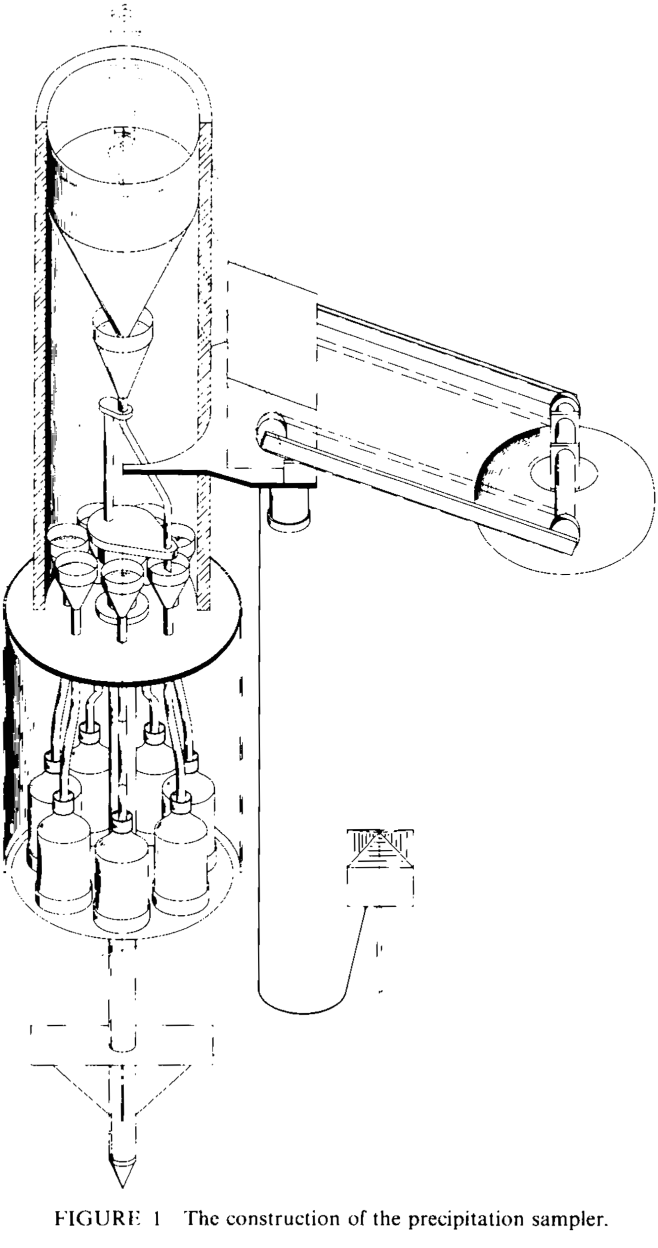

FIGURE 1 The construction of the precipitation sampler.

The samples are protected against direct sunlight to minimize the growth of algae. The sampling for this series of experiments was spread over a period of six months (April to October) in 1983 and 1984. In this period biological influences and high temperatures can be important factors causing deterioration of precipitation samples.

Sampling

The funnel and the collection bottles were cleaned with diluted nitric acid and doubly demineralized water before the start of each experiment. The samplers were activated if the weather-forecast indicated sufficient precipitation. At least 4 subsamples of 24 ml must be available to characterize the chemical composition of the precipitation sample for a period of one week, so the minimal sample size was about 100 ml, equivalent to 2.5 mm of precipitation. A subsample of 24 ml was taken immediately after the precipitation event and the sample bottle was replaced in the sampler. The next subsample was generally taken after 24 hours. Table I gives an overview of the subsamples taken in the fifteen experiments.

TABLE I

Overview of the subsamples taken in the fifteen experiments

Experiment	Sampling intervals in hours after precipitation event						
1[a]	0	2[b]	18[b]	24[b]	72	168	334
2[a]	0	2[b]	24[b]	101	190	334	
3[a]	0	27[b]	96	168	336		
4[a]	0	72	168	336			
5	0	25[b]	92	192	336		
6	0	26[b]	100	172	359	2163	
7	12	31[b]	81	176	351	1548	
8	10	38[b]	60	155	327	1528	
9	0	24[b]	361				
10	0	29[b]	76	202	341	1036	
11	0	25	72[b]	174	313	1008	
12	0	22[b]	94	312			
13	0	29[b]	75	173	342		
14	0	30[b]	75	175	360		
15	0	96[b]	288				

[a] Chromium was not analysed in this experiment.

[b] Only H, NH_4, SO_4^{2}, NO_3, Cl and F were analysed.

Sample pretreatment and analysis

A portion of 5 ml was taken from the subsample for the determination of H^+, NH_4^+, SO_4^{2-}, NO_3^-, Cl^- and F^-. The rest of the subsample was acidified to $pH = 1$ by means of nitric acid (supra pure) for analysis by Atomic Absorption Spectrometry and Induction Coupled Plasma Emission Spectrometry. The analysis of the not acidified portion of the subsample was carried out immediately.

H^+ and NH_4^+ were measured by Flow Injection Analysis combined with spectrophotometric detection. F^-, Cl^-, SO_4^{2-} and NO_3^- were determined by means of an Ion-Chromatograph equipped with a multiple detector system. Na, K, Mg, Ca, and Zn were measured by means of AAS using flame-techniques. For Pb, Cd and Cu a graphite furnace was employed. For the analysis of chromium ICP was employed. A more detailed description of the analytical methodology is given elsewhere.[9,10]

The accuracy of the computerized analytical methods used for the so-called bulk elements (H^+, NH_4^+, Na, K, Ca, Mg, Cl^-, SO_4^{2-}, NO_3^-) is 5% relative or better and determined by the fact that an automatic recalibration is carried out if the result of a standard differs more than 5% from the true value. The precision of the methods, between two successive recalibrations, is much better, in the order of 0.5 to 1% relative. The accuracy of the methods used for trace elements is typically 10% relative or better.

RESULTS

Elimination of outliers

The use of 8 identical samplers makes it possible to eliminate outliers caused by bird droppings, insects and other spurious factors which can influence the chemical composition of precipitation samples considerably.

The results of each set of 8 subsamples were tested whether a Gaussian distribution was present by means of w/s test (ratio between absolute spread and standard deviation). No significant deviations from Gaussian distribution were observed. Next, outliers were detected by means of a Dixon-test ($\alpha = 0.05$). If for 3 or more bulk elements outliers were detected in the results of a subsample, all results of that subsample were deleted because it was suspected that gross contamination had taken place. If for one or two bulk elements outliers were found, these results only were omitted from the data base. It should be noted however that only outliers caused by contamination, occurring during the sampling process, but also due to errors in sample pretreatment and analysis, are removed that way.

The number of outliers given in Table II under the heading "one or two outliers per subsample" gives the most likely upper limit of occurrences of contamination in the laboratory. The underlying assumption is that the chance of contamination for three or more bulk elements simultaneously is very slight.

So the conclusion is that less than 1.6% if of the 616 subsamples analysed for the bulk elements, have been possibly contaminated in the laboratory.

TABLE II

Outliers for all the results of the bulk- and trace elements

	Bulk elements	Trace lements
Total number of results	4959	2716
One outlier per subsample	51	66
Two outliers per subsample	28	22
Three or more outliers per subsample[a]	129	22

[a] The number of subsamples is 21 for the bulk elements and 6 for the trace elements.

Statistical evaluation of the results by means of the *F*-test

Usually linear regression analysis is applied to time series for the detection of changes in chemical composition. The drawback of this method is that a deviation in either the first or the last result of the series is not revealed in a sensitive way. So it was decided to apply an *F*-test to the results of each of the 15 experiments.

For each sampling interval per experiment maximal 8 results are obtained ($x_{i,j}$, i denotes the sampling interval, $i=1,2,\ldots,n$ and j the wet-only sampler, $j=1,2,\ldots,m$). The mean concentration per sampling interval C_i is computed by

$$C_i = \sum_{j=1}^{m} x_{i,j}/m$$

and the corresponding variance s_i^2 is calculated, for the same set of results, by

$$s_i^2 = \sum_{j=1}^{m} (x_{i,j} - C_i)^2/m(m-1).$$

The internal variance for n sampling intervals is calculated according to:

$$s_{\text{int}}^2 = n \Big/ \sum_{i=1}^{n} w_i \text{ (the statistical weight } w_i = 1/s_i^2\text{)}.$$

The external variance is computed from the mean concentrations (C_i) per sampling interval i and the overall mean concentration $(\bar{C})$ according to:

$$s_{\text{ext}}^2 = \frac{\sum_{i=1}^{n} w_i(C_i - \bar{C})^2/(n-1)}{\sum_{i=1}^{n} w_i/n}$$

$$\left(\text{the overall mean concentration } \bar{C} = \sum_{i=1}^{n} w_i C_i \Big/ \sum_{i=1}^{n} w_i\right)$$

The value F is calculated as $F = s_{\text{ext}}^2/s_{\text{int}}^2$

If the calculated F-values (for $\alpha = 0.05$) are smaller than a critical value, the results of the sampling intervals are assumed to be part of one population and no detectable change in chemical composition of precipitation is observed in that experiment.

The underlying assumption is that the results of all the sampling intervals should belong to the same population if no changes in chemical composition have taken place, or in other words, if the results of these sampling intervals are consistent.

Two corrections must be applied to the results of the F-test: (a) The automated analytical methods, employed in this study, are recalibrated if the results of standards differ more than 5% from the nominal values of those standards. This means that the mean concentration C_i can deviate 5% relative from the true value due to inacurracy of the calibration. If s_{int}^2 is small, the critical F-value can be exceeded due to this calibration inaccuracy without any real changes in the chemical composition of the samples. In view of all other uncertainties which occur in sampling and analysis of precipitation samples, we decided to accept the results of samples which showed s_{int} and s_{ext} values lower than 5% relative as consistent. This lower limit is chosen for practical reasons, not on strict statistical considerations. (b) Near the detection limits of the analytical methods a large scatter in C_i values can occur, which again does not reflect changes in chemical composition.

The results of the test are given in Table III. Inconsistent results caused by calibration inaccuracies or measurements of concentrations equal to the detection limits of the analytical methods are indicated. Completely consistent results are obtained for sodium, magnesium, nitrate, chloride and zinc for the whole set of results.

The less favourable results for the other elements can be a result of different processes. According to Mueller *et al.* the chemical composition changes very fast after sampling. The results of Ridder *et al.* indicate a more gradual process, so changes are observed as a function of elapsed time. To test the first hypothesis, the results of the first sampling interval (0 hours) of each experiment were omitted and the same procedure as described above was applied to the remaining data base. The second hypothesis was tested by omitting the results of the last sampling interval of each experiment. The results are given in Table IV.

There is no indication of rapid changes in concentration directly after sampling as only 8 of the 42 inconsistent results of the F-test, combining all elements and all experiments, become consistent after omitting the first result. No pattern can be recognized, so contrary to what was expected on basis of reports in the literature no great influence of the first sampling interval on the consistency of the results is observed.

Omitting the last results has a larger influence, 14 out of 42 F-test results become consistent, but again it is not possible to derive

TABLE III

The results of the F-test ($\alpha = 0.05$). Consistent results are indicated by (F). Inconsistent results caused by calibration errors (C) or concentrations equal to detection limits (D) of the analytical methods are also included.

	% of results passed as consistent	Experiment														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
H	60	C	C			F			C	C	F	D		C		C
NH_4	87	C	C	F	C	F	D	C	C	F	C		F		F	C
Na	100	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
K	73	C		F	F			C	F	F	F	C	F	F		F
Ca	87	F		F	F		F	F	F	F	F	F	F	F	F	F
Mg	100	F	F	F	F	C	F	F	C	F	F	F	F	F	C	F
SO_4	93	C	C	C	F	C	F	C	C		F	F	C	C	C	C
NO_3	100	C	F	C	F	C	F	C	F	F	F	F	F	C	C	C
Cl	100	C	C	F	F	F	F	C	C	F	F	F	F	F	F	F
F	73	F	F	C	D	F	F				F	D		F	F	C
Zn	100	F	F	F	F	F	D	F	F	F	F	F	F	F	F	F
Pb	67		C	F		C		C	C	F			F	C	F	F
Cd	53			C	D		F			F	F	F			F	F
Cu	53	F	F	F			F	C			F	F	F			
Cr	64	—	—			F				F	F	D		F	F	F
% of results passed as consistent	81	86	79	93	79	73	73	73	73	80	93	87	73	80	80	93

: Not analysed.

TABLE IV

A summary of the consistent results of the F-test from Table III (C), and the consistent results after omitting the results of the first sampling interval (1) or after omitting the results of the last sampling interval (L) are indicated

	Experiment														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
H	C	C			C			C	C	C	C	1	C		C
NH_4	C	C	C	C	C	C	C	C	C	C		C		C	C
Na	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
K	C	1	C	C	L		C	C	C	C	C	C	C	1	C
Ca	C	1	C	C	L	C	C	C	C	C	C	C	C	C	C
Mg	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
SO_4	C	C	C	C	C	C	C	C	L	C	C	C	C	C	C
NO_3	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Cl	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
F	C	C	C	C	C	C		L		C	C	L	C	C	C
Zn	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Pb		C	C	1	C	1	C	C	C	L		C	C	C	C
Cd	L	L	C	C	1	C			C	C	C	L	L	C	C
Cu	C	C	C		L	C	C			C	C	C	L	L	
Cr	—	—		—	C	L			C	C	C	1	C	C	C

—: not analysed.

generalized conclusions as no clear pattern is observed. If we do not take into consideration results from samples older than 400 hours, 11 results become consistent if we delete the last results. The level of consistency seems quite acceptable for the bulk elements, with the exception of H^+, caused by an unexplained spread in the results.

Statistical evaluation of the results by means of regression analysis

We have applied regression analysis on the pooled results for each element of the cleaned-up data base. For each experiment the concentrations for the sampling intervals within 400 hours after sampling, were divided by the mean concentration obtained from all sampling intervals of each experiment. In this way ratios were obtained for each element for all sampling intervals. Regression analysis was applied to all ratios for each element. In this way it is possible to investigate all results for one element of all experiments simultaneously.

The slope and the intercept, with the corresponding relative standard deviations are given in Table V. Figures 2–5 provide examples of plots of ratios versus time for H^+, NH_4^+, SO_4^{2} and NO_3^-.

On the basis of the calculated slope the expected uncertainty in the results of the bulk elements, analysed after a week (168 hours), is less than 5% relative, with the exception of potassium with an uncertainty of 8% relative. The uncertainties for the trace elements are generally higher, 13% for fluoride, 5% for zinc, 7% for lead, 1.5% for cadmium, 10% for copper and 0.5% for chromium.

If the samples are analysed after 400 hours the uncertainties for ammonium, sodium, magnesium, sulfate, nitrate and chloride are less than 5% relative. The uncertainties for H^+ (8%), potassium (20%) and calcium (8%) exceed this value. The uncertainties for the trace elements are 32% for fluoride, 12% for zinc, 16% for lead, 4% for cadmium, 24% for copper and 1% for chromium.

The fact that positive slopes were found by regression analysis for so-called "conservative compounds," compounds which are not subject to changes by e.g. biological activities, such as potassium, sulfate and chloride, points to contamination as a cause for the observed increase in nearly all concentrations. The samples were

TABLE V

Results of regression analysis of all experiments. Concentration ratios versus time in hours

Compound	Slope $\times 10^{-4}$	Stand. dev. $\times 10^{-4}$	Interc.	Stand. dev.
H^+	−1.9	1.2	0.99	0.02
NH_4^+	0.2	1.1	0.98	0.02
Na^a	0.8	0.2	0.99	0.004
K^a	5.0	0.8	0.91	0.01
Ca^a	1.8	0.5	0.97	0.01
Mg^a	1.1	0.3	0.98	0.005
SO_4^{2-}	0.9	0.5	0.98	0.01
NO_3^{-a}	1.0	0.3	0.99	0.005
Cl^{-a}	1.0	0.3	0.98	0.006
F^{-a}	8.0	2.4	0.86	0.03
Zn^a	2.8	1.2	0.93	0.02
Pb^a	3.8	0.9	0.92	0.02
Cd	1.2	1.3	0.96	0.03
Cu^a	5.7	1.0	0.89	0.02
Cr	0.3	4.1	1.03	0.07

[a] Correlation coefficient indicates a significant slope.

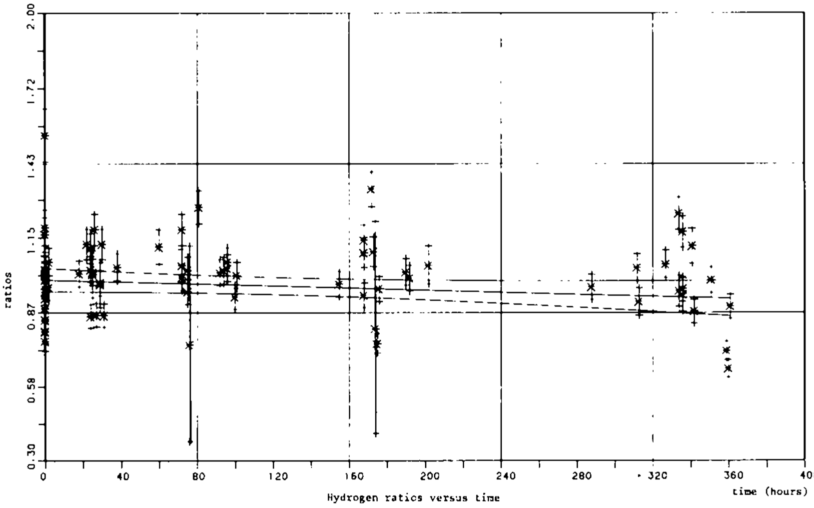

FIGURE 2 Hydrogen ratios versus time (hours).

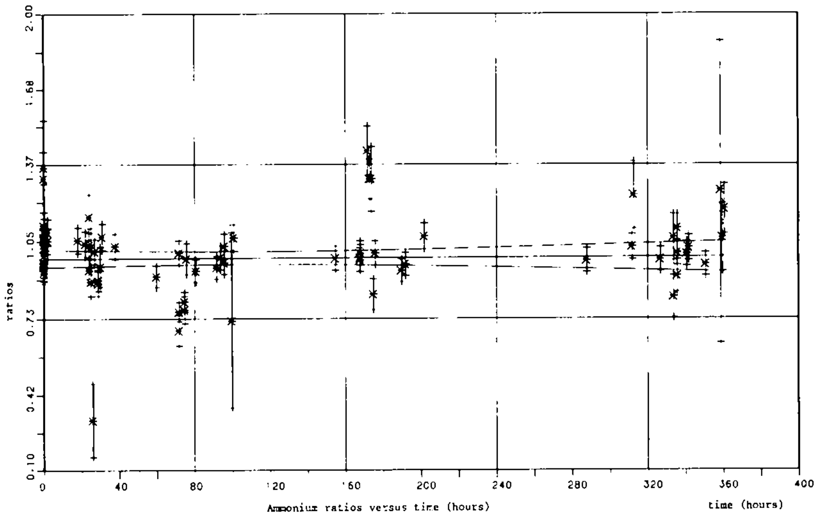

FIGURE 3 Ammonium ratios versus time (hours).

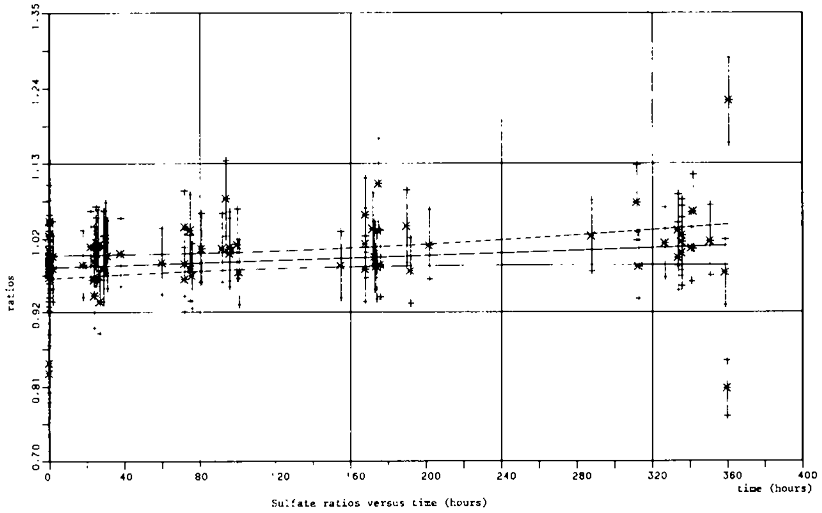

FIGURE 4 Sulfate ratios versus time (hours).

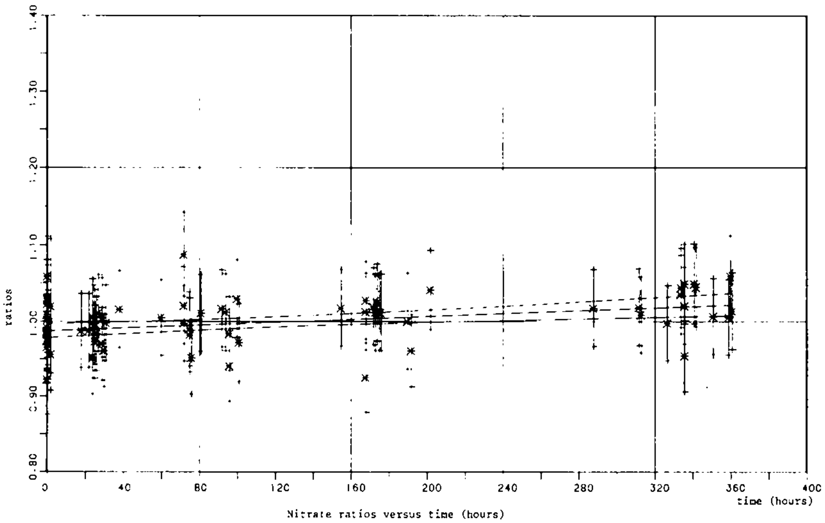

FIGURE 5 Nitrate ratios versus time (hours).

handled 5 times in average during each experiment in order to take subsamples. If we assume that the increase in concentrations is caused by contamination only, each handling of the samples has resulted in an average increase of about 1% relative for the bulk elements and about 3% relative for the trace elements fluor, zinc, lead, cadmium, copper, and chromium.

CONCLUSIONS

The stability of precipitation samples under field conditions in The Netherlands is acceptable for a period up to 1 week if uncertainties of about 5% relative for the bulk elements and of 10% for the trace elements are acceptable. The uncertainties increase to a level of 5-10% relative for the bulk elements and to 5-30% for the trace elements after a period of 400 hours. The results indicate that contamination during the sampling process is the dominant cause of increased concentrations of bulk- and trace elements. Contamination during sample pretreatment and analysis in the laboratory plays a minor role.

References

1. B. C. Madsen, *Atm. Env.* **16,** 2515 (1982).
2. L. Granat, On the deposition of chemical substances by precipitation, WMO-report, no. 368, pp. 71 78 (1974).
3. MAP3S, precipitation chemistry network, First periodic summary report, Battelle Pacific Northwest Laboratories, PNL-2402.
4. K. P. Mueller, G. Ahmeier, G. Gravenhorst, The influence of immediate freezing on the chemical composition of rain samples, in: *Deposition of Atmospheric Pollutants*, H. W. Georgii, J. Pankrath, eds. (D. Reidel, Publ. Comp.), pp. 125- 132, (1982).
5. T. B. Ridder, T. A. Buishand, H. F. R. Reijnders, M. J. 't Hart and J. Slanina, *Atm. Env.* **19,** 759 (1985).
6. R. G. De Pena, K. C. Walker, L. Lebowitz and J. G. Micka, *Atm. Env.* **19,** 151 (1985).
7. D. L. Sisterson, B. E. Wurfel, B. M. Lesht, *Atm. Env.* **19,** 1453 (1985).
8. Th. Gnauk, E. Brüggemann and W. Rolle, Nachrichten Mensch-Umwelt **13,** 60 77 (1985).
9. J. Slanina, V. D. I., *Berichte* **500,** 117 (1983).
10. J. Slanina, F. P. Bakker, P. A. C. Jongejan, L. van Lamoen and J. J. Möls, *Anal. Chim. Acta* **130,** 1 (1981).