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Letters to the Editor

A. J. Vermeulen^a

^a Department of Environmental Control, Provincial Waterboard, AE Overveen, The Netherlands

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Letters to the Editor

Dear Sir

With respect to the article "Collection and Analysis of Rainwater: Experimental Problems and the Interpretation of Results", published in *Intern. J. Environm. Anal. Chem.* 1979, vol. 7, pp. 161-176, I would like to make some remarks.

This article is about a research program on deposition and precipitation chemistry. Eight open and eight wet-only samplers, placed together on an open field near Den Helder, The Netherlands, were sampled three times a week. One of the conclusions was, that for many species the difference between the results of open and wet-only samplers was negligible.

To my opinion the results of this research have to be considered with some distrust.

In chapter 2.4 sub 2.4.1 we can read the following.

"All samplers were emptied three times a week on Monday, Wednesday and Friday. The sampling bottles were removed from the rainsamplers and closed immediately. All samplers were scrubbed with demineralized water, the water was allowed to drip out of the funnel during 10 minutes, and new weighed bottles were connected to the rain samplers".

My remarks are now as follows:

With respect to the open samplers (wet+dry deposition), the dry deposition is collected on the funnel surface and brought into the collecting bottles by rain.

On closer examination it will be obvious that the authors, while scrubbing the funnels, are losing a certain quantity of dry deposition. This last quantity can be very small if during the indicated sampling periods of two or three days, rain was falling just before the sampling bottles were changed, but it can be much more when rain did fall just after having connected new sampling bottles, and no more rain is falling during the rest of the sampling period of two or three days. It will be clear that, scrubbing the funnels every two or three days, during the whole sampling period of two or three months the lost part of dry deposition will increase with the number of dry days.

Hence during the period that this research was carried out, a great part of the dry deposition could have been lost and, in the extreme, the authors are comparing wet deposition with wet deposition!

In a recent article (Environmental Science and Technology, vol. 14, no. 7, July 1980) Hendry and Brezonik give results of research to the deposition ratio between wet-only and bulk rainsamplers. They did this research without scrubbing the funnels frequently. Hendry and Brezonik came to the conclusion that for a lot of ions dry fallout is of importance with respect to the total deposition (wet + dry fallout) and of comparable importance to rainfall with respect to the deposition of Ca, Na and Cl. (See table; in comparison with the results of Slanina *et al.*).

Ion	ratio bulk/wet-only deposition	Slanina <i>et al.</i>
Na	0.54	0.86
K	0.77	0.83
Ca	0.51	0.96
Mg	0.64	1.17
Cl	0.52	0.89
SO	0.89	1.00
PO ⁴ (ortho)	0.76	—
PO ⁴ (total)	0.40	—
NH ⁴	0.80	0.90
NO ₃	0.82	1.04

In table X and XI a correlation is given between SO_4^- and H^+ and NO_3^- and H^+ . From the results of those calculations some more or less important conclusions have been drawn by the authors, for example that HNO_3 and not H_2SO_4 is the predominant acid species in the North-western part of the Netherlands. I am surprised not to read a word about the sea-spray sulphate content of rainwater. Probably the authors simply forgot that their sampling location is situated close to the coast, which means that the concentration of sea-spray sulphate in rainwater is rather high. A very extensive research made by myself amongst other things in the considered area led to contents of sea-spray sulphate of 30 to 40% (on an average) of the total content of sulphate in rainwater. It will be obvious that in the calculation of the correlation SO_4^-/H^+ a correction for the quantity of sea-spray sulphate (Na_2SO_4) has to be made.

Under 2.4.2 we can read that samples less than 40 ml (aeq. to 0.1 mm rain) were discarded. However, because the inner diameter of the funnels is 22.3 cm, in my opinion all samples up to 1 mm rain were discarded.

Except for the most accurate handling and analyzing of the samples on the lab, in which I have all faith (I am well-known with the handling and

analyzing methods on the ECN), I have some doubts as to the validity of some of the conclusions drawn.

A. J. Vermeulen
Provincial Waterboard,
Department of Environmental Control,
Zijlweg 245,
2050 AE Overveen,
The Netherlands

Dear Sir,

This is with regard to Mr Vermeulen's remarks about our article "Collection and Analysis of Rainwater: Experimental Problems and the Interpretation of Results," Intern. J. Environ. Anal. Chem. Vol. 7 161-176 (1979). First of all we indeed discarded samples up to 1 mm rain instead of 0.1 mm as was erroneously mentioned.

Measuring dry deposition by comparing open and wet-only samplers is a most dangerous procedure: the scavenging efficiency of a rain sampler cannot be compared in any way with the scavenging efficiency of a wood or a lake.

We were mainly interested in the comparison of the two types of samplers only. If one does not very regularly clean the open samplers the results will be adulterated rapidly by bird droppings (very frequently in this part of the country), spider webs, insects, big soil particles and bacteria (which can induce changes in ammonia and nitrate content quite fast). So one had to choose between unreliable results or losses by frequently cleaning. We prefer the second choice.

Furthermore, if one does not clean the samplers at the beginning of a sample period, the dry deposition of the last period will always be attributed to the next one. This will influence further interpretation, especially if meteorological parameters are employed.

Statistically we could have lost 50% of the dry deposition, however, 20 of the 29 sampling periods occurred during front passages with prolonged and frequent rains during the sampling periods.

In our opinion the most important part of Mr. Vermeulen's remarks regards the influence of SO_2 or NO_x on the acidification of rain. Mr.

Vermeulen has correlated the SO_2 emission in The Netherlands with the H^+ concentration in the period 1956 to 1976. One must be very careful if aged data bases are used: At many occasions it is found that "trends" really are analytical artefacts if one goes further back than the late sixties. But apart from this difficulty, this approach of the origin of H^+ in rain is a fallacy. The typical conversion rates for SO_2 cited in literature are 1 to 4% per hour (Forrest *et al.* Atmosph. Environment vol. 13, pp. 1287–1297).

This means considering the mean wind velocity in The Netherlands of 6 m s^{-1} and the distance from De Bilt (where the H^+ data were taken) to the mean emission sources in The Netherlands of some 60 kilometers, that only 10% of the SO_2 is converted! On the other hand the conversion rates for NO_x can be as high as 14 % (Guicherit *et al.*, 11th Nato-CCMS Conference, 1980). The only realistic method would be to trace the precursor source regions for the sulfate coming down at the chosen spot, and then correlate the SO_2 emission to H^+ concentration in rain.

It is also doubtful that one can calculate the contribution of sulfuric acid versus nitric acid to acidification by looking at the sulfate and nitrate concentration of rain water. Acid components, in the form of aerosols or in droplets, can be neutralized e.g. by ammonia, during long range transport. Comparison of different parts of the world is a dangerous procedure in view of very different meteorological parameters.

For instance, further evaluation of our data indicates that the highest H^+ deposition takes place by rains in polluted marine air, not in rains of pure continental origin, as neutralization is much more complete in the latter case. The only way to investigate this problem in our opinion is to look at the correlation between certain species.

Correlations can lead to erroneous conclusions as well, hence other conditions must be met. In our case nearly stoichiometric ratios between the correlated species must be found before the conclusion can be drawn that two species e.g. H^+ and NO_3^- are present as HNO_3 . Correlations can also be found if these components which have a common source though not with stoichiometric composition. All sulfate values used for these calculations were corrected for sea-spray sulfate. This correction, however, is not very significant (5–10%) and data bases generated in The Netherlands which indicate 30–40% correction for sea-spray, should be checked immediately. The sea-spray correction has only a small influence on the correlations we find for 40 sampling periods.

Without sea spray correction species	corr. coef.	(wet deposition) found molar ratio
H^+ vs SO_4^{2-}	0.57	1.4
NH_4^+ vs SO_4^{2-}	0.71	2.1
H^+ vs NO_3^-	0.81	0.9
NH_4^+ vs NO_3^-	0.56	2.6
Na^+ vs SO_4^{2-}	-0.13	4
With sea spray correction species	corr. coef.	(wet deposition) found molar ratio
H^+ vs SO_4^{2-}	0.56	1.23
NH_4^+ vs SO_4^{2-}	0.72	1.9
H^+ vs NO_3^-	0.81	0.9
NH_4^+ vs NO_3^-	0.56	2.6
Na^+ vs SO_4^{2-}	-0.16	-4

The actual correlation coefficients are a bit different from those cited in the article, because we scrutinised our data base once again and deleted some highly suspicious samples.

We apologize for this somewhat lengthy reply, but the acid rain problem is for many areas in the world a rising menace. We therefore agree with Mr. Vermeulen on the importance that a correct scientific approach is chosen to identify important parameters.

J. Slanina
ECN, Energy Research Centre
Westerduinweg 3
Petten (NH)