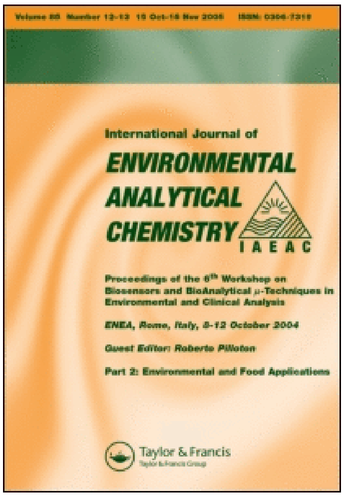

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Letter to the Editor

A. J. Vermeulen[a]
[a] Department of Environmental, Control of the Province of North-Holland, AE Overveen, The Netherlands

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Letter to the Editor

Dear Sir

With respect to the article "Collection and Analysis of Rainwater etc." (Slanina et al., vol. 7, pp. 161–176), my remarks on this article (vol. 9, pp. 221–223) and the answer of Mr. Slanina (vol. 9, pp. 223–225), I should like to make my final remarks as follows.

1. In his study he describes an uninterrupted series of 29 sampling periods. Each period enclosed 2 or 3 days. At the end of each period, the funnel of the open rainsampler was scrubbed consequently to remove contamination such as bird-droppings, insects etc. ..., but also part of the dry deposition (statistically 50% as stated now). I am glad Mr. Slanina admits that there is a loss, but why 50%?

Theoretically it is possible that rainfall occurs right at the beginning or right at the end of a sampling period. Having his scrubbing method in mind, there will be a loss of dry deposition either close to a hundred or to zero percent. On an average, the loss of dry deposition will be close to 50%, but then *only* with a proviso that there is statistically a sufficient number of sampling periods and *having rain in every* sampling period. It is this second restriction which is objectionable, because during a study, in practice dry and wet periods succeed one another and scrubbing the funnel at the end of a *dry* sampling period results in a loss of dry deposition of 100%.

In summary, it will be obvious that in practice, using Mr. Slanina's scrubbing method, the loss of dry deposition will be over 50%, raising with an increasing number of dry sampling periods.

In disregard of the way of sampling, Mr. Slanina stated in his article that the first goal of his study was to determine *the* ratio of total and wet deposition. However, as I explained above, a total/wet-only deposition ratio is strongly dependent on the dry/wet ratio of sampling periods. This makes it impossible to find a true ratio in a short period of time. It will be obvious that, to obtain a valid total/wet-only deposition ratio, one must first consider the total wet as well as the total dry deposition and second, it will take a long uninterrupted period of sampling to obtain that valid ratio.

In his letter Mr. Slanina said that one cannot compare results obtained in different countries. A fanciful idea, as he called it.

Of course one cannot. I used the Hendry and Brezonik figures however because of the similar study these authors did (except for Slanina's scrubbing method), to give an idea about a more realistic order of magnitude for the total/wet-only deposition ratio. It is a fact, that after making a correction for his loss of dry deposition, I found that the total/wet-only deposition ratios in his study approximate Hendry and Brezonik's, especially when we consider Slanina's ratios for small rainfalls ($\leqslant 2.5$ mm, table IX, Slanina's article). In the latter case, these ratios even show a greater influence of dry deposition as Hendry and Brezonik's. It is also evident that these small rainfalls frequently occur in the Netherlands (80% of the individual rains, Royal Dutch Meteorological Institute) and put their stamp on the total/wet-only deposition ratio.

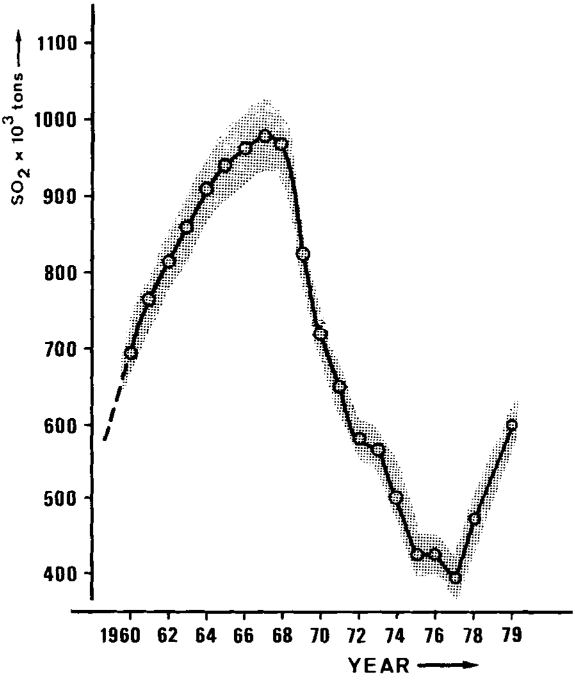

FIGURE 1 Data from National Bureau of Statistics.

2. Mr. Slanina thinks that HNO_3 and not H_2SO_4 is the predominant species in the rain acidification process. In my previous letter I already explained that due to a much smaller NO_x as SO_2 emission in the

Netherlands and besides the fact that NO_x gives one proton where SO_2 gives two when transformed into HNO_3 and H_2SO_4 respectively, it is very unlikely that NO_x is the predominant species. In a recent study on the relationship between the National SO_2-emission (fig. 1) and acidic rain for the centre of the Netherlands (fig. 2 and 2a), I found the very high correlation coefficiënt 0.82 over a period of 20 years (fig. 3). With respect to the trend in H^+ in the 1956–1968 period, however, Mr. Slanina suggests that this *constantly rising* trend (consisting of yearly averages) has been influenced by analytical artefacts ... I wonder, what is in his opinion wrong with the decreasing trend after the late sixties ...?

This decreasing trend now can be explained very easily. It is due to the very fast change over from oil to natural gas as the main fuel in the Netherlands. In a period of 5 years (1968 till 1972) the share of natural gas in the Dutch fuel consumption raised from 18% to over 50%!

In his letter Mr. Slanina said that a relationship as I found it, has to be a fallacy. He based his conclusion on the SO_2/SO_3 conversion rate, which should be 1–4% per hour. He calculated that at the De Bilt location (fig. 2

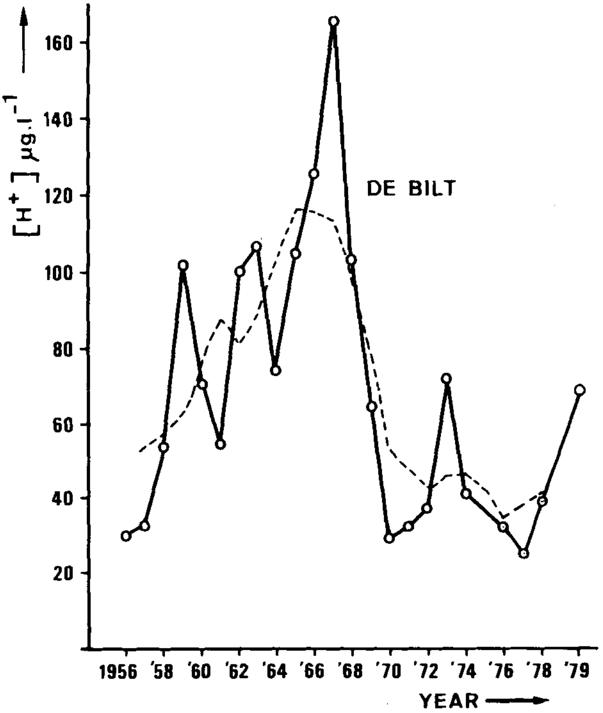

FIGURE 2 Result from own study (basic data from the Royal Dutch Meteorological Institute).

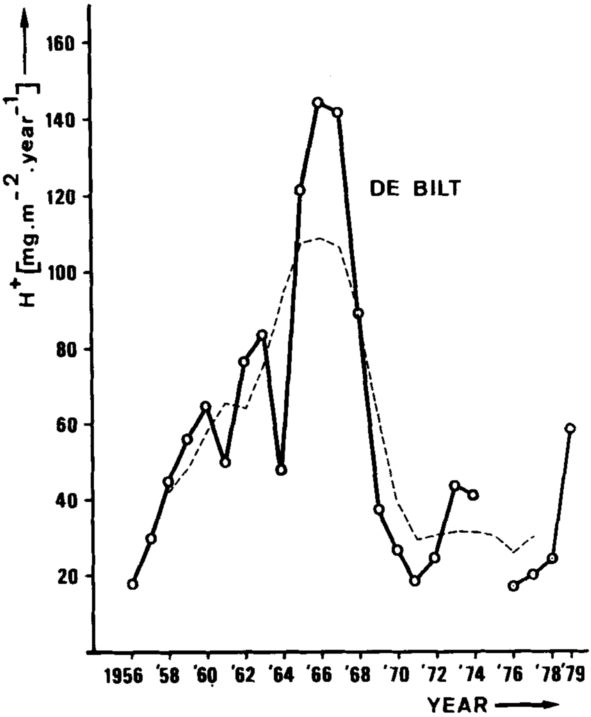

FIGURE 2a Result from own study.

and 2a) situated at a distance of 60 km from the main SO_2 sources in the Netherlands, only 10% could be converted into H_2SO_4. However, the conversion rate which he meant is hardly of any importance when we consider the acidification of rain in the surroundings of SO_2 source regions. The 1–4% is probably true, but those are figures for dry weather conditions. Under rainy weather conditions, the emitted quantity of SO_2 will be washed-out by raindrops rather effectively. Many well known authors (Granat and Högström) amongst other things did studies in the surroundings of SO_2 sources and found that during rain a great part of the SO_2 emitted was washed-out and deposited as sulfuric acid (conversion rate $\geqslant 95\%$) within a range of 60 to 100 km around the source. Granat (1973) made use of 78 rain samplers, Högström (1974) even of 100. In 1979 Högström repeated his study making use of a tracer; this study confirmed his earlier results that during rain more than 70% of the SO_2 emitted was washed-out and deposited within 80–120 km from the source, and on some days (drizzle) even within 30 km. Just as many other authors before, Högström found a significant relationship between the emitted and washed-out SO_2 on the one hand and the H^+ content of the rainwater on the other.

A lot of studies enhance the results of my study which show a significant relationship between the annual emission of SO_2 in the Netherlands and the concentration of H^+ in rainwater at the De Bilt location (fig. 3).

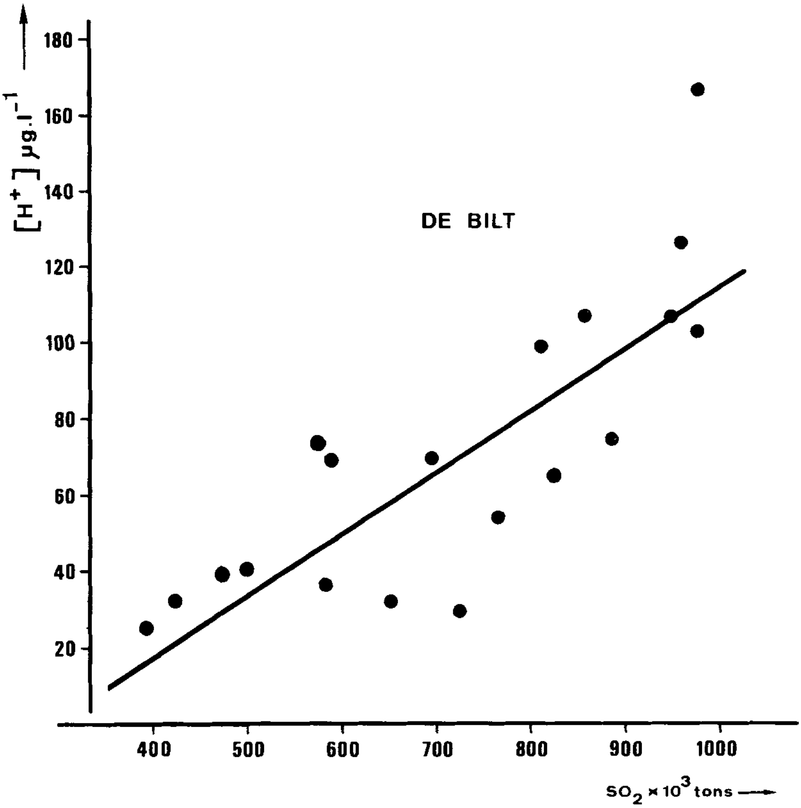

FIGURE 3 Result from own study.

3. Mr. Slanina stated in his letter that the conversion rate for NO_x is much higher than of SO_2, and well up to 14%. He refers to an article of Guicherit et al. In a personal communication Mr. Guicherit told me that "only in some incidental cases, under special conditions, conversion rates for NO_x of 14% were observed, but such a figure should also be possible for SO_2. The conversation rate for NO_x on a yearly basis is less than 5% per hour".

4. My last remark concerns sea-spray correction.

The influence of sea-spray sulfate can be considerable, especially on coast-sides. Usually an author indicates if $SO_4^=$ data have been corrected for sea-spray. Mr. Slanina did not, but in his letter he said that of course such a correction had been made, but, and I cite: "this correction 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*!". This makes me wonder again, since during 1975 and 1976 the province of North-Holland conducted a very extensive study into rainwater pollution. From a number of 22 locations, 11 sites were situated near the coast, hence comparable to his sampling location. On these sites, on a two years average, sea-spray sulphate ranged from 11 to 38% of the total $SO_4^=$ content of rainwater. On six sites this contribution was more than 20%. The analyses were carried out by Mr. Slanina's Analytical Department .... Perhaps the explanation is that Mr. Slanina based his study on the frequently scrubbed rain-sampler ....

I still put another question mark; it is not clear if the SO_4 figures in tables X. XI and XII of his article have been obtained with a frequently scrubbed open rain sampler (with all objections against it) or with the wet-only one.

A. J. Vermeulen
Department of Environmental
Control of the Province of
North-Holland,
Zijlweg 245,
P.O. Box 205,
2050 AE Overveen,
The Netherlands.