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Trend of the nitrate and ammonium content of precipitation water in Hungary for the last 80 years

By L. HORVÁTH, *Institute for Atmospheric Physics, P.O. Box 39, H-1675 Budapest, Hungary*

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ABSTRACT

The nitrate content of bulk precipitation samples in Hungary has increased about seven times relative to its original value, during the last 8 decades. At the same time, the concentration of ammonium ion has somewhat decreased. The increase of nitrate is significant in all seasons, especially in spring months. The ammonium concentration has decreased in fall and in winter, while it has increased in spring and summer. The present spring concentration maxima of nitrate and ammonium have developed since the turn of this century. The trends observed can be explained by the increased tropospheric concentration of air pollutants in this region.

1. Introduction

The study of nitrate and ammonium ions in precipitation water is of interest for many environmental problems. Nitrate and ammonium provide nutrients for different ecosystems and they can affect the acidity of precipitation or the acid deposition. It has been demonstrated that the concentration of nitric acid (nitrate) is continuously increasing relative to sulfuric acid (sulfate) (Galloway and Likens, 1981). On the other hand, on a global scale, ammonia is the only common basic substance in the atmosphere that can neutralize (partly or entirely) the acids formed from nitrogen oxides and sulfur dioxide. For these reasons, the variation of the acidity (pH) in the precipitation water can be related to the trend of nitrate and ammonium concentrations.

For the reliable detection of the temporal variation of nitrate and ammonium concentrations (or depositions), a rather long-term observation period is required. As regular measurements have generally begun in the 1950's, temporal trends can be studied only for recent decades. If we propose to detect the effect of human activity (i.e. of air pollution) on the chemical composition of the atmosphere, chemical data are required from the pre-industrialized period (from last century or from the beginning of the present century). However, such data are only rather sparsely available, mainly for North-West Europe and North America. Thus, at Rothamsted (England) there has been a significant increase of nitrate deposition, especially during the spring months from the middle of the 19th century (Brimblecombe and Pitman, 1980). At the same time, ammonium has remained practically constant. But the differences in sampling and analysis make the evaluation somewhat uncertain.

Similar results have been published for other parts of North-West Europe and eastern North America by Brimblecombe and Stedman (1982), who suggest that the anthropogenic NO_x emission is responsible for the observed increase of nitrate.

The temporal trend of the concentrations in precipitation can be detected by using the results of chemical analyses of snow and ice samples from Greenland. In this way Herron (1982) demonstrated that the concentration of nitrate is about twice as high in the snow derived after 1900 compared with the concentrations in the ice from the pre 1900s. A possible reason for the increase is the increased amount of the emitted nitrogen oxides by combustion, and the utilization of fertilizers. At the same time, in Antarctic samples no nitrate variation was found during the period mentioned.

For central east Europe, the long-term trend in precipitation composition has not yet been in-

vestigated. The aim of this paper is to detect the variation of nitrate and ammonium concentrations in precipitation samples collected in Hungary during the last 8 decades.

2. The data

In Hungary the first precipitation chemistry measurement was carried out in 1902 by Kazay (1904) in Ógyalla (λ = 18° 11′, φ = 47° 52′, presently in Czechoslovakia: Stara Dala), who measured only the concentration of nitrate and ammonium from an agrochemical point of view. The regular sampling and analysis began in the 1960s (Mészáros, 1965). In spite of a lack of continuous data, we make an attempt to detect the change of nitrate and ammonium concentrations since 1902. It should be emphasized that we are able to check the reliability of the earlier data presented by Kazay (1904) since the author gave a detailed description of the analytical methods used.

To determine the long-term trend of nitrate and ammonium the results from 3 measuring periods are used as follows.

(a) Measurements carried out by Kazay (1904) at Ógyalla in 1902.

(b) Measurements carried out by Kozák and Mészáros (1971) at 8 stations in Hungary over a period of 3 years (1968/70, the names of the stations with the geographical positions are given in Table 1).

(c) Measurements carried out during the last 3 years (1979/81) at 5–9 stations (the names of the stations with the geographical positions are given in Table 1).

The location of the sampling sites can be seen in Fig. 1. Monthly precipitation samples were collected by means of bulk collectors in each program. The concentration of nitrate and ammonium in 1902 was determined by the brucine and Nessler methods respectively, by using visual colorimetric titration. In recent programs, the nitrate is detected by the nitro-salicylate method, while ammonium is measured by the Nessler-reagent. In both cases, the concentrations are determined by a spectrophotometer.

Because of the differences between the analytical methods, it was necessary to compare the different procedures. For this reason, parallel analytical determinations were carried out using the visual colorimetric titration and spectrophotometric methods for nitrate and ammonium. The results of 17 parallel measurements carried out in normal precipitation samples were plotted for regression analysis. There were good linear relationships between visual and spectrophotometric results. The linear correlation coefficients were 0.98 and 0.92 for ammonium and nitrate, respectively. Taking the spectrophotometric methods as reference, the correction (multiplying) factors calculated from the regression lines are 1.09 and 0.65 for ammonium and nitrate, respectively. This means that Kazay

Table 1. *Geographical positions of the bulk precipitation sampling stations in Hungary*

No.	Sampling site	Sampling period	λ	φ
1	Ógyalla	1902	18°11′	47°52′
2	Bösárkány	1968/70	17°12′	47°42′
3	Varjakpuszta	1968/70	18°01′	46°41′
4	Budapest	1968/70	19°11′	47°26′
5	Jakabszállás	1968/70	19°36′	46°46′
6	Piszkéstető	1968/70	19°54′	47°55′
7	Szarvas	1968/70	20°32′	46°50′
8	Hortobágy	1968/70	21°06′	47°37′
9	Aranyosapáti	1968/70	22°16′	48°13′
10	Fonyód	1979	17°32′	46°43′
11	Zánka	1979	17°40′	46°53′
12	Balatonszemes	1979	17°46′	46°49′
13	Gamás	1979	17°48′	46°37′
14	Siófok	1979	18°01′	46°54′
15	Keszthely	1979/81	17°15′	46°45′
16	Tihany	1979/81	17°53′	46°54′
17	Balatonfüzfö	1979/81	18°02′	47°04′
18	Boglárlelle	1980/81	17°38′	46°46′
19	Budapest	1979/81	19°11′	47°26′

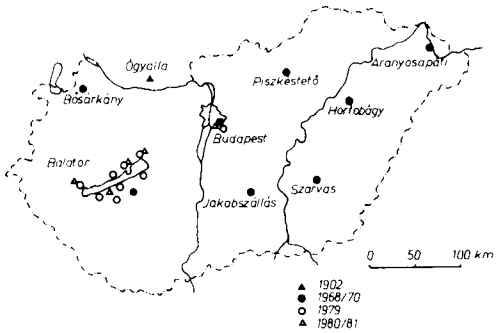

Fig. 1. Location of the Hungarian precipitation chemistry stations.

would have measured less nitrate and more ammonium if he had used our spectrophotometric methods.

3. Results

The yearly average chemical data together with the yearly average precipitation amounts for the periods (a), (b) and (c) are tabulated in Table 2. Yearly averages of the chemical data were calculated from monthly values by weighting the concentrations with the monthly precipitation amounts. It is to be noted that corrected data for 1902 were obtained by using the correction factors mentioned in paragraph 2. These corrected concentrations are used in the following part of this paper. Further, the data for 1968/70 and 1979/81 are average values calculated on the basis of monthly data of all the stations in Fig. 1. The yearly average concentrations of the nearest station to Ógyalla (Bösárkány) are also given in Table 2 for the period 1968/70, but the comparison of these concentrations with the results of other stations is rather difficult because of the extremely high annual precipitation amount at Bösárkány.

One can see from Table 2 that while the ammonium concentration has decreased from the turn of the century by around 20%, the nitrate content has increased by a factor of 6.6.

The wet deposition values can also be seen in Table 2. These figures show a similar picture because the yearly precipitation amounts have not changed significantly in the periods examined.

To check the significance of the differences of concentrations, a statistical test was performed. The Fisher test shows that the difference between the data from 1902 and 1979/81 is significant at $p = 0.1\%$ probability level. For the case of ammonium, the significant difference is caused by the higher annual variation of ammonium in 1902 compared to data from 1979/81 (Fig. 2).

It should be emphasized that temporal changes of nitrate and ammonium concentrations are not the same throughout the year. Thus the seasonal variations of ammonium and nitrate are different in 1902 and in 1979/81 (see Figs 2 and 3). In 1902, the seasonal variation of nitrate was not characteristic. During the last 8 decades, the nitrate concentrations have increased in all seasons, especially in spring (similar results are presented by Brimblecombe and Pitman, 1980 for deposition of nitrate). The seasonal variation of ammonium had a winter maximum and a summer minimum in

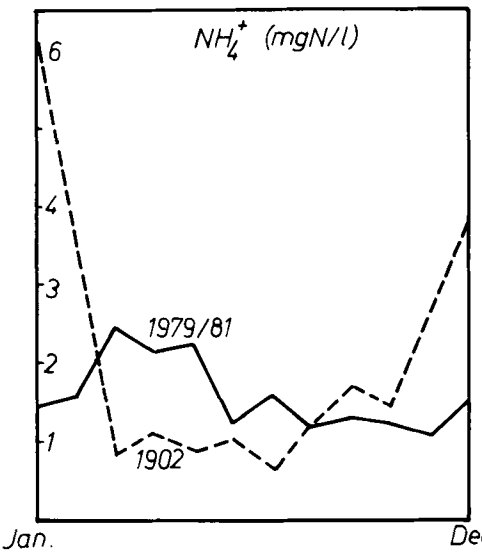

Fig. 2. Seasonal variation of the concentration of ammonium ion in precipitation water in Hungary.

Table 2. *Nitrogen content of bulk precipitation water and wet deposition in Hungary for the last 80 years*

Sampling site	Sampling period	Concentration (mg N l^{-1})		Deposition (g N m^{-2} yr^{-1})		p (mm yr^{-1})
		NO_3^-	NH_4^+	NO_3^-	NH_4^+	
Ógyalla	1902	0.19	1.61	—	—	629
Ógyalla (corrected)	1902	0.13	1.79	0.08	1.13	—
8 stations (nos. 2–9)	1968/70	0.83	1.43	0.53	0.91	638
Bösárkány	1968/70	1.00	0.95	1.13	1.07	1130
5–9 stations (nos. 10–19)	1979/81	0.86	1.50	0.50	0.87	581

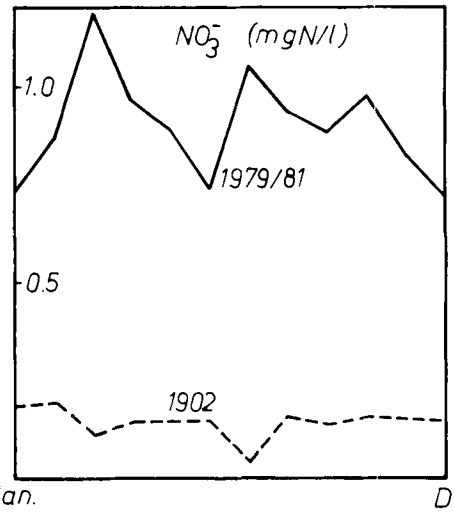

Fig. 3. Seasonal variation of the concentration of nitrate ion in precipitation water in Hungary.

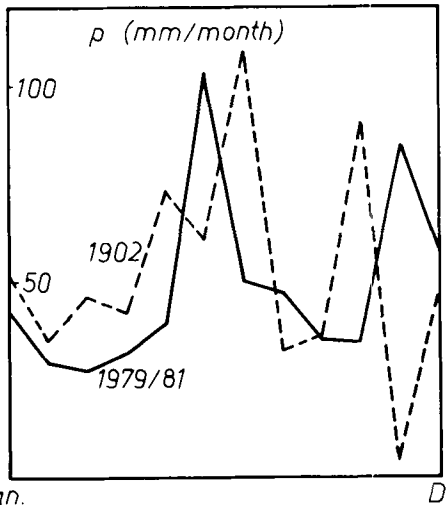

Fig. 4. Seasonal variation of the precipitation amount in Hungary for the two sampling periods.

1902. At present, the picture is markedly different. The maximum is in spring, similar to nitrate. This means that the ammonium concentrations have decreased in the winter and fall months and have increased in summer and especially in the spring months. Therefore, the present spring concentration maxima of nitrate and ammonium have developed since the turn of the century. Because of the similarity of the annual variations of the monthly precipitation amounts in 1902 and 1979/81 (Fig. 4), other factors than precipitation amount are responsible for the phenomenon mentioned.

Finally, the ammonium/nitrate ratio (expressed in N) was 13.8 in 1902, while at present it is 1.7. This means that the importance of nitrate in precipitation water has increased to a large extent compared to that of ammonium.

4. Discussion

The increased amount of nitrate in precipitation reported in previous papers (Brimblecombe and Pitman, 1980; Brimblecombe and Stedman, 1982; Herron, 1982) can also be detected in Hungary. This fact is evident, since the anthropogenic emission of NO_x (burning of fossil fuels, emission from vehicles) has been markedly increasing since the beginning of this century. The nitrate concentration measured in 1902 ($c = 0.13$ mg N l^{-1}) is only 15% of the present nitrate level ($c = 0.86$ mg N l^{-1}). This means that at least 85% of the present nitrate amount in precipitation water is due to anthropogenic effects, assuming that the strength of natural NO_x emission sources has not changed significantly during the period examined. However, a certain portion of the remaining 15% of nitrate may also be of anthropogenic origin as a consequence of the human activity at the turn of the century.

The ammonium concentration has slightly decreased during this century, in spite of the fact that ammonia emission from some sources has increased during this period (fertilizer production, coal combustion, traffic). As to animal husbandry, the main ammonia source (Bónis et al, 1980) remained constant, according to the data of KSH (1965, 1977). Taking into account the emission factors given by Bónis et al (1980), the ammonia emission in Hungary from the excrements of domestic animals between 1895 and 1911 and 1965 and 1976 was 76 and 75 Gg N yr^{-1}, respectively. This means that the strength of the main natural ammonia source (i.e., soil exhalation) may be responsible for the decrease of ammonium concentration in precipitation water. However, the large uncertainties in emission factors allow us only to draw a cautious conclusion.

Both the decrease of ammonium and the increase

of nitrate can increase the acidity. The changes of nitrate and ammonium concentrations from 1902 correspond to 73 μeq l^{-1} acid concentration (pH = 4.1). However, in Hungary, a considerable part of hydrogen ion in precipitation water is neutralized, mainly by soil-derived calcium compounds (Horváth, 1981).

The seasonal variation of ammonium and nitrate concentrations has markedly changed from the 1900s. Recently, characteristic spring maxima can be observed. The differences in the annual variations are not a consequence of the annual variation of the precipitation amount (Fig. 4). In particular, the high ammonium concentrations in January and December, 1902 were accompanied by nearly the same monthly precipitation amounts as in 1979/81.

One of the possible reasons for the difference in the annual variation of nitrate concentration may be the effect of increased human activity since the beginning of this century. Furthermore, the influence of increased anthropogenic emission in the annual variation of ammonium concentration cannot be excluded either.

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