On the spring maximum of the concentration of trace constituents in atmospheric precipitation

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ABSTRACT

The annual march of the concentration of different chemical components in atmospheric precipitation collected in different parts of Europe is presented. These annual marches show a characteristic spring maximum. On the basis of this finding the role of stratospheric ozone in the removal of tropospheric trace constituents is postulated.

1. Introduction

The removal of different trace gases from the troposphere by cloud and precipitation elements is of interest for many problems in air chemistry and pollution studies. In spite of this fact some details of chemical reactions in cloud and precipitation waters, leading to the removal of atmospheric gases, have remained an open question.

In this paper a possible reaction between ozone and other trace gases is postulated on the basis of the annual variation of the concentration of different soluble components in precipitation waters collected in Hungary and in different parts of Europe. This process leads to the oxidation and the subsequent removal of sulfur dioxide and nitrogen oxides from the atmosphere in agreement with laboratory experiments of Penkett (1972) and Penkett & Garland (1973).

2. Data used in the study

In Hungary during five years—from July 1, 1966 to June 30, 1971—four stations installed in a rural area were operated to collect monthly precipitation samples. The collectors were open not only during precipitation, that is the dry fallout is also included in the samples. From the samples the pH and electrical conductivity of the water as well as the concentration of sulfate, nitrate, ammonium, calcium and chloride ions were determined (but the conductivity and chloride data are not taken into consideration in this paper). The chemical analyses were made by nephelometric (SO_4^{--}, Cl^-) and colorimetric (other ions) methods. The position of the stations and the description of analytical procedures are published elsewhere (Kozák & Mészáros, 1971).

From the monthly data of the four stations gained during five years a common annual variation was calculated for each component (Mészáros, 1973). In the calculation of averages the data were weighted according to monthly precipitation quantities.

In addition to monthly values obtained for Hungary, data from five stations working in the Swedish network (the data were kindly supplied by the International Meteorological Institute, Stockholm) and those of one Soviet station (Drozdova et al., 1964) were selected according to their geographical position (see later). Data from Swedish stations were used for a period of 1965–69, while Soviet data were gained during 1958–61.

It is to be noted that some monthly values were omitted from the study since they did not seem to be representative (see the Appendix).

3. Annual variation of the composition of precipitation over Hungary

In Fig. 1 the data collected in Hungary are reproduced (Mészáros, 1973). The figure gives the annual variations of the concentration of different components in precipitation waters

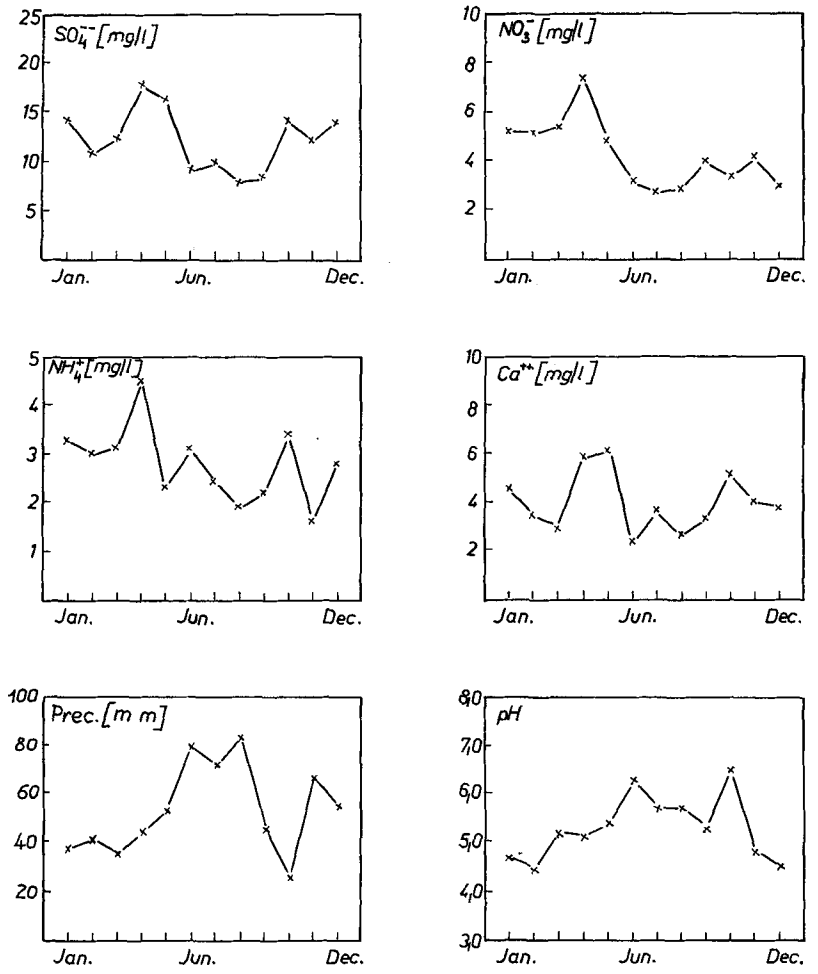

Fig. 1. Annual variation of the chemical composition and quantity of atmospheric precipitation over Hungary.

expressed in $mg.l^{-1}$ as well as the variation of pH and precipitation quantity. It can be seen that all components, except pH, have a spring maximum and a minimum during early fall or late summer. In the winter-time one can recognize a secondary maximum almost for all constituents. In the case of ammonium and calcium a small summer peak is also evident. The winter maximum is obviously a man-made effect while the small summer maximum is produced by natural soil sources. However, the time of the main maximum does not coincide with the time of the maximum strength of the above two sources placed on the Earth's surface. An exception is the annual variation of the pH, which is governed by the ratio of the sum of calcium and ammonium to that of sulphate and nitrate. Thus pH is generally greater when this ratio increases.

It is to be noted here that these Hungarian values are somewhat greater (mainly the calcium and ammonium) than those measured in different part of Europe (see later). This fact can be explained partly by the effect of lime containing soils of Hungarian Plain and partly by the ammonia production of agricultural (vegetation, animal husbandry) activity of this country (Kozák & Mészáros, 1971).

It is known that the concentration of different trace constituents also depends upon the quantity of precipitation (Junge, 1963). The spring maximum, however, cannot be explained by

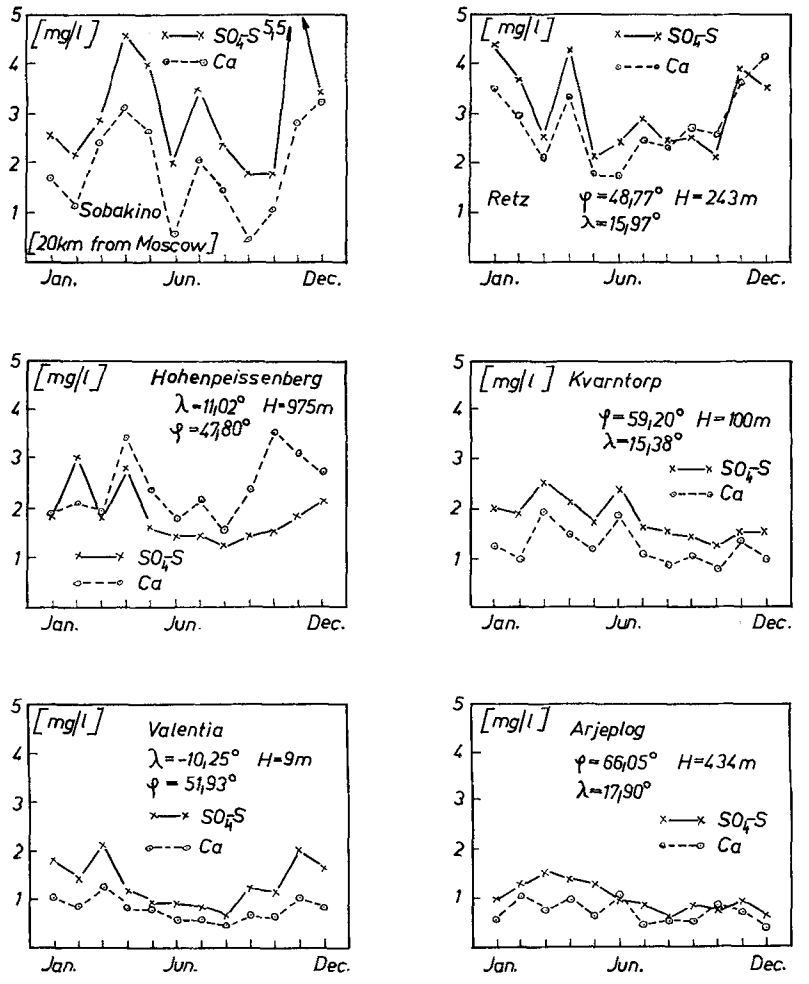

Fig. 2. Annual march of the concentration of sulfate sulfur and calcium in precipitation waters over different parts of Europe.

this effect since in this period the monthly precipitation quantity increases (see Fig. 1). The October peak, on the other hand, is probably caused by this relation because in this month the average precipitation quantity is very small.

4. Data from other European stations

To check the general validity of the spring maximum, data from five stations in the Swedish network and one from the European part of the Soviet Union were examined. The selection of stations was made along a direction from East to West and from South to North across Hungary. Fig. 2 gives the annual variation of the concentration of sulfate sulfur and that of calcium ions in precipitations. The three stations on the left side represent the direction from East to West, while the other three give the South–North direction. It can be seen that the continental, more polluted stations (Sobakino, Retz, Hohenpeissenberg) have annual variations very similar to those obtained for Hungary. One can further see that the spring maximum, except the calcium in Arjeplog, at the other three stations is also reflected. In these latter three cases, however, the absolute values are smaller and the peak is shifted from April to March.

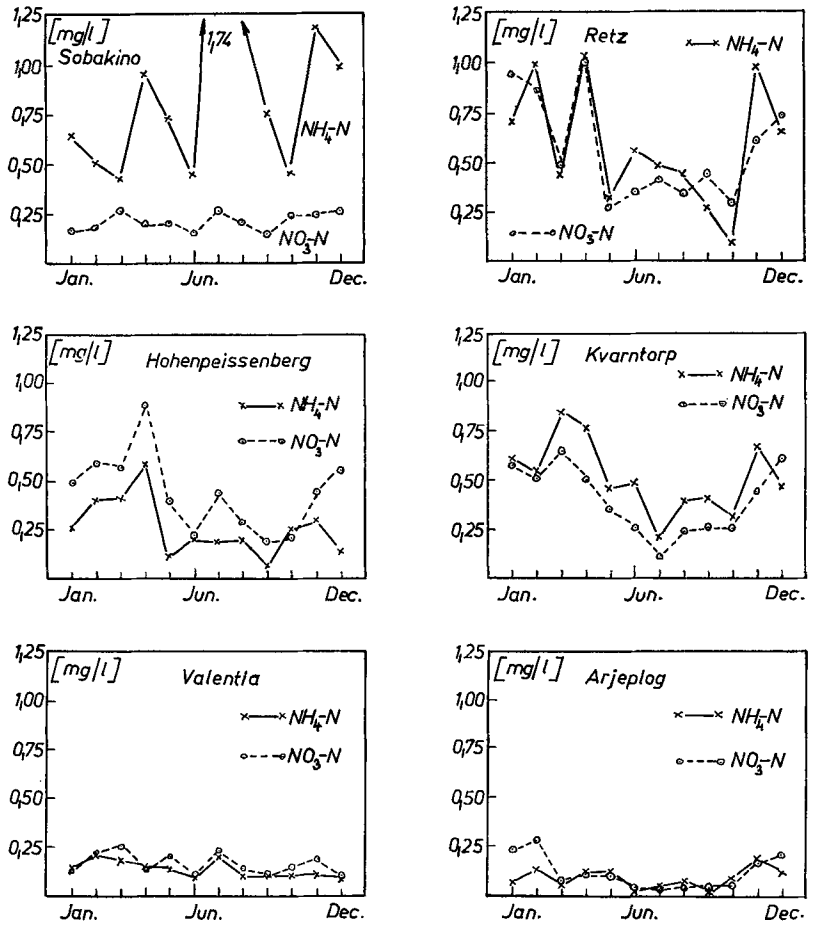

Fig. 3. Annual march of the concentration of ammonium nitrogen and nitrate nitrogen in precipitation waters over different parts of Europe.

The annual variation of ammonium and nitrate nitrogen is plotted in Fig. 3. For these components in Arjeplog and Valentia (less polluted places) pratically no annual variation was found. The spring maximum, however, is a general phenomenon for other stations. In Sobakino the summer ammonium peak is stronger than the spring one. Furthermore at this station the concentration of nitrate nitrogen in precipitation waters is surprisingly small (but the maximum is in March).

5. Possible explanation of the spring maximum

For the explanation of the spring maximum it is postulated that this phenomenon is caused by stratospheric ozone which has a maximum level in the troposphere during the spring (Junge, 1963). The ozone oxidizes sulfur dioxide and nitrogen oxides in cloud and precipitation waters. This process results in the formation of sulfuric and nitric acids, that is it decreases the pH of the atmospheric liquid waters. The increase of the concentration of hydrogen ions enhances the absorption rate of ammonia gas and the conversion rate of soil origin particulate materials (p.e.: calcium carbonate) to water soluble compounds. Thus the concentration of chloride ions in precipitation seems to be independent from the above process. The annual variation of the chloride, however, cannot give a check on the validity of the mechanism proposed. To the continental stations taken into

consideration the maritime chloride particles arrive by cyclones in the rear part of which the exchange between the stratosphere and troposphere bringing down the ozone is very strong. On the other hand much more chloride mass comes in the air of maritime locations if the sea billows, that is under cyclonic weather conditions.

It follows from Figs. 2 and 3 that the spring maximum is the most general for sulfate ions which makes possible that the reaction between ozone and sulfur dioxide is faster than that between ozone and nitrogen dioxide. Another possible explanation may be the lack of nitrogen oxides in cleaner atmosphere. This latter explanation means that sulfur gases are more widespread pollutants in Europe than nitrogen ones. The lack of atmospheric calcium and ammonia compounds during the spring in Arjeplog and Valentia may also explain that for these components no spring maximum was found at these stations.

Thus it results from the figures presented that, although the spring maximum is caused by stratospheric ozone, the process also depends upon the available concentration of trace constituents coming from the Earth's surface.

6. Discussion

The above hypothesis based on observational data can be considered a little speculative. It is to be noted, however, that it is in excellent agreement with the results of recent laboratory experiments carried out by Penkett (1972) and Penkett & Garland (1973). These laboratory works have shown that the oxidation of SO_2 by O_3 in fog droplets is a very fast process and the same is probably true for NO_2.

In the troposphere ozone concentrations of about 50 $\mu g/m^3$ are common. In Arosa, Switzerland, according to Götz & Volz (see Junge, 1963) the average concentration varies approximately between 30 $\mu g/m^3$ in winter and 60 $\mu g/m^3$ in late spring at 1 860 meters above sea levels. Maximum values are in order of 100 $\mu g/m^3$. The laboratory experiments of Penkett & Garland (1973) show that the sulfate amount formed in droplets is proportional to the ozone concentration of the air. At about a maximum ozone level mentioned the formation rate of sulfate is 0.88 mg/lit min in the liquid water, if the pH of this latter is 5 (temperature: 10°C, liquid water content: 0,1 ml m^{-3}, SO_2 concentration: 0.1 p.p.m.). It follows from these laboratory findings that the process is quite sufficient to explain the observational data presented in this paper even if ozone concentration is smaller than 100 $\mu g/m^3$ and the level of sulfur dioxide is smaller than that used during the experiments.

Thus it is concluded on the basis of these observations and laboratory experiments that stratospheric ozone plays an important part in the chemistry of tropospheric trace constituents and more exactly in the oxidation and removal of sulfur and nitrogen dioxide. This process probably also yields an important ozone sink in the troposphere.

Appendix

In the study the following monthly data from European stations were not taken into account:

1. In Hohenpeissenberg the monthly sulfur deposition is generally larger than 100 mg/m^2. In April 1965, however, for 135 mm precipitation quantity zero deposition is given. This figure may be in error, or, if it is true, it cannot be considered representative for a longer period.

2. In Arjeplog for June 1967, 302 mg/m^2 calcium deposition is given (43 mm precipitation quantity). For other summer months all values are smaller than 55 mg/m^2. If the 302 mg/m^2 was taken into consideration for June a 2.46 mg/l mean concentration would be received.

3. In Retz for October and November 1965 and for October, 1969 the following calcium depositions and precipitation quantities are given: 182 mg/m^2 (6 mm), 233 mg/m^2 (12 mm) and 115 mg/m^2 (3 mm), respectively. These values would result in a very high concentration which cannot be representative.

Finally it is to be noted that omissions mentioned in 2 and 3 do not touch the main conclusion of this paper.

REFERENCES

Drozdova, V. M., Petrenchuk, O. P., Selezneva, E. S. & Svistov, P. F. 1964. *Chemical composition of atmospheric precipitations over the European part of USSR* (in Russian). Gidromet. Izdat. Leningrad.

Junge, C. E. 1963. *Air chemistry and radioactivity*. Academic Press, New York and London.

Kozák, M. & Mészáros, E. 1971. Magyarországi csapadékvizek kémiai összetétele és mezögazdasági jelentösége. *Agrokémia és Talajtan 20*, 329–352.

Mészáros, E. 1973. A csapadékviz nyom-anyag koncentrációjának évi menete Magyarországon. *Időjárás, 77*, 304–310.

Penkett, S. A. 1972. Oxidation of SO_2 and other atmospheric gases by ozone in aqueous solutions. *Nature, Physical Sci. 240*, 105–106.

Penkett, S. A. & Garland, J. 1973. Oxidation of sulphur dioxide in artificial fogs by ozone. Presented at *Symposium on Atmospheric Trace Gases*, Mainz, Germany.

О ВЕСЕННЕМ МАКСИМУМЕ КОНЦЕНТРАЦИИ ТРАССЕРОВ В АТМОСФЕРНЫХ ОСАДКАХ

Представлен годовой ход концентрации различных химических компонент в атмосферных осадках, собранных в различных частях Европы. Эти годовые ходы имеют характерный максимум весной. На этой основе указывается на роль стратосферного озона в удалении трассеров из тропосферы.