On the distribution of ammonia in the middle and lower troposphere

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ABSTRACT

Ammonia has been measured under "pure air" conditions applying the Indophenol blue method after Bertheolot. Aircraft-ascents show a remarkable decrease of the NH_3-concentration when proceeding from the continent to the ocean. A number of aircraft-ascents were made to investigate the vertical distribution of onNH_3 and NH_4^+ They revealed a sharp decrease of the concentration in the ground layer of the troposphere approaching a constant concentration above 2 km altitude. Winter and summer values at 3 km altitude were around 1 $\mu g/m^3$ NH_3 and 4 $\mu g/m^3$ NH_3 respectively. Some conclusions on the formation of $(NH_4)_2$ SO_4-aerosols are drawn on the basis of the results obtained.

Introduction

The presence of ammonia in the atmosphere as ammonia gas or ammonium sulfate is a well-known fact. Although ammonium as a constituent of precipitation was analyzed as early as 1855 (Way, 1855), not until a hundred years later was a comprehensive survey of the distribution of NH_4^+ in precipitation given (Eriksson, 1952). In a review of nitrogen compounds in the atmosphere Georgii (1963) decribed the distribution of NH_3 at the ground for some continental stations. The general level of NH_3 for all stations was 4 to 20 $\mu g/m^3$ indicating a rather uniform distribution. Exceptionally high NH_3 concentrations were reported by Eggleton & Atkins (1972) from the Tees-side area near the northeast coast of the British Isles. It is generally accepted that mainly biogenic sources are responsible for the production of atmospheric NH_3 and these sources are predominantly located on the continents. Robinson & Robbins (1970) estimate the global NH_3 emission to the atmosphere to be $5\,900 \times 10^6$ tons per year including 4×10^6 tons/year coming from combustion-processes. Assumption of a background-concentration of 3–5 $\mu g/m^3$ NH_3 and the given emission-rate would indicate a tropospheric residence-time of about two days. This gives, however, only a vague estimation of the residence time which will depend very much on possible atmospheric reactions with NH_3 and therefore on the presence and concentration of reaction-partner in the atmosphere.

The mechanism of conversion of NH_3 into ammonium sulfate under atmospheric conditions has attracted much speculation during recent years. In spite of some valuable theoretical work and experimental studies in the laboratory significance of the different mechanism and reactions occuring in the atmosphere between NH_3 and SO_2 in the presence of solid particles or liquid water or by direct gas-phase reaction is still not well known, although Healy, McKay, Pilbeam and Scargill (1970) eliminate gas-phase reactions as major contributors to $(NH_4)_2SO_4$-particle formation. To make realistic assumptions on possible ammonium-sulfate formation in the free atmosphere it is necessary to know the distribution of SO_2, sulfate, NH_3 and NH_4^+ in the lower and middle troposphere, where, in the presence of clouds, this process is expected to take place. Earlier investigations by Georgii (1970) and Georgii and Vitze (1971) were mainly devoted to the sulfur components. More recently this work was extended to the ammonium compounds as a necessary further step for the understanding of the formation of sulfur-containing compounds.

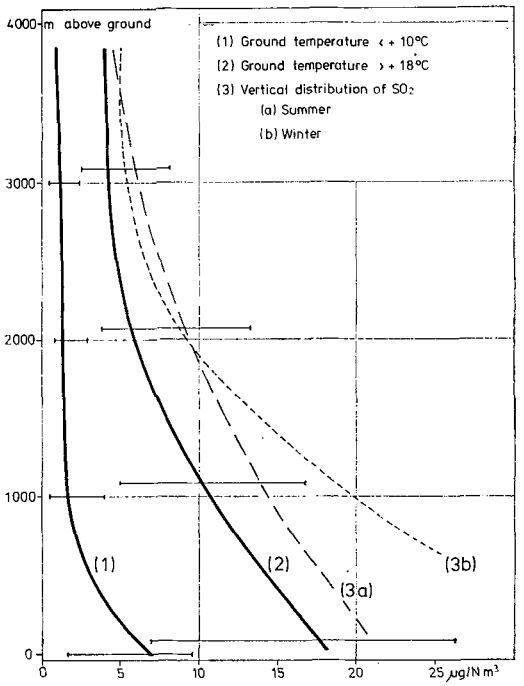

Fig. 1. Vertical distribution of NH_3 over Western Germany.

Results of NH_3 and aerosol measurements

From November 1969 to September 1972 a total of 75 aircraft-ascents were carried out over different areas of West Germany which were considered not directly influenced by pollution sources. The equipment for discontinuous sampling was identical with that described in connection with former investigations of gaseous sulfur components by Georgii & Jost (1964).

Automated wet chemical methods were used for the determination of ammonia. The indophenol-blue reaction after Berthelot applied by us is nearly identical with that described and used by Eggleton & Atkins (1972). The aircraft-ascents were carried out under clear air conditions. During several ascents NH_3 and SO_2 were sampled simultaneously. Besides the air sampling, vertical profiles of the relative humidity and the air temperature were measured. The sampling time increased with increasing altitude due to the decrease of the NH_3-concentration. In the middle troposphere roughly one hour's flight-time at each level was required to collect a sample containing a detectable NH_3-concentration.

The results show that the vertical distribution on NH_3 is determined by source strength at the ground, by vertical mixing and by possible sinks. Ths production rate depends very much on bacterial activity which again is a function of ground-temperature. This is reflected in a noticeable variation of NH_3 ground-concentration with temperature. We have therefore arranged our measurements into two categories, one for ground temperature above + 18°C (mainly summer values), the second including all measurements at ground-temperatures below + 10°C (mainly late fall, winter and early spring) In Fig. 1 we have entered the average vertical distribution of NH_3 for these two categories of ascents. We have also indicated the range of the fluctuation of individual measurements. From this diagram we can draw the following conclusions:

1. The vertical distribution of NH_3 is typical of that of a trace gas with the source at the ground.

2. The concentration of NH_3 decreases rapidly with altitude, reaching a constant background concentration in winter days about 1 500 m above ground, on warm days at about 3 000 m above ground.

3. On warm days the ground concentration is considerably higher. The difference amounts to a factor 3.

4. Seasonal differences of the NH_3-concentration are still noticeable at 3 000 m altitude above ground. The vertical transport of NH_3 is strongly affected by temperature inversions as well as convection.

5. The vertical distribution of NH_3 is compared with that for SO_2, which is discussed in detail by Jost (1974). In contrast to NH_3 the SO_2 content of the lower troposphere is higher during winter than during summer caused by higher anthropogeneous SO_2 production. At altitudes above 2 000 m the summer concentration of NH_3 is of the same order of magnitude as the SO_2-concentration, while during winter the NH_3-concentration is much below the SO_2 content of the middle troposphere. That means that only during the warm seasons is the supply of NH_3 to higher levels of the troposphere sufficiently large to be of any importance for the NH_3–SO_2 liquid water reaction suggested by Scott & Hobbs (1967) which leads to the formation of $(NH_4)_2SO_4$-aerosols.

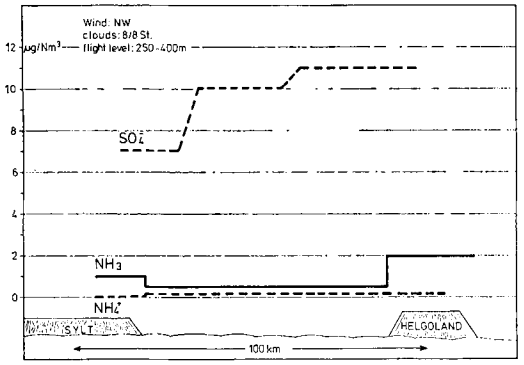

Fig. 2. Distribution of Trace-substance over the North Sea—4 Febr. 1971.

When proceeding from continental areas over the ocean we noticed a horizontal decrease of the NH_3-concentration. In air not influenced by advection from continental sources observations of the background-concentration of NH_3 can be made. Fig. 2 shows an example of this kind. During a flight over the North sea on 4 Feb. 1971 with strong advection of polar-maritime air masses from NW, the NH_3-concentration was as low as 0.3 to 1 $\mu g/m^3$, the higher values showing up only in the vicinity of islands. The same applies to the NH_4^+ concentration of the atmospheric aerosols no values above 0.3 $\mu g/m^3 NH_4$ were found on that flight in contrast to the considerable amounts of sulfate (7 to 12 $\mu g/m^3$) which were found. In this case the sulfate containing aerosols can hardly be ammonium sulfates formed under atmospheric conditions it can rather be assumed that the majority of sulfate is of maritime origin. The typical vertical distribution of

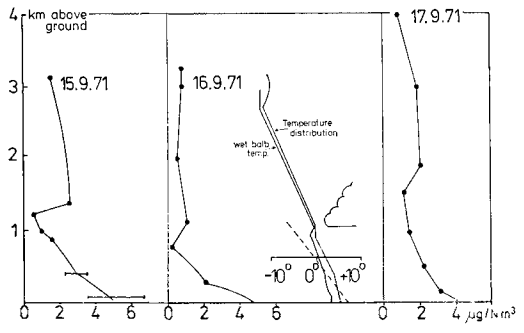

Fig. 3. Vertical distribution of NH_3 in upper Bavaria.

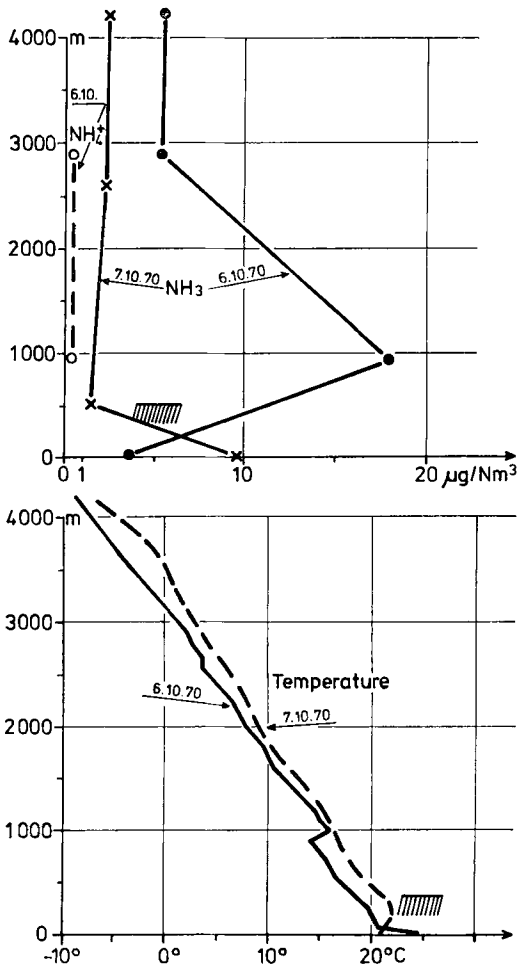

Fig. 4. Vertical NH_3-distribution over Bavaria.

NH_3 as found during individual aircraft-ascents is demonstrated in Fig. 3. This series of flight measurements was carried out between 15 and 17 Sept 1971 in Bavaria north of the Alps. The NH_3-concentration decreases in the lower part of the atmosphere, reaching values between 1 and 3 $\mu g/m^3$ in the layer above 2 km not directly influenced by ground activity.

A typical phenomenon is the accumulation of NH_3 below temperature inversions. During the flight on 15 Sept. a number of air samples were taken at low altitudes (300 m above ground) over areas which were expected to have different source-strengths of NH_3. We found significant differences in the NH_3-concentrations above a lake, rural country and extended wood-land. The lowest values were found over

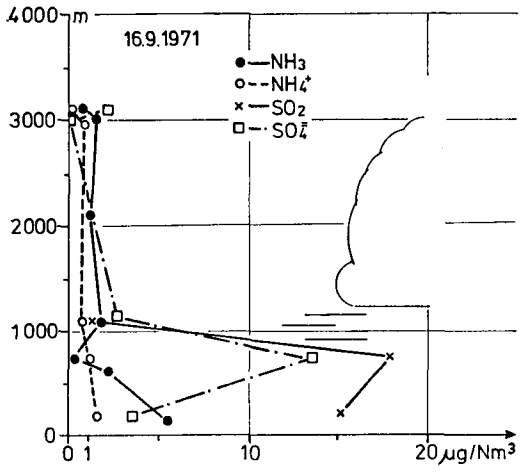

Fig. 5. Vertical distribution of trace-substances over Bavaria.

a lake. It can be concluded that different strength of natural ammonia-sources is still noticeable at several hundred meters altitude.

Another case study demonstrates the effect of Foehn on the north side of the Alps on the NH_3 concentration (Fig. 4). Strong advection of air masses from the South led to descending dry air on the North side of the Alps on 7 Oct. 1970. On 6 Oct. with prevailing south–westerly winds a rather high NH_3-concentration was observed in the lower troposphere with a peak-concentration below an inversion at approximately 1 000 m above the ground reaching nearly 20 $\mu g/m^3$. On 7 Oct. the picture has changed drastically. The wind had turned to southerly and a typical Foehn-situation predominated with dry air descending on the north side of the Alps and heavy rainfall south of the Alps. The wall of clouds in the south could clearly be recognised from aircraft. This led to a drastic reduction of the NH_3 concentration in the lower troposphere which was only about 1/5 of that of the previous day. At altitudes above 3 000 m the NH_3-concentration dropped from 6 to 3 $\mu g/m^3$ from 6 to 7 October. Part of this decrease can be explained by rainout and washout of the air passing the Alps from South to North. These findings are in agreement with earlier observations made with SO_2. They clearly show the influence of meteorological parameters on the concentration of atmospheric trace gases.

For a realistic appraisal of the contribution of NH_3 to the cycle of sulfur components in the atmosphere simultaneous analysis of the vertical distribution of gaseous and particulate sulfur and ammonium compounds is of particular interest. Fig. 5 shows the aircraft ascent made on 16 September 1971 when NH_3 and SO_2 as well as NH_4^+ and $SO_4^=$ in aerosols were measured synchroneously. The NH_3-distribution on that day has already been discussed. In contrast to NH_3 and NH_4-distribution, the SO_2 distribution and the distribution of sulfate in aerosols show high concentrations below an isothermal layer. SO_2 and SO_4-concentrations decrease strongly in and above a cloud layer. The great difference between the SO_2 and NH_3 concentration in the lower troposphere maybe explained by anthropogeneous SO_2-sources, possibly high chimneys at great distance. The NH_3/SO_2 ratio on that day, on one hand, and the $NH_4^+/SO_4^=$ ratio on the other, do not make it seem likely that a large quantity of ammonium sulfate can be produced under such conditions. An evaluation of a number of simultaneously measured NH_4^+ and $SO_4^=$ concentrations in atmospheric aerosols does not reveal a correlation between these two components. In continental airmasses we regularly find a surplus of sulfate compared with the stöchiometric ratio of ammonium and sulfate in ammonium sulfate. We can therefore conclude that at this stage the results of the investigation do not support the importance of the NH_3–SO_2-liquid water process. However, the number of simultaneous measurements is still too small to make more than a very preliminary statement. Further measurements are to be conducted in the vicinity of clouds. They will have to include the analysis of cloud-water and should be extended to the analysis of other possible reaction-partners of ammonia, for instance NO_2 and NO_3^-.

Acknowledgements

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О РАСПРЕДЕЛЕНИИ АММИАКА В СРЕДНЕЙ И НИЖНЕЙ ТРОПОСФЕРЕ

Концентрация аммиака измерялась в условиях «чистого воздуха» применением реакции с индофенолом синим по Бертело. Самолетные подъемы показывают заметное уменьшение концентрации NH_3 при переходе от континента к океану. Для изучения вертикального распределения NH_3 и NH_4^+ был сделан ряд самолетных подъемов. Они указывают на резкое уменьшение концентрации в приземном слое тропосферы с приближением ее к постоянному значению на высотах, больших 2 *км*. Зимой и летом значения концентрации NH_3 на высоте 3 *км* были вблизи 1 *мкг/м*^{3} и 4 *мкг/м*^{3}, соответственно. На основе полученных результатов были сделаны некоторые выводы об образовании аэрозолей $(NH_4)_2SO_4$.