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SHORT CONTRIBUTION

An investigation of the atmospheric HNO_3–NH_3–NH_4NO_3 equilibrium relationship in a cool, humid climate

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ABSTRACT

Simultaneous measurements of gaseous nitric acid and ammonia were made during summer, autumn and winter months in North-West England. Concentrations of HNO_3 and NH_3 lay within the ranges 0.03–0.36 ppb and 0.9–5.1 ppb respectively, gaseous HNO_3 accounting for only about 12% of total nitrate. Under the high humidity conditions prevalent during the work, the concentration data are consistent with the equilibrium of gaseous HNO_3 and NH_3 with solution droplets of NH_4NO_3.

1. Introduction

In recent years nitrates have been indicted increasingly as a major contributor to acid deposition, both dry and wet (Hileman, 1981). The acidic form of nitrate is nitric acid, HNO_3, and the relatively recent postulate that atmospheric concentrations of gaseous HNO_3 are controlled by an equilibrium of gaseous NH_3 and HNO_3 with particulate ammonium nitrate (Stelson et al., 1979) is thus of considerable importance:

$$NH_3(g) + HNO_3(g) \rightleftharpoons NH_4NO_3(s).$$

The testing of this equilibrium relationship for the atmosphere has been limited by the severe shortage of simultaneous measurements of HNO_3 and NH_3. Stelson et al. (1979) used the data collected by Spicer (1974) in West Covina, California, and Doyle et al. (1979) used measurements from Riverside, California. These are amongst the very few available data sets, all of which were collected at rather high air temperatures (e.g. Doyle et al. 27.3–37.3 °C; Stelson et al. 12–30 °C) and low humidities (Doyle et al. < 55%; Stelson et al. about 50% of data < 60%). In both studies, the data, especially at lower humidities, were found to be in qualitative agreement with equilibrium concentrations predicted from extrapolation of thermodynamic data (JANAF, 1971; Wagman et al., 1968; Brandner et al., 1962).

Solid ammonium nitrate at 25 °C deliquesces at relative humidities ⩾ 64%, and at 0 °C at r.h. ⩾77%, and hence then exists as solution droplets, which may contain other substances. In such circumstances the equilibrium relationship which applies to solid ammonium nitrate is not expected to hold, and it is predicted that the vapour pressures of HNO_3 and NH_3 will be dependent upon both relative humidity and solution pH (Tang, 1980). Consequently in more recent work, Stelson and Seinfeld (1982a, b) have used thermodynamic data to calculate the equilibrium vapour pressures of the gaseous components in equilibrium with NH_4NO_3 under varying conditions of relative humidity and solution pH.

Under British winter conditions, air temperatures rarely exceed 10 °C and humidity falls below 60%

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only infrequently. Since there were no data on the behaviour of NH_3 and HNO_3 under these conditions, and indeed few measurements of gaseous HNO_3 at all, a brief study was undertaken and is reported here. One disadvantage of working under these atmospheric conditions is that predicted concentrations of HNO_3 are very low and it is necessary to collect samples over 24-h periods. Ideally the equilibrium relationship should be tested with instantaneous measurements, but nonetheless 24-h measurements should conform in at least a qualitative sense, and are at present the best data available.

2. Experimental

Air samples were collected at the University Field Station at Hazlerigg, 4 km SSE of the town of Lancaster (North-West England). The site is rural and is used as grazing for sheep. Meteorological instruments are sited in an enclosure on the same site. The air sampler inlet was at a height of 1.8 m above ground level. The filtration equipment was freely ventilated by ambient air, and hence no temperature change occurred during sampling. Air was drawn directly to the pre-filter of the nitric acid sampler so as to avoid adsorption problems known to occur with inlet probes.

Gaseous HNO_3 was collected on an NaCl-impregnated filter preceded by a Teflon membrane filter (Gelman TF-450, 0.45 μm). The impregnated filters were prepared by immersing a Whatman No. 41 cellulose filter in a 5% aqueous NaCl solution, and drying under an infra-red lamp after draining off excess solution. The collected nitrate was extracted with deionized water (5 ml) and analysed colorimetrically (Harrison and McCartney, 1979).

Gaseous NH_3 was collected on a cellulose filter impregnated with $KHSO_4$ after pre-filtration of the air with a Teflon filter. The impregnation method and subsequent colorimetric analysis of ammonium ions by the phenol-hypochlorite method have been described elsewhere (Harrison and McCartney, 1979). The detection limits for analysis of HNO_3 and NH_3 in a 24-h air sample were 0.04 ppb and 0.03 ppb, respectively.

The particulate samples were analysed for major ion constituents. This included sulphate, by the barium chloranilate method; nitrate by copper catalysed hydroxylamine reduction to nitrite and azo dye formation; ammonium by the phenol-hypochlorite method; hydrogen ion by Gran titration, as well as other ions. Details of experimental procedures are reported elsewhere (Harrison and Pio, 1982).

3. Results and discussion

The sampling of NH_3 and HNO_3 from ambient air is itself fraught with difficulties, since the pre-filtration of an air stream to remove particulate NH_4^+ and NO_3^- is bound to upset the dissociation equilibrium to some degree. The alternative denuder method (Ferm, 1979) in which ammonia is removed from the air in a diffusion denuder prior to air filtration is also liable to upset this equilibrium, leading to further dissociation of particulate NH_4NO_3. In the sampling methodology used in this work, low pressure drops were maintained across the pre-filter (*ca.* 30 torr) and the apparatus was used at ambient temperatures to keep disturbance of the dissociation equilibrium to a minimum. Methods for HNO_3 collection and analysis have only been developed rather recently. It is known that HNO_3 depletion in inlet probes is a problem and hence no such probe was used in this work. The impregnated filter sampling technique for HNO_3 which was employed has recently been included in a comparative study of methods for analysis of this pollutant in ambient air (Spicer et al., 1982). It was found to be generally satisfactory, but yielded slight positive errors in HNO_3 concentration.

The air-sampling results appear in Table 1, and meteorological conditions in Table 2. The ammonia concentrations are fairly typical of those reported elsewhere (Harrison and McCartney, 1979, 1980). The HNO_3 levels, however, are considerably below other reported values. For example, in Southern California, Doyle et al. (1979) report concentrations of HNO_3 within the range 6–20 ppb, and Tuazon et al. (1981) found daily average HNO_3 levels of 13–32 ppb and daily maximum levels of 18–49 ppb during a multi-day smog episode. Measurements by Grennfelt (1980) in Sweden ranged up to 3.5 ppb HNO_3, but neither air temperatures, humidities nor ammonia concentrations were reported.

Table 1. *Results of air sampling*

Date	T.S.P. ($\mu g\ m^{-3}$)	SO_4^{2-} ($\mu g\ m^{-3}$)	Partic. NO_3^- ($\mu g\ m^{-3}$)	NH_4^+ ($\mu g\ m^{-3}$)	Partic. H^+ ($\mu g\ m^{-3}$)	HNO_3 (ppb)	NH_3 (ppb)	K_c (ppb^2)
1–2 May 1980	N.D.	12.9	3.8	5.2	0.020	0.36	2.0	0.72
2–3 May 1980	N.D.	4.0	3.5	1.9	0.010	0.17	1.7	0.29
23–24 June 1980	20	5.7	7.1	2.8	0.003	0.10	5.1	0.51
3–4 July 1980	21	5.3	2.7	2.3	0.010	0.24	3.7	0.94
7–8 July 1980	31	9.7	2.7	4.0	0.000	0.25	3.7	0.92
16–17 Sept. 1980	21	4.5	1.6	1.2	0.004	0.08	2.8	0.22
18–19 Sept. 1980	30	5.3	4.4	2.4	0.010	0.21	3.0	0.63
19–20 Sept. 1980	26	5.5	4.0	2.3	0.006	0.18	3.6	0.65
22–23 Oct. 1980	70	2.5	1.0	0.7	0.004	0.03	1.9	0.06
13–14 Feb. 1981	73	12.6	16.1	9.4	0.020	0.23	1.4	0.32
14–15 Feb. 1981	103	14.6	20.5	12.2	0.030	0.16	4.0	0.64
15–16 Feb. 1981	51	8.8	7.5	5.4	0.002	0.06	4.3	0.26
17–18 Feb. 1981	51	10.9	4.1	5.7	0.030	0.20	1.8	0.36
18–19 Feb. 1981	N.D.	4.1	2.1	1.8	0.006	0.05	0.9	0.05

N.D. = not determined.

Table 2. *Meteorological measurements*

Date	Temp. (max) (°C)	Temp. (min) (°C)	R.H. (max) (%)	R.H. (min) (%)	R.H. (med)* (%)	Rain (mm)	Sunshine (h)
1–2 May 1980	12.7	5.8	95	68	80	0.0	11.0
2–3 May 1980	13.6	4.1	84	45	63	0.0	11.0
23–24 June 1980	15.3	8.4	88	55	78	4.3	8.2
3–4 July 1980	16.1	11.4	92	64	82	6.5	2.3
7–8 July 1980	16.7	7.4	85	55	65	0.0	5.0
16–17 Sept. 1980	17.4	11.2	94	76	86	5.4	0.4
18–19 Sept. 1980	16.4	12.4	93	67	81	1.6	2.0
19–20 Sept. 1980	18.9	13.4	95	80	85	6.3	3.1
22–23 Oct. 1980	14.1	8.9	97	90	92	28.5	0.0
13–14 Feb. 1981	5.5	−0.7	77	47	65	0.0	0.0
14–15 Feb. 1981	4.9	−0.5	83	65	73	0.0	0.0
15–16 Feb. 1981	8.2	1.3	90	50	65	0.2	8.0
17–18 Feb. 1981	7.5	−1.1	85	60	72	0.0	3.0
18–19 Feb. 1981	3.2	−1.7	81	58	68	0.0	3.0

* Median relative humidity derived from continuous hygrometer records.

In our work the arithmetic mean ± s.d. of the ratio (HNO_3-nitrate) ÷ (total nitrate) is 0.12 ± 0.08 and hence gaseous inorganic nitrate represents only a small proportion of the nitrate mass. This is in marked contrast to the results of Grennfelt who found a considerably greater proportion of nitrate to be in the gaseous phase. It is, however, quite feasible that Grennfelt's measurements were carried out under conditions of higher atmospheric temperature and lower NH_3 concentration, both of which would favour HNO_3 relative to NH_4NO_3.

The range of humidities in our work (Table 2) is

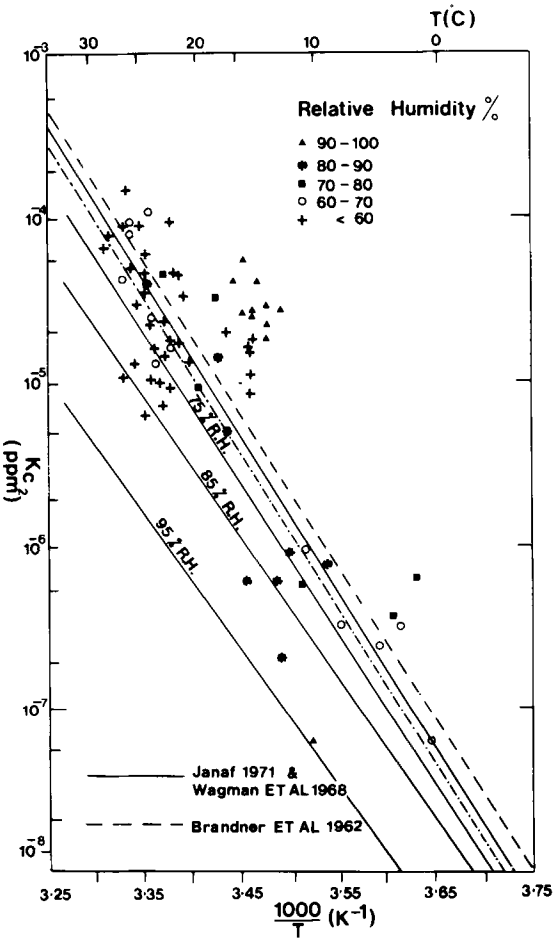

Fig. 1. The product $|HNO_3||NH_3| = K_c$ plotted versus $1000/T$ (K^{-1}). The lines (– – – and ——) indicate values calculated from equilibrium theory for solid ammonium nitrate using thermodynamic data from the sources indicated. The other lines are derived from the data of Stelson and Seinfeld (1982a, b); one (–·–·–) relates to solid ammonium nitrate and the others to solution droplets at the indicated relative humidities. The data points in the top left ($K_c > 10^{-6}$ ppm^2) are from Stelson et al. (1979) calculated from the data of Spicer (1974) for West Covina, California. The points in the lower right ($K_c < 10^{-6}$ ppm^2) are derived from our own data (Table 1).

generally above the point at which NH_4NO_3 becomes deliquescent at these air temperatures (Stelson and Seinfeld, 1982a). In Fig. 1 we have extended the Stelson et al. (1979) plot of Spicer's data to include our own, which lie in an entirely separate part of the graph. In addition, we have plotted theoretical equilibrium lines relating K_c ($= P_{NH_3} \cdot P_{HNO_3}$) to 1000/T for NH_4NO_3 solution droplets at various humidities, as well as for solid NH_4NO_3. The data have been abstracted from Stelson and Seinfeld (1982a) who found the effects of droplet pH to be relatively minor. For the purpose of the graph, the temperature of the sampling period was taken as the arithmetic mean of the daily maximum and minimum.

It is interesting that the inclusion of the lines for high relative humidities gives an excellent agreement with the theoretical equilibrium for the majority of the experimental points. Indeed, our data relate far better to the theoretical lines in relation to humidity than those of Spicer (1974) which tend to show increased values of K_c with humidity, contrary to the predictions of theory.

Given the use of 24-h sampling periods and the substantial variations in temperature and humidity which may occur during them, the agreement with theory is surprisingly good. The absence of any appreciable acidity in the aerosol (Table 1) is advantageous in limiting any possible deviations due to solution pH. Even one day of very heavy rainfall (28.5 mm on 22–23 October 1980) gives a good fit to the experimental line for 95% humidity (the observed humidity was 90–97%). The three points lying above the lines for solid ammonium nitrate all correspond to days with negative minimum temperatures and it is possible that the theory does not adequately embrace these circumstances.

In conclusion, it appears that at conditions of low temperature and high relative humidity, the NH_3–HNO_3–NH_4NO_3 equilibrium system conforms very well to the theoretical predictions of Stelson and Seinfeld (1982a, b) for solution droplets of NH_4NO_3.

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