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THE BUDGET OF OXIDISED NITROGEN SPECIES IN OROGRAPHIC CLOUDS

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Abstract—The transformation of NO_x as it passed through a hill-top cap cloud was investigated by
measuring (i) NO_x (NO and NO_2) and particulate nitrate concentrations on both sides of the hill,
(ii) nitrite and nitrate in cloud, and (iii) nitrous and nitric acid concentrations below cloud base. Results
from four periods during April and May 1993 are presented as part of a EUROTRAC GCE (Ground-based
Cloud Experiment) experimental campaign at Great Dun Fell, in Cumbria, England. The overall change in
NO_x in all four periods was less than 20%. On 22 April the air flow was from west to east, and NO_x
concentrations were very much larger than particulate nitrate concentrations. There was evidence for loss of
NO_x and production of nitrous acid as air passed through the cloud. During May the air flow was from east
to west; NO_x concentrations were much smaller, and similar to concentrations of particulate nitrate.
Differences in NO_x concentrations before and after cloud sometimes showed a loss of NO_x which was
greater than the combined measurement uncertainty. Changes in particulate nitrate concentrations were
close to the combined measurement errors. Concentrations of nitrate in cloud, however, were greater than
could be accounted for by particles alone, suggesting a significant input of HNO_3. Measurements below
cloud showed that as much as 25% of the cloud nitrate could be released as HNO_3 as cloud droplets
evaporated. These field measurements show that chemical processing of oxidised nitrogen does occur in
clouds, involving consumption of NO_x, and production of gaseous HNO_3 as cloud droplets evaporate. The
methods used to measure particulate nitrate concentrations, however, were not adequate to construct
a complete budget of oxidised nitrogen across the hill. © 1997 Elsevier Science Ltd.

Key word index: Field study, nitrogen oxides, cloud, NO_x, NO_y, HNO_3, HONO, nitrate, nitrite.

INTRODUCTION AND OBJECTIVES

The pathways by which nitrogen oxides (NO and
NO_2) in the gas phase are converted to nitrate in
cloud and rain are well known and have been used to
construct models of their transformation in the lower
atmosphere. Both homogeneous and heterogeneous
pathways are involved, although their relative
importance has generally not been quantified
(e.g. Heikes and Thompson, 1983; Lelieveld and
Crutzen, 1991).

Over the past five years, field experiments at Great
Dun Fell, in northwest England, have examined the
transformation of nitrogen oxides to nitrate by meas-
uring the changes in atmospheric composition as air is
advected through a stationary cap cloud on top of the
hill, treating the stationary cap cloud as an atmo-
spheric "reactor" (e.g. Colvile *et al.*, 1994, 1996a).
These measurements were consistent with nitrate pro-
duction from the reactive dissolution of NO_3 and
N_2O_5 radicals, formed in air upwind of the cloud.
Other potential reaction pathways were also

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described, involving the formation of nitrous acid (HONO) either upwind of cloud, or in cloud water (Cape et al., 1992).

As part of the ground-based cloud experiment (GCE) conducted under the auspices of EUROTRAC, measurements were made during April and May 1993 with the objective of quantifying the changes in total oxidised nitrogen (NO$_y$ = NO + NO$_2$ + HONO + HNO$_3$ + PAN + NO$_3^-$ particle + ⋯) in the gas and aerosol phase as an air mass passed through a cap cloud on the summit of Great Dun Fell. Gas and aerosol measurements were made upwind and downwind of the hill, and cloud water was analysed for nitrate and nitrite, in addition to other major ions. The objectives were:

(i) to quantify losses of NO and NO$_2$ (NO$_x$) across the hill, in order to investigate whether the cloud (as a "reactor") removed a significant quantity of NO$_x$ from the air mass;

(ii) to quantify gains in NO$_3^-$ in the aerosol phase, in order to assess the rate of nitrate production from the reaction of NO$_x$, the solution of nitric acid (HNO$_3$), the reaction of free-radicals (NO$_3$, N$_2$O$_5$), or from other unspecified reaction pathways.

Measurements were made at four experimental sites, Wharley Croft (WC), Mine Road (MR), the summit of Great Dun Fell (SU) and Moor House (MH) (see Choularton et al., 1996) for some or all of the experimental period.

METHODOLOGY

An overview of measurement methods is given in Choularton et al. (1996). Time resolution varied from 1 min (for gases such as NO and NO$_2$), to 8 h for some of the diffusion denuder measurements of nitrous and nitric acid. Details of methods for measuring oxidised nitrogen species are given below.

Instrumental methods

Total nitrogen oxides (NO$_y$) were measured only at Wharley Croft (WC), using a catalytic converter, in which the sampled air was mixed with CO and passed through a solid gold tube at 350°C (Fahey et al., 1985). All oxidised nitrogen compounds, including particles, were reduced to NO, which was measured using a Thermo-Environmental Model 42 chemiluminescent NO$_x$ analyser. A conversion efficiency of 100% was demonstrated for NO$_2$, by using a permeation tube source; suitable sources for other components were not available, and an effective conversion efficiency of 100% has been assumed in interpreting the data. For other gases the efficiency is likely to be in excess of 90% (Fahey et al., 1985), although the efficiency for nitrate particles is not known. The NO$_y$ measurements therefore give a lower bound to the true concentration of total oxidised nitrogen compounds in air. Air was sampled directly into the heated gold tube, as use of a sample inlet line as short as 1 m, made of PTFE (4 mm i.d.), had been shown previously (Colvile et al., 1994) to remove nitric acid. The NO$_x$ analyser was run continuously in NO mode, by-passing the internal thermal convertor, and was calibrated using a standard cylinder of NO in air (BOC Special Gases) diluted with pure air using a computer-controlled gas generator equipped with mass-flow controllers.

The output from the NO cylinder was cross-calibrated, using gas-phase titration with ozone, against a permeation tube containing N$_2$O$_4$ maintained in a thermostatted oven.

Nitrogen oxides (NO, NO$_2$, NO$_x$) were measured continuously at Wharley Croft (WC), Mine Road (MR) and Moor House (MH). At WC and MR, chemiluminescent analysers (Ecophysics CLD 770) were used to measure NO. NO$_2$ was measured using a photolytic convertor (Ecophysics PLC 760), which specifically photolyses NO$_2$ to NO. Calibration was by dilution of NO (as above), and the photolytic conversion efficiency for NO$_2$ was determined by automated gas-phase titration, or by comparison with the output from a permeation tube. At MH, NO and NO$_x$ were measured by a chemiluminescent NO$_x$ analyser (Thermo-Environmental 42S) with a thermal molybdenum convertor, calibrated using a diluted NO standard and NO$_2$ permeation tube, and cross-calibrated with the analyser at WC by means of a portable calibrator housing a permeation tube. This type of analyser responds quantitatively to PAN, and probably also to HONO, although HNO$_3$ would not have passed through the sampling inlet line (Colvile et al., 1994). All analysers were routinely calibrated before and after a designated experimental period.

At WC, annular denuders (Harrison et al., 1996) were operated for periods of 8 h to obtain an integrated value for HONO and HNO$_3$, and at MR annular denuders for HNO$_3$ were operated on an hourly basis.

Aerosol nitrate was sampled at WC and MH by both 5-stage Berner impactors and by Rotheroe-Mitchell high-volume samplers. The details of the particulate measurements, and the differences between them, are discussed by Choularton et al. (1996). In this paper, unless stated otherwise, particulate nitrate measurements refer to the Rotheroe-Mitchell (RM) samplers.

Cloud water for chemical analysis by ion chromatography was sampled by both active and passive collectors (Choularton et al., 1996).

Continuous measurements of nitrite in cloud were made using stopped-flow colorimetry, sampling cloud water from a passive gauge. The continuous system was calibrated before, during and after each experimental period using freshly made serially diluted solutions of NaNO$_2$ (A.R. grade) in distilled water. Concentrations of gaseous nitrous acid were inferred from continuous measurements of cloud water acidity and the use of Henry's Law (Cape et al., 1992). Acidity was measured continuously by mixing cloud water in a flow system with 1 M KCl solution, to provide a uniform high ionic strength prior to pH measurement using a combined micro-electrode. The pH measurement system was calibrated using dilute solutions of sulphuric acid over a range of concentrations between 10 and 1000 μM in place of the cloud water. This technique overcomes many of the problems associated with making pH measurements in solutions of low ionic strength (Galloway et al., 1979).

Estimates of precision and accuracy

Data were measured continuously from the gas analysers, and stored as 1 min averages, which were later combined to give 10 min average values. The limit of detection of the Ecophysics analysers for NO and NO$_2$ over a 10 min period was estimated, based on an unweighted multi-point calibration, to be better than 0.03 ppbV (parts in 10^9 by volume). The commercial "zero-air" source used for the calibration was further purified by passing the output over supported potassium permanganate (to oxidise NO to NO$_2$) followed by activated charcoal (to absorb NO$_2$). For the Thermo-Environmental NO$_x$ analysers, the precision is slightly poorer, estimated at around 0.05 ppbV over a 10 min period. Calibrations were performed before, during and after each intensive period of measurement; where a drift in the zero value of the Thermo-Environmental analyser occurred (typically of the order of 0.1 ppbV or less), linear interpolation

was used to correct the signal throughout the period of measurement. The Ecophysics analyser actively corrects for zero drift every measurement cycle. Span calibrations, typically at around 40 ppbV, showed variations in the response of less than 1 ppbV. The overall accuracy of the NO and NO_2 measurements at concentrations up to 5 ppbV is therefore likely to be within 0.1 ppbV. For the gold/CO convertor for NO_y, the values obtained must be seen as lower bounds, given the lack of information on conversion efficiencies for reduction of nitrate-containing particles to NO. However, the lack of a sampling inlet line means that gases such as HONO and HNO_3 are likely to have been measured with close to 100% efficiency.

Estimates of HONO in cloud, derived from simultaneous measurement of NO_2^- and H^+, are uncertain insofar as they rely on the establishment of Henry's Law equilibrium between the gas and aqueous phases after collection of the cloud droplets, to permit mixing and equilibration of droplets having potentially different chemical composition (Pandis and Seinfeld, 1991). In the system employed here, sampled cloud water and air were actively pumped from the passive collector through a phase-separator, where bulk liquid cloud water was continuously purged with ambient air, and was likely to be close to equilibrium. If a bias exists it would be in the direction of overestimating the computed gaseous HONO concentration.

The uncertainty in aerosol NO_3^- concentrations, including both sampling and analytical uncertainty, has been estimated as $\pm 15\%$ (Laj et al.,1996a), except for times when the aerosol sampler at MH was in cloud, when cloud droplets (and dissolved HNO_3) may have been sampled. Cloud water concentrations also have an uncertainty of around 15% (Laj et al., 1996b), to which has to be added the uncertainty in cloud liquid water content (Colvile et al., 1996b) in converting to equivalent gas-phase concentrations. The overall uncertainty in expressing cloud NO_3^- concentrations as ppbV equivalent is around $\pm 20\%$.

Comparison of data sets during monitoring

An example of the comparison of NO_x data from different sites may be seen in Fig. 1, which shows measurements at WC and MR on a day when cloud was not present. This figure illustrates a number of the features which must be taken into account when comparing data between sites. Measurements at WC (triangles) were relatively stable through the day, but changed abruptly at 0930 BST from around 8 ppbV to close to 1 ppbV, and thereafter rose slowly until midnight. By contrast, the data from MR are characterised by very large peaks (over 20 ppbV) superimposed on a much smaller background, which is different from the concentration at WC until 0930 BST, from when the two traces are in excellent agreement. The lack of agreement before 0930 was caused by sampling different air; the wind speed at MR was around $1 \, m \, s^{-1}$, and was even less at WC. From 0930 BST, as wind speed increased, the same air was sampled at both sites. However, the northerly wind direction at MR brought air contaminated by the exhaust from the diesel-powered electrical generator for that site across the measurement point, giving the periodic large concentrations.

SPATIAL VARIATION IN DATA

In the absence of rapid removal processes for NO_x from the atmosphere, either by dry deposition or by chemical reaction, the dynamic structure of the NO_x concentration can be used to ascertain whether or not the air flow was connected between the different sites, as illustrated above. This comparison provides additional information to that used on the basis of thermodynamic and meteorological information in determining the extent of flow connection (Colvile et al., 1996b). Examples will be seen in the case studies presented later, when not only evidence of connected
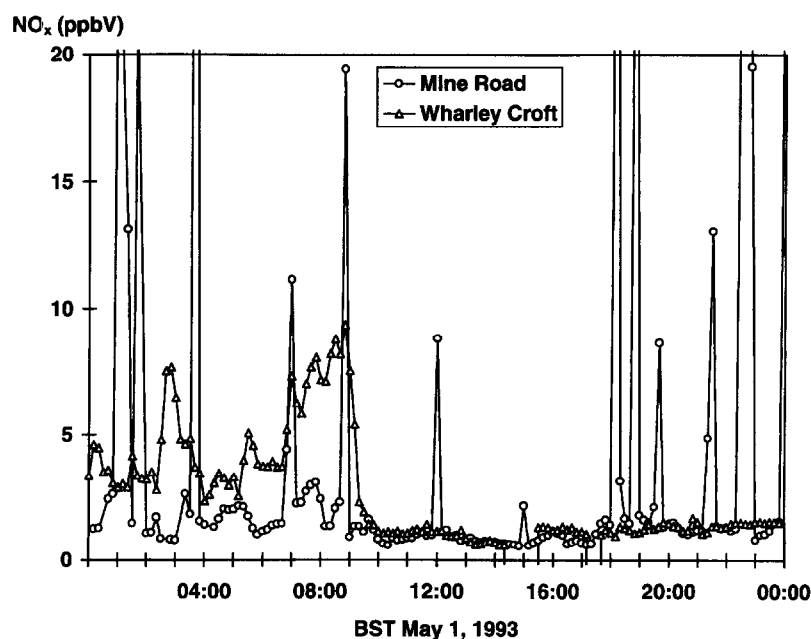

Fig. 1. Concentrations of NO_x (NO + NO_2) expressed as 10 min averages, at Wharley Croft (WC) and Mine Road (MR) on 1 May 1993.

flow, but also the effective time lag between sites, may be inferred from NO_x measurements.

CASE STUDIES OF NO_x TRANSFORMATION IN CLOUD

During the course of the measurement campaign there were 4 distinct periods for which sufficient data are available to investigate the possibility of NO_x consumption and NO_3^- production in cloud. Details of the meteorological conditions and chemical characteristics of the air mass during these periods will be found in Colvile et al. (1996b) and Swietlicki et al. (1996), respectively. There are, unfortunately, no periods when all the measurements were in operation at all sites.

Case study for 22 April 1993

A southwesterly airstream brought moist air over northwest England to Great Dun Fell. All sites were connected by the air flow, and site SU was in cloud throughout the period of intensive measurement (1600–2400 BST). Sites WC and MR were therefore upwind of the cap cloud on the summit. The surface wind direction was southerly, and surface wind speed was around $7 \, m \, s^{-1}$ at WC and MR, so that MR was approximately 16 min downwind of WC, but MH was only about 3 min downwind of MR, assuming horizontal homogeneity in the air flow. Figure 2 shows the relevant NO_x concentrations at the sites with data

(MR, upwind, and MH, downwind). The NO_2 convertor at WC was not in operation, but concentrations of NO_y were measured continuously. Overall, concentrations of NO_x were large, reflecting the passage of air over the industrialised region to the southwest of the measurement sites. With the exception of a period of around 40 min from 2130 BST there was a consistent decrease in NO_x concentration as the air mass moved across the hill, varying between 0 and 2 ppbV, suggesting reaction and transformation of NO_x during passage through the cloud, or dilution by entrainment of cleaner air. If reaction occurred, with production of nitrate, the aerosol data from upwind and downwind should show an increase in nitrate concentration. Air concentrations of nitrate aerosol, expressed as equivalent gas-phase NO_x for comparison with the gas data, are shown in Fig. 3. The large difference between the impactor data and the filter data upwind (WC) point to either a large contribution of HNO_3 (trapped on the filters), or to the exclusion of large particles from the impactor inlet. Measured HNO_3 and HONO concentrations at WC were small throughout most of the period, around 0.02 ppbV HONO and 0.03 ppbV HNO_3 (1600–2200 BST), suggesting that large particles were excluded from the impactor. The denuder data for the period 2210–0830 BST showed an increase in average HNO_3 concentration, to 0.08 ppbV, but no increase in HONO. The concentration of nitrate aerosol as small particles (measured by the impactor) was small, equivalent to
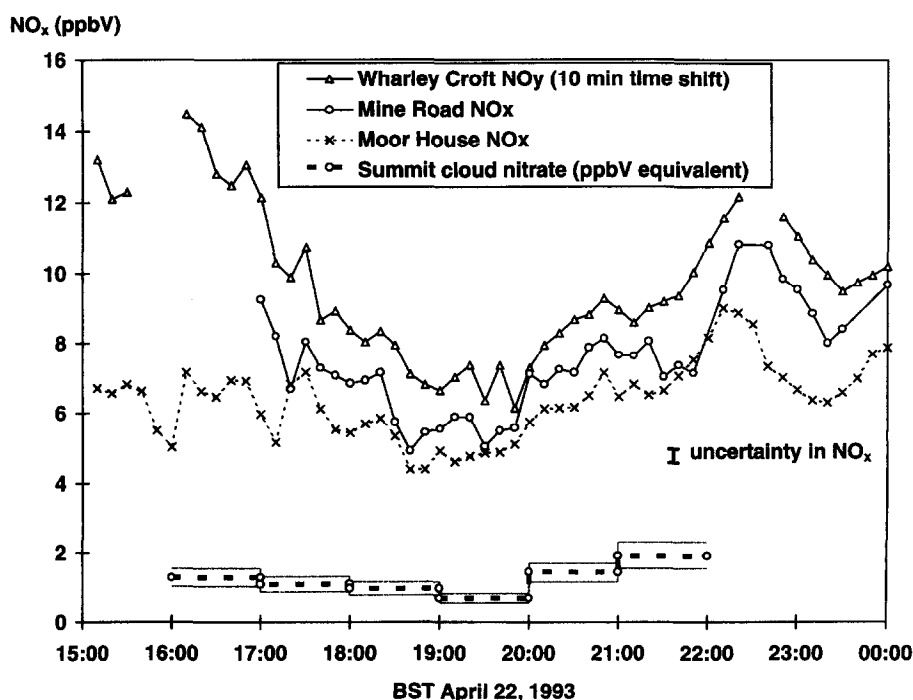

Fig. 2. NO_x and NO_y concentrations on 22 April 1993, and equivalent concentration of NO_3^- in cloud, expressed as NO_x in the gas phase. The overall uncertainty in cloud nitrate concentrations ($\pm 20\%$) is shown.
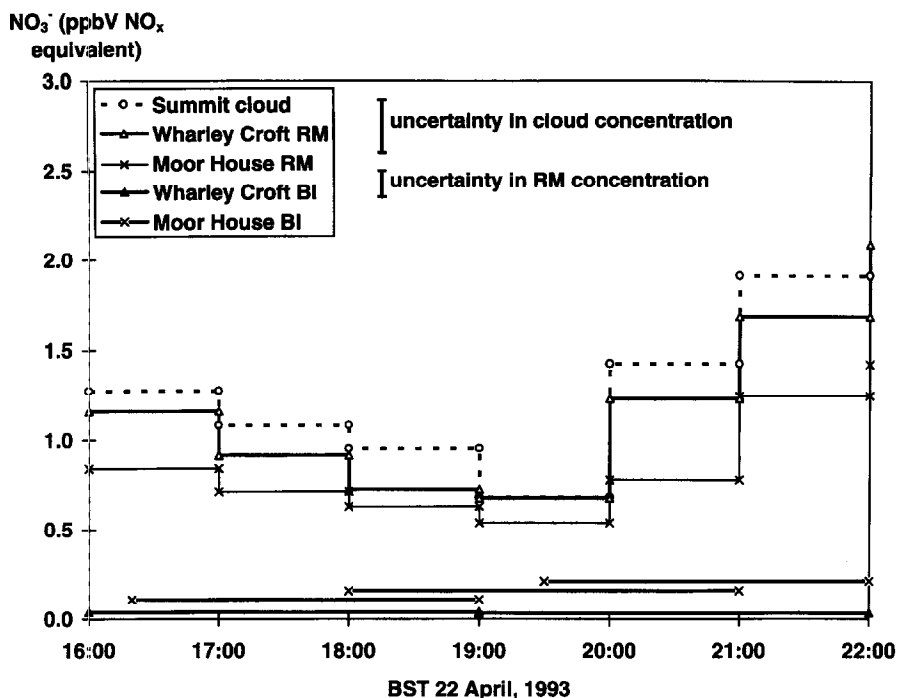
NO₃⁻ (ppbV NOₓ
equivalent)

Fig. 3. Nitrate aerosol concentrations from both Rotheroe-Mitchell (RM) filters and Berner-Impactors (BI), and nitrate concentrations in cloud at the summit, all expressed in terms of equivalent NO_x concentration. The upwind site on 22 April 1993 was Wharley Croft (WC).

around 0.05 ppbV NO_x. The total nitrate aerosol loading upwind (WC) measured by the filters was, however, the same as the calculated concentration in summit cloud water, and the difference between NO_y and NO_x, to within the combined error (Figs 2 and 3).

The particle loadings on the filters at MH throughout this experiment were systematically low compared with WC. All ions except sulphate had concentrations around 70% of WC; a regression analysis between WC and MH including all ions except sulphate between 1700 and 2200 BST had a slope of 0.72 and an r^2 of 0.95 ($n = 30$: 6 samples $\times 5$ ions). There was evidence of sulphate production in cloud during this period (Laj et al., 1996a; Wells et al., 1996). The impactor samples (smaller size-fraction) at MH, however, had greater nitrate concentrations than upwind, and showed a steady increase through the evening. Although the impactors only sampled a small fraction of the NO_3^- sampled by the RM filter samplers, the increase at MH relative to WC suggests a redistribution of nitrate across the particle size range, or the production of nitrate in cloud. There were no data for HNO_3 or HONO concentrations downwind of the summit.

Throughout this period there was a systematic reduction in both gaseous NO_x and particulate nitrate concentration in the air mass as it moved across the hill. There was, however, no evidence of large-scale entrainment of less polluted air (Colvile et al., 1996b),

which could have acted as a diluent on the whole air mass. The loss of nitrate measured on the particle filters could have been caused by a miscalibration of the sampled air volume at MH, as suggested by Wells et al. (1996), or by loss of material through deposition in light drizzle which was observed at the summit and at MH throughout the evening. Neither of these processes would have affected the NO_x concentrations. At the summit, the concentration of HONO inferred from measurements of NO_2^- and H^+ in cloud was between 0.02 and 0.03 ppbV until 2100 BST, when the concentration rose rapidly to over 0.4 ppbV. Before 2000 BST the acidity of the cloud water was very low, around pH 5.5, suggesting very little input of HNO_3 or N_2O_5 into the cloud from the gas phase, consistent with the measurements upwind. The concentration of acidity rose rapidly between 2000 and 2100 BST to around 90 μM, with an increase in SO_2 (Swietlicki et al., 1996) and non-marine Cl^- (Schell et al., 1996), and an increase in NO_3^- concentration of about 50 μM. The increase in nitrate in cloud over the hour, expressed in gas-phase equivalents, was 0.8 ppbV, and was matched by an increase in nitrate in the particle filter samples upwind (Fig. 3).

The gas-phase measurements throughout this case study suggest production of gaseous HONO, and possibly HNO_3, in cloud. Overall, between 0.5 and 2 ppbV NO_x were lost across the hill, with the largest losses occurring after 2200 BST. The available

measurements of HONO upwind (0.02 ppbV as an average through the period) suggest that after 2100 BST, HONO detected as nitrite in cloud water (up to 0.4 ppbV) was not derived from the solution of gas-phase HONO, but from reaction of NO_x in cloud. The apparent loss of total particle mass between the summit and MH and the lack of gas-phase HNO_3 data at MH prevent the confirmation of NO_x reaction in cloud through direct measurement of nitrate production.

Case study for 5–6 May 1993

The period considered here is between 1700 BST on 5 May and 0200 BST on 6 May. The air flow was from the northeast, making site MH upwind of the summit, and sites WC and MR downwind. There were no NO_x data available from MR during this period, but air flow appeared to be connected across the hill (Colvile et al., 1996b). Evidence for connected flow was also found in the NO_x data, with the fine structure upwind (MH) also seen some 30 min later downwind at WC (Fig. 4). The transit time between MH and WC calculated from surface wind speeds and directions was 30 min. There was a systematic decrease in NO_x concentration as the air passed over the hill through the cap cloud before 1930 BST, when NO_x concentrations were 2–3 ppbV, but no difference was detectable (within the combined uncertainty) later in the day when overall concentrations dropped below 0.5 ppbV. The fractional loss of NO_x between the sites

was 15–30% during the early evening. Particulate nitrate concentrations were small (equivalent to 0.2–0.3 ppbV NO_x) on both sides of the hill during the early evening, but increased after 2000 BST (Fig. 5). Before 2000 BST, nitrate concentrations from filters on both sides of the hill were smaller than the equivalent calculated concentrations from nitrate in cloud water, indicating a possible contribution of HNO_3 to cloud nitrate concentrations, and there was a small increase from MH (upwind) to WC (downwind), but this was close to the combined uncertainties. After 2000 BST, concentrations of nitrate on filters upwind were closely matched by the concentrations in cloud until just after midnight. Concentrations on filters downwind between 2000 BST and midnight were smaller, perhaps indicating dilution of the air by entrainment of cleaner air downwind of the summit (Colvile et al., 1996b). Between midnight and 0100 BST, however, there was a marked drop in nitrate concentrations upwind of the cloud, and apparent production of nitrate across the hill, coincident with a small, but significant, loss of NO_x between MH and WC (Fig. 4). Overall concentrations of (NO_y–NO_x) observed downwind varied between 0 and 1 ppbV, averaging about 0.5 ppbV, of which about half may be accounted for by the filter nitrate concentrations. Although nitric acid was detected immediately below cloud base downwind (MR) between 1800 and 2000 BST and between 0000 and 0200 BST, concentrations did not exceed 0.1 ppbV, and concentrations were
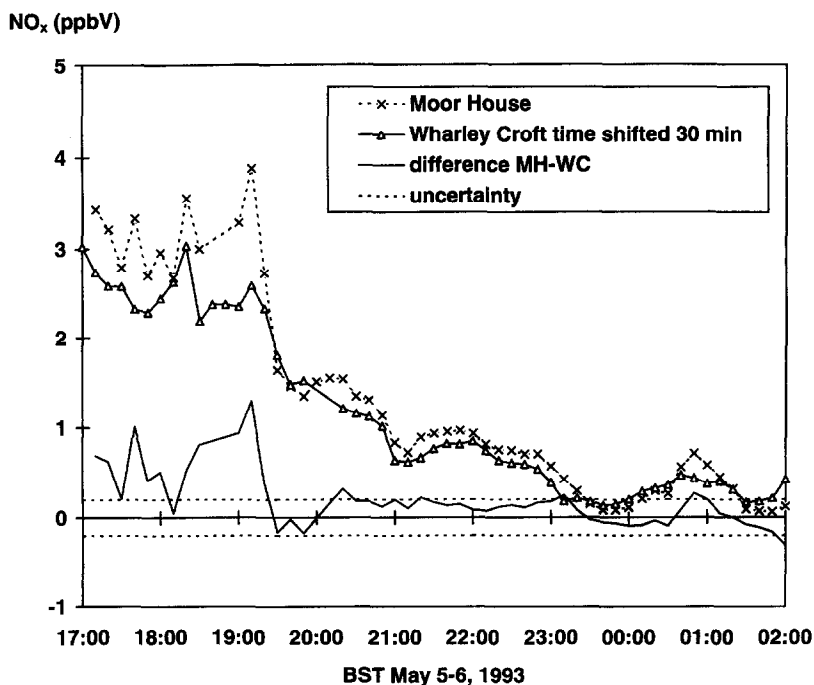

Fig. 4. Concentrations of NO_x upwind (Moor House) and downwind (Wharley Croft) of the summit on 5–6 May 1993. The time shift between the sites was taken as 30 min. Times are plotted relative to Moor House.
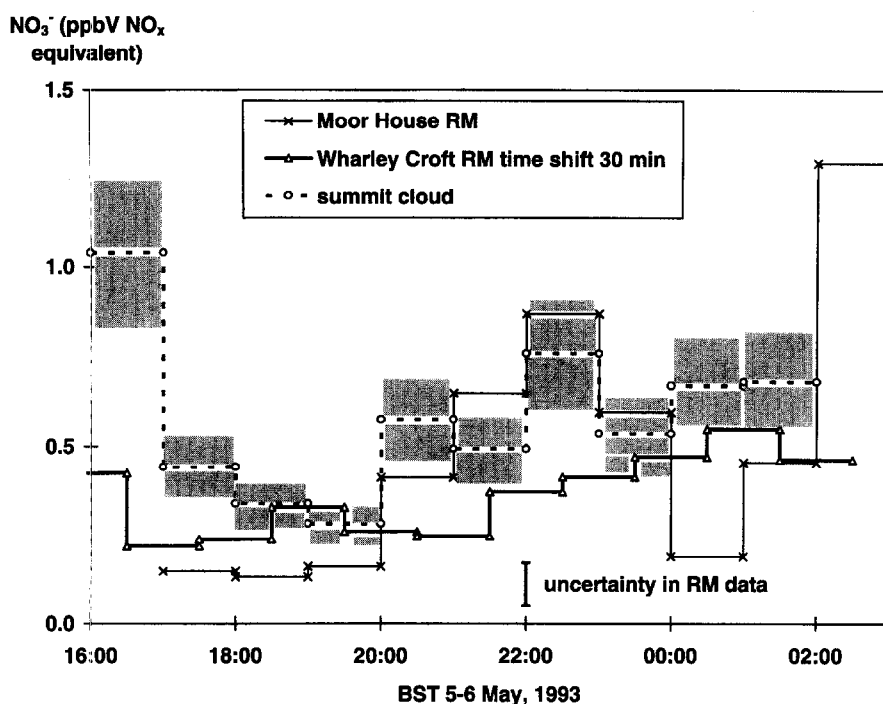
NO₃⁻ (ppbV NOₓ
equivalent)

Fig. 5. Particulate nitrate concentrations from Rotheroe-Mitchell filters, and cloud nitrate concentrations, on 5–6 May 1993, expressed as equivalent concentrations of NO_x. The shaded regions show the uncertainty in cloud nitrate concentrations. Data from Wharley Croft are shifted by 30 min to allow for transport from Moor House. Times are plotted relative to Moor House.

below the detection limit throughout the period at WC. Concentrations of HONO at WC were around 0.02 ppbV during the evening, and fell below the detection limit after 2300 BST. In the cloud, inferred HONO concentrations were larger, up to 0.3 ppbV at 1600 BST, falling to <0.1 ppbV after 1800 BST then rising to around 0.15 ppbV after dark, before falling again to 0.02 ppbV at midnight. Concentrations increased to almost 0.1 ppbV at 0030 BST before falling again, coincident with apparent nitrate production across the hill (see above).

There was evidence for significant loss of up to 1 ppbV NO_x across the hill before 2000 BST, which was matched by a smaller (0.1–0.2 ppbV) increase in nitrate, close to the measurement uncertainty. Thereafter, the concentrations of NO_x and nitrate were too small relative to the measurement errors to draw any clear conclusions, except for a short period at around 0030 BST, when there was an increase in nitrate across the hill of 0.3 ppbV, a loss of about 0.2 ppbV NO_x, an estimated HONO concentration in cloud of 0.1 ppbV, and measured HNO_3 concentrations immediately below cloud base of around 0.1 ppbV.

Case study for 9–10 May 1993

During the period of intensive measurement, from 2200 BST on 9 May to 0700 BST on 10 May the wind was from the northeast, making site MH upwind and site MR downwind. The calculated transit time from MH to MR was around 3 min. There are no data from

site WC. The concentrations of NO_x were small, less than or equal to 1 ppbV. However, concentrations at MH were 0.3 ppbV larger than at MR before 0230 BST (Fig. 6), indicating loss of NO_x as the air mass crossed the hill. There was some structure at MR after 0400 BST, which was not seen at MH, and which may have been caused by interference from diesel generators close to the summit of the hill (Fig. 6). Except for the period between 0500 and 0700 BST, when there was evidence of strong entrainment of air between the summit and MR (Arends, personal communication), there was little evidence that entrainment of air from higher in the atmosphere had an effect on the NO_x concentrations across the hill (Colvile et al., 1996b).

This small loss of NO_x across the hill could not be detected as an increase in the concentration of particulate nitrate across the hill (Fig. 7) because MH was in cloud for most of the period (Colvile et al., 1996b). The particulate nitrate concentrations from MH during cloud are systematically too low because of under-capture of cloud droplets by the Rotheroe-Mitchell collector. The equivalent NO_x concentrations at MH and in the summit cloud were in good agreement when MH was not in cloud. There was no cloud at WC, and although the flow across the hill appears to have been connected between MH and WC, the particulate nitrate concentrations from the Rotheroe-Mitchell (RM) collector were systematically lower at WC than at MH. The nitrate concentrations recorded in the Berner Impactor at WC were a factor
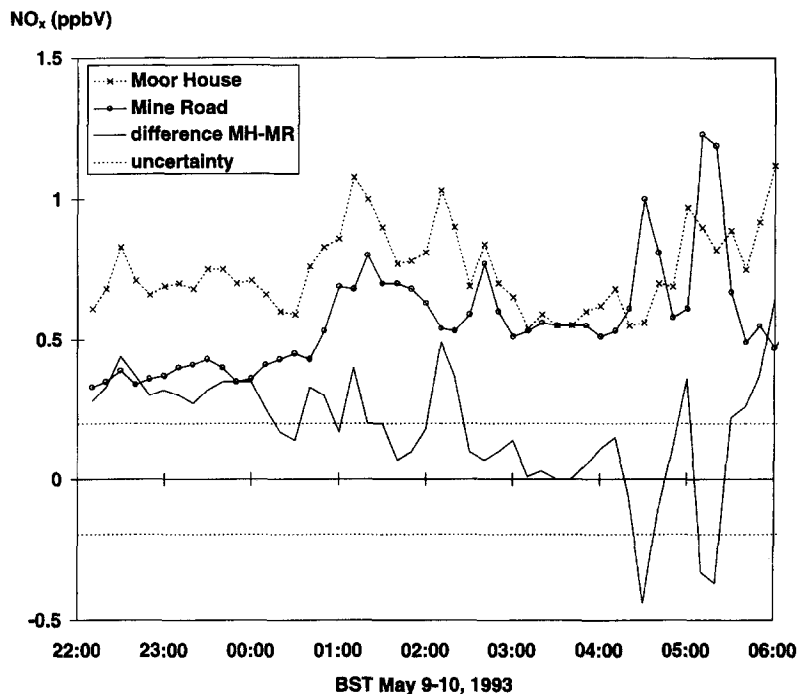
NO$_x$ (ppbV)

Fig. 6. Concentrations of NO$_x$ measured upwind (Moor House) and downwind (Mine Road) on 9–10 May 1993.
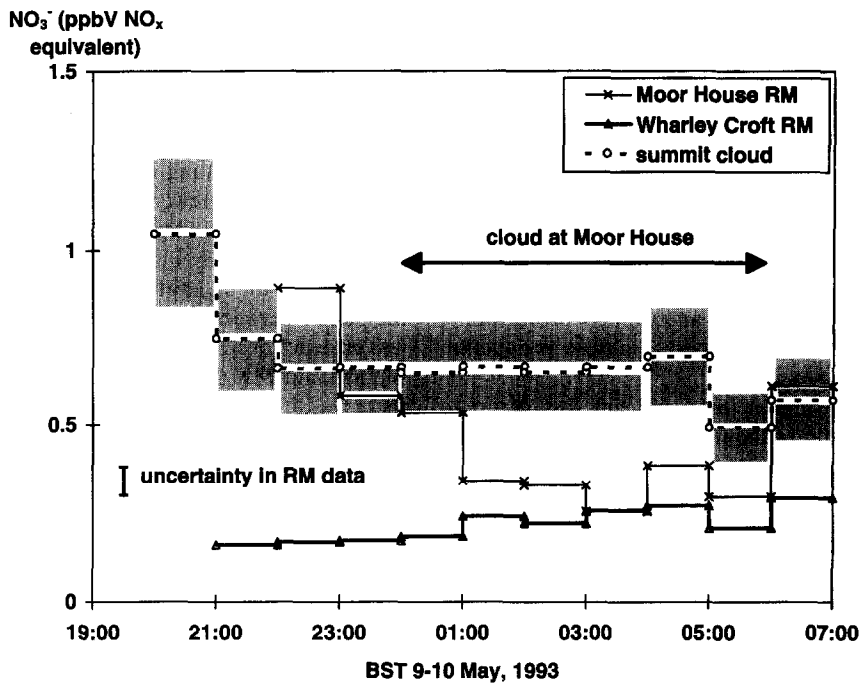
NO$_3^-$ (ppbV NO$_x$ equivalent)

Fig. 7. Particulate nitrate concentrations from Rotheroe-Mitchell filters, and cloud nitrate concentrations, on 9–10 May 1993, expressed as equivalent concentrations of NO$_x$. The shaded regions show the uncertainty in cloud nitrate concentrations.

of 2 greater than for the RM collector, but still smaller than the equivalent concentration in summit cloud, suggesting a problem with the operation of the RM collector.

Nitric acid was detected at MR, downwind of the cloud, between 2000 and 2200 BST, at a concentration of 0.1–0.2 ppbV. The denuder was operating with a cyclone attached to remove cloud droplets, as site

MR was continuously in cloud during this period; detection of measurable amounts of HNO_3 indicates degassing of HNO_3 from the evaporating cloud droplets. Loss of nitrate as HNO_3 may also be partly responsible for smaller measured nitrate concentrations at WC.

Gas-phase concentrations were small, but showed a detectable loss of NO_x across the hill before 0200 BST. The detection of gaseous HNO_3 at the downwind base of the cloud also suggests that oxidised nitrogen was being processed in the cloud, although there is no direct evidence of net production of nitrate from NO_x.

Case study on 11–12 May 1993

The wind direction was still northeasterly, with continuing low concentrations of NO_x, around 1 ppbV. Differences in concentration between the upwind site (MH) and downwind site (MR) were smaller than for the previous day, and within the measurement uncertainty (Fig. 8). Although there was no detectable loss of NO_x, there was a small but systematic increase in particulate nitrate concentrations between MH (upwind) and WC (downwind), up to 0.3 ppbV (NO_x equivalent) (Fig. 9). The small value for MH between 2200 and 2300 BST was caused by the site going into cloud, with a consequent drop in collection efficiency. The equivalent nitrate concentrations in cloud were very much larger, however, before 2300 BST suggesting that a large proportion of the cloud water nitrate was related to HNO_3 gas or radical precursors (NO_3, N_2O_5) rather than nitrate particles, as observed pre-

viously at this site (Colvile et al., 1994). Measurements of HNO_3 at MR, downwind of the summit, showed HNO_3 gas concentrations to be up to 0.4 ppbV at this time (Fig. 9), which presumably came from degassing of the evaporating cloud droplets (Colvile et al., 1996a).

For this period, there was no evidence of NO_x reaction in cloud, but the presence of HNO_3 downwind of the cloud, at concentrations approximately half those of the particulate nitrate, show that significant processing of oxidised nitrogen was occurring in cloud.

DISCUSSION AND CONCLUSIONS

Evaluation in terms of original objectives

(i) The measurement systems for NO_x across sites had a combined uncertainty of around 0.2 ppbV, which was similar to the magnitude of the differences seen across the hill for the last case study, but adequate to demonstrate significant differences between sites in the earlier studies. An added complication to the interpretation of the data in easterly flow is the possibility that "NO_x" at MH included PAN (peroxy acetylnitrate), which would have been detected by the thermal convertor there, but not detected by the photolytic convertors to the west of the summit (MR and WC). In general, PAN concentrations in Britain are small, and rarely exceed a few percent of the total NO_x concentration (PORG, 1993). The interpretation of differences in concentration upwind and downwind
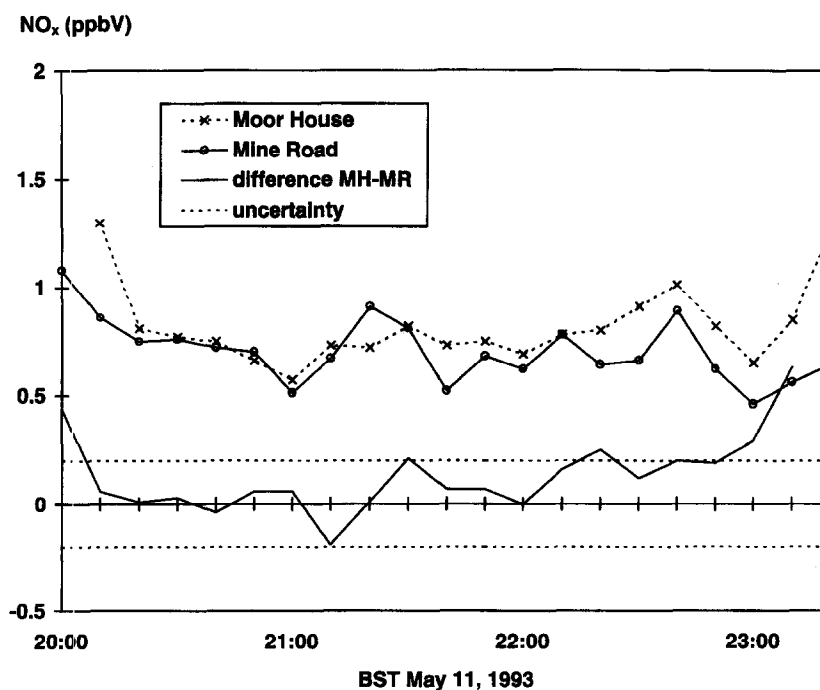

Fig. 8. Concentrations of NO_x upwind (Moor House) and downwind (Mine Road) on 11–12 May 1993.
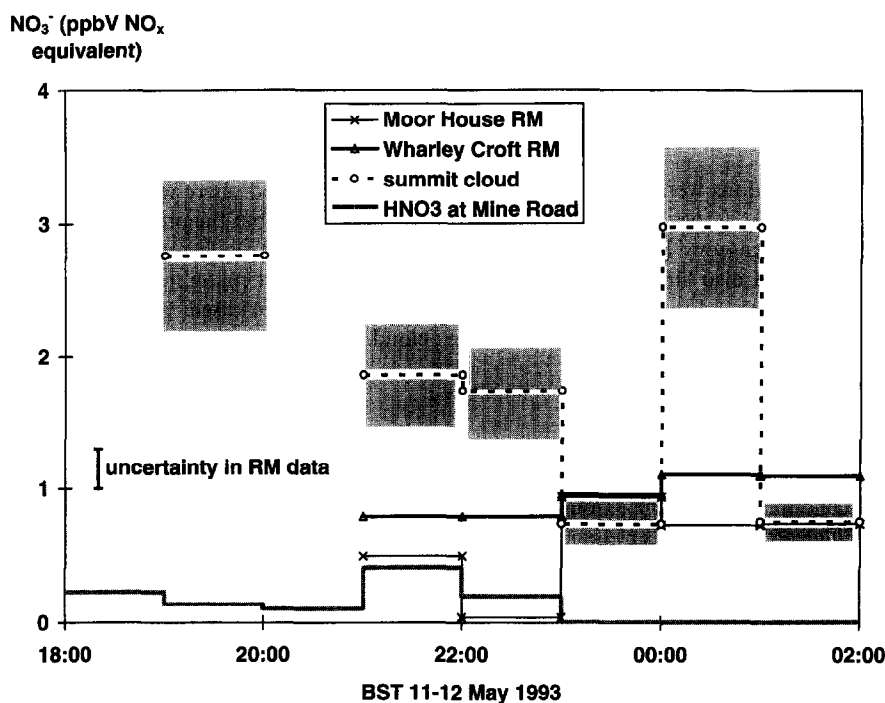
NO₃⁻ (ppbV NOₓ
equivalent)

Fig. 9. Particulate nitrate concentrations from Rotheroe-Mitchell filters, and cloud nitrate concentrations, on 11–12 May 1993, expressed as equivalent concentrations of NO_x. The shaded regions show the uncertainty in cloud nitrate concentrations. The concentration of HNO_3 downwind of the cloud is also shown.

of the hill cloud does not simply, however, rely on measurements of the gas-phase NO_x concentrations. Apart from the possibility of reaction in cloud, to produce nitrite or nitrate ions, the air mass may be diluted by entrainment of cleaner air over the hill, or by mixing into different depths of boundary layer. Moreover, in order for differences in mixing ratios to be ascribed to chemical reactions, there must be a continuity of air flow across the hill, so that the same air is sampled at all sites. This condition was established (Colvile et al., 1996b) for the first case study, in westerly flow, which also showed the greatest absolute difference in NO_x concentration across the hill, because of the large ambient concentrations. Only in this case study did the gas-phase NO_x concentration greatly exceed the concentration of nitrate particles or nitrate in cloud (Fig. 2). The relative difference in NO_x concentration across the hill was not large, amounting to no more than 15–20%, so that, for many of the other studies conducted at the same time, NO_x may be regarded as a tracer species (e.g. Wells et al., 1996).

The use of NO_x in this budget study, rather than NO and NO_2 separately, avoids complications caused by reaction of NO with ozone, or photolysis of NO_2, both of which change the ratio of NO to NO_2 on a time scale of tens of seconds but which leave the concentration of NO_x unchanged. Other gas-phase reactions, for example, the reaction of NO_2 with O_3 to

give NO_3 radicals, occur on much slower time scales, which would not significantly alter the total NO_x concentration during the transit time across the hill (up to 30 min).

(ii) Measurement of the aerosol nitrate and nitric acid concentrations proved to be inadequate as a means of determining whether or not NO_x had been transformed on passage through cloud. It is clear from the measurements, however, that both gas-phase and particle phase must be measured, because of the inter-conversion in cloud. Not only does HNO_3 dissolve in cloud water, increasing total nitrate concentration, but it appears from the data here, especially in the third and fourth case studies, that HNO_3 may be released as cloud droplets evaporate downwind from the hill summit. The difficulty of making a reliable measurement of aerosol nitrate, to include all particle sizes, yet without contamination by nitric acid, precludes complete speciation of airborne nitrate. It may be possible, however, to obtain concentration data for "total nitrate", to include both HNO_3 and aerosol nitrate. The measurements of NO_y provide a guide to the total oxidised nitrogen, but include gases such as PAN, which may be present in concentrations similar to those of HNO_3. Until a reliable method for calculating the conversion efficiency of aerosol nitrate is found, such measurements cannot provide concentration data suitable for constructing budgets.

Conclusions

Of the four case studies described above, only the first provides evidence of a significant loss of NO_x as air passed through the hill cloud on the summit of Great Dun Fell. The use of a gas analyser specific for NO_2, with a photolytic converter, upwind of the cloud means that any other oxidised nitrogen gases which would have been detected downwind by the thermal converter would cause a bias towards underestimating the loss of NO_x. Although it did not prove possible to construct a mass budget of nitrate across the hill, there was evidence from the impactor data of a transformation of the nitrate particle-size distribution. There was also evidence from measurements in cloud for the production of nitrite ions, which would have been released as nitrous acid (HONO) when cloud droplets evaporated. Of the other case studies, that on 5–6 May showed both a loss of NO_x and an apparent gain in particulate nitrate across the hill. There was also evidence in the later case studies, from measurements in and immediately below cloud, of a significant contribution of HNO_3 to the total nitrate in the atmosphere, even downwind of the cloud.

Any attempt to detect the reaction of NO_x in cloud, as in this field study, places very strict requirements on the precision and accuracy of gas and particle measurements, and on the measurement and interpretation of air flow and mixing across the hill (Kelly et al., 1989). In the studies described above, not all of the requirements were met, yet there is sufficient evidence, particularly from measurements of NO_2^- in cloud and HONO and HNO_3 concentrations below cloud, that passage of air through orographic clouds not only changes the partitioning of nitrate between the gaseous and particulate forms, but may also result in the reaction of NO_x to give HONO.

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