Pergamon

Atmospheric Environment Vol. 31, No. 16, pp. 2637–2648, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
1352-2310/97 $17.00 + 0.00

PII: S1352-2310(96)00229-4

OCCURRENCE AND FORMATION OF NITRATED PHENOLS IN AND OUT OF CLOUD

JENS LÜTTKE,*† VOLKER SCHEER,* KARSTEN LEVSEN,*
GEROLD WÜNSCH,‡ J. NEIL CAPE,§ KEN J. HARGREAVES,§
ROBERT L. STORETON-WEST,§ KARIN ACKER,
WOLFGANG WIEPRECHT¶ and BRIAN JONES||

*Fraunhofer Institut für Toxikologie und Aerosolforschung, Nikolai Fuchs Straße 1, D-30625 Hannover, Germany; ‡Institut für Anorganische und Analytische Chemie, Universität Hannover, Callinstraße 9, D-30167 Hannover, Germany; §Institute of Terrestrial Ecology, Edinburgh Research Station, Bush Estate, Penicuik EH26 0QB, U.K.; ¶Fraunhofer Institut für Atmosphärische Umweltforschung, Aussenstelle für Luftchemie, Rudower Chaussee 5 D-12484 Berlin, Germany; and ||AEA Technology, National Environment Technology Centre, Culham, Abington, Oxon OX14 3DB, U.K.

(*First received* 2 *November* 1995 *and in final form* 27 *July* 1996. *Published May* 1997)

Abstract—In this study, the concentrations of phenol, four nitrated phenols, their precursors and reactants in air and cloud water, are presented. The concentrations in air and cloud water were measured simultaneously at the summit of Great Dun Fell (GDF). The measured concentrations were compared with emission data, leading to the conclusion, that in particular dinitrophenols are formed by atmospheric reactions, while car exhaust accounts to a significant extent for the mononitrophenols observed. The experimental results point to a formation of dinitrophenols in the liquid phase (cloud droplets). This is corroborated by flow tube experiments which show that phenol in aqueous solution reacts with N_2O_5 and $ClNO_2$ to form nitrophenols. © 1997 Elsevier Science Ltd.

Key word index: Phenol, cloud water, nitrogen oxides, BTEX-aromatics, gas-phase reactions, liquid-phase reactions.

1. INTRODUCTION

The existence of nitrophenols in the atmosphere has been known since Nojima *et al.* (1975, 1976) first reported their identification by GC-MS in rain water. Moreover, the authors irradiated benzene or toluene/NO mixtures in a glass chamber with UV light and found a yellowish product consisting of nitrophenols and nitrocresols. From these experiments they concluded that nitrophenols are formed by photochemical reactions in the atmosphere during smog situations. Data on the occurrence of nitrophenols remained scarce (Nojima *et al.*, 1983; Leuenberger *et al.*, 1985, 1988), until their phytotoxic properties were discussed (Shea *et al.*, 1983; Schafer and Schönherr, 1985), and it was suggested that nitrophenols may represent one factor for the forest decline observed in Northern and Central Europe and other parts of the world (Rippen *et al.*, 1987). Since then nitrophenols have gained more attention and have been determined in rain water, fog, snow and plant leaves (Levsen *et al.*, 1990, 1993; Hinkel *et al.*, 1989; Richartz *et al.*, 1990), while measurements of nitrophenols in the gas phase have remained scarce (Leuenberger *et al.*, 1985; Nishioka and Lewtas, 1990). Herterich and Herrmann (1990) investigated the gas phase, rain water and the particulate phase in the atmosphere of two German hill sites. In their study they report on ratios between mono- and dinitrophenols, correlation of liquid phase 4-nitrophenol with the nitrate concentration and they discuss the formation, emission and deposition of nitrophenols. However, the sampling sites in this study were affected by primary emissions of nitrophenols from urban areas.

The formation of nitrophenols in combustion processes of motor vehicles was reported by Nojima *et al.* (1983) and more recently by Tremp *et al.* (1993), who found nitrophenols and nitrocresols in the exhaust gas of car engines in the mg m^{-3} range. Apart from these investigations of primary sources for nitrophenols, several theoretical approaches based on smog chamber studies were undertaken to explain an atmospheric formation of these compounds (Atkinson, 1989; Atkinson *et al.*, 1989, 1990; Atkinson and Aschmann, 1994; Grosjean, 1985; Nojima *et al.*, 1994).

---

† Author to whom correspondence should be addressed.

The degradation of pesticides such as parathion and parathion-methyl was investigated by various authors (Woodrow *et al.*, 1977; La Planche *et al.*, 1981; Bayer 1988a, b; Kishk *et al.*, 1976), who found that a major product of this degradation is 4-nitrophenol. This was also addressed in a report of GDCh (1992) in which the authors estimate a maximum input of $120\,\mathrm{t\,a^{-1}}$ of 4-nitrophenol into the environment, originating from the degradation of parathion and parathion-methyl used in the Federal Republic of Germany in 1989. Further entries of nitrophenols into the environment are possible from the combustion of coal and wood. However, due to insufficient data, the significance of these contributions remains unclear. The physicochemical properties of nitrophenols were studied by Schwarzenbach *et al.* (1988), who derived approximated Henry's law constants.

In this field study, gas- and liquid-phase concentrations of phenol and four nitrophenols, i.e. 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), and dinitroorthocresol (DNOC), in the air of a remote sampling site are reported. The data are supplemented by data on possible precursors, i.e. (benzene, toluene) with the aim of obtaining additional information on nitrophenol formation in the atmosphere.

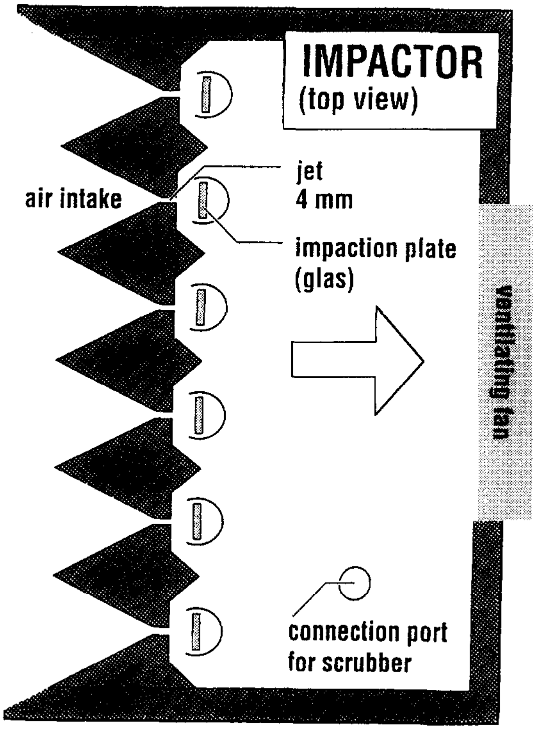


Fig. 1. Schematic overview of the cloud water collector (impactor).

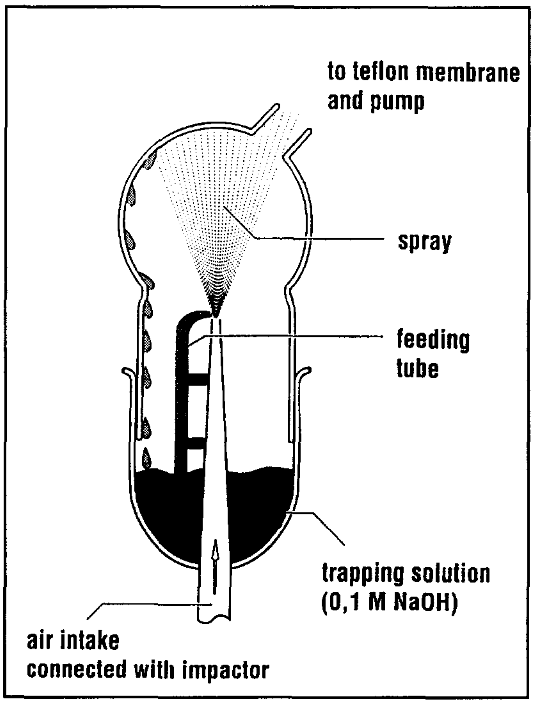


Fig. 2. Scrubber-unit, used for aerodispersive enrichment of gas-phase phenol and nitrophenols.

2. EXPERIMENTAL

2.1. *Sampling*

Sampling of phenolic compounds in gas phase and cloud water was performed on GDF Summit. BTEX-aromatics were sampled at Fell Gate (see Choularton *et al.*, 1997).

2.1.1. *Cloud water.* Cloud water was collected with an impactor based on the design of Marple and Willeke (1976) and Winkler (1992). This impactor was modified for trace organic compound analysis, and constructed exclusively from Teflon®, glass and stainless steel. The impactor consists of six parallel slit jets and the air is drawn through the impactor using four vacuum cleaners with a total sample volume of $500\,\mathrm{m^3\,h^{-1}}$ (Fig. 1). Running two of these impactors allowed sampling of up to 600 ml cloud water per hour. The calculated cut-off diameter for cloud droplets is 4 μm. Orientation to the wind direction was achieved by wind vanes. The sampling efficiency during the campaign varied between 50 and 65% of the measured liquid water content (LWC). Losses of cloud water during sampling were mainly due to blow off from the impaction plate or the sampling funnel at the bottom of the plate when the transport into the sample bottle was disturbed.

2.1.2. *Gas phase.* Gaseous phenolic compounds were collected by means of aerodispersive enrichment in scrubbers. This technique was introduced by Cofer *et al.* (1985) and Vecera and Janak (1987) and was employed for the first time to sample phenolic compounds in the atmosphere. Phenol and the four nitrophenols investigated, were enriched in the spray of a 0.1 M NaOH solution. Separation of air and spray was obtained by using a Teflon® membrane (5 μm pores). Four scrubber units (Fig. 2) were run in parallel allowing an air sample volume of $1.2\,\mathrm{m^3\,h^{-1}}$. The scrubbers were connected to the cloud droplet impactor by short Teflon® lines.

Using this set-up, all cloud droplets with diameters above the cut-off diameter of the impactor were separated off from the gas phase. The effective removal of the liquid phase was confirmed by measuring the volume of the trapping solution in the scrubbers. Only on one occasion (9 May), when the sampling lines between scrubber and impactor broke (turbulent wind of 20 m s^{-1}), were the scrubbers flooded with cloud water.

During cloud-free periods, the gas phase was sampled without connection to the cloud droplet impactor. During these events, the gas phase and the suspended particles were sampled.

2.1.3. *BTEX-aromatics.* BTEX-aromatics collected at Fell Gate were adsorbed on 2 g Tenax®, filled in stainless-steel tubes. The air was sampled with a flow of 100 ml min^{-1}. The total sample volume was 7 ℓ. This sampling unit was battery powered and portable. During sampling, the operator took care to prevent any contamination from generator exhaust and local car traffic.

2.1.4. *Oxides of nitrogen.* The sampling of nitrogen oxides, particulate nitrate and HNO_3 is described by Cape *et al.* (1997).

2.2. *Sample treatment and analysis*

2.2.1. *BTEX-aromatics.* Prior to sampling, steel tubes filled with Tenax® were baked at 250°C while flushing them with helium (quality 5.0) for at least 8 h. After baking, the tubes were closed with Swagelock® brass caps and stored in sealed glass bottles filled with helium. After sampling, the tubes were closed, cooled to 8°C and stored as described. Benzene and toluene were analysed by thermal desorption of the tubes into a GC-MS instrument. (Before thermal desorption, an internal standard, toluene-d_8, was injected onto the Tenax®.) The evaluation of the method revealed a standard deviation of $\pm 5\%$.

2.2.2. *Phenols.* The cloud-water samples were weighed and analysed for pH and conductivity in the field. Ring-deuterated internal standards (phenol-d_5, 2-nitrophenol-d_4, 4-nitrophenol-d_4, 2,4-dinitrophenol-d_3 and dinitroortho-cresol-d_2) were added immediately after sampling. The samples were stored in dark glass bottles. Extraction was performed on the following morning. Prior to solid-phase extraction with 4g C_{18}–material (according to Mußmann *et al.*, 1994), the samples were acidified to pH 1.5 (HCl) and about 50 g of NaCl was added. After extraction, the adsorbent was dried in a flow of nitrogen. For elution, 5 ml ethyl acetate was used. The extracts were sealed and stored in the dark at 4°C until analysed. Immediately before the analysis with GC-MS (instrument: VG 70SQ, selected ion monitoring) the extracts were reduced in volume to 0.5 ml by a gentle stream of nitrogen.

The 0.1 M NaOH solution from gas-phase sampling was treated in the same way. The deuterated internal standard was added to the combined (100 ml) trapping solution of the scrubbers immediately after sampling.

Field blanks were obtained by rinsing the impactor with clean water. They were processed and analysed in the same way as the real samples. Moreover, blanks of the trapping solution of the scrubbers were analysed. For blank values due to passive sampling of the Tenax® tubes, spare tubes not used during the campaign were analysed. Only in the trapping solution of the scrubbers were traces of phenol and 2-NP found. Gas phase values were corrected for these blanks.

3. RESULTS

3.1. *Concentrations of phenol and nitrophenols measured at GDF Summit*

The measured concentrations reflect a remote sampling site with low direct impact from rural areas. In comparison with previous rain water analysis in Hannover (Levsen *et al.*, 1990) and gas- and liquid- phase measurements in the south of Germany (Herterich and Herrmann, 1990) the nitrophenol

Table 1. Average concentration (ng m^{-3}) of phenol and nitrophenols measured in the air mass at GDF summit

		Phenol			2-NP			4-NP			2,4-NP			DNOC				
Day	Time BST	Liquid	Gas	Total	Liquid	Gas	Total	Liquid	Gas	Total	Liquid	Gas	Total	Liquid	Gas	Total		T°C
22 Apr	16:05–20:35	2.4	70.5	72.9	0.01	1.70	1.71	0.09	2.40	2.49	0.2	1.0	1.2	0.2	1.0	1.2	In cloud	5
27 Apr	19:53–01:00	6.1	18.3	24.4	0.02	0.80	0.82	0.03	1.20	1.23	0.8	1.6	2.4	0.5	1.1	1.6	In cloud	4
04 May	20:40–01:00		13.8	13.8		2.00	2.00		3.50	3.50		0.5	0.5		0.9	0.9	Air	4
05 May	16:07–20:50	3.0	20.8	23.8	0.03	1.12	1.15	0.72	6.40	7.12	0.2	8.5	8.7	0.1	1.7	1.8	In cloud	7
06 May	16:05–19:30		40.0	40.0		5.30	5.30		8.74	8.74		0.5	0.5		1.4	1.4	Air	10
08 May	17:15–22:20		47.8	47.8		0.80	0.80		20.4	20.4		0.1	0.1		0.2	0.2	Air	4
09 May	10:30–14:30		37.3	37.3		3.70	3.70		18.8	18.8		0.2	0.2		0.7	0.7	Air	4
09 May	19:35–03:00	4.0	**37.0**	**41.0**	0.36	**6.00**	**6.30**	1.60	**16.5**	**18.1**	1.1	**0.3**	**1.4**	1.0	**0.3**	**1.3**	In cloud	4
10 May	18:30–23:45	2.1	33.9	36.0	0.09	6.40	6.49	4.00	**35.0**	**39.0**	1.3	1.6	2.9	0.5	7.3	7.8	In cloud	6
11 May	19:30–22:25	0.6	27.2	27.8	0.10	1.30	1.40	1.04	30.4	31.4	0.3	7.2	7.5	0.4	**6.6**	**7.0**	In cloud	5

Note: Values in bold are calculated based on the cloud water concentration, LWC and the experimentally determined partitioning coefficients α_{wa} (reported by Lüttke and Levsen, 1997).

concentrations at GDF are low. The average total (gas and liquid phase) concentration at GDF was $\approx 14\,\mathrm{ng\,m^{-3}}$ for 4-NP. Recent (1994) measurements at Mt. Brocken in Central Germany (Lüttke and Levsen, to be published) show an average of $45\,\mathrm{ng\,m^{-3}}$ and a highest value of $360\,\mathrm{ng\,m^{-3}}$ for 4-NP.

3.2. *Total load of phenol and nitrophenols in the air at GDF Summit*

In Table 1 and Fig. 3, the results of the gas- and liquid- phase measurements are summarised. Cloud water concentrations of the compounds are expressed in gas-phase equivalents ($\mathrm{ng\,m^{-3}}$). The data for days with cloud events are based on the concentration of one 4 h gas-phase sample and the corresponding average cloud water concentration ($\mathrm{ng\,\ell^{-1}}$) of four 1 h samples which were multiplied with the liquid water content (LWC in $\ell\,\mathrm{m^{-3}}$). Since the gas- phase values from the cloud event on the 9 May could not be used (interrupted sampling line) and the value for 4-NP on 10 May and 2,4-DNP on 11 May could not be determined because of strong matrix interference in the observed mass channel, the values were calculated using the average liquid- phase concentration, the measured LWC and the average determined washout ratio ($\alpha_{wa} = C(\mathrm{water})/C(\mathrm{air})$; see also Lüttke and Levsen, 1997). In Table 1 the values obtained by calculation are indicated in bold. (As a result of the limited reproducibility of the determined mean washout ratio α_{wa}, the calculated values are less reliable but have been included to supplement the experimental data.)

Comparing the gas- and liquid-phase concentrations shown in Table 1, it can be seen that gaseous phenols make the major contribution to the total load in the air mass. Although we have determined high partitioning coefficients for the investigated phenols ($\alpha_{wa} \approx 10^5$) leading to substantial enrichment of these compounds in the liquid phase, the low LWC of the clouds limits mass accumulation and hence the contribution from the liquid phase to the total load of phenols in the air mass is low.

3.3. *Phenols in the gas phase*

Gaseous phenol and nitrophenols have been sampled during cloud events and cloud-free periods as shown in Table 1. Gaseous phenol is observed in a concentration range of $14\text{–}70\,\mathrm{ng\,m^{-3}}$. Among the nitrophenols, 4-NP is the most abundant compound ranging in concentration from $1.2\text{–}30\,\mathrm{ng\,m^{-3}}$. The other nitrophenols are observed in concentrations below $10\,\mathrm{ng\,m^{-3}}$. One additional sample was collected on the 7 May with a Teflon® impregnated

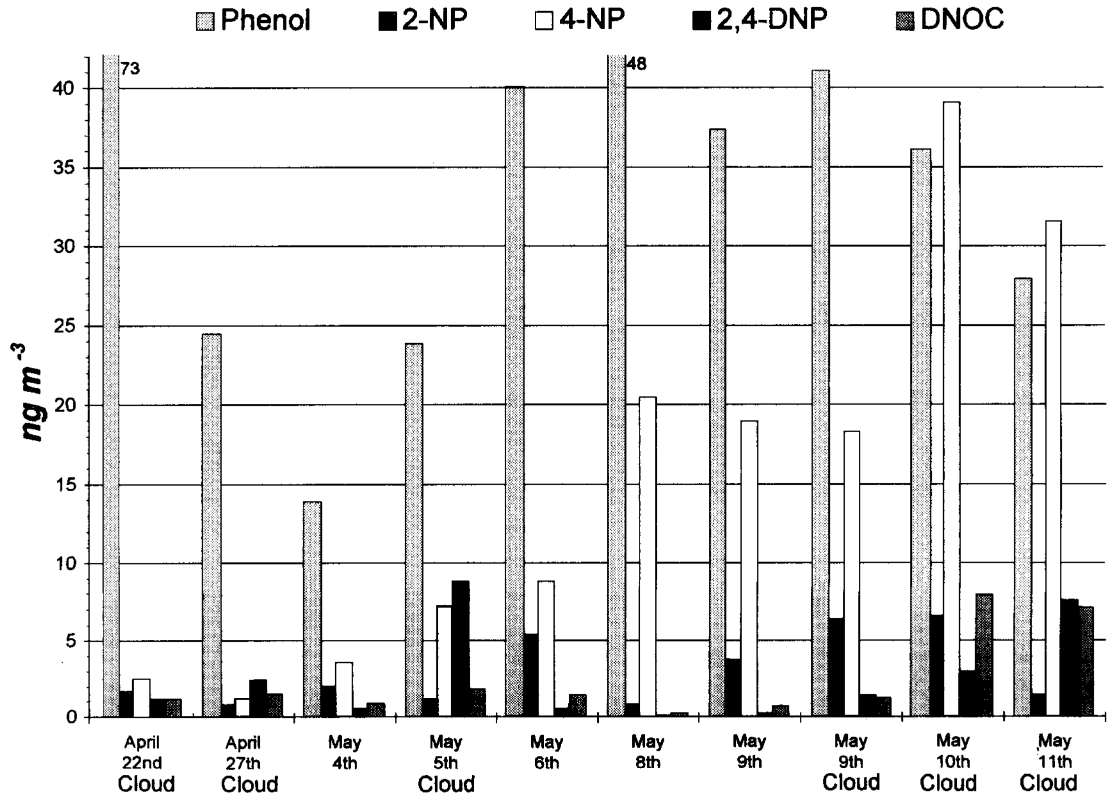


Fig. 3. Total load ($\mathrm{ng\,m^{-3}}$) of phenol and nitrated phenols in the air mass at GDF summit. Measuring periods with cloud events are indicated "Cloud".

Table 2. Average cloud water concentrations ($\mu g \ell^{-1}$) of phenol and four nitrophenols, derived from 1 h sampling intervals

Day	Phenol	2-NP	4-NP	2,4-DNP	DNOC
22 April	5.1	0.02	0.17	0.40	0.44
27 April	8.9	0.04	0.05	1.20	0.66
05 May	7.0	0.07	1.75	0.60	0.26
09 May	5.7	0.52	2.30	0.45	0.28
10 May	2.8	0.11	4.94	1.80	0.60
11 May	2.9	0.60	3.70	1.81	2.13

Table 3. Concentrations of benzene and toluene measured at Fell Gate (ng m^{-3})

Date	Time (BST)	Benzene	Toluene
22 April	16:00–18:00	410	850
	20:00–21:00	380	850
28 April	17:20–18:20	110	300
	19:05–20:05	190	540
04 May	17:05–18:05	560	710
	19:30–20:30	490	920
05 May	16:00–17:00	440	750
	17:45–18:45	480	670
	19:30–20:30	370	520
06 May	18:20–19:20	550	990
	19:20–20:20	590	1250
07 May	19:00–20:00	890	1590
	20:00–21:00	950	1090
08 May	16:45–17:45	1160	2190
	17:45–18:45	980	1560
	18:45–19:45	810	1880
09 May	10:19–11:19	440	1500
	19:10–20:10	940	2900
	22:47–23:47	780	1190
	23:47–00:47	610	790
10 May	17:41–18:41	1100	1800
	18:41–19:41	880	1540
11 May	20:35–21:35	600	780
	21:35–22:35	610	1240
	Mean	640	1190

glass-fibre filter attached to the sampling line. This filtration of the air leads to an almost total decrease of 4-NP (trace below detection limit 0.05 ng m^{-3}) in the gas phase, which is obviously due to the fact that 4-NP is bound to suspended particles (see also Lüttke and Levsen, 1997). The values from this day are not included in Table 1.

3.4. *Phenols in cloud water*

In Table 2, the average concentrations, derived from 1 h cloud water sampling intervals of the individual sampling days, are presented. Among the investigated compounds, phenol is observed in the highest concentrations with average concentrations between 2.8 and 8.9 $\mu g \ell^{-1}$ followed by 4-NP ranging from 0.18 to 5 $\mu g \ell^{-1}$. The other nitrophenols are less abundant with average concentrations below 2 $\mu g \ell^{-1}$ cloud water.

3.5. *Aromatic hydrocarbons*

In Table 3, the concentrations of benzene and toluene measured at Fell Gate are shown. When comparing the data with the data measured at the summit, it must be kept in mind that the air masses were not always connected (see Colvile *et al.*, 1997). For benzene and toluene the concentrations tend to rise during the campaign which to some extent correlates with the wind direction shift from west to east during the course of the measurements. In Fig. 4 the mixing ratios of benzene and toluene are compared with those of phenol and the sum of the investigated nitrophenols.

4. DISCUSSION

4.1. *General findings*

The presented data show an increase in the total nitrophenol load in the examined air mass during the course of the experiment (see Figs 4 and 5). 4-NP is the most abundant compound of the investigated nitrophenols, exceeding even the concentration of phenol on two occasions. This is in contrast with measurements in the south of Germany (Herterich and Herrmann, 1990) and results from measurements at Mt. Brocken in Central Germany (1994, Lüttke *et al.*, to be published) which show significantly higher values for 2-NP in relation to 4-NP (at Mt.Brocken the ratio 2-NP/4-NP was about 1). This lack of 2-NP at GDF might be the result of a faster photochemical degradation of 2-NP compared to 4-NP, leading to a depletion of 2-NP during the transport from urban areas to the remote sampling site GDF. Moreover, 2-NP reacts to form 2,4-DNP while 4-NP remains mostly unprocessed (see Section 4.3). The degradation rate of 2-NP was reported by Atkinson (1989) with $k_{OH} = 0.9 \times 10^{-12}$ cm^3 molecules^{-1} s^{-1}, to be similar to that of benzene $k_{OH} = 1.2 \times 10^{-12}$ cm^3 molecules^{-1} s^{-1}. OH$^\cdot$ degradation rate constants for 4-NP have not been reported in the literature. When assuming similar low OH radical degradation rates for the other nitrophenols, their lifetimes in the atmosphere are probably more affected by other processes like precipitation or other reactions (liquid phase) than by OH-radical-initiated reactions.

The observed increase of the sum of the investigated nitrophenols during the course of the experiment is not accompanied by an increase of the NO_x concentration which is shown in Fig. 5, where the average mixing ratio of NO_x, cloud water nitrate and particle bound nitrate (expressed as gas-phase NO_x equivalents) and the sum of all nitrophenols for each sampling day are compared (data for particulate nitrate are not available for all events). During the first five events the average ratio (NO_x/sum of NP) was 3×10^3 whereas in the last five events this ratio was 3.4×10^2.

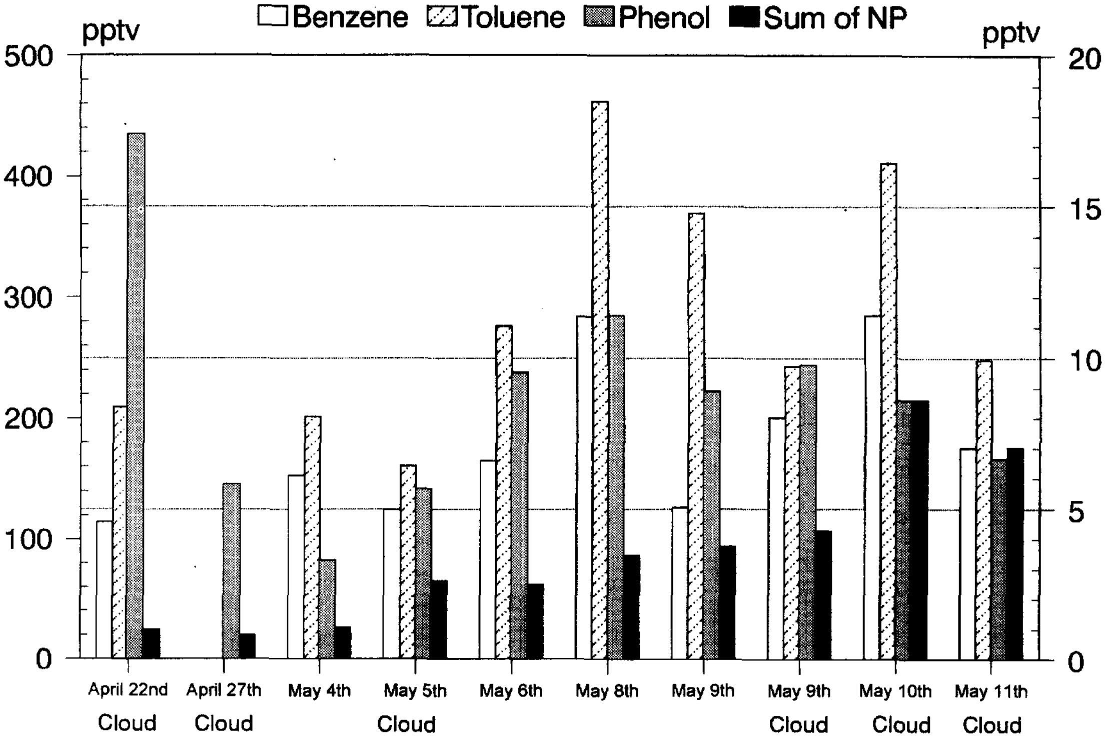
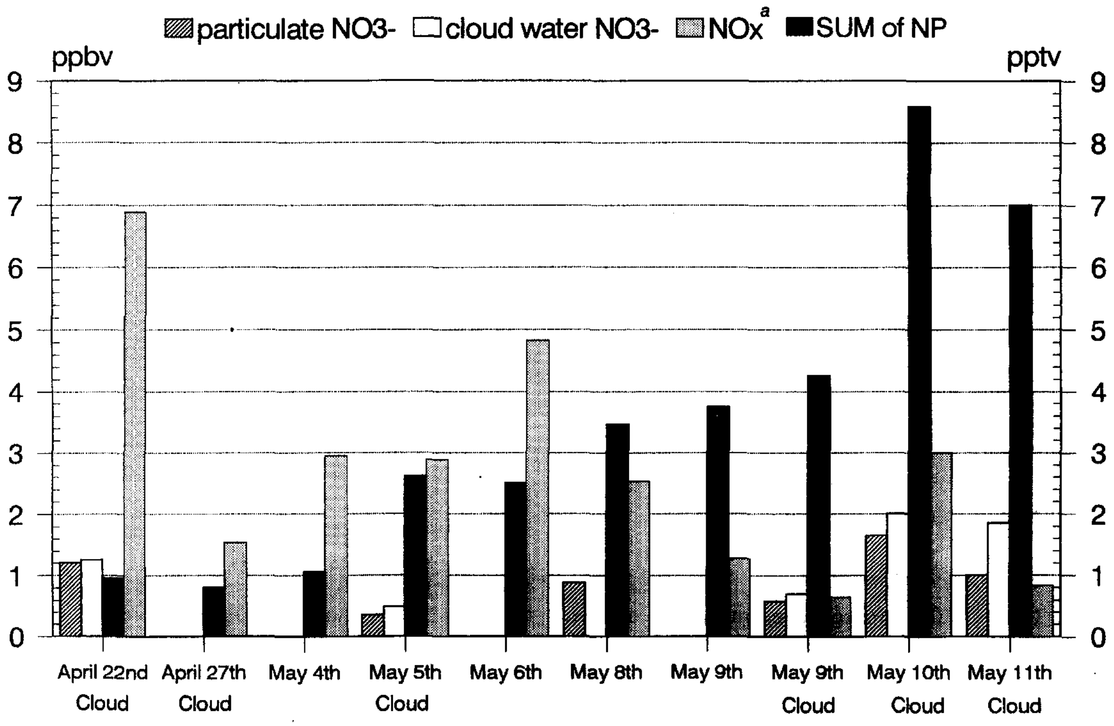


Fig. 4. Mixing ratios (pptv) of benzene, toluene (determined at Fell Gate), phenol and the sum of the investigated nitrophenols (determined at GDF summit). Note that benzene and toluene refer to the left axis (scale 500 pptv) and phenol and the sum of all nitrophenols refer to the right axis (scale 20 pptv). Measuring periods with cloud events are indicated "Cloud".



a = measured at Mine Road

Fig. 5. Average values for NO_x, cloud water and particulate nitrate (expressed as NO_x equivalents, ppbv) and the sum of all nitrophenols (pptv). Measuring periods with cloud events are indicated "Cloud".

Table 4. Average concentrations ($mg\,m^{-3}$) of benzene, toluene, phenol and nitrated phenols in the exhaust gas of motor vehicles

Benzene[a]	Toluene[a]	Phenol[a]	2-NP[b]	4-NP[b]	2,4-DNP[b]	DNOC[b]
250	350	6	1.2	0.8	< 0.01	< 0.01

[a] Rippen (1995).

[b] Tremp *et al.* (1993).

4.2. *Sources of phenol and nitrated phenols*

Two main sources of non-nitrated and nitrated phenols have been discussed in the literature. Atmospheric build-up by reactions in the troposphere and direct emission from motor vehicles.

4.2.1. *Emission by motor vehicles.* Data on the emission of benzene, toluene and phenol from motor vehicles have been reported repeatedly and are summarised by Rippen (1995). Data on the emission of nitrophenols from car exhaust were recently reported by Tremp *et al.* (1993). These data are summarised in Table 4. The major source of benzene and toluene in the northern hemisphere is car exhaust. The data show that the direct emission of 2,4-DNP and DNOC from car exhaust is only of minor importance. 2-NP and 4-NP are emitted in almost equal amounts. The mono-/dinitrophenol ratio is $\geqslant 100$.

4.2.2. *Formation of nitrated phenols by atmospheric reactions.* A mono-/dinitrophenol ratio of $\geqslant 100$ is in strong contrast to the results in this study, since on some days the dinitrophenol concentrations even exceed the mononitrophenol concentrations. Using benzene as a tracer for car exhaust (toluene reacts faster by a factor of 5), the initial ratios 2-NP/benzene and 4-NP/benzene $\approx (4 \times 10^{-3})$ in the exhaust gas may be compared with the ratios at the sampling site, where an average ratio of 2.8×10^{-3} (2-NP/benzene) and 8.4×10^{-3} (4-NP/benzene) was found.

From these data one may conclude that a significant fraction of the observed mononitrophenol concentration is explained by direct emissions and that most of the dinitrophenols found in the atmosphere originate from secondary nitration in the atmosphere. Since OH radical reaction rate constants for the investigated nitrophenols are not exactly known, these conclusions are tentative.

The gas-phase formation of phenol and nitrophenols from aromatic hydrocarbons was investigated by laboratory experiments. Atkinson *et al.* (1989, 1990) identified phenol as a reaction product of benzene, methyl nitrite, NO, NO_2 mixtures, irradiated at wavelengths $\geqslant 300$ nm, in smog chamber experiments. The authors report product yields from $OH^{\bullet}$-initiated reactions to be 24% for the reaction benzene → phenol. Since phenol reacts about 30 times faster with $OH^{\bullet}$, a steady state of 1% phenol based on the ambient benzene concentration is expected.

Moreover, the authors report ring-retaining product yields from OH-radical-initiated reactions to be 7% from the reaction toluene → benzaldehyde followed by reaction to the phenoxy radical, 20% from the reaction toluene → *o*-cresol and 5% from the reaction toluene → *m*- and *p*-cresol. The reaction of phenol and the cresols with NO_3 at room temperature is reported to be rapid with phenol: $3.6 \times 10^{-11}\,cm^3\,molecules^{-1}\,s^{-1}$ and *o*-cresol: $2.1 \times 10^{-11}\,cm^3\,molecules^{-1}\,s^{-1}$ leading to the formation of phenoxy and methylphenoxy radicals which are believed to react with NO_2 to yield nitrophenols and nitrocresols. Rate constants or pathways for the latter reactions and the reactions of mononitrophenols to dinitrophenols are not reported in the literature. Atkinson and Aschmann (1994) re-evaluated their data on nitroaromatic formation and concluded, that under typical tropospheric conditions, the hydroxycyclohexadienyl-type radicals (formed from the reaction of benzene and toluene with OH) react predominantly with O_2 instead of NO_2. Similar conclusions may be derived regarding the reaction of phenoxy radicals with NO_2 under atmospheric conditions.

Figure 4 shows the mixing ratios of benzene, toluene (determined at Fell Gate), phenol and the sum of the nitrophenols (determined at GDF Summit). When comparing the benzene/phenol ratio from car exhaust (42) with the average ratio observed at GDF Summit (21) it can be seen that, on average, half of the phenol observed at the sampling site must originate from direct emissions of phenol by cars or from other sources. Since phenol reacts fast with OH and NO_3 radicals (atmospheric lifetime with: $[NO_3] = 50$ pptv (10 min), $[OH] = 5 \times 10^5\,molecules\,cm^{-3}$ (14 h), Grosjean (1990)) and therefore is not transported over long distances, the phenol sources must have been rather close to the GDF. The data shown in Fig. 4 demonstrate that (with the exception of 22 April) during the entire campaign a similar trend is observed for the concentrations of benzene and phenol.

4.3. *Formation of dinitrophenols in the gas phase*

From Fig. 6 it can be seen that the concentrations of 2-NP and 2,4-DNP are anticorrelated (with the exception of 8 May), i.e. events with high concentrations of 2-NP show low concentrations of 2,4-DNP and *vice versa.* This observation is consistent with a nitration of 2-NP to yield 2,4-DNP (thus leading to a depletion of 2-NP) while 4-NP does not, or only to a minor extent, contribute to the formation of 2,4-DNP.

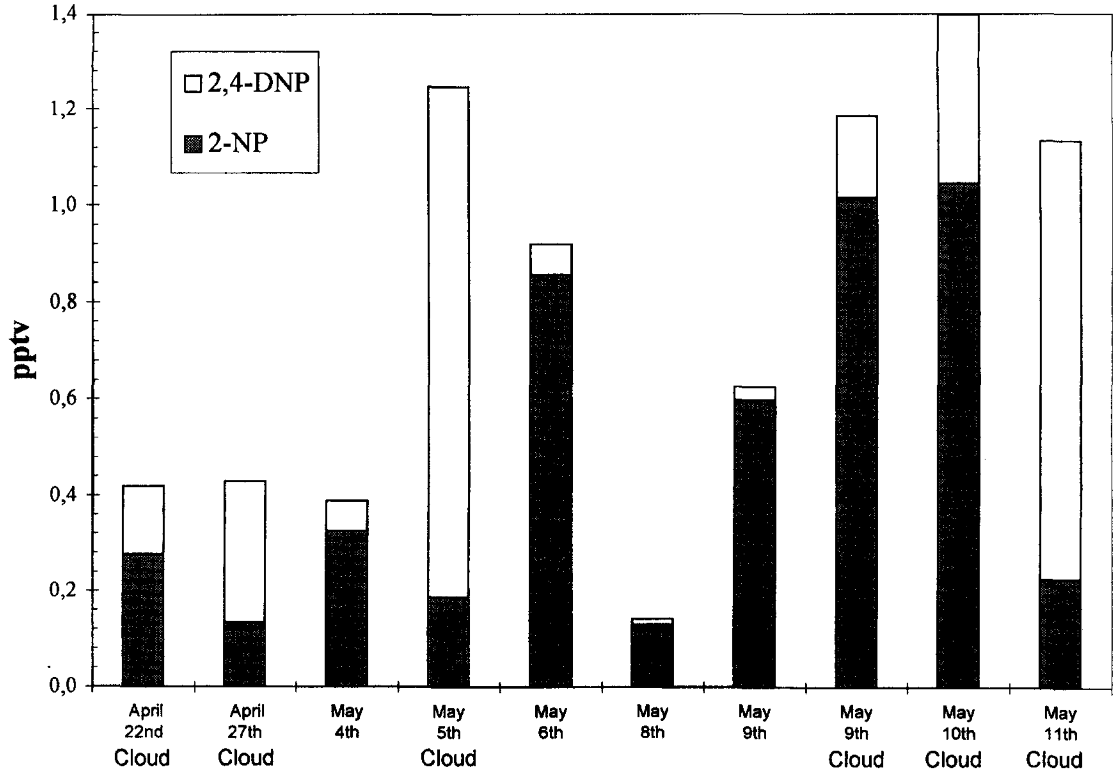


Fig. 6. Anticorrelation of the 2-nitrophenol and 2,4-dinitrophenol mixing ratios in the air mass at GDF summit. Measuring periods with cloud events are indicated "Cloud".

As discussed before (see also Lüttke and Levsen, 1997), there is experimental evidence from this study and from other authors (Nishioka and Lewtas, 1992; Herterich and Herrman, 1990; Nojima *et al.*, 1983) that 4-NP, in contrast to 2-NP, is mainly particle-bound and hence probably not available for gas-phase reactions which would also explain the longer lifetime of 4-NP (mentioned in Section 4.1).

4.4. *Nitrophenol formation in the liquid phase*

It can be seen from Table 5 that the molar mixing ratios of nitrophenols during the cloud events are higher and that the dinitro-/mononitrophenol ratio is higher compared to days with absence of clouds. This is an indication for a nitration of phenol and mononitrophenols in cloud droplets or in the water film on hygroscopic particles. The possibility of a tropospheric liquid-phase nitration of phenol in cloud droplets has not been considered in the past since there is a lack of a potent nitrating substance liberating substantial amounts of NO_2^+ for the electrophilic nitration of the aromatic ring.

Recent publications from Zetzsch and Behnke (1992) and Behnke *et al.* (1994) focused on $ClNO_2$ production by reactions of N_2O_5 with aqueous NaCl solutions or on deliquescent NaCl aerosol. Uptake coefficients were determined to be fast ($\gamma_{obs} = 3.2 \times 10^{-2}$) with $ClNO_2$, being the main product of the reaction with up to 100% yield.

Table 5. Molar mixing ratios (pptv) of nitrophenols in the air at the summit of GDF

Date	$\sum$ NP	$\sum$ m-NP[a]	$\sum$ d-NP[b]	
22 April	0.95	0.68	0.27	In cloud
27 April	0.80	0.33	0.47	In cloud
04 May	1.05	0.89	0.17	Air
05 May	2.61	1.34	1.27	In cloud
06 May	2.49	2.26	0.22	Air
08 May	3.46	3.42	0.04	Air
09 May	3.74	3.63	0.11	Air
09 May	4.25	3.94	0.31	In cloud
10 May	8.58	7.34	1.24	In cloud
11 May	7.00	5.30	1.71	In cloud
Average	4.03	3.15	0.88	In cloud
Average	2.68	2.55	0.13	Air

[a] m-NP = 2-NP, 4-NP.
[b] d NP = 2,4-DNP, DNOC.

Since $ClNO_2$ and N_2O_5 are very potent agents for nitration in solution, an experiment was carried out in order to investigate their potential for nitration in aqueous solutions (preliminary results, Scheer *et al.*, 1996). Phenolic solutions in the range of 10^{-1}–10^{-4} M were exposed to gaseous N_2O_5 and $ClNO_2$ in a wetted-wall flowtube reactor. Investigation of the phenolic solution (solid-phase extraction, GC/MS) revealed the production of 2-NP and 4-NP. A yield of 0.3% of these products based on the amount of $ClNO_2$ and of 0.07% yield based on the amount of N_2O_5 was found (10^{-4} M phenolic solution). The reaction of N_2O_5 and $ClNO_2$ depends on the concentration of the phenolic solution. In phenolic solutions acidified by HNO_3 (pH 1) and analysed in the same way, no nitrophenols were detected.

A possible reaction of phenol with the nitrate radical (present $< 1\%$ in N_2O_5) to form the phenoxy radical and subsequent reaction of the phenoxy radical with NO_2 can be excluded, since the experiments were carried out with ozone in excess. These preliminary results need to be examined in more detail.

Atmospheric nitration of phenols in cloud droplets by the reaction with nitrate radicals, analogous to the gas-phase nitration pathway mentioned in Section 4.2.2 is unlikely, because NO_2 has a low solubility in water and again, a reaction with dissolved O_2 might be favoured.

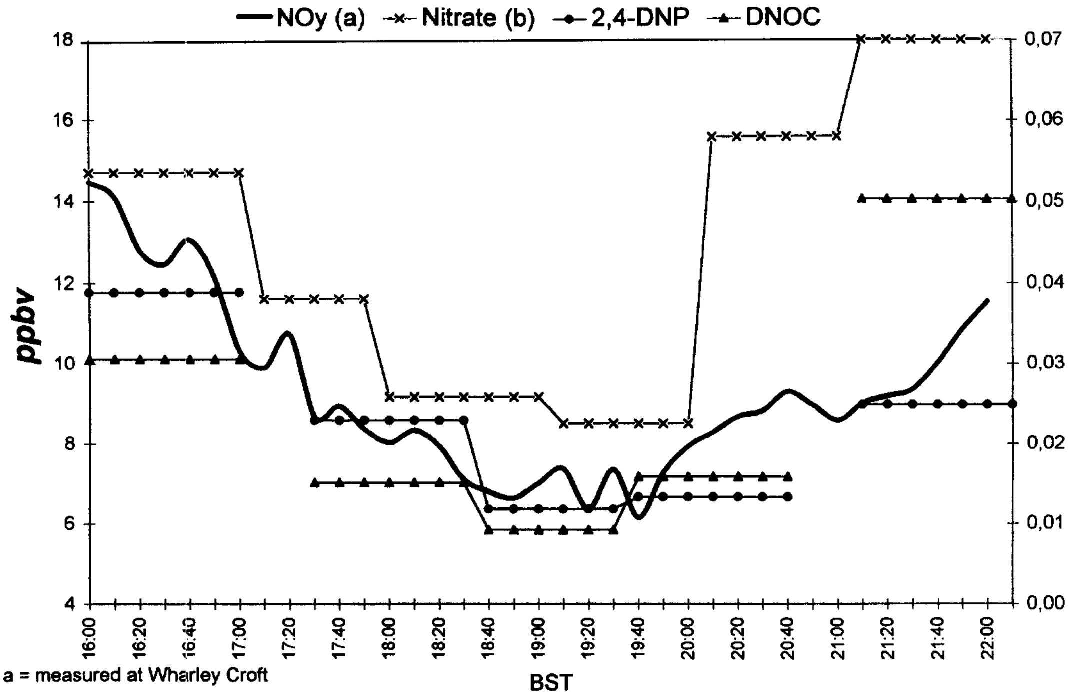
4.5. *Correlation of nitrophenols, oxides of nitrogen and nitrate*

There are two distinct periods for which suitable data are available for a more detailed investigation of any correlation between nitrophenol, nitrogen oxides and nitrate mixing ratios. These periods are presented in case studies.

For comparison of the liquid-phase nitrophenol concentrations (1 h time resolution) with the gas-phase values for NO_x and NO_y, the liquid-phase values are given in gas-phase equivalents pptv. Back-trajectories and details of the meteorological conditions for these periods will be found in Colvile *et al.* (1997). The detailed description of the NO_x fluxes over the hill and nitrate production in cloud is given in case studies found in Cape *et al.* (1997), while the pollution sources for these events are discussed by Swietlicki *et al.* (1997).

4.5.1. *The evening of* 22 *April* 1993. The NO_x concentration at this evening was the highest throughout the entire campaign, while the total nitrophenol load was the second lowest during the GDF experiment. This seems to be in contradiction with the assumption that nitrophenols are formed from a reaction involving NO_2.

From Fig. 7 it can be seen that during the course of the event the concentration of the dinitrophenols (2,4-DNP and DNOC) parallels those for nitrogen oxides and nitrate. This correlation is consistent with the mechanism proposed in Section 4.4. The concentrations of all four species decrease from the beginning of the sampling event (16:00 BST) to a minimum around (18:00–19:30 BST) and increase again until



a = measured at Wharley Croft

b = nitrate value multiplied by a factor of 5

Fig. 7. Measured NO_y concentrations on 22 April 1993, equivalent concentration of NO_3^- in cloud water expressed as gas phase NO_x (ppbv) and the dinitrophenol concentrations in cloud water expressed as gas-phase (pptv) equivalents.

the end of the measurements. Between 20:00 and 21:00 BST the nitrate concentration in the cloud water rises strongly. This nitrate production in cloud is attributed to uptake of NO_z (NO_y–NO_x) into the cloud water. This NO_z is believed to consist mainly of HNO_3 or N_2O_5 since the acidity of the cloud water increased between 20:00 and 21:00 BST with no major change in concentration of the other ions. Backtrajectories show that the air mass entering the sampling site moved southeast across the Atlantic Ocean and then turned towards northeast and moved straight to GDF. On the way up to the Pennines the rather clean (old) air mass crossed urban areas (e.g. Manchester, Liverpool) in the southwest of the sampling site and picked up some (fresh) pollution. As benzene and toluene concentrations were relatively low, but NO_x and SO_2 (the latter compound is an indicator of coal combustion) concentrations were high, the main source of pollution may have been coal firing and to a lesser extent car traffic. This freshly polluted air was transported within a relatively short time (3–5 h) along the Eden valley to the GDF. There was only little interchange between ground-level air mass and the higher cloud layer stretching out above the floor of the valleys on both sides of the Pennines. Both air masses were mixed shortly before the summit of GDF when the lower air mass was elevated into the cloud layer at the summit. Since the cloud water collectors were placed at the rim of the mountain there was little time for liquid-phase formation of nitrophenols (as postulated in Section 4.4) explaining why in spite of the high NO_x concentrations the nitrophenol level was low. While during this event the sum of all nitrophenols was low the dinitrophenols/mononitrophenols ratio was relatively high (0.4) which cannot be explained by direct emissions from car traffic. Most of the mononitrophenols in the old air mass already had reacted to dinitrophenols.

4.5.2. *The night of* 5–6 *May* 1993. In Fig. 8, the course of the NO_y concentration and the corresponding nitrophenol and nitrate values are shown. The 4-NP concentration rises between 20:00 and 21:00 BST while the concentrations of the dissolved dinitrophenols follow the declining NO_y concentrations. The rising 4-NP concentration is accompanied by a rising nitrate concentration and a rising acidity of the cloud water, which is again attributed to be due to uptake of NO_z.

Although the concentrations of NO_x and nitrate were lower than on 22 April the total concentration of the nitrophenols was higher. Backtrajectories show that the air mass originated from the North Atlantic, passed the North of Ireland, moved across Scotland to the North Sea, turned towards southwest and approached GDF from northeast. On their way across Scotland the air mass passed over densely populated regions (Glasgow–Edinburgh area) where it took up pollution. At 17:00 BST fairly high NO_x values

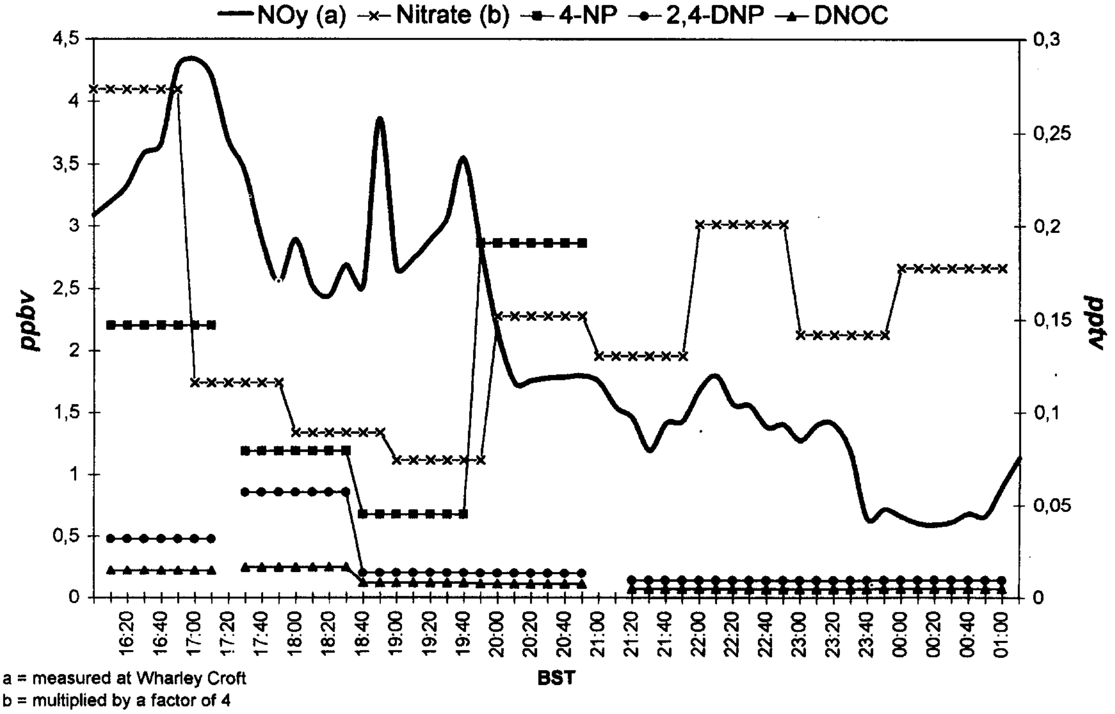


Fig. 8. Measured NO_y concentrations on 5 May 1993, equivalent concentration of NO_3^- in cloud water expressed as gas phase NO_x (ppbv), 4-nitrophenol and the dinitrophenol concentrations in cloud water expressed as gas-phase (pptv) equivalents.

(3 ppb) were measured at Moor House and Wharley Croft, which decreased steadily to below 0.5 ppb at around 24:00 BST. The cloud at the GDF Summit was part of an extensive cloud layer, stretching upstream over the lower hills east of GDF to the North Sea. The sampled air mass was transported in cloud for 100–400 min (see Colvile *et al.*, 1997). Thus, there was ample time for reactions in the cloud water since in contrast to the situation on the 22nd April the pollutants (e.g. NO_x, phenol) were transported in the cloud layer, which is consistent with a higher total nitrophenol concentration compared to the event on the 22nd of April and the proposed formation of nitrophenols in the liquid phase. Around 20:00 BST the character of the air mass reaching GDF changed from clearly anthropogenical to considerably more marine influenced (Swietlicki *et al.*, 1997). This change is accompanied by a sudden increase of the cloud water acidity and a rise in nitrate (cloud water and particulate) and 4-NP concentrations while the NO_x and NO_y concentrations decrease.

5. CONCLUSIONS

The occurrence and fate of phenol and four nitrophenols in the presence and absence of clouds were investigated in the air mass at the rural sampling site Great Dun Fell. The concentrations determined at this site were low compared to sampling sites in Central Europe which in particular holds for 2-NP. Amongst the investigated compounds, 4-NP is present in the highest concentrations. This is due rather to a slower degradation of 4-NP than to more emission or build-up since measurements in Central Europe revealed a ratio 2-NP/4-NP ≈ 1. In this investigation evidence for a substantial particle adsorption of 4-NP was found, which might account for the longer lifetime of this compound. A relation between 2-NP and 2,4-DNP is seen. From this anticorrelation a reaction of 2-NP to 2,4-DNP can be inferred, while this reaction is not observed for 4-NP. One explanation may be again the particle adsorption of 4-NP. The interaction of these compounds with the atmospheric liquid water is studied and it was found that air mass in cloud contains more dinitrophenols than air mass with absence of cloud. A possible explanation might be seen in the fact that the photochemical degradation of the compounds is reduced when the air mass is in cloud. Another explanation is the formation of nitrophenols in the liquid phase of clouds. A model experiment revealed that nitration of phenol in water films in the presence of gaseous N_2O_5 and $ClNO_2$ is possible. Further experimental work is necessary to prove the postulated formation of nitrated phenols in cloud droplets.

Acknowledgements—The authors thank Peter Mußmann and Claudia Koch for their help during the field campaign. Funding for the experiment was provided by the Bundesministerium für Bildung und Forschung, U.K. Department of Environment, Commission of European Union (Contract EV5V-CT94-0450), U.K. Department of Environment (Contract PEC07/12/32). The Environment Program of the European Commission DG IX provided travel grants to the GEC participants to meet and discuss the results of the present experiment. The Great Dun Fell Cloud Experiment 1993 was carried out within the EUROTRAC subproject GCE (Ground-based Cloud Experiment).

REFERENCES

Atkinson R. (1989) Kinetics and mechanisms of the gas-phase reactions of the hydroxylradical with organic compounds. *J. Phys. Chem. Ref. Data*, monograph 1.

Atkinson R. (1990) Gas phase tropospheric chemistry of organic compounds: a review. *Atmospheric Environment* **24A**, 1–41.

Atkinson R. and Aschmann S. (1994) Products of the gas-phase reactions of aromatic hydrocarbons: effect of NO_2 concentration. *Int. J. Chem. Kinet.* **26**, 929–944.

Atkinson R., Aschmann S., Arey J. and Carter W. (1989) Formation of ring retaining products from OH radical-initiated reactions of benzene and toluene. *Int. J.Chem. Kinet.* **21**, 801–827.

Bayer Company (1988a) E 605 forte, Parathion, Zusammenfassende Darstellung, Rückstände. Internal Report, Bayer AG Leverkusen Dok.-Nr. 0893P, 4s.

Bayer Company (1988b) ME 605 Spritzpulver, Parathion -methyl, Zusammenfassende Darstellung des Rückstandsverhaltens. Internal Report, Bayer AG Leverkusen Dok. Nr. 0896B, 4s.

Behnke W., George Ch., Scheer V. and Zetzsch C. (1994) Kinetic mechanism for the formation of $ClNO_2$ from the reaction of gaseous N_2O_5 with NaCl solution. In *Tropospheric Oxidation Mechanisms* (edited by Becker K. H.), Air pollution Research Report 54 (EUR 16171 EN), pp. 489–493. Comission of the European Communities, Brussels.

Cape J. N., Hargreaves, K. J., Storeton-West R. L., Jones B., Davies T., Colvile R. N., Gallagher M. W., Choularton T. W., Pahl S., Berner A., Kruisz C., Bizjak M., Laj P., Facchini M. C., Fuzzi S., Arends B. G., Acker K., Wieprecht W., Harrison R. M. and Peak J. D. (1997) Budget of oxidised nitrogen species in orographic clouds. *Atmospheric Environment* **31**, 2625–2636.

GDCh (1992) 2-Nitrophenol, 4-nitrophenol. BUA Stoffbericht 75. VCH, Weinheim (ISBN 3-527-28513-X).

Choularton T. W., Colvile R. N., Bower K. N., Gallagher M. W., Wells M., Beswick K. M., Arends B. G., Kos G. P. A., Fuzzi S., Lind L. A., Orsi G., Facchini M. C., Laj P., Gieray R., Wiesner P., Engelhardt T., Berner A., Kruisz C., Möler D., Acker K., Wieprecht W., Lüttke J., Levsen K., Bizjak M., Hansson H-C., Cederfelt S.I., Frank G., Mentes B., Martinsson B., Orsini D., Svenningson B., Swietlicki E., Wiedensohler A., Noone K. J., Pahl S., Winkler P., Seyffer E., Helas G., Jaeschke W., Georgii H. W., Wobrock W., Preiss M., Maser R., Schell D., Dollard G., Jones B., Davies T., Sedlak D. L., David M. M., Wendisch M., Cape J. N., Hargreaves, K. J., Storeton-West R. L., Fowler D., Hallberg A., Harrison R. M. and Peak J. D. (1997) The Great Dun Fell cloud experiment 1993: an overview. *Atmospheric Environment* **31**, 2393–2405.

Cofer W. R., Collins V. G. and Talbot R. WW. (1985) Improved aqueous scrubber for collection of soluble atmospheric trace gases. *Envir. Sci. Technol.* **19**, 557–560.

Colvile R. N., Bower K. N., Choularton T. W., Gallagher M. W., Wobrock W., Cape J. N., Hargreaves, K. J., Storeton-West R. L., Jones B., Wiedensohler A., Hansson H.-C., Wendisch M., Acker K., Wieprecht W., Pahl S., Winkler P., Berner A. and Kruisz C. (1997) Meteorology of the Great Dun Fell cloud experiment. *Atmospheric Environment* **31**, 2407–2420.

Grosjean D. (1985) Reactions of *o*-cresol and nitrocresol with NO_x in sunlight and with ozone–nitrogen dioxide mixtures in the dark. *Envir. Sci. Technol.***19**, 968–974.

Grosjean D. (1990) Atmospheric chemistry of toxic contaminants. Reaction rates and atmospheric persistance. *J. Air. Waste Man. Ass.* **40**, 1397–1402.

Herterich R. and Herrmann R. (1990) Comparing the distribution of nitrated phenols in the atmosphere of two German hill sites. *Envir. Technol.* **11**, 961–972.

Hinkel M., Reischl A., Schramm W. K., Trautner F., Reissinger M. and Hutzinger O. (1989) Concentration levels of nitrated phenols in conifer needles. *Chemosphere* **18**, 2433–2439.

Kishk F. M., El-Essawi T., Abdel-Ghafar S. and Abou-Donia M. B. (1976) Hydrolysis of methylparathion in soils. *J. Agric. Fd. Chem.* **24**, 305–307.

La Planche A., Bouvet M., Venien F., Martin G. and Chabrolles A. (1981) Modelisation de l'evolution du parathion dans le milieu natural sur un pilote de laboratoire. *Water Res.* **15**, 599–607.

Leuenberger C., Ligocki M. P. and Pankow F. (1985) Trace organic compounds in rain. 4. Identities, concentrations and scavenging mechanisms for phenols in urban air and rain. *Envir. Sci. Technol.* **19**, 1053–1058.

Leuenberger C., Czuczwa J., Tremp J. and Giger W. (1988) Nitrated phenols in rain: atmospheric occurrence of phytotoxic pollutants. *Chemosphere* **17**, 511–515.

Levsen K., Behnert S., Prieß B., Svoboda M., Winkeler H. D. and Zietlow J. (1990) Organic compounds in precipitation. *Chemosphere* **21**, 10377–1061.

Levsen K., Behnert S., Mußmann P., Raabe M. and Prieß B. (1993) Organic compounds in cloud and rain water. *Int. J. Envir. Analyt. Chem.* **52**, 87–97.

Lüttke J. and Levsen K. (1997) Phase partitioning of phenol and nitrophenols in clouds. *Atmospheric Environment* **31**, 2649–2655.

Marple A. and Willcke K. (1976) Impactor design. *Atmospheric Environment* **10**, 891–896.

Mußmann P., Levsen K. and Radeck W. (1994) Gaschromatographic determination of phenols in aqueous samples after solid phase extraction. *Fresenius J. Analyt. Chem.* **384**, 654–659.

Nishioka M. G. and Lewtas J. (1992) Quantification of nitro- and hydroxylated nitro-aromatic/ polycyclic aromatic hydrocarbons in selected ambient air daytime winter samples. *Atmospheric Environment* **11**, 2077–2087.

Nojima K. and Isogami C. (1994) Studies on photochemical reactions of air pollutants. XIII. Formation of nitrophenols by the reactions of three toluene oxides with nitrogen dioxide in air. *Chem. Pharm. Bull.* **42**, 2426–2429.

Nojima K., Fukaya K., Fukui S. and Kanno S. (1975) The formation of nitrophenols and nitrobenzene by the photochemical reaction of benzene in the presence of nitrogen monoxide. *Chemosphere* **2**, 77–82.

Nojima K., Fukaya K., Fukui S., Kanno S., Nishiyama S. and Wada Y. (1976) Formation of nitrophenols by the photochemical reaction of toluene in the presence of nitrogen monoxide and nitrophenols in rain. *Chemosphere* **1**, 25–30.

Nojima K., Kawaguchi A., Ohya T., Kanno S. and Hirobe M. (1983) Studies on photochemical reaction of air pollutants. X. Identification of nitrophenols in suspended particulates. *Chem. Pharm. Bull.* **31**, 1047–1051.

Richartz H., Reischel A., Trautner F. and Hutzinger O. (1990) Nitrated phenols in fog. *Atmospheric Environment* **12**, 3067–3071.

Rippen G. (1995) *Handbuch Umweltchemikalien.* Stoffdaten, Prüfverfahren, Vorschriften. ECOMED Verlagsgesellschaft, D-86899 Landsberg, Germany.

Rippen G., Zietz E., Frank R., Knacker T. and Klöpffer W. (1987) Do nitrophenols contribute to forest decline? *Envir. Technol. Lett.* **8**, 475–482.

Schafer W. E. and Schönherr J. (1985) Accumulation and transport of phenol 2-nitrophenol and 4-nitrophenol in plant cuticles. *Ecotox. Envir. Safe.* **10**, 239–252.

Scheer V., Lüttke J., George Ch., Levsen K., Frenzel A., Behnke W. and Zetzsch C. (1996) Atmospheric nitration of phenols in clouds by N_2O_5. *Proc. EUROTRAC Symp.* SPB Academic Publishing, Den Haag, The Netherlands.

Schwarzenbach R., Stierli R., Folsom B. and Zeyer J. (1988) Compound properties relevant for assessing the environmental partitioning of nitrophenols. *Envir. Sci. Technol.* **22**, 83–92.

Shea P. J., Weber J. B. and Overcash M. R. (1983) Biological activities of 2,4-dinitrophenol in plant-soil system. *Res. Rev.* **87**, 1–41.

Swietlicki E., Hansson H-C., Martinsson B., Mentes B., Orsini D., Svenningson B., Wiedensohler A., Wendisch M., Pahl S., Winkler P., Colvile R. N., Gieray R., Lüttke J., Heintzenberg J., Cape J. N., Hargreaves, K. J., Storeton-West R. L., Acker K., Wieprecht W., Berner A., Kruisz C., Facchini M. C., Laj P., Fuzzi S., Jones B. and Nason P. (1997) Source identification during the Great Dun Fell cloud experiment 1993. *Atmospheric Environment* **31**, 2441–2451.

Tremp J., Mattrel P., Fingler S., Giger W. (1993) Phenol and nitrophenols as tropospheric pollutants: emissions from automobile exhausts and phase transfer in the atmosphere. *Water Air Soil Pollut.* **68**, 113–123.

Vecera Z. and Janak J. (1987) Continuous aerodispersive enrichment unit for trace determination of pollutants in air. *Analyt. Chem.* **59**, 1494–1498.

Winkler P. (1992) Design and calibration of a fog water collector. *World Meteorological Organisation: Conf. on Instruments and Methods for Observation.* Vienna. WMO/TD-No 462, pp. 17–21.

Woodrow J. E., Seiber J. N., Crosby D. G., Moilanen K. W., Soderquist C. J. and Mourer C. (1977) Airborne and surface residues of parathion and ist conversion products in a treated plum orchard environment. *Arch. Envir. Contam. Toxicol.* **6**, 175–191.

Zetzsch C. and Behnke W. (1992) Heterogeneous photochemical sources of atomic Cl in the troposphere. *Ber. Bunsenges. Phys. Chem.* **96**, 488–493.