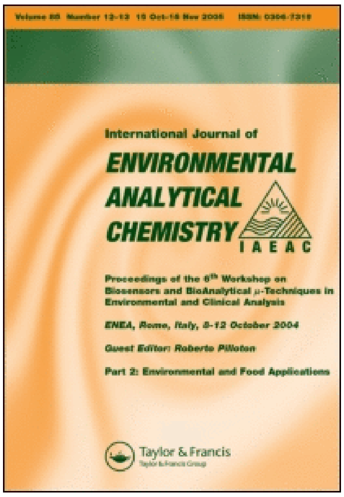


International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Phenols and Nitrated Phenols in Clouds at Mount Brocken

Jens Lüttke[a]; Karsten Levsen[a]; Karin Acker[b]; Wolfgang Wieprecht[b]; Detlev Möller[b]
[a] Fraunhofer-Institut für Toxikologie und Aerosolforschung, Hannover, Germany [b] Brandenburgische Technische Universität, Cottbus, Germany

To cite this Article Lüttke, Jens , Levsen, Karsten , Acker, Karin , Wieprecht, Wolfgang and Möller, Detlev(1999) 'Phenols and Nitrated Phenols in Clouds at Mount Brocken', International Journal of Environmental Analytical Chemistry, 74: 1, 69 — 89

To link to this Article: DOI: 10.1080/03067319908031417

URL: http://dx.doi.org/10.1080/03067319908031417

Intern. J. Environ. Anal. Chem., Vol. 74(1-4), pp. 69-89
Reprints available directly from the publisher
Photocopying permitted by license only

PHENOLS AND NITRATED PHENOLS IN CLOUDS AT MOUNT BROCKEN

JENS LÜTTKE[a], KARSTEN LEVSEN[a]*, KARIN ACKER[b], WOLFGANG WIEPRECHT[b] and DETLEV MÖLLER[b]

[a]*Fraunhofer-Institut für Toxikologie und Aerosolforschung, Nikolai-Fuchs-Str. 1, D-30625 Hannover, Germany and* [b]*Brandenburgische Technische Universität, D-03044 Cottbus, Germany*

(Received 02 April 1998; In final form 30 September 1998)

Two phenols and four nitrophenols have been determined in the gas and liquid phase of clouds during a field campaign in May 1994 at Mount Brocken (Germany). If the total amount in both phases is considered, 2-nitrophenol is the dominant compound which is mainly present in the gas phase while 4-nitrophenol is much more abundant in the liquid phase, which reflects the differences in the distribution constants. The experimental data suggest that mononitrophenols may partially originate from automobile exhaust while dinitrophenols are almost completely formed by atmospheric reactions. Furthermore, comparison of the concentration of dinitrophenols and the extent to which air masses are transported in clouds indicates that these compounds are mainly formed in cloud droplets.

Keywords: Clouds; phenols; nitrophenols; air pollution; phase partitioning

INTRODUCTION

Originally, pollution of the atmosphere by inorganic compounds (i.e. by automobile exhaust or power plants) was of primary concern not only for the scientific community, but also for legislative authorities and the public. The introduction of organic chemicals into the atmosphere has received increasing attention in recent years. More than 2000 compounds have been identified up to now in the atmosphere[1], where automobile exhaust is still the major source in most countries. These compounds may be removed from the atmosphere by abiotic degradation or by dry and wet deposition. Gaseous compounds may be scavenged by cloud droplets, where the scavenging efficiency largely depends on the vapour pressure and water solubility as reflected in Henry's constant[2]. Moreover, particle-bound

---

* Corresponding author. Fax: +49–511–5350–155. E-mail: levsen@ita.fhg.de.

compounds may also be efficiently scavenged by cloud droplets[3]. In principle, compounds scavenged by cloud droplets may undergo further reactions in the liquid phase, but for organic compounds so far such reactions have only been observed or suggested for formaldehyde and formic acid[4].

Among the organic compounds observed in the atmosphere, phenols and nitrated phenols have received particular attention as the former compounds are toxic to humans, while the latter compounds are known to be phytotoxic[5,6]. It was suggested that they may represent one factor for the forest decline observed in Central and Northern Europe and other parts of the world[7]. Nitrated phenols have first been identified in rainwater by Nojima et al.[8,9]. Since then scattered reports on the occurrence of these compounds in rain, fog and snow have appeared[10–16], while measurements of nitrophenols in the gas phase remained scarce[10,16,17].

Several sources for the origin of phenols and nitrated phenols have been identified. These compounds are formed in combustion processes of motor vehicles[18,19]. Based in part on smog chamber studies, it was demonstrated or at least suggested that phenols and their nitrated derivatives are formed by atmospheric reactions from benzene or alkylbenzenes[20–24, 38]. Little is known about further sources, in particular for nitrophenols. Coal and wood combustion may also lead to a further introduction of these compounds into the atmosphere. The biodegradation of the pesticides parathion and parathion-methyl leads to the release of nitrophenols into the environment[25], but hardly to an input into the atmosphere.

Within the EUROTRAC program (subproject "Ground based cloud experiments, GCE") we participated in a major field campaign at the Great Dun Fell in 1993 and reported concentrations of phenol and 4-nitrophenols in the gas and liquid phase of clouds at this relatively clean air site[26]. The partitioning of these compounds between the gas and the liquid phase was also investigated[27]. During most events of this campaign, phenol was the most abundant compound both in the gas and liquid phase, while among the four nitrophenols 4-nitrophenol dominated in the gas and the liquid phase. The results supported the assumption of a formation of nitrophenols (in particular dinitrophenols) in the liquid phase of the cloud droplets.

A further major field study was conducted at Mount Brocken (Germany) in June 1994 using in part advanced equipment. This site is situated in Central Europe and is more influenced by nearby urban pollution. The results from this campaign are reported and discussed here with a three-fold goal:

a. Does the type of the observed compound and its concentration reflect the more polluted site (as compared to the relatively clean air in Northern England)?
b. How does the concentration vary within one cloud event?
c. Is there additional or complementary information available, which supports the suggested formation of nitrophenols within cloud droplets?

EXPERIMENTAL

Site

The sampling site was located at the summit of Mount Brocken in the Harz mountains located in Northern Germany (s. map in Figure 1). Mount Brocken is by far the highest elevation in Northern Germany (1142 m). In contrast to the above mentioned mountain Great Dun Fell in Northern England where orographic clouds are frequent, Mount Brocken often projects into deep-drifting stratified clouds, which in June are mainly transported to this mountain by a northwesterly to southwesterly wind.

Sampling

Cloud water

Cloud water was collected using two identical impactors operated in parallel. They are based on the design of Marple and Willeke[28], and Winkler[29] and have been described previously. The total air volume sampled per impactor was ~ 500 m^3 h^{-1}, the calculated cut-off diameter ~ 4 μm. The sampling efficiency was determined to be 50–60 % of the liquid water content (LWC).

Gas phase

Gaseous phenols and nitrophenols were collected by means of aerodispersive enrichment in a specially designed scrubber (this scrubber technique was introduced by Cofer et al.[30], and Vecera and Janak[31]). A figure of a simple model was shown in the preceding publication[26]. For high volume sampling the scrubber was equipped with 16 spray units instead of one, each unit having a nozzle of 0.9 mm i.d. through which a volume of 345 L h^{-1} of air was sucked at a speed of 150 m s^{-1}. A total air volume of 5–7 m^3 h^{-1} could be sampled. (Details of the scrubber will be described elsewhere). In contrast to the original small scrubber, where the fine droplets are separated from the air using a Teflon membrane, in the present design the fine droplets leaving the scrubber were coagulated in a condenser cooled by water at room temperature and transported back to the trapping solution via a peristaltic pump.

To investigate a possible breakthrough of phenols, a stream of dry air with a well-defined concentration of phenols was introduced into the scrubber and the air leaving it passed through a trap filled with liquid nitrogen. No phenols were observed in this trap. (However, in events where one of the spray units did not operate properly, phenol was readily detected in the trap).

FIGURE 1 Location of the sampling site Mount Brocken (Germany)

The determination of the recoveries of phenols by the scrubber was difficult, as it was not possible to generate an air stream with a well-defined composition of all six phenols and nitrophenols at the same time. Rather, however, the non-volatile nitrophenols condensed in the glass tubes leading to the scrubber. With the relatively volatile phenol itself a recovery of 90 ± 3 % was found.

Chemicals

The following phenols and nitrophenols were investigated:

phenol
2-methylphenol (o-cresol) (2-MP)
4-methylphenol (p-cresol) (4-MP)
2-nitrophenol (2-NP)
4-nitrophenol (4-NP)
2,4-dinitrophenol (2,4-DNP)
2-methyl-4,6-dinitrophenol (dinitro-o-cresol) (DNOC)

In addition, the following deuterated standards were used:

phenol-d_5
2-methylphenol-d_4
2-nitrophenol-d_4
4-nitrophenol-d_4
2,4-dinitrophenol-d_3
2-methyl-4,6-dinitrophenol-d_2

For solid-phase extraction, a C_{18} adsorbent (Amchro) was used. All chemicals and solvents were purchased at the best quality available. The sodium hydroxide used in the scrubber may contain traces of phenol. This chemical was checked for phenol impurities before use.

Instrumental

A mass spectrometer (from Fisons Instruments, VG 70SQ, 70 eV, 220° C) was used in the selected ion monitoring mode. This mass spectrometer was usually operated at low mass resolution, $m/\Delta m = 1000$. Samples with interfering compounds were measured at $m/\Delta m = 5000$. The mass spectrometer was coupled with a gas chromatograph from Hewlett-Packard (HP 5890) using helium as carrier gas. Sample injection occurred either "on-column" or "split-splitless" using a column from J & W Scientific (DB 6.25) or Supelco (PTE-5) which are particularly suited for the analysis of phenols. If the sample was injected splitless, a retention gap was used. The dissolved organic carbon (DOC) was determined with an instrument from Maihak (Tocor 2) according to standardized procedures. For this determination, the aqueous sample was filtered with a silver membrane filter (0.2 µm) (Osmonics).

Sample treatment

The cloud water samples were analyzed for pH in the field. The deuterated internal standards were added immediately after sampling. The samples were stored in dark glass bottles. If possible, extraction was performed on the following morning using solid-phase extraction with 4g C_{18} adsorbent (Amchro). To this end, the samples were acidified to pH 1.5 (HCl) and 50 g of NaCl were added. It has been shown previously that quantitative extraction is possible by this method[32]. After extraction, the adsorbent was dried in a flow of nitrogen. For elution, 5 ml ethyl acetate were used. The extracts were sealed and stored in the dark at 4° C until analyzed. Before instrumental analysis, 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 with the scrubber was treated accordingly. The deuterated internal standards were added to the trapping solution of the scrubber immediately after sampling.

Field blanks were obtained by rinsing the impactor with pure water. These blanks were processed and analyzed in the same way as the real samples. Blanks of the trapping solution of the scrubbers were also analyzed. Only in the trapping solution of the scrubbers were traces of phenol and 2-NP found.

Liquid water content (LWC)

The liquid water content (LWC) of clouds was measured continuously by a laser forward scattering technique using a Gerber particulate volume monitor as described in detail in ref. 37.

RESULTS

Sampling period, meteorological conditions, back trajectories, general pollution level

In June 1994, six distinct cloud events at Mount Brocken were sampled, i.e. on June 2, June 4 and 5 (3 events), June 7 and June 10.

On June 2 (first event), there was a low pressure region over Central Europe. Stratocumulus clouds approached Mount Brocken with a southwesterly wind. Back trajectories (72 h) between 20:00 and 2:00 (the main sampling period) started in Southwest Europe and followed an almost straight line in a northeasterly direction to Mount Brocken. The general pollution level was relatively low for phenols and nitrophenols, but also for NO_2 ($NO_2 \leq 3$ ppbv, ≤ 6 $\mu g\ m^{-3}$) and NO_3^- (cloud water) ≤ 1 ppbv, ≤ 3 $\mu g\ m^{-3}$ (expressed as NO_2 gas phase equivalents).

On June 4 and 5, three cloud events could be sampled (June 4 from 12:00 to 14:00 (second event); June 5 from 0:15 to 5:00 (third event) and 18:00 to 22:00 (fourth event). During this period there was again a low pressure region over Germany. On June 4, air masses approached Mount Brocken with a southwesterly wind originating from Iceland and reaching the continent near Brittany (France), from where they proceeded directly in a straight line towards Mount Brocken. Similar conditions prevailed during events 3 and 4. During these events, air masses originated from the North Atlantic, passed Southern England and approached Mount Brocken with a northwesterly wind. The pollution level was again relatively low for phenols and nitrophenols, but also for NO_2 and NO_3^- ($NO_2 \leq 2$ ppbv ($\leq 4\ \mu g\ m^{-3}$), $NO_3^- \leq 0.6$ ppbv ($\leq 1{,}7\ \mu g\ m^{-3}$) NO_2 gas phase equivalents).

On June 7 (fifth event), the cloud event could be followed for almost 12 h. Again, a low pressure region prevailed over Germany where first a warm and later a cold front passed Mount Brocken. The air masses originated from the mid-Atlantic, passed over Central and Southern England, Belgium and the Ruhr Valley and approached Mount Brocken with a northwesterly to southwesterly wind. The air masses passed highly polluted areas, thus explaining the higher general pollution level for phenols and nitrophenols, but also NO_2 and NO_3^-. ($NO_2 \leq 7$ ppbv ($\leq 15\ \mu g\ m^{-3}$), $NO_3^- \leq 3.5$ ppbv ($\leq 10\ \mu g\ m^{-3}$) NO_2 gas phase equivalents).

On June 10 (sixth event), clouds could be monitored from 0:50 to 8:00 for ~ 7 h. Germany was again in a low pressure area. Air masses originated from the North Atlantic, passed over Northern and Central England and the Netherlands and reached Mount Brocken with a northwesterly wind. During the sampling period, the back trajectories shifted to the South. The air mass now passed over Southern England, Belgium and West Germany and approached Mount Brocken with a southwesterly wind. The general pollution level was again relatively high ($NO_2 \leq 4.5$ ppbv ($\leq 9\ \mu g\ m^{-3}$), $NO_3^- \leq 4$ ppbv ($\leq 12\ \mu g\ m^{-3}$) NO_2 gas phase equivalents).

The higher pollution level on June 7 and 10 compared with June 2 – 5 is also reflected by the other inorganic cations and anions, in particular SO_4^{2-}, Cl^-, NH_4^+ and Na^+. The DOC reached its highest value of ~ 28 mg/L on June 7 between 0.00 and 1.00 and remained high up to the end of the campaign. More details are available upon request.

Phenols and nitrophenols in cloud water

In Table I, the mean concentrations of the three phenols and four nitrophenols (μg/L) as well as the nitrate concentration (mg/L) and the dissolved organic carbon, DOC (mg/L), in cloud water are summarized for the six events. The individual data are also averaged over the entire campaign. The table reveals relatively high concentrations of nitrophenols and nitrate during the first event, lower pollution levels during the three following events and a strong increase towards the end of the campaign.

Surprisingly, 4-nitrophenol (4-NP) is by far the most dominant compound, ranging in concentrations from 6.4 – 46 µg/L (mean: 21 µg/L). The two dinitrophenols 2,4-dinitrophenol (2,4-DNP) and 2-methyl-4,6-dinitrophenol (dinitro-ortho-cresol, DNOC) are also found in very high concentrations (mean: 5.4 and 4.2 µg/L, resp.), while phenol and also the two methylphenols (MP) and 2-nitrophenol (2-NP) are found in relatively low concentrations (the concentration of 2-NP ranges from 0.11 to 0.45 µg/L, mean: 0.3 µg/L). The nitrate concentration roughly parallels that of the nitrophenols.

Table I also includes mean concentrations in the liquid phase during the Great Dun Fell campaign in 1993 in Northern England. As discussed below, during the Brocken campaign significantly higher 4-NP, 2,4-DNP and DNOC concentrations were observed compared with the Great Dun Fell campaign. (In the case of DNOC this difference is almost a factor of ten.) On the other hand, phenol is found in lower concentrations in cloud water at Mount Brocken.

Cloud water was collected at 1h intervals. Such time-resolved determinations give more detailed information on the source and formation of phenols. Figure 2 displays the concentrations of 4-NP, 2,4-DNP, DNOC and NO_3^- for the event on June 7, 1994 as a function of time, demonstrating clearly the close correlation of the concentrations of these three nitrophenols and nitrate. The observed time dependence of the nitrophenol concentration was less pronounced during the other events. Thus, similar correlations as shown in Figure 2 were not clearly visible during the other events.

Phenols and nitrophenols in the gas phase, total amount of phenols in both phases

Phenols and nitrophenols were also determined in the gas phase of clouds (interstitial air), as described in the experimental section. (The scrubber used for gas phase sampling had to be repaired in the field. As a result of the polymer used for this purpose, high blank values for phenol were found. Thus, phenol itself could not be determined in the gas phase).

The time-resolved data for 2-NP and 2,4-DNP are shown in Figure 3 as examples. (The complete data are available upon request). Figure 3 reveals that the concentration of the two nitrophenols in the interstitial air varies strongly with time. It is of interest that during the fifth event on June 7, the time dependence of 2-NP and 2,4-DNP differs significantly, as discussed below.

LE I Mean concentrations of phenols and nitrophenols (µg L^{-1}), nitrate (mg L^{-1}) and dissolved organic carbon (DOC, mg L^{-1}) in cloud water coll
e 1994 at Mount Brocken (Germany) and in April/May 1993 at Great Dun Fell (England)[a]

ent	*Date*	*Phenol*	*2-MP*	*3-/4-MP*	*2-NP*	*4-NP*	*2,4-DNP*	*DNOC*	*DOC*	*NO_3*
					Mount Brocken, June, 1994					
	02.06.94	6.2	0.25	1.3	0.14	24	7.9	6.1	7.2	9.4
	04.06.94	3.6	0.6	2.1	0.44	6.4	1.3	0.1	6.0	6.6
	05.06.94	1.2	0.1	0.6	0.17	18	2.0	1.1	4.3	2.4
	05.06.94	1.7	0.24	0.8	0.11	7.5	0.9	0.7	5.0	2.6
	07.06.94	2.9	0.5	1.9	0.24	24	10	10	11	16.2
	10.06.94	2.5	0.2	3.5	0.45	46	10	6.2	8.1	27.3
an	(µg L^{-1})	3.0	0.3	1.7	0.3	21	5.4	4.2		
	(nmol L^{-1})	32	2.7	16	1.8	150	29	20		
					Great Dun Fell, April-May, 1993					
an	(µg L^{-1})	5.4	n.d.	n.d.	0.2	2.2	1.0	0.7	n.d.	
	(nmol L^{-1})	57	n.d.	n.d.	1.7	16	5.4	3.7	n.d.	

IP = methylphenol, NP = nitrophenol, DNP = dinitrophenol, DNOC = dinitroorthocresol; n.d. = not determined.

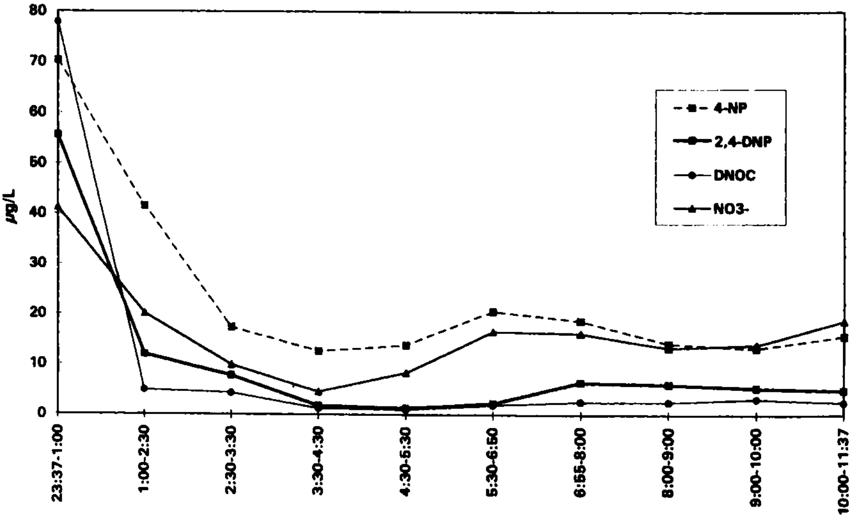
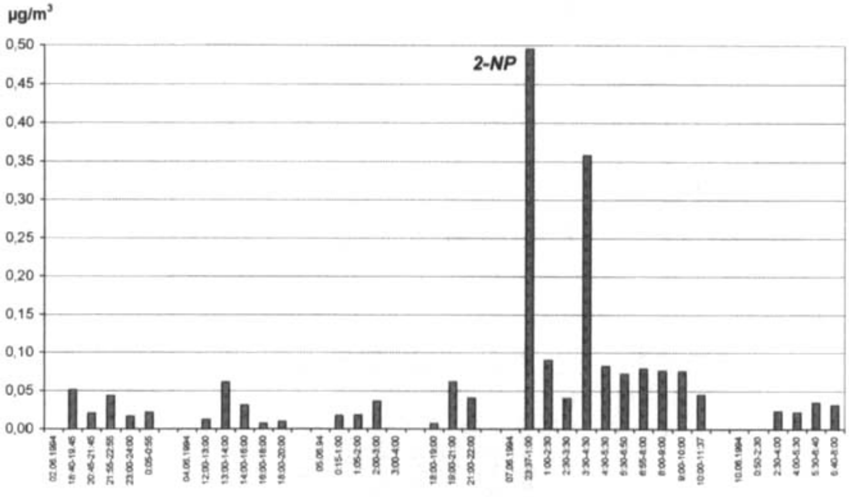


FIGURE 2 Concentration of four nitrophenols (µg/L) and nitrate in cloud water at Mount Brocken on 07. June 1994. (The concentrations of nitrate have to be multiplied by a factor of 1000, i.e. mg/L)



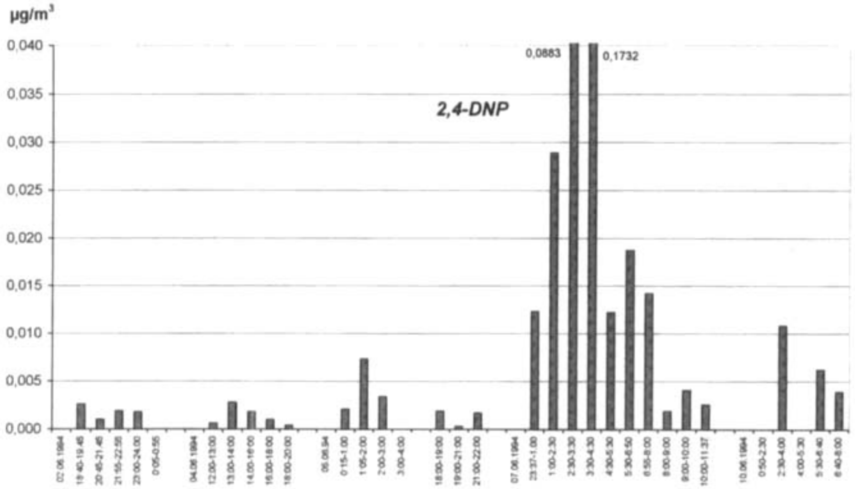


FIGURE 3 Concentration of two nitrophenols in the gas phase (interstitial air) during the entire campaign: (a) 2-nitrophenol (2-NP); (b) 2,4-dinitrophenol (2,4-DNP)

The average mixing ratio of the sum of two cresols and four nitrophenols in the gas and liquid phase is shown in Figure 4. This mixing ratio of the nitrophenols in both phases reflects the total pollution by these compounds better than the individual gas or liquid phase data. If the total mixing rate in both phases is considered, 2-NP is the dominant component which is mainly present in the gas phase, while 4-NP is much more abundant in the liquid phase. Moreover, the concentration of phenols and nitrophenols in cloud water as presented in Table I not only reflect the actual pollution level, but also the liquid water content (LWC) of the cloud: the rapidly increasing LWC during cloud formation may lead to a dilution of the cloud water sample which may be much faster than the subsequent new equilibration between gas and liquid phase. In Figure 4, the high pollution level during the 5th event, as already evidenced by inspection of the cloud water data, is again apparent.

Comparison with nitrogen dioxide and nitrate concentration

In Table I, the concentration of NO_3^- has already been compared with the concentrations of nitrophenols in cloud water. Figure 5 now compares the mixing ratio of the sum of all nitrophenols (pptv) with those of NO_2 and the concentra-

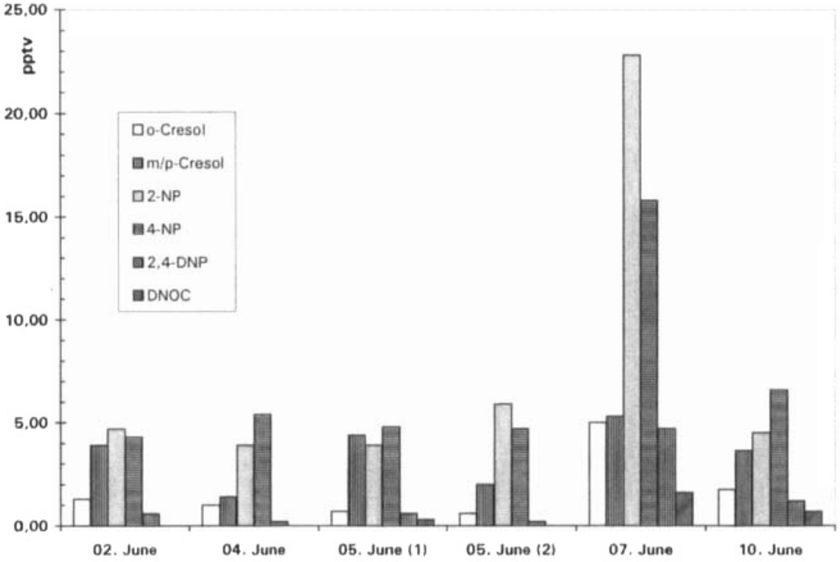


FIGURE 4 Mixing rates of total phenols and nitrophenols (sum of gas and liquid phase) during the entire campaign (mean values for each cloud event)

tion of nitrate (in cloud water, expressed as gas phase NO_2 equivalents, ppbv. It is obvious for the five events (in particular for the event on June 7) that high NO_2 and NO_3^- concentrations are accompanied by high nitrophenol concentrations, again demonstrating the high pollution load of the air masses during this event. It should be noted that neither NO_2 and NO_3^- are considered as precursors for nitrophenols. However, they may be taken as indicators for the presence of a nitrating agent.

Distribution between gas and liquid phase

The results of the Great Dun Fall campaign[27] demonstrated that the partitioning of the four nitrophenols (considered here) between the gas and the liquid phase is only in partial accordance with predictions by Henry's law (phenol and the two cresols are not considered, as these three compounds have not been determined in the gas phase in both campaigns). Equilibration of those compounds which strongly bind to particles, such as 4-NP and possibly partially 2,4-DNP and DNOC are not described by Henry's law.

The distribution constant α_{wa} (often referred to as scavenging or wash-out ratio, W_{wa}) is given by

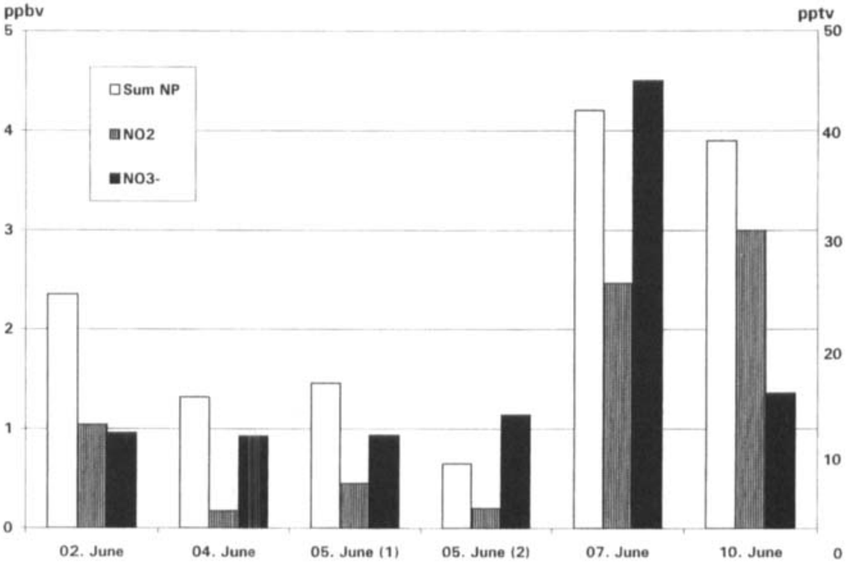


FIGURE 5 Mixing rates of sum of four nitrophenols (gas and liquid phase) in pptv, nitrogen dioxide (in ppbv) and nitrate (liquid phase, expressed as nitrogen dioxide gas phase equivalents in ppbv) (1 ppbv $NO_2 \approx 2.1\ \mu g\ m^{-3}$, 1 ppbv $NO_3^- \approx 2.9\ \mu g\ m^{-3}$, for pptv equivalents of nitrophenols see footnote in Table III)

$$\frac{\alpha_{wa} = C_{(water)}}{c_{(air)}} \tag{1}$$

If Henry's law applies

$$\frac{\alpha_{wa} = RT}{H(T)} \tag{2}$$

H may be determined experimentally or calculated from the saturation vapour pressure, p^0, and the aqueous solubility, $C^{sat}_{(W)}$, according to

$$H = \frac{p^0}{c^{sat}_{(w)}} \tag{3}$$

In Table II, the distribution constants for the four nitrophenols are listed for five cloud events. Also shown are the average distribution constants for each compound for the entire campaign. Finally, distribution constants determined experimentally by Tremp et al.[19] and calculated by Schwarzenbach et al.[33] for 20° C were included in Table II but corrected for an average ambient temperature of 6.5° C. (It has been shown previously that α_{wa} values at 6.5° C are higher than those at 20° C by a factor of ~ 2.5[27]). The individual data for a given compound as determined in this experiment show a large variation (by a factor of 8 in the case of 2-NP and even a factor of 29 in the case of 4-NP).

TABLE II Mean partition coefficients of nitrophenols, α_{wa}, of individual cloud events at Mount Brocken (June, 1994) and average partitioning coefficients, α_{wa}, of the entire Great Dun Fell campaign (April/May, 1993)[a]

Event[b]	*Date*	*2-NP*	*4-NP*	*2,4-DNP*	*DNOC*
		Mount Brocken, June, 1994			
1	02.06.94	5.0 E + 03	1.2 E + 06	4.5 E + 06	n.d.
2	04.06.94	1.5 E + 04	1.3 E + 05	1.5 E + 06	n.d.
4	05.06.94	6.6 E + 03	4.2 E + 05	1.1 E + 06	4.9 E + 05
5	07.06.94	2.7 E + 03	3.5 E + 05	1.2 E + 06	7.6 E + 05
6	10.06.94	2.3 E + 03	3.8 E + 06	1.4 E + 06	3.3 E + 06
	mean	8.4 E + 03	9.2 E + 05	3.3 E + 06	1.4 E + 06
		Great Dun Fell, April/May, 1993			
	mean	3.1 E + 04	1.4 E + 05	4.0 E + 05	3.2 E + 05
Tremp et al. (1993)[c]		4.8 E + 03	4.8 E + 06	7.0 E + 05	2.8 E + 05
Schwarzenbach et al. (1988)[c]		4.5 E + 03	1.8 E + 06	2.1 E + 05	1.4 E + 05

[a] NP = nitrophenol, DNP = dinitrophenol, DNOC = dinitroorthocresol.

[b] Data were incomplete for event 3.

[c] Corrected for 5° C by multiplication with 2.5 (ref. 27) (Average cloud temperature = 6.5° C).

If the average values for all five events are considered, 2-NP (which is not particle-bound at all) approximately agrees with the literature data (corrected for the temperature dependence). The same holds for 4-NP, while experimental values found for 2,4-DNP and DNOC are significantly higher compared with the (corrected) literature data.

Finally, a comparison with values from the Great Dun Fell campaign is of interest. The distribution constants for 4-NP, 2,4-DNP and DNOC determined at Mount Brocken in 1993 are significantly higher than those determined at Great Dun Fell.

Figure 6 compares, for the event of June 10, 1994, for the two compounds 2-NP and 4-NP, the contribution of the liquid phase with the total amount of the compound in both phases. (Note the different y scales). It is apparent from Figure 6a that the fraction of 2-NP in the liquid phase is almost negligible (below 0.5 %) compared with that of the gas phase. On the contrary, Figure 6b demonstrates that 4-NP in the liquid phase may contribute to the total amount of the compound in both phases between 20 and 50 %. This difference between 2-NP and 4-NP reflects the large variation in the distribution constants of these two compounds which differ by a factor of ~ 100, i.e. 4-NP (as a result of its low vapour pressure and the high water solubility) partitions to the aqueous phase much more effectively than 2-NP.

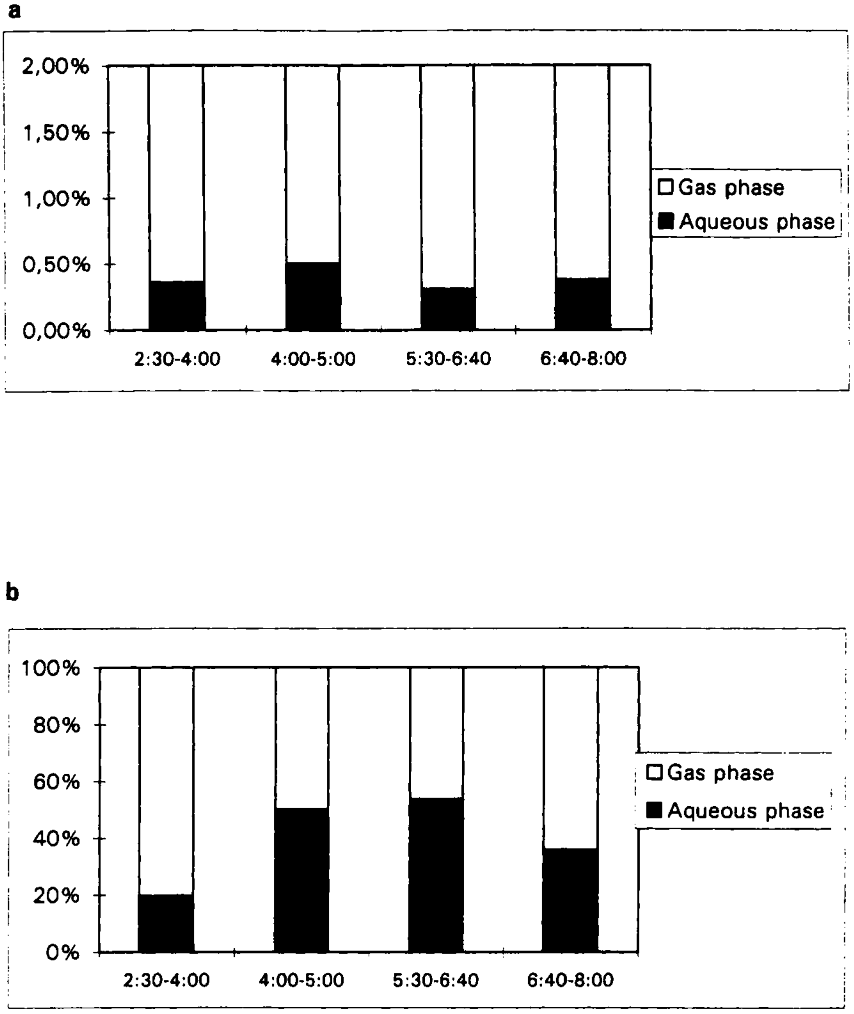


FIGURE 6 Distribution of two nitrophenols between gas and liquid phase on 10. June 1994: (a) 2-nitrophenol (2-NP); (b) 4-nitrophenol (4-NP)

The distribution constant between the gas and liquid phase does not only differ between different events, but also within one event. This variation was particularly pronounced during the 5th event (June 7, 1997). Figure 7 shows as example the distribution constants, α_{wa}, for the two mononitrophenols, 2-NP and 4-NP, demonstrating a parallel trend within the 12 h sampling interval with two pronounced minima.

DISCUSSION

Cloud water

The concentrations of the four nitrophenols and phenol determined in cloud water during the Brocken campaign differs significantly from those observed during the Great Dun Fell campaign:

First, the sum of all nitrophenols was much higher in cloud water collected at Mount Brocken compared with Great Dun Fell, clearly demonstrating the more polluted area in Central Europe, where plumes of highly polluted air masses reach Mount Brocken with westerly winds. One such plume was observed on June 7, 1994. Such high concentrations of phytotoxic nitrophenols may have a direct impact on mountain forests where deposition on tree leaves and needles may already occur without direct rainfall.

Only phenol itself was observed at Great Dun Fell in a higher concentration than at Mount Brocken, indicating that this compound is more rapidly degraded in the polluted area of Central Europe (inter alia by formation of nitrophenols).

Although 4-NP is found in significantly higher concentrations at Mount Brocken compared with Great Dun Fell, the observed mean value of 21 µg/L (150 nmol/L) is not exceptionally high for cloud water in Central Europe. Richartz et al.[15] found mean values for 4-NP of 20 µg/L (153 nmol/L) near Bayreuth (Bavaria, Germany), Herterich and Hermann[16] observed mean values of 17.5 µg/L (125 nmol/L) in the Alps and even an average of 57 µg/L (410 nmol/L) in the Fichtelgebirge, while much lower mean concentrations for this compound were reported for rain water[11,12,34,35].

Total amount of nitrophenols

Table III summarizes the total amount of the individual nitrophenols (both in the gas and liquid phase) for the six events as well as the mean values of all events. The table also contains the ratio of 2-NP/4-NP and the ratio of the mononitrophenols (2-NP and 4-NP) relative to the dinitrophenol 2,4-DNP

(Σ2-NP + 4-NP/2,4-DNP). For the latter ratio at Mount Brocken, a mean value of 29 was found while at Great Dun Fell this value was only 4.9. Many more mononitrophenols than dinitrophenols have been found in clouds at Mount Brocken. Assuming that mononitrophenols at least partially originate from automobile exhaust[19] and that they degrade further to form dinitrophenols, the results demonstrate that mainly freshly polluted air masses have reached Mount Brocken, while air masses at Great Dun Fell are more aged. This conclusion is also supported by the fact that a higher average ratio of 2-NP/4-NP is observed at Mount Brocken (1.0 ± 0.36) compared with Great Dun Fell (0.35 ± 0.2). Investigations of automobile exhaust by Tremp et al.[19] indicate a higher 2-NP/4-NP ratio in the exhaust (= 1.5) than in ambient air. We assume that gaseous 2-NP undergoes a more rapid degradation in the atmosphere than the (at least partially) particle-bound 4-NP, leading to lower ratios of 2-NP/4-NP in aged air masses at Great Dun Fell. (Note that during the Brocken campaign the pollution on June 7 (5th event) which most likely represents a freshly contaminated air mass, showed a particularly high ratio of 2-NP/4-NP, in support of this assumption).

TABLE III Mean mixing rates (pptv)[a], ratios of mixing rates and transportation in cloud (TIC, %) of four nitrophenols

Event	*date*	*2-NP*	*4-NP*	*2,4-DNP*	*DNOC*	*2-NP/4-NP*	*ΣNP/2,4 -DNP*	*TIC (%)*
1	02.06.94	4.7	4.3	0.6	< 0.1	1.1	16	41
2	04.06.94	3.9	5.4	0.2	< 0.1	0.7	55	10
3	05.06.94	3.9	4.8	0.6	0.3	0.8	27	42
4	05.06.94	5.9	4.7	0.2	< 0.1	1.2	58	4
5	07.06.94	22.8	15.8	4.7	1.6	1.4	8	63
6	10.06.94	4.5	6.6	1.2	0.7	0.7	9	30
	mean	7.6	6.9	1.3	0.4	1.0	29	

[a] for 2- and 4-NP 1 pptv ≈ 6.5 10^{-9} g m^{-3}; for 2,4-DNP 1 pptv ≈ 8.6 10^{-9} g m^{-3}; for DNOC 1 pptv ≈ 9.2 10^{-9} g m^{-3}.

Much higher concentrations of mononitrophenols than dinitrophenols have been observed in automobile exhaust[19]. Thus, the mononitrophenols found in the troposphere may at least partially result from direct automobile emissions, although these compounds may also be formed to a large extent by atmospheric reactions (nitration of alkylbenzene precursors). The situation is clearer for dinitrophenols which are almost exclusively formed by atmospheric reactions (see also ref. 26).

Formation of dinitrophenols in cloud droplets

Our results from the Great Dun Fell study[26] indicated that the formation of dinitrophenols by nitration of mononitrophenols mainly occurs within cloud droplets as the average concentrations of dinitrophenols in the gas phase were seven times higher on days when the sampling site was in clouds compared with cloud-free days. During the Brocken campaign discussed here, there was an independent experiment, which confirms this conclusion further: back trajectories were also calculated according to the "transport analysis programme" (TRAP 1). This programme allows the calculation of the relative time the air masses are transported in the cloud (TIC) in %. This TIC value is included in Table III. The table demonstrates that the TIC values of the 1st, 3rd, 5th and 6th events are much higher than those of the 2nd and 4th events. The ratio of the sum of the mononitrophenols to 2,4-dinitrophenol (Σ2-NP + 4-NP/2,4-DNP) directly reflects this transport in clouds. On days when the air masses reaching Mount Brocken are mainly transported in clouds, this ratio is low (mean = 15), while on days with little transport in clouds this ratio is much higher (mean: 57). Assuming that 2,4-dinitrophenol is formed in cloud droplets by nitration of mononitrophenols, a low ratio of the sum of mononitrophenols relative to 2,4-dinitrophenols is expected, if the air masses sampled are mainly transported in clouds as is indeed observed. Thus, these new data support our previous conclusion that dinitrophenols are mainly formed in cloud droplets. Independent laboratory studies reported by us[36] corroborate this conclusion further.

Partitioning of nitrophenols between the gas and liquid phase

As shown in section 3.5 and Table II, the observed partitioning of the four nitrophenols between the gas and the liquid phase only partially reflects the equilibrium predicted by Henry's law. An approximate agreement between the experimental data reported by Tremp et al.[19] and Schwarzenbach et al.[33] and the field data reported here is only observed for the two mononitrophenols, 2-NP and 4-NP. Noteworthy is the relatively good agreement for 4-NP, a compound which is largely particle-bound, for which a poor agreement based on field data of the Great Dun Fell campaign[27] was reported previously. In the present experiments, the interstitial air between the impactor and the scrubber was filtered, while in the previous experiments at Great Dun Fell non-filtered interstitial air entered the scrubber. Thus, particle-bound 4-NP is removed in the present experiment, explaining the better agreement between the partitioning coefficient determined in the laboratory and in the field. The discrepancies observed for 2,4-DNP and DNOC between laboratory and field experiments are not well understood, while the differences in the distribution constant between the two campaigns may again be the result of the different sampling procedures.

Table II reveals a considerable variation in the partitioning coefficients for the six sampling events. These variations in the partition coefficients were not only observed between distinct events, but also within one event, as shown in Figure 7 for the 5th event on June 7, 1997. These variations are real and must result from the cloud dynamics. During this event the boundaries of the cloud shifted significantly. At the beginning of the event the cloud base was near the sampling site at 1150 m, it decreased to almost 600 m within the following 7 h and then increased again to ~ 1200 m during the remaining period. The LWC increased significantly, i.e. from 30 mg/m^3 at 1:00 h to 800 mg/m^3 at 3:00 h showing strong fluctuations during the remaining sampling period. Moreover, the diameter of the droplets varied strongly during the whole event. These cloud dynamics were apparently faster than the establishment of the equilibrium between gas and liquid phase. Consider 2-NP as an example: if the partition coefficient determined in the laboratory at 7° C (~ 5 × 10^3, Tremp et al., 1993; Schwarzenbach et al., 1988) corrected for the temperature dependence, is considered to be correct, Figure 9 demonstrates that during part of the sampling campaign the cloud droplets were supersaturated by 2-NP while during other parts they were undersaturated.

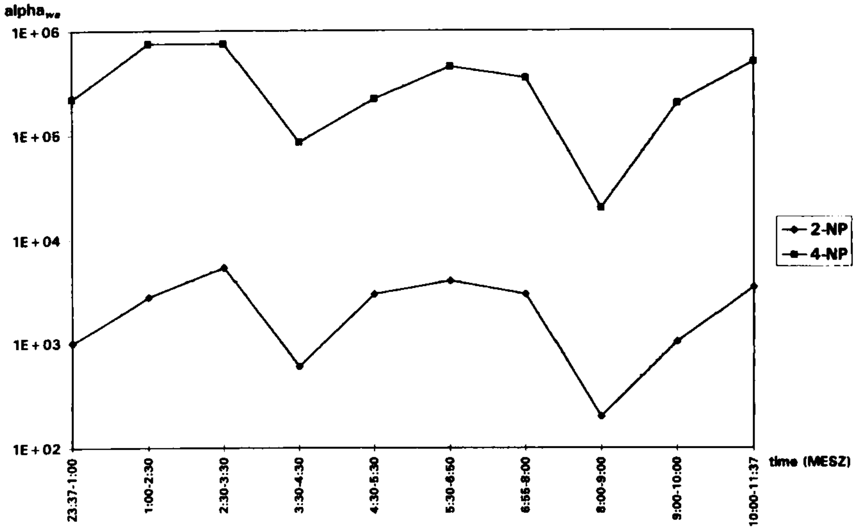


FIGURE 7 Variation of the partitioning coefficients of 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP) between liquid and gas phase during the cloud event on 07. June 1994

Acknowledgements

Financial support from the German Federal Ministry for Education, Research and Development (BMBF) is kindly acknowledged. We are grateful to Mr. M. Astratov for his assistance during the field campaign and to Dr. J. Kruppa for this help in preparing the manuscript.

References

[1] T.E. Graedel, D.E. Hawkins and L.D. Claxton, *Academic Press, 1986* (1986).

[2] M.P. Ligocki, C. Leuenberger and J. F. Pankow, *Atmos. Environ.*, **19**, 1609–1617 (1985).

[3] M.P. Ligocki, C. Leuenberger and J.F. Pankow, *Atmos. Environ.*, **19**, 1619–1626 (1985).

[4] P. Laj, S. Fuzzi, M.C. Facchini, J.A. Lind, G. Orsi, M. Preiss, R. Maser, W. Jaeschke, E. Seyffer, G. Helas, K. Acker, W. Wieprecht, D. Möller, B.G. Arends, J.J. Möls, R.N. Colville, M.W. Gallagher, K.M. Beswick, K.J. Hargraeves, R.L. Storeton-West and M.A. Sutton, *Atmos. Environ.*, **31**, 2589–2598 (1997).

[5] P.J. Shea, J.B. Weber and M.R. Overcash, *Res. Rev.*, **87**, 1–41 (1983).

[6] W.E. Schäfer and J. Schönherr, *Ecotox. Environ. Safe*, **10**, 239–252 (1985).

[7] G. Rippen, E. Zietz, R. Frank, T. Knacker and W. Klöpffer, *Environ. Technol. Letters*, **8**, 475–482 (1987).

[8] K. Nojima, K. Fukaya, S. Fukui and S. Kanno, *Chemosphere*, **2**, 77–82 (1975).

[9] K. Nojima, K. Fukaya, S. Fukui, S. Kanno, S. Nishiyama and Y. Wada, *Chemosphere*, **1**, 25–30 (1976).

[10] C. Leuenberger, M.P. Ligocki and F. Pankow, *Environ.Sci.Technol.*, **19**, 1053–1058 (1985).

[11] C. Leuenberger, J. Czuczwa, J. Tremp and W. Giger, *Chemosphere*, **17**, 511–515 (1988).

[12] K. Levsen, S. Behnert, B. Prieß, M. Svoboda, H.D. Winkeler and J. Zietlow, *Chemosphere*, **21**, 1037–1061 (1990).

[13] K. Levsen, S. Behnert and H.D. Winkeler, *Fresenius J. Anal. Chem.*, **340**, 665–671 (1991).

[14] K. Levsen, S. Behnert, P. Mußmann, M. Raabe and B. Prieß, *Intern. J. Environ. Anal. Chem.*, **52**, 87–97 (1993).

[15] H. Richartz, A. Reischel, F. Trautner and O. Hutzinger, *Atmos. Environ.*, **24A**, 3067–3071 (1990).

[16] R. Herterich and R. Herrmann, *Environ. Technol.*, **11**, 961–972 (1990).

[17] M.G. Nishioka and J. Lewtas, *Atmos. Environ.*, **11**, 2077–2087 (1992).

[18] K. Nojima, A. Kawaguchi, T. Ohya, S. Kanno and M. Hirobe, *Chem. Pharm. Bull.*, **31**, 1047–1051 (1983).

[19] J. Tremp, P. Mattrel, S. Fingler and W. Giger, *Water Air and Soil Pollution*, **68**, 113–123 (1993).

[20] R. Atkinson and S. Aschmann, *Int. J. Chem. Kin.*, **26**, 929–944 (1994).

[21] R. Atkinson, S. Aschmann, J. Arey and W. Carter, *Int. J. Chem. Kinet.*, **21**, 801–827 (1989).

[22] R. Atkinson, *Atmos. Environ.*, **24A**, 1–41 (1990).

[23] D. Grosjean, *Environ. Sci. Technol.*, **19**, 968–974 (1985).

[24] K. Nojima and C. Isogami, *Chem. Pharm. Bull.*, **42**, 2426–2429 (1994).

[25] GDCH, *VCH Verlagsgesellschaft* (1992).

[26] J. Lüttke, V. Scheer, K. Levsen, G. Wünsch, J.N. Cape, K.J. Hargreaves, R.L. Storenton-West, K. Acker, W. Wieprecht and B. Jones, *Atmos. Environ.*, **31**, 2637–2648 (1997).

[27] J. Lüttke and K. Levsen, *Atmos. Environ.*, **31**, 2649–2655 (1997).

[28] A. Marple and K. Willeke, *Atmos. Environ.*, **10**, 891–896 (1976).

[29] P. Winkler, *Vienna World Meteorological Organisation* TD-Nr. 462, 17–21 (1992).

[30] W.R. Cofer, V.G. Collins and R.W.W. Talbot, *Environ. Sci. Technol.*, **19**, 557–560 (1985).

[31] Z. Vecera and J. Janak, *Anal. Chem.*, **59**, 1494–1498 (1987).

[32] P. Mußmann, K. Levsen and W. Radeck, *Fresenius J. Anal. Chem.*, **348**, 654–659 (1994).

[33] R. Schwarzenbach, R. Stierli, B. Folsom and J. Zeyer, *Environ. Sci. Technol.*, **22**, 83–92 (1988).

[34] H.F. Schöler, K. Nick and M. Clemens, *Bornemann Verlag*, Bonn 1991 (1991).

[35] A.J. Geißler, *PhD thesis University of Bonn* (1994).

[36] V. Scheer, Ch. George, J. Lüttke, K. Levsen, W. Behnke, A. Frenzel and C. Zetzsch, *Proceedings of Eurotrac Symposium '98*, Ed.: P.M. Borrell, P. Borrell, T. Cvitas, K. Kelly and W. Seiler, Computanial Mechanis Publications, Southampton, UK, 1997, pp. 469–473.
[37] D. Möller, K. Acker and W. Wieprecht, *Atmos. Res.*, **41**, 321–335 (1996).
[38] R. Atkinson, S.M. Aschmann and J. Arey, *Environ. Sci. Technol.*, **26**, 1397–1403 (1992).