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CLOUD PROCESSING OF SOLUBLE GASES

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Abstract—Experimental data from the Great Dun Fell Cloud Experiment 1993 were used to investigate interactions between soluble gases and cloud droplets. Concentrations of H_2O_2, SO_2, CH_3COOH, HCOOH, and HCHO were monitored at different sites within and downwind of a hill cap cloud and their temporal and spatial evolution during several cloud events was investigated. Significant differences were found between in-cloud and out-of-cloud concentrations, most of which could not be explained by simple dissolution into cloud droplets. Concentration patterns were analysed in relation to the chemistry of cloud droplets and the gas/liquid equilibrium. Soluble gases do not undergo similar behaviour: CH_3COOH simply dissolves in the aqueous phase and is outgassed upon cloud dissipation; instead, SO_2 is consumed by its reaction with H_2O_2. The behaviour of HCOOH is more complex because there is evidence for in-cloud chemical production. The formation of HCOOH interferes with the odd hydrogen cycle by enhancing the liquid-phase production of H_2O_2. The H_2O_2 concentration in cloud therefore results from the balance of consumption by oxidation of SO_2, in-cloud production, and the rate by which it is supplied to the system by entrainment of new air into the clouds. © 1997 Elsevier Science Ltd.

Key word index: Cloud, soluble gases, Henry's equilibrium, in-cloud chemical reactions.

1. INTRODUCTION

The fundamental role of cloud droplets as a medium for chemical reactions has long been recognized (Jacob, 1986; Chameides and Davis, 1984; Calvert *et al*., 1986). This is because physical and chemical processes in multiphase systems significantly influence transport, distribution and removal of chemical species from the atmosphere. The interaction between cloud droplets and gaseous species is driven by numerous processes, including transport across the air–water interface and within the aqueous phase itself, aqueous-phase chemical reactions, and the mass transport of reaction products within the droplets (Schwartz, 1984; Warneck, 1986). In fact, aqueous-phase reactions potentially act either as sink or as source for atmospheric trace compounds, depending on the physical and chemical characteristics of the cloud droplets (Warneck, 1986). In turn, the chemical transformations in the liquid phase control the fate of gaseous species and/or their reaction products upon cloud dissipation.

A well-studied phenomenon is the aqueous-phase oxidation of S(IV), believed to account for a large fraction of sulphate aerosol present in the atmosphere (Hegg, 1985) and therefore to significantly modify the lifetime of sulphur species in the atmosphere. The overall effect of liquid-phase reactions in-cloud is more complex for chemical species, such as organic acids and H_2O_2, which can either be produced or consumed within the droplets. Substantial progress has been made in describing the equilibrium, kinetics

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and chemical evolution of atmospheric gaseous species upon incorporation into cloud droplets, but in-situ concurrent measurements of the gas and liquid concentrations of organic acids and odd hydrogen species in clouds are still needed to validate the theoretical studies. The Great Dun Fell cloud experiment 1993 (GDF) offers the opportunity to investigate gas–liquid interaction and its influence on the chemical composition of the air downstream of a cloud system (Choularton *et al.*, 1997). Several cloud episodes were studied in the experiment (Colvile *et al.*, 1997) and, during many of them, unambiguous modifications of the original air mass, due to aqueous-phase chemistry were monitored. Significant increases in aerosol SO_4^{2-} downstream of the cloud, compared to the aerosol entering the cloud, were detected (Laj *et al.*, 1997). These increases were related to S(IV) oxidation in the liquid phase, enhanced by the entrainment of reactants such as H_2O_2, into the cloud system. These findings are supported by the modelling of aerosol processing, showing a marked effect of SO_2 oxidation on the chemical evolution of the aerosol on which the droplet formed (Bower *et al.*, 1997). Losses of NO_x in cloud, followed by the outgassing of HONO and/or HNO_3, were noted during several of the cloud events (Cape *et al.*, 1997). Wells *et al.* (1997) showed that, during polluted conditions, NH_3 was consumed by cloud processing and decreased by up to 20%. Instead, during clean air conditions, NH_3 was outgassed from the aerosol. Furthermore, Wiedensohler *et al.* (1997) connected the outgassing of NH_3 to the production of new particles downstream of the cloud.

Other chemical species were affected by in-cloud chemical processes, in particular when the cloud acidity was changed. For example, the behaviour of gaseous species like H_2O_2, HCOOH, and CH_3COOH, is very sensitive to the chemical and microphysical properties of the droplets. This is because the gas/liquid equilibrium and pH dependencies of chemical reactions control the rate at which a given chemical species is either consumed or produced in the liquid phase. In the light of the chemical transformations monitored in the clouds at GDF, a more complete quantification of the processing of species like H_2O_2, HCOOH, CH_3COOH, and HCHO is required. This study is therefore an attempt to quantify the transformations of these chemical species in relation to the modifications of droplet chemistry induced by the in-cloud production of S(IV).

2. EXPERIMENTAL SET-UP AND METHODOLOGICAL APPROACH

A complete description of the GDF experiment, including the experimental set-up, techniques and sampling methodologies, is reported in Choularton *et al.* (1997). Here, we limit our description to the specific measurements relevant to this study. Gaseous phase concentration of SO_2, H_2O_2, CH_3COOH, HCOOH and HCHO were monitored continuously during the GDF field campaign. All gases were sampled in the interstitial air between cloud drops. The different sampling locations are indicated in Fig. 1. Cloud water sampling and cloud microphysical measurements were made at both Mine Road (MR) and Summit (SU) (Colvile *et al.*, 1997). Cloud water sampling was performed on a hourly basis. Determination of the bulk chemical composition of cloud droplets include analyses of major anions (SO_4^{2-}, NO_3^-, Cl^-), cations (Ca^{2+}, Na^+, K^+, Mg^{2+}, NH_4^+), and organic acids ($HCOO^-$, and CH_3COO^-) by ion chromatography, and free and bound formaldehyde and acetaldehyde by HPLC (Facchini *et al.*, 1992). It also includes measurements of S(IV) and H_2O_2 by continuous flow chemiluminescence fixing the concentration of both species immediately after collection (Maser *et al.*, 1994).

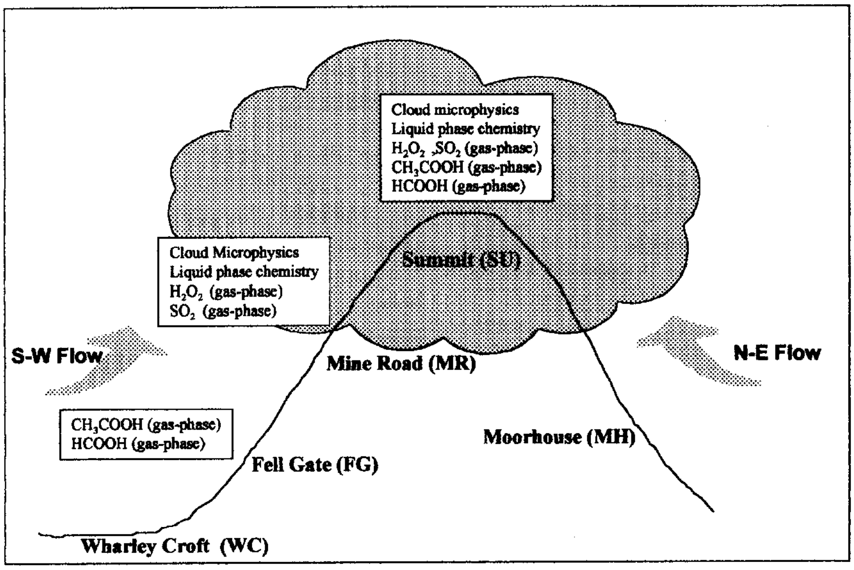

Fig. 1. Schematic view of the GDF experiment with measurements relevant to the present work, on the atmospheric sampling of gases and cloud water.

The Great Dun Fell 1993 campaign took place from 22 April to 12 May and was characterised by a sequence of cloud events described by Colvile *et al.* (1997). With the exception of the first cloud event on 22 April, unusual meteorological conditions compared to previous campaigns led to the formation of clouds in northeasterly flow conditions, resulting in the advection of polluted air masses (Colvile *et al.*, 1997). Cloud water sampling was performed during six cloud episodes, as reported in Table 1. Flow conditions as well as the location of cloud water sampling for each cloud event are also reported in Table 1.

As mentioned earlier, clouds were often sampled in conditions where both MR and SU were in-cloud. Exceptions are on 5/6 May (from 20:30), 11 May (until 23:30), during which cloud water was sampled at SU only, and on 22 April, during which MR was out of cloud and southeasterly flow conditions were prevailing (see Table 1). Most of the following discussion concerns time periods during which the height of cloud base allowed cloud water sampling at both SU and MR. Time periods of disconnected flow conditions, as defined by Colvile *et al.* (1997), were excluded from the study.

3. CHEMICAL COMPOSITION OF THE MULTIPHASE SYSTEM DURING THE CLOUD EVENTS

Air masses of different origins advected to the sampling sites, leading to substantial changes in cloud microphysics and droplet chemical composition during the different cloud episodes. Consequently, the concentration of chemical species in the aqueous phase is quite variable, ranging from 10 to 300 $\mu eq\,\ell^{-1}$ for SO_4^{2-}, 6 to 120 $\mu eq\,\ell^{-1}$ for NO_3^- and 5 to 225 $\mu eq\,\ell^{-1}$ for NH_4^+. On average, 75% of the ionic strength of cloud droplet solutions is accounted for by NH_4^+, SO_4^{2-} and NO_3^-. Concentrations of Na^+ and Cl^-, are also high (average concentrations of 110 and 60 $\mu eq\,\ell^{-1}$, respectively), as expected at a site influenced by maritime air masses. On average, the Cl/Na ratio lies below that of sea salt (0.5 as opposed to 1.16). This is probably due to the degassing of HCl from sea-salt particles in an acidic environment. On the other hand, organic acids ($HCOO^-$ and CH_3COO^-) only contribute between 1 and 4% of the ionic loading of the liquid phase. Free HCHO and HMSA are generally found at average concentrations lower than 1 μM. Mean values of cloud liquid water content (LWC), pH of the cloud droplets, and concentrations of SO_4^{2-}, NO_3^+, NH_4^+, S(IV), H_2O_2, $HCOO^-$, CH_3COO^-, and total HCHO in the aqueous phase for each cloud event are reported in Table 2. Clearly, aqueous-phase concentrations of major ions and organic acids were very high during the 11/12 May cloud episode but this is partly linked to the low LWC content of the cloud. Lower concentrations of NO_3^-, SO_4^{2-} and NH_4^+ are

Table 1. Major cloud sampling periods during the GDF campaign 1993, flow conditions, and presence of the cloud at MR

Cloud event	Sampling time	Wind direction	MR cloud
22 April	16:00–22:00	Southwesterly	No
5/6 May	16:00–02:00	Northeasterly	Until 20:30
9 May	00:00–12:00	Northeasterly	Yes
9/10 May	20:00–07:00	Northeasterly	Yes
10/11 May	18:00–00:00	Northeasterly	Yes
11/12 May	19:00–02:00	Northeasterly	From 23:30

Table 2. Liquid water content (LWC), cloud droplet pH, and concentration of SO_4^{2-}, NO_3^-, NH_4^+, S(IV), H_2O_2, an cloud at SU and MR averaged over each cloud episode. The standard deviations of the mean is indicated in bracket

EVENT	LWC ($mg\,m^{-3}$)		pH		SO_4^{2-} ($meq\,l^{-1}$)		NO_3^- ($meq\,l^{-1}$)		NH_4^+ ($meq\,l^{-1}$)		S(IV) (μM)	
	MR	SU	MR	SU	MR	SU	MR	SU	MR	SU	MR	SU
April 22	*n.d.*	0.47 *(0.08)*	*n.d.*	4.85 *(0.56)*	*n.d.*	0.14 *(0.04)*	*n.d.*	0.1 *(0.02)*	*n.d.*	0.4 *(0.1)*	*n.d.*	17.5 *(6.2)*
May 5/6	0.1 *(0.05)*	0.35 *(0.13)*	3.9 *(0.35)*	4.1 *(0.3)*	0.15 *(0.05)*	0.08 *(0.04)*	0.16 *(0.1)*	0.08 *(0.04)*	0.23 *(0.06)*	0.15 *(0.09)*	1.8 *(0.8)*	1.3 *(0.4)*
May 9	0.16 *(0.06)*	0.46 *(0.15)*	3.2 *(0.24)*	3.6 *(0.3)*	0.39 *(0.19)*	0.2 *(0.1)*	0.29 *(0.11)*	0.11 *(0.05)*	0.24 *(0.03)*	0.14 *(0.08)*	0.04 *(0.01)*	0.04 *(0.07)*
May 9–10	0.28 *(0.08)*	0.67 *(0.08)*	4.08 *(0.12)*	4.3 *(0.1)*	0.11 *(0.03)*	0.04 *(0.01)*	0.12 *(0.04)*	0.05 *(0.01)*	0.22 *(0.06)*	0.09 *(0.01)*	0.1 *(0.01)*	0.06 *(0.01)*
May 10–11	0.24 *(0.12)*	0.72 *(0.13)*	3.55 *(0.06)*	3.7 *(0.03)*	0.21 *(0.03)*	0.14 *(0.02)*	0.27 *(0.12)*	0.13 *(0.03)*	0.37 *(0.12)*	0.24 *(0.05)*	*n.d.*	0.7 *(0.3)*
May 11–12	0.06 *(0.01)*	0.25 *(0.11)*	4.34 *(0.04)*	4.2 *(0.12)*	0.3 *(0.08)*	0.24 *(0.15)*	0.57 *(0.16)*	0.34 *(0.25)*	0.81 *(0.17)*	0.64 *(0.38)*	*n.d.*	*n.d.*

b.d.l.: below detection limits; *n.d.*: no data.

Table 3. Gas phase concentrations and associated standard deviations of SO_2, H_2O_2, HCOOH, CH_3COOH, and HCHO in ppb at both MR and SU, averaged over the course of each fog episode.

Cloud	SO_2(ppb)		H_2O_2(ppb)		HCOOH (ppb)		CH_3COOH (ppb)		HCHO (ppb)
event	SU	MR	SU	MR	SU	FG	SU	MG	SU
22 April	4.82 (*2.61*)	2.4 (*0.44*)	0.03 (*0.09*)	*n.d.*	0.17 (*0.03*)	0.13 (*0.06*)	0.11 (*0.09*)	0.36 (*0.37*)	7.2 (*1.3*)
5/6 May	0.43 (*0.43*)	0.37 (*0.18*)	*n.d.*	0.32 (*0.27*)	0.28 (*0.07*)	0.61 (*0.01*)	0.19 (*0.21*)	0.20 (*0.05*)	2.3 (*1.4*)
9 May	4.2 (*4.3*)	0.86 (*0.8*)	0.16 (*0.2*)	0.27 (*0.24*)	0.13 (*0.09*)	0.38 (*0.11*)	0.08 (*0.06*)	0.17 (*0.04*)	1.2 (*0.22*)
9/10 May	0.28 (*0.08*)	0.16 (*0.04*)	0.08 (*0.04*)	0.15 (*0.07*)	0.2 (*0.02*)	0.49 (*0.09*)	0.11 (*0.4*)	0.22 (*0.11*)	1.3 (*0.26*)
10/11 May	4.19 (*1.55*)	0.74 (*0.17*)	0.02 (*0.01*)	0.04 (*0.02*)	0.25 (*0.04*)	0.56 (*0.30*)	0.15 (*0*)	0.39 (*0.15*)	2.18 (*0.65*)
11/12 May	0.31 (*0.19*)	0.28 (*0.07*)	*n.d.*	0.34 (*0.07*)	0.50 (*0.11*)	0.65 (*0.09*)	0.36 (*0.09*)	0.25 (*0.07*)	3.2 (*0.64*)

n.d.: no data.

measured during the 9/10 event in association to relatively high concentrations of organic acids. Very high levels of H_2O_2 are reported for the 9 May and 9/10 May events while the concentration of S(IV) is highest during 22 April and 5/6 May cloud events. The pH of the bulk cloud water solution varies between 3.2 (9 May) and 4.8 (22 April).

A similar comparison between the cloud episodes is made for gaseous species. Average concentrations and associated standard deviations of SO_2, H_2O_2, CH_3COOH, HCOOH and HCHO in the gas phase at each site and during each one of the cloud events are reported in Table 3. The gaseous-phase concentrations of H_2O_2 and SO_2 show behaviour similar to those of the liquid phase: highest concentrations of SO_2 are found during 22 April, while maximum concentration of H_2O_2 is found during 11/12 May. Note that the concentration of SO_2 is higher at SU than at MR, whereas that of H_2O_2 is higher at MR. Elevated levels of organic acids were measured during the nights of 5/6 May and 11/12 May. Obviously the concentrations of FG are higher than at SU, due to dissolution into cloud droplets. But it should be noted that the ratio of FG to SU concentration is usually higher for HCOOH than for CH_3COOH, except during 22 April. In this case, there is an apparent increase in HCOOH between FG and SU, although not paralleled by any change of CH_3COOH concentration. Hourly averages of HCHO concentrations in the cloud range from 1 to 8 ppb, with maximum values on the 22 April.

4. CLOUD PROCESSING OF SOLUBLE GASES

From the gas-phase concentrations in Table 3 it is clear that, for each cloud event, the average concentrations at SU differ from those at the other sites. In fact, going from SU to WC, gases either undergo degassing (as for CH_3COOH, HCOOH, and H_2O_2) or consumption (as for SO_2 and, in some cases, H_2O_2). Clearly, in the case of SO_2 and H_2O_2, consumption can be linked to the aqueous phase production of S(VI) (see Laj *et al.*, 1997). On the other hand, degassing is related to the dissolution of gas into cloud droplets, followed by degassing upon cloud dissipation. However, it could be questioned whether a dissolution/evaporation model can account for all these changes, or if, as for S(IV) conversion into S(VI), other chemical processes influence the distribution of gases at GDF. A direct comparison between the upwind and downwind concentrations of gases cannot be performed given the very limited information on gas-phase concentration available at the upwind site (MH). Therefore, a detailed quantification of possible loss or production of chemical compounds in cloud will be made by taking gas- and liquid-phase measurements into account. We will first investigate the behaviour of the SO_2–H_2O_2 system between SU and MR, before considering the possible aqueous-phase chemistry of HCHO, CH_3COOH, and HCOOH.

4.1. *The SO_2–H_2O_2 system in-cloud*

Investigation of the production of sulphate was performed by Laj *et al.* (1997) by means of an aerosol mass balance between concentrations upstream and downstream of the cloud, taking dynamic mixing into account. Production of aerosol sulphate was unambiguously detected on 22 April (17:00–22:00), 5/6 May (19:00–1:00), and 10 May (21:00–24:00) and confirmed by the model study of Wells *et al.* (1997). Comparison with liquid-phase measurements of sulphur species can therefore provide an independent check of these findings.

The incorporation and degassing of soluble gases into and from cloud droplets is theoretically described by Henry's law equilibrium. We calculated the deviation from the equilibrium for SO_2 and H_2O_2 using Henry's law constants, according to Winiwarter *et al.* (1994) and Noone *et al.* (1991), and taking into account pH and temperature of cloud droplets, as well as additional chemical equilibria in the liquid phase (i.e. formation of HMSA). The deviation from equilibrium is defined as the ratio between measured and theoretical liquid-phase concentrations. The results are shown in Fig. 2A–B, where deviations from the theoretical equilibrium are reported. Concentrations of SO_2 and H_2O_2 in the gas and liquid phases are much closer to equilibrium than during previous campaigns (Facchini *et al.*, 1992; Winiwarter *et al.*, 1994; Noone *et al.*, 1991). Large deviations of SO_2 are found for a few measurements (Fig. 2A). If samples with

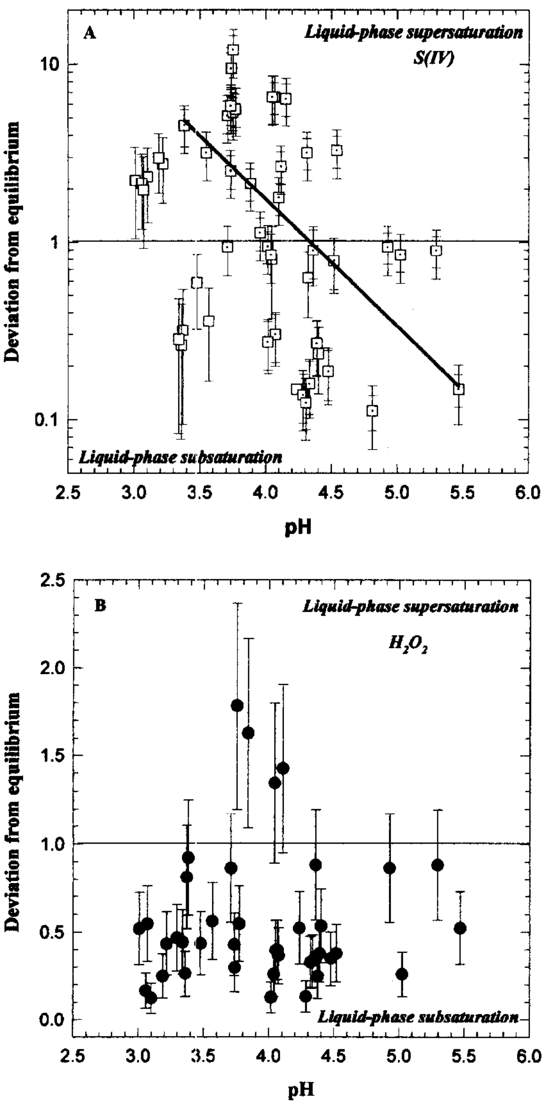

Fig. 2. Deviations from Henry's law equilibrium as a function of pH at SU for (A) SO_2, and (B) H_2O_2. The deviation from equilibrium is defined as the ratio between measured and theoretical liquid-phase concentrations. Deviation >1 corresponds to supersaturation of the liquid phase. Calculations are made according to Winiwarter *et al.* (1994), and Noone *et al.* (1991) taking into account additional equilibria in the liquid phase (i.e. formation of HMSA) as well as pH and temperature of cloud droplets. A linear regression excluding S(IV) values close to detection limits (non-dotted squares) is shown in (A).

S(IV) concentrations close to detection limits are excluded, the range of deviation from Henry's law equilibrium for SO_2 is relatively low (from 0.4 to 12) and a clear pH-dependency is found in agreement with other studies (Maser *et al.*, 1994). Deviations for H_2O_2 are in the range of 1 to 0.1, more frequently exhibiting undersaturation in the liquid phase. These deviations do not present any clear dependence upon pH (Fig. 2B). Such slight departures from Henry's law equilibrium towards the gas phase were also observed in previous work by Noone *et al.* (1991). Given the measurement uncertainty, we can conclude that the GDF clouds are often in, or close to, equilibrium with respect to the gas phase for SO_2 and H_2O_2.

4.1.1. *Evidence of* SO_2 *consumption between SU and MR.* Going into more detail, we can investigate the evolution of the equilibrium between SU and MR. Degassing (or uptake) of soluble gases by cloud droplets between SU to MR is, in principle, driven by the decrease of the cloud LWC as well as changes in cloud droplet pH and temperature. According to Henry's law, we can write

$$\frac{[X]_l^{SU}}{[X]_l^{MR}} = \frac{[X]_g^{SU}}{[X]_g^{MR}} \frac{L_4 H(pH^{SU}, T^{SU})}{L_3 H(pH^{MR}, T^{MR})} \tag{1}$$

where l refers to concentration in the liquid phase in μmol m^{-3} (i.e. aqueous-phase concentrations normalised to LWC to convert to atmospheric mixing ratios), g refers to the mixing ratio in the interstitial gas phase in ppb, L is the liquid water content of the cloud in g m^{-3}, and H the Henry's law constant, taking cloud water pH and air temperature into account. X refers to any chemical species measured in the gas and liquid phases at both sites. Therefore, knowing the concentrations in both gas and liquid phase at SU, it is possible to calculate the expected degassing from the liquid phase due to changing temperature and LWC from SU to WC. We can write

$$([X]_g^{MR})_{th} = [X]_g^{SU} \frac{[X]_l^{MR}}{[X]_l^{SU}} \frac{L^{MR} H(pH^{MR}, T^{MR})}{L^{SU} H(pH^{SU}, T^{SU})} \tag{2}$$

where $([X]_g^{MR})_{th}$ is the expected gas-phase concentration based on the actual gas-phase concentration at SU and liquid-phase concentration at both SU and MR. We can then compare $([X]_g^{MR})_{th}$ with the measured gas-phase concentration at MR ($[X]^{MR}$). As a first approximation, if $([X]_g^{MR})_{th} > [X]^{MR}$, the concentration in the gas-phase is lower than expected from the simple degassing of droplets, an indication of consumption within the liquid phase. On the contrary, if $([X]_g^{MR})_{th} < [X]^{MR}$, degassing is higher than expected, and this could be related to direct production in the liquid phase between SU and MR. It is implicitly hypothesised in this calculation that the droplets are chemically homogeneous and that the dissipation of small droplets by evaporation does not change the overall chemical composition (droplets smaller than 5 μm are not sampled by the cloud collectors). From a two-stage cloud impactor there are indications, albeit limited, that only weak size dependence is detected on the days of interest (basically from 5 to 12 May) but these measurements could have underestimated cloud inhomogeneities (Schell *et al.*, 1997).

Comparisons between theoretical and measured H_2O_2 and SO_2 concentrations are presented in Fig. 3. For both species, significant differences between

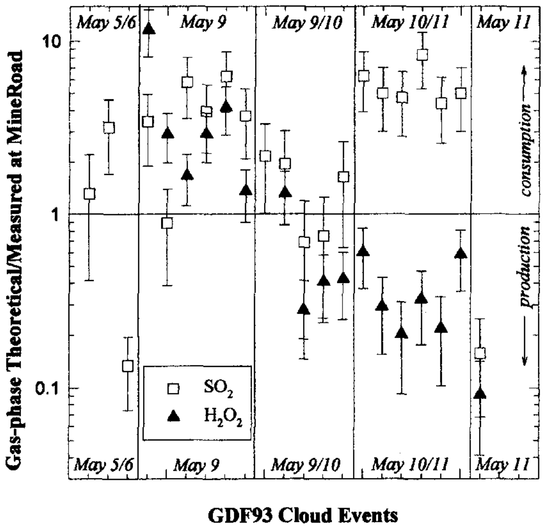

Fig. 3. Theoretical versus measured concentrations of SO_2 and H_2O_2 in the gas phase at MR for each cloud episode. Theoretical values are derived from equation (2). Values >1 indicate consumption between SU and MR. Vice versa, values <1 indicate production within the liquid phase.

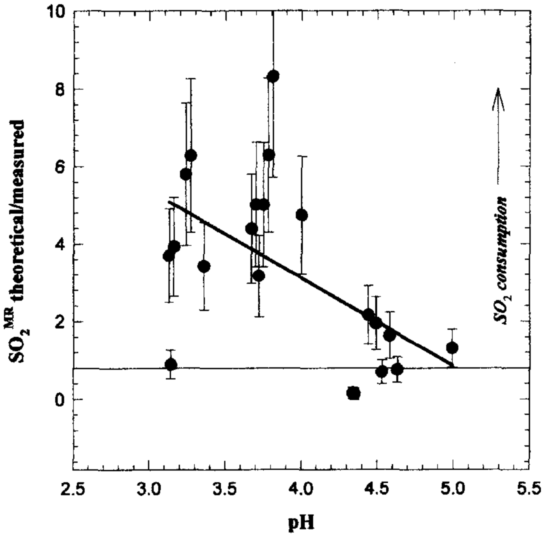

Fig. 4. Ratio between expected and measured gas-phase concentration of SO_2 at MR, as defined in equation (2), as a function of the pH of the liquid phase at SU. Values >1 indicate consumption of SO_2 between SU and MR.

measured and expected values are found. The degassing of SO_2 from the droplets due to cloud dissipation is close to equilibrium on 9/10 May. Instead, an apparent consumption of SO_2 occurs during 5/6, 9, and 10/11 May events and during the 11/12 May run (although this observation is based on only one data point). This conforms with aerosol mass increase downwind of the cloud (Laj *et al.*, 1997). This depletion varies considerably from one case to the next, but is in the range of 1 to 5 ppb overall, corresponding to 50 to 80% of the initial SO_2 concentration at SU.

The apparent loss of SO_2 does not arise from the formation of HMSA in the liquid phase. In fact, at GDF, with the exception of the 22 April event where pH was higher and HMSA formed, concentrations of HMSA remained in the order of a few $\mu mol\,\ell^{-1}$ throughout the experiment and cannot account for SO_2 loss. Instead, we can observe that the consumption/degassing of SO_2 is linked to the pH of the droplets at SU (Fig. 4), with higher consumption at lower pH, as expected from studies on the liquid-phase oxidation of SO_2 by H_2O_2 (Calvert *et al.*, 1984).

4.1.2. *The* H_2O_2 *chemistry at GDF.* We can see from Fig. 3 that, during the 9 May event and at the beginning of the 9/10 May event, consumption of SO_2 is associated with a depletion of H_2O_2. During these events, a clear SO_4^{2-} formation was detected by aerosol measurements (Laj *et al.*, 1997). In fact, previous studies have shown that, at GDF, oxidation of SO_2 occurs mostly via reaction with H_2O_2 (Chandler *et al.*, 1991). However, during the morning of 10 May and during the night of 10/11 May, there is an appa-rent production of H_2O_2 in the liquid phase (11 May, based on a single data point has not been considered). The calculated production is in the range of 0.1 to 0.05 ppb h^{-1} in the gas phase. During the night of 10/11 May, strong entrainment of new air into the cloud took place (Colvile *et al.*, 1997), possibly supplying H_2O_2 to the cloud system. On the contrary, entrainment was very limited during the morning of 10 May. The effects of entrainment are difficult to quantify because the composition of entrained air is unknown. We therefore cannot rule out that physical mixing of air increased the concentration of H_2O_2 downstream of SU. However, the limited entrainment during 10 May indicates that mixing is not the only factor acting on the distribution of H_2O_2 concentrations at GDF.

An alternative to this mixing/entrainment hypothesis is that production of H_2O_2 takes place via chemical reaction. It is very unlikely that H_2O_2 is produced directly below the cloud-base by reaction of hydroperoxy radicals:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \qquad (3)$$

In fact, given a daytime HO_2 concentration of 3×10^{-5} ppm, Stockwell (1995) computed an average formation rate of H_2O_2 of about 3×10^{-3} ppb min^{-1} in the gas phase. Taking into account that some of the measurements were performed during the night, and that the transit time from cloud base to MR is of a few tens of seconds, it is clear that this reaction cannot account for the production of H_2O_2. On the other hand, aqueous-phase production of odd hydrogen compounds in the liquid phase can also take place. It is linked to reactions with organic acids, as proposed by Jacob (1986) and Chameides and Davis (1984).

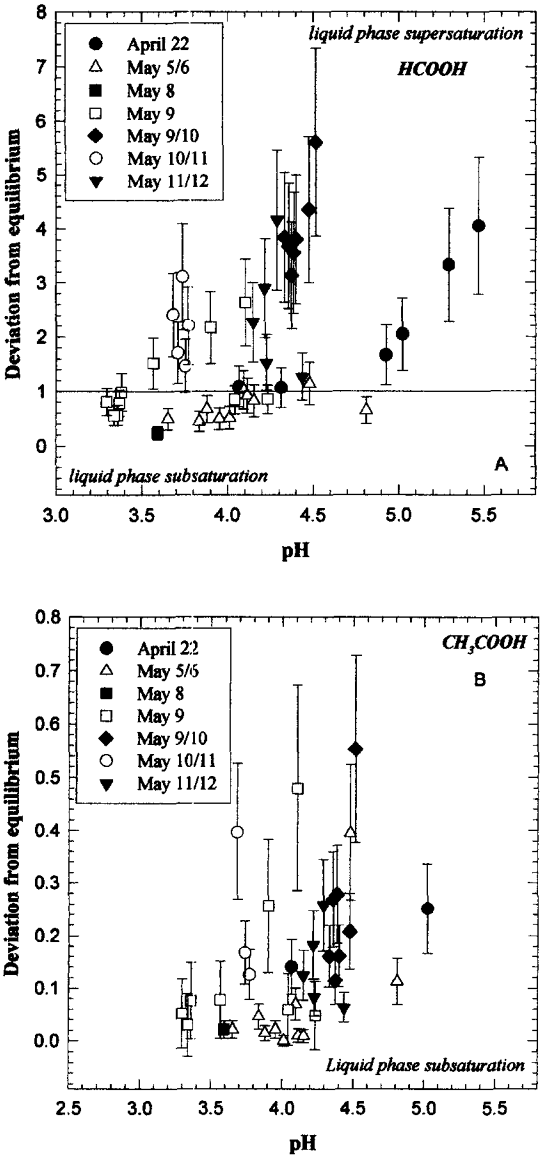

Fig. 5. Deviations from Henry's law equilibrium as a function of pH at the SU for (A) HCOOH and (B) CH_3COOH. The deviation from equilibrium is defined as the ratio between measured and theoretical liquid-phase concentrations. Deviation >1 corresponds to supersaturation of the liquid phase. Calculations are made according to Winiwarter *et al.* (1994) taking into account pH and temperature of cloud droplets.

This hypothesis can be verified since organic acids were monitored in both the liquid and gas phases.

4.2. *Chemistry of* HCOOH *and* CH_3COOH

We investigated the chemistry of organic acids at GDF, first by assessing the state of the equilibrium between gas and liquid phases. Deviations from Henry's law equilibrium for HCOOH and CH_3COOH are calculated according to Dong and Dasgupta (1986) and Winiwarter *et al.* (1994). Results are reported in Fig. 5A and B. For both species, deviations from equilibrium are lower than those found during previous experiments (Facchini *et al.*, 1992; Winiwarter *et al.*, 1994). CH_3COOH is always subsaturated in the liquid phase, whereas HCOOH is either sub- or supersaturated depending on the cloud event. The deviations of HCOOH from the equilibrium are clearly pH dependent with increasing supersaturation at higher pH (Fig. 5A). This is in contrast with previous studies (Facchini *et al.*, 1992; Winiwarter *et al.*, 1994). In addition, during the course of some of the cloud events (22 April, 9 May, and 9/10 May), there is a clear tendency towards increasing supersaturation, not observed for CH_3COOH.

Liquid-phase production of HCOOH takes place via the reaction of hydrated HCHO with OH (Chameides and Davis, 1984; Jacob, 1986):

$$CH_2(OH)_2 + OH \rightarrow HCOOH + HO_2 + H_2O. \quad (4)$$

Hydroxyl radical can form by the decomposition of O_3 in the liquid phase. The rate of reaction (4), and therefore the production of HCOOH, increases at low pH. However, at low pH, most of the HCOOH produced volatilises to the gas phase (Jacob, 1986).

At GDF, we can estimate the amount of HCOOH degassed between SU (in-cloud) and FG (out-of-cloud) considering the total amount of HCOOH present in the cloud system at SU. We defined the degassing factor as the difference between gas-phase HCOOH concentrations at FG and SU normalised by liquid-phase $HCOO^-$ concentrations at SU converted into $\mu mol\ m^{-3}$ of air:

Degassing factor =

$$\frac{HCOOH^{FG}_{gas(\mu mol\ m^{-3})} - HCOOH^{SU}_{gas(\mu mol\ m^{-3})}}{(LWC_{(\ell\ m^{-3})}\ x\ HCOOH^{SU}_{liquid(\mu mol\ \ell^{-1})})}.$$

The degassing factor is plotted as a function of pH in Fig. 6. Data from the 22 April cloud event are excluded from the figure because the degassing factor does not apply to southwesterly flow condition. Degassing took place on the morning of 9 May, during the nights of 9/10 May and 10/11 May (we have no data for the 5/6 May event) but not on 11/12 May. On 9 May and 9/10 May, it is paralleled by a degassing of CH_3COOH, which is, however, always relatively smaller than that of HCOOH. In addition, the degassing of HCOOH is a function of cloud droplet pH as seen in Fig. 6, with higher degassing at low pHs. The patterns of HCOOH in the gas phase are apparently linked to processes occurring in the liquid phase. As the pH of the droplets increases, an increasing fraction of HCOOH remains in the liquid phase, as reflected by greater supersaturation in the liquid phase at high pH (Fig. 5A). When pH decreases, production of HCOOH is enhanced but a larger fraction goes into the gas phase, as reflected in Figs 5A and 6. The transition pH for determining the behaviour of HCOOH is in the range 4–5 (Jacob, 1986) within the same range of pH measured at GDF. Gas and liquid

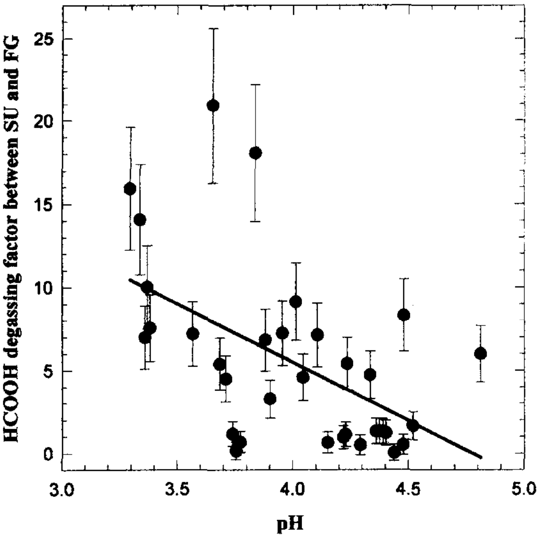

Fig. 6. Degassing factor of HCOOH between FG and SU (see text for the definition of the degassing factor), as a function of cloud droplet pH at SU. Values are fitted with a simple linear regression. Data of 22 April are excluded from the figure (southwesterly flow conditions).

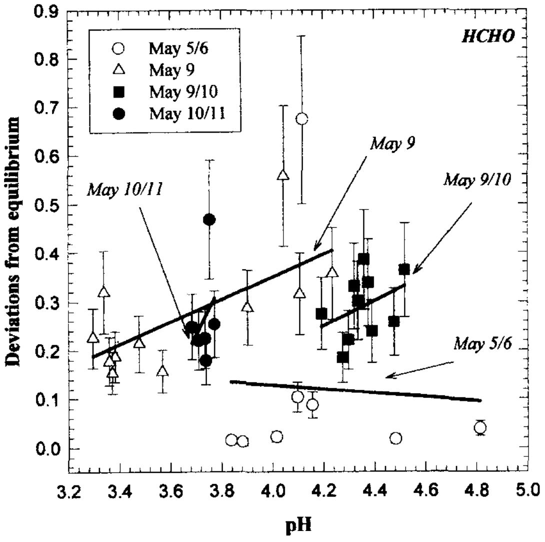

Fig. 7. Deviations from Henry's law equilibrium (as defined in Fig. 2) for HCHO as a function of pH at SU. Calculations are made according to Dong and Dasgupta (1986). Deviation >1 corresponds to supersaturation of the liquid phase. A simple linear regression is plotted for each cloud episode.

phase measurements therefore show strong indications of HCOOH production in the liquid phase. Similar HCOOH in-cloud production was also evidenced by Keene *et al.* (1995). CH_3COOH undergoes a behaviour different from HCOOH, possibly as a result of the limited production of CH_3COOH in the liquid phase (Jacob and Wofsy, 1988). The calculated sub-saturation in the liquid phase cannot be easily explained. However, it could partially result from the gas/liquid transfer limitation, in view of the short time available for establishing the equilibrium in the hill top cloud.

4.3. *Role of* HCHO

We can see from reaction (4) that the liquid-phase production of HCOOH depends upon the availability of hydrated HCHO. Gas-phase HCHO was measured only at SU. Therefore we have no indication on degassing or consumption as for other gases. We calculated the deviations from Henry's law equilibrium using the empirical function proposed by Dong and Dasgupta (1986). The results, presented in Fig. 7, show that, if on average HCHO deviations are not pH dependent, there is a positive correlation with pH during some of the cloud events (9 May, 9/10 May, and 10/11 May) during which HCOOH production is evidenced. The pH dependence certainly reflects the higher rate of reaction (4) at low pH. Measurements of HCHO in both liquid and gas phases therefore offer further support to the hypothesis of HCOOH production in the liquid phase.

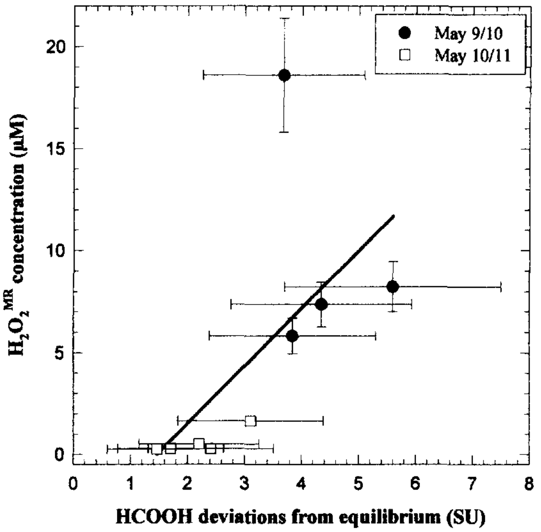

Fig. 8. Deviations of HCOOH from the Henry equilibrium (as defined in Fig. 2) as a function of H_2O_2 concentration in the liquid phase at SU (in µM) during time periods of H_2O_2 production, as derived from equation (2) and Fig. 3 (i.e. 9 May and 9/10 May).

4.4. *Link with odd-hydrogen chemistry*

Formation of HCOOH through reaction (4) also leads to the production of hydroperoxyl radical (HO_2). In turn, production of H_2O_2 takes place in the liquid phase through the following reaction (Schwartz, 1984; Jacob, 1986):

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (5)$$

Reactions (4) and (5) link liquid-phase production of H_2O_2 and HCOOH. In fact, during the periods of H_2O_2 production (9/10 May and 10/11 May), there is a positive correlation between supersaturations of HCOOH in the liquid phase at SU, and the resulting H_2O_2 concentrations in cloud at MR (see Fig. 8).

This is to be expected when reaction (4) occurs in cloud between SU and MR. Quantitative estimates for the production of HCOOH and H_2O_2 are of the same order (less than 0.1 ppb h^{-1}), which is close to the detection limits of the measurements. Additional measurements, as well as specific modelling of the cloud chemistry, are necessary to draw conclusions concerning this parallel production of HCOOH and H_2O_2 in cloud. In addition, it should be borne in mind that the entrainment of air into the cloud could also lead to the apparent degassing of H_2O_2. Both effects shall be taken into account in future studies.

5. CONCLUSIONS

The GDF experiment provided an opportunity to investigate the behaviour of SO_2, H_2O_2, HCOOH, CH_3COOH, and HCHO during the process of formation and dissipation of a hill cloud. Simultaneous measurements of atmospheric constituents in gas and liquid phases at different sites within and downwind of the hill cloud allowed an evaluation of gas/liquid interactions. During the evaporation of the clouds, gases appear to undergo either a degassing from the cloud droplets (as for HCOOH and H_2O_2) or, on the contrary, a depletion (as for SO_2 and H_2O_2, again depending on the event). Even though some of these effects could have resulted from the entrainment of new air into the cloud, we have, in some cases, clear evidence that they are also linked to chemical reactions in the liquid phase. Investigation of the SO_2–H_2O_2–HCOOH system in cloud showed that the behaviour of H_2O_2 is driven both by a direct consumption by reaction with SO_2, and in-cloud production associated to HCOOH formation. Reaction rates and possible degassing from the liquid phase are driven by the pH of the cloud droplets. Understanding the role of clouds in the processing and redistribution in the atmosphere of gaseous compounds, such as H_2O_2, requires a precise knowledge of chemical interactions in the liquid phase. The role of trace chemical species, such as organic acids, is of fundamental importance in the GDF cloud system.

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