Acidic gases (HCOOH, CH3COOH, HNO3, HCl, and SO2) and related aerosol species at a high mountain Alpine site (4360 m elevation) in Europe

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Acidic gases (HCOOH, CH$_3$COOH, HNO$_3$, HCl, and SO$_2$) and related aerosol species at a high mountain Alpine site (4360 m elevation) in Europe

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[1] During a field campaign performed at 4360 m elevation in the French Alps in summer 2004, atmospheric levels of acidic gases (HCOOH, CH$_3$COOH, HNO$_3$, HCl, and SO$_2$) and related aerosol species were investigated using mist chamber and denuder tube samplings. Sulfate aerosol levels greatly exceeded those of gaseous SO$_2$. Conversely, chloride, nitrate and particularly monocarboxylates were much more present in the gas phase than in the aerosol phase. On a molar basis, formic and acetic acids are the most abundant acidic gases ($\sim$14 nmol m^{-3} STP), followed by nitric acid (7 nmol m^{-3} STP), hydrochloric acid (1.7 nmol m^{-3} STP) and sulfur dioxide (0.8 nmol m^{-3} STP). These data gained in the free troposphere over Europe in summer are discussed and compared to those obtained during aircraft missions conducted over North America and the northwest Pacific near China. It is concluded that the concentrations of acidic gases and related aerosol species are quite similar in the free troposphere in summer over Europe and North America. Concentrations of sulfur and nitrogen species in the free troposphere are lower over Europe (and North America) than over the Pacific region located near China (a factor 5 and 2, respectively). Finally, measurements achieved in this study tend to indicate that secondary production is important for the atmospheric budget of carboxylic acids.

1. Introduction

[2] Because of their high solubility in water, acidic gases are important in atmospheric chemistry. Whereas the basics of the atmospheric cycle of inorganic gases like nitric acid and sulfur dioxide are rather well established, the case of light monocarboxylic acids is more complex (see *Chebbi and Carlier* [1996] for a review). Whatever the atmospheric acidic gas cycle is, its distribution throughout the atmosphere is not well enough known, particularly in the free troposphere. Similar to the situation for gases, our present knowledge of inorganic aerosol is far better than that of organic aerosol. The CARBOSOL project (present and retrospective state of the organic versus inorganic aerosol over Europe [*Legrand and Puxbaum*, 2007]) aims to document aerosol (organic and inorganic) in the free troposphere. To reach this goal, in addition to the year-round aerosol sampling made during two years at the Sonnblick Observatory (SBO, 47°03′N, 12°57′E) located at 3106 m above sea level (asl) in Austria [*Pio et al.*, 2007], a field campaign was conducted in summer 2004 at the Vallot Observatory (VO, 45°50′N, 6°51′E, 4360 m asl, French Alps) located 400 km westward from SBO. Since 1999, the site has been equipped with an automatic aerosol sampler supplied by a solar panel power device, that permits continuous sampling of inorganic aerosol [*Preunkert et al.*, 2002] as well as C$_2$-C$_5$ dicarboxylic acids [*Legrand et al.*, 2005]. A year-round study of sulfate aerosol performed at VO indicated that, in contrast to other high-elevation alpine stations such as SBO [*Kasper and Puxbaum*, 1998] or Jungfraujoch (3400 m asl in Switzerland) [*Baltensperger et al.*, 1997], VO is the only European sampling site which is located above the mixing layer in summer [*Preunkert et al.*, 2001].

[3] Because of the limited energy available at VO, high-volume aerosol sampling dedicated to study of the various organic compounds investigated during CARBOSOL [*Pio et al.*, 2007] was not possible as a continuous program. Thus, in summer 2004 a field campaign was organized during which a power generator was deployed at the site. In addition to the aim to document the organic aerosol load in the free troposphere, a secondary objective was to gain atmospheric aerosol data near to the Col du Dôme ice core drill site (4250 m asl), used in CARBOSOL to extract long-term past atmospheric trends organic aerosol from ice core records [*Legrand and Puxbaum*, 2007]. However, it was shown during CARBOSOL that the contribution of monocarboxylic acids to the dissolved organic carbon content of

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the Col du Dôme ice is relatively large compared to what is generally seen in precipitation at lower-elevation sites [*Legrand et al.*, 2007a]. That renders the interpretation of organic ice core records very complex and motivated the investigation of the atmospheric concentrations of mono-carboxylic acids near the ice core drill site. Since measurements of these species in the midtroposphere over Europe are very rare, we investigate also acidic gases ($HCOOH$, CH_3COOH, HNO_3, HCl, and SO_2) during the high-volume aerosol sampling field campaign at VO.

2. Site

[4] Samplings were performed at the Vallot observatory situated in the summit range of the Mont Blanc massif in the French Alps, 400 m southeast of the Col du Dôme ice core drill site. The observatory consists of a simple mountain shelter hut exclusively dedicated to scientific research. Snow and ice cover the vicinity to the southwest of the observatory whereas the northeast side is a precipice. The sampling lines were put on a platform set up on the snow 30 m southwest of the observatory. The power needed to run the pumps for sampling lines was provided by a power generator put on the north side of the observatory. The generator exhaust was piped away into the precipice with a 15 m long tube. During the 4 days of sampling the wind blew from southwest or southeast preventing generator exhaust from impacting the sampling lines. The absence of contamination by the generating set is confirmed by elemental carbon concentrations measured on the high-volume filter samples collected at the site between 1 and 4 September [*Legrand et al.*, 2007a], since the observed levels of ~50 ng m^{-3} STP are close to those expected at this elevation over Europe [*Fagerli et al.*, 2007].

[5] Samplings of acidic gases and aerosols were achieved during 3 days and two nights with continuous samplings from 1 September at 1000 UT to 2 September at 1130 UT, and from 3 September at 0700 UT to 4 September at 1500 UT. On 1 September 2004, France was under the influence of a ridge of high pressure extended from the Mediterranean Sea to England in connection with a high geopotential located over North Africa. Over the west of France a trough of low pressure extended to the Iberian Peninsula. The radio-sounding from Lyon, located 100 km from the Mont Blanc massif, indicated an unstable layer at 1200 m asl and a divergent air mass above, leading to a stable atmosphere. At VO, clear sky conditions prevailed until 2 September in the morning when convective clouds developed enough to reach the site. Riming conditions started at 1130 UT forcing us to stop sampling. Cloudy conditions ended in late afternoon. On 3 September VO experienced clear sky conditions but with respect to the situation of 1 September, air cooled by 2°C in altitude in relation to a cold drop over Portugal associated with a cutoff. On the other hand, in the boundary layer the temperature was 5°C higher on 3 September than on 1 September, and the atmosphere became unstable.

3. Methods

[6] Sampling of acidic gases was done by using mist chambers mounted behind a quartz filter, as well as denuder

tubes equipped with a backup quartz filter. The simultaneous use of the two sampling devices was motivated by several reasons. Handling of mist chambers is relatively easy and low blank values can be reached, leading to detection limits low enough to carry out samplings of a few hours, even at very remote places. However, aerosols trapped on the online filter upstream of the mist chambers can lead to substantial artifacts under certain environmental conditions. Furthermore, sampling of some acidic gases was found to be incorrect because of their sticking onto the wall of the Teflon tube located between the front aerosol filter and the inlet of the front mist chamber. For instance *Jourdain and Legrand* [2002] showed that gas samplings made in Antarctica suffer from a loss which can reach 50% for HCl and 100% for HNO_3, whereas no loss was observed for monocarboxylic acids. Denuder tubes require a more tedious handling than mist chambers, particularly during their coating and drying. The tube preparation generally leads to higher blank values than those of mist chambers and a sufficient sampling time is needed to achieve reliable measurements of low concentrations encountered at remote sites. Another potential problem in the use of denuder tubes is the limited capacity of the tube coating which could lead to a saturation of the coating and thus erroneous data. Therefore laboratory tests were made using 3 annular denuder tubes placed in series, in order to evaluate the collection efficiency of denuder tubes coated with solutions of different Na_2CO_3 concentrations. Results of the tests (not shown) suggest that given the lower atmospheric concentrations expected at 4000 m asl with respect to the ones in the laboratory the coating of tubes with a solution of Na_2CO_3 at 10^{-2} M (50% ultrapure water, 50% HPLC methanol) would be adequate for a typical sampling time of 12 hours.

[7] Two mist chambers were filled with 20 mL of purified water and run in series downstream of a high-purity quartz fiber filter (Whatman, QM-A, 47 mm diameter) with an air flow rate of 0.2 m^3 STP h^{-1}. During the day, 3 mist chamber samplings were done each covering 4 hours, whereas one sample was run over 12 hours during the night. The collection efficiency of the mist chamber device (defined as the mass trapped in the front chamber divided by the sum of masses trapped in the front and second mist chamber) ranged from 80 ± 10% for monocarboxylic acids and SO_2 to 70 ± 10% for HNO_3 and HCl. Such relatively low values are due to the presence of the second mist chamber in the sampling line which results in a higher resistance to air flow and causes less satisfactory nebulization in the first mist chamber compared to the second one. Concentrations were calculated using the total mass present in the first and in the second mist chamber. Several times during the campaign all glassware was washed with purified water produced by a Milli-Q 10 TS system (Millipore, Bedford, MA) and a Maxima HPLC system (Elga, High Wycome Bucks, England) run in series. To estimate the blank of the device the mist chambers were run for 20 s with the same water volume and quality as those used for the atmospheric sampling. The Maxima HPLC system provides an estimated dissolved organic carbon content of the water lower than 5 ppbC. Blank values were found to be low with respect to atmospheric concentrations for inorganic acids but became significant for carboxylic acids. Given the

Table 1. Comparison of HCOOH, CH₃COOH, HNO₃, HCl, and SO₂ Atmospheric Concentrations Derived by Using Mist Chambers and Denuder Tubes Deployed Between 1 September at 1000 UT and 4 September at 0730 UT (Arithmetic Means) at the Vallot Observatory

Species	Denuder Tubes, ng m^{-3}	Mist Chambers, ng m^{-3}
HCOOH	600 ± 435	632 ± 540
CH₃COOH	635 ± 360	825 ± 592
HNO₃	475 ± 200	35 ± 18
HCl	60 ± 34	40 ± 35
SO₂	55 ± 27	38 ± 35

20 mL of water used to fill the mist chambers and the volume of air sampled, mist chamber blank values corresponded to 59 ± 55 ng m^{-3} of formic acid and 51 ± 33 ng m^{-3} of acetic acid for the daytime samples. Concerning the nighttime samples, the three times larger volume of sampled air leads to three times lower blank values (20 ± 19 ng m^{-3} for formic acid and 18 ± 11 ng m^{-3} for acetic acid). Atmospheric concentrations of formic and acetic acid were corrected for these blank values. The accuracy of measurements is related to the accuracy of ion chromatography ($\sim$5%, see below) and the blank variability. For formic and acetic acids the accuracy is mainly driven by the blank variability (10% or less).

[8] A second gas sampling line consisted of 3 annular denuder tubes placed in series and coated with a 10^{-2} M solution of Na₂CO₃ (50% ultrapure water, 50% HPLC methanol) [*Ferm*, 1986; *Norton*, 1992]. A sampling time of 12 hours was applied during day and night. The sampling line was backed up with a high-purity quartz fiber filter (Whatman, QM-A, 47 mm diameter) and run at a flow of 0.32 m^3 STP h^{-1}. The soluble material stuck on the collecting surfaces of the tubes during sampling was extracted with 5 mL of purified water. Blank values of the coated tubes were close to 20 ± 10 ng m^{-3} for acetic acid, 14 ± 6 ng m^{-3} for formic acid, 11 ± 8 ng m^{-3} for HCl, 2 ± 1 ng m^{-3} for HNO₃, and 4 ± 2 ng m^{-3} for SO₂ for the air volume which was sampled over 12 hours. Atmospheric concentrations of all species were corrected by these blank values. The accuracy of atmospheric concentrations is mainly due to the accuracy of ion chromatography ($\sim$5%) for carboxylic acids, nitric acid and sulfur dioxide. For HCl the accuracy is lower (15%) because of the blank variability. The collection efficiency of denuder tubes (defined as the mass trapped in the front tube divided by the sum of masses trapped in the front, second, and third tube) was close to 85% for formic acid, HCl, and HNO₃, 72% for SO₂, and slightly lower for acetic acid (67%).

[9] Aerosols collected on the quartz fiber filters mounted behind the denuder tubes were analyzed for formate, acetate, chloride, nitrate, sulfate, ammonium and oxalate. Aerosols were extracted with 5 mL of purified water. Considering the 12 h sampling, the filter blank values are of 34 ± 8 ng m^{-3} for acetate, 17 ± 2 ng m^{-3} for formate, 21 ± 4 ng m^{-3} for chloride, 4 ± 1 ng m^{-3} for nitrate, 3 ± 1 ng m^{-3} for sulfate, 2 ± 1 ng m^{-3} for oxalate, and 8 ± 1 ng m^{-3} for ammonium. Atmospheric concentrations of all species were corrected by these blank values. The accuracy of analysis is mainly related to the blank variability for formate, acetate,

and chloride, and to ion chromatography accuracy for other ions.

[10] Anion measurements were made with a Dionex DX600 ion chromatograph equipped with an AS11 separator column and run with a quaternary gradient of eluents (H₂O, NaOH at 2.5 and 100 mM, and CH₃OH) as detailed by *Ricard et al.* [2002]. Cation measurements were made with a Dionex 500 ion chromatograph equipped with a CS12 separator column.

4. Results and Discussion

[11] Comparison of atmospheric concentrations derived from denuder samplings with those simultaneously carried out with mist chambers indicates a quite good agreement for acetic and formic acid (Table 1). The larger departure for acetic acid is related to the high level of this species encountered on 3 September, which here led to a saturation of the front tube of the sampling device as depicted by the similar mass trapped on the front and the second tube. Discarding this value the agreement between samplings with denuder tubes and mist chambers becomes better (500 ng m^{-3} STP instead of 567 ng m^{-3} STP). For HCl and SO₂, sampling made with denuders shows higher values than those with mist chambers (Table 1), likely because of a partial loss in the Teflon tube of mist chamber (section 3). This effect becomes dramatic for HNO₃ (475 ng m^{-3} STP from denuder tubes instead of 35 ng m^{-3} STP from mist chambers) confirming previous observations made by *Jourdain and Legrand* [2002].

[12] Figure 1 summarizes the measurements of gas phase samplings (HCl, HNO₃, and SO₂ from denuder tubes and monocarboxylic acids from mist chambers) together with those of aerosol sampled on the back up filters of denuder tubes. On 4 September the daytime denuder tubes were broken during handling and only aerosol data from the backup filter are available.

[13] The mean level of sulfate (400 ng m^{-3} STP) derived from back up filters of denuder tubes was close to mean summer levels (from April to September) observed in 2002 (405 ng m^{-3} STP) and 2004 (360 ng m^{-3} STP) on filters collected by the auto sampler run at VO. Similarly, the level of ammonium, another major component of aerosol, obtained during this short campaign (120 ng m^{-3} STP, Figure 1) is of the same order of magnitude as mean summer levels observed in 2002 and 2004 (160 ng m^{-3} STP) on auto sampler filters. Concentrations documented with the auto sampler during winter 2003–2004 (140 ng m^{-3} STP of sulfate and 40 ng m^{-3} STP of ammonium) are far lower that those recorded in summer and during the short 2004 campaign. These well-marked seasonal changes reflect distinct atmospheric conditions prevailing there because of the presence or absence of upward advection of air masses from the boundary in summer and winter, respectively [*Baltensperger et al.*, 1997; *Preunkert and Wagenbach*, 1998]. Thus we can conclude that atmospheric samplings made over a short time period at the beginning of September 2004 are very representative of mean summer conditions at that site.

4.1. Particulate Sulfate and Sulfur Dioxide

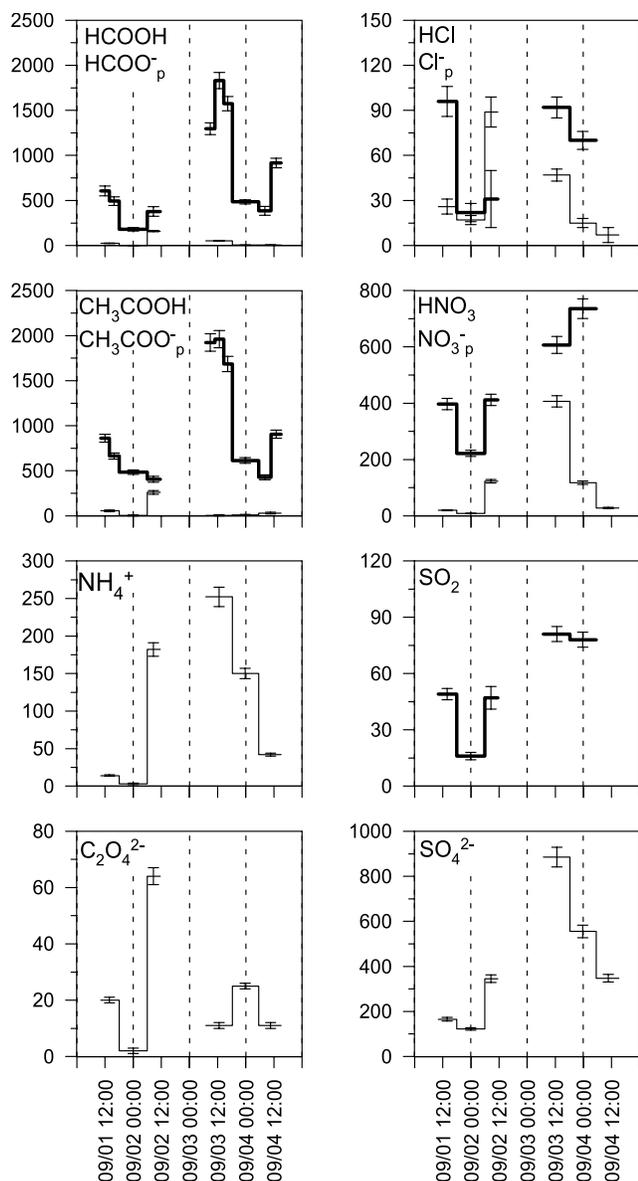[14] Mean concentrations of SO₄²⁻ and SO₂ derived from the denuder tubes at VO are 415 ng m^{-3} STP and 54 ng m^{-3}

Figure 1. Concentrations of gases (HCl, HNO_3, SO_2 from denuder tube sampling and HCOOH and CH_3COOH from mist chamber sampling) (thick line) and aerosols ($HCOO^-_p$, $CH_3COO^-_p$, NH_4^+, $C_2O_4^{2-}$, Cl^-_p, $NO^-_{3\,p}$, and SO_4^{2-} from the back up filters of denuder tubes) (thin lines) observed at the Vallot Observatory at the beginning of September 2004. All concentrations are in ng m^{-3} STP.

STP, respectively. During the CARBOSOL project a mean summer concentration of 960 ng m^{-3} STP of sulfate was found at SBO in 2003 and 2004 [*Pio et al.*, 2007] but SO_2 was not measured. For summer 1992 and 1993 *Kasper and Puxbaum* [1998] found mean summer values of 3020 ng m^{-3} STP of SO_4^{2-} and 430 ng m^{-3} STP of SO_2 at SBO. The decrease of sulfate concentrations by a factor of 3 from 1992–1993 to 2003–2004 at SBO is consistent with the decrease of anthropogenic SO_2 emissions since ~1980. At Payerne (Swiss plateau, 500 m asl), 2130 ng m^{-3} STP of sulfate and 740 ng m^{-3} STP of SO_2 were observed in summer 2002 [*Fjæraa*, 2006]. These data gained at different elevations indicate that the abundance of sulfate relative to sulfur dioxide increases with height. SO_4^{2-} to SO_2 mass ratios of 3 at Payerne, 7 at SBO and 8 at VO reflects the ongoing oxidation of sulfur dioxide into sulfate during upward transport of air masses from the boundary layer to the free troposphere.

[15] With respect to data previously gained in the free troposphere above various regions (Table 2) it appears that sulfur species over Europe are some four times more abundant than in the background free troposphere of Arctic regions. During ABLE-3A, data collected during transit flights off the east coast of United States and between Wallops Island (Virginia) and Thunder Bay (Ontario, Canada) show sulfur species in similar abundance as at VO (Table 2). In contrast, the free troposphere over the NW Pacific appears far more polluted with sulfur species which are some 5 times more abundant than over Europe.

4.2. Particulate Nitrate and Chloride Versus Nitric and Hydrochloric Acids

[16] The aerosol auto sampler deployed at VO since 1999 is equipped with nylon membrane filters mounted behind the quartz filters permitting investigation of total nitrate as well as total chloride. However, because of remobilization of nitrate and chloride from the quartz to the nylon filter during storage of filters, the partitioning between gaseous and aerosol cannot be investigated using this device [*Preunkert et al.*, 2002].

[17] The total nitrate level at VO was close to 600 ng m^{-3} STP at the beginning of September 2004. That is two times lower than the total nitrate level found in 1992–1993 at SBO [*Kasper and Puxbaum*, 1998] (Table 2). Since, in contrast to sulfur species, no dramatic decrease of nitrogen species emissions has taken place in Europe over the two last decades, this moderate decrease of total nitrate level from 1992–1993 at SBO to 2004 at VO is likely mainly related to the difference by more than 1000 m in elevation

Table 2. Comparison of Mean Concentrations (Arithmetic Means) Expressed in ng m^{-3} STP of Sulfur and Nitrogen Species and Carboxylic Acids Observed at the Vallot Observatory With Those Gained During Flight Campaigns Carried Out in Various Regions of the Free Troposphere

Sites or Aircraft Missions	Sampling Dates	SO_2	SO_4^{2-}	HNO_3	$NO^-_{3\,p}$	HCOOH	CH_3COOH	References
VO (4360 m asl)	Sep 2004	54	415	475	135	635	825	this work
SBO (3106 m asl)	Apr–Sep 1992–1993	430	3020	510	550	...	...	*Kasper and Puxbaum* [1998]
ABLE 3A (2 to 6 km, Arctic)	Jul–Aug 1988	...	100	110	25	145	200	*Talbot et al.* [1992]
ABLE 3A (2 to 6 km, North America)	Jul–Aug 1988	...	680	330	220	470	810	*Talbot et al.* [1992]
TRACE-P (4 km, NW Pacific)	Feb–Apr 2001	...	2200	800	550	...	...	*Dibb et al.* [2003]
TRACE-P (2–7 km, NW Pacific)[a]	Feb–Apr 2001	110	...	...	...	...	...	*Russo et al.* [2003]

[a]Median value.

between the two sites. Nitric acid generally dominates particulate nitrate at VO (Table 2) but as seen in Figure 1 the mass ratio of particulate nitrate to the sum of particulate nitrate and nitric acid is strongly variable from day to day. Close to a few percent at the beginning of the period (1 September) it increased to 20–40% during the daytime of 3 September. At the lower-elevation site of SBO *Kasper and Puxbaum* [1998] found a mass ratio of particulate nitrate to the sum of particulate nitrate and nitric acid close to 50% in summer and 20% in winter. During flights conducted during the TRACE-P campaigns near Asia, *Dibb et al.* [2003] observed a decrease of the mass ratio of particulate nitrate to the sum of particulate nitrate and nitric acid from 50% in the boundary layer to 30% and 5% at 4 km and 10 km elevation, respectively. The enhanced contribution of particulate nitrate seen at Vallot during the second part of the campaign which accompanied the increase of upward motion of air masses particularly on 3 September as mentioned in section 3 is consistent with a partitioning in favor of particulate nitrate at lower atmospheric levels.

[18] As for sulfur species, nitrogen species at VO are the same order of magnitude as those observed in the North American signal sampled during ABLE-3A (Table 2). Nitrogen species in the free troposphere over Europe (VO) and North America (ABLE-3A) are a factor two less abundant than over the NW Pacific. The difference between the NW Pacific and Europe is thus weaker for nitrogen species than for sulfur species. That is consistent with similar amounts of SO_2 and NO_2 emitted in western Europe in 2003 (2500 Gg of SO_2 and 3900 Gg of NO_2 [*Fagerli et al.*, 2007]) whereas emissions of SO_2 are almost twice than those of NO_2 in China (20,385 Gg of SO_2 and 11,347 Gg of NO_2 [*Streets et al.*, 2003]).

4.3. Particulate Carboxylates Versus Carboxylic Acids

[19] Between 1 and 3 September mean concentrations of total formic and acetic acids were close to 670 ng m^{-3} STP and 890 ng m^{-3} STP, respectively. The partitioning between gaseous and aerosol phases is strongly in favor of the gas phase (a factor of 60 for acetic and 115 for formic, Figure 1) which is expected given their high vapor pressure [*Talbot et al.*, 1988]. The mean levels of formic acid and acetic acid at VO are 635 ng m^{-3} and 825 ng m^{-3}, respectively. On a molar basis, formic and acetic acids are thus the most abundant acidic gases present in summer at 4300 m elevation over Europe ($\sim$14 nmol m^{-3} STP) followed by nitric acid (7 nmol m^{-3} STP), HCl (1.7 nmol m^{-3} STP) and SO_2 (0.8 nmol m^{-3} STP).

[20] For these two light carboxylic acids no data are available at SBO. Several studies of these species have been conducted in the boundary layer in Europe. For instance, *Puxbaum et al.* [1988] found 1800 ng m^{-3} of formic and 1050 ng m^{-3} of acetic acid in eastern Austria in July–August 1987. In western Germany *Hartmann et al.* [1989] found 1400 ng m^{-3} of formic and 2900 ng m^{-3} of acetic acid in September 1988. In the troposphere over Europe data are very rare, but during aircraft measurements made over Germany, *Reiner et al.* [1999] observed 430 ng m^{-3} STP of formic acid and 400 ng m^{-3} of acetic acid at 7 km. Since these measurements were achieved at the beginning of October 1991 we can expect higher values under full summer conditions. As reported in Table 2, the

levels of carboxylic acids at VO are similar to those observed during flights over North America. *Talbot et al.* [1992] and *Legrand et al.* [2003] concluded on the basis of the ABLE-3A campaign and from long-term Alpine ice core records, respectively, that formic and acetic acids present in the atmosphere are mainly of biogenic origin.

[21] With respect to formic acid levels observed in the European boundary layer ($\sim$1600 ng m^{-3}), those found at VO (635 ng m^{-3}) are relatively high. For instance the noble gas ^{222}Rn which has a lifetime of 5.5 days shows a typical decrease by a factor of 6.5 between the surface and 4.5 km at midlatitudes [*Liu et al.*, 1994]. Therefore, assuming a similar lifetime for ^{222}Rn and carboxylic acids [see, e.g., *Keene and Galloway*, 1988], we would expect 250 ng m^{-3} of formic acid at Vallot if only dilution with altitude is considered. The same conclusion holds true for acetic acid. Even if the highest value measured in the boundary layer (2900 ng m^{-3}) is considered, the observed level of acetic acid at VO (890 ng m^{-3}) is two times higher than expected (450 ng m^{-3}). Observations gained at VO therefore suggest the occurrence of secondary production of monocarboxylic acids within the troposphere, in addition to primary emissions from the boundary layer. Actually, there is theoretical as well as observational evidence for secondary photochemical sources for formic and acetic acids. Formic acid may be produced in the atmosphere by gas phase oxidation of reactive hydrocarbons [*Sanhueza et al.*, 1996] or aqueous phase HCHO oxidation [*Jacob*, 1986] whereas the reaction of peroxyacetyl radical with various peroxy radicals may be a source of acetic acid [*Madronich and Calvet*, 1990]. Recently more literature has become available on the formation of acetic acid that includes also the aqueous phase oxidation of methylglyoxal, an oxidation product of toluene and isoprene [*Lim et al.*, 2005; *Carlton et al.*, 2006]. However, the respective contributions to these different processes to the atmospheric budget of formic and acetic acids remain essentially unknown. Aircraft measurements from *Reiner et al.* [1999] showed decreasing values of formic acid between 7 and 10 km whereas those of acetic acid indicated a maximum at 9 km. *Reiner et al.* [1999] showed that it remains difficult to answer if either transport from the lower troposphere or acetone photolysis followed by reaction of CH_3COO_2 with HO_2 and CH_3O_2 controls the budget of acetic acid in these regions. During the nighttime of 1 September when subsidence of air mass took place at VO (section 2), we observe a very low level (3 ng m^{-3}) of ammonium, a species mainly related to surface emissions. Interestingly, at that time, whereas the formic acid level reaches the lowest concentration of the record (180 ng m^{-3}) the level of acetic acid remains relatively high (485 ng m^{-3}) (Figure 1). As a consequence, the acetic to formic acid mass ratio during the night 1 September is larger (2.7) than over the rest of the sampling campaign (1.2 ± 0.2). This observation supports the existence of an atmospheric source of acetic acid in atmospheric layers located above the VO site.

[22] The level of formic acid at VO is around 2.5 times lower than those observed in the European boundary layer. The decrease with height of this gaseous species is thus far weaker than that of aerosols. For instance the level of sulfate, close to 4000 ng m^{-3} STP in summer at surface sites in Europe [*Pio et al.*, 2007] is decreased to $\sim$400 ng m^{-3} STP at VO. Similarly the level of water soluble organic

aerosol (WSOC) is close to 2500 ng m^{-3} STP in summer at surface sites in Europe [*Pio et al.*, 2007] compared to ~150 ng m^{-3} STP at VO [*Legrand et al.*, 2007b]). This relatively high atmospheric abundance of formic acid at high elevation is also seen in precipitation. Indeed the dissolved organic carbon (DOC) present in precipitation, which is related to WSOC aerosol as well as organic gases which have been dissolved in the precipitation, is made up by a relatively large contribution of formic acid (12 ± 8%) [*Legrand et al.*, 2007a] compared to what is generally seen in precipitation at lower-elevation sites. For example, formic acid accounts for 2% of DOC in cloud water samples collected at Puy de Dome (1465 m elevation, center of France) [*Marinoni et al.*, 2004] and at Mount Rax (70 km southwest of Vienna, Austria) [*Löflund et al.*, 2002].

[23] As discussed by *Legrand et al.* [2007b], dicarboxylates such as oxalate aerosol also contribute much more to the DOC level of snow deposits at the Col du Dôme site than in precipitation occurring at lower elevations. A relative enrichment of the atmospheric concentrations of diacids with elevation is consistently observed by *Legrand et al.* [2007a]. On the basis of model simulations *Ervens et al.* [2004] suggested that oxidation of glutaric acid (C$_5$: HOOC(CH$_2$)$_3$-COOH) and glyoxylic acid (CHOCOOH) in the cloud aqueous phase represents an important atmospheric source of oxalic acid. As seen in Figure 1, the oxalate aerosol concentration stood out on 2 September (64 ng m^{-3} compared to 15 ng m^{-3} over previous and following periods), when the sampling was done just above the top of convective clouds (see section 2). This observation clearly supports the importance of aqueous phase cloud reactions for secondary production of oxalic acid. Such an observational proof for aqueous phase mechanisms was also recently provided by measurements made on aircraft by *Sorooshian et al.* [2006].

5. Conclusions

[24] This unique study of atmospheric levels of acidic gases (HCOOH, CH$_3$COOH, HNO$_3$, HCl, and SO$_2$) and related aerosol species conducted in summer at 4360 m elevation in the French Alps has shown that on a molar basis, formic and acetic acids represent there the most abundant acidic gases (~14 nmol m^{-3} STP) followed by nitric acid (7 nmol m^{-3} STP), HCl (1.7 nmol m^{-3} STP) and SO$_2$ (0.8 nmol m^{-3} STP). This abundance of monocarboxylic acids in the atmosphere above 4000 m elevation with respect to the boundary layer is likely related to the occurrence of secondary production of these species within the troposphere. It partly accounts for their higher contribution to the amount of dissolved organic carbon in snow deposits there compared to what is generally seen in precipitation at lower-elevation sites. These data gained in the free troposphere over Europe in summer are quite similar to values seen in the free troposphere in summer over North America. Concentrations of sulfur and nitrogen species in the free troposphere are lower over Europe (and North America) than over the Pacific region located near China (a factor 5 and 2, respectively).

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