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Michel Legrand, S. Preunkert, Corinne Galy-Lacaux, C. Liousse, D. Wagenbach. Atmospheric year-round records of dicarboxylic acids and sulfate at three French sites located between 630 and 4360 m elevation. *Journal of Geophysical Research: Atmospheres*, 2005, 110 (D13302), 1 à 11 p. 10.1029/2004JD005515 . insu-00374631

**HAL Id: insu-00374631**

**<https://insu.hal.science/insu-00374631>**

Submitted on 19 Feb 2021

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## Atmospheric year-round records of dicarboxylic acids and sulfate at three French sites located between 630 and 4360 m elevation

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Received 14 October 2004; revised 4 February 2005; accepted 18 March 2005; published 12 July 2005.

[1] An atmospheric year-round study of C2–C5 dicarboxylic acids (oxalic, malonic, succinic, malic, and glutaric) and sulfate was conducted in 2002 and 2003 at three remote western Europe continental sites located at different elevations (from 630 to 4360 m asl). Whatever the site and the season, oxalic acid is always the dominant diacid (average 64% of total dicarboxylic acids) followed by malonic acid (15% of total dicarboxylic acids). High correlation coefficients are observed between C3 (malonic), C4 (malic and succinic), and C5 (glutaric) acids and oxalic acid. These strong relationships between C2–C5 diacids support the hypothesis of a common production of these diacids through the aqueous phase chemistry of glutaric acid. Data gained at different elevations are here useful to compare the mass formation rates of sulfate and dicarboxylic acids. It is shown that in summer the decrease of the sum of dicarboxylic acids with height is far less pronounced than the decrease of sulfate (a factor of 2 instead of 6.8 from 630 to 4360 m asl). That demonstrates that the production of dicarboxylic acids occurs at up to 4300 m elevation while the production of sulfate from SO<sub>2</sub> mainly takes place between the boundary layer and 3000 m elevation. With respect to summer 2002 the sum of dicarboxylic acids was enhanced in summer 2003 (from 136 to 331 ng m<sup>-3</sup> STP at 2870 m asl, for instance) whereas a weaker increase is observed for sulfate (from 1700 to 2500 ng m<sup>-3</sup> STP at 2870 m asl). These changes are attributed to the particular summer 2003 conditions which led to enhanced level of oxidants (strengthened secondary productions) and warmer temperatures (enhanced emissions of biogenic precursors of diacids).

**Citation:** Legrand, M., S. Preunkert, C. Galy-Lacaux, C. Lioussé, and D. Wagenbach (2005), Atmospheric year-round records of dicarboxylic acids and sulfate at three French sites located between 630 and 4360 m elevation, *J. Geophys. Res.*, *110*, D13302, doi:10.1029/2004JD005515.

### 1. Introduction

[2] Numerous uncertainties still exist in estimating the direct and indirect impact of aerosols on climate, which is thought to be particularly large in industrialized regions. For the inorganic aerosol fraction as sulfate the production mechanisms as well as the thermodynamic and optical aerosol properties are relatively well known. For sulfate, numerous ground-based observations are available helping to reduce remaining uncertainties on chemical schemes and SO<sub>2</sub> emission inventories. Since the vertical distribution of sulfate in the atmosphere is important in modeling the radiative effect [Boucher *et al.*, 1998], atmospheric sulfate

data gained at high-elevated continental sites are also needed. In Europe, where the direct radiative effect of anthropogenic sulfate is believed to be most significant (together with eastern United States and Asia) [Charlson *et al.*, 1991], some multiyear sulfate data are available at elevations of up to 3000–3500 m asl (Mount Sonnblick at 3106 m asl, for instance [Kasper and Puxbaum, 1998]). However, year-round sulfate data gained at Vallot (4360 m asl, French Alps) indicate that Vallot is the only European sampling site located in summer above the mixed layer [Preunkert *et al.*, 2001].

[3] It is now well established that numerous organic compounds significantly contribute to the aerosol load of the atmosphere and thus to the radiative forcing of climate. In contrast to sulfate, more uncertainties exist about organics and in particular for secondary organic aerosol

species which are more oxygenated and hygroscopic than primary species [Saxena and Hildemann, 1996]. It has also been suggested that dicarboxylic acids significantly contribute to the organic aerosol mass [Satsumbayashi *et al.*, 1989].

[4] Oxalic acid (HOOC<sup>-</sup>COOH) is found to be the most abundant dicarboxylic acid present in the atmosphere of various regions followed by succinic (HOOCCH<sub>2</sub>CH<sub>2</sub>COOH) and/or malonic (HOOCCH<sub>2</sub>COOH) acid with concentrations of a few hundreds of ng m<sup>-3</sup> in urban regions [Kawamura and Ikushima, 1993; Sempere and Kawamura, 1994] to a few tens of ng m<sup>-3</sup> in the remote marine boundary layer [Baboukas *et al.*, 2000]. Although available atmospheric data are very sparse, they tend to show that oxalic acid levels at rural sites are not considerably different from those at urban sites [Limbeck and Puxbaum, 1999; Röhrl and Lammer, 2001]. Sources of dicarboxylic acids in the atmosphere remain unclear. Direct emissions from motor exhausts and soils have been identified as sources of oxalic acid [Kawamura and Kaplan, 1987; Grosjean, 1989]. Several field studies suggest that secondary productions of dicarboxylic acids are more important than direct emissions [Kawamura and Ikushima, 1993]. Whereas glutaric (HOOCCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOH) and succinic acids have been identified in laboratory studies as particulate products of the gas phase ozone-cyclohexene reactions [Hatakeyama *et al.*, 1985], no gas phase reactions are known to produce oxalic acid. Lee *et al.* [2003] found that individual aerosol particles containing high amounts of dicarboxylic acids also contain hydroxymethanesulfonate, a species exclusively formed in the aqueous phase from sulfur (IV) and HCHO. That suggests that in-cloud chemistry may be of importance, and Warneck [2003] proposed several pathways to the formation of oxalic acid in marine clouds. Other in-cloud processes were proposed by Ervens *et al.* [2003] that may act over continents.

[5] In this work we report on a year-round study of the chemistry of aerosols collected at three sites located in France between 630 and 4360 m asl. Analyses were focused on sulfate and C2–C5 dicarboxylic acids. The study covers 2 years, including the summer 2003, which was marked by extraordinary warm conditions in western Europe. We discuss seasonal variations of sulfate and dicarboxylic acids as observed at surface level as well as at the top of the mixed layer. The comparison of summer 2002 and 2003 is also used to reveal the role of secondary production for dicarboxylic acids.

## 2. Sampling and Methods

[6] Atmospheric samplings were conducted at three different sites located in France. Two sites, Lannemezan (LA, 630 m asl) and Pic du Midi (PdM, 2870 m asl), are located in the eastern Pyrénées. PdM is an atmospheric observatory whose access is restricted to research activities. LA is an annex of the laboratory of aerology located at a rural site on a large (~1500 km<sup>2</sup>) flat plateau along the pre-Pyrénées. The nearest large city (Toulouse, 146 m asl) is located 150 km away from LA. The third site (Vallot Observatory, VO, French Alps, 4360 m asl) is situated in the summit range of the Mont Blanc massif, roughly 500 km northeast to the Pyrenean sites.

[7] With the aim to gain reliable year-round data on the chemical aerosol composition above 4000 m elevation an automatic aerosol sampler was developed by Preunkert and Wagenbach [1998]. Filters were collected using the solar panel-powered device deployed at VO since September 1999. Prior to the beginning of 2003, sampling concentrated on summertime, and only a limited number of filters was obtained in winter because of a lack of energy during that season. The addition of new solar panels in March 2003 permitted for the first time the maintenance of a regular sampling during the winter 2003–2004. Air is sucked through a high-purity quartz fiber filter (Whatman, QM-A) placed in front of a nylon membrane filter (Gelman, Nylasorb). The typical flow rate of the device is 3 L STP per minute. In general, aerosol samples cover 7–10 days in summer and 20 days in winter. As shown by Preunkert *et al.* [2002], these conditions permit investigations of sulfate as well as oxalic acid. Investigations were here extended to other diacids. At PdM and LA where the energy supply is not limited, regular weekly aerosol samples were obtained at a flow rate of 14 L STP per minute using Gelman Zefluor (47 mm diameter, 0.5 μm pore size) Teflon filters.

[8] Oxalate (<sup>-</sup>OOC<sup>-</sup>COO<sup>-</sup>), malate (<sup>-</sup>OOCCH<sub>2</sub>CHOHCOO<sup>-</sup>), malonate (<sup>-</sup>OOCCH<sub>2</sub>COO<sup>-</sup>), succinate (<sup>-</sup>OOCCH<sub>2</sub>CH<sub>2</sub>COO<sup>-</sup>), glutarate (<sup>-</sup>OOCCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COO<sup>-</sup>), and tartarate (<sup>-</sup>OOCCHOHCHOHCOO<sup>-</sup>) were quantified with a Dionex 500 chromatograph equipped with an AS11 separator column and a gradient pump system permitting the use of a quaternary gradient of eluents (H<sub>2</sub>O, NaOH at 2.5 and 100 mM, and CH<sub>3</sub>OH) as detailed by Ricard *et al.* [2002]. Using a quarter of the filters collected at LA and PdM, the detection limits for major ions like sulfate are close to 1 ng m<sup>-3</sup> and are mainly related to the variability of filter blanks. The detection limit is 0.15 ng m<sup>-3</sup> for succinic acid and 0.5 ng m<sup>-3</sup> for oxalic acid because of the filter blank variability. The detection limit of other dicarboxylic acids is related to the accuracy of the ion chromatography (0.05 ng m<sup>-3</sup> for glutaric, malic, and tartaric and 0.5 ng m<sup>-3</sup> for malonic). These detection limits are close to winter levels of succinic and malonic acids at PdM. Using the whole filter collected at the VO, the detection limits are 2 ng m<sup>-3</sup> for sulfate, 0.5 ng m<sup>-3</sup> for oxalic and malonic acids, and 0.1 ng m<sup>-3</sup> for other dicarboxylic acids. Only the malonic acid levels in winter were so low there that they could not be always detected.

## 3. Data Presentation and Comparison With Previous Studies

[9] The summer 2003 was particular as a result of unusual hot and dry weather conditions that took place in western Europe. Therefore we compare in Table 1 dicarboxylic acids data gained at LA in summer 2002 only with those from previous studies carried out in summer at various low elevation sites. Summer 2002 data from high-elevated sites like PdM and VO were compared with those available at two high Alpine sites (Jungfraujoch and Mount Sonnblick).

[10] At LA, sulfate typically ranges from 1000 ng m<sup>-3</sup> in winter to 3300 ng m<sup>-3</sup> in summer which is similar to the 2000 and 2500 ng m<sup>-3</sup> in winter and summer,

**Table 1.** Concentrations of Dicarboxylic Acids as Measured in Winter and Summer at Surface Sites and in Summer at High-Elevated Sites<sup>a</sup>

Site	Sampling Time	Oxalic	Malonic	Succinic	Malic	Glutaric	Reference
<i>Surface Sites in Winter</i>							
Merseburg	Nov.–Dec. 1999 (22 samples)	57 (75%)	4.8 (6%)	4.2 (6%)	ND	<9.6 (<13%)	Röhl and Lammel [2001]
Tokyo	24–26 Feb. 1992	585 (64%)	117 (13%)	141 (15%)	32 (3%)	43 (5%)	Sempere and Kawamura [1994]
Los Angeles	20–30 Oct. 1984	485 (64%)	65 (8%)	157 (21%)	ND	51 (7%)	Kawamura and Kaplan [1987]
LA	Dec.–Jan.–Feb. 2002	46 (70%)	6.8 (10%)	6.3 (10%)	3.3 (5%)	3.6 (5%)	this work
<i>Surface Sites in Summer</i>							
Leipzig	July–Aug. 1998 (24 samples)	229 (64%)	66 (18%)	35 (10%)	ND	30 (8%)	Röhl and Lammel [2001]
K-pusztá	28 July to 12 Aug. 1998	269	22	5	ND	ND	Krivacsy et al. [2001]
Tokyo	22–23 July 1992	1516 (65%)	387 (17%)	265 (11%)	68 (3%)	85 (4%)	Sempere and Kawamura [1994]
Los Angeles	12–13 June 1984	382 (55%)	103 (15%)	154 (22%)	ND	54 (8%)	Kawamura and Kaplan [1987]
Vienna	June 1997 (three filters over 30 hours)	340 (48%)	244 (33%)	117 (16%)	ND	26 (3%)	Limbeck and Puxbaum [1999]
LA	June–July–Aug. 2002	95 (49%)	48 (24%)	20.4 (10%)	18.7 (10%)	12.9 (7%)	this work
<i>Mountain Sites (Summer)</i>							
Sonnblick	May 1997 (three filters over 30 hours)	153	22	14	ND	2.7	Limbeck and Puxbaum [1999]
Jungfraujoch	8 July to 5 Aug. 1998	49	15	11	ND	ND	Krivacsy et al. [2001]
PdM	June–July–Aug. 2002	80 (59%)	19.3 (14%)	12.2 (9%)	13.3 (10%)	10.6 (8%)	this work
VO	June–July–Aug. 2002	55 (57%)	20 (20%)	9.8 (10%)	7.1 (7%)	6.2 (6%)	this work

<sup>a</sup>Concentrations are in ng m<sup>-3</sup> STP. Numbers in parentheses refer to the contribution in mass of individual species to the sum of dicarboxylic acids. ND means not determined.

respectively, observed by Hjellbrekke [2003] at Payerne (Swiss plateau, 500 m asl). A quasi-absence of seasonal sulfate variations at surface levels has been reported over a large part of western Europe (see the compilation of data from European Monitoring and Evaluation Program (EMEP) of Kasibhatla et al. [1997]). This effect was interpreted as due to a doubling of SO<sub>2</sub> from summer to winter counteracted by less efficient conversion of SO<sub>2</sub> into sulfate due to lower H<sub>2</sub>O<sub>2</sub> levels in winter than in summer [Schaug et al., 1991]. At the low-elevation LA site, there is thus a striking enhancement of the mean summer sulfate over the respective winter level by typically a factor of 3. This observation argues not only for the expected higher SO<sub>2</sub> conversion rate during summer but also for a winter boundary layer at LA experiencing relatively weak SO<sub>2</sub> emissions and/or no extensive periods with strongly reduced vertical mixing like stable surface temperature inversions. Indeed, compared to similar rural sites located farther north (like Payerne), significantly lower winter sulfate values are seen at the LA site. Krivacsy et al. [2001] reported a mean sulfate value of 1080 ng m<sup>-3</sup> at the high Alpine Jungfraujoch Station in July 1998, which lies between the 1680 ng m<sup>-3</sup> at the PdM and the 480 ng m<sup>-3</sup> at VO.

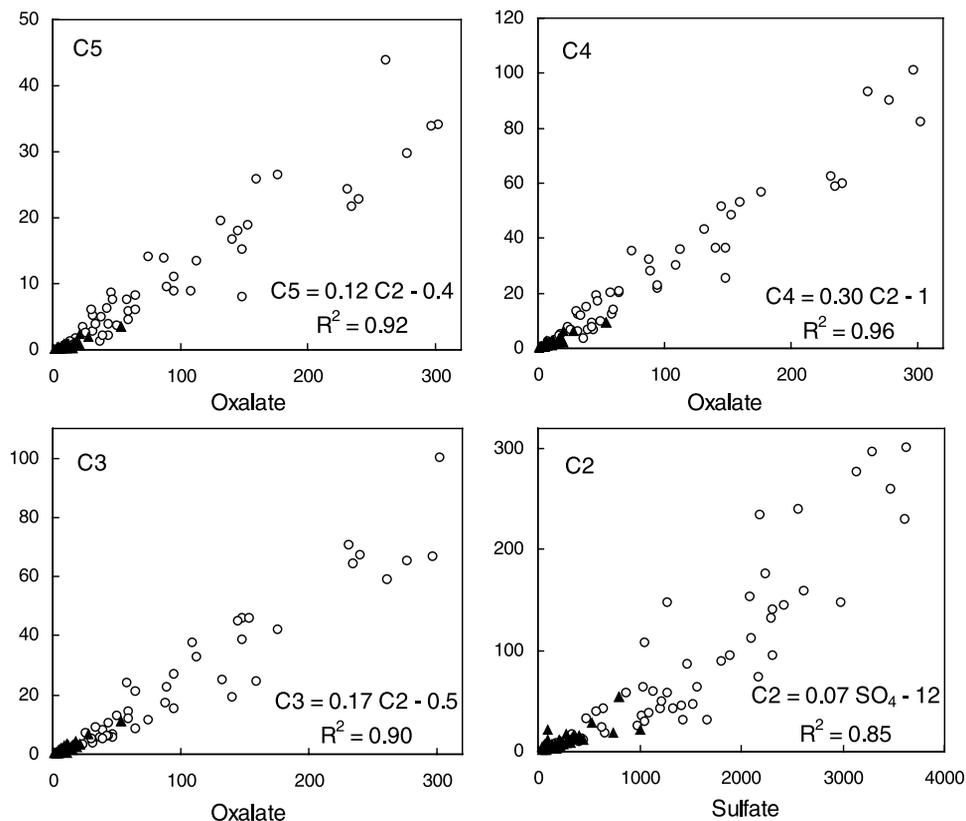
[11] Data on dicarboxylic acids present in the European atmospheric boundary layer are very rare. As shown in Table 1, winter levels of oxalic, malonic, and succinic acids at LA are very similar to those observed by Röhl and Lammel [2001] at a low-altitude rural site located in northern Germany but are 10 times lower than in large cities like Tokyo or Los Angeles (no data are available at European urban sites in winter). However, it is difficult to conclude that this difference reflects a large impact of vehicular emissions on the budget of dicarboxylic acids there since the Tokyo and Los Angeles data were documented only over a few days. Another study carried out over 1 year at Tokyo by Kawamura and Ikushima [1993] (not reported in Table 1) indicated mean annual values for oxalic (270 ng m<sup>-3</sup>), malonic (55 ng m<sup>-3</sup>),

succinic (37 ng m<sup>-3</sup>), and glutaric (11 ng m<sup>-3</sup>) acids. The twofold decrease of the total dicarboxylic acids from summer to winter reported by Kawamura and Ikushima [1993] would suggest typically 180 ng m<sup>-3</sup> oxalic acid in Tokyo during winter, which is roughly 4 times higher than the 50 ng m<sup>-3</sup> at rural European sites during that season.

[12] In summer, dicarboxylic acids at LA are 2 times less abundant than at the urban site of Leipzig. As for winter a comparison with studies carried out in other large cities like Los Angeles and Vienna is difficult given the very limited sampling time there. Considering only Leipzig data, we can conclude that the increase of dicarboxylic acids from rural to urban sites is close to a factor of 2 in summer.

[13] Dicarboxylic acids data outside this work only exist for summer at high-elevated sites. As seen in Table 1, those observed in July at the Jungfraujoch (3450 m asl) are clearly consistent with PdM and VO data.

[14] On the basis of the year-round data collected at LA, PdM, and VO we conclude that whatever the season, oxalic acid is always the major dicarboxylic acid. In summer the second more abundant diacid is malonic followed by malic, succinic, and glutaric (Table 2). Tartaric acid detected at the level of a few ng m<sup>-3</sup> represents a minor contribution to the sum of diacids, accounting for less than 2% only. In the following we therefore neglected tartaric acid when calculating the sum of dicarboxylic acids. In winter the contribution of malonic acid is lower than in summer, becoming closer to the contribution of succinic acid (Table 2). At all three sites, C3 (malonic), C4 (malic plus succinic), and C5 (glutaric) acids are well correlated with oxalic acid (see data from PdM and LA reported in Figures 1 and 2, respectively). These strong correlations are driven by the seasonal change of the vertical transport efficiency but may be enhanced additionally by the photochemical seasonality. Indeed, the correlations between C2 and C3–C5 are stronger than between C2 and sulfate (Figures 1 and 2), suggesting that



**Figure 1.** Linear regressions between C5 (glutaric), C4 (malic plus succinic), and C3 (malonic) versus C2 (oxalic) as well as oxalic acid versus sulfate at Pic du Midi. All concentrations are given in  $\text{ng m}^{-3}$  STP. Open circles refer to summer (April to September), and solid triangles refer to winter (October to March) samplings. Reported equations and correlation coefficients correspond to linear regressions obtained when all samples (winter and summer) are considered.

dicarboxylic acids are related to a common source and/or atmospheric formation process.

#### 4. Seasonal Variations Versus Elevation

[15] At LA, sulfate is 3.4 times higher in summer than in winter. As already mentioned, the more efficient photochemistry during summer contributes to the sulfate increase since more  $\text{SO}_2$  is converted into sulfate in summer than in winter. For instance, *Gregori* [1992] reported for 600 m elevation in the Alps that only a quarter of total sulfur is in the form of sulfate in winter whereas in summer, sulfate represents a half of total sulfur. As shown in Table 2, the total mass of dicarboxylic acids at LA increases from  $66 \text{ ng m}^{-3}$  in winter to  $195 \text{ ng m}^{-3}$  in summer, which is similar to seasonal contrast of sulfate. This suggests secondary photochemical productions to be important for dicarboxylic acids as well.

[16] The summer to winter sulfate ratio is higher at 2870 m asl (12.5) and 4360 m asl (4.4) than at 630 m asl (3.4). The lower ratio at VO than at PdM is due to the strong decrease of summer levels between these mountain sites (Table 2). At high-elevated sites the summer to winter ratio of total dicarboxylic acids is always higher than for sulfate (15 versus 12.5 at PdM and 12.3 versus 4.4 at VO).

[17] Summer and winter changes of sulfate and diacid levels versus height with respect to LA are summarized in

Figure 3. In winter, sulfate decreases strongly above 630 m elevation (by a factor of 7.2 at 2870 m asl and by 8.7 at 4360 m asl). The PdM and VO sites are clearly located in the free troposphere in winter. In summer the decrease of sulfate above 630 m asl remains close to a factor of 2 at 2870 m elevation but reaches a factor of 6.8 at 4360 m asl (Figure 3). The stronger decrease of sulfate with height in winter than in summer is due to a more efficient upward transport of air masses from the boundary layer in summer than in winter. In addition, the more complete conversion of  $\text{SO}_2$  into sulfate in summer than in winter likely contributes to the weaker decrease of sulfate in summer between 630 and 2870 m elevation. Indeed, at 1500 m elevation, for instance,  $\text{SO}_2$  still accounts for a quarter of total sulfur in summer [*Gregori*, 1992]. The more pronounced decrease of summer sulfate above 3000 m elevation may indicate that most of the  $\text{SO}_2$  has already been converted here into sulfate. For instance, at Mount Sonnblick (3106 m asl), summer  $\text{SO}_2$  levels are 10 times lower than sulfate levels [*Kasper and Puxbaum*, 1998].

[18] In winter the sum of dicarboxylic acids decreases above 630 m asl similarly to sulfate (Figure 3). A very different situation takes place in summer with a weak decrease of the sum of dicarboxylic acids (a factor of 1.4) and sulfate (a factor of 2) between LA and PdM. Even above 3000 m elevation, total diacids decrease more slowly than sulfate (a factor of 1.4 versus 3.5). This suggests that

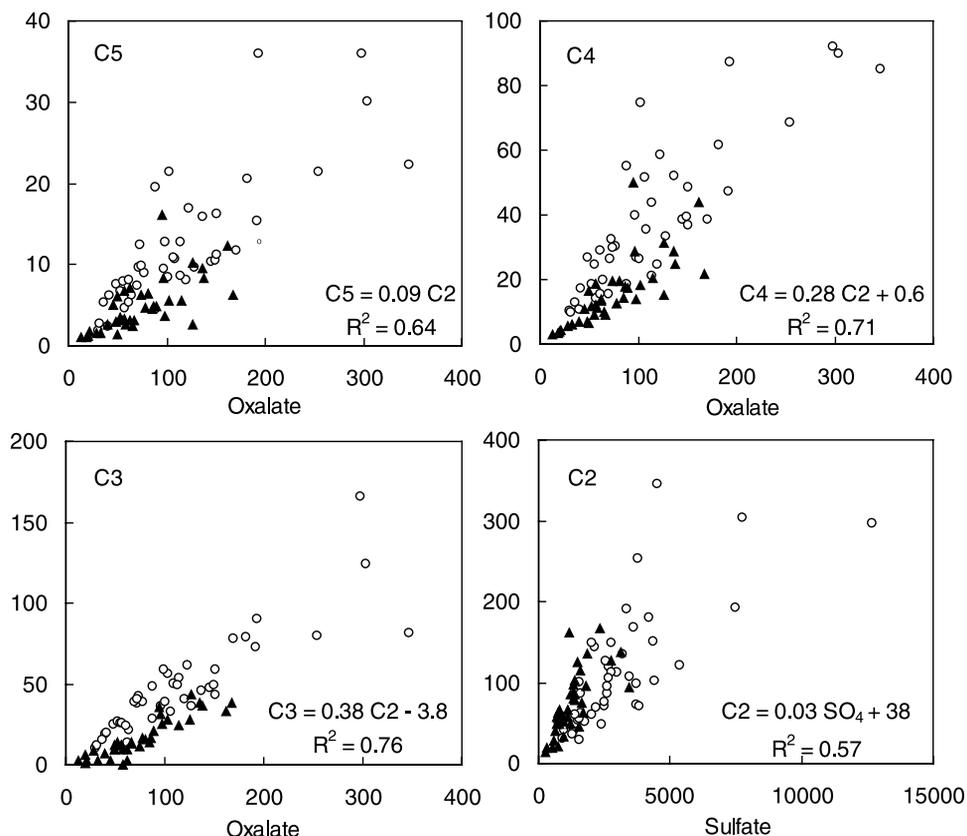


Figure 2. Same as Figure 1 but for Lannemezan (LA).

the secondary production of dicarboxylic acids continues to proceed in summer far above 3000 m elevation. As a result, the ratio of sulfate to total dicarboxylic acids (see  $r$  values in Table 2) decreases from 15 at low elevation sites to 5 at 4360 m asl.

## 5. Hot Summer 2003

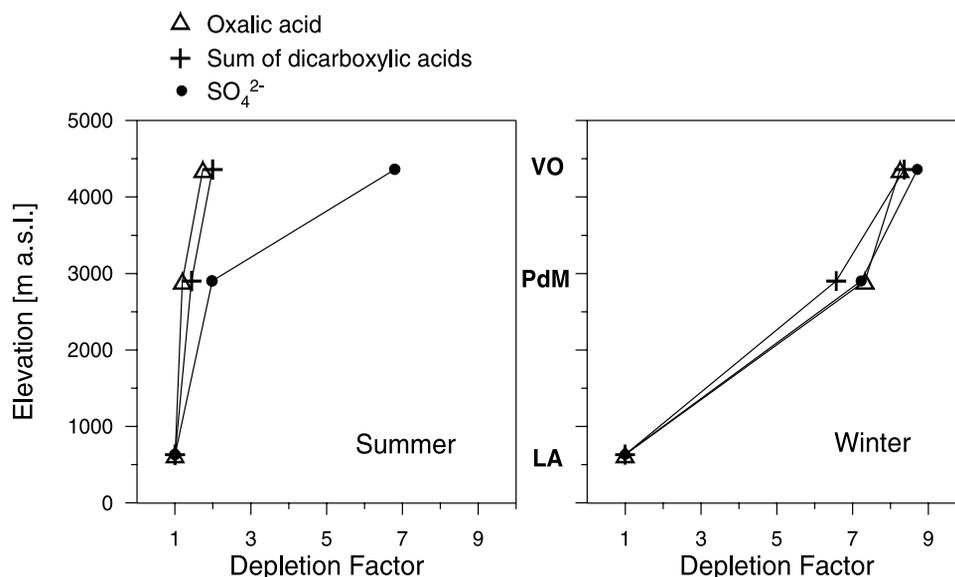
[19] At LA the mean levels of sulfate and total diacids over June–July–August (not shown) were enhanced by a factor of 1.2 and 1.5, respectively, in 2003 with respect to 2002. The chemical composition of aerosols sampled in 2002 and 2003 at the high-elevated sites of PdM and VO is shown in Figures 4 and 5, respectively. At PdM the sulfate level was enhanced by a factor of 1.5 in June–July–August 2003 compared to the situation in 2002. The increase from 2002 to 2003 is higher for the sum of dicarboxylic acids than for sulfate (a factor of 2.5 versus 1.5). The particular-

ities of summer 2003 are clearly seen by checking air temperatures and ozone mixing ratios measured at the site. For the 3 summer months the air temperature was 6.2°C in 2002 compared to 9.4°C in 2003 (Figure 4). This difference reflects the extraordinary warm conditions (the warmest since more than 100 years) that took place over western Europe in summer in 2003. Because of two breakdowns of the ozone monitor during thunderstorms at PdM the  $O_3$  mixing ratios were missed during the first 2 weeks in July and the second week in August 2002. In 2003, no data are available between 10 June and 8 July. Nevertheless, the mean summer ozone mixing ratio is found to be higher at PdM in 2003 (61 ppbv) than in 2002 (55 ppbv). This increase of ozone mixing ratios at 2870 m asl is related to the repetitive episodes of photochemical pollution that took place in the boundary layer of western Europe in 2003, possibly strengthened by a more efficient upward transport of air masses. As seen in Figure 6, summer levels of sulfate

Table 2. Mean Winter (December, January, and February) and Summer (June, July, and August 2002) Levels of Total Dicarboxylic Acids and Sulfate and of the Ratio (Denoted  $r$ ) of Sulfate to Total Dicarboxylic Acids<sup>a</sup>

Sites	SO <sub>4</sub>	Glutaric	Succinic	Malic	Malonic	Oxalic	Total Dicarboxylic Acids	$r$
LA (summer)	3326	12.9 (7%)	20.4 (10%)	18.7 (10%)	48 (24%)	95.3 (49%)	195	17
LA (winter 2002–2003)	976	3.6 (5%)	6.3 (10%)	3.3 (5%)	6.8 (10%)	46 (70%)	66	15
PdM (summer)	1682	10.6 (8%)	12.2 (9%)	13.3 (10%)	19.3 (14%)	80 (59%)	136	12
PdM (winter 2002–2003)	135	0.3 (3%)	<0.3 (3%)	0.5 (5%)	<1.1 (11%)	7 (78%)	9	15
VO (summer)	489	6.2 (6%)	9.8 (10%)	7.1 (7%)	20 (20%)	55 (57%)	98	5
VO (winter 2003–2004)	112	0.6 (8%)	0.5 (6%)	0.3 (4%)	<1.0 (13%)	5.5 (69%)	8	14

<sup>a</sup>Levels are in ng m<sup>-3</sup> STP. Numbers in parentheses refer to the contribution in mass of individual species to the sum of dicarboxylic acids.



**Figure 3.** Depletion factors with respect to the low-level site LA of sulfate, oxalic acid, and the sum of dicarboxylic acid levels at Pic du Midi (PdM) and Vallot Observatory (VO). Data points refer to (left) June–July–August means for summer and (right) December–January–February means for winter.

are significantly correlated with ozone mixing ratio ( $[\text{SO}_4] = 73 [\text{O}_3] - 1915$  with  $R^2 = 0.45$ ). Such a significant correlation between sulfate and ozone may reflect the fact that high temperatures have favored a more efficient vertical mixing of air masses in combination with a strengthened conversion of  $\text{SO}_2$ . Applying the  $\text{O}_3$ -sulfate relationship to the  $770 \text{ ng m}^{-3}$  increase of sulfate observed between summer 2002 and summer 2003, we calculate a respective increase of the  $\text{O}_3$  mixing ratio of 10.6 ppbv. This figure remains consistent with the observed ozone increase (6 ppbv), though  $\sim 30\%$  of the ozone data have been missed.

[20] As for sulfate, the sum of dicarboxylic acids is well correlated with the ozone mixing ratio in summer ( $[\text{total dicarboxylic acids}] = 14 [\text{O}_3] - 550$  with  $R^2 = 0.66$ ). Nevertheless, on the basis of this relationship an increase of  $\text{O}_3$  by 10.6 ppbv between 2002 and 2003 can only explain an increase by a factor of 2 of the sum of dicarboxylic acids between the two summers, suggesting additional parameter contributing to the increase of dicarboxylic acids between 2002 and 2003. As seen in Figure 6, whereas summer sulfate levels are almost not correlated with air temperature ( $R^2 = 0.2$ ), the sum of dicarboxylic acids in summer exhibits a significant correlation with air temperature ( $R^2 = 0.4$ ). The increase of air temperature from 2002 to 2003 ( $\sim 3^\circ\text{C}$ ) may have therefore contributed to the increase of the sum of dicarboxylic acids. In summary, the significant correlation of the sum of dicarboxylic acids with ozone and air temperature at PdM suggests that in addition to an enhanced upward transport their levels were higher in summer 2003 because of (1) an enhanced secondary production in response to an increase of oxidants induced by photochemical processes and (2) enhanced emission of their precursors in response to hot temperatures in the boundary layer.

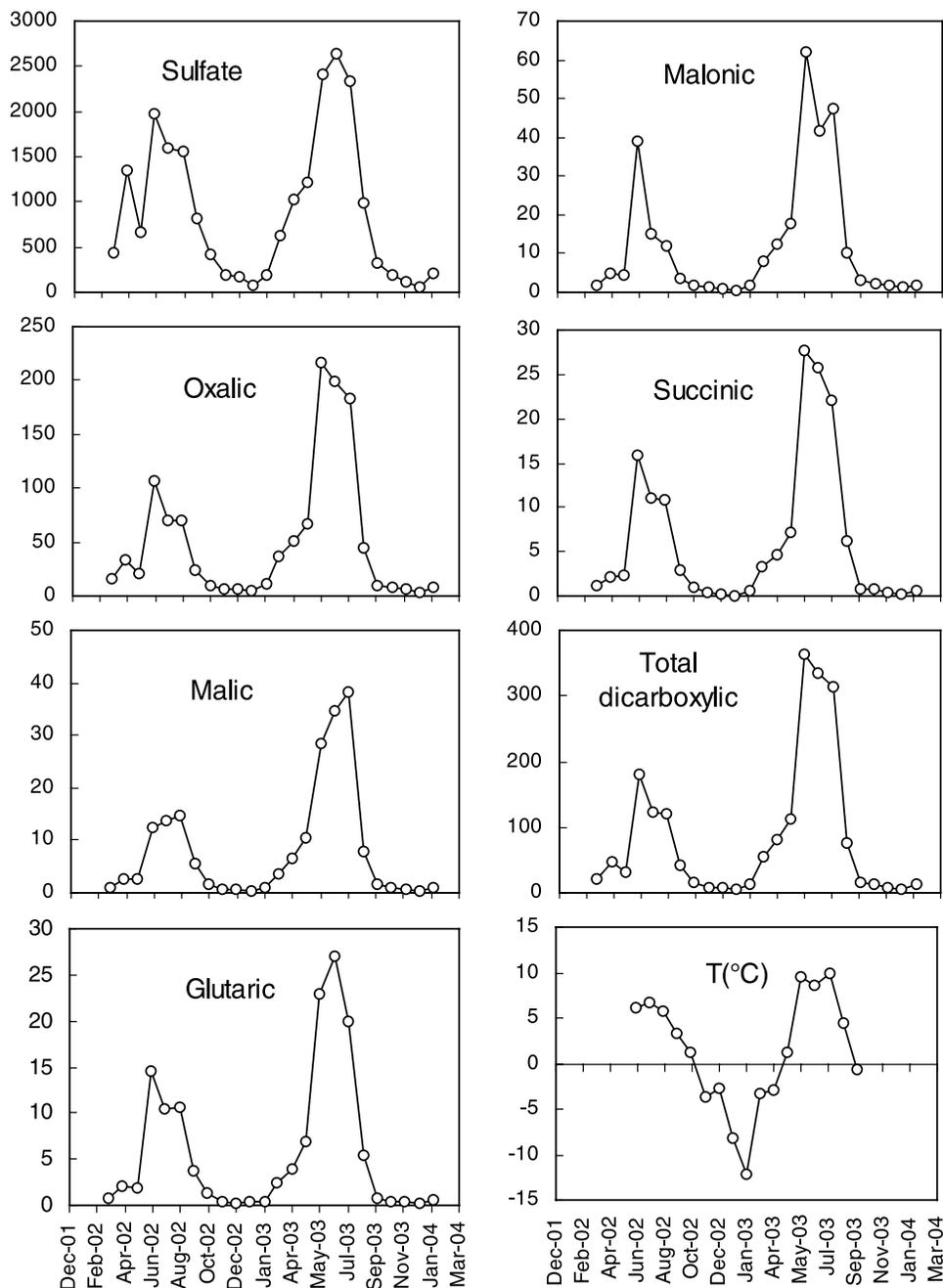
[21] As seen in Figure 5, the changes of sulfate and dicarboxylic acids from summer 2002 to summer 2003 at VO differ from those seen at PdM. The main change is here

a large distinct increase (by a factor of 4.2 for sulfate and 4.8 for the sum of dicarboxylic acids) during the first half of August with respect to the adjacent remaining summer 2003 levels. Apart from this period, sulfate and total diacids were enhanced in summer 2003 by a factor of 1.25 with respect to 2002. During the first half of August 2003, sulfate at VO reached  $2570 \text{ ng m}^{-3}$ , becoming close to levels observed in summer at PdM. Very likely, at that time the thickness of warm air mass was at its maximum as suggested by the record of temperature at VO (Figure 5). During that time the sum of dicarboxylic acids reached  $590 \text{ ng m}^{-3}$  at VO, which is twice as high as at PdM in summer and which indicates again that secondary production of dicarboxylic acids is still important at this elevation.

## 6. Discussions on the Origins of Dicarboxylates

[22] The preceding discussions have shown that dicarboxylic acids are very likely secondary products and that the processes involved in their productions are able to act up to 4300 m elevation. In addition, it is suggested that their gaseous precursors have sources which are strengthened by hot summer conditions.

[23] Two direct sources of dicarboxylic acids have been identified. First, soils containing microorganisms may produce dicarboxylates (mainly oxalate and phthalate) which can be thereafter emitted into the atmosphere. Other dicarboxylates like malonate and glutarate are 26 and 20 times less abundant than oxalate in soils. Kawamura and Kaplan [1987] found  $160 \text{ nmol g}^{-1}$  of oxalate in soils collected in downtown Los Angeles and  $4760 \text{ nmol g}^{-1}$  in bog sediments. On the basis of these values and assuming a typical mixing ratio of 13,700 ppm of calcium in soils [Vinogradov, 1959] we calculate an oxalate to calcium mass ratio ranging between 0.05 and 0.001. Given the mean calcium levels observed at LA in summer, for instance ( $225 \text{ ng m}^{-3}$  in 2002), we would expect soil-derived oxalate of less than



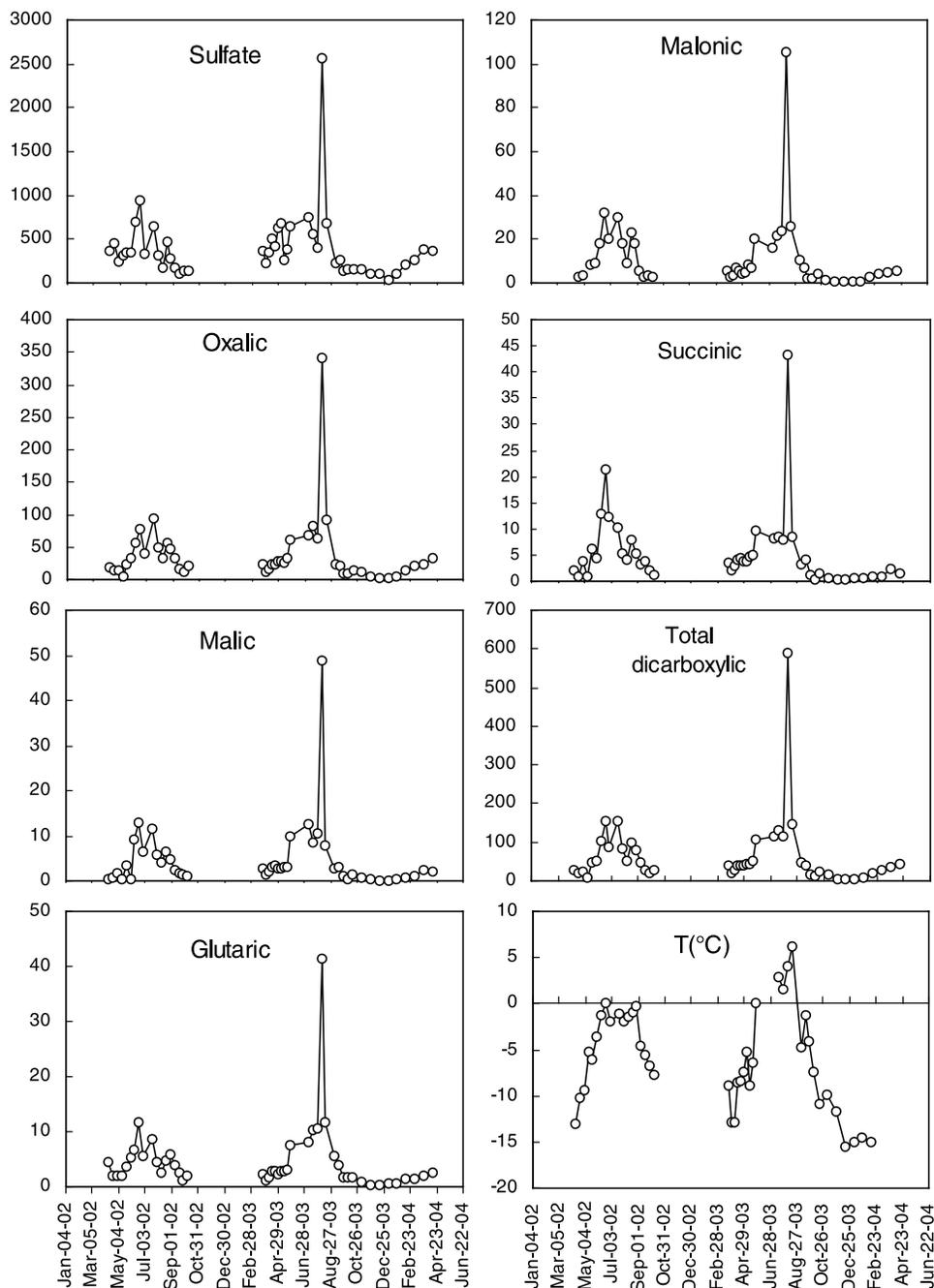
**Figure 4.** Monthly mean concentrations of sulfate and dicarboxylic acids (in  $\text{ng m}^{-3}$  STP) observed in 2002 and 2003 at PdM together with respective air temperature data.

$11 \text{ ng m}^{-3}$  which is 1 order of magnitude below the observed  $95 \text{ ng m}^{-3}$ . These considerations suggest that the contribution of soils to the atmospheric budget of oxalic acid is not important. This is also supported by the very different distribution of other dicarboxylic acids with a relative abundance of malonic acid in the atmosphere but not in soils.

[24] Biomass burning has been reported as a source of oxalic acid. Satellite imagery indicates that among western European countries, Portugal and France experienced in summer 2003 the worst forest fire season since 1980. For instance, in mid-September the total area burnt in Portugal

estimated from satellite imagery reached 380,000 ha (instead of 120,000 ha in 2002). In the beginning of September a forest area of 49,000 ha was burnt in France (instead of 20,000 ha in 2002). In Spain, 100,000 ha were burnt in both 2002 and 2003. However, forest fires very likely do not substantially contribute to the atmospheric budget of dicarboxylic acids since in 2003 they mainly occurred from mid-July to the end of September, whereas the level of dicarboxylic acids was already high in June (Figures 3 and 4).

[25] Among anthropogenic sources, direct emissions from car exhaust have been suggested as an important source of

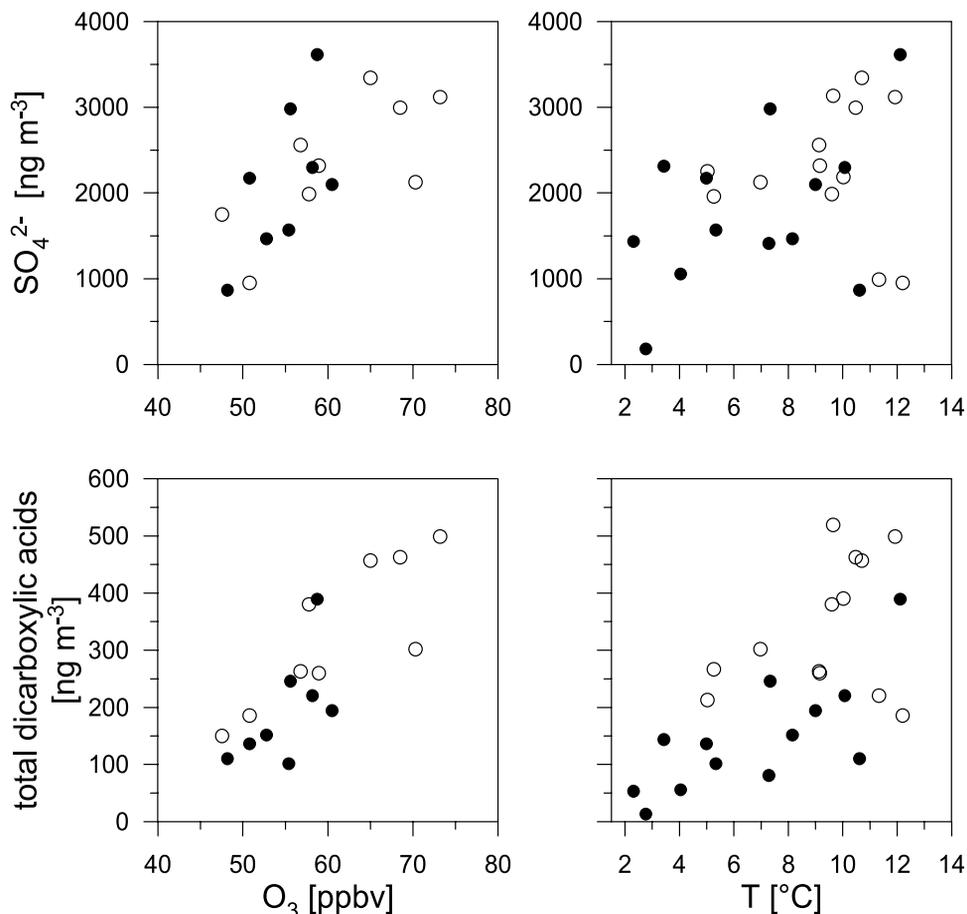


**Figure 5.** Atmospheric levels of sulfate and dicarboxylic acids at the high Alpine VO. Note that air temperatures are semiquantitative since they are measured inside the observatory (nonheated and nonhabitated).

oxalic acid. *Grosjean* [1989] indicated that 87 kg per day of oxalic acid are emitted by gasoline-powered vehicles in south California. *Kawamura and Kaplan* [1987] measured a 2.6 times higher emission of oxalic acid from diesel-powered vehicle emissions. Since daily emissions of ethene and propene by cars in France in 2000 (65 and 40 tons, respectively) are close to those for south California in 1989 (75 and 35 tons, respectively [*Grosjean*, 1992]), a crude estimate of direct emissions of oxalic acid by vehicles in France would suggest an upper limit of 0.3 tons per day. Assuming a mixed layer height of 3000 m in summer and

a typical characteristic time of 10 days, a concentration of  $1 \text{ ng m}^{-3}$  of oxalic acid only will be reached. Such an insignificant impact of anthropogenic combustion on the budget of oxalic acid in the low troposphere is also supported by the observed dominance of malonic over succinic acid in the atmosphere (Table 2), although succinic acid exceeds malonic acid by a factor of 2 to 3 in car exhausts [*Kawamura and Kaplan*, 1987].

[26] Whereas glutaric and adipic ( $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ ) acids have been identified in laboratory studies [*Hatakeyama et al.*, 1985] as



**Figure 6.** Interannual changes of sulfate and total dicarboxylic acids between summer 2002 (solid circles) and summer 2003 (open circles) at Pic du Midi versus ozone mixing ratios and air temperatures at the site. Individual data points refer to weekly samplings.

particulate products of the reaction of  $O_3$  with cyclohexene (a symmetrical alkene molecule similar to monoterpenes emitted by the biosphere), no gas phase reactions are known to produce oxalic acid. Warneck [2003] suggested that the aqueous phase of clouds may generate oxalic acid from glyoxal produced by oxidation of acetylene and from glycolaldehyde produced by oxidation of ethene. He estimates that these processes would lead to a concentration of oxalic acid ranging between 10 and  $70 \text{ ng m}^{-3}$ . Note that these processes are not producing other dicarboxylic acids. The recent study from Ervens *et al.* [2004], which deals with the formation of dicarboxylic acids in the continental atmosphere, also considers the production of glyoxal by toluene and the production of glycolaldehyde via isoprene oxidation as well as the aqueous phase reactions of adipic and glutaric acids produced by oxidation of cyclohexene. In this way, Ervens *et al.* [2004] estimated that the aqueous phase chemistry would lead to a total dicarboxylic acid level ranging in the continental atmosphere from  $150 \text{ ng m}^{-3}$  for clean to  $300 \text{ ng m}^{-3}$  for polluted conditions. These values are in the range of levels observed at the remote PdM and Vallot sites (Table 2). The predominance of oxalic over other dicarboxylic acids simulated by Ervens *et al.* [2004] is also consistent with observations. Aqueous phase reactions considered by Ervens *et al.* [2004] involve (1) the oxidation

of glyoxal and glycolaldehyde into oxalic acid and (2) a chain of reactions oxidizing C5 (glutaric) into C4 (succinic acid only), followed by the production of C3 and finally oxalic acid. As shown in section 3, at all three sites, strong correlations between C5, C4, and C3 and oxalic acid are observed. This finding supports the hypothesis of an aqueous phase oxidation of glutaric acid but does not exclude the importance of the other pathways which produce oxalic acid directly via glyoxylic acid ( $\text{HOOCCHO}$ ), as proposed by Ervens *et al.* [2004]. The relationships between C5, C4, and C3 versus C2 reported in Figures 1 and 2 indicates a weaker slope of the linear regressions in winter than in summer samples, particularly at LA (Figure 2). This difference and the weaker contribution of oxalic acid to the sum of diacid acids in summer with respect to winter at LA (Table 2) cannot be explained by the chain of reactions considered by Ervens *et al.* [2004]. A possible explanation may be related to a volatilization of oxalic acid at higher temperatures (particularly for LA in summer) as suggested by some previous studies [Limbeck *et al.*, 2001].

[27] Ervens *et al.* [2004] compared the dicarboxylic acid production with the production of sulfate for polluted and clean continental conditions. Whereas their simulated sulfate level resulting from aqueous  $\text{SO}_2$  oxidation was 2 orders of magnitude higher for polluted conditions com-

pared to clean air conditions, the sum of dicarboxylic acids was only reduced in clean air by a factor of 2. These simulations point out clearly the important role of biogenic isoprene and monoterpene emissions on the production of diacids. Since monoterpene and isoprene emissions are temperature-dependent [Kesselmeier and Staudt, 1999], this finding is consistent with the dicarboxylic acid increase observed between summer 2002 and summer 2003. Finally, Ervens *et al.* [2004] showed that compared to sulfate, aqueous phase production of dicarboxylic acids is less efficient, taking eight cloud cycles until a steady state is reached instead of three cycles in the case of sulfate. This figure would agree with our finding that secondary production of dicarboxylic acids continues to operate far above 3000 m elevation in contrast to sulfate, of which production mainly occurs below this elevation.

## 7. Summary and Conclusion

[28] The atmospheric year-round study of sulfate and dicarboxylic (oxalic, malic, malonic, glutaric, and succinic) acids was conducted in 2002 and 2003 at three remote western Europe continental sites located at different elevations (from 630 to 4300 m asl). Whatever the site and the season, oxalic acid is always the dominant diacid. It is shown that aqueous phase oxidation reactions are important for the atmospheric budget of diacids. As a consequence of the slower conversion of organic precursors into dicarboxylic acids with respect to the conversion of SO<sub>2</sub> into sulfate, the relative contribution of such water-soluble organic species with respect to sulfate is significantly enhanced above 3000 m elevation.

[29] The particular conditions that took place during summer 2003 have led to an increase of dicarboxylic acids by up to a factor of 2.5 with respect to summer 2002. It is shown that this increase was, in addition to transport changes, related to (1) enhanced level of atmospheric oxidants and (2) a larger emission of precursors among which monoterpenes and isoprene are good candidates. These findings cannot be ignored when examining the role of organic aerosols on the future climate at continental scale.

[30] Further works are needed to compare the rate of aqueous phase reactions of glutaric acid to those involving glyoxylic acid. That is mandatory to evaluate the respective contribution of natural (isoprene and monoterpenes) versus anthropogenic (toluene) gaseous precursors and will require measurements of intermediate products such as glyoxal and hydroxyacetaldehyde.

[31] **Acknowledgments.** This work has been supported by the European Environment and Climate program. Funding was provided by the European Community via contract ENV4-CT97 (ALPCLIM) and EVK2CT2001-00113 (CARBOSOL), the Centre National de la Recherche Scientifique (programme PNCA), and the Ministry for Science and Research of Baden-Württemberg within the collaboration program between Region Rhône-Alpes and Baden-Württemberg. We would like to thank the two anonymous reviewers for their very helpful comments on the manuscript.

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