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Online gas and aerosol measurement of water soluble carboxylic acids in Zurich

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[1] We discuss the diurnal and seasonal variability of low molecular weight organic acids in Zurich city on the basis of online quasi-continuous measurement in the gas and aerosol phase using a wet effluent diffusion denuder/aerosol collector (WEDD/AC) coupled to ion chromatography. The measurements were performed during August–September 2002 and March 2003. Acetic acid exhibited the highest concentration in the gas phase during all the measurement periods, followed by formic acid. Oxalic acid was predominantly found in the aerosol phase and often below the detection limit in the gas phase. In addition, filter samples were analyzed using ion chromatography–mass spectrometry (IC-MS) to provide more information on organic acids in the aerosol phase. From the offline IC-MS measurements, 20 monocarboxylic, dicarboxylic, and tricarboxylic acids were determined. In addition, more than 20 different masses were detected with the MS; however, identification of the organic acids was not possible. The sum of the carboxylic acids contributed on average 2% to the water soluble organic carbon (WSOC). The fraction of dicarboxylic acids to the WSOC was higher in summer compared to winter suggesting that dicarboxylic acids are mainly a result of photochemical reactions in summer whereas in winter they mainly result from primary sources.

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1. Introduction

[2] In the past much of the research concerning acid deposition focused on the strong inorganic acids such as sulfuric and nitric acid, and their precursors. However, organic acids which are far more numerous and diverse have scarcely been investigated. Recent evidence suggests that carboxylic acids are one of the dominant classes of organic compounds found in the atmosphere and ubiquitous in nature [*Narukawa et al.*, 2002; *Kerminen et al.*, 2000; *Kubatova et al.*, 2000; *Yao et al.*, 2004; *Baboukas et al.*, 2000]. Organic acids and in particular those having low carbon number and other functional groups such as hydroxyl and carbonyl are potentially hygroscopic [*Changgeng et al.*, 2001] and have been measured in the gas [*Sanhueza et al.*, 1996; *Meng et al.*, 1995] and aerosol phase [*Lee et al.*, 2003; *Mochida et al.*, 2003] as well as in wet precipitation in urban and rural areas [*Kawamura et al.*, 1996; *Fornaro and Gutz*, 2003]. The sources of these organic acids include direct emissions from anthropogenic and biogenic sources [*Kawamura and Kaplan*, 1987; *Graham et al.*, 2002; *Zervas et al.*, 2001; *Glasius et al.*, 2001; *Servant et al.*, 1991] and secondary production via the photo-oxidation of volatile organic compounds (VOCs) [*Madronich and Calvert*, 1990].

[3] Several gas and aerosol phase oxidation mechanisms are reported for the formation of organic acids. *Stephanou and Stratigakis* [1993] showed that C6 and C7 dicarboxylic acids were photo-oxidation products of anthropogenic cycloalkenes, while C12 to C26 dicarboxylic acids are produced by photo-oxidation of unsaturated fatty acids of biogenic origin. *Chebbi and Carlier* [1996] indicated liquid-phase oxidation of carbonyl compounds as a major source of some organic acids. *Fisseha et al.* [2004] also demonstrated the formation of a variety of organic acids from the photo-oxidation of trimethylbenzene in a smog chamber [*Kalberer et al.*, 2004].

[4] The most abundant forms of organic acids reported in the atmosphere are monocarboxylic and dicarboxylic acids. The partitioning of the organic acids to the gas and aerosol phase depends on the vapor pressure and relative humidity [*Khan et al.*, 1995]. Hence monocarboxylic acids, in particular formic and acetic acid, are predominantly present in the gas phase because of their high vapor pressure. The sources of these organic acids are however highly variable. For example, *Kawamura and Kaplan* [1987] demonstrated that formic and acetic acids could directly be emitted from

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car exhaust, and *Talbot et al.* [1988] reported direct emission of acetic and formic acid from biomass burning. Both authors point out a higher fraction of acetic acid compared to formic acid in the primary sources. On the other hand, formic acid is reported to be mainly produced via photochemical oxidation of volatile organic compounds (VOC) [*Sakugawa and Kaplan*, 1995].

[5] Several dicarboxylic acids were mainly found in the aerosol phase. Oxalic acid is the most abundant dicarboxylic acid reported in atmospheric aerosols followed by malonic and succinic acid [*Kawamura and Ikushima*, 1993; *Limbeck and Puxbaum*, 1999]. Atmospheric oxidation is reported as the major source of dicarboxylic acids [*Röhrl and Lammel*, 2001].

[6] Despite their importance in atmospheric chemistry, sampling of organic acids has been a challenge because of their semivolatile behavior. Filter sampling is the most widely used sampling method, however, it cannot provide high time resolution data and has a drawback due to the positive and negative artifacts associated with it. Other online methods such as gas chromatography (GC) or GC coupled to mass spectrometry (GC-MS) cannot be used for online measurement either because of the high polarity of organic acids. In addition measurements that provide both gas and aerosol data of the organic acids during the same period of time are very scarce.

[7] This paper therefore focuses on understanding diurnal and seasonal variations of low molecular weight organic acids in the gas and aerosol phase by using an online quasi continuous sampling and analysis of the organic acids. Low molecular weight organic acids in the gas and aerosol phase were collected in Zurich city during August–September 2002 and March 2003 using a wet effluent diffusion denuder aerosol collector (WEDD/AC) and measured online using ion chromatography (IC) coupled to the WEDD/AC. The full identification of the organic acids however was often hampered because of the resolution limitation of the IC. Hence additional filter samples were collected during the same period, and offline ion chromatography–mass spectrometry (IC-MS) measurements were performed to identify organic acids present in the aerosol which otherwise could not be identified with the online IC measurements.

2. Method

2.1. Sampling Site

[8] Sampling was made in Zurich city very close to the main train station. The site is an open space of ~1000 m^2 and is also used as air monitoring station by the Swiss national air pollution monitoring network (NABEL) and characterized as urban background site [*Putaud et al.*, 2004; *Hueglin et al.*, 2005]. The sampling for this study was performed in a measuring van, located close to the NABEL station. Both the measuring van and the NABEL station were operated by the Swiss Federal Laboratories for Materials Testing and Research (EMPA). Two sampling campaigns were made, the first one from 8 August to 30 September 2002 and the second from 3 to 30 March 2003.

2.2. Online Analysis

[9] Online sampling of the organic acids was performed with a wet effluent diffusion denuder/aerosol collector (WEDD/AC) which contains a flattened glass tube denuder with a dimension of 350 mm × 3 mm × 30 mm (L × H × W) and an aerosol mixing chamber as described in *Fisseha et al.* [2004] and *Zellweger et al.* [1999]. The inner surface of the denuder was coated with sodium silicate ($Na_2Si_4O_3$) and continuously wetted with ultra pure water (18MΩ × cm, Millipore Milli-Q) at a flow rate of 1.5 ml/min using an Ismatec peristaltic pump in counter flow to the air. At the lower end of the denuder, the effluent was pumped to a trace concentrator column for analysis by ion chromatography (IC).

[10] The particle collection system is based on the growth of particles under supersaturated conditions. In a mixing chamber (volume 250 ml) heated water vapor (100°C, flow rate 0.6 ml/min) was mixed with the air stream. The air is pumped further to a maze impactor, which is cooled down to 2°C. The water vapor condenses on aerosol particles and grows to droplets, which impact on the maze. The particle containing liquid was collected and concentrated on a second trace concentrator column. A more detailed description is given by *Simon and Dasgupta* [1995]. Air samples were taken at a flow rate of 4 l/min through the WEDD/AC for 1 hour, and the resulting effluents from both the denuder and aerosol collector were analyzed alternately using a Dionex ion chromatography system. Details of the IC are given elsewhere [*Fisseha et al.*, 2006]. Alternating analysis of the denuder and the particle collection system results in an overall temporal resolution of 2 hours.

2.3. Offline Analysis

[11] In addition to the online gas and aerosol phase measurements, offline analysis of organic acids in the particle phase was performed by IC-MS. Aerosol samples with a size cut of 10 μm were collected on quartz fiber filters with a diameter of 15 cm (Schleicher & Schuell) using a high-volume sampler at a flow rate of 0.5 m^3/min. Details of the sample handling are given by *Szidat et al.* [2004]. The water soluble organic carbon (WSOC) was extracted from the filters by ultrasonic extraction, and the concentrations of the organic acids in the aqueous extracts were determined by IC-MS. Circular filter pieces (14 mm diameter) were combusted using an elemental analyzer (Carlo Erba, EA-1108) before and after aqueous extraction, and the difference was defined as the WSOC concentration.

2.4. IC-MS

[12] A Dionex DX600 IC system was used for the online measurement which was equipped with an ion exchange ion pack AS 11 analytical column, an AG11 guard column, an ASRS auto suppressor with external water mode, an EG40 eluent generator having a capacity of delivering 100 mmol hydroxide solution and a conductivity detector. For the offline analysis, the IC system was coupled to a Dionex, MSQ™ mass spectrometer with a quadruple mass detector and an Enhanced Low-Mass Option (ELMO) enabling the measurement of also the smallest organic acid, formic acid. The mass spectrometer was operated in the negative mode to detect deprotonated compounds with a mass range of m/z 30–500.

2.5. Other Instrumentations

[13] Other parameters such as O_3, NO_2, CO, and PM10 were routinely determined at the same site by the Swiss

Table 1. Concentrations of Organic Acids Measured With the Online Method in the Gas and Aerosol Phase[a]

	August		September		March	
Compound	Gas, μg/m^3	Aerosol, μg/m^3	Gas, μg/m^3	Aerosol, μg/m^3	Gas, μg/m^3	Aerosol, μg/m^3
Acetic acid	1.25	0.09	1.09	0.27	1.97	0.21
Formic acid	0.61	0.17	0.24	0.16	1.07	0.49
Propanoic acid	0.03	N/A	0.16	N/A	0.11	0.05
Oxalic acid	N/A	0.05	N/A	0.03	N/A	0.06

[a] N/A, not available.

Federal Laboratories for Materials Testing and Research (Empa) throughout the year and these data were provided by Empa. Details of the instrumentation used at this site is reported elsewhere [*Fisseha et al.*, 2006].

3. Results and Discussion

3.1. Efficiency of the WEDD/AC

[14] The sampling efficiency of the WEDD/AC was measured for both the gas and the aerosol phase. A mixture of acetic and formic acid from a permeation source was passed through the denuder, and the collection efficiency was calculated to be at least 85% and 75% for acetic and formic acids, respectively at a flow rate of 4 l/min. Losses on the surface of the sampling line and some uncertainty due to the aging of the permeation source lowered the collection efficiency of the denuder. For the aerosol collector ammonium sulfate particles (particle diameter D_p 10–220 nm) were passed through the system and the collection efficiency of the aerosol collector was calculated to be 95%. Using a scanning mobility particle sizer (SMPS) less than 0.5% particle loss was observed in the denuder for particles greater than 50 nm.

3.2. Meteorology

[15] Primary meteorological variables were measured during the sampling periods by Empa. The mean temperature for the three sampling months was 19.9, 15, and 8.9°C for August, September and March respectively. The low temperatures in March resulted in a stagnant weather situation and correspondingly higher concentrations. Photochemical activity was highest in August.

3.3. Diurnal Variations

[16] Average ambient levels of all acids measured online are given in Table 1. Formic and acetic acid were the most abundant organic acids measured in the gas phase. The diurnal variations of organic acids as well as of other components are shown in Figure 1. It is seen that acetic acid resembles mostly those of the primary gaseous pollutants CO and NO_x, with a minimum in the afternoon, suggesting that among the measured organic acids primary sources are most important for acetic acid. However, a morning peak similar to CO and NO_x is not observed, suggesting that traffic is not as dominant a source as for CO and NO_x. Thus other sources such as wood combustion and biogenic emission [*Kesselmeier and Staudt*, 1999] could be potential additional sources of acetic acid in the area.

[17] For formic acid, the diurnal variation is roughly similar to acetic acid in March, but shows an afternoon maximum for August and September. This appears consistent with the suggestion that secondary sources are important in summer months whereas primary sources dominate in March, when temperature is lower and the nocturnal mixing height is lower as well [*Grosjean*, 1989]. Again, the absence of the morning rush hour peak is notable. The main sources of formic acid as discussed by *Chebbi and Carlier* [1996] are primary emission and secondary production. However, their relative importance is quite variable. *Khare et al.* [1997] reported a significant diurnal variation of formic acid for a semiurban site with an increase in formic acid concentration in the afternoon during the hours of high solar irradiation, indicating the importance of secondary formation. In our measurements photochemical activity was much stronger in August than September as seen from the ozone traces. This is also reflected in the lower and later afternoon peak of formic acid in September.

[18] Discrimination between acetic and propanoic acid was often difficult with IC such that the diurnal variation of propanoic acid should be interpreted with care. Tentatively, propanoic acid shows a similar diurnal variation as acetic acid with an indication of primary emission in September, while no clear diurnal variation is observed in August and March. Direct emission of propanoic acid from car exhaust was reported by *Kawamura et al.* [2000]. Secondary formation of propanoic acid was also reported by *Chebbi and Carlier* [1996] as an end product of the ozone-pentene reaction. In addition to these three major carboxylic acids, lactic acid, pyruvic acid, and glycolic acid were also occasionally detected in the gas phase but were often below the detection limit.

[19] Oxalic acid was the dominant identified dicarboxylic acid in the aerosol. Its diurnal variation shows a maximum in the afternoon during March and August, implying secondary production as the major source of oxalic acid in winter and summer, in contrast to the other organic acids. The low values in September with a maximum in the evening remain to be explained. Other dicarboxylic acids such as malonic and succinic acid were reported to be present in the atmosphere [*Kawamura and Ikushima*, 1993; *Limbeck and Puxbaum*, 1999]. However, from the online measurements, only oxalic acid was measured in a detectable range throughout the field campaign. The other dicarboxylic acids coeluted with the carbonate peak making the quantification impossible. Therefore the concentrations of these dicarboxylic acids are further discussed below on the basis of the offline IC-MS measurements conducted with the filter samples.

3.4. Seasonal Variations

[20] Figure 2 shows the seasonal variation of the average concentrations as well the partitioning to the gas and aerosol phase. As already seen in Figure 1, the highest and lowest concentrations of formic acid were found in March and September, respectively, varying by about a factor of four.

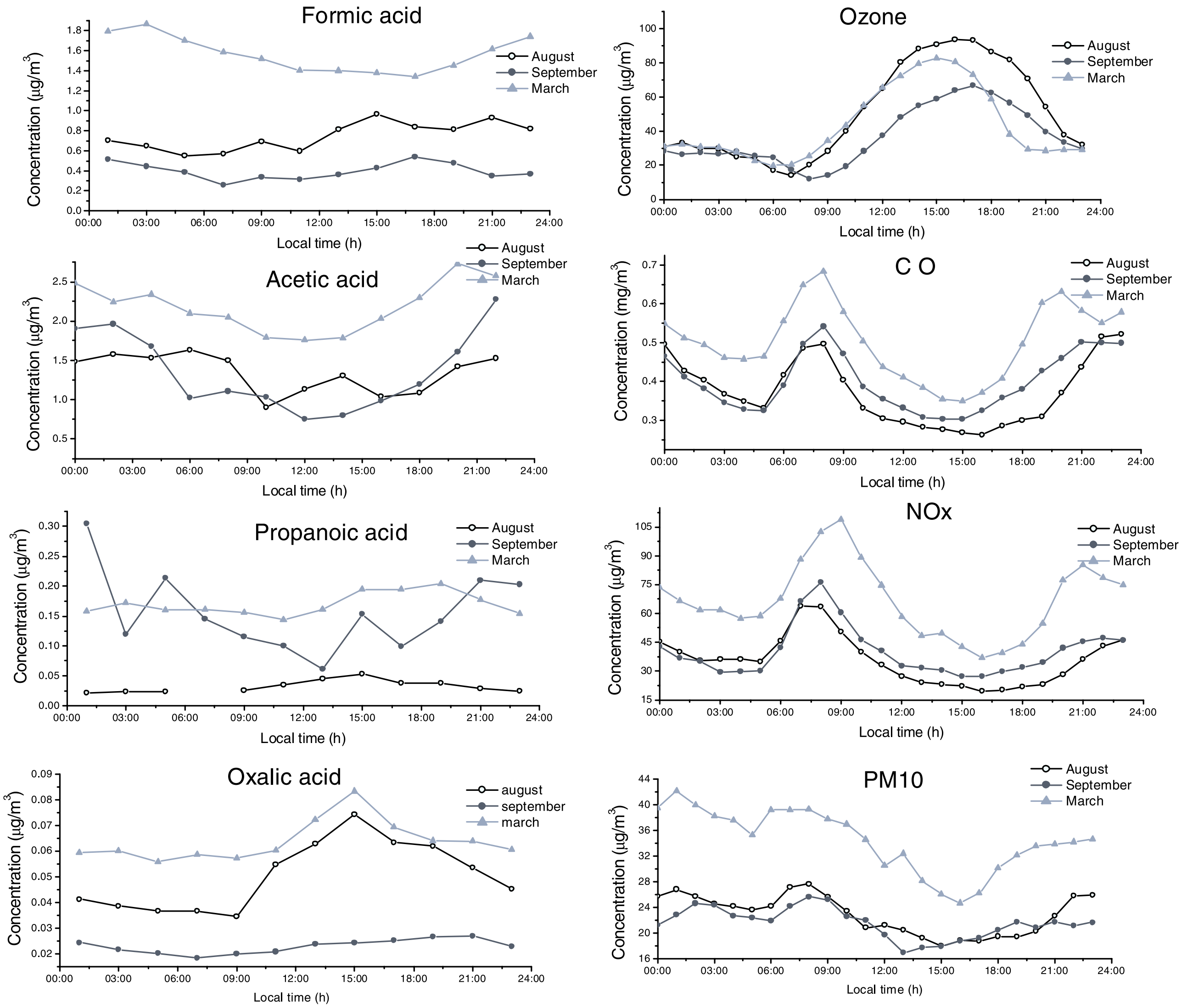

Figure 1. Average diurnal variations of organic acids (sum of gas and aerosol phase), gas phase pollutants and PM10 during the three months of the campaigns.

The elevated levels of formic acid concentration in March are explained by higher emissions due to room heating and a lower mixing height of the planetary boundary layer trapping the pollutants near the surface (which also results in much higher PM10 concentrations in March, as seen in Figure 1).

[21] A comparison with other cities reveals that the concentrations of formic acid in Zurich are much lower than those of major urban cities such as Claremont, California (14 μg/m^3) [*Grosjean*, 1990] or in São Paulo City, Brazil (9 μg/m^3) [*Souza et al.*, 1999] but comparable to semiurban sites such as Schenectady in the northeastern United States [*Khwaja*, 1995].

[22] The concentration of acetic acid is always higher than the one of formic acid, however, its seasonal variability is less pronounced, with the March value being approximately 1.5 times higher than the August and September values. Again, the Zurich data for acetic acid are lower than those from Brussels (11 μg/m^3) and rather comparable to those found in a semiurban area [*Granby et al.*, 1997].

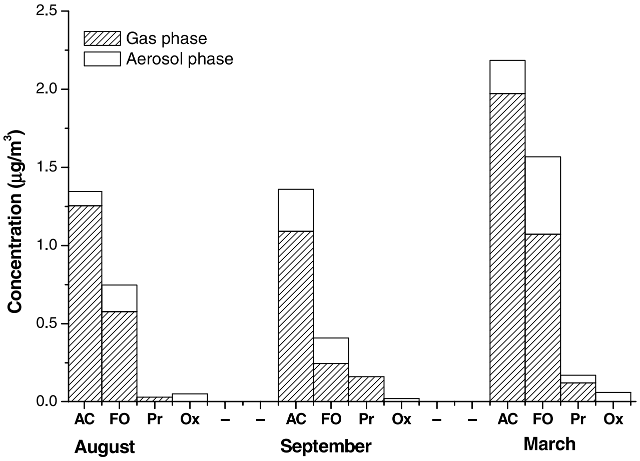

Figure 2. Average concentrations of acetic, formic, propanoic and oxalic acid in the gas and aerosol phase during the three sampling periods. AC, acetic acid; FO, formic acid; Pr, propanoic acid; and Ox, oxalic acid.

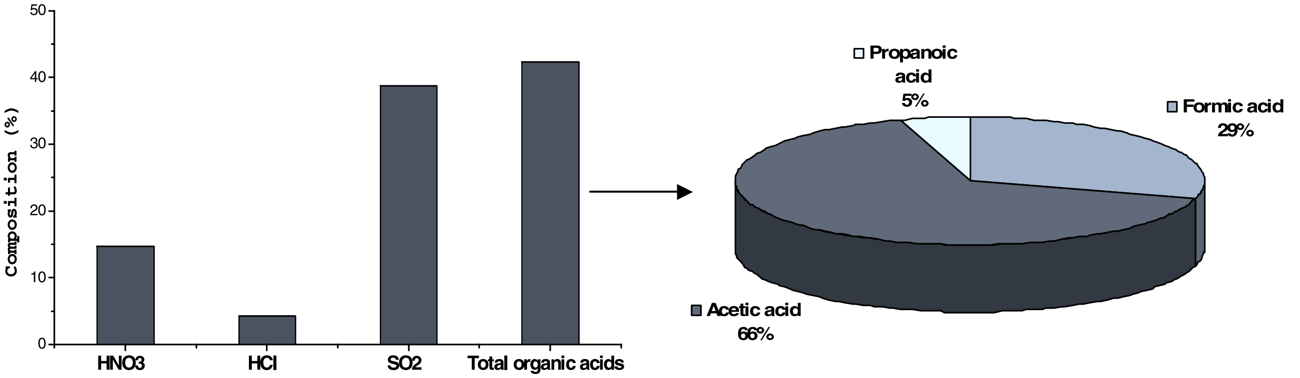

Figure 3. Contributions of the organic acids to the total acidity in the gas phase.

[23] *Khwaja* [1995] reported that the ratio of formic to acetic acid increases with the relative importance of secondary formation over direct emissions. *Talbot et al.* [1988] also found that air masses influenced by anthropogenic emissions have ratios less than unity. The automobile emission data reported by *Kawamura et al.* [1985] suggest that carboxylic acids are directly emitted by motor vehicles as incomplete products of fuel combustion and that the emissions are enriched in acetic acid compared to formic acid. A similar observation was also reported by *Talbot et al.* [1988] for tunnel studies. In our study, the formic to acetic acid ratio was always below 1, with an average value of 0.42. This would point to a dominance of primary sources; however, the diurnal variations in summer clearly indicated also a secondary source for formic acid. Oxalic acid showed a similar seasonal variation as formic acid (see also Table 1).

3.5. Gas/Aerosol Partitioning

[24] The concentrations of the monocarboxylic acids in the aerosol phase were very low compared to the corresponding gas phase concentrations (Figure 2). The predominance of the gas over the aerosol phase was more pronounced for acetic acid, with about 93% and 80% in vapor form in August and September, respectively. The average concentration of acetic acid measured in the aerosol phase was 0.16 $\mu g/m^3$. This value is lower than the one reported by *Khare et al.* [1998] for India (0.32 $\mu g/m^3$) but higher compared to the free troposphere (0.02 $\mu g/m^3$) [*Andreae et al.*, 1988]. The aerosol fraction was higher for formic acid than for acetic acid (Figure 2). Similarly, *Souza et al.* [1999] reported a higher fraction of formic acid in the aerosol phase compared to acetic acid. Although the vapor pressure of formic acid is higher compared to acetic acid, the higher acidity constant of formic acid probably results in

Table 2. Average Concentrations of Carboxylic Acids Measured in the Aerosol Using IC-MS

Molecular Weight	Number of Carbon	Acid	Summer Average ± (SD), ngC/m^3	Winter Average ± (SD), ngC/m^3
46	C1 (mono-)	formic	6.0 ± (2.6)	5.0 ± (2.6)
60	C2 (mono-)	acetic	1.0 ± (0.99)	0.5 ± (0.3)
74	C3 (mono-)	propanoic	0.6 ± (0.5)	0.8 ± (0.6)
76	C2 (mono-)	glyoxylic	0.9 ± (0.8)	0.7 ± (0.4)
88	C2 (mono-)	pyruvic	3.30 ± (1.4)	2.5 ± (1.2)
90	C2 (mono-)	lactic	1.88 ± (1.7)	1.5 ± (1.7)
90	C2 (di-)	oxalic	36.9 ± (13.9)	28.4 ± (11.3)
102	C5 (mono-)	valeric	0.96 ± (0.5)	0.7 ± (0.3)
104	C3 (di)	malonic	10.1 ± (4.7)	4.70 ± (3.4)
112	C5 (mono-)	furan carboxylic	2.2 ± (1.5)	2.0 ± (1.9)
116	C4 (di-)	fumaric	0.2 ± (0.1)	0.2 ± (0.1)
116	C4 (di-)	maleic	0.7 ± (0.2)	1.09 ± (0.6)
118	C4 (di-)	succinic	4.2 ± (2.1)	3.3 ± (2.4)
130	C5 (di-)	methylmaleic	1.1 ± (0.3)	1.0 ± (0.5)
132	C5 (di-)	glutaric	1.8 ± (0.7)	1.8 ± (1.2)
134	C4 (di-)	malic	7.6 ± (5.7)	4.0 ± (3.1)
146	C6 (di-)	adipic	2.4 ± (0.9)	2.1 ± (1.0)
150	C4 (di-)	tartaric	0.7 ± (0.9)	0.3 ± (0.3)
176	C6 (tri)	propane-1,2,3-tricarboxylic acid	2.7 ± (1.4)	0.6 ± (0.4)
192	C6 (tri-)	citric	1.3 ± (0.7)	0.6 ± (0.3)
138	Di	unidentified	7.8 ± (4.7)	9.3 ± (6.2)
140	Di	unidentified	7.3 ± (4.0)	7.8 ± (6.3)
148	Di	unidentified	77.9 ± (57.6)	36.4 ± (30.6)
158	Di	unidentified	0.9 ± (0.4) ±	0.6 ± (0.5) ±
164	Di	unidentified	38.7 ± (31.9)	34.6 ± (24.8)
188	Di	unidentified	8.0 ± (2.6)	3.9 ± (2.1)
190	Tri	unidentified	27.9 ± (15.5)	4.5 ± (2.8)
204	Tri	unidentified	6.6 ± (3.5)	1.1 ± (0.7)
206	Tri	unidentified	1.5 ± (0.8)	0.6 ± (0.3)

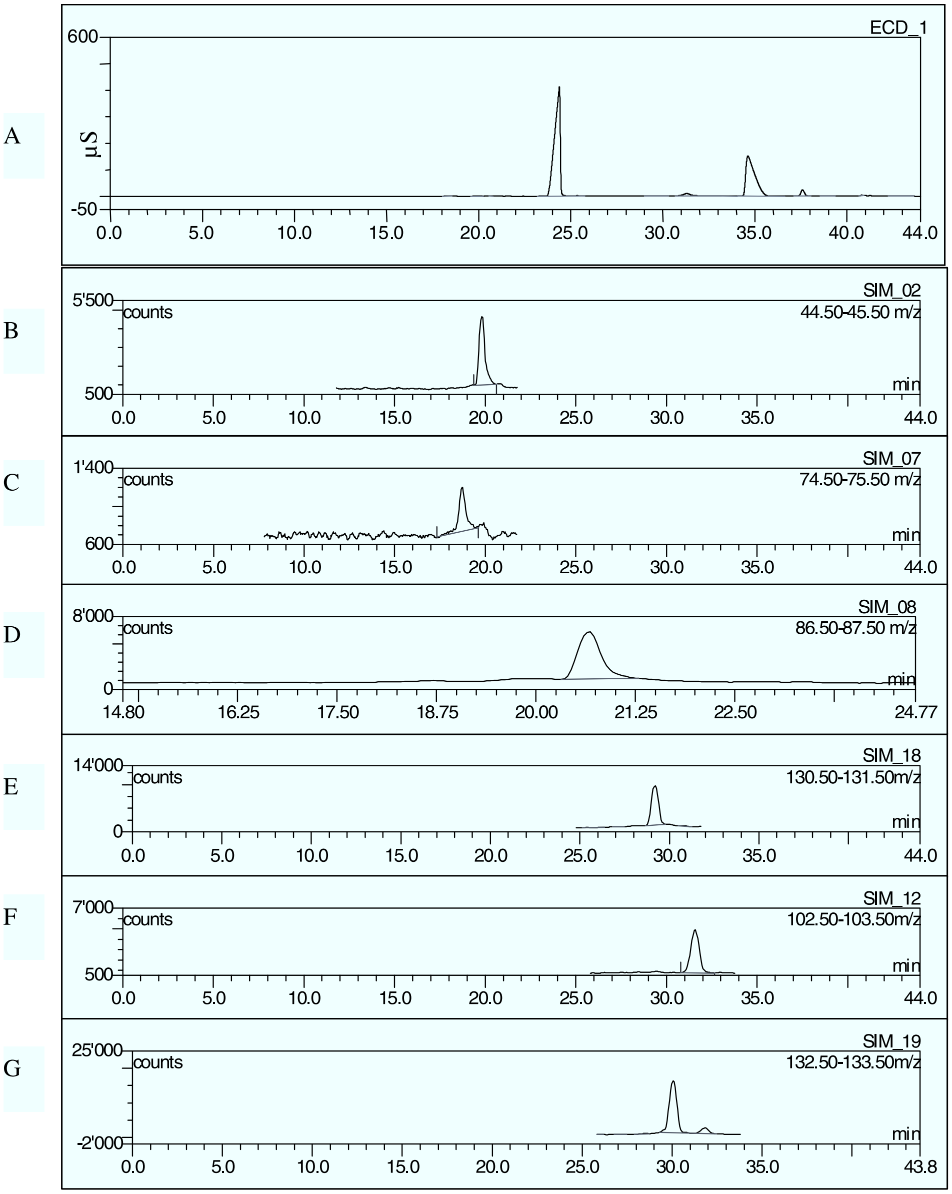

Figure 4. IC-MS chromatograms. (a) Chromatogram from the IC and (b–g) chromatograms for various masses.

a stronger aerosol partitioning than for acetic acid. In addition, the formation of formic acid in the condensed phase from the oxidation of formaldehyde on water droplets could result in a higher fraction of formic acid in the aerosol phase [*Seinfeld and Pandis*, 1998; *Jacob*, 1986]. However, this process depends on the pH of the solution. In contrast, *Khwaja* [1995] reported a higher partitioning of acetic acid into the aerosol phase compared to formic acid, however, the absolute value of formic acid for the month October (0.16 $\mu g/m^3$) was similar to the one measured in Zurich in September (0.16 $\mu g/m^3$).

[25] Oxalic acid was found mainly in the aerosol phase. Because of their low vapor pressure, dicarboxylic acids partition strongly to the particulate phase in the atmosphere [*Saxena and Hildemann*, 1996; *Chebbi and Carlier*, 1996].

[26] Because of their low reactivity, gaseous carboxylic acids are slowly removed from the atmosphere by chemical reactions [*Talbot et al.*, 1997]; their major sinks are wet and dry deposition [*Grosjean*, 1989]. Carboxylic acids and particularly monocarboxylic acids may thus be important in their contribution to acid rain. *Keene et al.* [1983] estimated that carboxylic acids may contribute up to 64% of the free acidity of the precipitation in nonurban environments. Figure 3 shows the concentrations of the organic acids in relation to the inorganic gas phase acids and SO_2. In total, the organic acids accounted for 42% of the total gas-phase acids, from which 66% were contributed by acetic acid. However, with respect to the total acid loading (including the aerosol phase) the contribution of organic acids is less (20%).

3.6. Offline IC-MS Analysis

[27] Table 2 shows the results of the IC-MS measurements. In total, 20 carboxylic acids were identified and

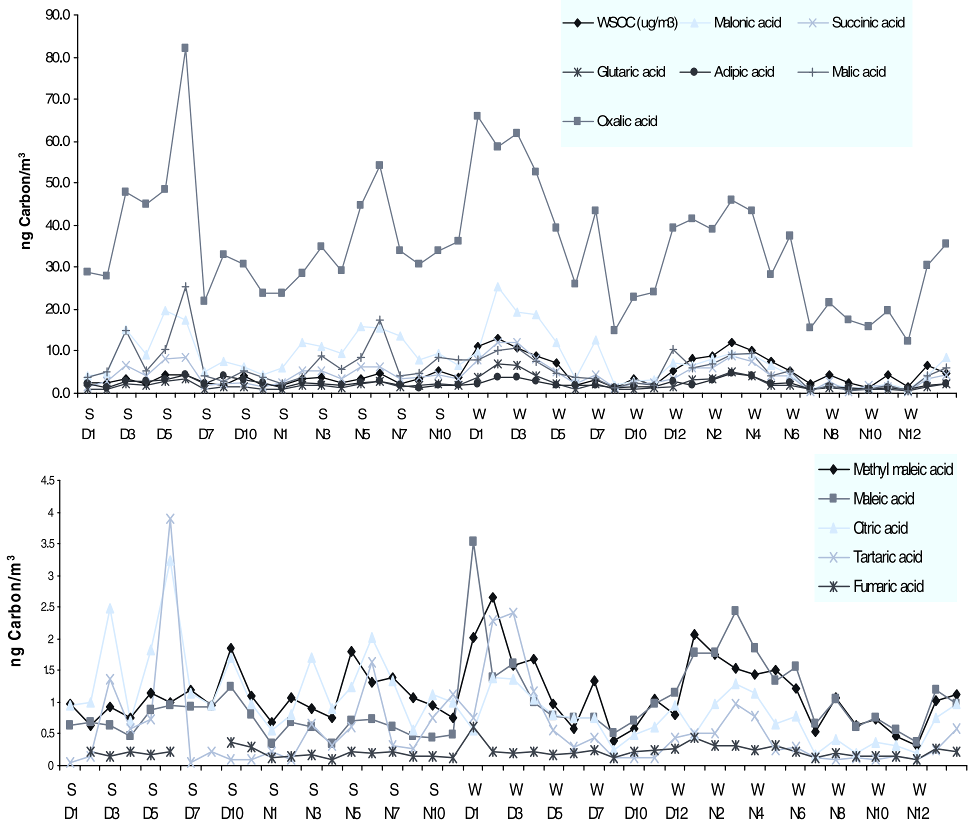

Figure 5. Concentrations of dicarboxylic organic acids and water soluble organic carbon (WSOC) in the measured filter samples. S, summer; W, winter; D, day; and N, night.

quantified, of which 8 were monocarboxylic, 10 were dicarboxylic and 2 were tricarboxylic acids. Most of the quantified carboxylic acids contained additional functional groups. Hydroxy-carboxylic acids were the most abundant classes of dicarboxylic acids next to aliphatic acids in the aerosol samples. Pyruvic acid was the only keto-acid identified. Most of the dominant species in the three compound classes had relatively short chain lengths of 2–5 carbons along with oxygenated functional groups. A branched chain saturated dicarboxylic acid (methylmaleic acid), two isomeric aliphatic unsaturated dicarboxylic acids, maleic (cis configuration) and fumaric (trans configuration), one cyclic dicarboxylic acid (furan 2-carboxylic acid) and 1,2,3-propanoic acid, a triacid which had recently been identified in urban and tropical aerosol [*Graham et al.*, 2002] were also detected in the MS from the filter samples. The MS enabled identification of compounds which could not be identified only from the IC measurements, because of their similar retention times (Figure 4). In addition, more than 20 unknown organic acids with m/z up to 249 were also detected with MS. 9 of these unidentified masses are given in Table 2. Although one can infer the number of possible carboxylic groups from the retention time of the compounds in the IC, it was difficult to determine the structure of the compounds just from the retention time and the mass. Hence, for unidentified masses, only the molecular weight and the possible number of acid groups are given. The concentrations of these organic acids were also estimated on the basis of the retention time of the nearest organic acid. However, the concentrations of these organic acids are not included in the calculated total concentration of organic acids in the aerosol. The IC-MS result revealed the potential of coupling the MS to the IC to identify compounds that might be of importance in different atmospheric processes. Although it was not possible for this study, online measurements with a WEDD-AC coupled to IC-MS might be even a more powerful tool to study the formation and fate of organic acids in the atmosphere.

[28] It is interesting to note that the concentrations of formic and acetic acid determined in the online measurements were typically 10 times higher than in the off-line measurements. This was not the case for oxalic acid. It may be speculated that during the filter sampling a large fraction of the aerosol bound monocarboxylic acids is lost, because of their high vapor pressure, in contrast to oxalic acid with a much lower vapor pressure. This again points to the importance of online measurements with lower artifact potential.

[29] Oxalic acid was by far the most abundant dicarboxylic acid (45%) on average, followed by malonic acid (10.8%) and malic acid (7.8%). In terms of carbon atoms however, C4 acids were dominant over C3 acids. A similar molecular distribution was observed in some aerosol samples collected from the North Pacific [*Kawamura and Usukura*, 1993], from Tokyo [*Kawamura and Ikushima*, 1993; *Sempéré and Kawamura*, 1994] and in other urban areas [*Yao et al.*, 2002]. Figure 5 shows that the concentrations of many of the prominent dicarboxylic acids were closely associated with WSOC, resulting in high correlation coefficients ($r^2 = 0.66$ to 0.88) among the C2, C3, C4, acids.

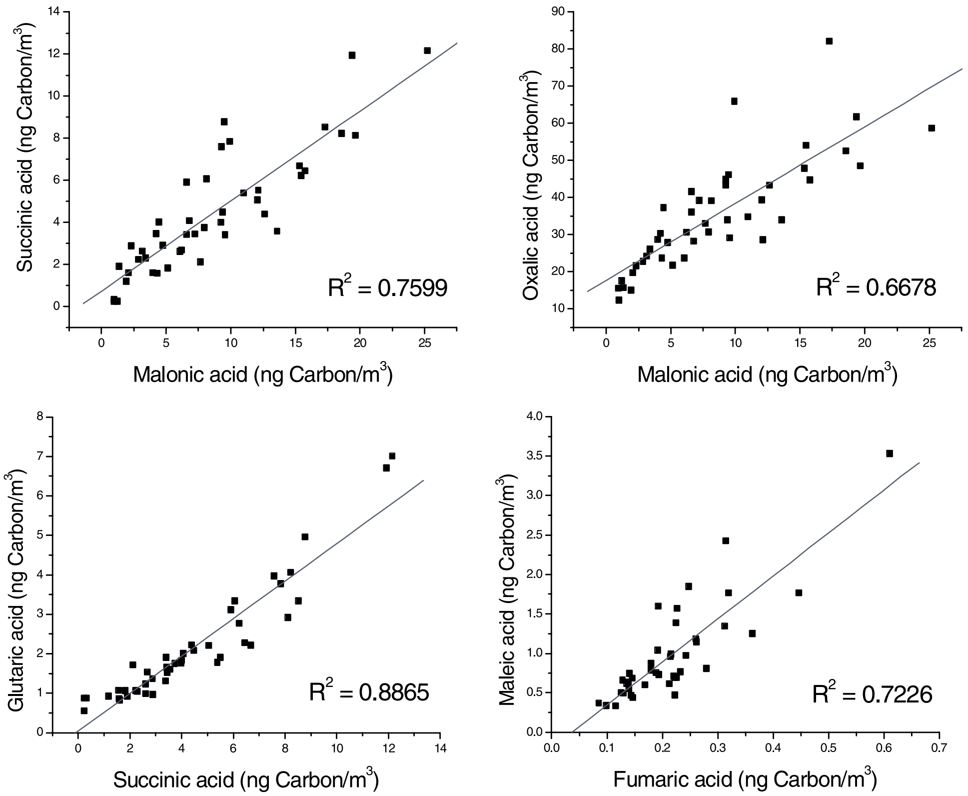

Figure 6. Correlations between selected dicarboxylic acids.

Figure 6 presents a few examples of these correlations. The high r^2 values for oxalic, malonic, and succinic acid suggest that the formation processes of these diacids are somehow related. Oxalic and malonic acids are likely produced in the atmosphere by photo-oxidation of succinic acid through intermediates such as malic acid [*Kawamura and Ikushima*, 1993]. *Kawamura and Gagosian* [1987] proposed that succinic, glutaric, and adipic acids are likely oxidation products of gaseous aliphatic monocarboxylic acids, which are in part produced by photo-oxidation of biogenic unsaturated fatty acids and other precursors. This consideration is consistent with the correlation found between succinic and glutaric acid (Figure 6). The two isomers, maleic and fumaric acid, measured in the aerosol samples also show a good correlation (Figure 6). *Kawamura and Sakaguchi* [1999] and references therein indicated that the cis configuration (maleic acid) is dominant in urban areas which is consistent with our observations.

[30] Table 3 presents the sums of identified monocarboxylic, dicarboxylic and tricarboxylic acids as well as their mass fraction of the WSOC from the filter analysis. In total, the carboxylic acids accounted for 0.85–4.5% (average 2%) of WSOC. Unidentified masses are not accounted for this calculation, but could be as high as 7% in total (Table 2). A similar value of 1.8% was reported by *Kawamura et al.* [2003] for the contribution of dicarboxylic acids to the total organic carbon in East Asia.

[31] Figure 7 presents the correlations of the sums of identified monocarboxylic and dicarboxylic acids with WSOC. It is seen that this correlation is weak for the monocarboxylic acids but substantially higher for the dicarboxylic acids. As noted above monocarboxylic acids may have been lost from the filter leading to their low contribution and correlation with WSOC. High concentrations of dicarboxylic acids were observed during the stagnant weather conditions in winter, which coincided with high WSOC concentrations. Interestingly, however, the fraction of carboxylic acids during winter was in general lower than in summer particularly during February with high pollutant concentration (Figure 8). This finding is similar to the one reported by *Graham et al.* [2002] who measured a high WSOC but a lower fraction of dicarboxylic acids during a forest fire. On the other hand *Yu et al.* [2005] indicated a higher percentage of organic acids for a stagnant

Table 3. Average Concentrations (±Standard Deviation) of Water Soluble Organic Carbon, Offline Total Monocarboxylic Acids and Offline Total Dicarboxylic Acids Measured in Zurich

Sample Label	WSOC, μg carbon/m^3	Monocarboxylic Acids, ng carbon/m^3	Dicarboxylic Acids, ng carbon/m^3	Total Organic Acid, ng carbon/m^3	% of Total Organic Acids
Summer day	3.0 (±1,0)	17.2 (±8,3)	69.2 (±35,7)	86.5 (±41,2)	2.9 (±1,0)
Summer night	3.5 (±1,1)	15.9 (±5,4)	64.6 (±18,3)	80.6 (±19,0)	2.5± (0,7)
Winter day	6.2 (±4,2)	18.7 (±10,6)	72.4 (±36,0)	91.0 (±43,8)	1.8± (0,7)
Winter night	5.8 (±3,4)	13.4 (±6,7)	48.0 (±25,2)	61.5 (±30,0)	1.2± (0,6)

weather period. They explained the high contribution of carboxylic acids with oxidation processes leading to the formation of organic acids. Hence the decrease in the organic acid fraction during the stagnant cold period in Zurich suggests a high contribution of the WSOC by combustion rather than oxidation.

4. Conclusions

[32] Online measurements are important in understanding sources and sinks of organic acids. The WEDD/AC method used in this paper for online sampling of gas and aerosol organic acids helps to understand the time variation of the organic acids in Zurich city. On the basis of these online measurements, acetic acid was found to be the dominant organic acid in the gas phase in all seasons with a concentration of 1.97 μg/m^3 in March and 1.09 μg/m^3 in September, followed by formic acid. The diurnal variations for formic and acetic acid indicate that acetic acid mainly results from primary sources (combustion and biogenic emissions) during all measurement periods whereas formic acid may result from oxidation and combustion during August while during March most of the formic acid results from primary sources. From the filter based offline IC-MS measurements, 20 carboxylic acids were identified and more than 20 unidentified mass signals were detected in addition. Oxalic acid was the dominant carboxylic acid among the identified organic acids in the aerosol with a concentration of 35ng/m^3, followed by malonic and maleic acid. In the filter measurements the quantified organic acids contributed 2% to the total WSOC. A decrease in the fraction of total organic acids in the WSOC was observed during stagnant cold weather conditions suggesting that the WSOC from biogenic combustion processes has a lower fraction of dicarboxylic acids than photo-oxidation. The IC-MS allows identification of coeluted compounds which otherwise would not be possible to identify with IC alone, however, many of these additional organic acids remain to be identified. Coupling the IC-MS to the WEDD/AC for online measurement may even provide a better result than the one reported here.

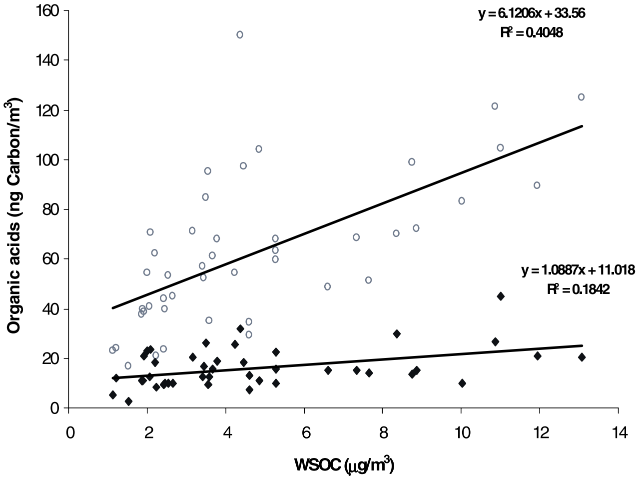

Figure 7. Correlations between WSOC and monocarboxylic acids (solid diamonds) and dicarboxylic acids (open circles).

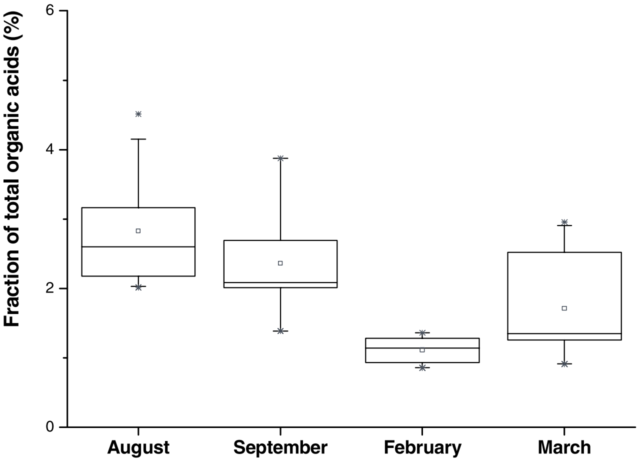

Figure 8. Fraction of the total organic acids in WSOC for the different months. The boxes indicate the median and the 25th and 75th percentiles, the open squares indicate the average, and the whiskers indicate the 1st and 99th percentiles.

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