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# Semivolatile behavior of dicarboxylic acids and other polar organic species at a rural background site (Nylsvley, RSA)

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## Abstract

In this study aerosol samples from the South African savanna were analyzed for their polar organic constituents. Samples were collected with a front/back-up filter tandem system of quartz fiber filters (dual filter strategy). In all samples ( $n = 15$ ) dicarboxylic acids and a variety of phthalates, aldehydes and monocarboxylic acids were observed. Oxalic acid was the dominating compound with an average amount of  $79.2 \text{ ng m}^{-3}$  on the front filter and  $11.3 \text{ ng m}^{-3}$  on the back-up filter. The presence of significant concentrations of dicarboxylic acids on the back-up filter was rather unexpected. There are two possible sources to explain the presence of individual compounds on the back-up filter – particle penetration through the front filter or adsorption of compound parts from the gas phase. Interpretation of the data indicates that the dicarboxylic acid concentrations on the back-up filters appear to be caused by the adsorption of gaseous organic species. Dicarboxylic acids semivolatile behavior is evident with this results. This conclusion refutes the commonly held view that dicarboxylic acids in the atmosphere were associated with the aerosol phase only. Additionally, it was found that the distribution of dicarboxylic acids between the gas and particle phase in the atmosphere is not only dependent on their vapor pressures. The actual gas phase concentration appears to be more determined by the chemical properties of the particles than by pure physical influences. Surprisingly, malonic acid exhibits an anomaly, as it does not show a semivolatile tendency. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Organic aerosol; Sampling artifacts; Oxalic acid; Malonic acid; Succinic acid; Ambient aerosols

## 1. Introduction

Monocarboxylic acids and dicarboxylic acids have been identified as major constituents of the organic aerosol (e.g. Cautreels and Van Cauwenberghe, 1976; Grosjean et al., 1978; Rogge et al., 1993). They have been found in aerosol samples from urban, continental background and remote marine sites (e.g. Satsumabayashi et al., 1989; Kawamura et al., 1996). The presence of these

compounds in the atmosphere may result from primary emissions (e.g. Kawamura and Kaplan, 1987; Legrand and De Angelis, 1996) or from secondary photochemical reactions (e.g. Grosjean et al., 1978; Kawamura and Sakaguchi, 1999). Generally, the predominance of oxalic acid, followed by malonic and succinic acid was shown for aerosols from distinctly different sites (Kawamura and Ikushima, 1993; Limbeck and Puxbaum, 1999a). Until now these major constituents of the polar organic aerosol have not been observed in the gas phase in measurable quantities (Saxena and Hildemann, 1996), therefore, in the atmosphere, they are considered to be associated with the aerosol phase. For example, Clegg et al. (1996) reported that oxalic acid in the atmosphere partitions almost completely into aqueous aerosols, except under conditions of combined low relative humidity,

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low aerosol pH and temperatures greater than about 15°C.

It appears straightforward to define particulate organic compounds as those existing in a condensed phase while suspended in the atmosphere. But atmospheric aerosols are known to contain not only nonvolatile compounds, there are always some semivolatile species present. The sampling of those semivolatile compounds is rather difficult. Generally, organic aerosol samples are collected with pre-combusted quartz fiber filters. But filter collection of organic aerosol is complicated for compounds with semivolatile behavior by artifact errors. The fraction of organic material retained on conventional quartz filters can vary greatly (Appel et al., 1983). If vapor-phase carbonaceous material is retained by sorption on the filter fibers and/or on previously collected particles, this represents a positive error for determining the concentration of particulate carbon ("positive artifact"). Conversely, carbon volatilized from the particle phase during and after sample collection represents a negative error in particulate carbon sampling ("negative artifact"). McDow and Huntzicker (1990) have shown that adsorption of organic vapors to the particles on the filter or to the filter substrate itself makes a substantial contribution to the total organic carbon. Thus leads to an overestimation of the organic content of aerosols. For the correction of this adsorption artifact a dual filter strategy is recommended (Fitz, 1990) to yield more accurate ambient organic particulate concentrations. Eatough et al. (1993) describe a different method for the correction of adsorbed carbon in which a sampling system consisting of diffusion denuders, quartz filters and charcoal impregnated filters (BYU Organic Sampling System; BOSS) are used to distinguish between positive and negative artifacts. During sampling gaseous compound parts originally present under ambient conditions, were separated from the aerosol particles with the denuder system. Afterwards with the filter stack system the particles were collected and additional from the front filter evaporated compound parts were absorbed on the charcoal filter (determination of the negative artifact).

Data, however, about sampling artifacts for individual semivolatile compounds is very sparse. Some studies were reported on potentially toxic or mutagenic compounds like chlorinated or polyaromatic hydrocarbons (e.g. Coutant et al., 1988; Gundel et al., 1995). But for the semivolatile behavior of the main polar organic aerosol constituents only information for phthalic acid esters and monocarboxylic acids is available (Cautreels and Van Cauwenberghe, 1978). Here we report about the observation of a semivolatile behavior of oxalic acid and related polar organic compounds. Sample collection was performed at a biogenically dominated background site – the Nylsvley Nature Reserve in the savanna of South Africa. Aerosol samples were collected using a dual filter sampling strategy to determine the distribution of total

carbon and polar organics between front and back-up filters.

## 2. Experimental

### 2.1. Site description

Samples were collected at the Nylsvley Nature Reserve (NNR) in northeastern South Africa (24°39'S, 28°24'E). The NNR is situated on a plateau at approximately 1000 m elevation in a southern African subtropical savanna biome. A detailed description of the vegetation at NNR is given in Scholes and Walker (1993) and Guenther et al. (1996). The NNR is well suited for background measurements as there is a well-equipped environmental research station operated by the University of the Witwatersrand and tourist traffic is very sparse. The next larger settlements and industrial units are more than 100 km away. Thus, NNR can be regarded as a representative site for the subtropical southern African savanna.

### 2.2. Sampling

A set of 16 weekly aerosol samples was collected from 15 October 1997 to 04 February 1998. Sampling was performed with a low-volume sampler (flow rate about 151 min<sup>-1</sup>) and an open-face-sampling head containing two quartz fiber filters in series (front and back-up filter – dual filter sampling strategy). The sampling head was placed 1.9 m above the ground, which was covered with grass, with the filter facing downwards. For rain protection the sampling head was situated under a shelter which was mounted on a pole with the open side down. Sampling intervals were from 165 to 170 h (around one week) with sample changes from approximately 10:00 to 15:00 h every full week. The sampling volume was measured with an electronic gas meter (Eurometers Ltd. E6) and converted to STP (273 K, 1013 hPa). Sampling substrates for front filters and back-up filters were pre-combusted quartz fiber filters (Pallflex 2500 QAT-UP, 47 mm Ø). To exclude any contamination from the sampling procedure itself, field blanks were collected by purging sample air for 30 s through the filter. After sampling, the filters were stored in petri dishes inside a refrigerator at 4°C. The complete sample set was sent to Vienna by express mail and stored in a refrigerator until the time of analysis.

### 2.3. Analysis/sample preparation

Analytical target compounds in the aerosol were polar organic compounds such as carboxylic acids and related compounds. To allow a simultaneous determination of C2–C9 dicarboxylic acids and C8–C18 monocarboxylic acids the aerosol samples were analyzed by a slightly

modified version of the method of Limbeck and Puxbaum (1999b). To obtain the oxygenated compounds from the aerosol samples, a half from each filter was extracted two times with a methanol/acetone/organic free water-solution using ultrasonic agitation. The combined extracts were diluted with water. Afterwards the samples were separated into different classes of organic compounds using a C18 solid-phase extraction (SPE) cartridge [IST, 221-0020-H]. After a conditioning step, the aqueous sample solution was pulled through the SPE-cartridge with a vacuum flask. The resulting aqueous solution then contained the unretained compounds such as dicarboxylic acids. This solution was carefully reduced to a final volume of about 100  $\mu\text{l}$  with a nitrogen blow down system at 90°C. This aqueous residue was diluted with 1-propanol and spiked with 2-bromododecanoic acid as an internal standard. This solution was treated with a  $\text{BF}_3$ -propanol complex to obtain the propyl-esters. After the addition of a saturated aqueous NaCl solution the dicarboxylic acid esters were extracted with cyclohexane and analyzed by GC/MS. The adsorbed compounds like monocarboxylic acids, aromatic compounds alcohols or aldehydes were eluted from the SPE-cartridge with pure methanol. The achieved solution was treated with a  $\text{BF}_3$ -methanol complex to obtain the corresponding methyl-esters. After the addition of 12-bromo-1-dodecanol as an internal standard, the solution was diluted with saturated aqueous NaCl solution. From this solution the weakly polar organic compounds were extracted with cyclohexane. The GC/MS-analysis was performed using a HP® 5890 Series II GC equipped with a capillary column (HP® INNOWax 19091N-133, 30 m, 0.25 mm ID, 0.25  $\mu\text{m}$  film thickness) and a mass selective detector (HP® 5971 A). The quantification was based on a calibration function for the complete procedure that has been determined with standard solutions and the internal standards. The absolute amount of an individual compound necessary for detection with the described method is about 10–50 ng. This detection range translates to a minimum sample quantification range of 25–150 ng. With the used sample volumes of about 140–160  $\text{m}^{-3}$  air for the aerosol samples, quantification limits in a range of 0.2–1  $\text{ng m}^{-3}$  could be achieved. For the calculation of the absolute amount of an individual compound, the corresponding field blanks were considered.

Total Carbon (TC) was determined with a carbon analyzer modified after a set up described by Puxbaum and Rendl (1983). One aliquot of the second half of the filter ( $\varnothing$  12 mm) was burnt in an oven at 1000°C in an oxygen stream and the  $\text{CO}_2$  evolved was determined with a NDIR analyzer (Maihak UNOR 6B). No measures were taken to remove carbonates from the filter punches prior to combustion. For the determination of sulfate via ion-chromatography (Dionex®; analytical column AS4A-SC, suppressor ASRS I recycle mode, conductivity detection, eluent 1.8 mM  $\text{Na}_2\text{CO}_3$  and 1.7 mM

$\text{NaHCO}_3$ ) another aliquot of the filter ( $\varnothing$  12 mm) was used, which was extracted for 20 min ultrasonically in 3 ml of ultra pure water (Kasper and Puxbaum, 1994).

### 3. Results

In the aerosol samples certain dicarboxylic acids, monocarboxylic acids, phthalates, phenols and aldehydes could be identified and quantified. The most abundant compounds were oxalic acid followed by malonic acid and succinic acid. This result for the major polar aerosol constituents was expected because dicarboxylic acids were known as dominant constituents of the organic aerosol (Kawamura and Ikushima, 1993; Limbeck and Puxbaum, 1999a). In addition some weakly polar organic compounds were identified. For example in sample 3 (29 October–5 November 1997) hexadecanoic acid was found with a concentration of 14.4  $\text{ng m}^{-3}$ , octadecanoic acid with 5.1  $\text{ng m}^{-3}$  and dibutylphthalate with 1.9  $\text{ng m}^{-3}$  on the front filter. A different result was obtained for sample 10 (10–17 December 1997), where octadecanoic acid was the most abundant weakly polar organic compound with 6.7  $\text{ng m}^{-3}$  followed by dibutylphthalate with 5.2  $\text{ng m}^{-3}$  and hexadecanoic acid with 4.8  $\text{ng m}^{-3}$ . For more details see Table 1 with additional results from other identified and quantified compounds from samples 3 and 10. The results obtained from the back filters for the weakly polar compounds were also included in Table 1, indicating that many of the compounds present at the front filters were also observed on the back-up filters. The compound concentrations in Table 1 and generally all other aerosol concentration data are given as mass concentrations reduced to standard temperature and pressure, STP (273 K, 1013 hPa). Interestingly, these weakly polar organic compounds were not present in all samples with concentrations above the quantification limits. In samples with a lower TC content (below 1  $\mu\text{g m}^{-3}$ ) they were observed only with amounts, which were not significantly different from the field blanks. Therefore, it was not reasonable to calculate an average amount over all samples. A possible explanation for this result could be that no prevention was taken to avoid sample oxidation during collection. For example, unsaturated acids could be converted by photo-oxidation into dicarboxylic acids, ketoacids and aldehydes (Kawamura and Gagosian, 1987). Monocarboxylic acids might react with radicals or other oxidants present and thus become converted to oxidized products, thereby making them inaccessible for analysis.

Also, for total carbon (TC) a partitioning between front and back-up filters was observed. Values between 1.29 and 4.99  $\mu\text{g C m}^{-3}$  TC on the front filters, and TC concentrations in the range of 0.14–0.49  $\mu\text{g C m}^{-3}$  at the back-up filters were obtained. In Table 2 the averages ( $n = 15$ ) for front and back-up filter concentrations for

Table 1

Weakly polar organic compounds, results from sample 3 (29 October–5 November 1997) and sample 10 (10–17 December 1997)

Compound	29 October–5 November 1997		10–17 December 1997	
	Frontfilter (ng m <sup>-3</sup> )	Backfilter (ng m <sup>-3</sup> )	Frontfilter (ng m <sup>-3</sup> )	Backfilter (ng m <sup>-3</sup> )
Nonanale	0.7	< <sup>a</sup>	<	<
Decanoic acid	0.3	<	2.2	0.9
Dodecanoic acid	0.3	0.2	0.8	0.2
Tetradecanoic acid	0.3	<	0.5	<
Branched aldehyde (C13/14)	1.1	0.5	0.5	<
Pentadecanoic acid	0.5	<	<	<
Hexadecanoic acid	14.4	8.7	4.8	2.9
Hexadecenoic acid	<	0.5	<	0.4
Heptadecanoic acid	0.7	0.2	<	<
Octadecanoic acid	5.1	2.3	6.7	1.2
Octadecenoic acid	<	0.9	<	0.3
Diisobutylphthalate	1.7	1.7	1.7	0.9
Dibutylphthalate	1.9	2.9	5.2	2.4
Total carbon	2650	460	2190	270

<sup>a</sup> < Indicates concentration below quantification limit.

Table 2

Strong polar organic compounds, present in all front filter samples mean values ( $n = 15$ )

Compound	Frontfilter (ng m <sup>-3</sup> )				Backfilter (ng m <sup>-3</sup> )			
	Average	Median	Min.	Max.	Average	Median	Min.	Max.
Pyruvic acid	5.6 ± 5.0	3.8	0.9	19.9	1.2 ± 0.6	1.0	< <sup>a</sup>	3.7
Oxalic acid	79.2 ± 42	73.8	14.8	179.5	11.3 ± 7.4	7.2	2.7	40.2
Glyoxylic acid	10.8 ± 6.9	9.4	0.9	21.5	1.7 ± 1.8	0.9	<	6.1
Malonic acid	51.7 ± 57	29.7	3.0	227.8	0.2 ± 0.2	0.1	<	0.6
Isoglutaric acid	1.5 ± 0.7	1.4	0.7	3.4	0.5 ± 0.2	0.5	0.3	1.3
Succinic acid	13.1 ± 7.1	11.3	4.8	31.1	3.3 ± 1.1	2.9	1.3	10.1
Glutaric acid	1.9 ± 0.9	1.9	0.7	4.0	0.7 ± 0.3	0.7	0.3	1.8
Adipic acid	2.6 ± 3.6	1.8	0.6	15.9	0.8 ± 0.5	0.7	<	1.9
Pimelic acid	1.3 ± 0.7	1.0	0.5	2.9	0.5 ± 0.3	0.5	<	1.1
Suberic acid	1.8 ± 1.3	1.6	0.9	6.2	0.6 ± 0.3	0.6	<	1.4
Azelaic acid	5.0 ± 2.5	4.3	1.6	10.9	1.3 ± 0.6	1.1	0.5	3.4
Phthalic acid	1.5 ± 1.6	0.9	0.2	6.6	0.2 ± 0.3	0.2	<	1.0
Total carbon	2477 ± 806	2234	1291	4985	292 ± 93	265	135	486
Sulfate	2878 ± 978	2749	1039	4465	46 ± 32	57	1	85

<sup>a</sup> < Indicates concentration below quantification limit.

TC are reported. Additionally, for the highly polar dicarboxylic acids a distribution between front and back-up filter was found. Because these compounds were present in all samples with concentrations distinctly different from the field blanks, the averages over all samples were

calculated (Table 2). The inorganic nonvolatile compound sulfate was determined on the front filters with concentrations in the range of 1.04–4.47 μg m<sup>-3</sup>, on the back-up filter sulfate was present with a concentrations of less than 2% of the front filters.

## 4. Discussion

### 4.1. Front/back-up filter distribution – semivolatile behavior

The observation of notable amounts of dicarboxylic acids and other polar organic compounds at the back-up filters may have three different reasons:

- (a) *Particle penetration*: Possible for all present particles. If the filter efficiency for fine particle collection is low, particle penetration through the front filter may cause the presence of individual organic compounds at the backup filter.
- (b) *Positive artifact*: Possible for compounds co-existing in particulate and gaseous phase (semivolatile behavior). Upon sampling with quartz fiber filters the gaseous phase might be adsorbed on the quartz fibers of the front and back up filter.
- (c) *Negative artifact*: Possible for compounds with semivolatile behavior. A compound deposited on the front filter may partially evaporate during sampling and adsorb on the back-up filter, in particular as a result of changing equilibrium conditions (e.g. temperature).

In the following section the different reasons for the occurrence of individual organic compounds on the back-up filters are discussed. As a reference we also compare the front to back-up filter distributions for the determined dicarboxylic acids with the results for the nonvolatile inorganic compound sulfate.

The presence of monocarboxylic acids, phthalates, phenols and aldehydes on the back filter could be explained with the adsorption of gaseous compounds. From earlier investigations the possibility of vapor adsorption on quartz fiber filters is known (Cadle et al., 1983). Their results indicate that adsorption of gaseous organic compounds can be a significant part of the total collected organic amount. So the presence of significant concentrations of semivolatile compounds on quartz fiber back-up filters is not surprising. Possible sources are ambient organics originally in the vapor phase (positive artifact) or volatilized off organic particulate matter collected on the front filter (negative artifact).

The presence of dicarboxylic acids and related compounds on the back-up filters (Table 2) was a surprising result because until now these compounds have not been reported to occur in the gaseous phase (Saxena and Hildemann, 1996). We had therefore to consider another possible pathway, that being the penetration of particles through the front filter. The part originating from penetration through the front filter could be described with the determined concentrations for the inorganic non-volatile compound sulfate. For an easier comparison the front to back-up filter distribution was calculated for TC and sulfate. The part collected on the front filter (F) is

given by  $c_F/(c_F + c_B)$ , the part collected on the back-up filter (B) was calculated according to  $c_B/(c_F + c_B)$ , where  $c_F$  is the concentration on the front filter and  $c_B$  is the concentration determined on the back filter. Because negative artifact and adsorption effect vary with sampling time (different temperature, pressure, humidity, etc.) no consistent front to back distribution ratios were expected. Therefore the averages over all 15 samples were used. We exclude particle penetration as a major reason for the occurrence of higher fractions of dicarboxylic acids at the back-up filters because for sulfate only 1.7% of the total sulfate (sum of front and back-up filter) was observed at the back-up filter. Therefore we assume that the part derived by penetration through the front filter is 1.7% at maximum. Essentially it might be lower, because it is possible that a part of the determined back-up filter sulfate originates from adsorption and oxidation of sulfur dioxide on collected particles (Liberti et al., 1978). For the investigated strong polar compounds a shift to higher parts on the back-up filters was observed compared to TC and sulfate (Fig. 1). Surprisingly, malonic acid exhibits an anomaly as compared to the other dicarboxylic acids. The relative amount at the back-up filter ( $c_B/(c_F + c_B)$ ) is about 1.3% and thus even less as for sulfate. On the other hand, on average 13–30% of the other dicarboxylic acids are observed at the back-up filter. It is rather unlikely that this increase is due to particle penetration through the front filter because sulfate and the major constituents oxalic acid, malonic acid and succinic acid were observed with similar particle size distributions (Meszaros et al., 1997). For TC we derived that 88.9% were collected on the front filters and 11.1% on the back-up filters. The occurrence of dicarboxylic acids at the back-up filter appears to be caused by the adsorption of gaseous organic species. This conclusion appears to be confirmed by OC/EC studies of McDow and Huntzicker (1990) who found OC on the front and back filters, but nonvolatile EC was only determined on the front filters. They suggested that the lack of EC on the back-up filters rules out significant transmission of particles through the front filters, and thus the presence of OC on the back-up filters can only be explained by adsorption of organic vapors. Additionally, our findings are supported by those of Turpin et al. (1994) who reported that quartz fiber filters were essentially 100% efficient in removing aerosol particles, therefore the occurrence of a compound on the back-up filter had to have occurred via the gas phase. Preliminary unpublished results from a laboratory study performed in Vienna have certified that evaporation of particulate dicarboxylic acids and adsorption on quartz fiber filters are possible.

We have to assume that the TC distribution between back-up and front filter (B/F) depends on the composition of the carbonaceous aerosol fraction. Higher parts of semivolatile organics in the aerosol may increase the

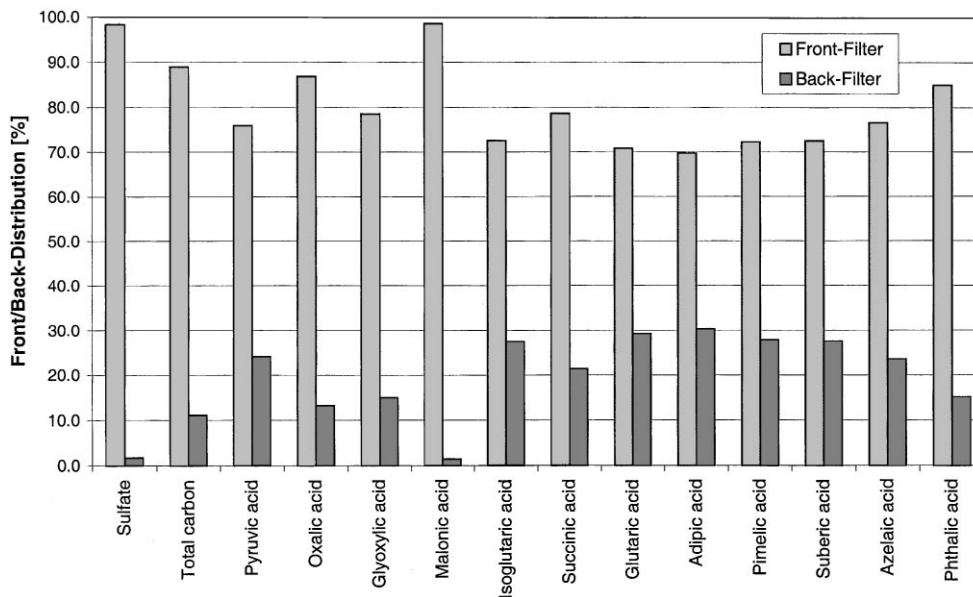


Fig. 1. Partitioning of individual compounds between front and back-up filter.

fraction collected on the back filter, while nonvolatile compounds may cause a shift to higher parts on the front filter. This nonvolatile carbonaceous aerosol fraction, which shows the same particle behavior as sulfate, is expected to contain high molecular weight compounds like cellulose or other biopolymers (Kunit and Puxbaum, 1996; Havers et al., 1998) and/or highly polar multifunctional compounds (Hoffmann et al., 1997). This fraction also contains elemental carbon, which is not volatile and therefore not susceptible to adsorption and volatilization errors during sampling. From the investigated polar organic compounds a lower ratio B/F was observed only for malonic acid as compared to TC. All other dicarboxylic acids and related compounds were found with higher parts on the back-up filter related to TC (see Fig. 1) – we regard them as compounds with semivolatile behavior. This conclusion appears to be confirmed by studies of Kerminen et al. (1999). Their measurements of particulate dicarboxylic acids in the Arctic atmosphere revealed that differences in dicarboxylic acid concentrations between Berner low-pressure impactor (BLPI) and virtual impactor (VI) samples are caused by evaporation losses and sorption of gaseous diacids on the VI filters, respectively.

#### 4.2. Gas phase/particle phase distribution – quantification problems

For the interpretation of the observed front and back-up filter results it has to be considered that adsorption of gaseous compound parts on quartz fiber filters could be incomplete. Unknown amounts of a semivolatile

substance could be lost during sample collection – leading to an underestimation of the total amount (sum of gas phase and particulate matter concentration). Preliminary results from a further sampling campaign at the Nylsvey Natural Reserve with a third quartz filter behind the front and back-up filters has shown that in dependence of the temperature the collection efficiency for the dual filters ranges from about 85–100%. The amount collected on the third filter varied for different compounds from nondetectable to about 5% of the total collected amount at 25°C and 15% at 35°C. Therefore, we conclude for the present study that the total amount is determined with an uncertainty of around 10% for the more volatile compounds (e.g. oxalic acid or succinic acid) and about 5% for the less volatile compounds (e.g. malonic acid). The dual filter results could be used as an acceptable approximation for the total amount of individual compounds present in the atmosphere.

As described earlier, possible sources for the adsorption of individual compounds on the back-up filters are organics originally in the vapor phase under ambient conditions or volatilized particulate matter from the front filter. With the used sampling strategy it is not possible to distinguish between these two artifact types. From earlier investigations of McDow and Huntzicker (1990) a dependence of the collected amount of organic aerosol on quartz fiber filters from the face velocity is known (the filter face velocity is the volumetric flow rate divided by the exposed area of the filter). They showed that an increase of the face velocity of the sampled air (in a range from 10 to 120 cm s<sup>-1</sup>), under the condition of constant volumetric sampling rate, significantly

decreased the apparent concentration of particulate organic carbon. In this study the samples were collected under conditions with face velocities about  $16 \text{ cm s}^{-1}$ , which should minimize the volatilization of particulate matter. Nevertheless, this negative sampling artifact might be considered as a possible source for the presence of polar organic compounds on the back-up filters. Reconciling these two artifact types there are two possible contrary pathways for the interpretation of the obtained front and back-up filter results: (a) the determined back-up filter amounts descends only from adsorption of compound parts originally present in the vapor phase during sampling (results explained only with the positive artifact) or (b) completely from adsorption of volatilized particulate matter previously collected on the front filter (results explained only with the negative artifact). In the last years several articles focused on the positive artifact (e.g. Appel et al., 1979; Cadle et al., 1983; Ligocki and Pankow, 1989), with the outcome that adsorption of organic vapors on collected particulate matter and on the filter medium itself is possible. Results from Appel et al. (1989) revealed that this positive sorption artifact is playing an important role on the fresh filter medium and for short sampling volumes and/or low particulate carbon loadings. This result is confirmed by Turpin et al. (1994), when they found that longer sampling periods reduce the percentage of collected material that is adsorbed vapor. For the correction of this adsorbed amount on the front filter Fitz (1990) has recommended to subtract the carbon concentration on the back filter from that of the front filter to yield more accurate ambient organic particulate concentrations. Using this correction method it must be considered that the particulate phase could be underestimated if the adsorbed amount on the back-up filter originates not only from compound parts originally

present in the vapor phase. Table 3 shows for each determined dicarboxylic acid the distribution gas phase to particulate matter and the “total collected amount” calculated according to the method described by Fitz (1990) [“particulate matter” =  $c_F - c_B$ ; “gas phase” =  $2 \times c_B$ ].

On the other hand, the loss of semivolatile organic compounds from particles during sampling has been demonstrated by Eatough et al. (1993). In this case the actual fraction of organic material in fine particles may have been underestimated due to losses of the semivolatile particulate organic fraction. This sampling error could be corrected by adsorption of the evaporated compound parts on a back-up filter. If we assume that the back-up filter concentrations in our study originate from evaporated front filter aerosols only, we derive the results shown in Table 4 for particulate matter (“particulate matter” =  $c_F + c_B$ ) and for particle loss during sampling (“particle loss” =  $c_B$ ). The disadvantage of this method for the correction of the negative sampling artifact is that the particulate phase could be overestimated if the adsorbed amount on the back-up filter originates from other sources as well as from losses of semivolatile particulate compounds evaporated from the front filter. Generally, the gas to particle distributions reported in Tables 3 and 4 are averages calculated from the individual gas to particle ratios for the 15 samples.

Using these two different approaches for the interpretation of obtained front and back-up filter results, it must be considered that in addition to sorption on the filter material, adsorption on previously collected particulate matter is possible. Therefore, the concentrations for individual compounds listed in Tables 3 and 4 have to be regarded as the limiting cases. For the correct determination of an individual compound in gas phase and particulate matter different sample collection methods have

Table 3

Gas/particle distribution for all determined dicarboxylic acids (mean values  $n = 15$ ). Results calculated considering only the “positive artifact”: = > “part. Matter” =  $c_F - c_B$ ; “gas phase” =  $2c_B$

Compound	Part. matter ( $\text{ng m}^{-3}$ )	Gas phase ( $\text{ng m}^{-3}$ )	Total amount ( $\text{ng m}^{-3}$ )	Part. Matter (%)	Gas phase (%)
Pyruvic acid	$4.1 \pm 5.1$	$2.2 \pm 1.3$	$6.3 \pm 4.9$	61.4	38.6
Oxalic acid	$67.9 \pm 40$	$22.6 \pm 15$	$90.4 \pm 48$	73.7	26.3
Glyoxylic acid	$7.8 \pm 7.2$	$3.3 \pm 3.6$	$11.0 \pm 8.1$	70.1	29.9
Malonic acid	$51.5 \pm 58$	$0.4 \pm 0.3$	$51.9 \pm 57$	97.3	2.7
Isoglutaric acid	$0.9 \pm 0.6$	$1.1 \pm 0.3$	$2.0 \pm 0.8$	45.1	54.9
Succinic acid	$9.7 \pm 6.5$	$6.7 \pm 2.1$	$16.4 \pm 8.4$	57.3	42.7
Glutaric acid	$1.2 \pm 0.9$	$1.5 \pm 0.5$	$2.7 \pm 1.1$	44.9	55.1
Adipic acid	$1.8 \pm 3.6$	$1.7 \pm 1.0$	$3.5 \pm 3.8$	48.5	51.5
Pimelic acid	$0.7 \pm 0.6$	$1.0 \pm 0.6$	$1.8 \pm 0.8$	48.4	51.6
Suberic acid	$1.2 \pm 1.2$	$1.3 \pm 0.6$	$2.4 \pm 1.3$	54.5	45.5
Azelaic acid	$3.7 \pm 2.7$	$2.7 \pm 1.2$	$6.3 \pm 2.4$	64.6	35.4
Phthalic acid	$1.2 \pm 1.6$	$0.3 \pm 0.5$	$1.5 \pm 1.7$	69.9	30.1
Total Carbon	$2185 \pm 815$	$583 \pm 193$	$2769 \pm 864$	78.9	21.1

to be developed to distinguish between positive and negative artifacts.

#### 4.3. Gas-phase presence of dicarboxylic acids

Each compound is distributed between the gas phase and the condensed phase. The proportion between par-

Table 4

Gas/particle distribution for all determined dicarboxylic acids (mean values,  $n = 15$ ). Results calculated considering only the “negative artifact”: = > “part. Matter” =  $c_F + c_B$ ; “part. loss” =  $c_B$

Compound	Part. matter (total amount) ( $\text{ng m}^{-3}$ )	Particle loss (evaporation) during sampling	
		( $\text{ng m}^{-3}$ )	(%)
Pyruvic acid	$6.3 \pm 4.9$	$1.2 \pm 0.6$	24.1
Oxalic acid	$90.4 \pm 48$	$11.3 \pm 7.4$	13.1
Glyoxylic acid	$11.0 \pm 8.1$	$1.7 \pm 1.8$	14.9
Malonic acid	$51.9 \pm 57$	$0.2 \pm 0.2$	1.3
Isoglutaric acid	$2.0 \pm 0.8$	$0.5 \pm 0.2$	27.5
Succinic acid	$16.4 \pm 8.4$	$3.3 \pm 1.1$	21.4
Glutaric acid	$2.7 \pm 1.1$	$0.7 \pm 0.3$	29.2
Adipic acid	$3.5 \pm 3.8$	$0.8 \pm 0.5$	30.3
Pimelic acid	$1.8 \pm 0.8$	$0.5 \pm 0.3$	27.8
Suberic acid	$2.4 \pm 1.3$	$0.6 \pm 0.3$	27.5
Azelaic acid	$6.3 \pm 2.4$	$1.3 \pm 0.6$	23.4
Phthalic acid	$1.5 \pm 1.7$	$0.2 \pm 0.3$	15.1
Total Carbon	$2769 \pm 864$	$292 \pm 93$	11.1

ticulate matter and gaseous phase varies with the vapor pressure of the investigated compound (Appel et al., 1983). The equilibrium vapor pressures of the determined dicarboxylic acids range from  $8\text{E} - 5$  to  $1\text{E} - 7$  mm Hg at room temperature (vapor pressures taken from Saxena and Hildemann, 1996). At the point that the gas-phase concentration of a given compound exceeds its equilibrium vapor pressure, an amount corresponding to the excess is assigned to the aerosol phase (Pandis et al., 1992). Therefore, we could expect for compounds with decreasing vapor pressures a decrease of the gas-phase concentrations. But contrary to this approach we derived the results shown in Fig. 2. Except for malonic acid we observed a decrease of the atmospheric gas-phase concentration with decreasing vapor pressure, but not logarithmically as expected. Fig. 2 shows that the observed gas-phase concentration for oxalic acid is about 3 times higher compared to succinic acid although the vapor pressure is about 10 times higher. For adipic acid the vapor pressure is about 1000 times lower compared to oxalic acid, but for the gas-phase we have observed only a 10 times lower concentration (see also Fig. 2). This discrepancy is not explainable with uncertainties in analysis, therefore we conclude that the gas/particle partition is not only dependent on the vapor pressure. We have to consider other physical and chemical processes influencing the gas phase to particle phase distribution. For example, adsorption onto available particle surfaces or absorption into a liquid phase of an individual compound will allow some gas to particle conversion to occur even when the gas-phase pressure is below its saturation vapor pressure (Pankow, 1994). Accounting

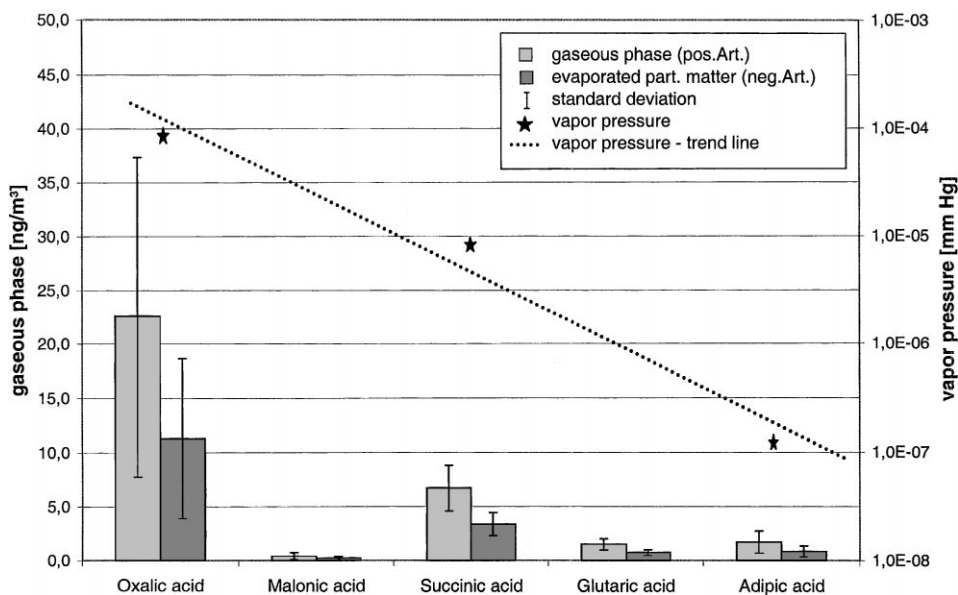


Fig. 2. Gas-phase concentrations and vapor pressures of selected dicarboxylic acids (present in the vapor phase under ambient conditions or volatilized part. matter).



for such effects the different behavior for malonic acid might be explained. A possible reason for the absence of notable amounts of malonic acid on the back-up filters is that malonic acid might be associated with metals or other inorganic aerosol compounds. This assumption is supported by findings of Kerminen et al. (2000), when they suggested that most of the malonic acid is associated with sea-salt particles and therefore malonic acid has a contrary size distribution compared to oxalic acid.

In conclusion, the most likely explanation for the observed difference in behavior between individual dicarboxylic acids in our experiment is the different chemical and physical nature of these compounds. In equilibrium systems the gas to particle partitioning can be described by means of the vapor pressure only, however, for atmospheric conditions other compound properties (e.g. hygroscopic or deliquescent manner) and interactions with the environment (e.g. absorption or salt formation) must be considered.

## 5. Conclusions

- Interpreting the whole data set we have shown that the dicarboxylic acid concentrations on the back-up filters appear to be caused by the adsorption of gaseous organic species. With this result a semivolatile behavior of dicarboxylic acids is evident.
- With the used dual filter sampling strategy it was not possible to distinguish between positive artifact (adsorption of compound parts originally present in the vapor phase) and negative artifact (adsorption of compound parts volatilized off particulate matter collected on the front filter).
- For the interpretation of our results the two extreme cases of only a positive artifact or only a negative artifact were considered, which lead to a concentration range for particulate matter and the gaseous phase. For example the gaseous phase concentration varied from not present under ambient sampling conditions (results explained by the negative artifact) to about 38% (mean for 12 different dicarboxylic acids and related compounds) of the total sampled amount (results explained with the positive artifact).
- The distribution of dicarboxylic acids between gas and particle phase in the atmosphere appears not directly related to the vapor pressures. Absorption and/or adsorption effects on less volatile materials in the particulate matter seem to have an effect. For example, the observed “gas-phase” concentration for oxalic acid is 5 orders of magnitude lower than the equilibrium gas-phase concentration over the pure compound. Thus the actual gas-phase concentration appears to be more dependent on the chemical properties of the particles than the pure physical influences.

- Interpreting our results we suggest that for all earlier studies, where sampling was performed with quartz fiber filters, the reported results for dicarboxylic acids and related compounds are possibly incorrect. This is because in dependence of the sampling site and the sampling conditions an unknown amount of vapor has always been collected on the quartz fiber filters and has possibly evaporated off the filter. These sampling artifacts might lead to an overestimation of the particulate fraction, respectively, to an underestimation of the “total” atmospheric occurrence. Therefore, future studies should be focused on the development of dedicated procedures to avoid sampling artifacts for the collection of carbonaceous aerosol constituents.

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