

Low-Molecular Weight Dicarboxylic Acids and Glyoxylic Acid: Seasonal and Air Mass Characteristics

ANDREAS RÖHRL^{†,‡} AND
GERHARD LAMMEL^{*,†,§}

Max-Planck-Institut für Meteorologie, Bundesstrasse 55,
20146 Hamburg, Germany, Universität Hamburg, Institut für
Anorganische und Angewandte Chemie, Germany, and
Universität Hamburg, Meteorologisches Institut, Germany

Low-molecular weight dicarboxylic acids are important constituents of the organic fraction of atmospheric particulate matter in remote and polluted regions. The knowledge on their sources is sparse, however, and organic aerosols in general need to be better characterized. Observations of C₂–C₅ α,ω-dicarboxylic acids (DCAs oxalic, malonic, succinic, and glutaric acid) and C₂ oxomono-carboxylic acid (glyoxylic acid) from rural and urban sites in different seasons in Germany are reported using filter sampling and ion chromatography. The C₂–C₅ DCAs accounted for (by average) 0.07–0.51 μg m⁻³ at the various sites corresponding to 3.4–23 mg g⁻¹ of total suspended particulate matter and glyoxylic acid for < 0.18–0.28 mg g⁻¹. Both, the transport of air masses over the continent and the summer season favored the occurrence of the acids. Secondary photochemical formation dominated the sources. It was found that for central Europe the anthropogenic emissions are more important than the biogenic emissions for all the acids determined and most important for oxalic acid. The biogenic precursors play a significant role for malonic acid. The influence of the marine sources was detectable for malonic and glutaric acid.

1. Introduction

Particulate organic matter constitutes a major fraction of ambient aerosols. Our knowledge on its composition is in general insufficient to judge on the possible implications for the aerosol optical properties, cloud nucleation properties, and human health.

Carboxylic acids are late products in the photochemistry of hydrocarbons. Due to the low vapor pressures these compounds are almost exclusively partitioning into the particulate phase (except of the C₁–C₆ monocarboxylic acids, MCAs) and contribute significantly to the water-soluble fraction (1). Besides the MCAs the low molecular weight, C₂–C₅ dicarboxylic acids, oxalic (HOOC–COOH), malonic (HOOC–CH₂–COOH), succinic (HOOC–CH₂–CH₂–COOH), and glutaric acid (HOOC–CH₂–CH₂–CH₂–COOH) constitute a major fraction of the organic particulate matter. The first unambiguous observations of DCAs in the atmosphere were made more than twenty years ago (2). Until now, only

a few studies had been conducted (3–9), and two of these were from Europe (8–9).

Observations at various locations demonstrated that oxalic acid (C₂) usually contributes the largest fraction, one- to two-thirds by mass. Oxomono-carboxylic acids (oxoMCAs) are less significant (4–5, 10). In urban air (Los Angeles, Tokyo) elevated concentrations of DCAs (ca. 0.5–3.0 μg m⁻³ = 0.05–1.4% of particulate mass) coincided with elevated concentrations of photooxidants (4, 6, 11). High concentrations were also observed obviously related to large forest fires (12) pointing to either primary emission or secondary formation. In the marine boundary layer Kawamura and Usukura (5) observed 0.02–1.0 μg m⁻³, and at a continental baseline station Limbeck and Puxbaum (9) found 0.2 μg m⁻³.

We determined C₂–C₅ DCAs and glyoxylic acid (CH(O)–COOH, i.e., C₂-oxoMCA) at three rural and two urban sites during summer and winter in Germany. The analysis of the results is led by the aim to characterize the distribution and the influences of source types, i.e., primary or secondary, biogenic or anthropogenic. Findings from field experiments can be valuable contributions to elucidate atmospheric chemical decay paths.

2. Methodology

Experimental: Sites and Sampling. Samples were taken from 5 sites in Germany: one coastal rural site (Kap Arkona on Rügen island, 54°41'N/13°26'E, February–March 1998), two inland rural sites (Merseburg, located some 160 km SW of Berlin, 51°21'N/11°58'E, November–December 1999, and Falkenberg, located some 80 km SE of Berlin, 52°13'N/14°08'E, July–August 1998), and two urban sites, one at the rim of a major conurbation (Eichstätt, located some 20 km NW of the center of Berlin, 52°42'N/13°08'E, July–August 1998) and one site located in a major conurbation (Leipzig, 51°19'N/12°25'E, July–August 1999).

The sampling locations were chosen in a way such that local influences were minimized. The rural sites are not influenced by local pollution sources other than traffic on minor roads. At the urban sites (Eichstätt and Leipzig) influences from sources in the conurbation cannot be excluded and will be discussed below.

The Merseburg and Leipzig sites were located opposite, western and eastern ends of the same, the Halle-Leipzig-Bitterfeld conurbation with ca. 1 million inhabitants. Air was sampled from the height of the urban canopy (roof top, inlet ca. 16 and 21 m above ground, respectively). The Leipzig site was distanced ca. 2 km from the city center and ca. 5 km from the eastern, i.e., mostly leeward end of the conurbation. In Merseburg sampling took place on a building situated at the western rim of the town, directly adjacent to a rural area. We classify Merseburg "rural" here, because this building during the measurements was almost exclusively exposed to winds from western directions. At Eichstätt and Falkenberg air was sampled from 2.5 m above the ground in flat terrain. At Kap Arkona sampling took place from ca. 6 m above the ground and ca. 50 m above sea level some 20 m from the cliff.

The weather was almost dry during the summer campaigns (very few light precipitation events) but not during the winter-time campaigns (frequent precipitation). The ground was snow-covered during part of the Kap Arkona campaign. Summary statistics of the meteorological conditions at the sites during the sampling periods are listed in Table 1.

Total suspended particulate matter, TSP, was continuously collected on quartz fiber filters (Munktell MK360, 15 cm diameter) using a high-volume sampling device (Digitel) with

* Corresponding author phone: +49-40-41173-362; fax: +49-40-441787; e-mail: lammell@dkrz.de.

[†] Max-Planck-Institut für Meteorologie.

[‡] Universität Hamburg, Institut für Anorganische und Angewandte Chemie.

[§] Universität Hamburg, Meteorologisches Institut.

TABLE 1: Summary Statistics of Meteorological Conditions and of Carboxylic Acid Concentrations, c_i (ng m⁻³), and Particulate Matter Mass Fractions, x_i (mg g⁻¹), at the Sites^a

	Kap Arkona		Merseburg		Falkenberg		Eichstätt		Leipzig	
temp (°C)	4	(-1)–(+9)	4	(-3)–(+10)	19	(10–37)	18	(13–26)	18	(8–33)
rel humidity (%)	89	(50–100)	74	(44–94)	72	(31–99)	72	(33–99)	63	(41–91)
wind speed (m s ⁻¹)	10	(2–15)	5	(0–15)	3.1	(1–10)	2.7	(1–4)	2.2	(0.1–6)
	c_i (ng m⁻³)									
C ₂ -DCA	147	(20: 21–432)	57	(22: < 4.4–157)	343	(17: 173–699)	251	(22: 76–637)	229	(24: 64–497)
C ₃ -DCA	18	(20: < 3.7–41)	4.8	(22: < 7.5–21)	64	(17: 15–128)	56	(22: < 2.1–104)	66	(24: 11–108)
C ₄ -DCA	< 19	(20: < 67)	4.2	(22: < 4.4–18)	25	(17: 8.7–100)	18	(22: < 14–51)	35	(24: 11–94)
C ₅ -DCA	11	(20: < 4.8–66)		(22: < 9.6)	21	(17: 6.5–70)	10	(22: < 2.8–31)	30	(24: < 8.9–74)
C ₂ -oxoMCA		(20: < 6)		(22: < 4.0)		(17: < 6)		(22: < 6)	8.4	(24: < 4.8–20)
	x_i (mg g⁻¹)									
C ₂ -DCA	6.97	(19: 1.87–11.2)	2.94	(22: < 0.3–5.03)	15.5	(21: 10.1–25.1)	8.74	(22: 2.92–16.7)	8.00	(24: 1.49–16.4)
C ₃ -DCA	0.98	(19: < 0.36–1.92)	0.27	(22: < 0.20–0.58)	2.81	(21: 1.26–4.95)	1.96	(22: < 0.12–3.43)	2.20	(24: 0.66–3.26)
C ₄ -DCA	< 0.86	(19: < 1.74)	0.21	(22: < 0.14–0.51)	1.1	(21: 0.40–2.9)	0.64	(22: < 0.58–1.4)	1.20	(24: 0.40–2.3)
C ₅ -DCA	0.46	(19: < 0.47–2.08)		(22: < 0.70)	0.92	(21: 0.56–2.80)	0.37	(22: < 0.61–1.68)	0.99	(24: < 0.27–2.44)
C ₂ -oxoMCA		(19: < 0.16)		(22: < 0.15)		(21: < 0.13)		(22: < 0.11)	0.29	(24: < 0.15–0.51)

^a Data listed as "mean (hourly minimum – hourly maximum)" and "time weighted mean (number of samples: minimum-maximum)", respectively.**TABLE 2: Dicarboxylic Acid Concentrations, c_i (ng m⁻³), and Mean TSP (μ g m⁻³) for Classes of Air Mass Origin, Marine, Marine-Continental 1, and Marine-Continental 2 (See Text)^a**

all sites				Kap Arkona (winter)		Merseburg (winter)		Falkenberg (summer)		Eichstätt (summer)		Leipzig (summer)	
Marine													
C ₂ -DCA	81	(13: < 21–180)	50	(5: 21–59)					148	(3: 120–180)	98	(5: 64–168)	
C ₃ -DCA	22	(13: < 4.0–74)	5.3	(5: < 4.0–8.6)					15	(3: < 5.0–35)	42	(5: 11–74)	
C ₄ -DCA	7 ± 2	(13: < 2.6–111)	< 6.8	(5: < 13)						(3: < 25)	12	(5: < 10–17)	
C ₅ -DCA	10	(13: < 5.3–42)	3.9	(5: < 5.3–8.3)						(3: < 11)	17	(5: < 9.8–42)	
C ₂ -oxoMCA	4	(13: < 5.3–8.6)		(5: < 6)						(3: < 6)	6	(5: < 5.3–8.6)	
TSP	18.1		8.4						21.9		29.5		
Marine-Continental 1													
C ₂ -DCA	202	(50: 16–489)	214	(11: 21–432)	44	(10: 16–84)	284	(10: 173–457)	220	(11: 76–473)	235	(8: 82–489)	
C ₃ -DCA	36	(50: < 3.7–108)	20	(11: < 3.7–41)		(10: < 8.2)	50	(10: 15–84)	58	(11: 26–104)	76	(8: 44–108)	
C ₄ -DCA	16 ± 5	(50: < 2.7–259)	< 26	(11: < 68)		(10: < 4.6)	17	(10: 9–24)	19	(11: 10–51)	37	(8: 16–94)	
C ₅ -DCA	15	(50: < 4.6–74)	16	(11: < 4.8–32)		(10: < 4.6)	17	(10: 6.5–29)	12	(11: < 2.8–31)	26	(8: < 8.9–74)	
C ₂ -oxoMCA	4	(50: < 4.6–20)		(11: < 6)		(10: < 4.6)		(10: < 6)		(11: < 6)	9.8	(8: < 4.8–20)	
TSP	24.9		29.4		14.3		17.6		30.0		33.3		
Marine-Continental 2													
C ₂ -DCA	281	(14: 72–637)			104	(6: 72–157)	453	(3: 445–465)	377	(3: 189–637)	427	(2: 357–497)	
C ₃ -DCA	56	(14: < 7.4–104)			7.8	(6: < 7.4–21)	94	(3: 80–104)	70	(3: 51–92)	84	(2: 78–91)	
C ₄ -DCA	23	(14: < 4.3–63)			9.4	(6: < 4.3–18)	30	(3: 24–39)	14	(3: 13–14)	53	(2: 43–63)	
C ₅ -DCA	18	(14: < 3.2–61)				(6: < 7.0)	24	(3: 22–27)	6.5	(3: < 3.2–10)	60	(2: 58–61)	
C ₂ -oxoMCA	3	(14: < 4.6–11)				(6: < 4.6)		(3: < 6)		(3: < 6)	11	(2: 10–11)	
TSP	30.0				27.7		28.9		32.4		30.3		

^a DCA data listed as the following: time-weighted means (number of samples: minimum-maximum). Data which could not be attributed to air mass class were disregarded here. For derivation of means of data subsets which include values below the detection limit, these were set equal to half the detection limit.

an upper cutoff at ca. 23 μm (according to the manufacturer). This type of sampling is a common method for organic particulate matter used by various groups (13). Filters were exposed for periods of 3 to 48 h at flow rates of ca. 0.42 $\text{m}^3 \text{min}^{-1}$. Negative sampling artifacts, e.g. evaporative losses, and positive artifacts, e.g. reaction of gaseous precursors on the filters, cannot be excluded, however.

Experimental: Sample Handling and Analysis. TSP mass was determined by differential weighing of the filter membranes after equilibration to constant relative humidity (ca. 50%) prior to and after sampling. TSP mass at this humidity deviates only little from dry particulate mass (14). The samples were kept frozen until analysis. The filter membranes were extracted with pure water (ultrasonic agitation, Seralpur). The extracts were filtered and analyzed with an ion chromatography system (Dionex, AS11–HC column). The applied eluent gradient swept from 0.5 to 16 mmol L^{-1} sodium hydroxide and from 0 to 20% methanol (similar to earlier work (8, 15)). A methanol free eluent was used for the Kap Arkona samples. With this eluent C_4 -DCA cannot be determined unambiguously but instead the sum of C_4 -DCA and another C_4 diacid (malic acid). Thus, upper limits for C_4 -DCA are given for the Kap Arkona samples. Detection limits achieved corresponded to 10 to 50 ng for the acids investigated. They were determined as the mean plus 3 standard deviations of the field blank value or, if higher, the level corresponding to $S/N = 10$ in chromatograms. Species recovery rates based on multiple standards application on filter membranes were $100.9 \pm 2.9\%$, $100.1 \pm 2.6\%$, $99.9 \pm 3.0\%$, $98.6 \pm 3.1\%$, and $93.7 \pm 5.9\%$ for the C_2 – C_5 DCAs and glyoxylic acid, respectively. Based on multiple standard determination the uncertainty due to chemical analyses is estimated to be $< 4\%$ for C_3 -, C_4 - and C_5 -DCA, $< 10\%$ for C_2 -DCA, and $< 20\%$ for C_2 -oxoMCA (based on 2 σ). Peak identity was confirmed by addition of authentic standard substances.

Elemental analyses were performed using X-ray fluorescence (X-LAB, Spectro A.I.) of parts of the untreated filters (ca. 8 cm^2). The method was described in detail (16).

Data Analysis: Air Mass Classification. We classified the samples according to the air mass origin and trajectory as follows: For samples from Merseburg, Falkenberg and the urban sites the classification was based on 72 h near-ground back-trajectories analyzed with a state-of-the-art weather forecast model (German Weather Service, DWD, or NOAA). All air masses originated in the North Atlantic. The samples were grouped into 3 categories (cf. Figure 1, Table 2): Marine air masses which underwent only little influence from the continent and, in particular, had not passed industrialized regions (northern sector, henceforth called “marine”), marine air masses which experienced continental influence during rather rapid transport from the Atlantic over parts of western Europe (western sector, “marine-continental 1”) and air masses of marine origin which resided over western, southern or central Europe for considerable time (“marine-continental 2”). Samples associated with trajectories covering more than one sector are considered ambiguous and are disregarded in Table 2. Furthermore, from the class marine-continental 1 all data presumably influenced by a nearby conurbation were excluded based on wind direction at the site and trajectory analyses. (This rule had to be applied only for the Falkenberg data as related to the Berlin conurbation.)

For the coastal site (Kap Arkona) we differentiate between two classes, namely advection from the sea (i.e. wind directions between 270° and 100°) and advection from land (i.e. wind directions between 100° and 270°). Air advected to the site during the campaign was marine and originated in the North Atlantic region or, less frequently, in the Arctic (according to weather analyses; Berliner Wetterkarte). Thus, we classify air masses advected from sea and from land to

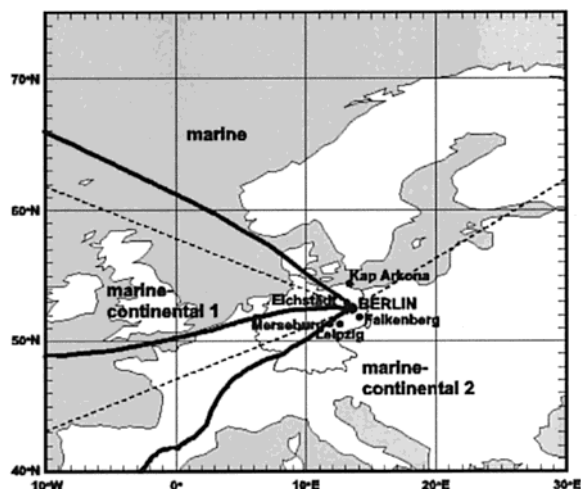


FIGURE 1. 1: Classification of samples according to air mass trajectory within 72 h prior to reach the sites based on near-ground back-trajectories. The map shows exemplary trajectories (from summer 1998) for each of the classes.

TABLE 3: Particulate Matter Elemental Concentrations (ng m^{-3}) during the Field Campaign in Kap Arkona, Time-Weighted Means of 2 Groups of Samples, Advection from the Sea and from Land

	Cl	Ca	S	Al	Fe
from sea	650	280	360	40	98
from land	360	170	900	120	140

the marine and marine-continental 1 classes, respectively (Table 2). Support for this classification of air masses is furthermore provided by the results of particulate matter elemental analysis: The marine aerosol sources are traced by high (sea-salt) Cl and a weak negative correlation between Ca and Fe, $r_{\text{Ca/Fe}} = -0.38$. The continental aerosol source mineral dust is traced by high Al and Fe levels, a high correlation between Ca and Fe ($r_{\text{Ca/Fe}} = 0.70$) and high S (Table 3) and major anions (17) (not reported here).

Data Analysis: Ratios of Concentrations and Mass Fractions. We apply a novel approach to interpret observational data of atmospheric trace constituents: Processes which together constitute the atmospheric cycling of particulate matter secondary trace substances may affect selectively either the atmospheric concentrations, c_i ($\mu\text{g m}^{-3}$) (with i denoting an individual compound) or the particulate phase mass fractions, $x_i = c_i/c_{\text{TSP}}$ ($\mu\text{g g}^{-1}$). Qualitative information on the significance of the processes can be gained from a systematic combined analysis of these two types of data: A high boundary layer will usually cause a low atmospheric concentration (because primary or precursor sources at the ground are diluted into a large volume), but the particulate phase mass fraction will not systematically differ from the situation in a low boundary layer. And a high precipitation frequency during air mass transport leads to a low atmospheric concentration but does not affect the particulate phase mass fraction of one of the components in a systematic way (except in aerosols which are to a high degree externally mixed). These processes and tendencies are visualized in Figure 2. Additional information about influences underlying the data set can be gained when data subsets combining samples of common properties are examined: In general terms, with $p1$ and $p2$ denoting contrasting properties, the observation of parallel (such as both high, i.e., $c_{i,p1}/c_{i,p2} > 1$ and $x_{i,p1}/x_{i,p2} > 1$, or both low, i.e., $c_{i,p1}/c_{i,p2} < 1$ and $x_{i,p1}/x_{i,p2} < 1$, ratios of concentrations and mass fractions) or selective behavior (such as $x_{i,p1}/x_{i,p2}$

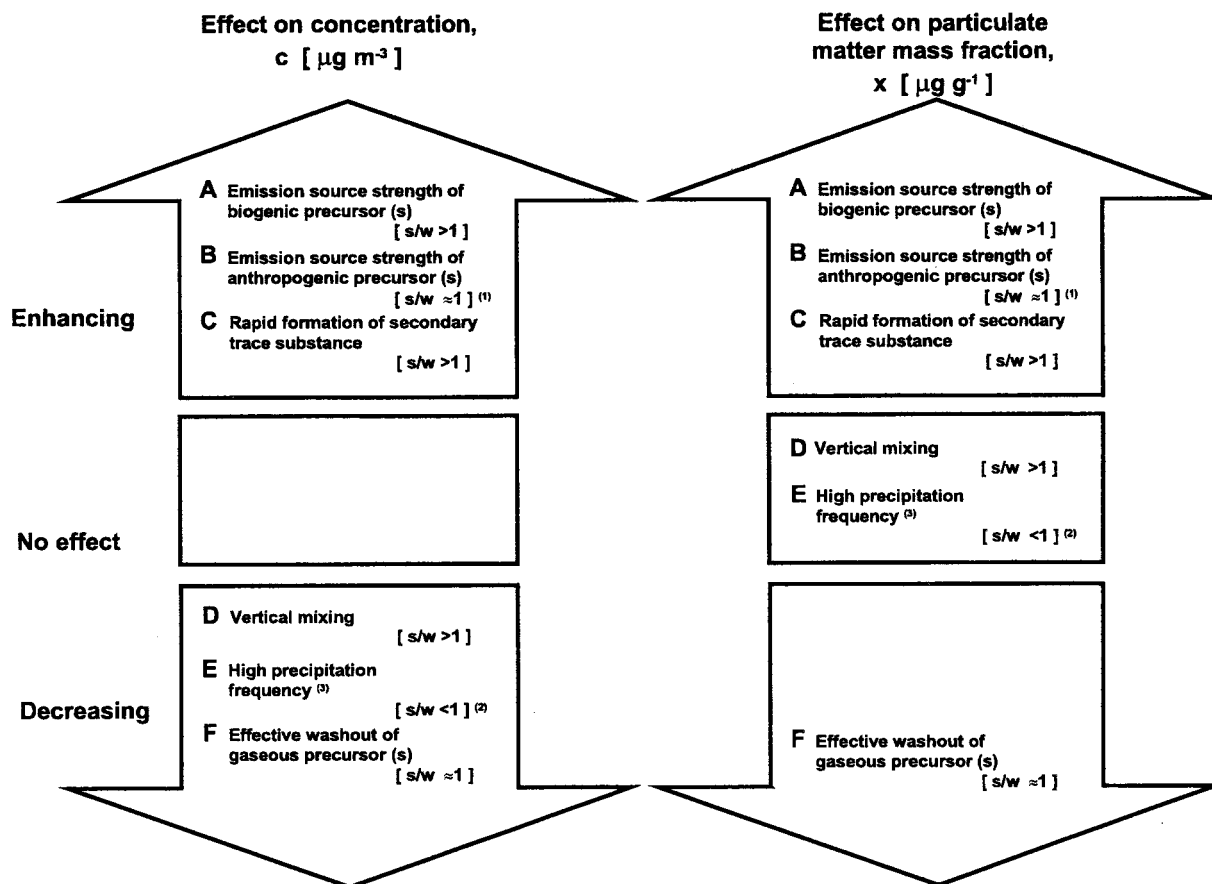


FIGURE 2. 2: Direction of effects (enhancing, none, decreasing) on atmospheric concentration, c ($\mu\text{g m}^{-3}$), and the particulate phase mass fraction, x ($\mu\text{g g}^{-1}$), and seasonal preferences of processes which together constitute the atmospheric cycling of a secondary organic trace substance which predominantly partitions to the particulate phase (such as a DCA). $s/w > 1$, $s/w \approx 1$, and $s/w < 1$ denote seasonal preference to summer, no general seasonal preference, and preference to winter, respectively. (Footnotes): (1) For most substances, but not necessarily for those emissions linked to human activities with seasonal preference (such as e.g. agriculture). (2) In Central Europe, the periods of the winter campaigns were much wetter than the periods of the summer campaigns. (3) Except for aerosols which are to a high degree externally mixed. In these aerosols, small decreasing or enhancing effects are expected as a consequence of the trace substances mass size distribution.

> 1 but $x_{i,p1}/x_{i,p2} < 1$ or vice versa) allows for identifying tendencies which provide additional information related to the differentiation between $p1$ and $p2$. When applying this approach, we rely upon the assumption that nonsystematic differences, on $c_{i,p}$ or $x_{i,p}$, will at least to some extent level out in the data ensembles. We report on analyses of seasonal (then $p1$ = summer, $p2$ = winter) and air mass class (then $p1$ = marine-continental, $p2$ = marine) data subsets in the following section.

3. Results and Discussion

DCA Occurrence: Overall Results and Site Characteristics. During each campaign more than 20 samples were obtained. The overall results are presented in Table 1: Concentration levels of C_2 - to C_5 -DCAs were < 0.01 – $0.9 \mu\text{g m}^{-3}$ (by average $0.26 \mu\text{g m}^{-3}$) in individual samples, corresponding to < 0.06 – 2.7% (by average 1.1%) of (almost dry) total suspended particulate matter (TSP).

The mean concentration levels of C_2 - to C_5 -DCAs for the different sites are 0.07 – $0.51 \mu\text{g m}^{-3}$ corresponding to 0.34 – 2.3% of TSP. The ranges of atmospheric concentrations at individual sites and for individual acids span 1–2 orders of magnitude. The lowest concentration and particulate matter mass fractions were observed at the inland, rural site Merseburg (accounting for $0.073 \mu\text{g m}^{-3}$ and 3.9 mg g^{-1}), somewhat higher at the coastal, rural site Kap Arkona ($0.23 \pm 0.01 \mu\text{g m}^{-3}$ and $8.7 \pm 0.4 \text{ mg g}^{-1}$; the uncertainty is caused

by the C_4 -DCA upper bounds), higher at the urban sites, Eichstätt and Leipzig ($0.34 \mu\text{g m}^{-3}$ and 11 mg g^{-1} , $0.35 \mu\text{g m}^{-3}$ and 11 mg g^{-1} , respectively) and highest at the rural site Falkenberg ($0.42 \mu\text{g m}^{-3}$ and 21 mg g^{-1}).

In comparison with previous observations of DCA occurrence at urban and rural sites (Table 4) two points should be emphasized: At Falkenberg DCAs account for the largest fraction of particulate matter ever observed except in the Antarctic atmosphere. The levels obtained at the urban sites are at the lower end of such observations (and lower than in Falkenberg). Based on time-weighted averaging of the data from rural sites on one hand and urban sites on the other hand, the urban environment seems to “add” $0.13 \mu\text{g m}^{-3}$ and causes a 50% increase compared to the advected “rural” air. Such a conclusion would be misleading, however, because the results from urban sites are based on summer-time data only and, hence, are biased by the seasonal variability of DCA sources and sinks (see below). The site effect will therefore be smaller ($< 0.13 \mu\text{g m}^{-3}$) or even insignificant. When secondary formation was important on the time scale of hours or urban areas were sources of precursor emissions, we expect increased concentrations downwind of urban areas. This applies to the Leipzig (located at the downwind margin of the Halle-Leipzig-Bitterfeld conurbation under conditions of W and NW winds, i.e., ca. 35% of the sampling time) and Falkenberg (downwind of Berlin under conditions of NW winds, i.e., 21% of the sampling time) sites. In

TABLE 4: Overview of Mean Concentrations, c (ng m^{-3}), and Particulate Phase Mass Fractions, x (mg g^{-1}), of the Sum of C_2 - C_5 Dicarboxylic Acids at Various Sites during Summer and Winter Months^a

		n^d	c	x	ref
Remote Sites					
summer	Arctic (Canada)	9	ca. 14 ^b	nd ^c	(10)
summer	Arctic (Finland)	12	ca. 40	nd ^c	(8)
summer	Antarctic (Syowa)	1	77	43.8	(7)
summer	Central N Pacific	6	233	0.6	(5)
summer	Sonnblick Mtn.	3	172	nd ^c	(9)
winter	Arctic (Canada)	10	ca. 15	nd ^c	(10)
Rural Sites					
summer	Falkenberg	21	419	20.9	this study
winter	Arkona	20	229 \pm 11	9.1 \pm 0.2	this study
winter	Merseburg	22	73	3.9	this study
Urban Sites					
summer	Tokyo	8	700	7.1	(4)
summer	Tokyo	2	2250	12.8	(6)
summer	Wien	3	725	nd ^c	(9)
summer	Eichstadt (near Berlin)	22	335	11.4	this study
summer	Leipzig	24	351	11.0	this study
winter	Tokyo	5	530	3.4	(4)
winter	Tokyo	2	890	5.0	(6)

^a Literature data from months other than Jun-Aug ("summer" for northern hemisphere samples) or Dec-Feb ("winter") were discarded. ^b Highest concentrations observed in spring (polar sunrise) and autumn. ^c nd = no data available. ^d n = number of samples.

particular, the high DCA values from Falkenberg suggest that the urban plume might have contributed: The DCA concentrations of those samples collected at the site which were most exposed to winds from the directions of the Berlin conurbation (50% of the time within a 48 h period) were distinctly higher by a factor of 2.0 (i.e. 0.58 vs 0.30 $\mu\text{g m}^{-3}$, factors of 1.7–2.9 for the individual acids) than of samples simultaneously collected in Eichstadt (i.e. upwind of Berlin). This indicates that the urban area contributed to some extent to the DCA levels at Falkenberg.

With glyoxylic acid accounting for < 4.8–20 ng m^{-3} (Table 1) relatively low levels of this acid were observed in Leipzig (and below detection limits at the other sites) compared to concentrations between 26 and 68 (rural site in autumn (17)) and 174–238 ng m^{-3} (Tokyo in summer (6)). The results could be biased by a negative sampling artifact such as oxidative losses on the quartz fiber filters. This reasoning is supported by somewhat lower concentrations associated with longer sampling intervals (means of 8.1 and 11.2 ng m^{-3} for sampling intervals of 23 and 11.5 h, respectively). Such a process would imply a positive, though relatively much smaller artifact for the product of the oxidation, C_2 -DCA. A similar process was recently suggested to explain differences between impactor and polycarbonate filter sampling of DCAs (8).

Air mass type and season certainly contributed to the differences between the sites (Table 2), and these characteristics are examined based on data which aggregate sites in the following.

DCA Occurrence: Air Mass Characteristics. The average concentration levels of the sum of the C_2 – C_5 DCAs were 0.12, 0.27, and 0.42 $\mu\text{g m}^{-3}$ in marine and the continentally influenced air masses of the classes marine-continental 1 and marine-continental 2, respectively. The larger continental influence of the latter class corresponds to distinctly higher concentrations. By time-weighted average and aggregating the two classes of continentally influenced air, the continental influence seems to add $c_{\text{marine-continental}} - c_{\text{marine}} = 0.18 \mu\text{g m}^{-3}$ (time-weighted average) of DCAs and cause a doubling of the concentration in summer and a tripling in winter (Table 5a). The particulate mass fractions show the same behavior, with ca. 7, 11, and 14 mg g^{-1} . Moreover, the acids were very similarly distributed in the various classes, with oxalic acid accounting for 68–76%, malonic for 13–18%, and succinic and glutaric acid for both 5–8%. Concentration levels of the

individual acids increased from class to class (Table 2). The distributions, when disaggregated to the site level, deviate only little from this trend: The relative contribution of C_2 -DCA is highest at the rural sites, Kap Arkona, Merseburg, and Falkenberg (77%, 83%, and 77%, respectively), while the contribution of C_3 -DCA is highest at the urban sites, Leipzig and Eichstadt (21% and 17%, respectively), and C_4 -DCA at Leipzig (9%).

DCA Occurrence: Seasonal Characteristics. The seasonal influence leads to ca. 2.1-fold higher concentrations in summer ((1.9 \pm 0.1)-fold in continentally influenced air and (2.7 \pm 0.1)-fold in marine air; the uncertainties, again, result from the upper limits for C_4 -DCA in Kap Arkona samples; cf. Table 5b), an increase which corresponds to $c_{\text{summer}} - c_{\text{winter}} = 0.19 \mu\text{g m}^{-3}$ of DCAs (time-weighted averages). From this we conclude that the influence of the summer season on the occurrence of DCAs is of similar significance than the influence of transport over the continent (above). Note, that that the seasonal variation of the particulate phase as a whole is less pronounced as for the DCAs.

The continental influence on the occurrence of the acids, expressed as $c_{\text{i,marine-continental}}/c_{\text{i,marine}}$, is less in the summer-time than in the winter-time (2.1 and 2.9 \pm 0.2; Table 5a). It is least for C_5 -DCA and not detectable for glyoxylic acid. Given the seasonal preferences of biogenic (summer maximum) and anthropogenic (by and large insignificant seasonality (18)) hydrocarbon emissions, this seasonal pattern of acid concentrations indicates that the terrestrial biogenic sources are less important than anthropogenic sources for all the acids and least important in the case of C_5 -DCA and C_2 -oxoMCA—at least on a time scale of less than 2 days in which the air parcel has been subject to terrestrial emissions. We gain additional indications from the combined analysis of concentrations and particulate phase mass fractions.

A tendency for increasing particulate phase mass fractions due to the continental influence is only observed for the C_2 – C_4 DCAs and only in the summer-time ($x_{\text{i,marine-continental}}/x_{\text{i,marine}} = 1.9$ –2.9, Table 5a). The same tendencies are obtained for the concentrations ($c_{\text{i,marine-continental}}/c_{\text{i,marine}}$, Table 5a) in summer, while in the winter-time continentally influenced air masses of the concentrations of all acids are higher, a factor of 2.9 \pm 0.2, than in the winter-time marine air masses. This can be explained by the processes which affect c_i and x_i differently (namely D and E in Figure 2): A

TABLE 5: Ratios of Time-Weighted Mean C₂-C₅ Dicarboxylic and C₂-Oxomonocarboxylic Acid Concentrations, c ($\mu\text{g m}^{-3}$), and the Particulate Phase Mass Fractions, $x = c/c_{\text{TSP}}$ ($\mu\text{g g}^{-1}$), in (a) Air Masses of Different Origin and (b) Different Seasons, Marine and Marine-Continental (See Text) Based on Aggregation of Data from All (5) Sites^a

Section (a)				
season	$C_{\text{marine-continental}}/C_{\text{marine}}$ ($\mu\text{g m}^{-3}$)/($\mu\text{g m}^{-3}$)		$x_{\text{marine-continental}}/x_{\text{marine}}$ ($\mu\text{g g}^{-1}$)/($\mu\text{g g}^{-1}$)	
	summer	winter	summer	winter
TSP	0.97	3.0		
C ₂ -oxoMCA	0.92	nd ^b	0.95	nd ^b
C ₂ -DCA	2.7	3.1	2.9	1.0
C ₃ -DCA	1.8	2.7	1.9	0.85
C ₄ -DCA	2.6	>0.2	2.9	>0.1
C ₅ -DCA	1.4	2.8	1.5	0.86
sum of C ₂ -C ₅ DCAs	2.1	2.9 ± 0.2	2.6	0.90 ± 0.12

Section (b)				
air mass classes	$C_{\text{summer}}/C_{\text{winter}}$ ($\mu\text{g m}^{-3}$)/($\mu\text{g m}^{-3}$)		$x_{\text{summer}}/x_{\text{winter}}$ ($\mu\text{g g}^{-1}$)/($\mu\text{g g}^{-1}$)	
	marine-continental	marine	marine-continental	marine
TSP	1.1	3.3		
C ₂ -oxoMCA	>1.9	nd ^b	>1.5	nd ^b
C ₂ -DCA	1.9	2.2	2.0	0.67
C ₃ -DCA	4.6	6.9	4.6	2.0
C ₄ -DCA	>1.4	>1.8	>1.5	>0.5
C ₅ -DCA	1.8	3.8	1.9	1.1
sum of C ₂ -C ₅ DCAs	1.9 ± 0.1	2.7 ± 0.1	2.2 ± 0.1	0.82 ± 0.05

^a Data which could not be attributed to air mass class were disregarded here. Ratios of total suspended particulate matter, TSP, data are given, too. The absolute values of TSP are 25.6 and 6.6 for summer and winter means, respectively, and 26.4 and 17.6 for marine-continental and marine air means, respectively. ^b nd = no data.

low boundary layer and a high precipitation frequency prevailed in the winter-time but not in the summer-time. In the summer-time, concentrations and particulate matter mass fractions air mass tendencies behave the same ($C_{\text{marine-continental}}/C_{\text{marine}} \approx x_{\text{marine-continental}}/x_{\text{marine}}$, Table 5a)—but are different for the individual acids with distinctly higher values of the C₂-C₄ DCAs. No such species selection is observed in the winter-time ($C_{\text{marine-continental}}/C_{\text{marine}} \approx 3 \cdot x_{\text{marine-continental}}/x_{\text{marine}}$, Table 5a). This can be explained by those processes which do not differentiate between c_i and x_i (A, B, C, and F in Figure 2) and have a seasonal preference to the summer (hence, A and C only): The differentiation was either caused by biogenic emissions of precursors of the C₂-C₄ DCAs (but not of the other acids) or a more rapid formation of these acids (or both). Another feature of the data provides additional indications in this context: Oxalic acid shows a moderate sensitivity for the seasonal influence (Table 5b) but a large sensitivity for the continental influence (Table 5a): The winter mean concentration of oxalic acid is $0.14 \mu\text{g m}^{-3}$ which corresponds to half of the summer value (factors of 1.9 and 2.2 higher in different air mass classes), while the winter mean concentration of C₃-DCA is $0.013 \mu\text{g m}^{-3}$, which corresponds to only one-fifth of the mean summer value (factors of 4.6 and 6.9 in different air mass classes; cf. Table 5b). Given the seasonal variabilities of the anthropogenic and biogenic precursor emissions, we conclude that the anthropogenic sources are most prominent for oxalic acid formation, while terrestrial biogenic emissions play a larger role besides the anthropogenic emissions for malonic acid. In combination with the above argumentation it is, furthermore, indicated that oxalic acid was more rapidly formed photochemically.

The processes in the atmospheric cycling of DCAs which tend to enhance the atmospheric concentrations in the summer-time were more efficient in marine compared to continentally influenced air masses ($C_{\text{summer}}/C_{\text{winter}}$ in marine > $C_{\text{summer}}/C_{\text{winter}}$ in continentally influenced air; Table 5b). This signal is largest for C₃- and C₅-DCA. It points to the

existence of marine biospheric sources of the DCA precursors, in particular for C₃- and C₅-DCA which have been identified in the context of earlier work (5, 7).

Acids Precursors Sources: Correlation and Elemental Composition. We use the particulate matter elemental composition to trace the sources of the particulate matter (19, 20). The Merseburg data set was not included in this kind of analysis because so many DCA data were below the detection limit (Table 2), and no correlation of the C₄-DCA in marine air masses are reported because of the small data set.

The contribution of mineral dust to the aerosol composition is obvious through the correlation of Ca and Fe ($r = 0.52-0.97$) at all and K at most of the sites. Pb, a tracer for vehicle traffic, was correlated with Zn ($r = 0.87-0.88$) and Fe ($r = 0.51-0.55$) at the rural sites.

The C₂-C₃ DCAs ($r = 0.54-0.66$), and to a lesser extent the C₄-DCA, were correlated with nonsea salt sulfur (nss-S) at the urban sites but not so at the rural sites. The pattern becomes more clear when disaggregated into air mass classes rather than sites (Table 6): The cluster of particulate K, Ca, and Fe is obvious in continentally influenced air, and there is a high correlation between Zn and Pb in the class marine-continental 2. There is no correlation of the DCAs with sea-salt (traced by the Cl content), the aerosol related to vehicle traffic (traced by the Pb content), or other elements covered by the analyses (K, Zn). In marine air and less in continentally influenced air the sum of the DCAs is highly correlated with nss-S. We derived nss-S assuming that sea-salt aerosol is the exclusive source for particulate Cl which is certainly justified for marine air. nss-S is an indicator for photochemistry (as formed from oxidation of SO₂ by photooxidants in the gas and aqueous phases) in the air mass history on the time-scale of several days. We attribute the weak correlation between DCAs and nss-S in continentally influenced air to a systematic error in the determination of nss-S content which leads to overestimation: There are additional, anthropogenic sources of Cl over land and Cl will be partly removed from

TABLE 6. Air Mass Classified Correlation Coefficients, r_{ij} , of Time-Weighted Mean Mass Fractions of Particulate Matter Constituents

i/j	marine	marine-continental	
		1	2
n ^a	13	40	8
K/Ca/Fe ^b	0.28	0.85	0.75
Pb/Zn	0.00	0.16	0.84
C ₂ -C ₅ DCAs/Cl	-0.27	-0.23	-0.79
C ₂ -C ₅ DCAs/nss-S ^c	0.68	0.20	0.54
C ₂ -C ₅ DCAs/Pb	-0.18	0.18	0.16
C ₂ -C ₅ DCAs/Zn	0.44	0.10	0.10
C ₂ -DCA/C ₃ -DCA	0.57	0.70	0.62
C ₃ -DCA/C ₄ -DCA		0.48	0.57
C ₄ -DCA/C ₅ -DCA		0.65	0.87
C ₃ -DCA/C ₅ -DCA	0.38	0.52	0.28
C ₂ -DCA/C ₄ -DCA		0.47	0.34
C ₂ -DCA/C ₅ -DCA	0.20	0.51	0.27

^a n = number of samples. ^b Mean value of three r_{ij} . ^c nss-S = nonsea-salt sulfur.

the sea-salt aerosol (as HCl). In general, nss-S and Pb are internally mixed to a high extent (21, 22) and can be considered representative for the submicrometer size fraction. For marine air (the only class where nss-S is an appropriate indicator) the DCAs are correlated with nss-S but not with Pb ($x_{Pb} = 260 \mu\text{g g}^{-1}$), indicating that the size distributions of these three constituents to deviate considerably. Remarkably large discrepancies between the mass size distributions of C₂-C₅ DCAs were recently reported from a remote site in northern Europe (8). We conclude that the DCAs are obviously decoupled from (i.e. they are likely externally mixed with) the major natural aerosol components sea-salt and mineral dust and the particles containing vehicle traffic Pb emissions which supports the perception of the dominance of secondary sources.

The DCAs are in general correlated with each other which is most pronounced in the air mass class marine-continental 1. C₅-DCA was, however, distinctly less coupled to C₂ and C₃-DCA (Table 6).

To summarize the results, it was found that secondary photochemical formation is a very, we speculate the most, important source for the low-molecular weight DCAs, while there is no significant indication for primary sources. The influences of both terrestrial as well as marine precursor emissions were identified. For central Europe the anthropogenic emissions are more important than the biogenic terrestrial emissions for all the acids determined. The latter play a significant role for malonic acid. The occurrence of malonic and glutaric acid is also influenced by marine, presumably biogenic emissions.

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