

## Carbonaceous aerosol over the Indian Ocean: OC/EC fractions and selected specifications from size-segregated onboard samples

C. Neusüß,<sup>1</sup> T. Gnauk, A. Plewka, and H. Herrmann

Institut für Troposphärenforschung, Leipzig, Germany

P. K. Quinn

Pacific Marine Environmental Laboratory, NOAA, Seattle, Washington, USA

Joint Institute for the Study of the Atmosphere and Ocean, University of Washington, Seattle, Washington, USA

Received 4 January 2001; revised 1 October 2001; accepted 15 October 2001; published 15 October 2002.

[1] Concentrations and mass fractions of organic carbon, elemental carbon, and numerous organic species have been determined for submicrometer and supermicrometer particles in the Indian Ocean on the cruise of the R/V Ron Brown during INDOEX in February/March 1999. The total carbon (TC) concentration was low for air masses originating from the southern hemisphere of the Indian Ocean, where only small amounts of organic carbon (OC) could be detected in supermicrometer (sea salt) particles. The OC concentration was typically more than one order of magnitude higher in the northern Indian Ocean, where continental air masses were encountered, both for submicrometer and supermicrometer particles. Elemental carbon (EC) was mostly found in submicrometer particles, increasing up to more than two orders of magnitude in the northern part compared to the southern part of the Indian Ocean. The mass fraction of carbonaceous material was in the range of 6–15% and 2–12% for submicrometer and supermicrometer particles, respectively, with the higher values for more polluted air masses. A high degree of mixing with light scattering material is the main reason for high-absorption coefficients. The absorption efficiency is higher for lower mass fractions of EC. Various short-chain dicarboxylic and hydroxylated dicarboxylic acids have been determined. Dicarboxylic acids were mostly found in supermicrometer particles, whereas hydroxylated dicarboxylic acids showed up mainly in submicrometer particles. Alkanes and polycyclic aromatic hydrocarbons have been found in small amounts, leading to the conclusion that an important part of the organic material is of secondary origin. This is confirmed by the good correlation of the sum of carboxylic acids with OC, nitrate with a less pronounced correlation with sulfate. However, low OC/EC ratios indicate the existence of primary OC. **INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; **KEYWORDS:** carbonaceous aerosol, size distribution, organic particulate matter

**Citation:** Neusüß, C., T. Gnauk, A. Plewka, H. Herrmann, and P. K. Quinn, Carbonaceous aerosol over the Indian Ocean: OC/EC fractions and selected specifications from size-segregated onboard samples, *J. Geophys. Res.*, 107(D19), 8031, doi:10.1029/2001JD000327, 2002.

### 1. Introduction

[2] The amount, chemical composition, and the size distribution of atmospheric aerosol particles govern their impact on climate and toxicity. Carbonaceous material is a major fraction of atmospheric aerosol particles [e.g., Heintzenberg, 1989]. Elemental carbon (EC) is of special interest due to its light-absorbing properties. Organic carbon (OC) contributes to scattering characteristics of atmospheric par-

ticles, for example, Penner [1995] and also contributes to the absorption of light [e.g., Zappoli *et al.*, 1999].

[3] Several studies about carbon concentrations in polluted continental environments and some for marine environments exist reviewed by Duce *et al.* [1983], Heintzenberg [1989], Penner [1995], and Heintzenberg *et al.* [2000]. However, there are only very limited data available for size-separated OC and EC measurements. Due to different sources and effects such measurements are necessary, especially in marine environments, where anthropogenic sources influence mainly fine particles, which are mixed with natural sea salt particles with the main mass in the coarse mode. Some examples for the size distribution of OC and EC can be found in the works of Countess *et al.* [1981], McMurry and Zhang

<sup>1</sup>Now at Bruker Saxonia Analytik GmbH, Leipzig, Germany.

[1989], *Nunes and Pio* [1993], *Berner et al.* [1996], and *Kleemann et al.* [1999]. These studies, however, are dealing with polluted, continental aerosol samples. *Heintzenberg* [1982] and *Kaneyasu and Murayama* [2000] studied the size distribution of black carbon (BC) in marine samples.

[4] With the exception of natural biomass burning EC entirely results from anthropogenic combustion processes, whereas OC can have several sources. These include direct emission due to incomplete combustion of fossil fuel or biomass and the atmospheric conversion of volatile organic compounds (VOCs) into less volatile species which subsequently transfer into the particulate phase. Direct particle emission as well as the emission of particle OC precursors occur as a result of both anthropogenic and natural processes.

[5] The knowledge about processes and budgets involving particulate organic material is rather incomplete. One reason is the fact that typically only 10% of the organic carbon is assigned to single species [*Rogge et al.*, 1993a] although larger amounts of OC have been identified either in aged air masses [*Neusüß et al.*, 2000a] or by including more generalized groups of compounds such as macromolecular species [*Zappoli et al.*, 1999]. Second, to date the methods to sample organic material and to separate OC from EC are not well characterized [*Countess*, 1990; *Hering et al.*, 1990; *Huebert and Charlson*, 2000; *Jacobsen et al.*, 2000].

[6] A large variety of organic species contribute to the OC [e.g., *Rogge et al.*, 1993a; *Saxena and Hildemann*, 1996]. Particle organic composition influences the physico-chemical properties of aerosol particles. For example, humidity growth of organics-containing particles is enhanced or decreased with respect to inorganic ions [*Saxena et al.*, 1995] and surface tension may be influenced [*Shulman et al.*, 1996; *Facchini et al.*, 1999] by organics.

[7] Dicarboxylic acids are a main fraction of the known organic material in atmospheric particles [*Saxena and Hildemann*, 1996]. Several measurements indicate their ubiquitous occurrence [e.g., *Kawamura et al.*, 1996a; *Kawamura and Sakaguchi*, 1999]. Photochemical processes appear to be the main sources of low molecular weight dicarboxylic acids. Direct sources such as combustion of fossil fuels are of negligible importance. For sources of organic acids in atmospheric particles see *Schauer et al.* [1996] and references therein.

[8] In this contribution detailed information is presented on the concentration and particle size distribution of (i) EC, (ii) OC, and (iii) selected organic species in the marine boundary layer aerosol over the Indian Ocean sampled during the intensive field phase of the Indian Ocean Experiment (INDOEX) [*Lelieveld et al.*, 2001]. Organic species include low molecular weight dicarboxylic acids, polycyclic aromatic hydrocarbons (PAH), and alkanes.

[9] A large number of different methods exist for the determination of particulate OC and EC. The method applied here and in other recent aerosol field studies from our laboratory [*Müller*, 1999; *Neusüß et al.*, 2000a, 2000b, 2002] is described in detail and discussed in view of the variety of other existing methods. Results obtained here are discussed in the context of the radiative properties of the Indian Ocean aerosol (cf. also *Quinn et al.* [2002b]). Regional influence on the aerosol composition are discussed by air mass analysis applying 4-day back trajectories [*Quinn et al.*, 2002b]. The data on particulate content of EC, OC, and

speciated organic compounds are linked together and put into context with results from other recent field campaigns.

## 2. Methods

### 2.1. Sampling

[10] Air was isokinetically sampled about 10 m above sea level in front of the ship's stack. Only air masses without contamination, indicated by number of particles and relative wind speed and direction, were sampled. To this end, sampling was automatically switched off when particle number concentration rapidly increased, the relative wind direction was forward of the beam or the relative wind speed was below 3 m/s. The air was heated slightly (2–10°C) to sample air at a constant level of 55% RH. For a detailed description of the aerosol sample inlet see *Quinn et al.* [2002a].

[11] Three-stage multistage cascade impactors [*Berner et al.*, 1979] were used to determine carbon and organic species. The 50% aerodynamic cutoff diameters,  $D_p$ , were 10, 1.1, and 0.18  $\mu\text{m}$ , respectively. Thus, supermicrometer particles were collected in the size range  $1.1 \mu\text{m} < D_p < 10 \mu\text{m}$  and submicrometer particles in the range  $0.18 < D_p < 1.1 \mu\text{m}$ . The sampling flow rate was 30 l/min.

[12] Aluminum foil was used to sample for the determination of organic and elemental carbon (OC/EC). Tedlar film was used as the substrate for the subsequent analysis of organic ions by capillary electrophoresis (CE). In the latter case Pyrofoil<sup>TM</sup> covered part of the Tedlar film in order to determine semivolatiles organic species by Curie point pyrolysis-gas chromatography/mass spectrometry (CPP-GC/MS) from the same sample.

[13] The impactors sampling for the analysis of carbon were equipped with two quartz fiber filters in series behind the impaction plates to account for particles with  $D_p < 0.18 \mu\text{m}$ . The second filter should account for positive artifacts due to adsorption of gas phase organics. However, during this campaign the difference of the two filters was in the range of field blanks. Consequently, values of the backup filters are disregarded. The error caused by this procedure is small as can be concluded from the carbon size distributions discussed below.

[14] In total, 41 samples for the determination of carbon have been taken continuously in time intervals of 12–48 h, depending on the available aerosol concentration. Mean concentrations are reported as time-averaged values. 7 samples have been analyzed for organic species.

[15] Furthermore, a 7-stage multistage cascade impactor (50% cutoffs: 0.18/0.3/0.54/1.1/2.0/4.1/10.3  $\mu\text{m}$ ) was used to obtain three examples of the size distribution of carbon.

### 2.2. Carbon

[16] Carbon was determined in this study separating OC/EC with a thermographic method using a commercial carbon analyzer (C-mat 5500, Ströhlein, Germany) consisting of a free programmable combustion furnace (IR 05) followed by a resistance oven (D03 GTE) holding the CuO catalyst (to convert carbon quantitatively to carbon dioxide) at 850°C, and a NDIR detector measuring the IR absorption of the formed carbon dioxide. Analyses were carried out placing samples in a quartz tube positioned in the center of the IR oven and heating rapidly under different conditions. As carrier gases in a first step nitrogen (5.0) for OC

volatilization at 590°C and in a second step oxygen (4.5) for EC combustion at 650°C were applied. In between the two runs the IR furnace was cooled down to 50°C to avoid EC losses during flushing with oxygen. The duration of each run was 8 min and thermograms of every run were stored in a computer. Quantification was performed by integration of the area below the thermogram curve.

[17] The OC-defining temperature of 590°C was chosen with respect to the same Curie point temperature of the sampling foils employed simultaneously to detect organic single species by CPP-GC/MS (see beneath). Aluminum foils are the most appropriate substrate for impactor sampling (carbon-free production process resulting in low blank values, cheap). The melting point of 659°C restricts the EC determination to this temperature. However, tests with carbon black and natural soot (sampled on quartz filters) show that only 2–3% of the TC evolves between 650°C and 850°C. Thus, EC (and TC) does not contain carbonate carbon evolving at temperatures > 650°C [Petzold and Nießner, 1996].

[18] Calibration of the instrument was performed using external standards (e.g., a solution of potassium hydrogen phthalate containing 10 µg C in 100 µl solution). Fivefold EC analysis of 62 high volume samples result in a coefficient of variation of 4.7%.

[19] The detection limit of the carbon analyzer was determined to be 0.3 µg carbon. Several field blanks have been taken by handling the aluminum foils in the same matter as the sampled substrates, but without drawing air through the impactors. Field blank mean values (averaged over 9 blanks) were  $5.8 \pm 1.1$  µg and  $1.3 \pm 0.5$  µg for OC and EC, respectively, resulting in detection limits (95% confidence level) of 0.16 µg/m<sup>3</sup> and 0.07 µg/m<sup>3</sup> for OC and EC, respectively, for a typical day/night sampling period. Since the sampling period was extended up to a whole day (in one case up to two days) for clean air masses the detection limit is proportionately lower. These values can be taken as uncertainty for the chemical analysis, apart from below mentioned OC/EC-split. Sampling artifacts are unknown and therefore have not been corrected for.

[20] OC/EC-separation can be carried out in many different ways. Methods have been developed including extraction steps to remove OC with organic solvents, acids, bases and water [Cadle and Groblicki, 1980; Japar et al., 1984; Kuhlbusch, 1994; VDI 2465 Bl.1, 1996]. Dry thermal desorption methods under an inert gas [Malissa et al., 1976; Cadle et al., 1980; Ogren et al., 1983; Ulrich et al., 1990; VDI 2465 Bl.2, 1997], air [Cadle and Groblicki, 1980; Cadle et al., 1981] or oxygen atmosphere [Malissa et al., 1976; Novakov, 1982; Cachier et al., 1989; Lavanchy et al., 1999] with a wide range of conditions also have been applied. Furthermore, combinations of both wet and dry methods have been used [Iwatsuki et al., 1998; Zappoli et al., 1999]. In addition, optical pyrolysis correction procedures have been developed and incorporated in existing instruments [Johnson et al., 1981; Huntzicker et al., 1982; Japar et al., 1984; Chow et al., 1993].

[21] With respect to the highly desirable comparability of carbon measurement values from different research groups inter-laboratory method comparison studies were performed [e.g., Cadle and Mulawa, 1990; Countess, 1990; Shah and Rau, 1991]. Our laboratory participated in the Germany-internal VDI/DIN-comparison experiment for EC determi-

nation [Neuroth et al., 1999] and in the International Aerosol Carbon Round Robin Test Carbon Shoot Out Stage I [Schmid et al., 2001] as well as Stage II [manuscript in preparation].

[22] All experiments have shown sufficient comparability of TC values but a wide variety in the results of OC and EC determinations. A survey of the results seems to show a tendency for higher EC values by pure thermographic methods resulting in lower OC. However, the basis in these comparisons is the mean value of all participants, the true value remains unknown.

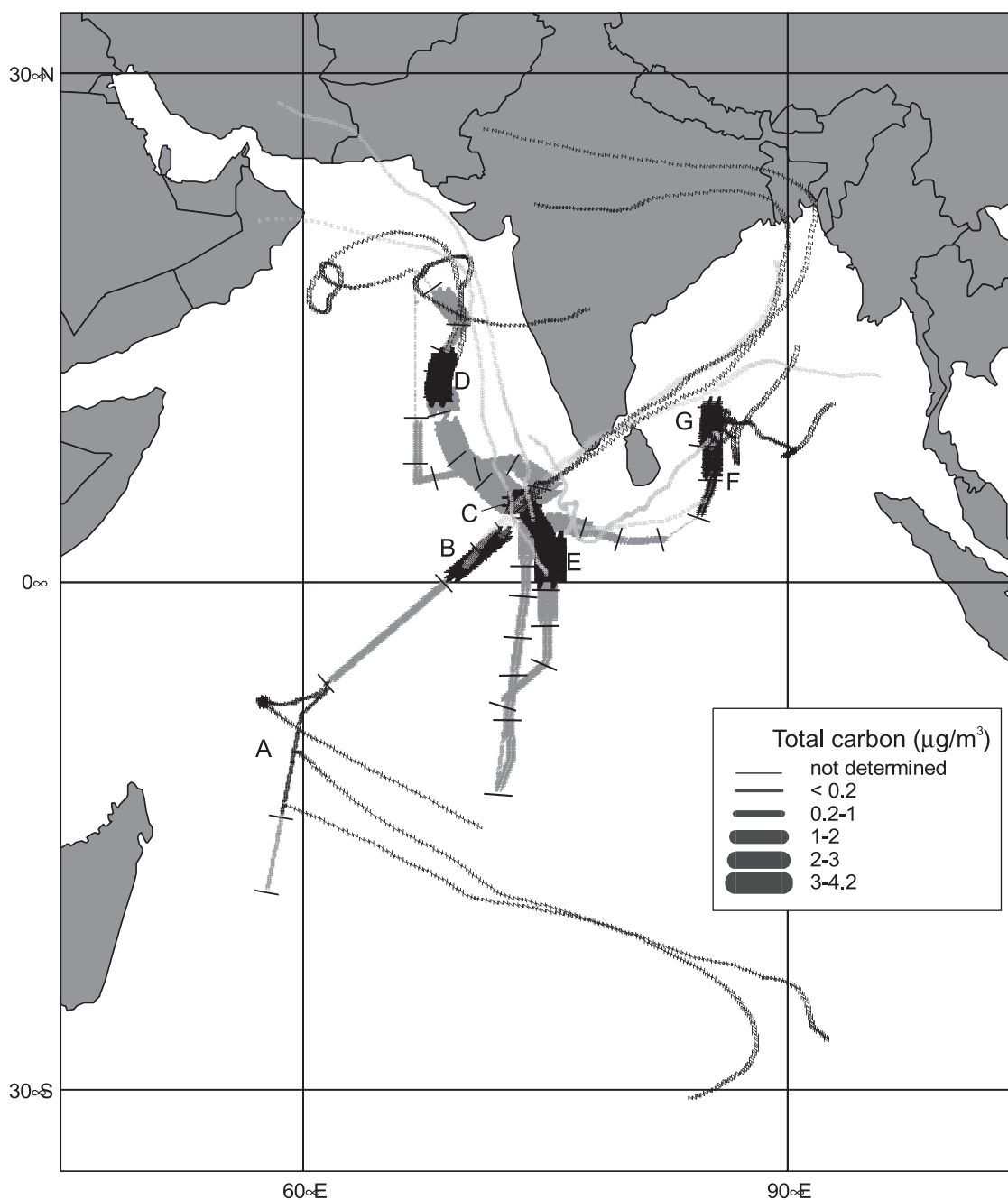
[23] Compared to extraction methods thermal desorption methods are easier to practice, in fact they seem to be the only reliable method for impactor samples since extraction of impactor foils bears the risk of washing away part of the sample.

[24] With thermal desorption methods a main difficulty consists of the definition of an OC/EC separation point that enables complete OC volatilization without EC losses or EC artifact formation by charring processes during volatilization.

[25] From test series with organic compounds relevant in atmospheric processes it was evident that 590°C over 8 min may not be sufficient for quantitative volatilization in all cases. For methanesulfonate (MSA) or dicarboxylic acids losses of 5–20% were observed, whereas PAHs like pyrene or benzo[ghi]perylene were found to be volatilized quantitatively. Higher temperatures up to 850°C led to higher OC yields indicating that the incomplete OC determination was not only caused by charring processes during heating but also by incomplete volatilization. Detailed results will not be presented here since the degree of volatilization of ionic compounds (accounting for the least volatile species) strongly depends on total ionic composition. For example, oxalic acid, a major aerosol constituent (see below), will dissociate in wet particles and, in the presence of calcium (as part of sea salt), possibly form the less soluble calcium oxalate. This species decomposes by heating to form CaCO<sub>3</sub> (which is stable against further thermal decomposition up to 650°C and higher) and CO (which will be measured as CO<sub>2</sub>). Thus, in the case of total transformation to calcium oxalate only 50% of oxalic acid would be determined as OC. Comparable reactions might occur for other ionic compounds. Such phenomena have been observed in the analysis of atmospheric aerosol particles [Novakov and Corrigan, 1995].

[26] With respect to oxidizing methods for the separation of OC and EC the volatilization procedure used here has the important advantage of being short in time (8 min versus 1–3 h) which makes it suitable for the large number of samples resulting from size-fractionating and long term analysis. Nevertheless, charring is expected to be higher. This means that the method applied here provides a lower limit for OC and upper limit for EC. Higher OC volatilization temperatures result in higher OC/EC ratios. For some samples in central Europe the difference between 590°C and 650°C has been determined to be in the range of 15%. However, an upper temperature limit of about 650°C due to the melting point of aluminum exists.

[27] In summary, there is no generally accepted procedure for OC/EC separation until now, all results are depending of the method applied and therefore results from different experiments are difficult to compare. The method used here leads typically to lower OC/EC ratios compared to related techniques. However, the lack of positive sampling artifact



**Figure 1.** Total carbon concentration (OC + EC, submicrometer + supermicrometer) along the Ronald H. Brown cruise trip during INDOEX. The dark marked parts indicate periods with organic specification (A–G). For the beginning and the end of these samples, isentropic 7-day backtrajectories ending in 950 hPa are shown. The ship position is indicated for the start and stop times of the carbon samples.

and the short analysis time provides are main advantages of the applied methods. The OC/EC determination development and characterization will be discussed elsewhere in more detail [Gnauk et al., in preparation].

[28] To convert organic carbon (OC) to organic matter (OM) a conversion factor of 1.6 is used. This value results from an estimation for strongly anthropogenic influenced aerosols based on a recent study by *Turpin and Lim* [2000]. Although the specification of organic material that the cited study is based on was incomplete, such conversion factors are necessary to derive mass fractions of organic material.

The results discussed in this paper show that during the INDOEX campaign highly oxidized material (i. e. carboxylic acids that would result in a large conversion factor) was found to a much larger extent than low oxidized material (i. e. alkanes, PAHs etc. that would result in low conversion factors). Thus, the use of a factor of 1.6 is expected to be a conservative estimation of organic matter.

### 2.3. Absorption

[29] The absorption for submicrometer and supermicrometer particles was determined at 550 nm and 55% RH by



**Table 1.** Number of Samples, Concentration of OC and EC, Mass Fraction of OM and EC, and Absorption Coefficient for the Different Air Masses

	Southern Indian Ocean <sup>a</sup> ( <i>n</i> = 3) <sup>b</sup>		Indian Subcontinent ( <i>n</i> = 6)		Arabia/Indian Subcontinent ( <i>n</i> = 9)		Northern Indian Ocean ( <i>n</i> = 5)		Arabian Sea/Coastal India ( <i>n</i> = 3)		Bay of Bengal ( <i>n</i> = 2)	
	Sub	Super	Sub	Super	Sub	Super	Sub	Super	Sub	Super	Sub	Super
TC conc. [ $\mu\text{g}/\text{m}^3$ ]	0.05	0.08	2.47	0.73	1.06	0.69	0.19	0.40	0.76	0.39	1.20	0.18
OC conc. [ $\mu\text{g}/\text{m}^3$ ]	0.04	0.07	0.81	0.61	0.55	0.59	0.08	0.36	0.35	0.33	0.46	0.13
EC conc. [ $\mu\text{g}/\text{m}^3$ ]	0.01	0.01	1.67	0.12	0.51	0.10	0.12	0.04	0.41	0.05	0.74	0.05
OC/EC ratio	3.4	6.6	0.5	5.1	1.1	5.9	0.7	8.7	0.8	6.6	0.6	2.7
Mass fraction of OM [%]	5.0	1.6	6.6	11.1	9.6	5.9	3.9	5.5	6.7	8.5	5.5	4.9
Mass fraction of EC [%]	0.9	0.2	8.5	1.4	5.6	0.6	3.6	0.4	5.0	0.8	5.6	1.1
Mass fraction of TCM <sup>c</sup> [%]	5.9	1.8	15.1	12.5	15.2	6.5	7.5	5.9	11.7	9.3	11.1	6.0
Abs. coeff. [ $10^{-6} \text{ m}^{-1}$ ]	0.24	0.01 <sup>d</sup>	16.3	0.83 <sup>d</sup>	6.5	0.25 <sup>d</sup>	2.0	0.09 <sup>d</sup>	5.8	0.37 <sup>d</sup>	11.7	0.66 <sup>d</sup>

<sup>a</sup> Best estimate: detection limit for these sampling periods (95%-level): OC:  $0.06 \mu\text{g}/\text{m}^3$ , EC:  $0.02 \mu\text{g}/\text{m}^3$ .

<sup>b</sup> *n* = number of samples.

<sup>c</sup> Total carbonaceous matter TCM = OM + EC.

<sup>d</sup> Difference of total and submicrometer absorption coefficients.

measuring the change in transmission through a filter with a Particle Soot Absorption Photometer (PSAP, Radiance Research). Measured values were corrected for scattering, spot size, flow rate and the manufacturer's calibration according to *Anderson et al.* [1999] and *Bond et al.* [1999].

#### 2.4. Organic Specification

[30] Aliphatic and hydroxylated organic acids as well as semivolatile compounds were determined using a combined method of capillary electrophoresis (CE) and Curie point pyrolysis-gas chromatography/mass spectrometry (CPP-GC/MS). Both methods require only small sample amounts and avoid extensive purification or derivatization procedures.

[31] Briefly, for determination of organic acids the Tedlar films were cut into small pieces and leached into 0.75 mL pure water. After filtration the solutions were analyzed by capillary zone electrophoresis with indirect UV detection. A *p*-amino-benzoic acid based electrolyte (pH 9.5) and detection at 254 nm is applied. Quantification is performed by comparing the peak areas with those of external standards.

[32] Semivolatile compounds were determined by heating the exposed Pyrofoil<sup>®</sup> (Fe-Ni-alloy) rapidly due to absorption of a radio frequency magnetic field by the ferromagnetic material. At the Curie point temperature (here  $590^\circ\text{C}$ ), which is reached within milliseconds, the ferromagnetism changes to paramagnetism and the heating effect ceases. The volatile and semivolatile organic compounds evaporate from the foil and are flushed into the GC by helium. The substances were separated by a CP-Sil-5 capillary and identified by a quadrupole mass spectrometer with an electron impact ionization source (Trio 1000). The quantification is performed by comparing the peak areas with those of internal deuterated standards and calculating response factors with external standards, respectively. The methods are described in detail in the work of *Neusüß et al.* [2000a].

#### 2.5. Mass

[33] Particle mass was obtained by weighing the substrates before and after sampling. A Cahn Model 29 microbalance was used at a relative humidity of  $33 \pm 3\%$ . Thus, the mass includes water associated with the sampled particles at 33% RH. A detailed description of the weighing procedure is given by *Quinn and Coffmann* [1998].

[34] The weighing was performed for samples taken by a two stage impactor resulting in mass concentrations for supermicrometer particles ( $D_p = 1.1\text{--}10 \mu\text{m}$ ) and submicrometer particles ( $D_p < 1.1 \mu\text{m}$ ). Therefore, the submicrometer mass includes particles with  $D_p < 0.18 \mu\text{m}$ , in contrast to the submicrometer carbon mass. From mass size distributions with 7-stage impactors (as for the size segregated carbon with a filter behind the last stage) a factor converting the mass of particles with  $D_p < 1.1 \mu\text{m}$  to the mass of particles with  $D_p = 0.18\text{--}1.1 \mu\text{m}$  can be derived. This factor was determined to be  $0.95 \pm 0.01$  and  $0.85 \pm 0.05$  for polluted and clean air masses, respectively, and was used for correction.

### 3. Results

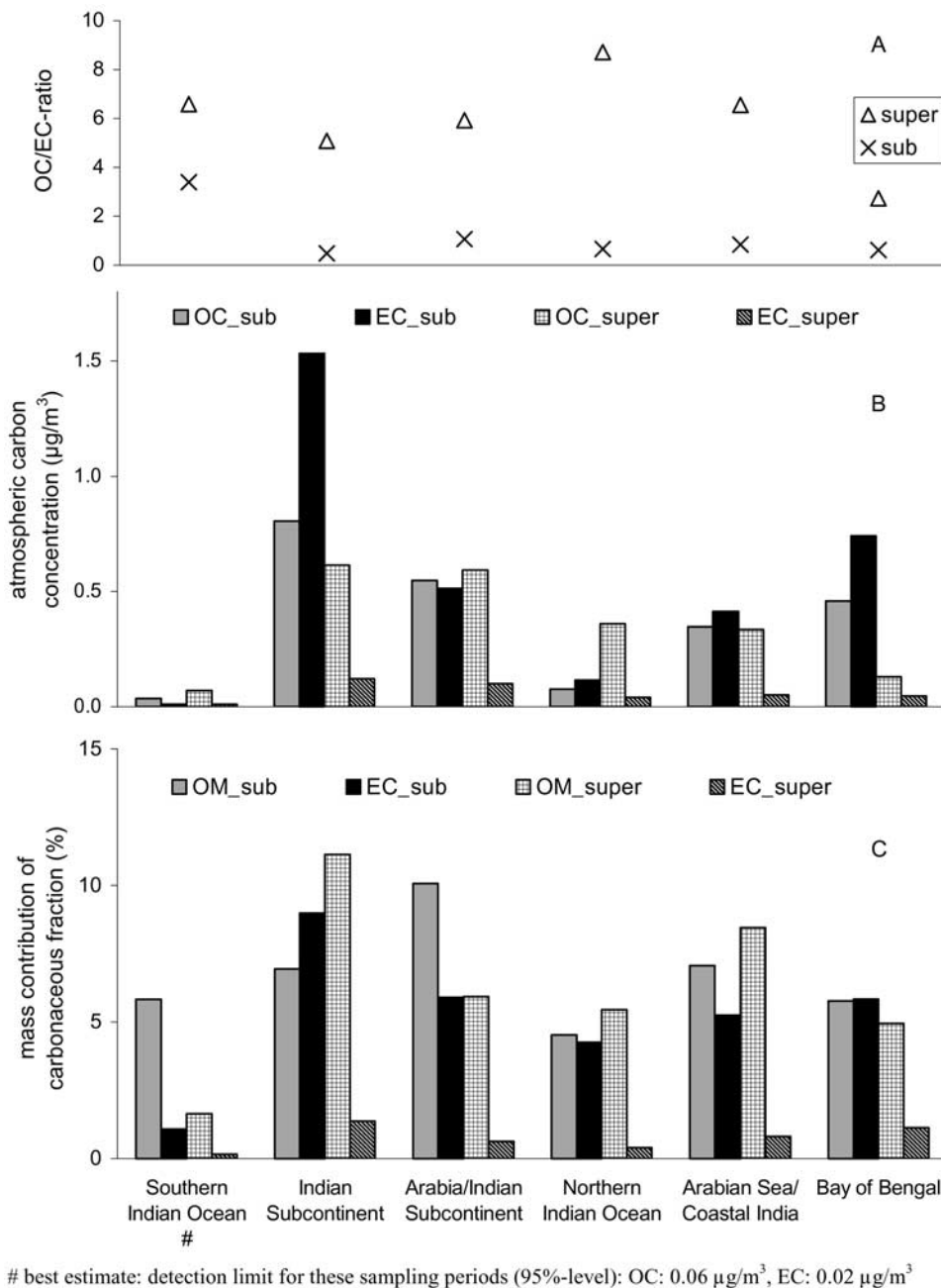
#### 3.1. Meteorological Context

[35] In Figure 1 the cruise track of the Ronald H. Brown during INDOEX is shown. The results of the organic specification of the dark colored sampling periods (A–G) will be presented and discussed below. For the latter samples back trajectories ending in 500 m calculated with HY-SPLIT 4 are shown [cf. *Quinn et al.*, 2002b] (available at <http://www.noaa.gov/ready-bin/fnl.pl>).

[36] Despite an southwesterly flow bringing pristine air from the southern Indian Ocean in the beginning of the cruise, a northerly to westerly airflow generally dominated. Thus continentally air mainly from India was transported over a large part of the Indian Ocean. Air and seawater temperature were always higher than  $25^\circ\text{C}$ , partly slightly above  $30^\circ\text{C}$ . The relative humidity was mostly higher than 70%. Only short rain events occurred on the first leg between Mauritius and the Maldives and in the Gulf of Bengal, however, probably only accounting for a reasonable wash out in the latter case. For details of the meteorological circumstances see the work of *W. P. Ball et al.* (Bulk and size-segregated aerosol composition: Continental impacts during INDOEX 1999, submitted to *Journal of Geophysical Research*, 2001).

#### 3.2. Organic and Elemental Carbon

[37] Along with the cruise track the total carbon (TC) concentration is shown in Figure 1. The TC concentration



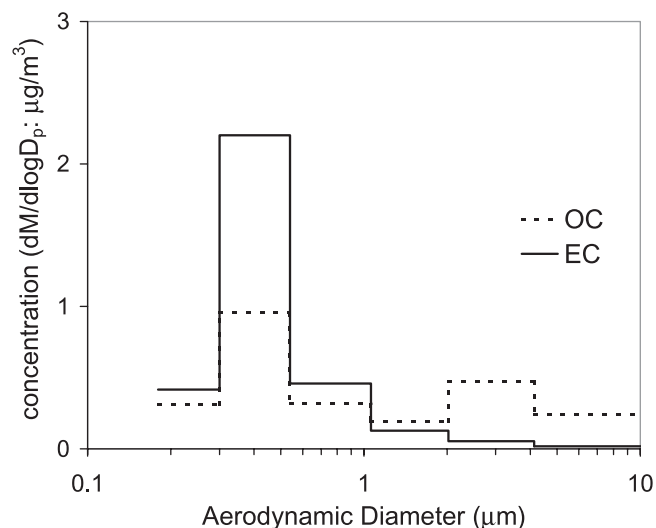
**Figure 2.** Submicrometer and supermicrometer OC/EC ratio (A), carbon concentration (B), and mass fraction (C) for different air masses.

ranged between only partly detected (supermicrometer OC) on the order of magnitude of  $0.1 \mu\text{g}/\text{m}^3$  in the southern Indian Ocean to more than  $4 \mu\text{g}/\text{m}^3$  southwest of India in the area of the Maldives. These differences are due to distinctly different air masses encountered by the research vessel during the cruise through the Indian Ocean.

[38] The main data on carbon concentration and content and absorption coefficients of the particles for different air masses are summarized in Table 1. Furthermore, OC and EC concentrations (2 a) and OM and EC mass fractions (2 b) for the different air masses are shown in Figure 2. The air mass categories “East Indian Subcontinent” and “Central Indian Subcontinent” used by Quinn *et al.* [2002b] are

combined into “Indian Subcontinent” here and the air mass category “Arabia” is not used due to the lack of data.

[39] The atmospheric concentration of carbon for air masses from the southern hemisphere is much lower than for air masses from the northern hemisphere. This is most pronounced for EC, which is up to more than two orders of magnitude higher in the Indian Ocean during airflow from the north. In these air masses the concentration of OC in coarse particles, which are dominated by sea salt particles [Quinn *et al.*, 2002b] is a factor of 5–10 higher than in the pristine southern air. The samples of the Bay of Bengal air masses, however, show only a slight increase in supermicrometer OC concentration compared to the southern



**Figure 3.** Example of the size distribution of organic and elemental carbon during INDOEX (AS-Coastal India).

hemisphere air masses. EC is found mainly in submicrometer particles, whereas OC is found both in sub- and supermicrometer particles.

[40] An example of the size distribution of OC and EC for the “Arabian Sea/Coastal India” air mass is presented in Figure 3. EC shows a maximum in the size range  $0.3 \mu\text{m} < D_p < 0.54 \mu\text{m}$ . OC has its maximum in the same size fraction but in addition a second maximum in the range  $2 \mu\text{m} < D_p < 4.1 \mu\text{m}$  corresponding to the sea salt mode. A very similar size distribution both for OC and EC is observed for a sample from “Arabian Sea/Indian Subcontinent”, which was taken 13 days earlier. The submicrometer maximum is very weak and shifted to larger particles ( $0.54 \mu\text{m} < D_p < 1.1 \mu\text{m}$ ) in the third sample, which was taken at the farthest north in the Arabian sea, with very low carbon concentrations.

### 3.3. Organic Species

[41] By CPP-GC/MS alkanes, fatty acids and partly polycyclic aromatic hydrocarbons (PAHs) could be detected. Fatty acids, however, could not be quantified due to bad peak shapes in the GC. PAHs have been detected in levels close to the detection limit in samples B, C, and G. Phenanthrene showed the highest concentration, followed by fluoranthene and pyrene, respectively. Concentrations were higher in submicrometer particles compared to supermicrometer particles. The sum of these three species for sub- and supermicrometer particles was in the range of  $0.2\text{--}0.5 \text{ ng/m}^3$ .

[42] The typical pattern of alkanes is shown in Figure 4. Only small differences between the various air masses were observed both for the pattern and the concentration of alkanes. Hence, no concentration of single alkanes are reported.

[43] The anions of oxalic ( $C_2$ ), malonic ( $C_3$ ), succinic ( $C_4$ , including methylmalonic acid), tartaric ( $C_3\text{OH}$ ), malic acid ( $C_4\text{OH}$ ), tartaric ( $C_4(\text{OH})_2$ ) and methanesulfonic acid (MSA) were found regularly. In some samples glutaric ( $C_5$ ), adipic ( $C_6$ ) and azelaic acid ( $C_9$ ), including their respective isomers, were tentatively identified.

[44] The concentrations of organic acids measured during INDOEX are shown in Table 2. The area of sampling can be identified from Figure 1. The first sample (A) corresponds to air masses from the southern hemisphere. All the others are more or less anthropogenically influenced from the Indian subcontinent and regions nearby, thus leading to representative values for organics measured in northern hemisphere air masses during INDOEX.

[45] Organic acid concentrations are lowest for the clean case and highest for those samples where the mass and carbon concentrations are highest as well (cp. Figure 2).

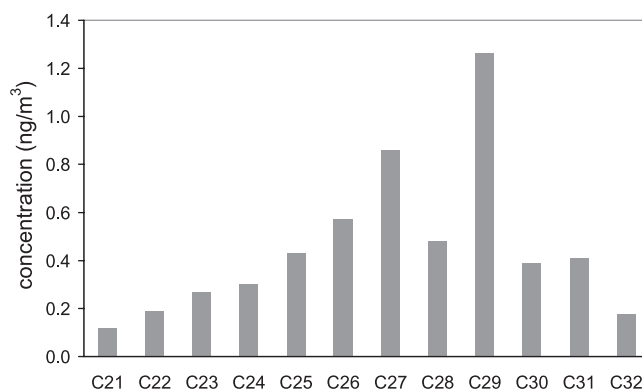
[46] Oxalic acid is the most abundant organic acid in aerosol particles, followed by malonic and succinic acid for coarse mode particles. Nevertheless, malic and tartaric acid are almost as concentrated and sometimes exceed the oxalic acid concentration in submicrometer particles.

## 4. Discussion

### 4.1. Organic and Elemental Carbon

[47] The OC/EC ratios (Table 1) are between 3 and 7 for clean air masses and supermicrometer particles in the polluted case, which can be attributed to the low EC content in this particles. Low OC/EC ratios ( $0.5\text{--}1.1$ ) are found for submicrometer particles in the polluted air masses, which is similar to values found in central Europe by applying the same analytical method [Neusüß *et al.*, 2002]. OC/EC ratios close to 1 also were found in urban aerosols by Countess *et al.* [1981] and Ohta *et al.* [1998], where the first group applied a similar analytical procedure as described here. However, higher OC/EC ratios even close to source were observed in several other studies [Gray *et al.*, 1986; Brémond *et al.*, 1989; Crutzen and Andreae, 1990; Castro *et al.*, 1999]. The differences are expected to be at least partly due to different sampling and analytical methods. However, the low OC/EC ratios found here are close to those observed during INDOEX by Mayol-Bracero *et al.* [2002], applying a different sampling and analytical approach.

[48] Concentrations of particulate carbon measured in marine environments have been reviewed by Penner [1995]. For the southern marine hemisphere organic carbon concentrations of  $0.13\text{--}0.23 \mu\text{g/m}^3$  (one value of  $0.53 \mu\text{g/m}^3$ ) are reported. Our values for comparable air masses



**Figure 4.** Alkane pattern of submicrometer particles of sample C.

**Table 2.** Concentration of Organic Species in Seven Samples During the Cruise<sup>a</sup>

	A Southern Indian Ocean		B Indian Subcontinent		C Indian Subcontinent		D Arabia/Indian Subcontinent		E Arabia/Indian Subcontinent		F Arabian Sea/Coastal India		G Bay of Bengal	
	Sub	Super	Sub	Super	Sub	Super	Sub	Super	Sub	Super	Sub	Super	Sub	Super
Oxalate	0.9	18	18	90	59	98	47	77	23	171	17	25	20	55
Tartrate	n.d.	n.d.	n.d.	2.5	8.9	n.d.	8.3	n.d.	3.3	n.d.	1.3	n.d.	2.8	n.d.
Malonate	n.d.	8.6	n.d.	35	13	47	3.6	33	2.5	41	2.7	11	1.6	8.2
Tartrate	n.d.	1.8	21	n.d.	55	n.d.	28	n.d.	19	n.d.	9.8	n.d.	6.4	n.d.
Malate	n.d.	1.2	15	5.4	51	8.7	21	4.4	13	8.2	8.0	n.d.	9.3	1.5
Succinate <sup>b</sup>	n.d.	n.d.	n.d.	5.5	7.8	9.3	2.2	11	n.d.	14	n.d.	n.d.	n.d.	2.2
Glutarate <sup>b</sup>	n.d.	n.d.	4.9	n.d.	14	n.d.	3.9	2.7	4.3	n.d.	n.d.	n.d.	2.6	n.d.
Adipinate <sup>b</sup>	n.d.	n.d.	2.6	n.d.	11	n.d.	2.0	1.0	2.4	n.d.	n.d.	n.d.	2.0	n.d.
Σ carboxylic acids	0.9	29	61	139	219	163	116	129	66	234	39	36	44	67
MSA	9.2	28	22	3.1	33	5.5	28	5.9	2.2	4.2	12	n.d.	16	n.d.

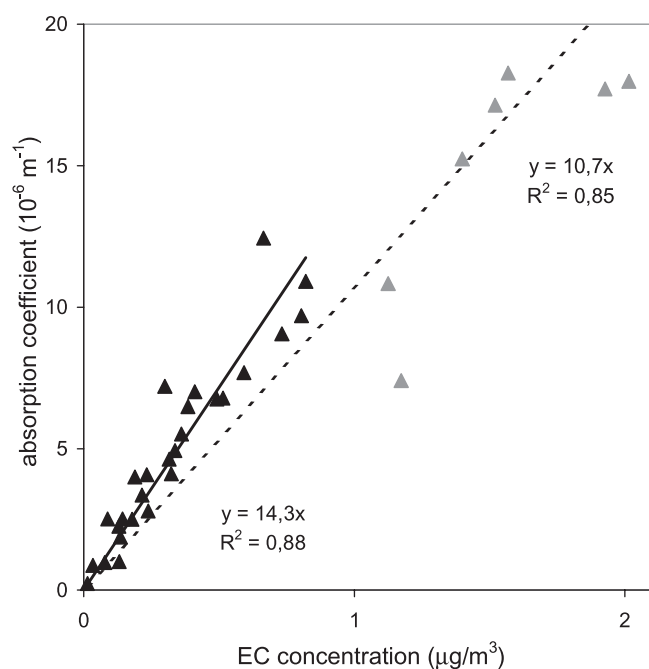
<sup>a</sup> All values are expressed in ng/m<sup>3</sup>.  
<sup>b</sup> Including isomers of same carbon numbers.

are at the lower limit of these concentrations. OC is mostly associated with supermicrometer particles, containing mainly sea salt. Since sea salt concentration depends strongly on wind speed [Fitzgerald, 1991] a variation in OC concentration with wind speed is expected, but could not be observed here, due to few samples without pollution influence. Penner [1995] summarized OC concentrations for 12 remote marine locations in the northern hemisphere, resulting in mean values of 0.2–0.8 μg/m<sup>3</sup>. Our measurements in the northern Indian Ocean resulted in mean values for the different air masses in the range of 0.4–1.2 (Figure 2). The EC concentrations measured here in the northern hemisphere are similar to remote continental concentrations in the United States [Penner, 1995] and to measurements in Falkenberg, Germany during the Lindenberg Aerosol Characterization Experiment (LACE) [Neusüß et al., 2002].

[49] For the different trajectory groups the differences in the atmospheric concentrations are much higher than those in their mass fraction contribution (Figure 2). This indicates that the change in the carbon concentration is dominated by phenomena that affect all chemical components, like dilution, dry and wet deposition. However, slightly higher mass fractions of carbon are found for air masses with higher carbon concentrations. The carbonaceous fraction of particulate mass for the polluted air masses is in the range of 8–15% for submicrometer particles (6–12% for supermicrometer particles). This is lower than what is generally observed in anthropogenically influenced continental air masses close to sources [e.g., Gray et al., 1986; Heintzenberg, 1989; Eatough et al., 1996; Neusüß et al., 2002]. The differences cannot be explained by the occurrence of seasalt, since seasalt does not account for a large fraction of submicrometer particles [Quinn et al., 2002b]. Nevertheless, the fact that the carbon amount over the northern Indian Ocean is somewhat higher than what was observed in aged anthropogenically influenced marine air masses from Europe during ACE-2 [Quinn et al., 2000] implies that the ratio of carbonaceous to sulfur emission (gaseous plus particulate phase) is higher in southern Asia than it is in Europe. The reason is probably the higher degree of biomass burning in Southeast Asia (S. A. Guazzotti et al., Characterization of pollution outflow from India and Arabia: Biomass burning and fossil fuel combustion, submitted to *Journal of Geophysical Research*, 2001, hereinafter referred to as Guazzotti et al., submitted manuscript, 2001) compared to Europe, which is in agreement with estimates based on emission budgets [Penner et al., 1993; Mayol-Bracero et al., 2002; Dickerson et al., 2002; M. Reddy and S. Venkataraman, A 0.25° × 0.25° inventory of aerosol and sulphur dioxide emissions from India, I, Fossil fuel combustion, submitted to *Atmospheric Environment*, 2001; M. Reddy and S. Venkataraman, A 0.25° × 0.25° inventory of aerosol and sulphur dioxide emissions from India, II, Biomass combustion, submitted to *Atmospheric Environment*, 2001]. Examples of aerosol composition showing lower amounts of soluble ions in India [Kulshrestha et al., 1998] than in Europe [Neusüß et al., 2002] confirm this conclusion.

[50] The absorption of submicrometer particles measured with a PSAP is correlated to the EC concentration (submicrometer) for all INDOEX samples in Figure 5. For low carbon concentrations (EC < 1 μg/m<sup>3</sup>) a good regression is





**Figure 5.** Absorption coefficient versus EC concentration for submicrometer particles during INDOEX.

found. An absorption efficiency of around  $14 \text{ m}^2/\text{g}$  is found for all air masses except the most polluted cases (“Indian Subcontinent”). Absorption efficiencies are summarized for different air masses and size classes in Table 3.

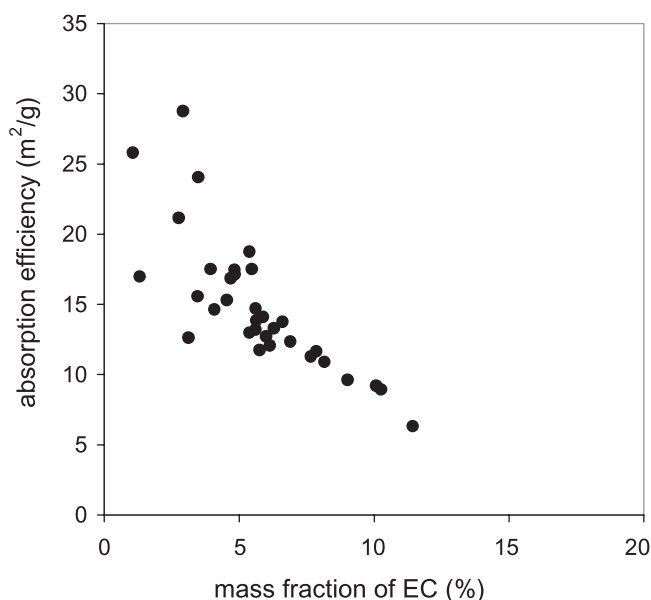
[51] The good correlation indicates the following. First, EC is responsible for most of the absorption of the aerosol. Second, absorption and EC measurements are in principle internally consistent. Furthermore, the absorption efficiencies obtained here are comparable to the mean level of previous studies [Lioussé *et al.*, 1993]. Nevertheless, the absorption efficiency depends on the methods used. Other OC/EC-separations, using oxygen or accounting for charring effects, usually lead to lower EC-fractions. To correct here for this would increase the absorption efficiency to levels above those previously reported of about  $10 \text{ m}^2/\text{g}$  [Lioussé *et al.*, 1993; Petzold *et al.*, 1997]. The difference could be due to low mass fractions of EC during INDOEX, compared to measurements close to sources and a higher degree of mixing of absorbing carbon with scattering

**Table 3.** Absorption Efficiency for Different Air Masses and Particle Size<sup>a</sup>

Air Mass Type	Absorption Efficiency, $\text{m}^2/\text{g}$	
	$D_p < 1.1 \mu\text{m}$	$D_p < 10 \mu\text{m}$
Southern Indian Ocean	...	...
Indian Subcontinent	$10 \pm 1$	$10 \pm 2$
Arabia/Indian Subcontinent	$15 \pm 5$	$13 \pm 4$
Northern Indian Ocean	$15 \pm 2^b$	$13 \pm 3$
Arabian Sea/Coastal India	$14 \pm 3$	$13 \pm 3$
Bay of Bengal	$16 \pm 4$	$16 \pm 4$

<sup>a</sup>The range given corresponds to one standard deviation.

<sup>b</sup>One outlier ( $29 \text{ m}^2/\text{g}$ ) removed.



**Figure 6.** Absorption efficiency versus mass fraction of EC for submicrometer particles.

material, what is necessary to yield absorption efficiencies of larger than  $10 \text{ m}^2/\text{g}$  [Martins *et al.*, 1998; Fuller *et al.*, 1999] and what was observed by means of single particle analysis by Guazzotti *et al.* (submitted manuscript, 2001). This view is further confirmed by the dependence of the absorption efficiency on the mass fraction of EC as shown in Figure 6. The decrease of the absorption efficiency with the increase of mass is likely to be due to an internal mixture of absorbing material [Lioussé *et al.*, 1993] and has also been found by Petzold *et al.* [1997]. Moreover, theoretical calculations by Martins *et al.* [1998] confirm the quantity of the measured absorption efficiency. During INDOEX 5% EC content lead to an absorption efficiency of around  $15 \text{ m}^2/\text{g}$  (Figure 6). For particles in the size range around  $0.3 \mu\text{m} < D_p < 0.5 \mu\text{m}$  (maximum in the observed size-distribution in Figure 3) with 5% EC the calculations by Martins *et al.* [1998] using a core-shell model yield absorption efficiencies around  $15 \text{ m}^2/\text{g}$ .

#### 4.2. Organics

[52] To obtain hints on the sources of the particles odd-even-number of the alkanes (carbon preference index, CPI) were calculated. Independent of particle size the CPI values were found to be in the range of 1–2, being indicative of mainly anthropogenic input. Fossil fuel emissions lead to CPI indices close to 1.0 [Simoneit and Mazurek, 1982]. For alkanes, emitted from plant waxes, CPI-values up to 11 are described [Schneider and Gagosian, 1985; Simoneit, 1989]. But the lack of odd to even carbon number preference may not necessarily be the sign of anthropogenic origin, as n-alkanes from the marine biota also show CPIs close to one, though at a much lower concentration levels [Eichmann *et al.*, 1979].

[53] The concentration of low molecular weight dicarboxylic acids measured in the pristine Indian Ocean is similar to values measured under clean conditions in the Pacific

**Table 4.** Account of Organic Compound Classes as Part of Mass, OC, and TC

	A (Clean)		B-G (Polluted)	
	Sub	Super	Sub <sup>a</sup>	Super <sup>a</sup>
	<i>Fraction of Mass, %</i>			
C <sub>2</sub> -C <sub>6</sub> dicarb. acids	0.1	0.7	0.30 (0.19-0.52)	1.54 (0.54-2.17)
C <sub>3</sub> -C <sub>4</sub> hydroxyl. dicarb. acids	0.0	0.1	0.38 (0.14-0.57)	0.05 (n.d.-0.13)
Σ alkanes	0.7	0.2	0.07 (0.03-0.11)	0.14 (0.03-0.71)
MSA	0.8	0.8	0.17 (0.12-0.29)	0.03 (n.d.-0.05)
Total	1.6	1.8	0.98 (0.56-1.32)	1.83 (0.66-2.81)
	<i>Fraction of OC, %</i>			
C <sub>2</sub> -C <sub>6</sub> dicarb. acids	b	15.0	2.5 (0.9-3.1)	6.0 (3.9-14.5)
C <sub>3</sub> -C <sub>4</sub> hydroxyl. dicarb. acids	b	1.9	2.9 (1.1-4.3)	0.4 (n.d.-0.5)
Σ alkanes	b	10.9	1.2 (0.5-2.7)	2.6 (0.8-19.7)
MSA	b	6.7	0.5 (0.2-0.8)	0.06 (n.d.-0.1)
Total	b	34.5	8.1 (2.8-8.5)	8.9 (6.4-34.6)
	<i>Fraction of TC, %</i>			
C <sub>2</sub> -C <sub>6</sub> dicarb. acids	b	13.0	1.1 (0.5-1.6)	4.7 (3.3-10.6)
C <sub>3</sub> -C <sub>4</sub> hydroxyl. dicarb. acids	b	1.7	1.2 (0.5-1.7)	0.3 (n.d.-0.4)
Σ alkanes	b	9.5	0.6 (0.2-1.1)	2.2 (0.8-14.4)
MSA	b	5.9	0.2 (0.1-0.4)	0.06 (n.d.-0.1)
Total	b	30.1	3.1 (1.5-4.2)	6.9 (6.2-25.4)

<sup>a</sup>Median (range).

<sup>b</sup>Carbon below detection limit.

[Matsumoto *et al.*, 1998; Kawamura and Sakaguchi, 1999], in the Arctic [Talbot *et al.*, 1992; Li and Winchester, 1993; Kerminen *et al.*, 1999] and in the North Atlantic [Neusüß *et al.*, 2000c] (C<sub>2</sub>: 6-24 ng/m<sup>3</sup>). Lower values have only been reported for the Antarctic and Arctic, C<sub>2</sub>: 2-10 ng/m<sup>3</sup> [Kawamura *et al.*, 1996a,b]. These values are relatively close together and seem to be the result of a chemistry in remote areas. The concentration of the carboxylic acids in the polluted air masses during INDOEX (Table 2) is in the same range as observed for relatively unpolluted locations in Europe [e.g., Mészáros *et al.*, 1997; Kerminen *et al.*, 2000; Neusüß *et al.*, 2000c], North America [Khawaja, 1995], or South Africa [Limbeck and Puxbaum, 1999], but lower than that what is partly found in urban aerosol samples [e.g., Sempéré and Kawamura, 1994; Souza *et al.*, 1999].

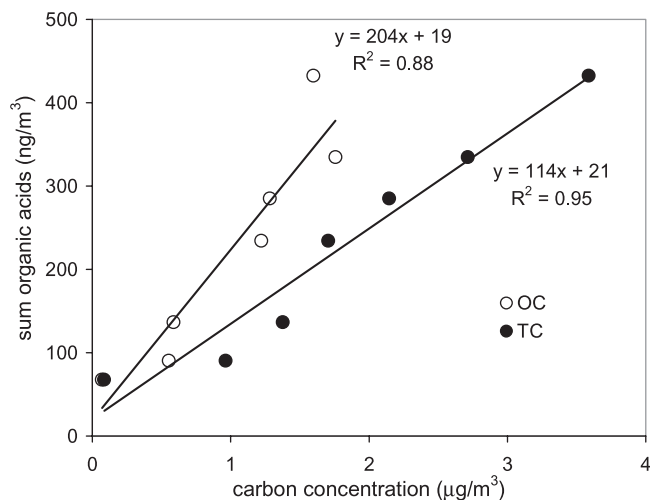
[54] The contribution of the selected organic compounds to OC, TC and mass is summarized in Table 4. The carboxylic acids account for 2-7% of the fine organic carbon and up to 15% of coarse OC. This is in the same range as measured in the highly polluted cities of Los Angeles (3-5% in fine particles [Rogge *et al.*, 1993a]) and Tokyo (4-15% for particles with  $D_p < 10 \mu\text{m}$  [Sempéré and Kawamura, 1994]).

[55] The contribution of the determined dicarboxylic acids to total particle mass ( $0.4 \geq 2\%$ ) also is in the same range as that measured by several groups in rural and urban areas in the USA and Japan [Rogge *et al.*, 1993a; Sempéré and Kawamura, 1994; Khawaja, 1995; Lawrence and Koutrakis, 1996].

[56] Especially low molecular weight nonhydroxylated dicarboxylic acids are found in the coarse mode. This is in agreement with measurements during ACE-2 [Neusüß *et al.*, 2000c], in the Pacific Ocean [Matsumoto *et al.*, 1998], and in the Arctic [Li and Winchester, 1993; Kerminen *et al.*, 1999]. This demonstrates the need of measurements up to  $D_p = 10 \mu\text{m}$  and avoidance of sampling only fine particles.

[57] The OC fraction of sea salt particles (coarse mode) is higher for polluted air masses. Short-chain carboxylic acids account for up to 15% of this OC. This indicates that the coarse mode OC consists in polluted cases mainly of secondary organic compounds, probably associated with sea salt particles.

[58] In Figure 7 the concentration of carboxylic acids versus organic and total carbon is shown for the sum of sub- and supermicrometer particles. The sum of dicarboxylic acids (as well as oxalic acid alone) show a linear dependence with both OC and TC. Furthermore the regressions through the datapoints confirms a linear dependence for nitrate ( $R^2 = 0.85$ ) and sulfate ( $R^2 = 0.67$ ). This indicates similar sources for dicarboxylic acids (and precursors) and particulate carbon, nitrate, and to a lesser extent, sulfate. Different conversion rates of precursors also


**Figure 7.** Regression of the sum of carboxylic acids to OC and TC.

may be responsible for the better correlation of carboxylic acids to nitrate relative to sulfate, since the sampled air masses are expected to have different ages with respect to anthropogenic emissions.

[59] The sources of low molecular weight dicarboxylic acids and even more hydroxylated dicarboxylic acids are still not well characterized. Several studies show that fossil fuel combustion is not an important source of dicarboxylic acids. Neither vehicles [Rogge *et al.*, 1993b; Schauer *et al.*, 1999] nor oil [Rogge *et al.*, 1997; Neusüß *et al.*, unpublished results, 2001], gas [Rogge *et al.*, 1993c], or coal burning (C. Neusüß *et al.*, unpublished results, 2001) emit significant amounts of low molecular weight dicarboxylic acids (C<sub>2</sub>–C<sub>4</sub>). Biomass burning seems to contribute to the atmospheric concentration of oxalate and probably other acids [Andreae *et al.*, 1988; Lefter *et al.*, 1994; Rogge *et al.*, 1994; Allen and Miguel, 1995; Narakuwa *et al.*, 1999], although it is not clear whether they are directly emitted.

[60] Generally, low molecular weight carboxylic acids are mainly photochemically produced in the atmosphere [Chebbi and Carlier, 1990], which is confirmed by reaction chamber results [Hatakeyama *et al.*, 1985, 1987; Behnke *et al.*, 1999] and modeling approaches [Schauer *et al.*, 1996]. However, the exact formation mechanisms are still unclear. Nevertheless, there are several indicators that the measured dicarboxylic acids during INDOEX are mainly produced photochemically in the atmosphere from gaseous precursors: The observed mass fraction of oxalate (0.4 ≥ 2%) is much higher than what is observed in biomass burning particles (0.01–0.15%) [Allen and Miguel, 1995]. Low molecular weight dicarboxylic acids are mainly found in the sea salt dominated coarse mode. Due to a low temperature of decomposition (138°C [Lide, 1992]) the occurrence of malonic acid (Table 2) cannot be explained by direct emission.

[61] Together with low amounts of alkanes and PAHs as primary pollutants, these facts indicate that the OC is at least partly photochemically produced in the atmosphere.

## 5. Conclusions

[62] Concentrations and mass fractions of organic carbon, elemental carbon and numerous organic species have been determined for submicrometer and supermicrometer particles in the Indian Ocean on the cruise of the R/V Ron Brown during INDOEX.

[63] A strong influence of southern Asia on the concentration of particulate carbonaceous material has been observed. OC concentration was typically more than one order of magnitude higher in the northern compared to the southern Indian Ocean, both for submicrometer and supermicrometer particles. EC was mostly found in submicrometer particles, increasing up to more than two orders of magnitude in the northern part compared to the southern part of the Indian Ocean. The mass fraction of carbonaceous material was in the range of 6–15% and 2–12% for submicrometer and supermicrometer particles, respectively, with the higher values for more polluted air masses.

[64] A high degree of mixing with scattering material in conjunction with low mass fractions of elemental carbon (relative to close-to-source measurements) results in high absorption efficiencies. The absorption efficiency is lower

for higher mass fractions (corresponding to higher concentrations) of elemental carbon.

[65] Differences in reaction pathway or vapor pressure are probably the reason for the occurrence of dicarboxylic acids in supermicrometer particles, whereas hydroxylated dicarboxylic acids show up mainly in submicrometer particles. A large amount of organic material is probably of secondary origin since alkanes and polycyclic aromatic hydrocarbons have been found only in small amounts. This is confirmed by the good correlation of the sum of carboxylic acids with OC, EC, nitrate, and, to a lesser extent, sulfate. However, low OC/EC ratios argue for the existence of primary OC. Source studies of OC and EC in Southeast Asia are badly needed.

[66] **Acknowledgments.** We thank Brigitte Gerlach for laboratory assistance and the crew of the R/V Ron Brown. Financial Support of the Bundesministerium für Bildung, Wissenschaft, Forschung und Technik (BMBF) under contract 01 LA-9830/0 is acknowledged. HH acknowledges support by the “Fonds der Chemischen Industrie”.

## References

- Allen, A. G., and A. H. Miguel, Biomass burning in the Amazon: Characterization of the ionic component of aerosols generated from flaming and smoldering rainforest and savannah, *Environ. Sci. Technol.*, **29**, 486–493, 1995.
- Anderson, T. L., D. S. Covert, J. D. Wheeler, J. M. Harris, K. D. Perry, B. E. Trost, D. J. Jaffe, and J. A. Ogren, Aerosol backscatter fraction and single scattering albedo: Measured values and uncertainties at a coastal station in the Pacific Northwest, *J. Geophys. Res.*, **104**, 26,793–26,807, 1999.
- Andreae, M. O., et al., Biomass-burning emissions and associated haze layers over Amazonia, *J. Geophys. Res.*, **93**, 1509–1527, 1988.
- Behnke, W., M. Elend, U. Krüger, and C. Zetzsch, The influence of NaBr/NaCl on the Br-catalysed production of halogenated radicals, *J. Atmos. Chem.*, **34**, 87–99, 1999.
- Berner, A., C. Lurzer, F. Pohl, O. Preining, and P. Wagner, The size distribution of the urban aerosol in Vienna, *Sci. Total Environ.*, **13**, 245–261, 1979.
- Berner, A., S. Sidla, Z. Galambos, C. Kruisz, R. Hitznerberger, H. M. ten Brink, and G. P. A. Kos, Modal character of atmospheric black carbon size distribution, *J. Geophys. Res.*, **101**, 19,559–19,565, 1996.
- Bond, T. C., T. L. Anderson, and D. Campbell, Calibration and intercomparison of filter-based measurements of visible light absorption by aerosols, *Aerosol Sci. Technol.*, **30**, 582–600, 1999.
- Brémond, M.-P., H. Cachier, and P. Buat-Ménard, Particulate carbon in the Paris region atmosphere, *Environ. Technol. Lett.*, **10**, 339–346, 1989.
- Cachier, H., M.-P. Brémond, and P. Buat-Ménard, Determination of atmospheric soot carbon with a simple thermal method, *Tellus*, **41B**, 379–390, 1989.
- Cadle, S. H., and P. J. Groblicki, An evaluation of methods for the determination of organic and elemental carbon in particulate samples, *Gen. Motors Res. Publ. GMR-3452*, Gen. Motors, Warren, Mich., 1980.
- Cadle, S. H., and P. A. Mulawa, Atmospheric carbonaceous species measurement methods comparison study: General Motors results, *Aerosol Sci. Technol.*, **12**, 128–141, 1990.
- Cadle, S. H., P. J. Groblicki, and D. P. Stroup, Automated carbon analyzer for particulate samples, *Anal. Chem.*, **52**, 2201–2206, 1980.
- Cadle, S. H., P. J. Groblicki, and P. A. Mulawa, Problems in the sampling and analysis of carbon particulate, *Gen. Motors Res. Publ. GMR-3935*, Gen. Motors, Warren, Mich., 1981.
- Castro, L. M., C. A. Pio, M. Harrison, and D. J. T. Smith, Carbonaceous aerosol in urban and rural European atmospheres: Estimation of secondary organic carbon concentrations, *Atmos. Environ.*, **33**, 2771–2781, 1999.
- Chebbi, A., and P. Carlier, 1996, Carboxylic acids in the troposphere, occurrence, sources, and sinks: A review, *Atmos. Environ.*, **30**, 4233–4249, 1990.
- Chow, J. C., J. G. Watson, L. C. Pritchett, W. R. Pierson, C. A. Frazier, and R. G. Purcell, The DRI thermal/optical reflectance carbon analysis system: Description, evaluation and applications in U.S. air quality studies, *Atmos. Environ.*, **27A**, 1185–1201, 1993.
- Countess, R. J., Interlaboratory analyses of carbonaceous aerosol samples, *Aerosol Sci. Technol.*, **12**, 114–121, 1990.



- Countess, R. J., S. H. Cadle, P. J. Groblicki, and G. T. Wolff, Chemical analysis of size-segregated samples of Denver's ambient particulate, *J. Air Pollut. Control Assoc.*, **31**, 247–252, 1981.
- Crutzen, P. J., and M. O. Andreae, Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, *Science*, **250**, 1669–1678, 1990.
- Dickerson, R. R., M. O. Andreae, T. Campos, O. L. Mayol-Bracero, C. Neusuess, and D. G. Streets, Analysis of black carbon and carbon monoxide observed over the Indian Ocean: Implications for emissions and photochemistry, *J. Geophys. Res.*, **107**(D19), 8017, doi:10.1029/2001JD000501, 2002.
- Duce, R. A., V. A. Mohnen, P. R. Zimmerman, D. Grosjean, W. Cautreels, R. Chatfield, R. Jaenicke, J. A. Ogren, E. D. Pellizzari, and G. T. Wallace, Organic material in the global troposphere, *Rev. Geophys. Space Phys.*, **21**, 921–952, 1983.
- Eatough, D. J., D. A. Eatough, L. Lewis, and E. A. Lewis, Fine particulate chemical composition and light extinction at Canyonland National Park using organic particulate material concentrations obtained with a multi-system, multichannel diffusion denuder sampler, *J. Geophys. Res.*, **101**, 19,515–19,531, 1996.
- Eichmann, R., P. Neuling, G. Ketseridis, J. Hahn, R. Jaenicke, and C. Junge, n-Alkane studies in the troposphere: I. Gas and particulate concentrations in the north Atlantic air, *Atmos. Environ.*, **13**, 587–599, 1979.
- Facchini, M. C., M. Mircea, S. Fuzzi, and R. J. Charlson, Cloud albedo enhancement by surface-active organic solutes in growing droplets, *Nature*, **401**, 257–259, 1999.
- Fitzgerald, J. W., Marine aerosols: A review, *Atmos. Environ.*, **25A**, 533–545, 1991.
- Fuller, K. A., W. C. Malm, and S. M. Kreidenweis, Effects of mixing on extinction by carbonaceous particles, *J. Geophys. Res.*, **104**, 15,941–15,954, 1999.
- Gray, H. A., G. R. Cass, J. J. Huntzicker, E. K. Heyerdahl, and J. A. Rau, Characteristics of atmospheric organic carbon and its elemental carbon particle concentration in Los Angeles, *Environ. Sci. Technol.*, **20**, 580–589, 1986.
- Hatakeyama, S., T. Tanonaka, J.-h. Weng, H. Bandow, H. Takagi, and H. Akimoto, Ozone-cycloalkene reactions in air: Quantitative analysis of particulate products and the reaction mechanism, *Environ. Sci. Technol.*, **19**, 935–942, 1985.
- Hatakeyama, S., M. Ohno, J.-h. Weng, H. Takagi, and H. Akimoto, Mechanism for the formation of gaseous and particulate products from ozone-cycloalkene reactions in air, *Environ. Sci. Technol.*, **21**, 52–57, 1987.
- Heintzenberg, J., Size-segregated measurements of particulate elemental carbon and aerosol light absorption at remote Arctic locations, *Atmos. Environ.*, **16**, 2461–2469, 1982.
- Heintzenberg, J., Fine particles in the global troposphere, a review, *Tellus*, **41B**, 149–160, 1989.
- Heintzenberg, J., D. S. Covert, and R. van Dingenen, Size distribution and chemical composition of marine aerosols: A compilation and review, *Tellus B*, **52B**, 1104–1122, 2000.
- Hering, S. V., et al., Comparison of sampling methods for carbonaceous aerosols in ambient air, *Aerosol Sci. Technol.*, **12**, 200–213, 1990.
- Huebert, B. J., and R. J. Charlson, Uncertainties in data on organic aerosols, *Tellus*, **52B**, 1249–1255, 2000.
- Huntzicker, J. J., R. L. Johnson, J. J. Shah, and R. A. Cary, Analysis of organic and elemental carbon in ambient aerosols by a thermal-optical method, in *Particulate Carbon: Atmospheric Life Cycle*, edited by G. T. Wolff and R. L. Klimisch, pp. 79–88, Plenum, New York, 1982.
- Iwatsuki, M. T. Kyotani, and K. Matsubara, Fractional determination of elemental carbon and total soluble and insoluble organic compounds in airborne particulate matter by thermal analysis combined with extraction and heavy liquid separation, *Anal. Sci.*, **14**, 321–326, 1998.
- Jacobsen, M. C., H.-C. Hansson, K. J. Noone, and R. J. Charlson, Organic atmospheric aerosols: Review and state of the science, *Rev. Geophys.*, **38**, 267–294, 2000.
- Japar, S. M., A. C. Szkarlat, R. A. Gorse Jr., E. K. Heyerdahl, R. L. Johnson, J. A. Rau, and J. J. Huntzicker, Comparison of solvent extraction and thermal-optical carbon analysis methods: Application to diesel vehicle exhaust aerosol, *Environ. Sci. Technol.*, **18**, 231–234, 1984.
- Johnson, R. L., J. J. Shah, R. A. Cary, and J. J. Huntzicker, An automated thermal-optical method for the analysis of carbonaceous aerosol, in *ACS Symposium Series 167*, pp. 223–233, Am. Chem. Soc., Washington, D.C., 1981.
- Kaneyasu, N., and S. Murayama, High concentration of black carbon over middle latitudes in the North Pacific Ocean, *J. Geophys. Res.*, **105**, 19,881–19,890, 2000.
- Kawamura, K., and F. Sakaguchi, Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, *J. Geophys. Res.*, **104**, 3501–3509, 1999.
- Kawamura, K., H. Kasukabe, and L. Barrie, Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations, *Atmos. Environ.*, **30**, 1709–1722, 1996a.
- Kawamura, K., R. Sempéré, Y. Imai, Y. Fujii, and M. Hayashi, Water soluble dicarboxylic acids and related compounds in Antarctic aerosols, *J. Geophys. Res.*, **101**, 18,721–18,728, 1996b.
- Kerminen, V.-M., K. Teinilä, R. Hillamo, and T. Mäkelä, Size-segregated chemistry of particulate dicarboxylic acids in the Arctic atmosphere, *Atmos. Environ.*, **33**, 2089–2100, 1999.
- Kerminen, V.-M., C. Ojanen, T. Pakkanen, R. Hillamo, M. Aurela, and J. Meriläinen, Low molecular weight dicarboxylic acids in an urban and rural environment, *J. Aerosol Sci.*, **31**, 349–362, 2000.
- Khwaja, H. A., Atmospheric concentrations of carboxylic acids and related compounds at a semiurban site, *Atmos. Environ.*, **29**, 127–139, 1995.
- Kleemann, M. J., L. S. Hughes, J. O. Allen, and G. R. Cass, Source contributions to the size and composition distribution of atmospheric particles: Southern California in September 1996, *Environ. Sci. Technol.*, **33**, 4331–4341, 1999.
- Kuhlbusch, T. A. J., Schwarzer Kohlenstoff aus Vegetationsbränden: Eine Bestimmungsmethode und mögliche Auswirkungen auf den globalen Kohlenstoffzyklus, Ph.D. thesis, Univ. of Mainz, Mainz, Germany, 1994.
- Kulshrestha, U. C., A. Saxena, N. Kumar, K. M. Kumari, and S. S. Srivastava, Chemical composition and association of size-differentiated aerosols at a suburban site in a semi-arid tract of India, *J. Atmos. Chem.*, **29**, 109–118, 1998.
- Lavanchy, V. M. H., H. W. Gäggeler, S. Nyeki, and U. Baltensperger, Elemental carbon (EC) and black carbon (BC) measurements with a thermal method and an aethalometer at the high-alpine research station Jungfraujoch, *Atmos. Environ.*, **33**, 2759–2769, 1999.
- Lawrence, J., and P. Koutrakis, Measurement and speciation of gas and particulate phase organic acidity in an urban environment, *J. Geophys. Res.*, **101**, 9159–9169, 1996.
- Lefer, B. L., R. W. Talbot, and R. C. Harris, Enhancement of acidic gases in biomass burning impacted air masses over Canada, *J. Geophys. Res.*, **99**, 1721–1737, 1994.
- Relieveld, J., et al., The Indian Ocean Experiment: Widespread air pollution from South and South-East Asia, *Science*, **291**, 1031–1036, 2001.
- Li, S. M., and J. W. Winchester, Water soluble organic constituents in Arctic aerosols and snow pack, *Geophys. Res. Lett.*, **20**, 45–48, 1993.
- Lide, D. R., (Ed.), *CRC Handbook of Chemistry and Physics*, 73rd ed., CRC Press, Boca Raton, Fla., 1992.
- Limbeck, A., and H. Puxbaum, Organic acids in continental background aerosols, *Atmos. Environ.*, **33**, 1847–1852, 1999.
- Lioussé, C., H. Cachier, and S. G. Jennings, Optical and thermal measurements of black carbon aerosol content in different environments: Variation of the specific attenuation cross-section, sigma ( $\sigma$ ), *Atmos. Environ.*, **27A**, 1203–1211, 1993.
- Malissa, H., H. Puxbaum, and E. Pell, Zur simultanen relativkonduktometrischen Kohlenstoff- und Schwefelbestimmung in Stäuben, *Fresenius Z. Anal. Chem.*, **282**, 109–113, 1976.
- Martins, J. V., P. Artaxo, C. Lioussé, J. S. Reid, P. V. Hobbs, and Y. Kaufman, Effects of black carbon content, particle size, and mixing on light absorption by aerosols from biomass burning in Brazil, *J. Geophys. Res.*, **103**, 32,041–32,050, 1998.
- Matsumoto, K., I. Nagao, H. Tanaka, H. Miyaji, T. Iida, and Y. Ikebe, Seasonal characteristics of organic and inorganic species and their size distributions in atmospheric aerosols over the northwest Pacific ocean, *Atmos. Environ.*, **32**, 1931–1946, 1998.
- Mayol-Bracero, O. L., R. Gabriel, M. O. Andreae, T. W. Kirchstetter, T. Novakov, J. A. Ogren, P. J. Sheridan, and D. Streets, Carbonaceous aerosols over the Indian Ocean during INDOEX: Chemical characterization, optical properties, and probable sources, *J. Geophys. Res.*, doi:10.1029/2000JD000039, in press, 2002.
- McMurry, P. H., and X. Q. Zhang, Size distributions of ambient organic and elemental carbon, *Aerosol Sci. Technol.*, **10**, 430–437, 1989.
- Mészáros, E., T. Barcza, A. Gelencsér, J. Hlavay, G. Kiss, Z. Krivácsy, A. Molnár, and K. Polyák, Size distribution of inorganic and organic species in the atmospheric aerosol, *J. Aerosol Sci.*, **28**, 1163–1175, 1997.
- Müller, K., A 3 year study of the aerosol in northwest Saxony (Germany), *Atmos. Environ.*, **33**, 1679–1685, 1999.
- Narukawa, M., K. Kawamura, N. Takeuchi, and T. Nakajima, Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, *Geophys. Res. Lett.*, **26**, 3101–3104, 1999.
- Neuroth, R., L. Laskus, and D. Dahmann, Interner VDI/DIN-Ringversuch zur Bestimmung von elementarem Kohlenstoff, *Gefährst. Reinhalt. Luft*, **59**, 91–94, 1999.
- Neusüß, C., M. Pelzing, A. Plewka, and H. Herrmann, A new analytical approach for size-resolved speciation of organic compounds in atmospheric aerosol particles: Methods and first results, *J. Geophys. Res.*, **105**, 4513–4527, 2000a.



- Neusüß, C., D. Weise, W. Birmili, H. Wex, A. Wiedensohler, and D. Covert, Size-segregated chemical, gravimetric and number distribution-derived mass closure of the aerosol in Sagres, Portugal during ACE-2, *Tellus*, 52B, 169–184, 2000b.
- Neusüß, C., E. Brüggemann, and H. Herrmann, Organic acids in atmospheric aerosol particles: Results from different field campaigns in Europe, *J. Aerosol Sci.*, 31, S238–S239, 2000c.
- Neusüß, C., H. Wex, W. Birmili, A. Wiedensohler, C. Koziar, B. Busch, E. Brüggemann, T. Gnauk, M. Ebert, and D. S. Covert, Characterization and parameterization of atmospheric aerosol number, mass, and chemical size distributions in central Europe during LACE 98 and MINT, *J. Geophys. Res.*, doi:10.1029/2001JD000514, in press, 2002.
- Novakov, T., Soot in the atmosphere, in *Particulate Carbon: Atmospheric Life Cycle*, edited by G. T. Wolff and R. L. Klimisch, pp. 19–41, Plenum, New York, 1982.
- Novakov, T., and C. E. Corrigan, Influence of sample composition on aerosol organic and black carbon determinations, presented at Chapman Conference on Biomass Burning and Global Change, AGU, Williamsburg, Va., 13–17 March, 1995.
- Nunes, T. V., and C. A. Pio, Carbonaceous aerosols in industrial and coastal atmospheres, *Atmos. Environ.*, 27A, 1339–1346, 1993.
- Ogren, J. A., R. J. Charlson, and P. J. Groblicki, Determination of elemental carbon in rainwater, *Anal. Chem.*, 55, 1567–1572, 1983.
- Ohta, S., M. Hori, S. Yamagata, and N. Muraio, Chemical characterization of atmospheric fine particulates in Sapporo with the determination of water content, *Atmos. Environ.*, 32, 1021–1025, 1998.
- Penner, J. E., Carbonaceous aerosols influencing atmospheric radiation: Black and organic carbon, in *Aerosol Forcing of Climate: Report of the Dahlem Workshop on Aerosol Forcing of Climate*, edited by R. J. Charlson and J. Heintzenberg, pp. 91–108, John Wiley, New York, 1995.
- Penner, J. E., H. Eddleman, and T. Novakov, Towards the development of a global inventory for black carbon emissions, *Atmos. Environ.*, 27A, 1277–1295, 1993.
- Petzold, A., and R. Niessner, Coulometrische Messung der Rußbelastung in der Außenluft - Verfahrensentwicklung und Anwendung an Meßstellen unterschiedlicher Belastung, *Gefahrst. Reinhalt. Luft*, 56, 173–177, 1996.
- Petzold, A., C. Kopp, and R. Niessner, The dependence of the specific attenuation cross-section on black carbon mass fraction and particle size, *Atmos. Environ.*, 31, 661–672, 1997.
- Quinn, P. K., and D. J. Coffman, Local closure during the First Aerosol Characterization Experiment (ACE 1): Aerosol mass concentration and scattering and backscattering coefficients, *J. Geophys. Res.*, 103, 16,575–16,596, 1998.
- Quinn, P. K., T. S. Bates, D. J. Coffman, J. E. Miller, D. S. Covert, J. P. Putaud, C. Neusüß, and T. Novakov, A comparison of aerosol chemical and optical properties from the first and second aerosol characterization experiments, *Tellus*, 52B, 239–257, 2000.
- Quinn, P. K., D. J. Coffman, T. S. Bates, T. L. Miller, J. E. Johnson, K. Voss, E. J. Welton, and C. Neusüß, Dominant aerosol chemical components and their contribution to extinction during the Aerosols99 cruise across the Atlantic, *J. Geophys. Res.*, doi:10.1029/2000JD900577, in press, 2002a.
- Quinn, P. K., D. J. Coffman, T. S. Bates, T. L. Miller, J. E. Johnson, E. J. Welton, C. Neusüß, M. Miller, and P. Sheridan, Aerosol optical properties during INDOEX 1999: Means, variability, and controlling factors, *J. Geophys. Res.*, 107(D19), 8020, doi:10.1029/2000JD000037, 2002b.
- Rogge, W. F., M. Mazurek, L. M. Hildemann, and G. R. Cass, Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation, *Atmos. Environ.*, 27A, 1309–1330, 1993.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit, Sources of fine organic aerosol: 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks, *Environ. Sci. Technol.*, 27, 636–651, 1993.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit, Sources of fine organic aerosol: 5. Natural gas home appliances, *Environ. Sci. Technol.*, 27, 2736–2744, 1993.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit, Sources of fine organic aerosol: 6. Cigarette smoke in the urban atmosphere, *Environ. Sci. Technol.*, 28, 1375–1388, 1994.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit, Sources of fine organic aerosol: 8. Boilers burning no. 2 distillate fuel oil, *Environ. Sci. Technol.*, 31, 2731–2737, 1997.
- Saxena, P., and L. M. Hildemann, Water-soluble organics in atmospheric particles: a critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem.*, 24, 57–109, 1996.
- Saxena, P., L. M. Hildemann, P. H. McMurry, and J. H. Seinfeld, Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.*, 100, 18,755–18,770, 1995.
- Schauer, J. J., W. F. Rogge, L. M. Hildemann, M. A. Mazurek, and G. R. Cass, Source apportionment of airborne particulate matter using organic compounds as tracers, *Atmos. Environ.*, 30, 3837–3855, 1996.
- Schauer, J., M. J. Kleemann, G. R. Cass, and B. R. T. Simoneit, Measurement of emissions from air pollution sources: 1. C<sub>1</sub> through C<sub>30</sub> organic compounds from medium duty diesel trucks, *Environ. Sci. Technol.*, 33, 1578–1587, 1999.
- Schmid, H., et al., Results of the “Carbon Conference” international carbon round robin test stage I, *Atmos. Environ.*, 35, 2111–2121, 2001.
- Schneider, J. K., and R. B. Gagosian, Particle size distribution of lipids in aerosols off the coast of Peru, *J. Geophys. Res.*, 90, 7889–7898, 1985.
- Sempéré, R., and K. Kawamura, Comparative distributions of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban atmosphere, *Atmos. Environ.*, 28, 449–450, 1994.
- Shah, J. J., and J. A. Rau, Carbonaceous species methods comparison study: Interlaboratory round robin interpretation of results, Research Division, California Air Resources Board, Final Rep. G2E-0024, Sacramento, CA, 1991.
- Shulman, M. L., M. C. Jacobsen, R. J. Charlson, R. E. Synovec, and T. E. Young, Dissolution behavior and surface tension effects of organic compounds in nucleating cloud droplets, *Geophys. Res. Lett.*, 23, 277–280, 1996.
- Simoneit, B., Organic matter of the troposphere: V. Application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations, *J. Atmos. Chem.*, 8, 251–275, 1989.
- Simoneit, B. R. T., and M. A. Mazurek, Organic matter of the troposphere: II. Natural background of biogenic lipid matter in aerosol over the rural western United States., *Atmos. Environ.*, 16, 2139–2159, 1982.
- Souza, S. R., P. C. Vasconcelos, and L. R. F. Carvalho, Low molecular weight carboxylic acids in an urban atmosphere: Winter measurements in Sao Paulo city, Brasil, *Atmos. Environ.*, 33, 2563–2574, 1999.
- Talbot, R. W., A. S. Vijgen, and R. C. Harris, Soluble species in the Arctic summer troposphere: Acidic gases, aerosols, and precipitation, *J. Geophys. Res.*, 97, 16,531–16,543, 1992.
- Turpin, B. J., and H. Lim, Species contribution to PM 2.5 concentrations: Revisiting common assumptions for estimating organic mass, *Aerosol Sci. Technol.*, in press, 2000.
- Ulrich, E., C. Beckmann, and G. Israel, The characterization of carbon species in particulate matter by successive thermal desorption, *J. Aerosol Sci.*, 21, S609–S612, 1990.
- VDI-Richtlinie 2465 Bl. 1, Messen von Ruß (Immission): Chemisch-analytische Bestimmung des elementaren Kohlenstoffs nach Extraktion und Thermodesorption des organischen Kohlenstoffs, Beuth, Berlin, 1996.
- VDI-Richtlinie 2465 Bl. 2, Messen von Ruß (Immission): Thermographische Bestimmung des elementaren Kohlenstoffs nach Thermodesorption des organischen Kohlenstoffs, Beuth, Berlin, 1997.
- Zappoli, S., et al., Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility, *Atmos. Environ.*, 33, 2733–2743, 1999.

T. Gnauk, H. Herrmann, C. Neusüß, and A. Plewka, Institut für Troposphärenforschung, Permoserstr. 15, 04318, Leipzig, Germany. (gnauk@tropos.de; cne@bsax.de; herrmann@tropos.de; plewka@tropos.de)  
P. Quinn, Pacific Marine Environmental Laboratory, NOAA, 7600 Sand Point Way NE, Seattle, WA 98115, USA. (quinn@pmel.noaa.gov)