

# **The chemical composition of the size-segregated atmospheric aerosol**

## **Results from ACE-2, MINT, LACE**

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### **Introduction**

The chemical composition of the atmospheric aerosol is an essential information to determine its influence on chemical transformations in the atmosphere, on climate, and on cloud formation. There are considerable gaps of knowledge with regard to different aerosol types and their respective size distribution. Especially size-resolved and simultaneous measurements of ionic and carbonaceous material are rare in the literature. Moreover, the specification of the carbonaceous material is still far away to be complete. Here results from three field campaigns in Europe are presented. These campaigns focused on closure studies and characterization of the atmospheric aerosol, especially with regard to its influence on radiative forcing.

### **Methods**

The field campaigns took place in Sagres, Portugal (ACE-2: June/July 1997), Melpitz (Leipzig), Germany (MINT: November 1997), and in Falkenberg (Berlin), Germany (LACE: July/August 1998). The setup was the same for all field campaigns. Two 5-stage low pressure cascade impactors (Berner-type; 50%-cut-offs: 0.05/0.14/0.42/1.2/3.5/10  $\mu\text{m}$ ) were used to determine the mass and chemical composition of the atmospheric aerosol. In one impactor aluminum foils were used to sample for mass and carbon. The second impactor runs with Tedlar foils to determine ionic compounds. Both weighting and sampling were performed at 60% relative humidity. The time resolution was typically 12 h.

The mass of the samples was determined by weighting the foils before and after exposure. The microbalance was placed in a box with a constant humidity of about 60 %, which was provided by a saturated NaBr solution and continuously controlled. The foils were conditioned in this box for at least 12 h before weighting.

The exposed Tedlar foils were cut into small pieces, leached in 1 or 1.5 ml of deionised water, which was then filtered and analyzed by capillary zone electrophoresis. A fused silica capillary with an inner diameter of 75  $\mu\text{m}$  and a total length of 70 cm (63 cm to the detector) was used. The applied electrical field was 420 V/cm. The buffer used to determine anions consists of an aqueous solution of p-aminobenzoate (10 mMol/l), NaOH (resulting in a pH of 9.6), and 8 mMol/l. Indirect detection is performed with a diode array detector working at  $\lambda = 254 \text{ nm}$  (Röder and Bächmann, 1995). The buffer to separate the main inorganic cations contains Imidazol (5.5 mMol/l), phosphoric acid (5 mMol/l) and 18-crone-6 ether (2.5 mMol/l, to separate ammonium and potassium; Beck and Engelhardt, 1992; Yang *et al.*, 1994). For every sample, a blank value was determined by analyzing a part of the foil without sample deposit. Blank values never reached values of significance compared to the chemical mass of the corresponding samples.

Carbon is determined with a thermographic. The sample is placed in a quartz tube and heated rapidly to a specific temperature. To separate between organic and elemental carbon the procedure of Petzold, [1995] is applied: In a first step the sample is heated under nitrogen to 500 or 590 °C. Those carbon compounds which evaporate under these conditions are referred to as volatile carbon. In a second step the sample is heated under oxygen to 650 °C, where all carbon except carbonate is oxidized. The evaporated carbon is completely oxidized to  $\text{CO}_2$  ( $T = 850 \text{ }^\circ\text{C}$ , CuO - catalysator), which is analyzed with an IR-detector. Quantification is performed by running external standards.

The water amount is calculated on the base of hygroscopic growth factors determined for single particles by an HTDMA for particles in the fine mode and calculated on the base of values from the literature for the coarse mode (assuming only sea-salt and  $\text{NaNO}_3$ , in the measured ratio). The classification of the air mass is performed using backward trajectories and additional measurements of meteorological parameters and gaseous species ( $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{O}_3$ ).

## **Results and Discussion**

Mean values and typical examples for the size-resolved chemical composition of the atmospheric aerosol are presented in Figures 1-3. Large differences in the mass concentration are obvious as well as different chemical composition with regard to both size (within the same sample) and air mass type. Generally, chemically and gravimetrically determined mass agree well, although calculation of the water amount is not complete. Only those species are shown,

which have a significant contribution to mass. E.g. potassium and calcium were most of the time abundant, but never accounted for more than a few percent of the mass.

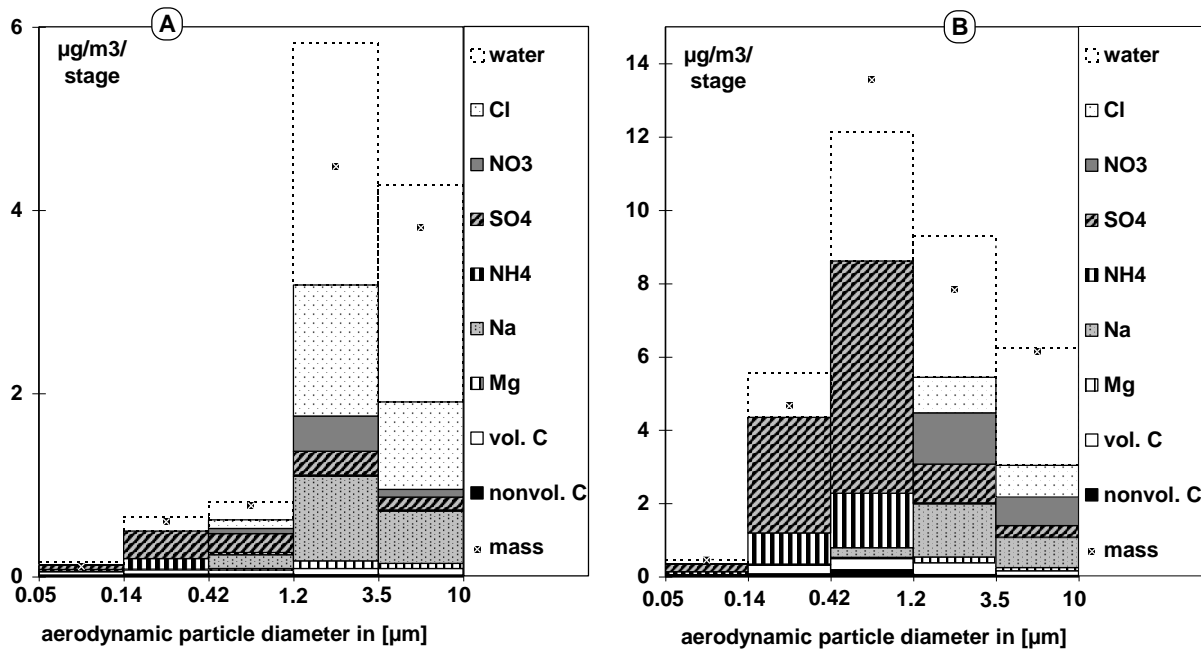


Figure 1: Chemical and mass size distribution of main compounds for clean marine air (A) and long range transported pollution from Central Europe (B) in Sagres (ACE-2).

Case A and B (Figure 1) represents clean marine air (mean of 5 samples) and polluted marine air (mean of 6 samples; long range transported pollution over the Atlantic Ocean to Portugal, without regional influence). The coarse mode ( $D_p > 1.2 \mu\text{m}$ ) consists of sea-salt, where the chloride is partly replaced by nitrate (stronger in the case of polluted air masses). The difference of the air mass is mainly characterized by high sulfate concentration in the fine mode ( $D_p < 1.2 \mu\text{m}$ ). The carbon concentration shows only slight increase.

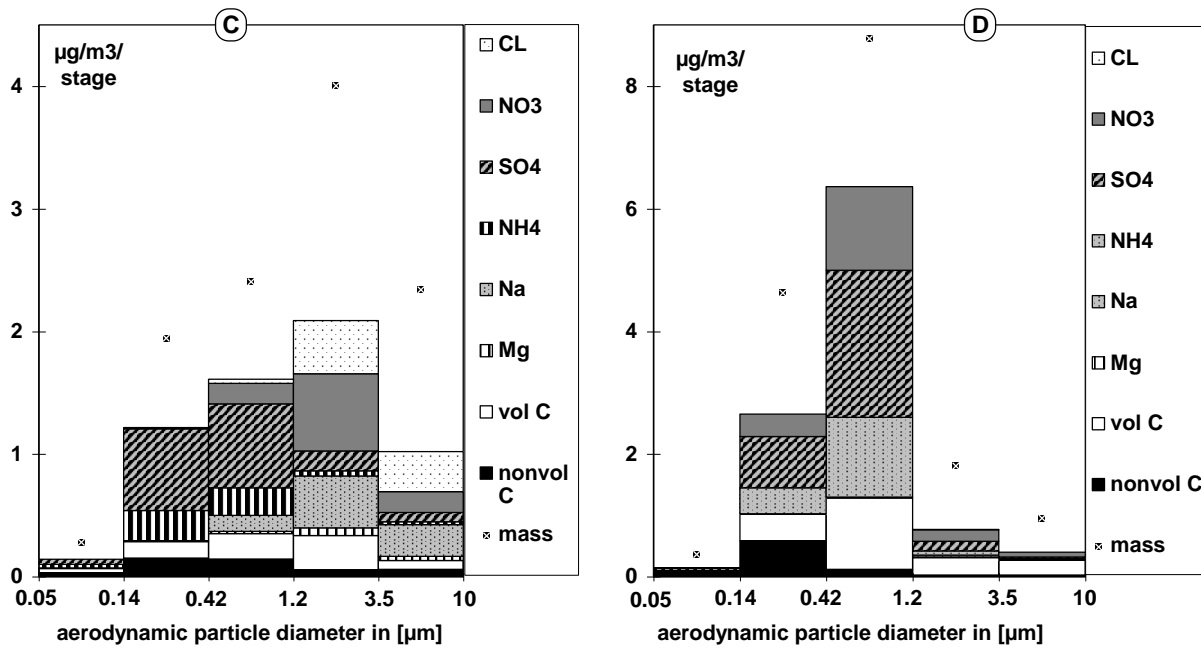


Figure 2: Chemical and mass size distribution of main compounds for marine air (C) and continental air (D) in Falkenberg, Berlin (LACE).

Figure 2 shows two cases of the composition of the atmospheric aerosol in Central Europe during LACE. Case C represents an air mass from the northwest (North Atlantic, Northern British Islands, North Sea). Case D a continental air mass from Poland. In both cases the carbon concentrations are higher than in Portugal. The marine influenced case C shows modified sea-salt aerosols in the coarse mode. The size distribution of nitrate is similar to that of sodium, indicating that all nitrate is fixed on sea-salt. In contrast, nitrate in the continental aerosol (D) shows the same size distribution as sulfate.

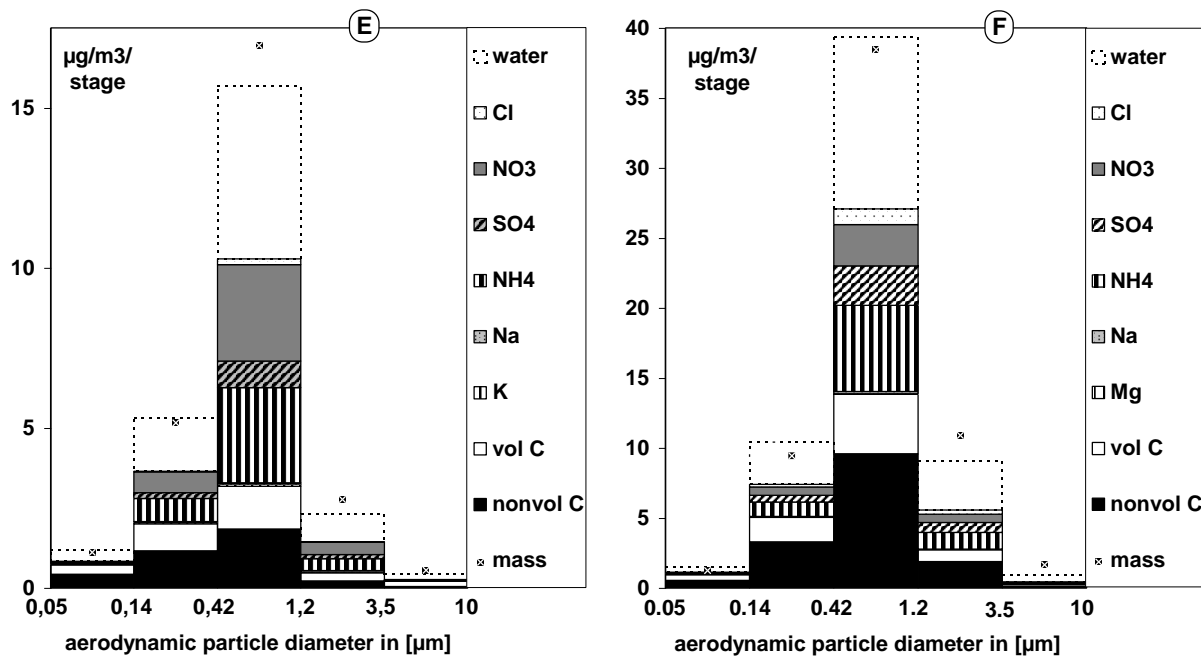


Figure 3: Chemical and mass size distribution of main compounds for westerly flow (E) and easterly air masses (F) in Melpitz, Leipzig (MINT).

Compared to ACE-2 and LACE significant higher mass concentration were observed during November 1997 in Melpitz, Leipzig (Figure 3). Especially in the case of weak winds from the east in combination with a strong inversion high concentration of carbon, sulfate, nitrate, and ammonium were observed. In the case of westerly winds (from Leipzig, 50 km away) the mass concentration was lower, but the amount of nitrate relatively higher. In both cases the coarse mode shows no difference in chemical composition with regard to the fine mode, indicating a growth of the anthropogenic particles into size ranges larger 1.2 μm in diameter. The carbon content makes up to more than 50% of the chemically determined mass.

One of the main advantages of the capillary electrophoresis is the simultaneous determination of inorganic and organic ions. Several dicarboxylic and hydroxylated dicarboxylic acids could be determined. As representative examples the size distributions for two different aerosol types are presented in Figure 4. The relative concentration of the different species is the same for both cases: Decreasing concentration of dicarboxylic acids with increasing carbon number. The size distribution is similar within the same air mass and class of species.

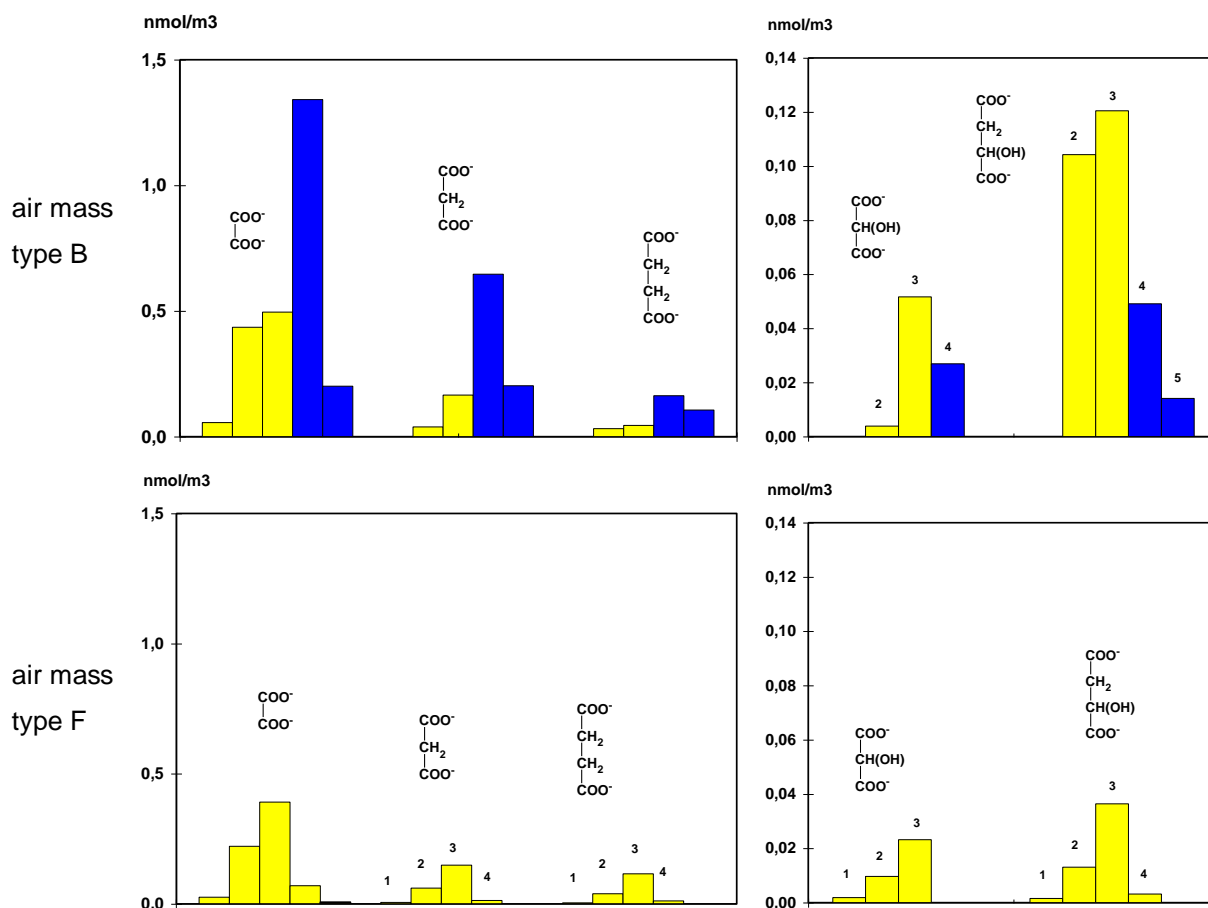


Figure 4: Size distribution of dicarboxylic and hydroxylated dicarboxylic acids for polluted marine air in summer 1997 during ACE-2 (top) and a polluted continental air mass in November 1997 during MINT (bottom). Dark bars indicate mainly sea-salt containing particles.

A strong indication for photochemical production is the fact that the concentration of all dicarboxylic acids were significantly higher in Portugal (and LACE) than during MINT, although the carbon concentration were much lower (more than an order of magnitude). Another hint for photochemical production is the fact that dicarboxylic acids are found partly on sea-salt particles (51% for oxalic acid as mean for all samples from Portugal, ACE-2). Significant marine sources can be excluded since the concentration depend on the degree of pollution (correlation with non-sea-salt sulfate). Indeed, it might be possible, that an exchange over the gas phase is responsible for the size distribution. This could explain the difference to hydroxylated dicarboxylic acids, which are less volatile and show smaller amounts in the coarse mode (Although different production mechanism in/on the aerosol could be responsible). On the other hand dicarboxylic acids (oxalic acids) never have been measured in the gas phase apart from source studies (*Saxena and Hildemann, 1996*). Moreover, the size distribution of e.g. oxalic acid and malonic acid are similar although the  $pK_s$  differ ( $pK_{Oxal} = 1.2$ ;  $pK_{Succ} = 4.2$  (*Lide, 1992*). The dissociated acids are not expected to be volatile.

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