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Dust composition and mixing state inferred from airborne composition measurements during ACE-Asia C130 Flight #6

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Abstract

In this study ~3.5 min average bulk aerosol composition data recorded from aircraft during ACE-ASIA C130 Flight #6 are used to investigate the extent of fine particle ($D_{p\ 50} < 1.3\,\mu m$) mixing among various inorganic aerosol particle constituents. Dust-laden air masses that had mixed with urban air pollutants over the Beijing and Tianjin region were subsequently recorded in the marine boundary layer over the Yellow Sea during the ACE-ASIA mission. An analysis of correlations and molar ratios between cations and anions suggest that dust particles are largely composed of $CaCO_3$ (i.e., the dust particles are fresh), and that NH_4^+ and K^+ are likely associated with SO_4^{2-} and NO_3^-. The results point to an external mixture of mineral dust and urban pollutant particles. Aerosol simulations carried out assuming various degrees of internal mixing (by Ca^{2+} mass) between dust and urban particles indicate the observed $2NH_4^+$–SO_4^{2-} association exists only when most of the fine-mode dust particles exist externally to SO_4^{2-}. In this case, the degree of external mixing (by Ca^{2+} mass) is estimated to be larger than 70%.

Keywords: Dust mixing state; Ion association; Aerosol thermodynamic modeling; ACE-ASIA campaign

1. Introduction

Atmospheric aerosols are a mixture of various chemical components because they are emitted directly from multiple sources and are secondarily produced by various atmospheric processes. Many researchers have investigated the degree to which atmospheric aerosols are mixed or segregated (e.g., Covert and Heintzenberg, 1984; Zhang et al., 1993; Cooke and Wilson, 1996; Haywood et al., 1997; Kleeman et al., 1997). Two limiting cases are possible for the degree of aerosol mixing (or segregation): (1) internal mixtures and (2) external mixtures. In the internal aerosol mixture, particles of the same size bins are assumed to have the same chemical composition, whereas, in the external mixture, particles of the same size bin have a different chemical composition. The degree to which aerosol particles mix influences the aerosol chemical composition and determines the aerosol chemical evolution as well as the particle's physical and optical properties.

Measurements of mineral dust, urban pollutants, and sea salt aerosol were made during the Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia), conducted in the spring of 2001 in East Asia. The

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experiment was a large multi-investigator study involving ground, ship, and airborne measurements, during the time of year when dust storms are most frequent and intense.

In this study, the degree of fine particle mixing is investigated by an indirect method (hereafter, the fine particles are defined as aerosols with diameters nominally smaller than 1.3 μm). Tests are performed on measurements from the ACE-ASIA experiment, and one specific measurement leg from ACE-ASIA C130 Flight #6 is focused on to investigate the aerosol mixing state. The case was encountered in the marine boundary layer (MBL) over the Yellow Sea on April 11, 2001, and contains a complicated mixture of dust, sea-salt, and polluted urban aerosols. Measurements of fine particle ionic composition from the particle into liquid sampler coupled to a dual channel ion-chromatograph (PILS-IC) with an integration period of 3 min 24 s (Weber et al., 2001; Orsini et al., 2003) are used to investigate correlations and molar ratios between various particulate ionic compounds and the results are qualitatively compared to the predictions from a thermodynamic "closed-mode" aerosol model simulation (Jacobson et al., 1996; Meng et al., 1998). This is a unique approach whose benefits and limitations are presented in this paper.

2. Experimental procedures

The PILS-IC measured fine-particle inorganic chemical composition on the C130. In this instrument, sample air is drawn through denuders to remove interfering gases and then rapidly mixed with saturated water vapor. The resulting supersaturated water condenses on the sampled ambient particles that subsequently grow to sizes that are easily captured by inertial impaction onto a small wetted area. With the addition of a small transport flow (~0.1 ml/min), the resulting liquid flow containing the water-soluble aerosol components is analyzed continuously via anion and cation chromatography. Based on baseline noise from the measurements of ambient air, detection limits are calculated to be in the range of 40–60 ng/m^3 for cations (NH_4^+, Ca^{2+}, Mg^{2+}, K^+, Na^+) and approximately 10–20 ng/m^3 for anions (SO_4^{2-}, NO_3^-, Cl^-). Although it is possible to measure additional ions with the PILS-IC (e.g., carbonate, organic compounds), they were not measured during these airborne experiments since they entail substantially longer integration times for chromatographic separation, thus limiting the sampling rate.

During this experiment, the instrument was operated with a 4-min sampling cycle, with a 3 min 24 s sample integration period (Weber et al., 2001; Orsini et al., 2003). In these experiments the PILS-IC measurements only provided fine-mode aerosol composition, where the fine-mode is defined here as particles with aerodynamic diameter less than nominally 1.3 μm. At this diameter, the PILS instrument has a 50% collection efficiency. However, the measurement does include larger particles. For example, particles of 2 μm are sampled with an efficiency of approximately ~20%. For more detailed explanations and an experimentally measured efficiency curve, the reader can refer to Maxwell-Meier et al. (2004).

3. Results and discussions

3.1. ACE-ASIA C130 Flight #6

The aerosol mixing state in a chemically complex environment that includes mineral dust particles, polluted urban aerosol particles, and sea-salt particles is analyzed. This type of aerosol mixture was frequently observed during the ACE-Asia experiment. Here the focus is on a portion of the ACE-ASIA C130 Flight #6.

3.1.1. Air trajectories

ACE-ASIA C130 Flight#6 was flown over the Yellow Sea on April 11, 2001. The flight track and 5-day backward trajectories along the flight track are shown in Fig. 1. The aircraft measurements were conducted along a North-South flight track on 124°E longitude between 33° and 37°N latitude. In this analysis we focus on the air masses encountered between 2:15 and 3:11 UTC since they contain both high Ca^{2+} and SO_4^{2-} concentrations, indicating that the measurements are highly impacted by dust and anthropogenic particles. The

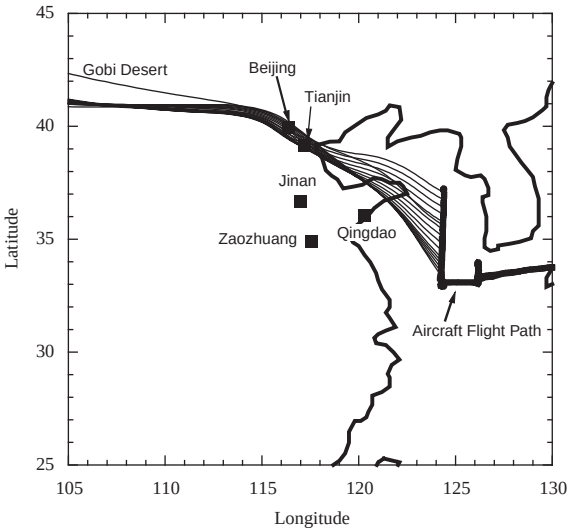

Fig. 1. C130 Flight #6 backward air mass trajectories along the C130 flight track.