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Ion balance and acidity of size-segregated particles during haze episodes in urban Beijing

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Abstract: In this study, we investigated how the ion balance of size-segregated particles causes variations in aerosol acidity and atmospheric processing on clean versus hazy days using a 9-stage sampler. We calculated the ratios (in charge equivalents，$R_{C/A}$) between measured cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) and anions (SO_4^{2-}, NO_3^- and Cl^-) for different aerosol size fractions. The ratios were typically close to unity in the accumulation mode, and increased significantly when the particle size increased or decreased. In the coarse size range (aerodynamic diameter > 2.1 μm), high $R_{C/A}$ values were most likely caused by the CO_3^{2-} and HCO_3^- content of the mineral dust. In contrast, the high $R_{C/A}$ values for submicron aerosols (< 1.1 μm) were likely caused by the presence of water-soluble organic anions. The $R_{C/A}$ values for all size fractions were lower on hazy days than clean days, indicating that aerosol acidity was enhanced on polluted days. The SO_4^{2-} and NO_3^- contents in fine particles were completely neutralized as the $R_{C/A}$ values for $PM_{2.1}$ approached unity, and mean values of $R_{C/A}$ were 1.34 and 1.16 during the transition and polluted periods, respectively. The lowest $R_{C/A}$ values were observed in the size fraction with the highest concentrations of SO_4^{2-}, NO_3^- and NH_4^+ (SNA) and concentrations of SNA increased with the increasing aerosol acidity. Significant correlations between $[NO_3^-]/[SO_4^{2-}]$ and $[NH_4^+]/[SO_4^{2-}]$ during NH_4^+-rich conditions in fine size fractions indicated fine mode NO_3^- in Beijing was mainly formed by gas-phase homogeneous reaction between the ambient NH_3 and HNO_3.

Key words: Ion balance; acidity; size distribution; haze

1. Introduction

Atmospheric particulate matter (PM) is an important pollutant that has been linked to adverse health effects, visibility reduction and climate change (Liang et al., 2016;