

Major ion composition in aerosol: As an new indicator of chlorine deficiency

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A large part of sodium and chlorine in aerosol particles are derived from surface seawater as sodium chloride (sea-salt; NaCl). Sodium chloride in aerosol is altered to sodium nitrate (NaNO₃) and sulfate (Na₂SO₄) by the reaction with nitric acid (HNO₃) and sulfuric acid (H₂SO₄) in atmosphere, respectively. In these reactions, gaseous HCl is emitted from sea-salt particles to the atmosphere, which is called as chlorine deficiency. These are important chemical reactions to anthropogenic N, in the process of transport from continent to open ocean, and to H₂SO₄ as scavenging process in atmosphere (Akimoto, 2014). However, detail processes of the chemical reaction and size-dependence of aerosol particles on this reaction are not clear. In order to clarify these reactions/processes in aerosol, we employed mass fractions (MF) parameter to size-fractionated aerosol particles obtained from land/continent and ocean. Direct speciation of Na was also conducted by soft X-ray absorption fine structure (XAFS) spectroscopy to intercompare the abundance ratio of Na species to those estimated by MF.

Size-fractionated aerosol particles on land were collected by a high volume cascade impactor at Higashi-Hiroshima from December 2012 to March 2014. Marine total suspended particulate (TSP) and size-fractionated aerosol particles were collected in the *R/V Hakuho-Maru* research cruises of KH-12-4 (the North Pacific Ocean: from 23th August to 3rd October 2012) and KH-13-4 Leg. 4 (the Bay of Bengal: from 31th July to 14th August 2013), respectively. Major ionic concentrations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻ and SO₄²⁻) in aerosol samples were determined by an ion chromatography after appropriate pretreatment. MF parameters were calculated as $[X]_{eq}/[\text{total anion}]_{eq}$ (X: Cl⁻, NO₃⁻ and nssSO₄²⁻). Direct speciation of Na in continental size-fractionated aerosol particles were conducted by XAFS spectroscopy on BL-10, SR-center, Ritsumeikan University.

MF[Cl⁻]_{eq} was inversely correlated with both MF[NO₃⁻]_{eq} and MF[nssSO₄²⁻]_{eq} in continental coarse aerosol particles. It can be said that the chlorine deficiency is explained by the reaction with NO₃⁻ and/or nssSO₄²⁻. The regression line for MF[Cl⁻]_{eq}-MF[nssSO₄²⁻]_{eq} was -2.16. As for MF[Cl⁻]_{eq}-MF[NO₃⁻]_{eq}, the regression line shows -1.03, and this regression line satisfies the equation of y=1-x. Thus, HNO₃ has large contribution as a reactant of NaCl in the urban atmosphere. Furthermore, chemical reaction of NaCl with HNO₃ and H₂SO₄ preferentially occur on the small aerosol particles because further decrement of MF[Cl⁻]_{eq} was found in smaller size of aerosols compared with that of large aerosol particles. The speciation analysis with XAFS spectroscopy showed comparable results with that obtained from MF analysis using the high reacted aerosol samples from continent (MF[Cl⁻]_{eq} : MF[NO₃⁻]_{eq} : MF[nssSO₄²⁻]_{eq} =18:56:23). As for marine aerosol samples from the North Pacific Ocean, dominant reactant of NaCl is H₂SO₄. On the other hand, the reaction of NaCl occurs with both NO₃⁻ and SO₄²⁻ above the Bay of Bengal.

As a consequence, MF is very useful tools to find dominant reactant of NaCl and Na chemical species as a result of chlorine deficiency in both continental and marine aerosol particles.

Keywords: atmospheric chemistry, aerosol, Na, XAFS spectroscopy