Atmospheric Aging of Internally Mixed Sea Salt and Organic Particles: Surprising Reactivity of NaCl with Weak Organic Acids

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Abstract

Atmospheric aging of internally mixed sea salt/organic particles has been largely overlooked in the atmospheric aerosol chemistry. Atmospheric aging, and in particular hydration-dehydration cycles of mixed sea salt/organic particles, result in chloride depletion. Surprising reactivity of NaCl with weak organic acids (present in the atmosphere) result in chloride depletion and formation of organic salts. Field evidence is presented showing that chloride components in sea salt particles may effectively react with organic acids releasing HCl gas to the atmosphere, leaving behind particles depleted in chloride and enriched in the corresponding organic salts. These reactions in aerosol are driven by high volatility and irreversible evaporation of the HCl product from drying particles. These field observations were corroborated in a set of laboratory experiments where NaCl particles mixed with organic acids were found to be depleted in chloride. Combined, the results indicate that substantial chemical reactivity of sea salt particles with secondary organic aerosols that has been largely overlooked in the atmospheric aerosol chemistry. Atmospheric aging, and in particular hydration-dehydration cycles of mixed sea salt/organic particles may result in formation of organic salts that will modify the acidity, hygroscopic and optical properties of aged particles.

Acid displacement reactions of sea salt chlorides with inorganic acids (present in the atmosphere) result in chloride depletion:

\[ \text{NaCl (aq)} + \text{HA (aq, g)} \rightarrow \text{NaA (aq)} + \text{HCl (aq, g)} \]

where HA denotes weak organic acids such as (nitric acid), H2SO4, sulfuric acid, and CH3COOH (acetic acid). These reactions release volatile HCl (g) to the atmosphere. The remaining particles are enriched in the corresponding salts and depleted in chloride.

Low volatility carboxylic acids are inherent constituents of SOA formed from both biogenic and anthropogenic precursors. Hence, particles of mixed NaCl/soa composition may undergo similar reaction processes. These reactions would liberate HCl(g) and promote the formation of organic salts in the particle phase.

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Complementary Laboratory Studies

Chemical imaging analysis of internally mixed sea salt/organic particles collected on board the Department of Energy (DOE) G-1 aircraft during the 2010 Carbonaceous Aerosols and Radiative Effects Study (CARES) was performed using electron microscopy and X-ray spectroscopy techniques. Substantial chloride depletion in aged sea salt particles was observed. This depletion could not be explained by the known atmospheric reactivity of sea salt with inorganic nitric and sulfuric acids.

Field evidence is presented showing that chloride components in sea salt particles may effectively react with organic acids releasing HCl gas to the atmosphere, leaving behind particles depleted in chloride and enriched in the corresponding organic salts. While formation of the organic salts products is thermodynamically favored for bulk aqueous chemistry, these reactions in aerosol are driven by high volatility and irreversible evaporation of the HCl product from drying particles. These field observations were corroborated in a set of laboratory experiments where NaCl particles mixed with organic acids were found to be depleted in chloride. Combined, the results indicate that substantial chemical reactivity of sea salt particles with secondary organic aerosols that has been largely overlooked in the atmospheric aerosol chemistry. Atmospheric aging, and in particular hydration-dehydration cycles of mixed sea salt/organic particles may result in formation of organic salts that will modify the acidity, hygroscopic and optical properties of aged particles.

Acid displacement reactions of sea salt chlorides with inorganic acids (present in the atmosphere) result in chloride depletion:

\[ \text{NaCl (aq)} + \text{HA (aq, g)} \rightarrow \text{NaA (aq)} + \text{HCl (aq, g)} \]

where HA denotes chloride salts of sea water, and HA are atmospheric acids such as HNO3, (nitric acid), H2SO4, (sulfuric acid), and CH3COOH (acetic acid). These reactions release volatile HCl (g) to the atmosphere. The remaining particles are enriched in the corresponding salts and depleted in chloride.

Low volatility carboxylic acids are inherent constituents of SOA formed from both biogenic and anthropogenic precursors. Hence, particles of mixed NaCl/soa composition may undergo similar reaction processes. These reactions would liberate HCl(g) and promote the formation of organic salts in the particle phase.

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