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Mixed Chloride Aerosols and their Atmospheric Implications: A Review

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ABSTRACT

Natural and anthropogenic chloride aerosols make up a significant fraction of atmospheric particulate matter and play important roles in the boundary layer chemistry. Here we provide a review of the mixing characteristics of chloride aerosols and the subsequent atmospheric implications, which are rarely considered in current field and modeling studies. Single-particle analytical techniques have shown that a large fraction of chlorides mix internally with other components, in particular inorganic salts and organic matters, instead of existing separately. In marine and coastal regions, high proportions of chloride aerosols usually mix with inorganic substances (e.g., Mg, Ca, K, N, S), while small quantities of them are coated by organic matter. In forest, grassland, and agricultural areas, most chlorides in biomass burning particles mix with or are coated by organics. In industrialized urban areas, the chloride aerosols often co-exist with heavy/transition metals (e.g., Zn, Pb) and are coated by organic materials in aged plumes. Moreover, secondary chlorides also mix with mineral dusts, nitrates, and sulfates. The mixing of chloride aerosols with insoluble substances can inhibit their hygroscopic properties, which in turn affects the cloud condensation nuclei activation and heterogeneous reactivity. The encasing of chloride aerosols within light-absorbing substances changes their optical properties and subsequently causes atmospheric warming. This paper emphasizes the complexity of the mixing of chloride aerosols, as well as the potential atmospheric implications thereof, and proposes some research topics deserving future study.

Keywords: Chloride aerosol; Mixing state; Hygroscopicity; Reactivity; Optical properties.

INTRODUCTION

Chloride aerosols have been identified as a major constituent of atmospheric particulate matter, and play important roles in tropospheric chemistry (Erickson and Duce 1988; Carslaw *et al.*, 2010; Laskin *et al.*, 2012). They exist in various chemical forms and different sizes in diverse locations. In marine and coastal regions, sea salts, dominated by sodium chloride, contribute a large fraction to the mass and number concentrations of aerosols, most of which exist in super-micro particles (Erickson and Duce 1988; Gong *et al.*, 2002; O'Dowd and de Leeuw, 2007). In forest, grassland, and agricultural areas, aerosols containing potassium chloride contribute almost half of the number concentration of fine particles in biomass burning plumes (Pratt *et al.*, 2011). In industrialized urban areas, aerosols containing metal chlorides contribute as much as 73% to the fine particles emitted in industrial smoke (Moffet *et al.*, 2008a). Chloride aerosols can be activated via reactions with strong acids or acid anhydrides, and in turn further anticipate the tropospheric chemistry. Previous field studies have confirmed that particulate-phase chlorides (e.g., sodium chloride and potassium chloride) react with sulfuric acid and/or nitric acid to release gas-phase HCl, which further reacts with NH_3 to produce ammonium chloride or with dust to produce chloride-dust (Sullivan *et al.*, 2007a). Recent studies have revealed that the heterogeneous reactions of N_2O_5 on chloride aerosols release $ClNO_2$, which serves as an important source of Cl atoms (Osthoff *et al.*, 2008; Thornton *et al.*, 2010; Wang *et al.*, 2016).

With the development and application of single-particle analytical techniques, detailed information has been obtained on the chemical constituents and mixing states of individual aerosols, showing that a large fraction of chloride aerosols mix with other substances, which alters the behavior of chloride aerosols. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can be used to identify the size and elemental distribution of individual chloride aerosols in the atmosphere, together with the mixing characteristics with other constituents (Barkay *et al.*, 2005; Laskin *et al.*, 2006; Adachi and Buseck, 2008; Chi *et al.*, 2015). The recently developed aerosol time-of-

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fight mass spectrometry (ATOFMS) can provide the size and chemical composition of a large number of individual aerosols in real time (Moffet *et al.*, 2008b; Bi *et al.*, 2011; Prather *et al.*, 2013). These single-particle techniques have provided new insights and a deeper understanding of the mixing characteristics of chlorine-rich aerosols including sea salts, particles in biomass burning plumes and industrial smoke, and secondary chloride aerosols. Andreae *et al.* (1986) unexpectedly found that a large fraction of mineral substances and sulfates in the marine boundary layer were internally mixed with sodium chlorides. Subsequently, several field studies have confirmed that a significant proportion of sea salts are internally mixed with sulfates and nitrates (Mouri *et al.*, 1993; Laskin *et al.*, 2002; Li *et al.*, 2003a), while other research has revealed that the chloride components in sea salts acquire a coating of organic surfactants in polluted coastal environments or even at remote islands (Tervahattu *et al.*, 2002a, b; Laskin *et al.*, 2012; Chi *et al.*, 2015). Electron microscopy and single-particle mass spectrometry have indicated that potassium chlorides in biomass burning smoke mix with soot and organics, and some even acquire an organic surface coating (Silva *et al.*, 1999; Li *et al.*, 2003b). In urban areas, field studies have detected plentiful submicron metal chloride containing particles, which are typically mixed with carbonaceous materials in combustion emissions (Moffet *et al.*, 2008b; Li *et al.*, 2009; Geng *et al.*, 2010; Hu *et al.*, 2015). Additionally, in long-range transport dust plumes over the Pacific, Sullivan *et al.* (2007b) observed that a large amount of secondary particulate chlorides (produced from gas-phase HCl) was internally mixed with dust particles. The mixing of various chloride aerosols with other substances, particularly insoluble and light-absorbing materials, may significantly alter the hygroscopic, reactivity, and optical properties, as well as their effect on the climate, thus causing the apparent deviation between model predictions and ambient observations. In spite of the above studies, the current knowledge on the mixing state of chloride aerosols is generally fragmentary, and a comprehensive understanding is required.

This study reviews the currently available, scattered studies on mixed chloride aerosols (the major field campaigns are shown in Fig. 1) to obtain a clearer understanding of their mixing properties and the subsequent atmospheric implications. First, we provide a brief introduction to the commonly used single-particle analytical methods. Then, we summarize the previous results on the composition of mixed chloride aerosols, their mixing characteristics, the co-existing constituents and the necessary conditions for aerosol mixing, according to a classification into sea salt, biomass burning particle, industrial smoke dust, and secondary chloride particle. Finally, we summarize and discuss the effect of the mixing of chloride aerosols on the hygroscopicity, reactivity, and optical properties of the particles.

ANALYTICAL TECHNIQUES FOR PARTICLE MIXING STATE

The development of single-particle techniques has allowed substantial progress in research into particle mixing states, and offers considerable advantages compared with the

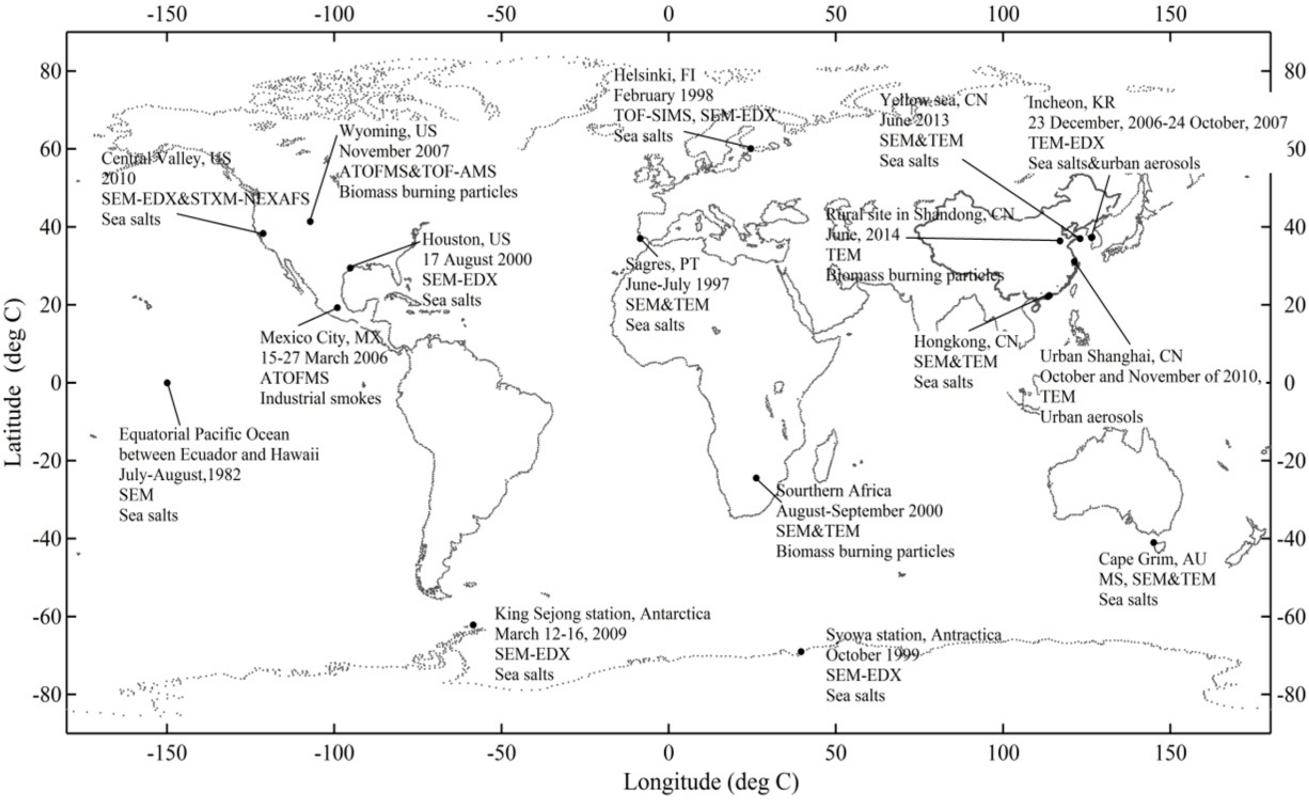

Fig. 1. Map showing the previous field studies on mixing characteristics of chloride aerosols with various techniques.

traditional analytical methods for bulk aerosols. Bulk aerosol analytical methods (e.g., online and offline ion chromatography and aerosol mass spectrometry) provide only information on the concentrations of different components for large amounts of particles. To obtain the mixing characteristics of different constituents in individual particles, several advanced single-particle techniques have been applied or developed in the past decades, including SEM, TEM, ATOFMS, scanning transmission X-ray microscopy with near-edge X-ray absorption fine-structure spectroscopy (STXM-NEXAFS), nanoscale secondary-ion mass spectrometry (NanoSIMS), and time-of-flight secondary-ion mass spectrometry (TOF-SIMS).

SEM is a widely used technique in which the surface of a single particle is imaged by scanning it with a high-energy beam of electrons in a raster scan pattern. SEM equipped with energy-dispersive X-ray spectrometry (EDX) is an effective approach for identifying the surface composition (elemental mapping) of individual particles with diameters greater than 100 nm. The mixing characteristics of different constituents in the surface layer of the particle can be obtained from information on the shape and chemical composition by SEM-EDX (Barkay *et al.*, 2005; Laskin *et al.*, 2006; Pachauri *et al.*, 2013).

TEM is an electron microscopic technique in which a beam of electrons is transmitted through the particle. TEM-EDX can be used to readily observe the mixing state, structure, and elemental composition of the entire particle (Li *et al.*, 2003a; Adachi and Buseck, 2008; Li *et al.*, 2016a). Note that the ordinary EDX can only detect elements heavier than carbon and the TEM requires labor-intensive operation. The application of ultra-thin window detectors in SEM and TEM permits the detection of light elements and thus achieves nearly total element analysis. In addition, the TEM and SEM suffer from a defect of possible changes of particle samples in the microstructure, composition, and mass (e.g., semi-volatile compounds) during examination.

STXM-NEXAFS can also image the particle shape, albeit with poor resolution. This combined method provides information on the spatially resolved bonding and oxidation state of the investigated particles with enhanced chemical sensitivity. STXM-NEXAFS can be used to obtain the mixing properties of certain specific constituents, particularly organics and light-absorbing components (Moffet *et al.*, 2010; Laskin *et al.*, 2012; Ault *et al.*, 2013a).

ATOFMS is an online, field-deployable form of aerosol mass spectrometry that couples aerodynamic particle sizing with time-of-flight mass spectrometry in a single instrument. ATOFMS provides real-time, high-time-resolution data on the sizes, compositions, and mixing properties of individual particles (Dall'Osto *et al.*, 2004; Dall'Osto and Harrison, 2006; DeCarlo *et al.*, 2006; Moffet *et al.*, 2008a, b; Bi *et al.*, 2011). It provides good statistic information on single particles; however, the specific components of the particles are difficult to identify from the mass spectra.

Recently, TOF-SIMS and NanoSIMS have been used to study single particles. In these methods, a primary-ion beam is fired at the particle surface, and the secondary ions produced by the impact are detected by advanced mass spectrometers. TOF-SIMS and NanoSIMS provide the distributions of all elements and isotopes, as well as certain molecules, at the particle surface with very high sensitivity, accuracy, and lateral resolution. Compared with TOF-SIMS, NanoSIMS generally has higher sensitivity and a higher lateral and mass resolution and obtains more detailed information on the mixing of particles (Hagenhoff, 2000; Tervahattu *et al.*, 2002b, 2005; Marino *et al.*, 2006; Ghosal *et al.*, 2014; Chi *et al.*, 2015; Li *et al.*, 2016b).

MIXING CHARACTERISTICS OF CHLORIDE AEROSOLS IN ATMOSPHERE

Mixing of Chlorides in Sea Salts

Generally, a large fraction of the chlorides in sea salts are internally mixed with inorganic materials in the atmosphere and co-exist with many different substances (see the schematic diagrams in Fig. 2). In the relatively clean atmosphere over the Pacific Ocean, Atlantic Ocean, and coastal Antarctica, field observations have indicated that much of the sodium chloride in fresh sea salts is capped by a small quantity of other inorganic elements (as shown in Fig. 2(a)) (Andreae *et al.*, 1986; Murphy *et al.*, 1998; Li *et al.*, 2003a; Hara *et al.*, 2005; Li *et al.*, 2016a; Young *et al.*, 2016). For example, Andreae *et al.* (1986) observed by SEM that regular sodium chloride crystals contacted with various silicates and sulfates in the equatorial Pacific Ocean between Ecuador and Hawaii, and Li *et al.* (2016a) observed by SEM and TEM that square sodium chloride particles were associated with certain amounts of magnesium chlorides and calcium sulfates in the Yellow Sea of China. In coastal regions with anthropogenic influences, the compositions and mixing characteristics of sea salts significantly change along with the atmospheric transport and aging processes. A fraction of the particulate chlorides in sea salts is converted into gas-phase compounds (e.g., HCl and $ClNO_2$), with most of the remaining chlorides completely encased within a large quantity of inorganic elements (as shown in Fig. 2(b)) (e.g., Mg and S at Cape Grim (Murphy *et al.*, 1998), K, Ca, and S in Incheon (Geng *et al.*, 2010), Mg, K, Ca, and S in Antarctica (Hara *et al.*, 2005), and Mg, N, and S in Houston, Macao, and Hong Kong (Laskin *et al.*, 2002; Li *et al.*, 2010, 2016a)). Amorphous sodium chloride particles were found to be completely bound with sodium nitrates and sodium sulfates in coastal Hong Kong (Li *et al.*, 2016a). An investigation of sea spray aerosols generated in the laboratory by Ault *et al.* (2013b) showed that elemental redistribution occurred within the sea salt particles, and their internal structures were altered by reaction with nitric acid. In addition, field studies have found that the chlorides in sea salts were closely bound with aluminum compounds in the coastal town of M'Bour, Senegal (Deboudt *et al.*, 2010), and iron compounds in the industrial region of Dunkerque (Choël *et al.*, 2010).

Besides co-existing with other inorganic matter, a significant fraction of the chlorides in sea salts also mix with organic compounds in polluted coastal regions (see the schematic diagrams in Fig. 3). The identified organic species co-existing with sea salts varies by location (e.g., fatty acids

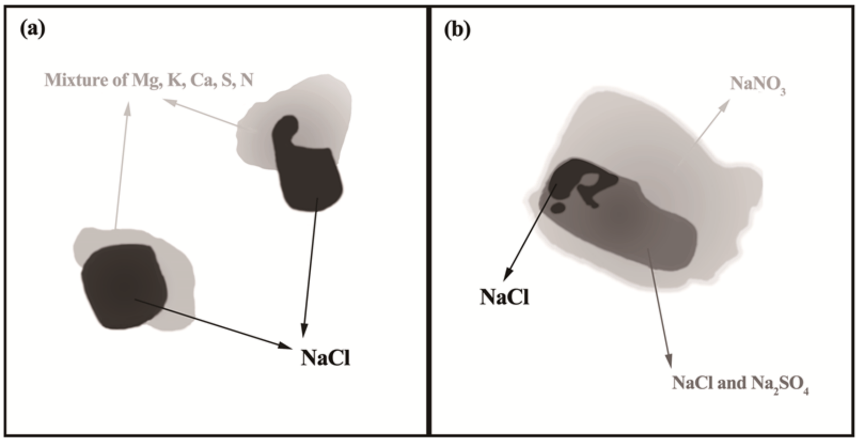

Fig. 2. Schematic diagrams showing the mixing of chlorides in sea salts with inorganic substances, referred from Li *et al.* (2016a). (a) Typical square NaCl attaching with the mixture of Mg, K, Ca and S in the fresh sea salt; (b) Shapeless NaCl enclosed by Na_2SO_4 and $NaNO_3$ in the aged sea salt.

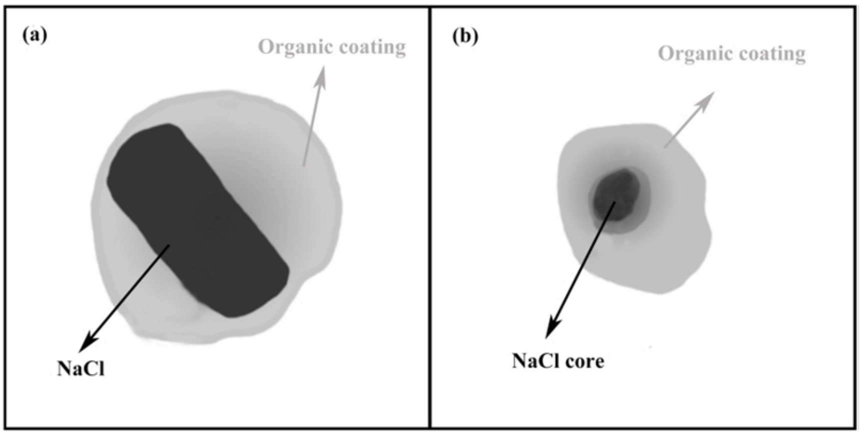

Fig. 3. Schematic diagrams showing the chlorides in sea salts coated by organic matters, referred from Ault *et al.* (2013a) and Chi *et al.* (2015). (a) A typical fresh sea salt (square NaCl) and (b) an aged sea salt (NaCl core) coated by organic materials.

in Helsinki (Tervahattu *et al.*, 2002a, b), methanesulfonates in King George Island, Antarctica (Maskey *et al.*, 2011), and multiple organic compounds at Cape Grim (Middlebrook *et al.*, 1998; Murphy *et al.*, 1998) and in coastal central California (De Bock *et al.*, 2000)). In the sea salts mixed with organics, most of the sodium chlorides were surface-coated by organic materials. Laskin *et al.* (2012) found by SEM-EDX and STXM-NEXAFS that the chloride core in aged sea salts was coated by a substantial C-containing constituent layer. Subsequent ocean-in-lab experiments with sea spray aerosols generated from sea water after the addition of biological and organic materials also discovered an apparent organic coating layer at the surface of the sodium chloride core (Ault *et al.*, 2013a; Prather *et al.*, 2013).

Mixing of Chlorides in Biomass Burning Particles

Chloride aerosols from biomass burning normally mix with carbonaceous materials in young smoke and are completely coated by organics after partial replacement in aged smoke (see the schematic diagrams in Fig. 4). Li *et al.* (2003b) investigated chloride aerosol particles from biomass burning in the southern African boundary layer and free troposphere using TEM. In fresh biomass burning plumes, most of the chlorides existed as potassium chloride, and the potassium chloride crystals contacted with carbonaceous materials. Further biomass burning experiments in the open field by Li *et al.* (2016a) confirmed that the co-existing carbonaceous materials could be either organic matter or soot, and their mixing characteristics varied depending on the type of biomass fuel and the burning conditions. Geng *et al.* (2010) also observed chlorides in tar ball particles generated from household wood combustion in Incheon in winter. In aged biomass burning smoke, potassium chlorides were partly replaced by potassium sulfates and potassium nitrates through heterogeneous reactions, and the remaining chlorides and potassium were completely coated by organic compounds (Li *et al.*, 2003b).

Mixing of Chlorides in Industrial Smoke

Chloride aerosol particles directly emitted in industrial smoke mostly co-exist with transition/heavy metals. Geng *et al.* (2010), using TEM, observed abundant Zn/Pb/Cl-

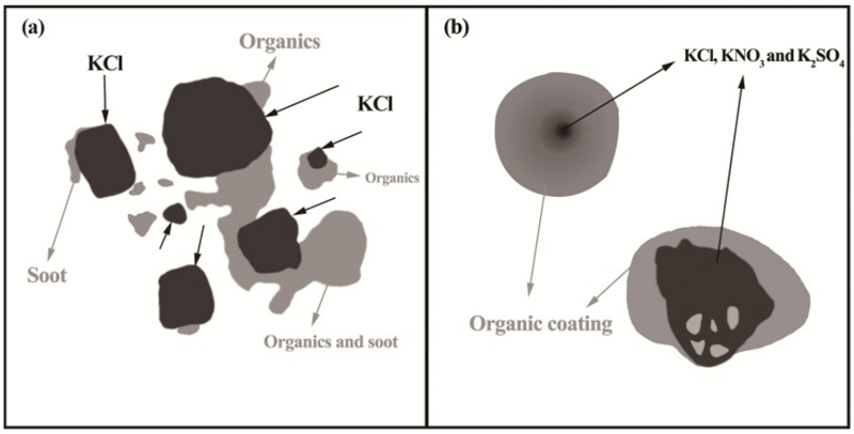

Fig. 4. Schematic diagrams showing the mixing characteristics of chlorides in biomass burning particles, referred from Li *et al*. (2003b) and Li *et al*. (2016a). (a) KCl crystals touching with organics and soot in young biomass burning smokes. (b) Shapeless KCl, and secondary K_2SO_4 and KNO_3 coated by organic compounds after aging processes in aged smokes.

containing particles in polluted urban Incheon, which were attributed to industrial processes and coal-fired power generation. The gas-phase zinc and lead chlorides emitted from high-temperature combustion sources condensed into solid-phase submicron Cl-containing particles upon cooling (Hu *et al.*, 2003). Online measurements of single particles by ATOFMS in an industrial/residential section of Mexico City by Moffet *et al.* (2008a, b) demonstrated that the metal/Cl-containing particles accounted for a large fraction of the fine-mode particles, and the fraction reached 73% in the early morning hours. Other studies have also observed numerous micron-sized Zn/Pb/Cl-containing particles in lead smelter plumes (Ettler *et al.*, 2005), in incinerator fly ash (Tan *et al.*, 2002; Zhang *et al.*, 2009), in mixed urban plumes (Lu *et al.*, 2012), and in haze episodes (Li *et al.*, 2009; Hu *et al.*, 2015). The chloride particles from industrial smoke were often coated by organic matter after aging (see the schematic diagram in Fig. 5). TEM images of aerosol particles collected in urban Shanghai by Fu *et al.* (2012) clearly showed that zinc chloride particles from industrial plumes were completely enclosed within organic compounds.

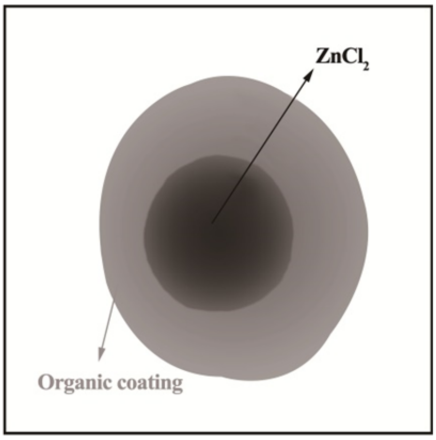

Fig. 5. Schematic diagram showing the typical industrial $ZnCl_2$ particle coated by organic matters, referred from Fu *et al*. (2012).

Mixing of Secondary Chloride Particles

The secondary chloride aerosols produced by the reaction of HCl with alkaline substances (e.g., NH_3 and mineral dusts) often mix with dust, nitrate, and sometimes sulfate. Sullivan *et al.* (2007b) observed a large fraction of chlorides mixing with mineral dusts (i.e., Al, Ca, and Fe compounds) in long-range transport dust plumes by using ATOFMS during shipboard measurements over the Pacific Ocean between Hawaii and Japan. Further study by Sullivan *et al.* (2007a) showed that the abundant chlorides in dust particles originated from the heterogeneous reactions of HCl released from chemically aged sea salt particles. The newly added secondary chlorides in the mixed dust particles contributed 4–9% of the individual dust particle mass, and secondary chloride-containing dust particles constituted as much as 65% of the total dust particles during a major dust storm. Tobo *et al.* (2010) also noticed the chloride depletion in sea salt particles and a coatings containing $CaCl_2$ on the surface of dust core at Kanazawa site during an Asian dust storm period. Moreover, Sullivan *et al.* (2007b) observed a significant fraction of secondary chloride particles mixing with nitrates (14.8% of the chloride-dust and nitrate-dust particles) and a small proportion mixing with sulfates (0.8% of the chloride-dust and sulfate-dust particles).

ATMOSPHERIC IMPLICATIONS OF MIXED CHLORIDE AEROSOLS

Alteration to Hygroscopicity and Cloud Condensation Nuclei Activation

The mixing of chloride aerosols with other inorganic and organic constituents (as summarized in Table 1) can significantly alter their hygroscopicity and further influence the activation of cloud condensation nuclei (CCN) when compared with the pure chloride salts. Salt particles primarily consisting of pure hydrophilic chlorides are hygroscopic, with deliquescence relative humidity (DRH) values of around 80% (e.g., 75.3% for NaCl, 84.2% for KCl, and 80.0% for NH_4Cl at 298 K) (Tang *et al.*, 1978; Tang and Munkelwitz, 1993). The mixing of chloride salts with other inorganic salts,

Table 1. Summary of mixed chloride aerosols in atmosphere.

Type	Location	Chloride form	Mixed element or substance	Mixing pattern
Sea salts	Marine and coastal region	NaCl, minor $MgCl_2$	Mg, Ca, K, N, S, organics	Enclosed with inorganics, coated by organics
Biomass burning particles	Vegetation covered area	KCl	N, S, K, soot, organics	Touching with or coated by carbons, replaced by N and S
Industrial smokes	Industrialized city	Zn-Pb-Cl	Metals, organics	Co-existing with metals, coated by organics
Secondary chloride particles	Marine and other locations	NH_4Cl, $CaCl_2$	Al, Ca, Fe, N, S	Mixed with dust, nitrates, and minor sulfates

particularly low-DRH salts like nitrates and hydrosulfates, heavily decreases the DRH of the mixed aerosol particles and thus enhances their CCN activation. Wexler and Seinfeld (1991) compared the DRHs of mixtures of nitrates, chlorides, and sulfates and those of the individual salts, and found apparent decreases in DRH after mixing. Wise *et al.* (2009) observed a significant reduction in deliquescence humidity when sodium chloride was mixed with a small amount of various inorganic substances, with the DRH dropping to 66% for laboratory-synthesized sea salts and to 57% for natural sea salts. For sulfate-coated and Mg-rich chloride-coated sea salt particles collected from the ambient atmosphere, Semeniuk *et al.* (2007a) also observed that the initial water uptake occurred at lower relative humidity (RH) than for common marine aerosol particles, and the coated sea salts underwent a complex multi-step deliquescence. Nevertheless, the mixing of chlorides with less hygroscopic (i.e., organic compounds) and insoluble substances (e.g., soot) can significantly suppress their hygroscopicity and CCN efficiency. Semeniuk *et al.* (2007b) investigated the hygroscopic behavior of single particles of potassium chlorides mixing with organic matter at RH values of 0–100%, and found that the mixed chloride particles did not appear to deliquesce. For ambient particles comprising organic substances and chloride and/or other inorganic components, online field measurements indicated that the CCN efficiency decreased from 12.8 ± 6.1% to 4.5 ± 2.6% when the organic fraction increased from 10–20% to 30–40% (Zhang *et al.*, 2012).

Change in Heterogeneous Reactivity

Changes in the liquid water and soluble chloride contents in mixed chloride aerosols subsequently affect the reactivity of the chlorides in related heterogeneous reactions. Generally, the mixing of chlorides with inorganic salts tends to promote reactivity, while mixing with or coating by less hygroscopic and insoluble substances is prone to suppress reactivity. Saul *et al.* (2006) determined the reactive uptake coefficient of nitric acid on both pure sodium chlorides and sodium chlorides mixed with magnesium chlorides at RH values of 10–85%, and found that the uptake coefficient on the mixed chloride aerosols remained high (> 0.1) even at 10% RH, and was much higher than that on pure sodium chloride aerosols. This enhancement suggests that the displacement of chloride by nitrate is facilitated by the mixing of chlorides. Stewart *et al.* (2004) also observed a higher N_2O_5 uptake coefficient on natural sea salts (e.g., 0.048 at 50% RH) than that on pure sodium chlorides (e.g., 0.033 at 50% RH), but they attributed this phenomenon to the variation in the salt size, which led to a limitation in the uptake rate on small particles. An investigation of the heterogeneous loss of N_2O_5 on submicron sea salt particles with a hexanoic acid coating by Thornton and Abbatt (2005) showed that the presence of millimolar levels of hexanoic acid greatly decreased the N_2O_5 uptake coefficient by a factor of 3–4 (i.e., approximately from 0.025 to 0.008, at 70% RH).

Effects on Optical Properties and Radiative Forcing

The mixing of chloride aerosols with organic matter alters not only the hygroscopicity but also the optical properties of the aerosols, which has a further effect on the radiative forcing. Generally, mixing with non-absorbing organic matter suppresses the uptake of water, particularly at high humidity, and thus reduces the aerosol scattering efficiency and the subsequent cooling effect on the atmosphere. Abo Riziq *et al.* (2007) measured the optical properties of mixed chloride particles and found that the extinction efficiency of mixed particles of sodium chloride with glutaric acid decreased significantly in comparison with pure sodium chloride particles. A modeling study by Randles *et al.* (2004) predicted that an internal mixture of 90% sodium chloride with 10% non-absorbing organics would cause 3% less cooling than 100% sodium chloride particles in the visible spectrum over clear-sky oceans. The mixing of chloride with light-absorbing substances (e.g., black carbon (soot) and brown carbon (nitroaromatic compounds, humic-like substances, and imidazoles)) generally enhances the absorption of light and/or decreases the scattering of light by aerosols when compared with the individual components, and thus causes a warming effect. Mallet *et al.* (2004) compared the single-scattering albedos of internally mixed sea salt with black carbon particles, the corresponding externally mixed particles, and unmixed sea salts at a coastal industrialized region in France, and found that the single-scattering albedo of the internally mixed particles (0.75) was significantly lower than those of the externally mixed particles (0.85) and unmixed sea salts (0.99). A modeling study by Randles *et al.* (2004) predicted that the internal mixing of 90% NaCl with 10% mildly absorbing organic compounds would substantially reduce the radiative cooling compared with 100% NaCl aerosols. In addition, Hoffer *et al.* (2006) found that humic-like substances in biomass burning particles at a tropical pasture site in Brazil contributed 50% to the absorption of light by aerosols at 300 nm and 7% for the entire spectrum. Chakrabarty *et al.* (2010) also reported that the presence of brown carbon in biomass burning particles collected from a laboratory chamber led to an increase in light absorption and the radiative forcing efficiency. The global mean radiative forcing of biomass burning aerosols is approximately 0.04 W m^{-2}, with a median of 0.02 W m^{-2} (Forster *et al.*, 2007).

FUTURE PERSPECTIVES

A number of field studies on single particles have confirmed that a large fraction of the chloride aerosols from various sources are internally mixed with other inorganic and organic substances in diverse locations. Laboratory experiments and a few field measurements and modeling simulations have provided some evidence that the mixing of chloride aerosols with other constituents has significant effects on their hygroscopicity, CCN activity, heterogeneous reactivity, optical properties, and radiative forcing when compared with the pure chloride salts. However, additional studies are required to obtain a comprehensive understanding of the mixing characteristics of chloride particles and their subsequent atmospheric effects, including (a) more field studies on the mixing properties of chloride aerosols in megacity centers, suburban areas, and rural locations to fully understand the influences of anthropogenic activities on the mixing state as well as the mixing processes; (b) further laboratory studies to clarify the complex effects of different mixing patterns on the size, density, morphology, porosity, hygroscopicity, reactivity, and optical properties of chloride aerosols; (c) the development and improvement of modeling techniques by taking into account the mixing state of the chloride aerosols and the subsequent changes in their physical and chemical properties; and (d) modeling simulations to evaluate the potential environmental effects (e.g., radiative forcing, CCN activation, and precipitation) of mixed chloride aerosols.

CONCLUSION

In this review, we have summarized the existing studies and findings on the mixing characteristics of chloride aerosols, and the atmospheric consequences of this mixing. Besides the traditionally used SEM and TEM, several new single-particle techniques have been developed and applied in research on the mixing state and chemical composition of aerosol particles, including STXM-NEXAFS, ATOFMS, TOF-SIMS, and NanoSIMS. Field studies in various locations have shown that a large proportion of chlorides internally mix with other inorganic and organic constituents rather than existing alone. Specifically, sodium chlorides in fresh sea salts are usually attached to a small quantity of other inorganic substances, while in aged sea salts they are completely encased within a large quantity of inorganic materials. Sodium chlorides in polluted coastal regions also co-exist with multiple organic compounds, with an organic layer coated on the surface. Potassium chlorides in biomass burning particles are generally attached to carbonaceous materials in young smoke, and they are completely coated by organic matter in aged smoke. Most chloride aerosols emitted in industrial smoke are mixed with transition/heavy metals, and a coating of organics and/or sulfates appears on aged particles. In addition, some secondary chlorides are produced by the reactions of HCl with alkaline substances, and can mix with mineral dusts, nitrates, and sulfates. The mixing of chloride with other components can significantly alter the physical and chemical properties of the aerosol particles. Generally, mixing with inorganic salts enhances the hygroscopicity, heterogeneous reactivity, and CCN activation of the aerosols, while mixing with organic matter suppresses these traits. The mixing of chloride aerosols with organic compounds can decrease the scattering of light or increase its absorption by aerosols, thus leading to a warming effect to the atmosphere. With consideration of the apparent effects of mixing on the properties of chloride aerosols and subsequently on the climate and the limited current studies in this community, we also provide suggestions for necessary future research.

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