https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020

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Impact of organic acids on chloride depletion of inland transported sea spray aerosols

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https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020

Atmospheric Chemistry and Physics Discussions

Highlights

1. Half of the sea salt aerosol (SSA) particles could be assigned as the biological origin.
2. Organic acids considerably contribute to chloride depletion of SSA particles.
3. Biological organic coatings may inhibit heterogeneous reactions of SSA particles.

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

Abstract. Heterogeneous reactions on sea spray aerosols (SSA) are the main pathway to drive the circulation of chlorine, nitrogen, and sulfur in the atmosphere. The release of Cl will significantly affect the physicochemical properties of SSA. However, the impact of organic acids and mixing state on chloride depletion of SSA is still unclear. Hence, the size and chemical composition of individual SSA particles during the East Asian summer monsoon were investigated by a single particle aerosol mass spectrometer (SPAMS). According to the chemical composition, SSA particles were classified into SSA-Aged, SSA-Bio and SSA-Ca. In comparison to the aged Na-rich SSA particles (SSA-Aged), some additional organic species related to biological origin were observed in SSA-Bio, and each of two types accounts for approximately 50% of total SSA particles. SSA-Ca may associated with organic shell of Na-rich SSA particles, which only accounts for ~3%. Strongly positive correlations between Na and organic acids (including formate, acetate, propionate, pyruvate, oxalate, malonate, succinate, and glutarate) were observed for the SSA-Aged ($r^2 = 0.52$, $p < 0.01$) and SSA-Bio ($r^2 = 0.61$, $p < 0.01$), indicating the significance of organic acids in the chloride depletion during inland transport. The contribution of these organic acids to the chloride depletion is estimated to be up to 34%. Interestingly, the degree of chloride depletion is distinctly different between SSA-Aged and SSA-Bio. It is most probably attributed to the associated organic coating in the SSA-Bio particles, which inhibit the displacement reactions between acids and chloride. As revealed from the mixing state of SSA-Bio, Cl / Na ratio increases with increasing phosphate and organic nitrogen, which is known to originate from biological activities. This finding provides some basis for the

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

improvement of modeling simulations in chlorine circulation and a comprehensive understanding of the effects of organics on chloride depletion of SSA particles.

Keywords:

Sea spray aerosols; individual particles; chloride depletion; mixing state; organic acids.

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020

Atmospheric Chemistry and Physics Discussions

1 Introduction

As one of the largest natural sources of aerosols, sea spray aerosols (SSA) have a global flux of 2000-10000 Tg yr^{-1} (Gantt and Meskhidze, 2013) and global average distribution of 10.1 μg m^{-2} (Ma et al., 2008). SSA are highly complex mixtures, and the chemical composition and mixing state of original SSA depends on the components of local seawater and the mechanisms of formation (Wang et al., 2017). While fresh SSA particles contain approximately 90% sodium chloride (NaCl) in mass, multiphase reactions considerably affect the chemical composition and mixing state, and subsequently, the physical and chemical properties of SSA. The multiphase reactions of SSA, as have been widely reported in field experiments and laboratory studies (Ault et al., 2014; Ghorai et al., 2014; Ryder et al., 2015; Trueblood et al., 2016; Bondy et al., 2017; Martin et al., 2017; Bertram et al., 2018), drive the circulation of elements (e.g., C, O, N, S, P, Cl) affecting tropospheric chemistry and global ecosystem (Finlayson-Pitts, 2003).

As one of the most important reactions, chloride depletion, as shown in R1, in SSA by interacting with acidic species modifies the physicochemical properties of SSA.

$$HA_{(g \text{ or } aq)} + NaCl_{(aq \text{ or } s)} \rightarrow NaA_{(aq \text{ or } s)} + HCl_{(g \text{ or } aq)} \quad \text{(R1)}$$

where NaCl represents the major component of SSA, and HA represents acidic species (e.g., HNO_3, H_2SO_4, and organic acids). Generally, inorganic acids are considered as the major contributors to chloride depletion in SSA (Dasgupta et al., 2007; Laskin et al., 2012; Chi et al., 2015), represented as:

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020

Atmospheric Chemistry and Physics Discussions

$$HNO_{3\,(g\text{ or }aq)} + NaCl_{(s\text{ or }aq)} \rightarrow NaNO_{3\,(aq)} + HCl_{(g\text{ or }aq)} \quad (R2)$$

$$H_2SO_{4\,(g\text{ or }aq)} + NaCl_{(s\text{ or }aq)} \rightarrow Na_2SO_{4\,(aq)} + HCl_{(g\text{ or }aq)} \quad (R3)$$

However, growing evidence indicates that inorganic acids cannot fully explain the chloride depletion (Laskin et al., 2012). It is therefore proposed that organic acids should be included to further explain the mechanism of chlorine depletion in aged SSA (Ault et al., 2013; Wang and Laskin, 2014; Wang et al., 2015). Similarly, the heterogeneous reactions on SSA with organic acids (R-COOH) can be described as:

$$R\text{-}COOH_{(g\text{ or }aq)} + NaCl_{(s\text{ or }aq)} \rightarrow R\text{-}COONa_{(aq)} + HCl_{(g\text{ or }aq)} \quad (R4)$$

$$NaNO_{3\,(aq)} + R\text{-}COOH_{(g\text{ or }aq)} \rightarrow HNO_{3\,(g\text{ or }aq)} + R\text{-}COONa_{(s\text{ or }aq)} \quad (R5)$$

(*s*, solid; *aq*, aqueous; and *g*, gaseous)

The physicochemical properties of SSA could be substantially altered through the production of organic salts (Trueblood et al., 2016; Bertram et al., 2018). With ubiquitous existence in the atmosphere, some typical organic acids, such as formic acid, acetic acid, and oxalic acid, may potentially contribute to chloride depletion. Mochida et al. (2003) suggested that organic acids (e.g., oxalic acid and succinic acid) should be considered in the models in order to predict chloride depletion accurately. Through investigating the interactions between the pure NaCl and carboxylic acids in the laboratory, Laskin et al. (2012) even suggested interactions between carboxylic acids and NaCl was the main contribution of chloride depletion. Consistently, Ghorai et al. (2014) observed that some dicarboxylic acids might cause obvious chloride depletion under a specific meteorological condition. These dicarboxylic acids (e.g., malonic acid and succinic acid) are ubiquitous in urban and marine aerosols (Kawamura and Bikkina,

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

94 2016), which may come from the polluted continental outflow and the open ocean
95 (Bikkina et al., 2015).

96 Given the potential contribution of organic acids to the chloride depletion, the
97 understanding of the relative contribution and the influencing factors is still unclear.
98 The investigation of factors that affect chloride depletion is indispensable to understand
99 the ageing process of SSA and the ability to serve as cloud condensation nuclei (CCN)
100 (Drozd et al., 2014; Wang et al., 2015). The morphology of fresh SSA particles is core-
101 shell structure, which consists of salt-core dominated by sodium chloride and outer shell
102 covered by K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^- and organic components (Laskin et al., 2012;
103 Collins et al., 2014; Chi et al., 2015). These organic components such as alkanes, fatty
104 acids, sugars, dicarboxylic acids and phosphate may emitted from phytoplankton and
105 bacteria in the sea surface microlayer (SSML) (Gaston et al., 2010; Bikkina et al., 2015;
106 Cochran et al., 2017a; Cochran et al., 2017b; Wang et al., 2017), and the chemical
107 composition and size distribution of SSA particles could be greatly changed by wave
108 breaking. In recent literature, organic coatings on the particles resulted from
109 atmospheric oxidation of hydrocarbons of biogenic and anthropogenic origin may
110 significantly regulate uptake of N_2O_5 (Folkers et al., 2003; Ryder et al., 2015).

111 In the present study, a single particle aerosol mass spectrometer (SPAMS) was
112 used to investigate the particle size, chemical composition and ageing degree of
113 individual SSA particles after long-range inland transport during the summer monsoon,
114 to reveal the relative contribution of organic acids on chloride depletion and the
115 influencing factors. The displacement reactions on the SSA particles with various types

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

of organic acids are considered, and the results suggest a significant impact of organic acids on chloride depletion during inland transport. The influence of biogenic organics in the chloride depletion was also discussed.

2 Materials and Methods

2.1 Field site description

The sampling site is located at Nanling national background station (Mt. Tianjing, 24°41′56″ N, 112°53′56″ E; 1690 m a.s.l.), which was approximately 350 km north of the South China Sea and 200 km north of the Pearl River Delta (PRD) region. It is also surrounded by a national park forest (273 km^2), where there were barely anthropogenic pollutants. However, under the influence of the East Asian summer monsoon, the air mass originated from the South China Sea might cross the PRD region to the sampling site. As can be seen in *Supplement* Fig. S1, four major cluster back trajectories of air masses originated from the South China Sea and Indo China Peninsula transported across inland regions to the sampling site within 72 h. During the sampling period, the average relative humidity was 87%, the average temperature was 26.3°C, the wind direction was mainly southwesterly, and the average wind speed was 10 m s^{-1}. More detailed information on the meteorological data can be found in *Supplement* Fig. S2.

2.2 Instrumentation

Individual particles were analyzed using a SPAMS (Hexin Analytical Instrument Co., Ltd., China) from 11 May to 3 June 2018. The SPAMS was used to on-line measure

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

the size and chemical composition of individual particles. The design and principles of SPAMS have been reported in detail previously (Li et al., 2011). Briefly, the aerosols are drawn into the aerodynamics lens. Then the collimated particles beam through two continuous laser beams (Nd: YAG laser, 532 nm) with a pace of 6 cm. The obtained time of flight and velocity are corresponding to the vacuum aerodynamic diameter. The velocity of an individual particle is applied to trigger the pulse laser (Nd: YAG laser, 266 nm). Subsequently, the generated ion fragments are detected by a bipolar time-of-flight mass spectrometer. Standard polystyrene latex spheres of 0.2-2.2 μm were used to calibrate vacuum aerodynamic particle sizes (d_{va}) of the measured individual particles.

It is also noted that aerosols were sampled through two parallel inlets. The first one is a ground-based counterflow virtual impactor (GCVI model 1205, Brechtel Manufacturing Inc., USA), sampling the cloud residual particles, dried from cloud droplets (with size larger than 8 μm) during cloud event (i.e., when the relative humidity was higher than 95% and the visibility was lower than 3 km) (Zhang et al., 2017). The other one is a $PM_{2.5}$ sampling inlet, delivering fine particles during cloud free periods.

2.3 Classification of SSA

The general characteristic peaks of SSA particles include *m/z* 23 $[Na]^+$, 39 $[K]^+$, 46 $[Na_2]^+$, 62 $[Na_2O]^+$, 63 $[Na_2OH]^+$, 81 $[Na_2{}^{35}Cl]^+$ and 83 $[Na_2{}^{37}Cl]^+$ (Collins et al., 2014; Arndt et al., 2017; Martin et al., 2017). There are some additional organic peaks of biological origin (such as at *m/z* 58 $[C_2H_5NHCH_2]^+$, 59 $[N(CH_3)_3]^+$, 74

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

157 $[(C_2H_5)_2NH_2]^+$, -26 $[CN]^-$, -42 $[CNO]^-$, -63 $[PO_2]^-$, -79 $[PO_3]^-$, etc.), besides sodium-
158 related peaks in SSA particles (Ault et al., 2014; Sultana et al., 2017b). In this study,
159 SSA particles were identified by the presence of peaks at *m/z* 23, 46, 62, 63, 81 and 83,
160 which was coincident with the previous study at the same site reported by Lin et al.
161 (2019). In addition, these organic signals are also considerable for identification of SSA
162 particles, when the above sodium related peaks exist.

163 A total of ~2 million detected particles were clustered into several groups using an
164 Adaptive Resonance Theory neural network (ART-2a) (Song and Hopke, 1999) with a
165 vigilance factor of 0.75, a learning rate of 0.05 and a maximum of 20 iterations. Based
166 on the above representative peaks, ~50 000 SSA particles were identified. Three types
167 of SSA particles with distinct mass spectral characteristics were obtained, including
168 ~25 000 SSA-Aged, ~25 000 SSA-Bio and 1 500 SSA-Ca, respectively. We note that
169 the mass spectral characteristics of SSA for the cloud residual particles ensemble those
170 for the cloud-free particles. And therefore, we focus on the influence of long-range
171 transport, rather than in-cloud process, on the modification of SSA.

172 ## 3. Results and discussion

173 ### 3.1 General characteristics of inland transported SSA particles

174 Figure 1 provides the averaged positive and negative ion mass spectra of three
175 types of SSA particles. SSA-Aged is characterized by prominent ion signature for *m/z*
176 at 23 $[Na]^+$, 39 $[K]^+$, 40 $[Ca]^+$, 46 $[Na_2]^+$, 62 $[Na_2O]^+$ and 63 $[Na_2OH]^+$. Some
177 contributions from *m/z* 24 $[Mg]^+$, 56 $[Fe]^+$ or 56 $[CaO]^+$, 81 $[Na_2{}^{35}Cl]^+$, 83 $[Na_2{}^{37}Cl]^+$,

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

178 108 $[Na_2NO_3]^+$ and 165 $[Na_2SO_4]^+$ were also observed. These mass spectral
179 characteristics are similar to those in previous literature (Hughes et al., 2000; Collins et
180 al., 2014; Sultana et al., 2017a). This type of SSA particles with a significant ion marker
181 of Na is typically represented as Na-rich sea salt particles. In the negative ion spectra,
182 abundant nitrate were observed due to the ratio of *m/z* at -46 $[NO_2]^-$, -62 $[NO_3]^-$, and -
183 147 $[Na(NO_3)_2]^-$, in contrast to weak chlorine ion signal at *m/z* -35 $[^{35}Cl]^-$ and -37 $[^{35}Cl]^-$,
184 indicating that the particles have undergone partial but not fully atmospheric ageing
185 (Hughes et al., 2000; Sultana et al., 2017b). Several peaks are assigned as organic acids,
186 such as formate at *m/z* -45 $[HCO_2]^-$, acetate at *m/z* -59 $[C_2H_3O_2]^-$, propionate at *m/z* -73
187 $[C_2HO_3]^-$, pyruvate at *m/z* -87 $[C_3H_3O_3]^-$, oxalate at *m/z* -89 $[C_2HO_4]^-$, malonate at *m/z*
188 -103 $[C_3H_3O_4]^-$, succinate at *m/z* -117 $[C_4H_5O_4]^-$, and glutarte at *m/z* -131 $[C_5H_7O_4]^-$
189 (Lin et al., 2019), which may be related to algal activity in the SSML or conversion of
190 second organic aerosols (SOAs) in the atmosphere (O'Dowd et al., 2014).

191 Compared with SSA-Aged, the averaged ion spectra of SSA-Bio are more
192 complex. SSA-Bio had significant additional signals from biological organic matter
193 (i.e., organic nitrogen and phosphate), besides the general characteristics of the SSA-
194 Aged particles (Prather et al., 2013; Guasco et al., 2014). While these markers might
195 also be associated with dust (Zawadowicz et al., 2017), it is most likely attributed to
196 biological markers herein, since there is negligible ion marker (e.g., Al, Ti, Si) for dust.
197 Distinct characteristics of amines (58 $[C_2H_5NHCH_2]^+$, 59 $[N(CH_3)_3]^+$) were presented
198 in the positive spectra, which is similar to the results in a prior laboratory study (Sultana
199 et al., 2017a). Besides, the source of amines could also be influenced by the formation

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

of secondary species (such as animal husbandry and biomass burning) during transport (Cheng et al., 2018). The organic nitrogen (i.e., -26 $[CN]^-$, -42 $[CNO]^-$) has been assigned to the ionization of amino acids in previous studies (Abneesh et al., 2005; Czerwieniec. et al., 2005). Phosphate peaks at *m/z* -63 $[PO_2]^-$ and -79 $[PO_3]^-$ are likely assigned as the ionization of components such as phospholipids in biological cells (Fergenson, 2004; Collins et al., 2013; Cochran et al., 2017a; Cochran et al., 2017b; Nguyen et al., 2017). It is noted that SSA-Bio should be regarded as the SSA population influenced by biological activity (Prather et al., 2013). In addition, the peaks of *m/z* 56 represents $[CaO]^+$ / $[KOH]^+$ or $[^{56}Fe]^+$. In contrast to SSA-Aged, those aforementioned organic acids exhibited higher peak signal in SSA-Bio. Similar to SSA-Aged, inorganic acids (-46 $[NO_2]^-$, -62 $[NO_3]^-$ and -97 $[HSO_4]^-$) with strong ion signals were also observed. Despite of the different mass spectral pattern, the behavior and inland transport of SSA-Aged and SSA-Bio may be similar. As can be seen in Fig. S1, the relative proportions of them keep stable in the different air masses. They also exhibit similar size distribution, concentrating in size range of 0.4-0.7 μm and peaking around 0.5 μm (Fig. S3).

SSA-Ca is identified by relatively higher contributions from calcium-related compounds at *m/z* 40 $[Ca]^+$, 56 $[CaO]^+$, 57 $[CaOH]^+$, 75 $[Ca^{35}Cl_2]^+$, 77 $[Ca^{37}Cl_2]^+$, and 113 $[(CaO)_2H]^+$, whereas associated with smaller sodium peak than other types. The negative spectra are dominated by nitrate, sulfate, organic nitrogen, phosphate and chloride. This SSA population has been previously classified as "organic-carbon-dominated (OC)" (Prather et al., 2013; Collins et al., 2014), likely resulted from the

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

coating of Na-rich particles through crystallization and precipitation (Sultana et al., 2017a; May et al., 2018). The mass spectral characteristics of the Ca-rich SSA particles are quite similar to those of lake spray aerosols (Axson et al., 2016; May et al., 2018). However, SSA-Ca only accounts for a negligible fraction (3.2%) and thus will not be covered in the following discussions.

3.2 Contribution of organic acids to the chloride depletion in the SSA particles

The linear correlations based on peak area between Na and chloride, sulfate, nitrate, and organic acids in the SSA-Aged and SSA-Bio particles are shown in Fig. 2. As expected, there are strong correlations between Na and nitrate in both the SSA-Aged ($r^2 = 0.79$, $p < 0.01$) and SSA-Bio ($r^2 = 0.86$, $p < 0.01$) particles. In addition, more than 99% of SSA particles are internally mixed with nitrate (Fig. 3). This indicates that chemistry in Reaction 2 (R2) is prevalent during long-range transport (Bondy et al., 2017). This is also consistent with previous studies regarding that nitric acid is a major contributor to chloride depletion (Zhao and Gao, 2008; Chi et al., 2015; AzadiAghdam et al., 2019). It is probably because the concentration of its precursor NO_x (4.67 μg m^{-3}) suppresses those of other acids in the south China sector (Wang et al., 2016; Wu et al., 2019).

Strong positive correlations between Na and organic acids are also observed in both the SSA-Aged ($r^2 = 0.52$, $p < 0.01$) and SSA-Bio particles ($r^2 = 0.61$, $p < 0.01$). Furthermore, very high number fractions (NFs) of organic acids are also found in SSA-Aged (72%) and SSA-Bio (59%), as shown in Fig. 3. This indicates the possible

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

243 presence of organic salts in SSA particles and the substantial contribution of organic
244 acids to the chloride depletion. The detailed mixing state between SSA particles and
245 several detected organic acids, as shown in Fig. S4, indicates that formate, oxalate,
246 malonate, and glutarate are the dominant salts. The relative peak area (RPA) ratio (acids
247 / (sulfate + nitrate + organic acids)) is further applied to roughly evaluate the relative
248 contribution of different acids (nitric acid, sulfuric acid, and organic acids) to the
249 chloride depletion of SSA particles (Fig. S5). In the ageing process of the SSA particles,
250 nitrate occupies a large proportion in the SSA-Aged (63-96%) and SSA-Bio particles
251 (64-95%), respectively. Notably, chloride depletion attributed to organic acids could
252 account for 2–34% in the SSA-Aged particles and 2–29% in the SSA-Bio particles. The
253 relative contribution of organic acids to chloride depletion has been reported to be
254 higher than 30% at the eastern United States coast (Braun et al., 2017) and up to 40%
255 in Southeast Asia (AzadiAghdam et al., 2019). The contribution of sulfuric acids (0-
256 10% versus 0-18 %) is the lowest, although it shows positive correlation ($r^2 = 0.24$, $p <$
257 0.01 versus $r^2 = 0.54$, $p < 0.01$) for the SSA-Aged and SSA-Bio particles, respectively
258 (Fig. 2). In addition, similar variations in peak areas of sulfate, nitrate and organic acids
259 were observed in the SSA-Aged and SSA-Bio particles throughout the sampling period
260 (Fig. S6), indicating a close connection of the formation mechanism between inorganic
261 and organic acids.

262 **3.3 Effect of particle type on chloride depletion**

263 Cl / Na value is typically applied to evaluate the ageing degree of SSA particles

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

(Laskin et al., 2012; Bondy et al., 2017). There is a significant difference of Cl / Na between the SSA-Aged (1.9%) and SSA-Bio (5.4%) particles (Fig. 4). This result reflects less chloride remaining in the SSA-Aged, attributed to more severe ageing. It might also be supported by relatively weak positive correlation ($r^2 = 0.46$, $p < 0.01$) between Na and Cl (Fig. 2). This result may be explained by the influence of chemical composition and mixing state on the evolution of the SSA particles (Collins et al., 2014; Quinn et al., 2015; Sultana et al., 2017b). Additionally, concentration calculation was also further quantified the chloride depletion percentage using the following equation:

$$\%Cl^- \text{ depletion} = (1.81 \times [Na^+] - [Cl^-]) / (1.81 \times [Na^+]) \times 100\% \quad (R6)$$

where $[Na^+]$ and $[Cl^-]$ are mass concentrations ($\mu g\ m^{-3}$), and 1.81 is the typical mass ratio of Cl / Na in seawater (Zhao and Gao, 2008; Braun et al., 2017; AzadiAghdam et al., 2019). The overall $\%Cl^-$ for the total SSA particles varying from 55% to 99% with an average of 78% (detailed in *Supplement* Table S1), which is similar to the previous filed study in the PRD region reported by Chen et al. (2016). However, SSA particles are not the only source of chlorine ion in the atmosphere (Lightowlers et al., 1988). The excess $[Cl]^-$ produced by fuel combustion could lower the $\%Cl^-$, which might explain the weak difference between the two assessment methods of ageing degree of SSA particles. Hence, both assessment methods could effectively evaluate the chloride depletion of SSA particles supported by a positive correlation ($r^2 = 0.47$, $p < 0.01$) (Fig. S7).

Further analysis indicates that organic matter of biological origin might play an important role in such inhibition of chloride depletion in the SSA-Bio particles. It is

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

supported by the relationship between peak area ratio of Cl / Na and the biological origin markers (-26 $[CN]^-$, -42 $[CNO]^-$, -63 $[PO_2]^-$ and -79 $[PO_3]^-$) described in section 3.1. As shown in Fig. 5, peak area ratio of Cl / Na exhibits an increasing trend with both phosphate (-63 $[PO_2]^-$, -79 $[PO_3]^-$) and organic nitrogen (-26 $[CN]^-$ and -42 $[CNO]^-$). This direct evidence indicated phosphate might have a considerable effect on chloride depletion in SSA particles. The relationship between Cl / Na and organic nitrogen is also consistent with that reported in our previous filed observations at the same site (Lin et al., 2019). Previous laboratory study results have also shown that reactivity could be inhibited by the organic matter of biological origin (Ault et al., 2014). As shown in Fig. S8, transmission electron microscopy (TEM) images clearly show NaCl core and organic coating of the SSA particles with various thicknesses. The thicker organic coating may inhibit the reactive uptake of $HNO_{3\,(g)}$ or $N_2O_{5\,(g)}$ to SSA particles (Folkers et al., 2003; Ryder et al., 2014; Ryder et al., 2015), resulting in a less released Cl to the atmosphere. Such organic coatings are mostly composed of long-chain hydrocarbon, saccharides, carbohydrate, amine and anionic surfactant (Jayarathne et al., 2016; Bertram et al., 2018), and thus have stronger hydrophobicity and probably inhibit the occurrence of Cl transport of convection and diffusion (Bondy et al., 2017).

4. Conclusion and atmospheric implication

We investigated the chloride depletion of SSA particles after long-range inland transport in south China, during a monsoon season. The SSA particles still account for ~3% of the observed submicron particles and are extensively internally mixed with

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

various acids. While the contribution of nitric acid dominates over other acids to the chloride depletion, our results suggest that the role of organic acids should not be neglected. Up to 34% of chloride depletion could be explained by diverse organic acids. Our results add to the growing body of evidence that carboxylic acid may play a significant role in acid displacement reactions (Ma et al., 2013). Given the substantial influence of organic acids on the hygroscopic properties of SSA (Ghorai et al., 2014), such processes may affect CCN / IN activities and lifetime of SSA (Knopf et al., 2014), and thus should be considered in models to predict the climate impact of SSA accurately. Currently, the calculation model of organic acids (especially water-soluble organic compounds) to chloride depletion is still limited (Laskin et al., 2012; Xu et al., 2013). Peng et al. (2016) suggested organic salts produced by NaCl react with dicarboxylic acids inhibit the volatilization of HCl that is resulting in less chloride depletion. Our data may improve the understanding of chloride depletion responsible for mixing state of diverse organic acids in the future study.

In addition, we stress that there is a SSA type (e.g., SSA-Bio) likely attributed to the biogenic origin, exhibiting distinctly different chloride depletion, in comparison with the commonly observed SSA-Aged type. Our data indicate that organic matter of biological origin might play an essential role in such inhibition of chloride depletion in the SSA-Bio particles. As previously reported, the presence of organic coatings on SSA particles could effectively influence the heterogeneous reactivity of SSA particles (Ryder et al., 2015; Bondy et al., 2017). Considering the considerable contribution (~50%) of the SSA-Bio particles to the overall SSA, such information should be useful

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020


Atmospheric Chemistry and Physics Discussions

329 to improve that model results for the climate impact of SSA.

330

331 ## Author contributions

332 GHZ, LL, and XHB designed the research. BJS, GHZ, and LL analyzed the data,
333 and wrote the manuscript. YZF, XBD, YC, YXY and WS conducted sampling work
334 under the guidance of GHZ, LL, and XHB. DHC had an active role in supporting the
335 sampling work. YZF performed the laboratory analysis of individual particles by
336 TEM/EDS. All authors contributed to the discussions of the results and refinement of
337 the manuscript.

338 **Data availability.** Data are available on request from Lei Li (lileishdx@163.com).

339 ## Acknowledgement

340 This work was supported by the National Nature Science Foundation of China (No.
341 41905106), Guangdong International Science and Technology Cooperation Project
342 (2018A050506020) and Guangdong Foundation for Program of Science and
343 Technology Research (Grant No. 2019B121205006).

344 **Competing interests.** The authors declare that they have no conflict of interest.

345 ## References

346 Abneesh, S. M. E., Pitesky, Paul T, Steele, Herbert J, Tobias,David P, Fergenson, Joanne

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Preprint. Discussion started: 8 June 2020

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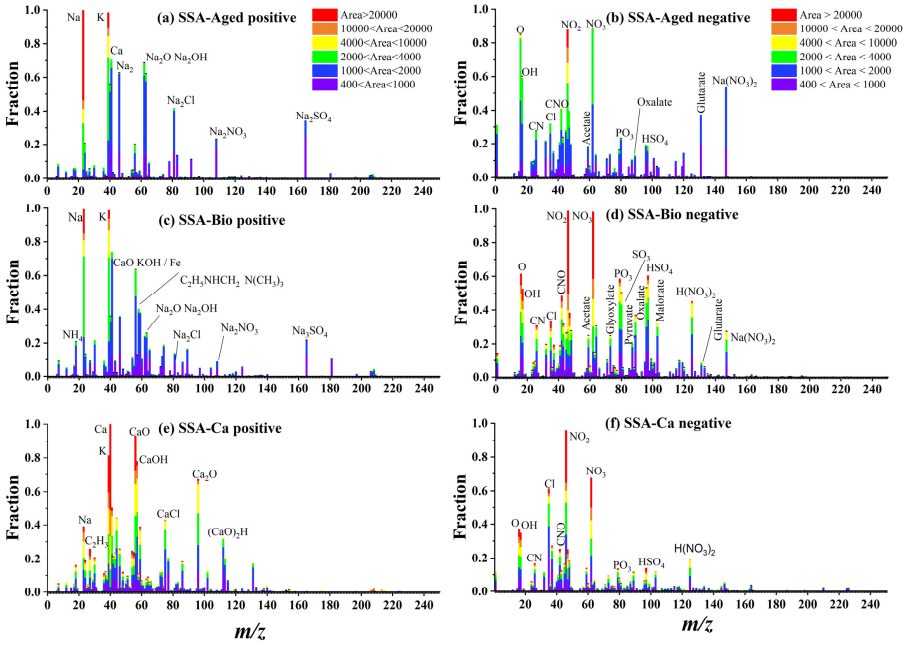
Atmospheric Chemistry and Physics Discussions

613 # Figures

614

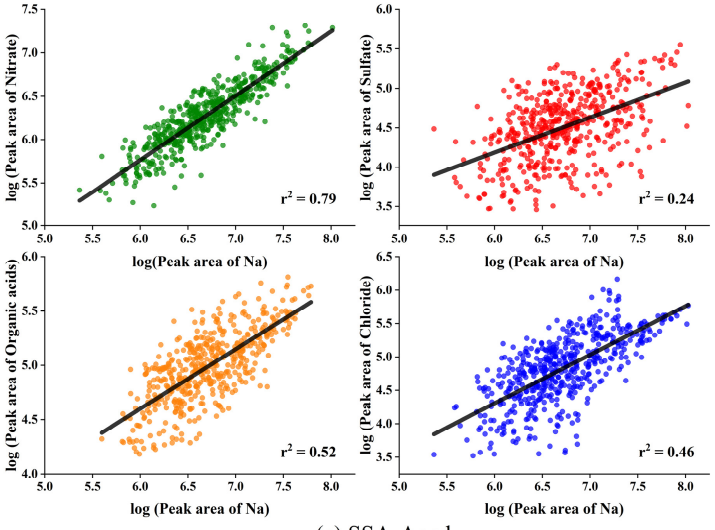


615

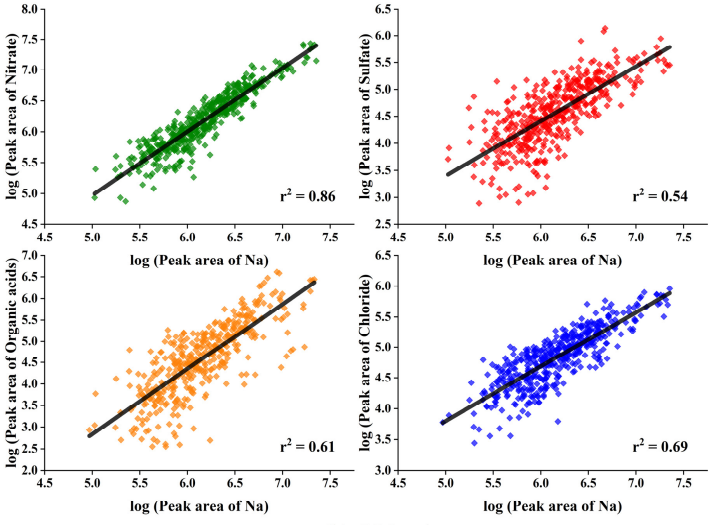
616 Figure 1. The averaged digitized positive and negative ion mass spectra of the major
617 types of SSA particles.

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020

Atmospheric Chemistry and Physics Discussions



618 (a) SSA-Aged



619 (b) SSA-Bio

620 Figure 2. Correlations between hourly mean peak area of Na (*m/z* 23) and sulfate (*m/z*
621 -97), nitrate (*m/z* -46 and 62), organic acids (*m/z* -45, -59, -73, -87, -89, -103, -117 and
622 -131) and chloride (*m/z* -35 and -37) in the SSA-Aged and SSA-Bio. The data is
623 logarithmically transformed to follow a normal distribution.

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020

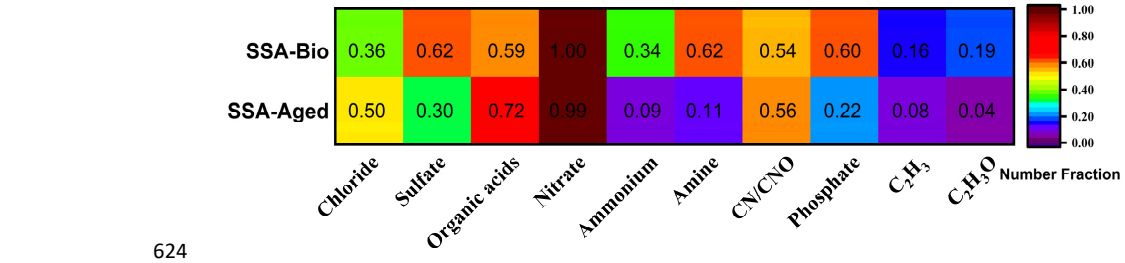
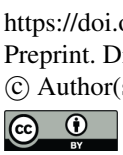
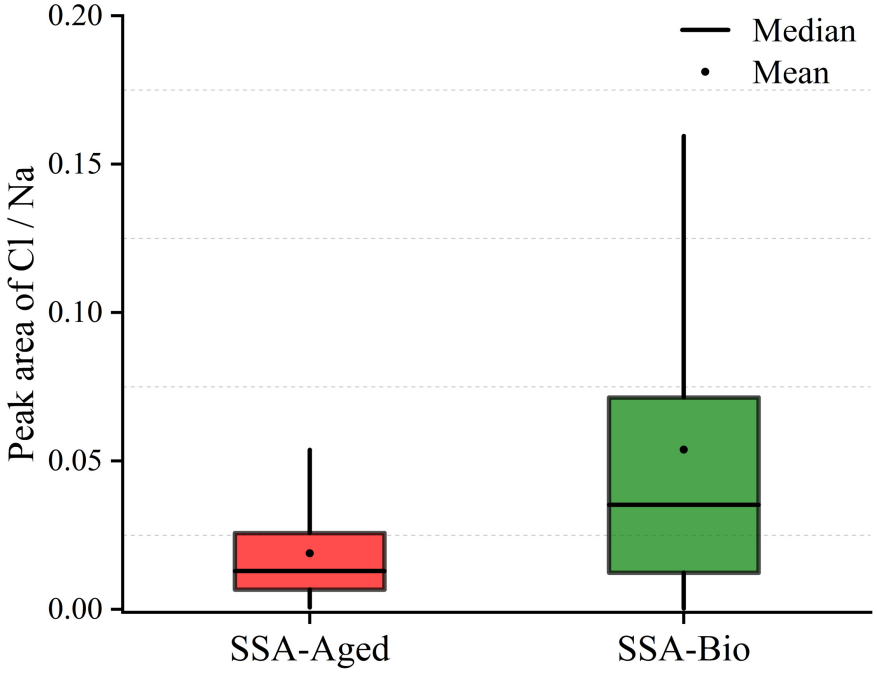


Figure 3. Hourly mean number fractions (NFs) of major component in the SSA-Aged and SSA-Bio. The major component includes chloride (*m/z* -35 or -37), sulfate (*m/z* -97), organic acids (*m/z* -45, -59, -73, -87, -89, -103, -117 or -131), nitrate (*m/z* -46 or -62), ammonium (*m/z* 18), amine (*m/z* 58 and 59), organic nitrogen (*m/z* -26 or -42), phosphate (*m/z* -63 or -79), and organic carbon (*m/z* 27 and 43).

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020



Atmospheric Chemistry and Physics Discussions

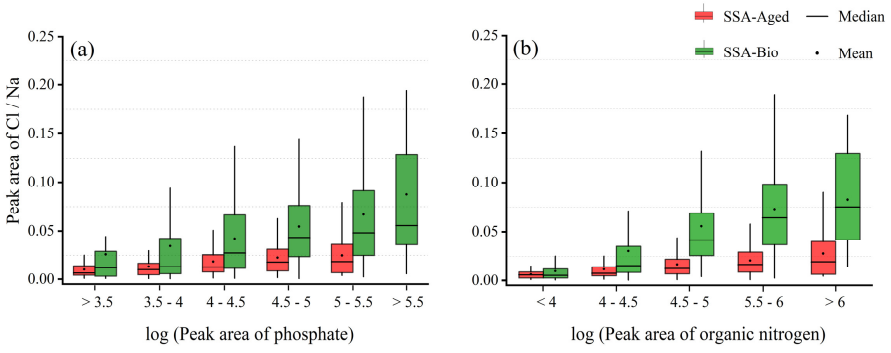


631

632 Figure 4. A box and whisker plot of hourly mean peak area of Cl / Na in SSA-Aged
633 and SSA-Bio. In the box and whisker plot, the lower and upper lines of the box denote
634 the 25 and 75 percentiles, respectively. The lower and upper edges denote the 10 and
635 90 percentiles, respectively.

https://doi.org/10.5194/acp-2020-443
Preprint. Discussion started: 8 June 2020

Atmospheric Chemistry and Physics Discussions



636

637 Figure 5. The logarithmical peak area of phosphate (*m/z* -63 and -79) and organic

638 nitrogen (*m/z* -26 and -42) varied as a function of hourly mean peak area ratio of Cl /

639 Na.