

1 **Organic amine weakens chloride depletion in coastal**
2 **atmosphere**

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11 **Abstract.** Chloride depletion from sea salt aerosols (SSA) is frequently observed in polluted coastal
12 regions, and despite they severely impact air quality and human health, the influencing mechanism of
13 alkaline species in this phenomenon remains incompletely understood. Here, we conducted laboratory
14 experiments to investigate the effect of alkaline species including NH_3 and an organic amine
15 (dimethylamine, DMA) on chloride depletion and the subsequent formation of organic chlorinated
16 compounds. Results showed that alkaline species could weaken chloride depletion caused by acidic
17 gases, mainly due to acid-base neutralization. Specifically, chloride depletion in the presence of NO_x
18 decreased from 20.1% to 15.8% when NH_3 concentration increased from 100 to 300 ppb. Chloride
19 depletion also decreased from 18.6% to 13.5% with DMA concentration increasing from 50 to 150 ppb.
20 The weakening effect of DMA on chloride depletion is more pronounced than that of NH_3 , primarily
21 DMA stronger alkalinity and nucleation ability. These alkaline species exhibit a stronger reduction of
22 chloride depletion in the presence of SO_2 than in the presence of NO_x . The detection of organic
23 chlorinated products, formed via active chlorine-induced oxidation, is consistent with the role of
24 alkaline species in weakening chloride depletion, which subsequently results in the reduction of active
25 chlorine. These findings suggest that alkaline species, more specifically organic amines, are significant
26 factors influencing chloride depletion in the coastal atmosphere, further improving our understanding
27 of this phenomenon.

28 **1 Introduction**

29 Sea salt aerosols (SSA), primarily composed of sodium chloride, are abundant in coastal areas and play
30 a key role in cloud nucleation with high light scattering efficiency (Zhang and Chan, 2023; Zhou et al.,
31 2025). Chloride depletion, referred to as the removal of chloride ions from SSA and frequently
32 observed in the coastal atmosphere (Bian et al., 2014; Duan et al., 2024; Su et al., 2022), accelerates
33 their aging process of SSA, profoundly influencing visibility, global climate and the earth-atmosphere
34 radiative balance (Ghosh et al., 2020; Edwards et al., 2024; Su et al., 2022). This process also affects
35 the atmospheric oxidation capacity by producing Cl_2 , HCl , Cl^\bullet , and other reactive species (Hoffmann et
36 al., 2019; Chen et al., 2024b; Dai et al., 2025). However, significant discrepancies exist between field
37 observations and model predictions of chloride depletion with an average absolute difference of 20%
38 (Nolte et al., 2008; Nolte et al., 2015; Su et al., 2022), highlighting the need for a deeper understanding

39 of its underlying mechanisms.

40 Alkaline species such as NH_3 and organic amines have been suspected to affect chloride depletion (Su
41 et al., 2022). Gaseous ammonia (NH_3), the most abundant alkaline species in the atmosphere, plays an
42 important role in the formation of atmospheric particles (Behera et al., 2013; Lan et al., 2024; Wang et
43 al., 2020). A field study found a relatively low level of chloride depletion in the Antarctic winter, and
44 the large amount of ammonia emitted by penguins has been hypothesized to be responsible for this
45 phenomenon (Rankin and Wolff, 2003). Dimethylamine (DMA, $(\text{CH}_3)_2\text{NH}$), a predominant organic
46 amine in the atmosphere, has a stronger alkalinity than ammonia and could compete with ammonia in
47 reactions with acidic species, despite its atmospheric concentration being much lower than that of
48 ammonia (Chen et al., 2022; Xie et al., 2018; Liu et al., 2024a). However, to the best of our knowledge,
49 there is currently no experimental evidence illustrating the role of alkaline species in chloride depletion.

50 The influence of organic amines remains overlooked in model predictions (Nolte et al., 2015),
51 highlighting a critical gap for accurately predicting chloride depletion in amine-rich coastal or
52 agricultural-marine interfaces.

53 Organic chlorinated compounds are important indicators of chloride depletion. They can be formed
54 from the oxidation of volatile organic compounds (VOCs) by reactive chlorine species (e.g., Cl^\bullet , Cl_2^\bullet ,
55 etc.) generated during the chloride depletion process (Zhang and Chan, 2023; Wennberg et al., 2018;
56 Wang et al., 2022b). Once formed, some organic chlorinated compounds with low volatility can
57 partition into the particle phase, contributing to the formation of secondary organic aerosols (SOA). For
58 example, it is estimated that organic chlorinated compounds can contribute up to 15% of the total SOA
59 in polluted areas with sufficient chlorine and VOC emissions (Liu et al., 2024c). Organic chlorinated
60 compounds have been observed during chloride depletion in our previous study in the presence of
61 isoprene (Song et al., 2025), an important biogenic VOC emitted from ocean and terrestrial plants (Yu
62 and Li, 2021; Zhang et al., 2025; Zou et al., 2023). Understanding the formation of organic chlorinated
63 compounds would not only help elucidating the influence of alkaline species on chloride depletion but
64 also provide significant implications for the chlorine cycle.

65 To investigate the roles of alkaline species, including NH_3 and DMA, in chloride depletion,
66 experiments on reactions involving SSA particles, alkaline species, acidic gases, and/or isoprene were
67 conducted in a chamber. We characterized the changes in chloride depletion and further analyzed the
68 subsequent formation of corresponding organic chlorinated compounds to explore the reasons for their

69 changes. This study provides a comprehensive understanding of chloride depletion from SSA, which
70 may be crucial for more accurately predicting this phenomenon in coastal atmospheres.

71 2 Materials and methods

72 2.1 Chamber experiments

73 To study the effect of alkaline species on chloride depletion, three groups of experiments were designed:
74 NaCl particles + NH₃/DMA (control experiments), NaCl particles + H₂O₂ + NO_x/SO₂ + NH₃/DMA,
75 and NaCl particles + H₂O₂ + isoprene + NO_x/SO₂ + NH₃/DMA. Here, the shifting ratios of ammonia to
76 DMA are in the range 0.67-6, which falls within the ranges observed in diverse coastal environments
77 (0.1-110) (Smith et al., 2007; Chen et al., 2022; Berner and David Felix, 2020; Liu et al., 2022; Liu et
78 al., 2024b; Liu et al., 2023; Du et al., 2021). Although the initial concentrations of alkaline species used
79 in the experiments were higher than the ambient levels, this consideration was necessary for laboratory
80 experiments within a short time scale to tackle their influence on chloride depletion. Details of
81 experimental conditions are provided in Table 1. All experiments were conducted in a 1.5 m³ indoor
82 chamber consisting of 60 μm Teflon film within a temperature-controlled environment, surrounded by
83 black light lamps (F40BLB, GE) with the center irradiation wavelength of 365 nm as the light source.
84 The chamber was equipped with a set of online instruments for measuring physical and chemical
85 parameters. The concentration of aerosol particles was measured using a scanning mobility particle
86 sizer (SMPS, Grimm, Germany), which is composed of a differential mobility analyzer (DMA, 55-L,
87 Grimm, Germany) and a condensation particle counter (CPC, 5416, Grimm, Germany). The
88 concentrations of NO_x and isoprene in the chamber were monitored using a NO–NO₂–NO_x analyzer
89 (Model 42i, Thermo Scientific, USA) and a gas chromatograph coupled with a flame ionization
90 detector (GC-FID 7890B, Agilent Technologies, USA). H₂O₂ acted as the source of OH radicals. The
91 initial concentrations of other substances (H₂O₂, alkaline gases, etc.) were calculated based on the
92 chamber volume and the injection volume.

93 **Table 1. Summary of experimental conditions and results.**

Experiment ^a	[Isoprene] ₀	[H ₂ O ₂] ₀	[NO _x] ₀	[SO ₂] ₀	[NH ₃] ₀	[DMA] ₀	RH	T	Cl ⁻ /Na ⁺
	(ppb)	(ppm)	(ppb)	(ppb)	(ppb)	(ppb)	(%)	(°C)	(mM/mM) ^c
C.1					100		72	20	0.989±0.019

C.2				100	71	20	0.994±0.020
N.1		4	141		69	23	0.755±0.015
NA.1		4	138	100	69	21	0.798±0.016
NA.2		4	139	200	72	21	0.822±0.017
NA.3		4	139	300	72	20	0.841±0.017
ND.1		4	146	50	69	21	0.813±0.017
ND.2		4	147	100	71	21	0.849±0.017
ND.3		4	141	150	71	22	0.864±0.018
S.1		4	300		67	22	0.704±0.009
SA.1		4	300	100	70	23	0.825±0.017
SA.2		4	300	200	70	23	0.839±0.017
SA.3		4	300	300	69	23	0.849±0.017
SD.1		4	300	50	70	22	0.851±0.017
SD.2		4	300	100	71	22	0.865±0.018
SD.3		4	300	150	70	23	0.878±0.018
IN.1 ^b	667	4	150		72	20	0.770±0.016
INA.1 ^b	621	4	140	100	71	22	0.784±0.016
INA.2	604	4	161	300	69	23	0.791±0.016
IND.1 ^b	601	4	152	100	68	22	0.814±0.017
IND.2	668	4	146	150	70	20	0.866±0.018
IS.1 ^b	776	4	300		68	20	0.655±0.008
ISA.1 ^b	604	4	300	100	70	20	0.790±0.016
ISA.2	601	4	300	300	71	21	0.800±0.016
ISD.1 ^b	629	4	300	100	70	21	0.897±0.018
ISD.2	594	4	300	150	69	22	0.961±0.020

94 ^aAbbreviations used in experimental codes correspond to the reactants introduced into the chamber.
95 “N”, “S”, “A”, “D”, and “I” stand for NO_x, SO₂, NH₃, DMA, and isoprene, respectively. C.1 and C.2
96 are control experiments.
97 ^bExperiments were repeated to collect aerosol particles for composition measurement by
98 UPLC/ESI-HR-Q-TOFMS.
99 ^cErrors in Cl⁻/Na⁺ were calculated by error propagation considering Cl⁻ and Na⁺ errors derived from
100 their IC calibration curve.

101 The chamber was thoroughly cleaned using O₃ and purified air, and exposed to UV lamps for at least
102 12 h before each experiment. Relative humidity (RH) in the chamber was adjusted by the proportion of
103 dry and wet air. Subsequently, SSA particles produced by atomizing NaCl solution with an atomizer
104 (Model 3076, TSI, USA) were introduced into the chamber. Based on the experimental design, known
105 volumes of other reactants (i.e., H₂O₂ (Aladdin, 30 wt% in H₂O), inorganic gases (NH₃, NO, etc)
106 (Qingdao Deyi Gas Company, 500 ppm balanced in N₂), DMA (Aladdin, 40 wt% in H₂O), and isoprene
107 (Macklin, >99%)) were introduced into the chamber. After the reactants were adequately mixed for 20
108 minutes, the black light lamps were turned on to initiate the reaction. The experiment lasted for two
109 hours, after which aerosol particles generated during the experiment were collected onto quartz filters
110 and 47 mm polytetrafluoroethylene (PTFE) filters and stored at -20 °C until offline analysis.

111 **2.2 Particle analysis**

112 The concentrations of inorganic ions were measured by ion chromatography (IC, Dionex ICS-600,
113 Thermo Scientific, USA). Aerosol particles collected on the quartz filters were first extracted in 5 mL
114 of ultrapure water (Milli-Q, Millipore, France) by ice sonication for 45 min. The extract was then
115 filtered through a 0.22 μm polyethersulfone syringe filter and injected into the ion chromatography
116 instrument via a six-way valve with a 250-μL loop. The separation of anions and cations was achieved
117 using a Dionex IonPac AS19 column (4 × 250 mm) with an AG19 guard column (4 × 50 mm, Dionex
118 Ionpac) for anions, and a Dionex IonPac CS12A column (4 × 250 mm) with a CG12A guard column (4
119 × 50 mm, Dionex Ionpac) for cations. A 20 mM potassium hydroxide solution was used as the anionic
120 eluent, while a 20 mM methanesulfonic acid solution was employed for cationic elution. The flow rate
121 for both eluents was maintained at 1 mL min⁻¹. The degree of chloride depletion was characterized by
122 the mole ratios of Cl⁻/Na⁺. The Cl⁻/Na⁺ value for fresh SSA is around 0.999, while lower Cl⁻/Na⁺ ratios
123 in SSA indicate the occurrence of chloride depletion.

124 The formation of organic chlorinated compounds was characterized using ultra-high performance
125 liquid chromatography (UPLC, UltiMate 3000, Thermo Scientific, USA) coupled with electrospray
126 ionization high-resolution quadrupole time-of-flight mass spectrometer (ESI-HR-Q-TOF-MS, Bruker
127 Impact HD, Germany). Prior to measurements, aerosol particles collected on PTFE filters were
128 extracted twice using 5 mL methanol (Optima® LC/MS grade, Fisher Scientific, USA) by sonication in
129 an ice bath for 30 min. The extract was filtered through a PTFE syringe filter (0.22 μm) to remove

130 impurities, and then concentrated under a gentle nitrogen gas (99.999%, Qingdao Deyi Gas Company).
131 The dried extract was reconstituted in 200 μL of a 1:1 (v:v) mixture of methanol and ultrapure water
132 containing 0.1% formic acid (Optima® LC/MS grade, Fisher Scientific, USA). Sample extracts (10 μL)
133 were analyzed using an Atlantis T3 C18 column (100 \AA , 3 μm particle size, 2.1 mm \times 150 mm, Waters,
134 USA). The mobile phase comprised 0.1% formic acid in ultrapure water (A) and 0.1% formic acid in
135 methanol (B). A 60 min gradient elution with a flow of 200 $\mu\text{L min}^{-1}$ was performed as follows: B
136 initially maintained at 3% for the first 3 minutes, gradually increased to 50% from 3 to 25 minutes, and
137 then rose to 90% from 25 to 43 minutes. The fraction of B was reduced back to 3% between 43 and 48
138 minutes, and maintained at 3% until 60 minutes to re-equilibrate the column.

139 Mass spectrometric data were analyzed with Bruker Compass Data Analysis version 4.2 Build 383.1
140 software. The molecular formulas of organic chlorinated compounds were assigned as
141 $\text{C}_{2-40}\text{H}_{2-80}\text{O}_{0-40}\text{N}_{0-3}\text{S}_{0-2}\text{Cl}_{1-2}$ within a ± 5 ppm mass tolerance, with restrictive conditions applied to
142 exclude unreasonable formulas: $1 \leq \text{H}/\text{C} \leq 3$, $0.2 \leq \text{O}/\text{C} < 1.5$, $0 \leq \text{N}/\text{C} \leq 0.5$, $0 \leq \text{S}/\text{C} \leq 1$, $\text{S}/\text{O} \leq 0.25$, 0
143 $<$ double bond equivalent (DBE)/ $\text{C} < 1$. The organic chlorinated compounds were reliably identified
144 based on their isotopic mass and intensity, but the identified formulas containing isotopes (e.g., ^{13}C , ^{18}O ,
145 ^{34}S , and ^{37}Cl) were not further discussed. The carbon oxidation state (OS_{C}) and DBE of the assigned
146 molecular formula ($\text{C}_c\text{H}_h\text{O}_o\text{N}_n\text{S}_s\text{Cl}_j$) were calculated as follows:

$$147 \quad \text{DBE} = 1 + \frac{2c - (h+j) + n}{2} \quad (1)$$

$$148 \quad \text{OS}_{\text{C}} \approx 2 \times \frac{\text{O}}{\text{C}} - \frac{\text{H}}{\text{C}} \quad (2)$$

149 The toxicity of identified organic chlorinated compounds was analyzed based on their possible
150 chemical structures using Toxicity Estimation Software Tool (T.E.S.T., V.5.1.2, USEPA) to estimate
151 their oral rat pLD_{50} ($-\log_{10}(\text{pred})$, mol kg^{-1}), developmental toxicity, and mutagenicity.

152 2.3 Box model

153 The Framework for 0-D Atmospheric Modeling (F0AM) (Wolfe et al., 2016) was used to further
154 investigate the impact of alkaline species on chloride depletion. The gas phase reactions used in this
155 study were derived from the Master Chemical Mechanism (MCM) v3.3.1 (<http://mcm.york.ac.uk/>)
156 (Jenkin et al., 2015). Based on the heterogeneous reactions integrated in our previous work (Song et al.,
157 2026), we further incorporated the acid-base neutralization reactions into the mechanism, with a rate

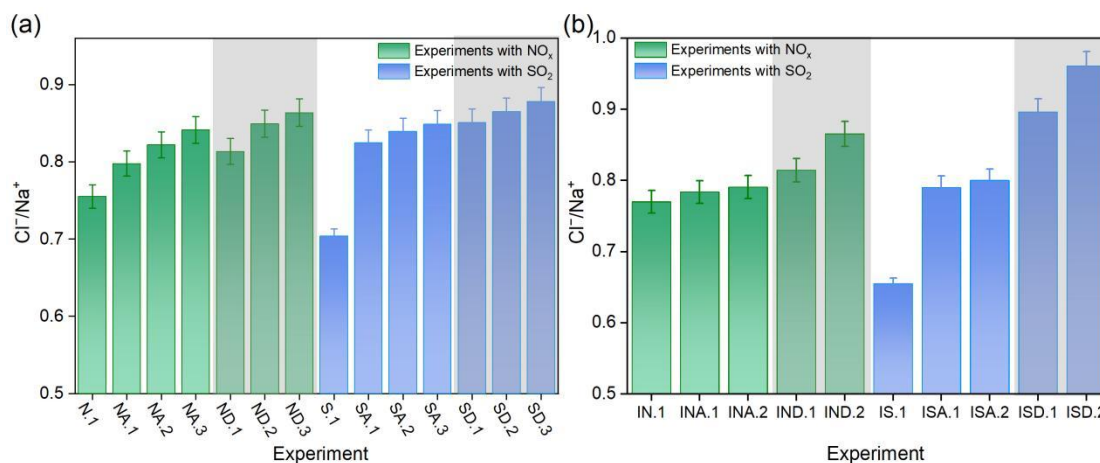
158 constant of $2.64 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction between NH_3 and HNO_3 (Behera and
159 Sharma, 2012). The initial conditions in the model were set to match those of the chamber experiments.

160 **3. Results and discussion**

161 **3.1 Effects of NH_3 on chloride depletion**

162 A series of experiments were designed with varying initial concentrations of alkaline species in the
163 presence of acid gases, i.e., SO_2 and NO_x , to evaluate the effect of alkaline species on chloride
164 depletion (Table 1). Although NH_3 addition induced no significant change in chloride depletion in the
165 absence of SO_2 and NO_x (Exp. C.1), it could significantly hinder this process in their presence (Fig. 1a).
166 For example, the mole ratios of Cl^-/Na^+ increased from 0.798 to 0.841 when the concentration of NH_3
167 raised from 100 to 300 ppb under constant NO_x (Exp.NA.1-NA.3), while this ratio was 0.755 when
168 only NO_x was present (Exp.N.1). This corresponds to a reduction in chloride depletion from 20.1% to
169 15.8%. In these experiments, $\text{NO}_2 + \text{OH}$ or $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ reactions could lead to the formation of nitric
170 acid (HNO_3), which can induce chloride depletion through the replacement reaction (Su et al., 2022;
171 Xu et al., 2021). The suppressed chloride depletion by NH_3 can be attributed to the neutralization
172 reaction between NH_3 and HNO_3 that generates NH_4NO_3 particles (Behera et al., 2013). Although
173 NH_4NO_3 is unstable (Behera et al., 2013; Lan et al., 2024), ammonium ions were detected in these
174 experiments. Furthermore, the time series of the HNO_3 and Cl atoms exposure were simulated using
175 F0AM for Exp.N.1-NA.3 (Fig. S1). The exposure of HNO_3 and Cl atoms decreased after NH_3 addition,
176 further supporting the crucial role of the reaction between NH_3 and HNO_3 in reducing chloride
177 depletion. As shown in Table S1, the exposure of HNO_3 and Cl atoms also decreased after the addition
178 of NH_3 (0-20 ppb), demonstrating that the observed mechanisms persist at near-ambient concentrations.
179 In the presence of SO_2 , the effect of NH_3 on reducing chloride depletion is even more pronounced. For
180 example, the addition of 300 ppb NH_3 (Exp.SA.3) reduced SO_2 -induced chloride depletion from 29.5%
181 (Exp.S.1) to 15.0%. This can be explained by the generation of $(\text{NH}_4)_2\text{SO}_4$ via the reaction of NH_3 with
182 sulfuric acid (H_2SO_4), which is produced from the oxidation of SO_2 by OH radicals (Lan et al., 2024;
183 Behera et al., 2013). As shown in Fig. S2, ammonium ion was detected in Exp.SA.1-SA.3. Notably, the
184 $\text{H}_2\text{SO}_4 + \text{NH}_3$ reaction is much more thermodynamical and kinetically favorable than the $\text{HNO}_3 + \text{NH}_3$
185 reaction (Behera et al., 2013). This may be the reason why the reduction in chloride depletion was more

186 significant in experiments SA.1-SA.3 compared to experiments NA.1-NA.3. Our findings further
 187 support the hypothesis formulated from field studies that ammonia can reduce chloride depletion
 188 (Rankin and Wolff, 2003; Braun et al., 2017; Zhan et al., 2017; Chen et al., 2016; Yao et al., 2003;
 189 Ghosh et al., 2020).



190

191 **Figure 1. Dependences of Cl⁻/Na⁺ ratio on the concentrations of different alkaline species in the (a) absence**
 192 **and (b) presence of isoprene. The experiments with a grey background indicate the addition of DMA.**

193 Isoprene was further introduced into the experimental chamber with various initial NH₃ concentrations
 194 to study the combined effect of alkaline gases with isoprene and acidic gases (Fig. 1b). Similar to the
 195 above experiments without isoprene, NH₃ can reduce the chloride depletion caused by acidic gases,
 196 with a more pronounced weakening effect in the presence of SO₂. Notably, the addition of isoprene
 197 reduced the ability of NH₃ to weaken chloride depletion, resulting in its relative enhancement. For
 198 instance, chloride depletion was 20.8% in the experiment with isoprene and NH₃ (Exp.INA.2),
 199 significantly higher than 15.8% in the experiment without isoprene (Exp.NA.3). Slightly different
 200 values, namely 19.9% and 15.0% were observed in Exp.ISA.2 and Exp.SA.3, respectively, which can
 201 be attributed to the reaction of NH₃ with SOA constituents such as organic acids, or other species
 202 generated from the oxidation of isoprene to form nitrogen-containing organic compounds (Li et al.,
 203 2024; Wu et al., 2021; Wennberg et al., 2018; Bates et al., 2023). This leads to reduced NH₃ for
 204 neutralizing acid-induced chloride depletion.

205 3.2 Effects of DMA on chloride depletion

206 DMA was introduced into the reaction system to investigate its influence on chloride depletion. Similar
 207 to NH₃, DMA also caused negligible chloride depletion in the absence of acidic gases (Exp.C2, Table

208 1). In the presence of acidic gases, the weakening effect of chloride depletion becomes more
209 pronounced with increasing DMA concentrations (Fig. 1a). For example, chloride depletion decreased
210 from 18.6% to 13.5% as DMA concentration increased from 50 to 150 ppb in the presence of NO_x
211 (Exp.ND.1-ND.3). In the presence of SO₂ in Exp.SD.1-SD.3, it ranged from 12.1% to 14.8%, lower
212 than that in Exp.S.1 (29.5%). This is mainly because DMA, with a high vapor pressure, can react with
213 inorganic acids (e.g., HNO₃, H₂SO₄, etc.) produced during the reaction to form aminium salts with
214 lower vapor pressure (Wang et al., 2010; Murphy et al., 2007; Nielsen et al., 2012). Moreover, DMA
215 can effectively promote cluster formation with H₂SO₄ or HNO₃, thereby generating DMA-H₂SO₄,
216 DMA-H₂SO₄-H₂O clusters, and other nucleation systems (Chen et al., 2024a; Loukonen et al., 2010;
217 Zhang et al., 2019). The aforementioned mechanisms can all reduce chloride depletion induced by
218 inorganic acids.

219 As shown in Fig. 1a, chloride depletion in Exp.ND.2 (15.0%) was lower than that in Exp.NA.1 (20.1%).
220 Similarly, it was lower (13.4%) in Exp.SD.2 than in Exp.SA.1 (17.4%). Despite the DMA
221 concentration is lower than that of NH₃, chloride depletion in the presence of DMA (Exp.SD.1) was
222 still weaker than that in the presence of NH₃ (Exp.SA.1). This can be attributed to DMA having a
223 stronger alkalinity (Chen et al., 2022; Sauerwein and Chan, 2017; Xie et al., 2018), and a more
224 effective nucleation ability (Ortega et al., 2012; Kupiainen et al., 2012) than NH₃. According to a
225 theoretical study by Zhang et al. (2019), DMA is more likely than NH₃ to approach the air-nanoparticle
226 interface, where the probability of its heterogeneous reaction with H₂SO₄ can increase. Notably, the
227 neutralization efficiency of alkaline species can be affected by the particle phase state. When the phase
228 state of particles changes from liquid to semisolid state, the neutralization efficiency of DMA may be
229 relatively inhibited compared to that of the more mobile NH₃ (Sauerwein and Chan, 2017; Derieux et
230 al., 2019). The viscosity of SSA particles in our experiments was calculated to be 1.89-1.98 Pa·s
231 (details in the Supplement), being significantly lower than the 10² Pa·s threshold for
232 liquid-to-semisolid phase transition (Derieux et al., 2018). This suggests that the SSA particles in this
233 study existed in liquid state, and the neutralization efficiency of both ammonia and DMA was not
234 constrained by phase transition.

235 Following the addition of isoprene, the weakening effect of DMA on chloride depletion in the presence
236 of NO_x was not significantly different from that of experiments without isoprene. Nonetheless, this
237 addition enhanced the weakening effect of DMA on chloride depletion in the presence of SO₂. Chloride

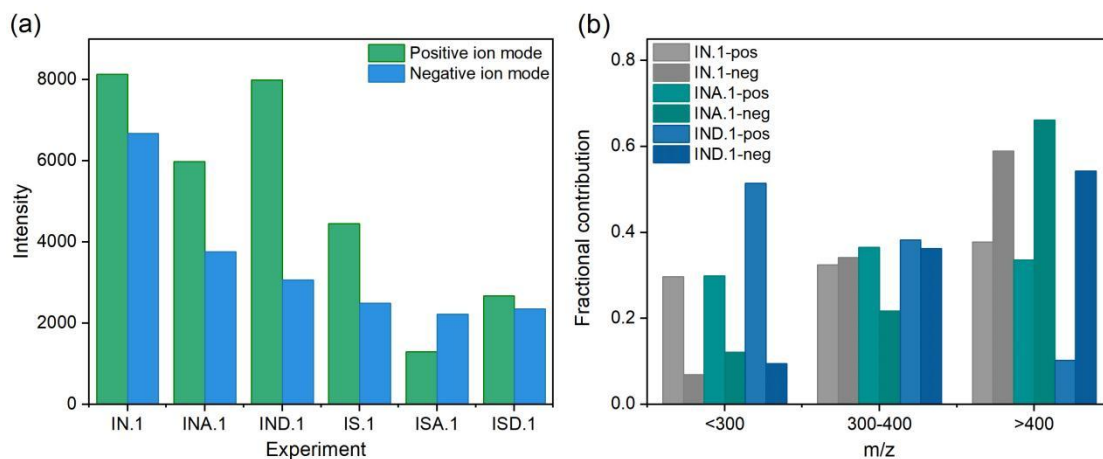
238 depletion in Exp.ISD.2 was 3.8%, significantly lower than that in Exp.SD.3 (12.1%). This can be
239 explained by the fact that organic acids produced from the oxidation of isoprene enhance DMA-H₂SO₄
240 nucleation, with a stronger enhancement effect observed at lower H₂SO₄ concentrations (Wang et al.,
241 2022a; Lu et al., 2020). Isoprene oxidation products can react with H₂SO₄ to form organic sulfates
242 (Armstrong et al., 2022; Wach et al., 2020), leading to a reduction in H₂SO₄ concentration within the
243 reaction system.

244 **3.3 Formation of organic chlorinated compounds**

245 The molecular composition of organic chlorinated compounds was analyzed, using
246 UPLC/ESI-Q-TOF-MS, to further explore the effect of active chlorine on chloride depletion. Fig. S3
247 presents the mass spectra of organic chlorinated compounds in the presence of acidic and alkaline gases.
248 Mass spectra in both positive and negative ion modes contained numerous peaks, with compositions in
249 the presence of NO_x being more complex than those in the presence of SO₂.

250 **3.3.1 Effects of alkaline species in the presence of NO_x**

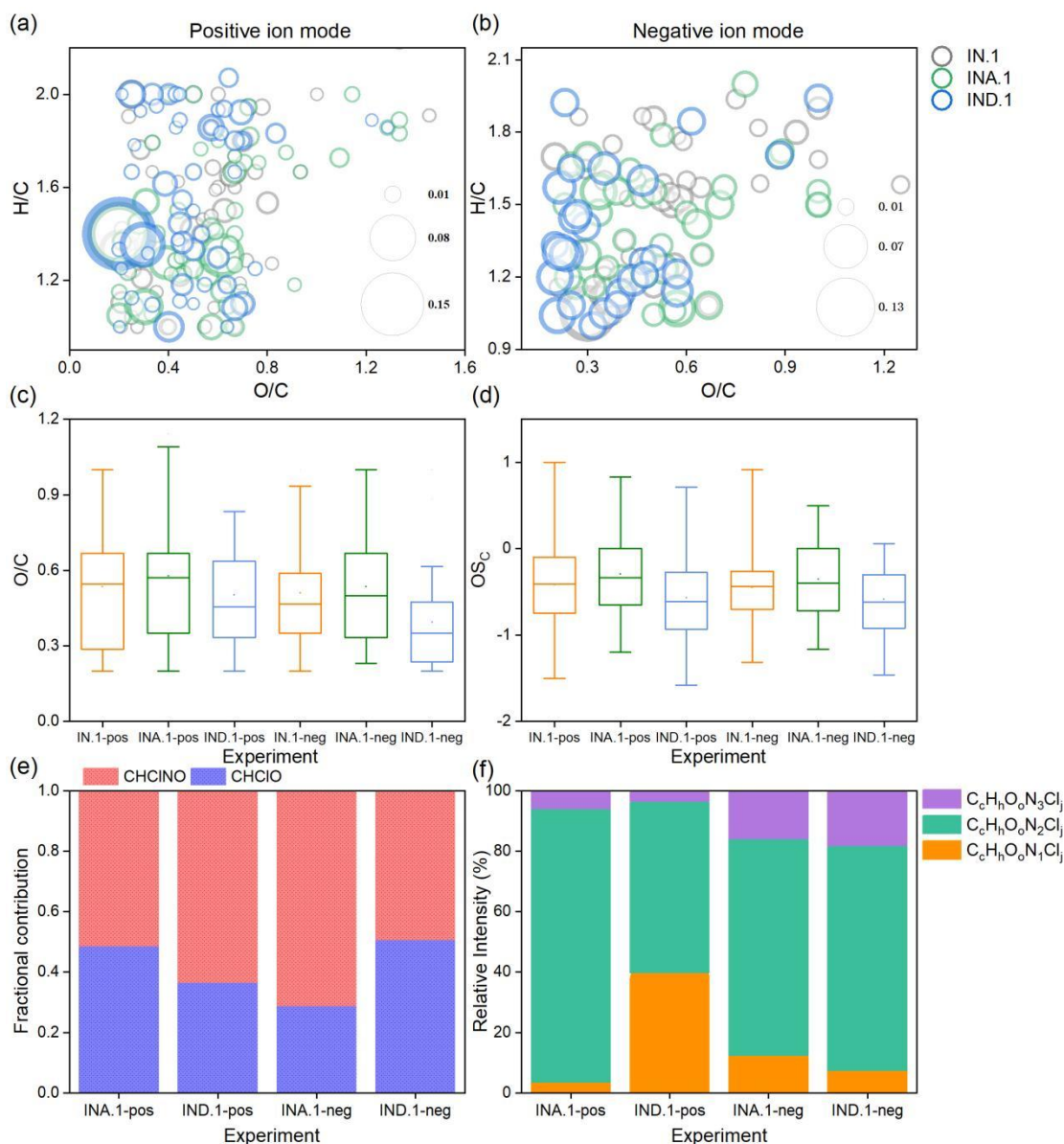
251 As shown in Fig. 2a, the total signal intensity of the organic chlorinated compounds detected in the
252 presence of alkaline species (Exp.INA.1 and Exp.IND.1) was lower than that in their absence
253 (Exp.IN.1), indicating that the alkaline species reduce the formation of organic chlorinated compounds
254 during the chloride depletion process. The identified organic chlorinated compounds were classified
255 into three categories: $m/z < 300$, $300 \leq m/z \leq 400$ and $m/z > 400$ (Fig. 2b). The molecular weight
256 distribution of products shifted with the addition of alkaline species. In the experiment without alkaline
257 species (Exp.IN.1), molecules with high molecular weight ($m/z > 400$) had the highest proportion. In
258 contrast, DMA reduced the proportion of high molecular weight molecules ($m/z > 400$), while
259 increasing the intensity of molecules with m/z values in the ranges $m/z < 300$ and $300 \leq m/z \leq 400$
260 (Exp.IND.1) as shown in Fig. 2b. This suggests that the presence of DMA facilitates the formation of
261 organic chlorinated compounds with lower molecular weight, which can be attributed to the stronger
262 neutralization of the acidity by DMA, thereby inhibiting the acid-catalyzed polymerization reaction to
263 generate high molecular weight molecules (Du et al., 2023). The lower proportion of organic
264 chlorinated oligomers produced in Exp.IND.1 further supports this speculation (Fig. S4).



265

266 **Figure 2. (a) Total signal intensity of identified organic chlorinated compounds for different experiments. (b)**
 267 **Distribution of identified molecules under different experimental conditions.**

268 The Van Krevelen (VK) diagrams based on O/C and H/C ratios are presented in Fig. 3a-3b. The H/C
 269 and O/C ratios of organic chlorinated compounds are primarily distributed in the ranges of 0.9-2.0 and
 270 0.1-1.0. As shown in Fig. 3c, the organic chlorinated compounds produced in the presence of NH₃
 271 (Exp.INA.1) exhibited the highest O/C ratio, which can be attributed to the presence of more hydroxyl,
 272 carbonyl, and carboxyl functional groups. The OS_C of organic chlorinated compounds in Exp.INA.1
 273 was also higher, indicating that NH₃ enhances the degree of oxidation of organic chlorinated
 274 compounds (Fig. 3d). Conversely, the O/C ratio and OS_C of organic chlorinated compounds were low
 275 in the presence of DMA (Exp.IDA.1). Fig. S5 shows that the proportion of dichlorinated compounds in
 276 the presence of DMA is lower than that in the presence of NH₃, indicating that less active chlorine was
 277 produced in the presence of DMA and its multi-generation oxidation was inhibited. This result further
 278 supports that the weakening effect of DMA on chloride depletion is significantly more effective than
 279 that of NH₃ as mentioned above. Some organic chlorinated compounds (e.g., C₅H₇ClO₄, C₈H₁₁ClO₅,
 280 and C₈H₁₃ClO₆) detected in this study have also been reported in field observations (Chen et al., 2023),
 281 indicating that chloride depletion could be a source thereof in the ambient environment. These
 282 compounds were identified in our previous study and their formation pathways were proposed (Song et
 283 al., 2026).

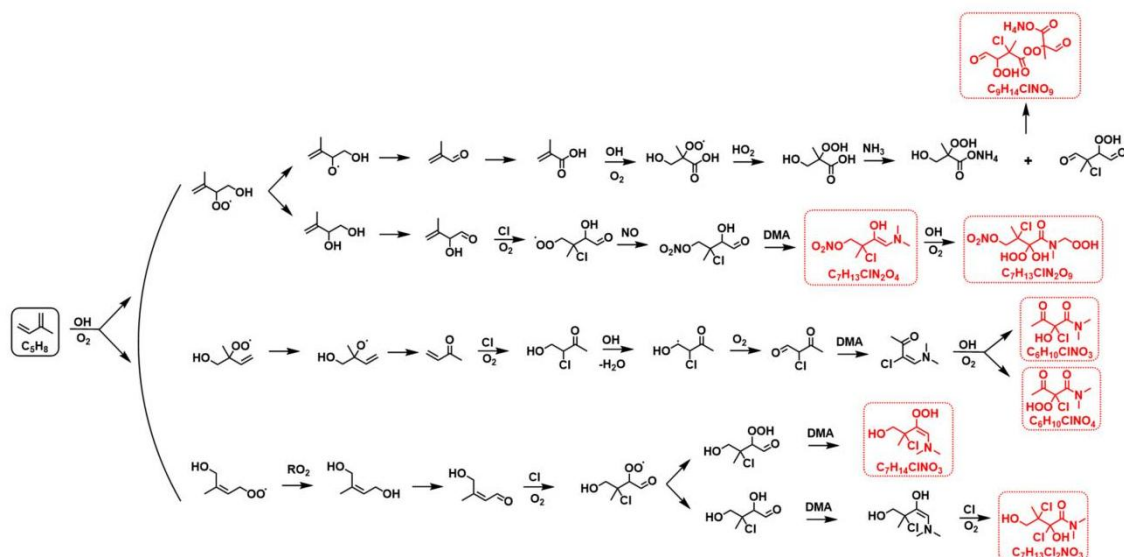


284
 285 **Figure 3. Van Krevelen diagram of organic chlorinated compounds for different experiments with NO_x in the**
 286 **(a) positive and (b) negative ion modes. The circle size represents the proportion of organic chlorinated**
 287 **compounds. (c) OS_C and (d) DBE of organic chlorinated compounds for different experiments with NO_x. (e)**
 288 **Fractional contribution to the total unique molecules by CHCINO and CHCIO compounds in the presence of**
 289 **alkaline species. (f) Nitrogen atom distribution of CHCINO compounds in the presence of alkaline species for**
 290 **different experiments with NO_x.**

291 As shown in Fig. S6, many unique molecules were detected in the experiments with alkaline species
 292 (Exp.INA.1 and Exp.IND.1), in addition to some compounds also detected in Exp.IN.1. In the
 293 experiment in the presence of NH₃ (Exp.INA.1), 42 and 30 unique molecules were detected in the
 294 positive and negative ion modes, respectively. When DMA was present (Exp.IDA.1), 45 and 25 unique
 295 organic chlorinated compounds were identified in the positive and negative modes, respectively. These
 296 findings suggest that alkaline species alter the molecular composition of organic chlorinated

297 compounds. The identified chlorinated species predominantly consisted of CHClO and CHClNO
298 compounds, with the proportion of CHClNO being higher than that of CHClO (Fig. 3e). The CHClNO
299 compounds primarily consist of N₂ products (Fig. 3f), and their formation is favored by high humidity
300 (Yang et al., 2025). Representative CHClNO compounds include C₉H₁₄ClNO₉, C₇H₁₃ClN₂O₄,
301 C₆H₁₀ClNO₃, etc. Fig. 4 presents the formation mechanism of these compounds. Specifically, isoprene
302 is oxidized by OH radicals to form key intermediates, which can be further oxidized by Cl radicals,
303 yielding organic chlorinated monomers (e.g., C₄H₅ClO₂, C₅H₉ClO₃, C₅H₉ClO₄). These monomers can
304 be converted into organic chlorinated oligomers through dehydration reactions or acid-catalyzed
305 accretion reactions. Notably, NH₃ and DMA can react with these organic chlorinated compounds
306 through acid-base neutralization to produce CHClNO compounds. For instance, NH₃ can react with
307 C₄H₈O₅ to form C₄H₁₁NO₅. C₄H₁₁NO₅ and C₅H₇ClO₄ can undergo an accretion reaction to form
308 C₉H₁₄ClNO₉. In addition, DMA can react with the aldehyde function of organic chlorinated compounds
309 to form carbinolamines, which then dehydrate to form enamine compounds (e.g., C₇H₁₃ClN₂O₄ and
310 C₇H₁₄ClNO₂). These enamine compounds can be further oxidized by OH and Cl radicals to produce the
311 observed CHClNO compounds (e.g., C₆H₁₀ClNO₃, C₇H₁₃Cl₂NO₃, C₇H₁₃ClN₂O₉).

312 The toxicity prediction results of these organic chlorinated compounds are presented in Table S2.
313 Results show that C₇H₁₃ClN₂O₄ compounds have the highest pLD₅₀ values and are classified as class 3,
314 indicating that they have considerable potential for acute toxicity. Notably, the predicted developmental
315 toxicity values for the compounds listed in Table S2 have been classified as the highest hazard level,
316 and they also pose mutagenicity risks. This highlights the necessity to conduct in-depth research on the
317 toxicity of organic chlorinated compounds in the coastal atmosphere.

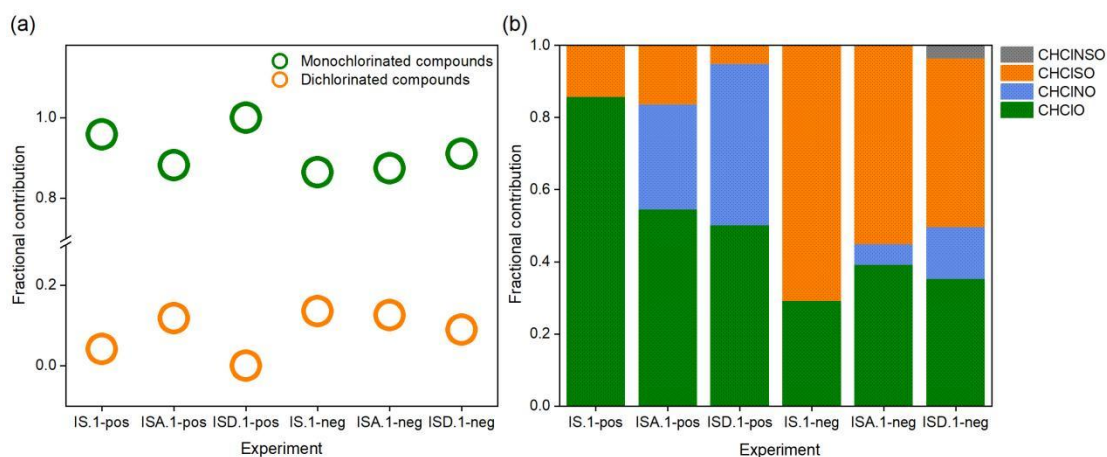


318

319 **Figure 4. (a) Formation mechanism of representative CHCINO compounds. The red boxes indicate the**
 320 **detected CHCINO compounds in our experiments.**

321 3.3.2 Effects of alkaline species in the presence of SO₂

322 In the presence of SO₂, the addition of NH₃ and DMA both significantly reduced the abundance of high
 323 molecular weight compounds (Fig. S7) and the total signal intensity of organic chlorinated compounds
 324 (Fig. 5a), which can be attributed to a reduced activation of chloride ions. This might be due to the fact
 325 that the addition of alkaline species reduces the production of gaseous HCl as a result of acid-base
 326 neutralization reactions and further diminishes the source of active chlorine (Edwards et al., 2024;
 327 Song et al., 2025). In addition, chloride ions can be activated into active chlorine by strong oxidants
 328 (OH radicals, O₃, etc.) (Zhang and Chan, 2023; Su et al., 2022). DMA can compete with chloride ions
 329 for these oxidants, thereby limiting the activation of chloride ions and reducing the generation of active
 330 chlorine species (Møller et al., 2020). The proportion of dichlorinated compounds in Exp.ISD.1 was
 331 significantly lower than that in Exp.IS.1 (Fig. 5a), mainly due to the reduction of active chlorine that
 332 inhibited its multi-generation oxidation. This further explains that the weakening effect of DMA on
 333 chloride depletion is enhanced in the presence of isoprene and SO₂.



334

335 **Figure 5. (a) Fractional contribution of monochlorinated and dichlorinated compounds in the total organic**
 336 **chlorinated compounds for different experiments with SO₂. (b) Fractional contribution to the total organic**
 337 **chlorinated compounds by different compounds.**

338

As shown in Fig. 5b, in experiments with SO₂, the products detected in the positive ion mode mainly
 339 consisted of CHCLO compounds, while the proportion of CHCISO compounds was the highest in the
 340 negative ion mode. This may be related to the different sensitivities of the compounds in different ion
 341 modes. CHCINO and CHCINSO compounds (including C₇H₁₅CIN₂O₆, C₁₃H₁₉CIN₂O₆, C₁₈H₃₅CIN₂SO₈,
 342 etc.) were also detected in experiments in the presence of alkaline species and SO₂. As mentioned
 343 above, the CHCINO compounds can be formed through the acid-base neutralization reaction or the
 344 reaction of DMA with aldehyde function. These compounds can react with H₂SO₄ through
 345 esterification reactions to form CHCINSO compounds. The observed higher proportion of CHCINO
 346 compounds in Exp.ISD.1 than that in Exp.ISA.1 (Fig. 5b) may result from the stronger ability of DMA
 347 to react with organic acids or carbonyl compounds (Smith et al., 2021). Moreover, autoxidation via a
 348 unimolecular reaction, being an important oxidation pathway for DMA in the atmosphere, facilitates
 349 the formation of hydroperoxy amides (Møller et al., 2020). Overall, alkaline gases affect the formation
 350 of active chlorine during chloride depletion, and alters the composition of organic chlorinated
 351 compounds.

352

4. Conclusions

353

The complexity of atmospheric pollutants in coastal environments hinders the understanding of the
 354 mechanisms influencing chloride depletion. This study explored the detailed effects of NH₃ and DMA
 355 on this phenomenon. The results demonstrated that NH₃ and DMA could weaken the chloride depletion
 356 induced by acidic gases, with DMA exhibiting a more substantial weakening effect than NH₃. This

357 difference in their impact is primarily due to DMA's stronger alkalinity and nucleation ability, which
358 enable it to interact more effectively with acidic species than NH₃. Although the concentration of DMA
359 in the atmosphere is lower than that of NH₃, its impact on chloride depletion is essential. The current
360 results further reveal that considering only the effects of acidic gases may lead to deviations in the
361 prediction of chloride depletion. This underscores the necessity to examine the role of alkaline species,
362 especially organic amines, in future field studies of chloride depletion.

363 The mass spectrometry results showed that the presence of alkaline species also reduces the formation
364 of organic chlorinated compounds, indicating that the generation of active chlorine is inhibited during
365 chloride depletion. This can be attributed to the fact that the alkaline species reduce the generation of
366 gaseous HCl through acid-base neutralization reactions, and can compete with chloride ions for
367 oxidants, thereby further reducing the production of active chlorine. This further supports the idea that
368 alkaline species could weaken the chloride depletion process. Additionally, the presence of alkaline
369 species, especially DMA, promotes the formation of low-molecular-weight organic chlorinated
370 compounds by neutralizing acidity, thereby inhibiting acid-catalyzed polymerization and the formation
371 of high-molecular-weight compounds. The addition of alkaline species was observed to alter the
372 composition of organic chlorinated compounds, with several identified unique products that were not
373 present under acidic conditions. This suggests that alkaline species not only inhibit chloride depletion
374 but also influence the overall chemical composition of the atmosphere by altering the chlorination
375 pathways of organic compounds. The current results strengthen our understanding of the mechanism
376 influencing chloride depletion, and provide a ground for the future identification of organic chlorinated
377 compounds in ambient samples.

378 The initial concentrations of alkaline species used in the experiments were higher than the ambient
379 levels. Moreover, the complex atmospheric chemical reactions were simplified in this study to
380 eliminate the interference from other factors. Future studies should consider evaluating the effects of
381 composition and phase state of aerosols on the mechanism and the extent of chloride depletion.

382 **Data availability**

383 Experimental data can be found at <https://doi.org/10.5281/zenodo.18795123> (Song and Du, 2026).

384 **Supplement**

385 The supplement related to this article is available online at:

386 **Author contributions**

387 LD and AS designed the experiments, and AS carried them out. AS performed data analysis with
388 assistance from LD, KL, and LX. AS wrote the paper with contributions from all co-authors, and
389 co-authors commented on the paper.

390 **Competing interest**

391 The contact author has declared that none of the authors has any competing interests.

392 **Acknowledgements**

393 We thank Guannan Lin from the State Key Laboratory of Microbial Technology of Shandong
394 University for help and guidance with UPLC/ESI-HR-Q-TOF-MS measurements.

395 **Financial support**

396 This work was supported by National Key Research and Development Program of China
397 (2023YFC3706203), National Natural Science Foundation of China (U25A20787, 22376121), and
398 Intramural Joint Program Fund of State Key Laboratory of Microbial Technology
399 (SKLMTIJP-2025-02).

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