Reply to Anonymous Referee #1

We sincerely thank the Referee for the careful review and thoughtful comments, which are very helpful in improving our manuscript. We have addressed a point-to-point response to the comments and modified the manuscript accordingly. For clarity, the Referee's comments are reproduced in blue, authors' responses are in black and changes in the manuscript are in red.

Review of "Organic amine weakens chloride depletion in coastal atmosphere" by Song et al.

In this study, Song et al. convincingly show that bases such as NH_3 and amines should be accounted for in studies of chloride depletion. This is a nice message since past work on the topic is more fixated on acids and doesn't consider the bases which can counteract the action of acids to deplete chloride from sea salt. A more specific and interesting result is that the weakening effect of dimethylamine on chloride depletion is more than that of ammonia due to stronger alkalinity and nucleation ability. Their methods are robust and based on chamber experiments; I especially appreciated that they studied the formation of corresponding organic chlorinated compounds as a result of sea salt reactions.

1. The topic is of interest to the journal. The presentation quality was somewhat fair with English editing work needed still. Figure quality can be improved as well. I support publication subject to the authors addressing my comments below.

Response:

We have carefully conducted an English editing of the manuscript and improved the quality of the figures.

Major Comments:

2. How significant really are these somewhat small changes in chloride depletion (20.1% to 15.8% and 18.6% to 13.5%)? Are these even significant changes, and if so, what

could the implications be of these changes in the atmosphere? Please in your response build more text as well into the paper to discuss the implications of this study as right now it is unclear to readers.

Response:

Due to the inherent limitations of laboratory chamber studies (e.g., wall effects), experiments of this nature are typically conducted over relatively short timescales. Consequently, the results obtained may be less pronounced than those observed in field measurements. In our specific experiments, the chloride depletion, measured after two hours of reaction, was lower than that observed in field measurements after extended atmospheric aging. For example, chloride depletion in the experiment without alkaline species (Exp. N.1) was 24.4%, lower than that observed in field studies (43-98%) (Cvitešić Kušan et al., 2020; Rastogi et al., 2020; Yu et al., 2021). As shown in Fig.1, the trend of the weakening of chloride depletion was very significant after the addition of alkaline species, and errors in Cl^-/Na^+ were much smaller than the variation value. In the actual atmospheric environment, longer reaction times would likely result in a more pronounced weakening effect of alkaline species on chloride depletion. Moreover, although the absolute changes in chloride depletion after adding alkaline species are relatively small, the relative change is quite significant. Compared with experiment N.1, the inhibition rates of ammonia and dimethylamine on chloride depletion were 17.6%–35.2% and 23.8%–44.8%, respectively. Therefore, these changes in chloride depletion (20.1% to 15.8% and 18.6% to 13.5%) would likely be quite significant if extrapolated to real atmospheric conditions.

Although many field observation studies have hypothesized that ammonia (NH_3) can reduce chloride depletion (Rankin and Wolff, 2003; Yao et al., 2003; Braun et al., 2017; Ghosh et al., 2020), its mechanism and the extent of its impact, and those of alkaline species in general, remain unclear. This study conducted laboratory experiments to investigate the extent of the influence of two important alkaline species (ammonia and dimethylamine (DMA)) on chloride depletion, and analyzed the underlying mechanisms of their effects. Results showed that alkaline species could weaken chloride depletion caused by acidic gases, mainly due to acid-base neutralization. This further supports the hypothesis from field studies that ammonia can reduce chloride depletion. Furthermore, we found that the weakening effect of DMA on chloride depletion is more pronounced than that of NH_3. But the influence of organic amines in the model prediction of chloride depletion has not been taken into account, highlighting the gap to predict Chloride depletion in amine-rich coastal or agricultural-marine interfaces. The results of the current study reveal that considering only the effects of acidic gases may lead to deviations in the prediction of chloride depletion. This study provides a comprehensive understanding of chloride depletion from SSA, which may be crucial for more accurately predicting chloride depletion in coastal atmospheres. In addition, the mass spectrometry results strengthen our understanding of the mechanism influencing chloride depletion, and provide a ground for the future identification of organic chlorinated compounds in ambient samples. We have further clarified these in the revised manuscript.

Lines 195-197, Page 9:

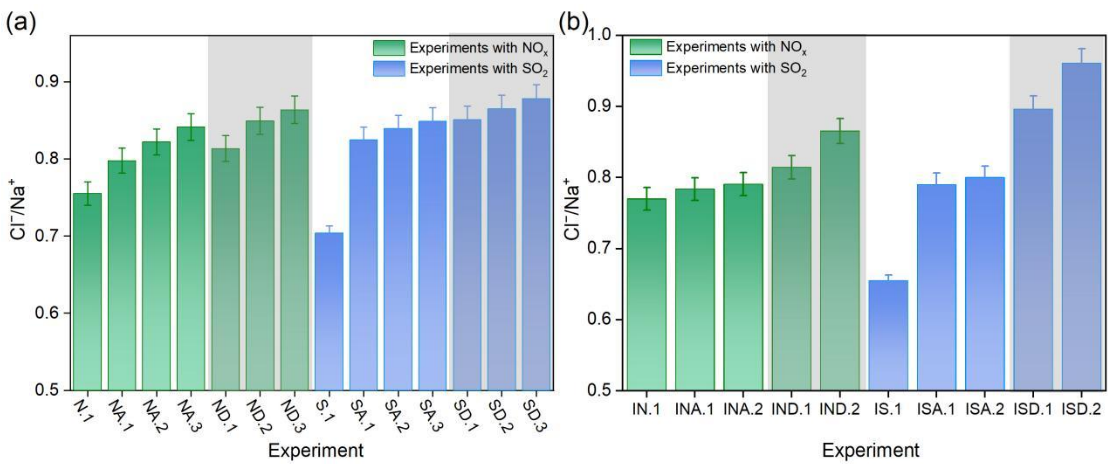

Figure 1. Dependences of Cl^{-}/Na^{+} ratio on the concentrations of different alkaline species in the (a) absence and (b) presence of isoprene. The experiments with a grey background indicate the addition of DMA.

Lines 26-29, Page 2:

These findings suggest that alkaline species, more specifically organic amines, are significant factors influencing chloride depletion in the coastal atmosphere, further improving our understanding of this phenomenon.

Lines 71-72, Page 4:

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

Lines 191-194, Page 9:

Our findings further support the hypothesis formulated from field studies that ammonia can reduce chloride depletion (Rankin and Wolff, 2003; Braun et al., 2017; Zhan et al., 2017; Chen et al., 2016; Yao et al., 2003; Ghosh et al., 2020).

Lines 368-371, Page 17:

The current results further reveal that considering only the effects of acidic gases may lead to deviations in the prediction of chloride depletion. This underscores the necessity to examine the role of alkaline species, especially organic amines, in future studies of chloride depletion.

Lines 385-387, Page 17:

The current results strengthen our understanding of the mechanism influencing chloride depletion, and provide a ground for the future identification of organic chlorinated compounds in ambient samples.

3. Could the authors provide a brief subsection in their paper to discuss limitations of their study and potential errors/uncertainties in the context of how future work along these lines can build on these results? Also, what can observational-based studies do differently than before in light of the results of this work?

Response:

To quickly tackle the mechanism by which alkaline species affect chloride depletion, we used initial concentrations of alkaline species that were higher than the ambient levels. In most chamber experiments, the relatively high initial reactant concentration is important to clarify complex reaction processes in a short time scale (Kong et al., 2024; Zhang et al., 2024). Moreover, the complex atmospheric chemical reactions were simplified in this study to eliminate the interference from other factors.

The composition and phase state of aerosols may further affect the degree and mechanism of chloride depletion, which is the direction for future research efforts.

Field observations have revealed the potential impact of NH_3 on chloride depletion (Rankin and Wolff, 2003; Yao et al., 2003; Braun et al., 2017; Ghosh et al., 2020). This study further quantifies the degree of this impact through experiments and analyzes the influencing mechanism, providing more sufficient evidence for field studies. Additionally, field observations only considered the impact of NH_3 on chloride depletion, with no exploration of the role of organic amines. Our findings underscore the necessity to discuss the inclusion of alkaline species in the chloride depletion process, especially organic amines. Finally, highlights chloride depletion as a potential source of atmospheric organic chlorinated compounds, which should be considered in future field studies. We have updated this in the revised manuscript.

Lines 80-82, Page 4:

Although the initial concentrations of alkaline species used in the experiments were higher than the ambient levels, this consideration was necessary for laboratory experiments within a short time scale to tackle their influence on chloride depletion.

Lines 388-392, Page 17:

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

Lines 191-194, Page 9:

Our findings further support the hypothesis formulated from field studies that ammonia can reduce chloride depletion (Rankin and Wolff, 2003; Braun et al., 2017; Zhan et al., 2017; Chen et al., 2016; Yao et al., 2003; Ghosh et al., 2020).

Lines 368-372, Page 17:

The current results further reveal that considering only the effects of acidic gases may lead to deviations in the prediction of chloride depletion. This underscores the necessity to examine the role of alkaline species, especially organic amines, in future field studies of chloride depletion

Lines 385-387, Page 17:

The current results strengthen our understanding of the mechanism influencing chloride depletion, and provide a ground for the future identification of organic chlorinated compounds in ambient samples.

Minor Comments:

4. Abstract: Near the beginning the authors don't provide any details of the methods and readers wont know how the results were obtained (e.g., is this a lab study, field work, or modeling?).

Response:

We have modified the abstract in the revised manuscript to highlight the type of study we conducted.

Lines 13-15, Page 2:

Here, we conducted laboratory experiments to investigate the effect of alkaline species including NH_3 and an organic amine (dimethylamine, DMA) on chloride depletion and the subsequent formation of organic chlorinated compounds.

5. Line 147-148: hard to understand this sentence "Despite NH3 addition…"

Response:

This sentence has been revised.

Lines 167-169, Page 8:

Although NH_3 addition induced no significant change in chloride depletion in the absence of SO_2 and NO_x (Exp. C.1), it could significantly hinder this process in their presence (Fig. 1a).

6. Data Availability: This statement is somewhat weak in that data should typically be archived at a public site with a DOI number.

Response:

A new description of data availability is provided in the revised manuscript.

Lines 393-394, Page 18:

Data availability

Experimental data can be found at https://doi.org/10.5281/zenodo.18795123.

References

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