

Dear Editor and reviewers,

Thank you very much for your comment on our manuscript “**Mechanistic insights into chloroacetic acid production from atmospheric multiphase VOC-chlorine chemistry (DOI: 10.5194/egusphere-2024-3137)**”.

We have cautiously considered all of the comments and responded as follows. Comments from the reviewers are shown in black *Italic* font. Response from the authors is shown in blue regular font. Revisions are shown in red regular font. The line numbers provided here refer to the ones in the revised manuscript.

Referee #1:

Li et al. present observations of chloroacetic acid at a rural site in Hong Kong and showed that its formation cannot be fully explained by existing mechanisms. They propose two potential pathways for its production: (1) isoprene and its oxidation products, and (2) multiphase reactions. The draft is well-structured, and the results are clearly presented. However, I suggest the authors address the following comments before the manuscript is accepted for publication in ACP:

Response: Thank you for your valuable suggestions. We have responded to your comments point by point below and added the discussion in the revised manuscript.

1. The estimation of the reactive uptake coefficient relies on linear relationship models based on several OVOCs. I recommend evaluating the accuracy of this linear model and discussing the uncertainties associated with these uptake coefficients.

Response: More regression evaluation indexes are provided to assess the accuracy of the linear relationship model. As shown in Fig. S11c, the linear relationship model between $\Delta_r G_{\text{hyd}}$ and $\lg\lambda$ exhibits the best correlation. The model's standard deviation (SD) is used for sensitivity testing of the predicted uptake coefficients (Fig. S12). We include a discussion of the effects of reactive uptake coefficients of Cl-OVOCs on simulated chloroacetic acid levels in the revised manuscript:

Lines 226 – 232: “A sensitivity analysis of the effects of reactive uptake coefficients of Cl-OVOCs on simulated chloroacetic acid levels using our updated model was also conducted (Fig. S12). Results show that a one standard deviation change ($\lg\gamma \pm \text{SD}$) in the predicted reactive uptake coefficients for Cl-OVOCs results in either a 5% increase or an 11% decrease in the simulated peak of chloroacetic acid. Our study underscores the significance of heterogeneous reactions in the production of chloroacetic acid and other organic acids, highlighting the necessity for more precise reaction parameters in future research.”

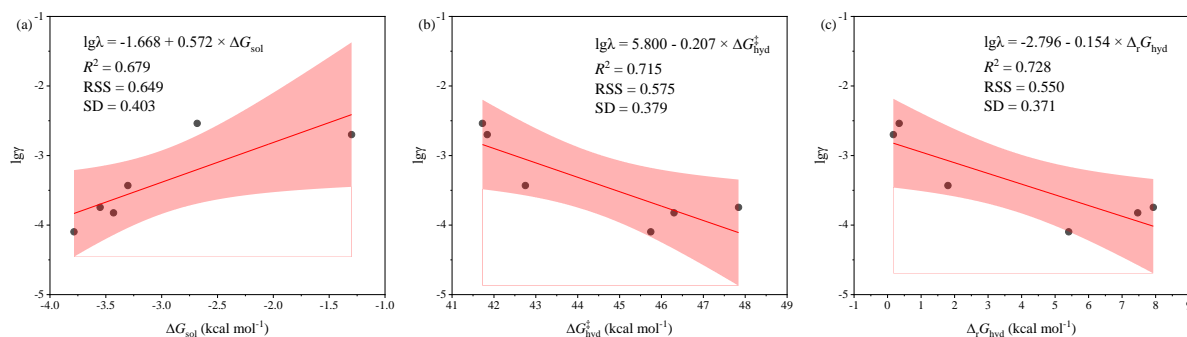


Figure S11. Linear relationships between Gibbs free energy of diol reactions and reactive uptake coefficients of carbonyls. (a) ΔG_{sol} as the solvation energy of carbonyls; (b) $\Delta G_{\text{hyd}}^{\ddagger}$ and (c) $\Delta_r G_{\text{hyd}}$ as the Gibbs free energy barriers and changes in the hydration reactions of carbonyls; λ as the reactive uptake coefficients; R^2 as the coefficient of determination; RSS as the residual sum of squares; SD as the standard deviation.

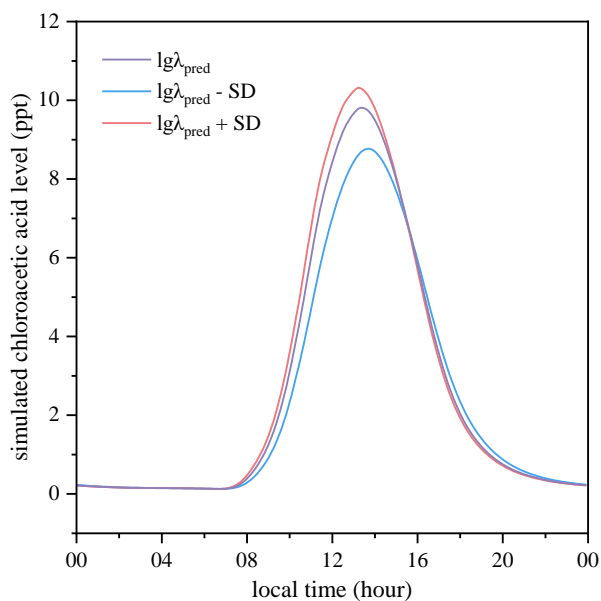


Figure S12. Sensitivity testing of the effects of reactive uptake coefficients of Cl-OVOCs on simulated chloroacetic acid and Cl-OVOC levels using our updated model. λ_{pred} are the predicted reactive uptake coefficients of Cl-OVOCs according to the linear relationship model between $\Delta_r G_{\text{hyd}}$ and $\lg \lambda$, and SD is the standard deviation.

2. The updated gas-phase chlorine chemistry and VOC-Cl model predict Cl-OVOCs concentrations up to 1 ppb, which significantly exceeds the observed values. The authors should provide an explanation for this large discrepancy.

Response: In our simulation, the model considering only gas-phase VOC-Cl chemistry predicts high concentrations of Cl-OVOCs, mainly chloro-formaldehyde, chloro-acetaldehyde, and chloroacetone. The high yields of chloro-containing aldehydes and ketones predicted by our gas-phase model are consistent with the results of the gas-phase chamber experiment, but they do not match the field observations. To reconcile the overestimation of chloro-containing aldehydes and ketones and the underestimation of chloroacetic acid, we proposed multiphase chemistry including the reactive uptake of Cl-OVOCs and heterogeneous conversion of chloro-acetaldehyde to chloroacetic acid. A comparison of our gas-phase model simulation results with observations is presented in the last paragraph of section 3.2:

Lines 175 – 178: “Our updated gas-phase alkene + Cl^{*} reactions explain only 8% of the observed chloroacetic acid concentration and significantly overestimate Cl-OVOCs. The photochemical formation of chloroacetic acid and Cl-OVOCs results in their simulated diurnal cycles of daytime increase and nighttime decrease, failing to replicate the observed patterns. The inconsistency between simulated and observed results of chloroacetic acid and Cl-OVOCs implies possible missing sinks or sources.”

3. The inclusion of both updated gas-phase chemistry and heterogeneous reactions increases the simulated levels of chloroacetic acid by 32–56%. I suggest adding a discussion on the potential role of other missing mechanisms to account for the remaining gap.

Response: Other missing sources have been discussed in the last paragraph of section 3.3.

Lines 232 – 242: “With the aforementioned updates, the box model significantly improved its ability to simulate chloroacetic acid. However, there is still a discrepancy between the updated simulations and field measurements, which may result from the uncertainty in the parameters we use and other factors affecting chloroacetic acid. For example, previous studies have reported the RH dependence of the reactive uptake coefficients of aldehydes and

organic acids (Chen et al., 2021; De Haan et al., 2018; Gen et al., 2018; Tong et al., 2010; Zeineddine et al., 2023). Other reactions of aldehydes in aerosols such as $\cdot\text{OH}$ oxidation, sulfite addition and Maillard-like reactions with reduced nitrogen species could compete with hydrolysis (Shen et al., 2024; Tang et al., 2022), potentially suppressing the yield of organic acids from the multiphase conversion of aldehydes. α -Chloro- β -ketones such as chloroacetone may also contribute to chloroacetic acid formation through atmospheric heterogeneous chemistry, supported by our QC calculations. In addition to alkenes, other VOCs of high molecular weight, such as ethylbenzene, may serve as precursors of chloroacetic acid (Cui et al., 2021). Moreover, chloroacetic acid may be produced as a disinfection by-product from the chlorination of dissolved organic matter in the aqueous phase (Jahn et al., 2024).”

4. Line 193: Considering the slow rate of hydrolysis reactions, how do QC calculations support the plausibility of chloroacetic acid formation via multiphase processes? This result appears contradictory.

Response: Our original manuscript investigates only the hydrolysis of OVOCs with water monomer to compare the relative energies of their hydrolysis thereby estimating the reactive uptake coefficients of Cl-OVOCs through QC calculations and linear relationship models. Considering the aqueous and acidic nature of aerosols, we investigated the hydrolysis of OVOCs with water dimer ($(\text{H}_2\text{O})_2$), water trimer ($(\text{H}_2\text{O})_3$), and sulfuric acid (H_2SO_4) in our revised version (Fig. 5). Results showed that multiple water molecules or acid catalysts involved in the hydrolysis reaction significantly reduce the energy barrier. Our QC calculations in the revised manuscript support the plausibility of chloroacetic acid formation via multiphase processes. The revised manuscript is as follows:

Lines 193 – 200: “The calculated energy barrier of chloro-acetaldehyde hydrolysis with a water molecule reaches $37.5 \text{ kcal mol}^{-1}$, which is reduced by the water dimer and trimer to 25.2 and $21.3 \text{ kcal mol}^{-1}$, respectively. Considering the acidic nature of aerosol, a molecule of sulfuric acid catalyzes chloro-acetaldehyde hydrolysis with an energy barrier of $6.1 \text{ kcal mol}^{-1}$. Multiple water molecules or acid catalysts involved in the hydrolysis reaction significantly lower the energy barrier, indicating the rapid hydrolysis feasibility of chloro-acetaldehyde in atmospheric aerosols. QC calculations also indicate that chloroacetic acid readily forms from chloroethyl-diol undergoing $\cdot\text{OH}$ oxidation and O_2 abstraction due to the low energy barriers in both gas and aqueous phases, as depicted in Fig. 5b. The QC calculations support the plausibility of the multiphase formation of chloroacetic acid.”

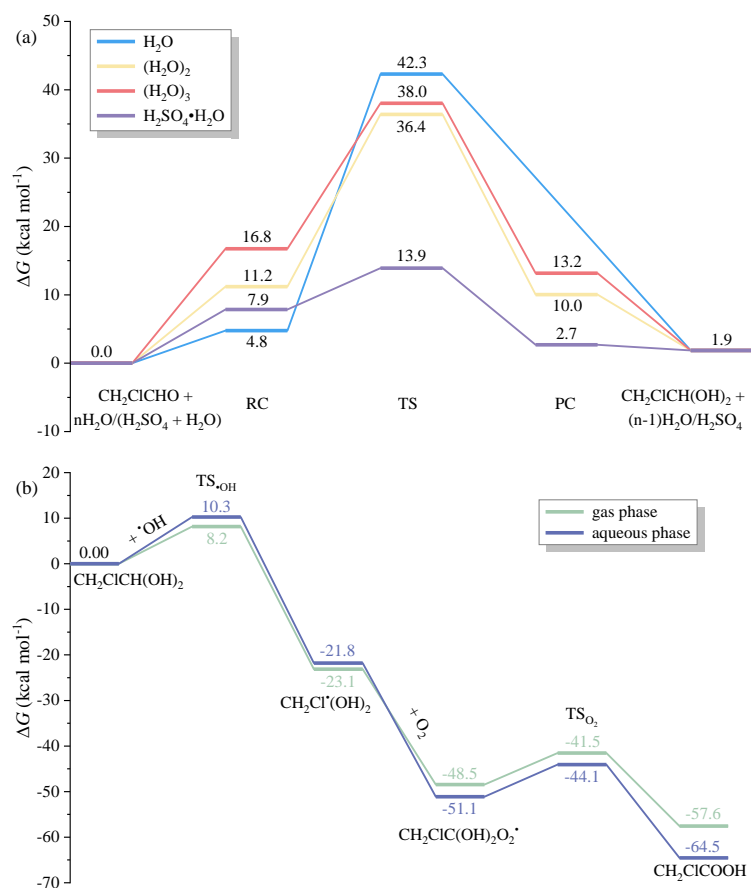


Figure 5. QC-calculated potential energy surfaces of the multiphase conversion of chloroacetic acid from chloroacetaldehyde at 298 K. (a) The hydrolysis potential energy surfaces of chloroacetaldehyde with water monomer (H_2O), water dimer ($(\text{H}_2\text{O})_2$), water trimer ($(\text{H}_2\text{O})_3$), and sulfuric acid (H_2SO_4) in aqueous phase; (b) potential energy surfaces of the conversion of chloroethyl-diol to chloroacetic acid in gas and aqueous phases. TS denotes the transition state connecting reactants and products, RC and PC denote reactant complexes and product complexes.

5. Lines 131–134 and Figure S1: The correlation coefficient between S_a and $\text{C}_2\text{H}_3\text{O}_2\text{Cl}$ is not strong enough to indicate a robust correlation. Please address this limitation.

Response: The correlation coefficients for S_a and $\text{C}_2\text{H}_3\text{O}_2\text{Cl}$ levels were 0.44 and 0.54 in 2020 and 2021, respectively, which are “moderately” correlated. The inappropriate statement below has been corrected or removed from the revised manuscript.

Lines 128 – 130: “Daytime S_a and jNO_2 were moderately positively correlated with the $\text{C}_2\text{H}_3\text{O}_2\text{Cl}$ level (Fig. S1), suggesting that aerosols and solar radiation could be involved in $\text{C}_2\text{H}_3\text{O}_2\text{Cl}$ formation.”

~~“We also found a stronger correlation between S_a and $\text{C}_2\text{H}_3\text{O}_2\text{Cl}$ than between S_a and Cl_x (Fig. S1), suggesting that the $\text{C}_2\text{H}_3\text{O}_2\text{Cl}$ formation may directly involve heterogeneous reactions.”~~

6. Figure 1: Why are the observed $\text{C}_2\text{H}_3\text{O}_2\text{Cl}$ levels higher in 2020 compared to 2021? Can this discrepancy be explained by the proposed mechanisms?

Response: Our proposed mechanism for chloroacetic acid formation indicates that reactive chlorine concentrations, precursor levels (primarily isoprene), and heterogeneous reaction processes impact the simulated levels of chloroacetic acid. The higher concentrations of observed chloroacetic acid in 2020 compared to 2021 can be partially attributed to elevated reactive chlorine species despite lower average isoprene concentrations in 2020.

Complex components of the aerosol would also influence the formation of chloroacetic acid. For example, higher SO₂ concentrations in 2021 compared to 2020 (Tab. 2) may suppress the hydrolysis reaction of aldehydes in aerosols, thereby reducing chloroacetic acid production. The limitations of our updated model are discussed:

Lines 236 – 238: “Other reactions of aldehydes in aerosols such as [•]OH oxidation, sulfite addition and Maillard-like reactions with reduced nitrogen species could compete with hydrolysis (Shen et al., 2024; Tang et al., 2022), potentially suppressing the yield of organic acids from the multiphase conversion of aldehydes.”

7. *Figure 4: The model-simulated diurnal cycle of Cl-OVOCs does not match the observed diurnal pattern of C₂H₃O₂Cl shown in Figure 1. Please explain this inconsistency.*

Response: The simulated diurnal cycle of chloroacetic acid using our gas-phase model does not match the observed diurnal pattern, which is modified by adding heterogeneous sources and sinks. A comparison of our gas-phase model simulation results with observations is presented in the last paragraph of section 3.2:

Lines 175 – 178: “Our updated gas-phase alkene + Cl[•] reactions explain only 8% of the observed chloroacetic acid concentration and significantly overestimate Cl-OVOCs. The photochemical formation of chloroacetic acid and Cl-OVOCs results in their simulated diurnal cycles of daytime increase and nighttime decrease, failing to replicate the observed patterns. The inconsistency between simulated and observed results of chloroacetic acid and Cl-OVOCs implies possible missing sinks or sources.”

8. *Figure 4: The gray shading representing C₂H₃O₂Cl is not visible in the plot. Please clarify or correct this issue.*

Response: Compared to other Cl-OVOCs, very low concentrations of C₂H₃O₂Cl could not be visualized in Fig. 4. C₂H₃O₂Cl was removed from Fig. 4 and the caption added “The diurnal profiles of C₂H₃O₂Cl (maximum 1.6 ppt) are not visible”.

Reference

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