

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 #2:

The manuscript “Mechanistic insights into chloroacetic acid production from atmospheric multiphase VOC-chlorine chemistry” by Li et al. describes the potential heterogeneous processes of chloroacetic acid production in observations at Hong Kong by performing quantum chemical calculations and chemical box model simulations. The formation mechanism of chloroacetic acid in the atmosphere is poorly understood, as such, I feel this study, which provides a comprehensive assessment of this chemistry, is of interest to the community and falls within the scope of ACP. The manuscript is also well written and organized. I recommend publication after addressing the following points.

Response: Thank you for your encouraging comments and valuable suggestions. Please find our point-by-point response below.

1. Page 3, line 93-: I am not very sure whether a linear relationship analysis between hydrolysis of OVOCs and their reported γ values could be used to predict γ of Cl-VOCs. For N_2O_5 in liquid water maybe it is fine as its bulk hydrolysis rate is quite fast, and there are no other significant processes in pure liquid water. But here, the hydrolysis rates of Cl-VOCs are slow, oxidation in aqueous phase also plays a role, and the composition in aerosol water is really complicated. Please discuss whether these factors would have an impact.

Response: Considering the aqueous and acidic nature of aerosols., we reinvestigated the hydrolysis of chloroacetaldehyde by water dimers, water trimers and sulfuric acid. As shown in revised Fig. 5, the energy barrier for the hydrolysis of chloroacetaldehyde to form diol by water trimer is reduced to 21.3 kcal mol⁻¹, which means that this reaction rate reaches $2.8 \times 10^{-3} \text{ s}^{-1}$ based on the TST theory. Even one molecule of sulfuric acid catalyzes the hydrolysis of chloroacetaldehyde with an energy barrier of 6.1 kcal mol⁻¹ and a reaction rate constant of $2.8 \times 10^8 \text{ s}^{-1}$. The reaction rate for the $\cdot\text{OH}$ oxidation of chloroacetaldehyde is $10^{-6} - 10^{-3} \text{ s}^{-1}$, which was estimated based on the $\cdot\text{OH}$ concentrations in the aerosol ($[\cdot\text{OH}]_{\text{aq}}$) as $10^{-15} - 10^{-12} \text{ M}$ in the tropospheric aqueous phase (Herrmann et al., 2010) and the reaction rate constant as $3.82 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Huang et al., 2021). The $\cdot\text{OH}$ oxidation of chloroacetaldehyde may compete with hydrolysis in marine areas with high $[\cdot\text{OH}]_{\text{aq}}$. The fate of chloroacetaldehyde in aerosols depends on the aerosol components, such as concentrations of $\cdot\text{OH}$ and sulfuric acid. In our revised manuscript, QC calculations support the possibility of multiphase formation of chloroacetic acid, and the competing reactions of aldehyde hydrolysis in aerosols are mentioned:

Lines 236 – 238: “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. ”

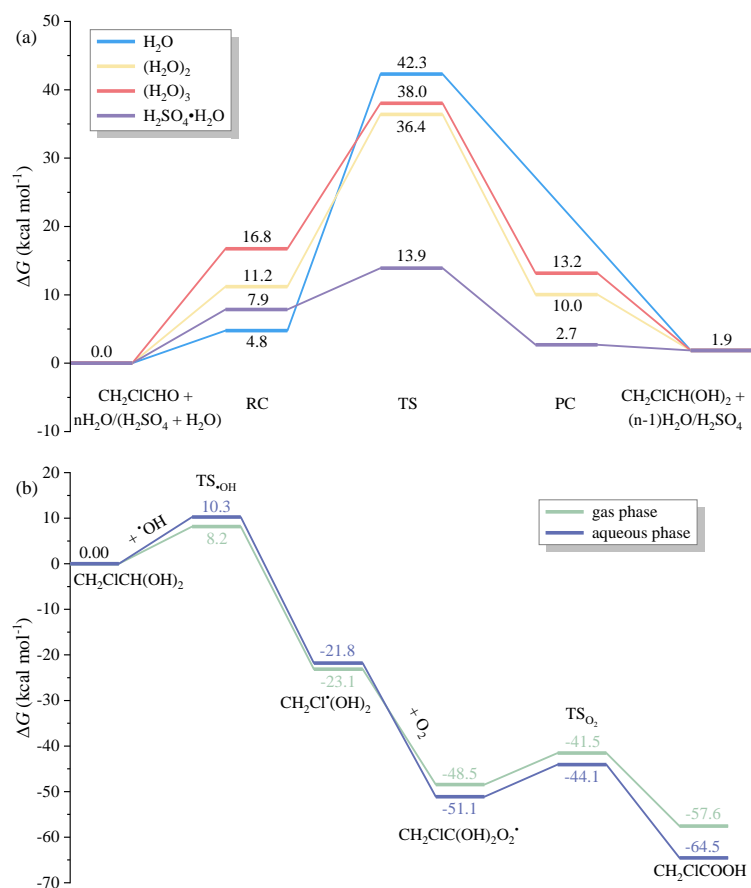


Figure 5. QC-calculated potential energy surfaces of the multiphase conversion of chloroacetic acid from chloroacetaldehyde at 298 K. (a) The hydrolysis potential energy surfaces of chloroacetaldehyde with water monomer (H_2O), water dimer ($(\text{H}_2\text{O})_2$), water trimer ($(\text{H}_2\text{O})_3$), 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.

2. It seems that the method for deriving γ also assumes that gas-phase diffusion limitations were negligible, is this true? Please clarify.

Response: The resistor model provided a concise formulation for estimating the reactive uptake coefficient, γ , of the trace gas (Davidovits et al., 2011). In the model, the elemental steps of heterogeneous uptake kinetics include gas-phase diffusion, mass accommodation, and solubility/reactivity in liquids, as expressed:

$$\frac{1}{\gamma} = \frac{1}{\Gamma_{\text{dif}}} + \frac{1}{\alpha} + \frac{1}{\Gamma_{\text{rxn}} + \Gamma_{\text{sat}}}$$

where Γ_{dif} is the gas-phase diffusion limitation, α is the mass accommodation coefficient, Γ_{rxn} and Γ_{sat} describe the liquid-phase reaction and solubility processes.

For typical submicrometer-sized aerosol particles in the atmosphere, gas-phase diffusion does not usually limit uptake coefficients unless the uptake coefficient is large. Previous studies have also reported that gas-phase diffusion was not the primary limitation on observed uptake coefficients at $\text{RH} \leq 98\%$ (De Haan et al., 2018).

So, we assume that the gas-phase diffusion limitations of OVOCs were negligible.

By the way, mass accommodation coefficients for formaldehyde, acetaldehyde and glyoxal were reported as 0.02, < 0.03 and 0.023, respectively (Jayne et al., 1992; Schweitzer et al., 1998). Considering their uptake coefficients at

the 10^{-3} level, we infer that interfacial mass accumulation is also not a limiting factor for the reactive uptake of aldehydes.

Solution process and chemical reactions in the liquid phase may dominate the uptake of aldehydes. We therefore used the free energy of dissolution and the hydrolysis reaction energy difference of OVOCs to build linear relationship models, as shown in Fig. S11 in the *Supporting Materials*. The result shows that the model based on the latter has a better correlation. The uptake of OVOCs deserves further study.

The assumption is clarified in the manuscript:

Lines 205: “Note that we assume that gas-phase diffusion limitations of OVOCs were negligible, given their low uptake coefficients.”

3. Page 3, line 70, please also report measurement accuracy.

Response: The uncertainty associated with the sensitivity of $C_2H_3O_2Cl$ arises from multiple factors, including the concentration of the calibration gas (2.76%), the flow and temperature control system (2%), wall losses in the calibration tube (5%), and variations due to relative humidity (2%). Additionally, accounting for the uncertainty in wall losses within the inlet tube (5%) and peak fitting during data processing (1%), the overall uncertainty in the measurement of $C_2H_3O_2Cl$ was estimated to be 11.1% using the basic formula for error propagation.

$$\frac{\sigma_f}{f} = \sqrt{\left(\frac{\sigma_a}{a}\right)^2 + \left(\frac{\sigma_b}{b}\right)^2}$$

where σ_f is the error in the result $f = a \times b$ or $f = \frac{a}{b}$, and σ_a, σ_b are the errors in a and b, respectively. As your comment, measurement accuracy was added.

Lines 73 – 74: “The total uncertainty of the measured chloroacetic acid was estimated to be 11.1%.”

4. Page 5, first paragraph: it seems that the correlations could be mostly attributed to diurnal variation, is this true? Considering the diurnal variation of oxidants, VOCs and other emissions, it is not surprised to have chloroacetic acid, aerosol mass, photolysis rate, etc. all peak in daytime. Similarly, correlation with RH could also be due to the diurnal variation of humidity.

Response: To reduce the effect of diurnal variation on correlation analysis, the correlations between $C_2H_3O_2Cl$, meteorological factors, and chemical constituents from 10:00 – 14:00 during the two observation periods were examined, as shown in revised Fig. S1. Results show that inorganic reactive chlorine levels, photolysis rates and aerosol surface area concentrations and relative humidity can be regarded as related to CAA levels with correlation coefficient greater than 0.5 or less than -0.5 during 10:00 - 14:00, although the coefficients are smaller than those during all day.

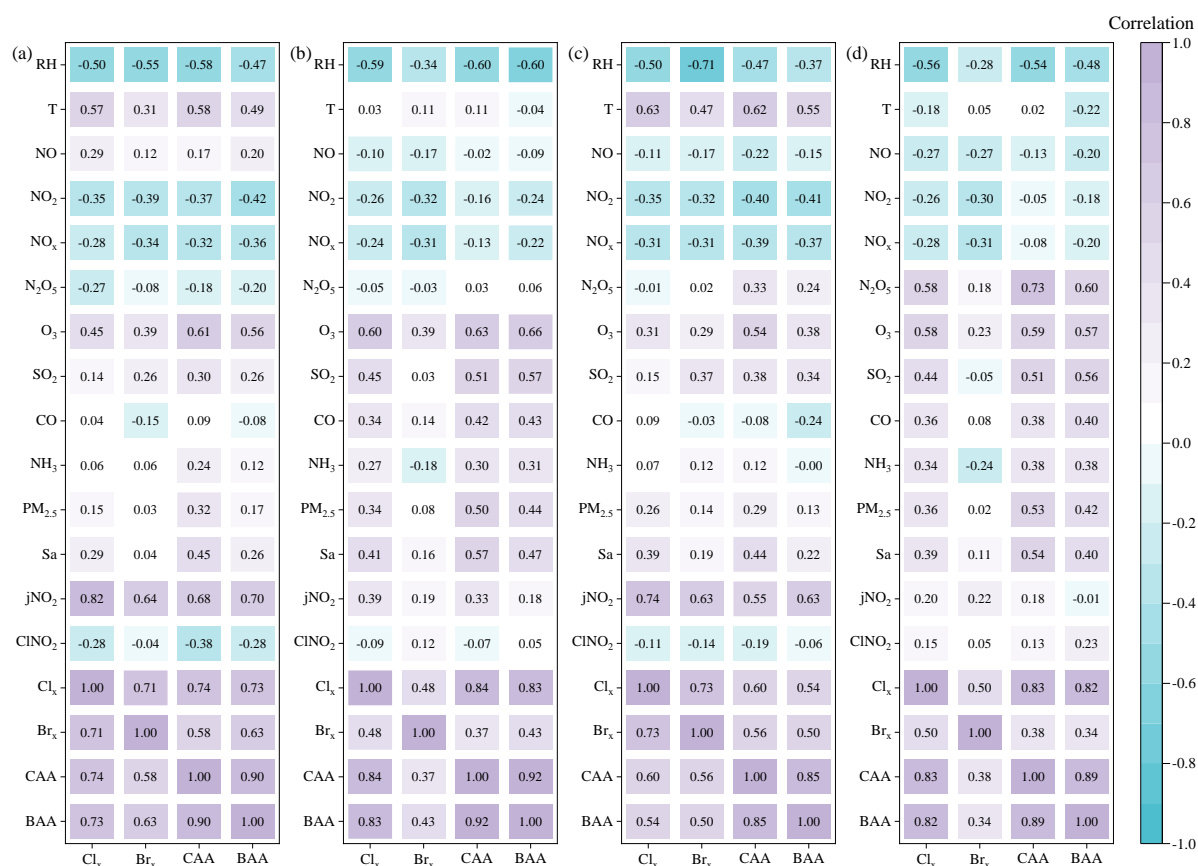


Figure S1. The correlation coefficients between important meteorological factors and CAA concentration (a) during all day in 2020, (b) during all day in 2021, (c) during 10:00 – 14:00 in 2020 and (d) during 10:00 – 14:00 in 2021. Cl_x = 2 × Cl₂ + HOCl + BrCl, and Br_x = 2 × Br₂ + BrCl. All data are 1-h averages.

5. Page 5, line 150-152: the energy barrier (~8 kcal mol⁻¹) between IM1 and IM2 is unclearly shown in the 3-D relaxed scan (Fig. 2). Texts on the axes need to be clearer.

Response: We have redrawn Fig. 2 for clarity.

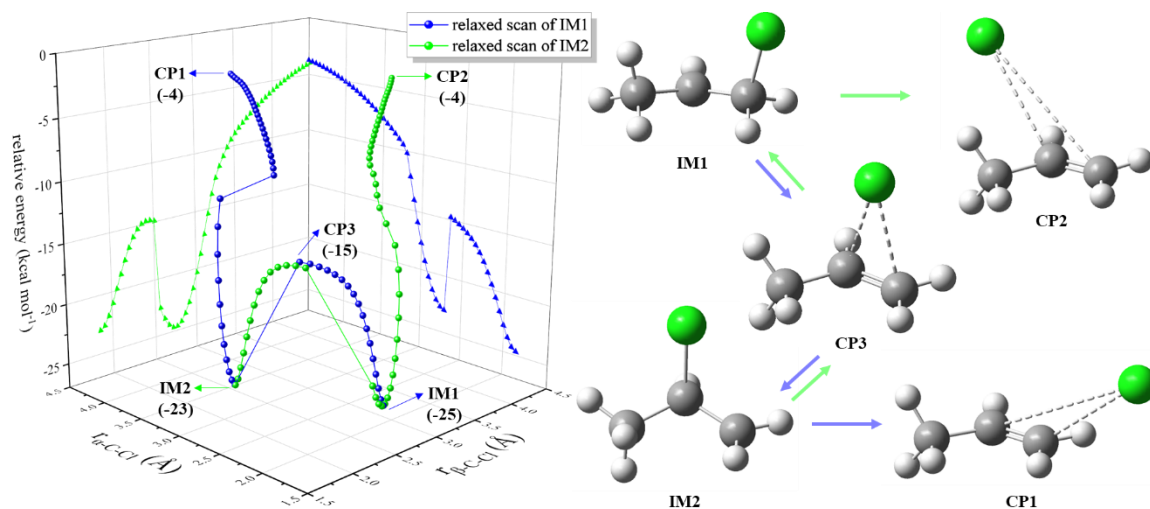


Figure 2. Relaxed scan of Cl⁺ addition to propene (C₃H₆). IM1 and IM2 are intermediates for Cl⁺ addition to alpha-C and beta-C of propene, and CP1, CP2 and CP3 are the complexes derived from scans of IM1 and IM2 in terms of bond lengths (r) of alpha-C-Cl and beta-C-Cl as variables, respectively. Scanned potential energy surfaces of

IM1 (in blue) and IM2 (in green) take the total energy of the reactants Cl[•] + propene as zero for reference. Energy in brackets in kcal mol⁻¹.

6. According to Figure 1, 4, 6, and 8, it seems that the diurnal variation of Cl-OVOCs/chloroacetic acid can only be represented by adding a reactive uptake, and cannot be resolved by adding another gas formation pathway related to oxidants levels. Is this correct? If so, this could be evidence to support the importance of multiphase process. Also, does adding reactive uptake change the diurnal pattern of precursors?

Response: Comparing the simulated results of chloroacetic acid and Cl-OVOCs in scenarios I – IV (Figs. 4 and 8), adding another gas formation pathway can increase their simulated levels but not change their simulated diurnal patterns. In scenario V, adding the reactive uptake of chloroacetic acid matches the simulated and observed pattern (Fig. 8), which can be seen as evidence of the atmospheric multiphase process. As shown in Figs. 4 and 6, adding reactive uptake also changes the diurnal pattern of Cl-OVOCs. We make Tab. 1 and Fig. 8 clearer for diurnal patterns, and the simulated and observed diurnal patterns of Cl-OVOCs and chloroacetic acid are discussed:

Lines 223 – 226: “As discussed in Section 3.2, the gas-phase chlorine chemistry of alkenes accounts for only 8% of the observed chloroacetic acid level and fails to explain the observed diurnal cycle. Adding reactive uptake of chloroacetic acid on aerosols aligns the simulated and observed daily variation, and including the heterogeneous source of chloroacetic acid increases the simulated level to 24 % – 48 % of the observed level (Fig. 8).”

Table 1. Model scenarios

Scenario	Precursor			Uptake of Cl-OVOCs and chloroacetic acid ^a	Heterogeneous formation of chloroacetic acid ^b
	C ₂ H ₄	C ₃ H ₆	C ₅ H ₈		
I	√				
II		√			
III			√		
IV	√	√	√		
V	√	√	√	√	
VI	√	√	√	√	√

^aThe reactive uptake of Cl-OVOCs on the aerosols is based on estimated uptake coefficients derived from QC calculations, excluding the heterogeneous formation of chloroacetic acid, and the γ value for chloroacetic acid is assumed to be the same as that for acetic acid (Wang et al., 2020). ^bThe yield of chloroacetic acid from the reactive uptake of chloro-acetaldehyde is estimated as twice that of oxalic acid from aqueous-phase photochemical reactions involving glyoxal (Carlton et al., 2007).

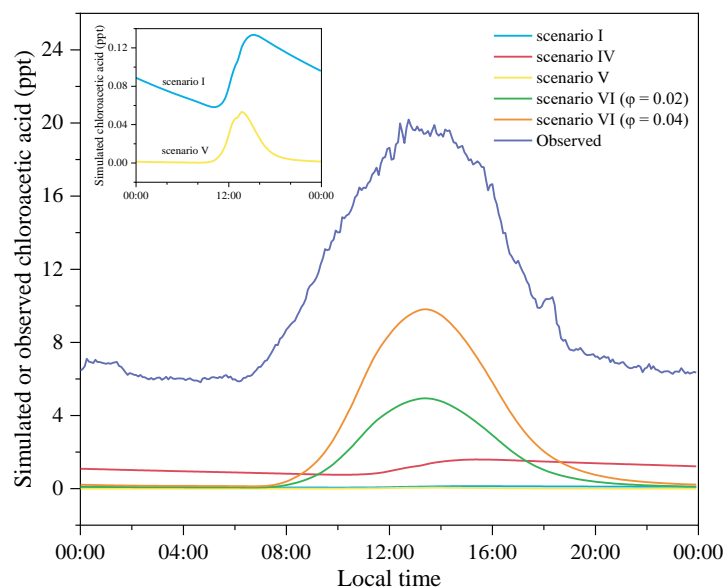


Figure 8. Comparison of measured and simulated diurnal profiles of chloroacetic acid.

7. Figure 8 has not been mentioned in the main text, please add it to the corresponding description.

Response: It has been added to the last paragraph of section 3.3.

8. Figure 8: Why does adding reactive uptake (scenario VI) decrease chloroacetic acid level at night (compare to scenario IV)?

Response: This may result from uncertainties in the reactive uptake coefficients of Cl-OVOCs and other missing sources of chloroacetic acid. Budget analyses (Fig. R1) on scenario VI revealed that heterogeneous loss of chloroacetic acid reduces its simulated concentration at night. Previous research has reported that the reactive uptake coefficients of methylglyoxal increase as RH increases, while those of glyoxal and organic acids decrease at high RH (Chen et al., 2021; De Haan et al., 2018; Gen et al., 2018; Tong et al., 2010; Zeineddine et al., 2023). Adding RH-dependent reactive uptake coefficients to the model may improve the simulated diurnal pattern of chloroacetic acid at night. Chlorination of natural organic matter and other organic matter in the aqueous phase may also produce chloroacetic acid, which may act as the nighttime source of chloroacetic acid. The limitation discussion on our simulation results is added in the revised manuscript:

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).”

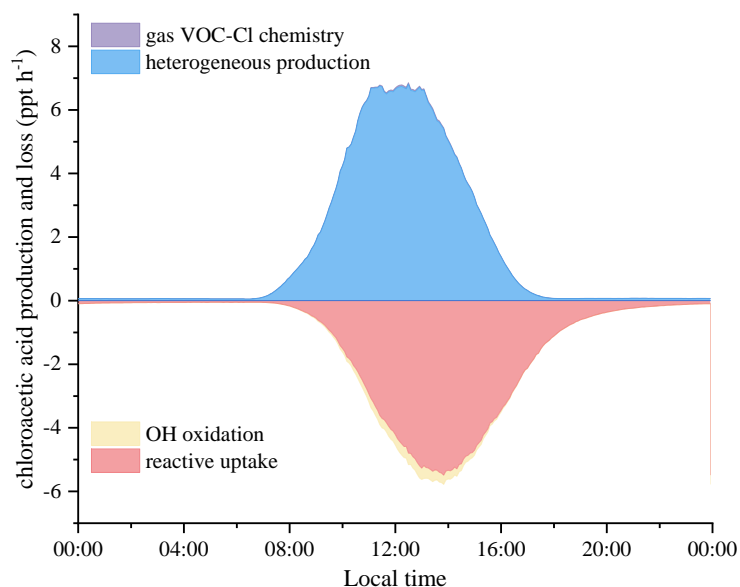


Figure R1. Diurnal variation of chloroacetic acid production and loss rates on scenario VI in Table 1.

9. I might suggest adding description for simulated contribution from heterogeneous reactions of chloroacetaldehyde to the observed chloroacetic acid in abstract and conclusion.

Response: It has been added.

Abstract:

“Box model simulation with multiphase chemistry reveals that the heterogeneous conversion of chloroacetaldehyde to $C_2H_3O_2Cl$ can contribute 24% – 48% of the observed levels.”

Conclusion:

“Adding the heterogeneous processes of these Cl-OVOCs to the MCM model explains 24% – 48% of the observed chloroacetic acid levels and exhibits a diurnal pattern similar to the observations, reducing the gaps between observed and simulated results.”

10. Abstract: “multiphase processes in VOC-Cl chemistry” in the last sentence may lead to confusion. It sounds like a multiphase process involve gas VOC with oxidation by Cl in aqueous phase. Please consider rephrase.

Response: We revise “multiphase processes in VOC-Cl chemistry” to “multiphase processes in atmospheric organic acid formation”.

Reference

- Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H.-J., and Ervens, B.: Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, *Atmos. Environ.*, 41, 7588–7602, <https://doi.org/10.1016/j.atmosenv.2007.05.035>, 2007.
- Chen, X., Zhang, Y., Zhao, J., Liu, Y., Shen, C., Wu, L., Wang, X., Fan, Q., Zhou, S., and Hang, J.: Regional modeling of secondary organic aerosol formation over eastern China: The impact of uptake coefficients of dicarbonyls and semivolatile process of primary organic aerosol, *Science of The Total Environment*, 793, 148176, <https://doi.org/10.1016/j.scitotenv.2021.148176>, 2021.
- Cui, H., Chen, B., Jiang, Y., Tao, Y., Zhu, X., and Cai, Z.: Toxicity of 17 Disinfection By-products to Different Trophic Levels of Aquatic Organisms: Ecological Risks and Mechanisms, *Environ. Sci. Technol.*, 55, 10534–10541, <https://doi.org/10.1021/acs.est.0c08796>, 2021.
- Davidovits, P., Kolb, C. E., Williams, L. R., Jayne, J. T., and Worsnop, D. R.: Update 1 of: Mass Accommodation and Chemical Reactions at Gas–Liquid Interfaces, *Chem. Rev.*, 111, cr100360b, <https://doi.org/10.1021/cr100360b>, 2011.
- De Haan, D. O., Jimenez, N. G., De Loera, A., Cazaunau, M., Gratien, A., Pangui, E., and Doussin, J.-F.: Methylglyoxal uptake coefficients on aqueous aerosol surfaces, *J. Phys. Chem. A*, 122, 4854–4860, <https://doi.org/10.1021/acs.jpca.8b00533>, 2018.
- Gen, M., Huang, D. D., and Chan, C. K.: Reactive Uptake of Glyoxal by Ammonium-Containing Salt Particles as a Function of Relative Humidity, *Environ. Sci. Technol.*, 52, 6903–6911, <https://doi.org/10.1021/acs.est.8b00606>, 2018.
- Herrmann, H., Hoffmann, D., Schaefer, T., Brüner, P., and Tilgner, A.: Tropospheric Aqueous-Phase Free-Radical Chemistry: Radical Sources, Spectra, Reaction Kinetics and Prediction Tools, *ChemPhysChem*, 11, 3796–3822, <https://doi.org/10.1002/cphc.201000533>, 2010.
- Huang, Y., Xu, H., Chen, B., Pan, H., and Qiu, Z.: Insights into chloroacetaldehydes degradation by 254 nm ultraviolet: Kinetics, products, and influencing factors, *Journal of Environmental Chemical Engineering*, 9, 104571, <https://doi.org/10.1016/j.jece.2020.104571>, 2021.
- Jahn, L. G., McPherson, K. N., and Hildebrandt Ruiz, L.: Effects of relative humidity and photoaging on the formation, composition, and aging of ethylbenzene SOA: Insights from chamber experiments on chlorine radical-initiated oxidation of ethylbenzene, *ACS Earth Space Chem.*, 8, 675–688, <https://doi.org/10.1021/acsearthspacechem.3c00279>, 2024.
- Jayne, J. T., Duan, S. X., Davidovits, P., Worsnop, D. R., Zahniser, M. S., and Kolb, C. E.: Uptake of gas-phase aldehydes by water surfaces, *J. Phys. Chem.*, 96, 5452–5460, <https://doi.org/10.1021/j100192a049>, 1992.
- Schweitzer, F., Magi, L., Mirabel, P., and George, C.: Uptake Rate Measurements of Methanesulfonic Acid and Glyoxal by Aqueous Droplets, *J. Phys. Chem. A*, 102, 593–600, <https://doi.org/10.1021/jp972451k>, 1998.
- Shen, H., Huang, L., Qian, X., Qin, X., and Chen, Z.: Positive Feedback between Partitioning of Carbonyl Compounds and Particulate Sulfur Formation during Haze Episodes, *Environ. Sci. Technol.*, 58, 21286–21294, <https://doi.org/10.1021/acs.est.4c07278>, 2024.
- Tang, S., Li, F., Lv, J., Liu, L., Wu, G., Wang, Y., Yu, W., Wang, Y., and Jiang, G.: Unexpected molecular diversity of brown carbon formed by Maillard-like reactions in aqueous aerosols, *Chem. Sci.*, 13, 8401–8411, <https://doi.org/10.1039/D2SC02857C>, 2022.
- Tong, S. R., Wu, L. Y., Ge, M. F., Wang, W. G., and Pu, Z. F.: Heterogeneous chemistry of monocarboxylic acids on α -Al₂O₃ at different relative humidities, *Atmos. Chem. Phys.*, 10, 7561–7574, <https://doi.org/10.5194/acp-10-7561-2010>, 2010.
- Wang, Y., Zhou, L., Wang, W., and Ge, M.: Heterogeneous Uptake of Formic Acid and Acetic Acid on Mineral Dust and Coal Fly Ash, *ACS Earth Space Chem.*, 4, 202–210, <https://doi.org/10.1021/acsearthspacechem.9b00263>, 2020.
- Zeineddine, M. N., Urupina, D., Romanias, M. N., Riffault, V., and Thevenet, F.: Uptake and reactivity of acetic acid on Gobi dust and mineral surrogates: A source of oxygenated volatile organic compounds in the atmosphere?, *Atmos. Environ.*, 294, 119509, <https://doi.org/10.1016/j.atmosenv.2022.119509>, 2023.