

RC1: Jeff Snider, University of Wyoming

The manuscript adds to a body of measurements of retention during riming. A retention coefficient increases from zero to one in the limit that volatilization to the gas phase does not occur during riming. In that limit the material is scavenged from the gas phase, via its incorporation in a graupel particle, opening the possibility for vertical transport and removal.

The measurements evaluated in this contribution can help improve understanding of new particle formation (NPF).

More broadly, the investigation casts a spotlight on parameterizing retention in terms of Henry Law solubility.

The authors should consider my critiques and reply with a revised manuscript.

We thank Jefferson Snider for the supportive review and the valuable and constructive comments/suggestions that helped to improve our manuscript. We have carefully revised the manuscript accordingly. Below you will find our point-by-point responses. Reviewer comments and suggestions are written in black, responses in blue. Changes in the manuscript are marked with "".

L36-37

As scientists we are striving to better understand tropospheric chemistry - the associated roles of aerosol and cloud processes – while aiming to reliably model what is happening. That is clear. However, the Introduction seems overly focused on the upper troposphere and on organic compounds. What is depicted in Figure 1 is also important for latitudes other than tropical and for compounds other than IVOC and SVOC. Sulfur dioxide and sulfuric acid fall into the camp of compounds not mentioned at this point in the Introduction. My recommendation is that you adjust somewhat, so that readers are not left with the impression that the motivating uncertainty is only scenarios in deep convective clouds, or in tropical deep convective clouds, or that the uncertainty only applies to the cloud processing of organic compounds.

We thank Jefferson Snider for drawing our attention to the fact that the motivation focused only on organics. We have adapted the text to provide a broader range of background knowledge.

L31: “The rate of NPF formation is strongly dependent on the concentration of low volatile vapors, the temperature and the number of particles that are present. Low-volatility vapors are for example sulfuric acid, which is formed from the reaction of sulfur dioxide and hydroxyl radicals or via oxidation of dimethyl sulfide, as well as highly oxidized organic compounds (Xiao et al., 2023; Williamson et al., 2019; Andreae et al., 2018; Kerminen et al., 2018; Twohy et al., 2002).”

L32-35

The statement that tropical convection does not produce sinks for small particles (and condensable vapors) needs clarity. If sinks (aerosol surface?) are missing, then this can accelerate NPF. But, if tropical convection also removes gaseous precursor, then NPF is decelerated. In this context, what is known about non-tropical convection?

We have adapted the text to provide more clarity. The reviewer is correct in pointing out that retention is also an important factor in non-tropical convection. We have included this in the introduction by referring to aircraft measurements and the associated determination of the scavenging efficiencies of water-soluble compounds.

L34: “A common explanation for the presence of this high number of small particles at high altitudes is the uplift of condensable vapors with simultaneous removal of existing aerosol particles in deep convective clouds. This removal of larger particles reduces the sinks for small particles and condensable vapors, supporting NPF (Clarke et al., 1998). However, Williamson et al. (2019) showed that tropical convection does not lead to uniquely low particle numbers for larger particles. They then argue that there must be a stronger source of condensable vapors at high altitudes in the marine tropics than in other regions and that most of the models used underestimated available organic matter at high altitudes and predict less NPF in these regions. It is therefore important to investigate the possible transport mechanism of organic precursor components that could lead to NPF at high altitudes (Bardakov et al., 2022).

Among other mechanisms, deep convection plays an important role in the transport of trace substances and aerosols into the upper troposphere. In this region, these substances have a longer atmospheric lifetime, thereby increasing the likelihood of long-range transport. Additionally, they can contribute to NPF (Bardakov et al., 2022; Barth et al., 2007a; Barth et al., 2007b). The fraction that arrives in the upper troposphere is influenced by the liquid phase and mixed-phase scavenging of the substances. Aircraft measurements from the USA in thunderstorm inflow and outflow regions demonstrate that water-soluble trace gases, such as H₂O₂, are removed with efficiencies between 79% and 97%, which are also influenced by the process of retention (Bela et al., 2018; Barth et al., 2016).”

L53 – 54

It’s not clear what is implied by “autoxidation.”

Thank you for this comment. We have modified the sentence to the manuscript to hopefully clarify what is implied by autoxidation.

L65: “Highly oxygenated organic molecules (HOMs) exhibit a sufficient low vapor pressure for NPF (Bianchi et al., 2019), however, their formation via autoxidation, a rapid OH-radical–induced oxidation process in the atmosphere, is suppressed at low temperatures (Stolzenburg et al., 2018)”

L85 – 88

In those prior investigations, were drops or droplets collected from regions that were not supercooled? If that was the case, then this statement is not obviously true.

We thank Jefferson Snider for the clarification. It is not clear from the measured samples whether they were supercooled droplets. We have therefore softened our conclusion.

L99: “Measurements of rain, hail and cloud water have already shown that they contain a-pinene oxidation products and nitrophenols (Spolnik et al., 2020; Desyaterik et al., 2013; Ganranoo et al., 2010). It is therefore likely that these compounds are also present in the supercooled droplets within mixed phase zones of clouds.”

L103

Is the “simulated graupel” here the same as the “captive floated” target discussed later?

The two terms are used synonymously. The text has been adapted to make this clearer.

L200: “To produce the simulated graupel, a silicon mold was filled with ultra-pure water and frozen. The graupel were “captive floated” to avoid the loss of graupel and any contamination on contact with the wind tunnel walls.”

2.2 Growth Regimes

During wet growth, broadly speaking, the sample is at ~ 0 oC, droplets are collected, some of that material adds to the mass of the sample, and some is shed. Your observation is that $T > -3$ oC (this is an ambient temperature threshold, correct?) make for “no freezing.” Could this be because the simulated graupel (and the bar) are thermally coupled to a warmer apparatus?

We would like to thank for pointing out this possibility of thermal coupling. The -3°C is the ambient temperature. The Teflon-coated bars are attached to the wind tunnel wall, so it cannot be completely ruled out that the effect may be also due to thermal coupling with warmer surfaces. However, we assume that the effect is more likely to be due to the surface. Teflon is hydrophobic, so that at warmer temperatures the supercooled droplets may not freeze on the hydrophobic surface upon collision.

A comment: Saying that the layer is freezing “very slowly” is confounding an already difficult concept. I will argue that, during wet growth, the freezing rate of an element of input liquid is impossible to calculate. In contrast, during dry growth, freezing rate can be calculated because shape, mass, and boundary conditions are constrained. Rates are fast (the impacted droplet is small, and the temperature gradient is reasonably large) and the characteristic time is small ($\ll 1$ s).

It is correct that “very slowly” is confounding. We have adapted the sentence in the manuscript to provide more clarity.

L129: “During wet growth, the freezing rate of an element of liquid input is rather low in comparison to dry growth conditions.”

I like how you have tied with the theoretical work of Michael and Stuart (2009) and brought in your observations of impinged droplets forming larger surface elements. What is the evidence that there is no shedding?

The statement is based on observations and not on a measurement, so we cannot exclude with 100% certainty that shedding has taken place. However, we were unable to observe any visible shedding of droplets. Furthermore, at an inflow velocity of only 3 m/s, which is low compared to the fall velocity of hail in the atmosphere, we do not expect any shedding to occur. We have adapted the sentence to make the statement more specific.

L138: “However, unlike the study of Michael and Stuart (2009), it was not observed that the droplets shed off during these experiments.”

L160 –

You present `_normalized_` number and `_normalized_` mass distributions. Why can't this method be used to quantify LWC?

In principle, it is possible to use the number or the mass distribution to calculate the LWC, but the method would be less accurate. The sample volume is relatively small and therefore the uncertainty is larger. For this reason, we decided to use the method presented in the manuscript, which is more precise.

L174 –

Can you reference a thesis, dissertation, or publication where the distance between the rime collector (s) and the sprayer is documented? If not, please specify that distance.

We would like to thank the reviewer for this comment. The distance is now specified.

L190: “The distance between the sprayer and the experimental section is approx. 3 m (Jost, 2012).”

L180 – 182

This needs better clarity. The apparatus captured droplets on an impaction substrate where they froze to form rime. Subsequently you melted the sample and measured the concentration of analyte in the liquid. Please revise for clarity.

We have changed the description a bit and hope that it is now easier to follow.

L190: “In the experimental section, the supercooled droplets collided with three different surfaces, which were used as rime ice collectors and froze on them. (...) The ice samples were collected after each experimental run and stored at -25 °C until they were melted for the chemical analysis.”

L191 –

There is a typo in this sentence. The same typo is on L348.

We would like to thank the reviewer for pointing out the typing errors, which have now been corrected.

L200 –

Why were the melted samples filtered? Is it possible that analyte (or IC) was lost or gained during this step?

We would like to thank Jefferson Snider for pointing out the possible impairment. The samples are filtered to remove possible particles, such as dust, and thus protect the HPLC system. We have investigated the influence of filtration, and no significant difference was found.

L208: “For analysis, the ice samples were melted and filtered through polyamide (PA) membranes (pore size: 0.20 µm; Altmann Analytik) to remove potential particles, but without affecting the concentration of the analytes.”

L212 –

What is “a. u.”? This occurs twice in this Section.

We thank the reviewer for noticing the missing explanation. a. u. stands for arbitrary unit. The software of the mass spectrometer does not display the nitrogen flow in an actual unit, but only as a numerical value in a. u.. We have added the explanation to the manuscript.

L220: “Sheath gas and auxiliary gas flow was 40 and 20 a. u.(arbitrary unit) respectively.”

L234 –

The sentence has “nebulizer” but Figure 2, and the equations, have “sprayer.” These are the same thing, I believe. “Nebulizer” and “nebulization” also appear later in the manuscript. Please use consistent terminology.

Nebulizer and sprayer are used as synonyms. We have carefully gone through the manuscript again to ensure consistent naming.

L248 –

It is important to know if the other nitrophenol isomer, the one with the larger KH, was tested for desorption.

What about other $KH < 105 \text{ M atm}^{-1}$ compounds? For example, was the desorption of pinanediol tested? These $KH < 105 \text{ M atm}^{-1}$ compounds partition mostly into the gas phase, assuming phase equilibrium.

We thank the reviewer for this statement. Only the desorption for 2-nitrophenol was determined, as the method with the liquid nitrogen finger was not suitable for this substance. As the other substances including pinanediol all have a retention of around 1, we assumed that desorption has no significant influence on the results. In addition, it was tested for pinic acid that the two measurement methods (using the LN finger or the sprayer blank, with the assumption $D = 1$) do not differ significantly for substances with high retention coefficients, indicating that desorption has no significant influence for this kind of substances. Therefore, we decided to use the LN finger because it is more accurate (the sample distance is assumed to be too short to allow for a noticeable influence of desorption for compounds with high H^*), and we do not need to measure the desorption correction coefficients for all substances.

L250: "Equation 1 and 2 yield identical results for compounds with a desorption correction coefficient of approximately 1. This is illustrated using pinic acid as a representative example in the Supplement (Figure S3)."

L255 –

Longer exposure time in the wind tunnel, with two sprayers compared to four sprayers, is consistent with the discussion of nitrogen volumetric flow rates. With four sprayers, the nitrogen flow rate is larger, and so, the exposure time is smaller. Based on that, I'm expecting longer exposure time with two sprayers, more liquid-to-gas desorption with two sprayers, and a smaller "desorption correction coefficient" with two sprayers. Larger "desorption correction coefficient", with two sprayers, is contrary to Figure 4. Because the fit lines are converging toward smaller temperature, this may not matter. But it's important to get the interpretation of Figure 4 correct.

We want to thank Jefferson Snider for the thorough reading and questioning of the results. The droplets produced when using four sprayers have a longer residence time in the tunnel as a lower nitrogen flow per spray nozzle is used. Even though the total flow rate is higher (24 L/min compared to 20 L/min with two sprayers), this flow rate is divided between four sprayers so that the nitrogen flow rate per sprayer is lower and the exposure time of the droplets is therefore longer. We have included additional measured points in the figure to give a more accurate representation of the data. We now used all the measurements for one linear fit because the slopes and y-axis intercepts of the different nitrogen fluxes are not significantly different, and this gives us better statistics. We have revised the section on desorption based on a comment from Amy L. Stuart. We have decided to include the section on desorption in the supplement rather than the manuscript (see Supplement: desorption correction procedure).

L286 –

A period is missing.

We would like to thank the reviewer for pointing out the missing period, which have now been corrected.

L283 -

How is your result, for pinanediol, an exception to that reported in Jost et al. (2017)? Chemically, the pinanediol (1, 2) is structurally different from the formaldehyde diol.

Pinanediol is an exception, as the data of Jost et al. (2017) indicate that substances with a Henry's law constant comparable to that of pinanediol have a temperature dependence and a lower retention coefficient, which was not the case in our measurements.

Table 4 and its footnotes –

The footnotes, and associated citations, are obscuring this aspect of the presentation. Why can't the US EPA citation be "US EPA, 2012"? Related to this, please see my comment below about the two Henry constants you present (Table 4) for the two structural isomers.

We thank the reviewer for this comment. We cite the US EPA in this way because this is the citation style recommended by the provider.

L436 –

The 2 nitrophenol isomer may form an intramolecular hydrogen bond, possibly weakening its binding to solvent (water). This same rationale might also explain why the Henry constants are so markedly different. There is some discussion of this in the chemical literature. Please provide some insight, and reference citations, in your revision.

We thank the reviewer for this remark. We added a paragraph about this topic to our manuscript.

L448: "The different arrangement allows for the formation of an intramolecular hydrogen bond between the OH and the nitro group in 2-nitrophenol. This can result in the non-dissociated form being stabilized, which may explain why 4-nitrophenol exhibits greater solubility than 2-nitrophenol. This could be due to the fact that 4-nitrophenol undergoes easier solvation and displays the capacity to form intermolecular hydrogen bonds. This property may also be responsible for the observed differences in Henry's law constants and retention (Achard et al., 1996; Schwarzenbach et al., 1988). In contrast to the bond method used in this study, the group method of the HENRYWIN™ software predicts the same Henry's law constant for both isomers."

L438 (and Table 4) –

It is not clear how you arrived at the different Henry constants for the two structural isomers. Did these values come from HENRYWIN? Here (L438) you state that the two isomers are predicted to have the same KH. Also (L365), you state that "The calculated values of H^* are listed in Table 4. Since there are no measured Henry's law constants nor reaction enthalpies for some of the more complex organic compounds, these were predicted using the HENRYWIN software which provides the values for 298 K." This is confusing.

Two different prediction methods can be used with the HENRYWIN software. The group method and the bond method. The data in Table 4 and in the figure were all obtained using the bond method. In L438 it is pointed out that it is important to have reliable predictions or measurements for H^* . For the two nitrophenols, the same value would be obtained using the group method, which does not seem to make physical sense. The text has been adapted so that it is hopefully no longer confusing.

L367: "Since there are no measured Henry's law constants nor reaction enthalpies for some of the more complex organic compounds, these were predicted using the bond method of the HENRYWIN™ software which provides the values for 298 K."

L452: "In contrast to the bond method used in this study, the group method of the HENRYWIN™ software predicts the same Henry's law constant for both isomers. This clearly shows the importance of reliable prediction or measurement of H^* and the importance of chemical structure."