

“Retention of Pinene Oxidation Products and Nitro-aromatic Compounds during Riming”

By C. Borchers et al. (2024) for EGUsphere

Reviewed by 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.

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.

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?

L53 – 54

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

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.

L103

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

2.2 Growth Regimes

During wet growth, broadly speaking, the sample is at $\sim 0^\circ\text{C}$, droplets are collected, some of that material adds to the mass of the sample, and some is shed. Your observation is that $T > -3^\circ\text{C}$ (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?

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).

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?

L160 –

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

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.

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.

L191 –

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

L200 –

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

L212 –

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

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.

L248 –

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

What about other $K_H < 10^5 \text{ M atm}^{-1}$ compounds? For example, was the desorption of pinanediol tested? These $K_H < 10^5 \text{ M atm}^{-1}$ compounds partition mostly into the gas phase, assuming phase equilibrium.

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.

L286 –

A period is missing.

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.

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.

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.

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 K_H . 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.