Atmos. Chem. Phys. Discuss., 12, C3244–C3251, 2012
www.atmos-chem-phys-discuss.net/12/C3244/2012/
© Author(s) 2012. This work is distributed under
the Creative Commons Attribute 3.0 License.

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Organics in environmental ices: sources, chemistry, and impacts" *by* V. F. McNeill et al.

Anonymous Referee #1

Received and published: 5 June 2012

Overview.

The manuscript reviews recent field, laboratory, and modeling studies of the chemistry and physics of organic compounds in snow and ice. The authors have done a good job focusing on work published since the Grannas et al. (2007) review of snow chemistry in ACP, which makes the current manuscript a useful addition. I also appreciate the focus on organic molecules, which is new. This is a nice piece of work that should be published after the comments below are addressed.

Major Comments.

1. My main recommendation is that the review should be more critical. That is, it should more carefully analyze the studies that are presented. There are three categories of

analysis in the current manuscript: (a) Simply listing a certain paper and the topic it studied; (b) Describing the main results from the study; (c) Describing the main results, comparing them to results from other work, and making a recommendation if the results do not agree. In the manuscript there are examples of all three levels of analysis.

(a) Frankly, text in category "a" is of little use to a reader. To give one example (Page 8889, lines 22 – 27): "Experiments at variable substrate concentration in the condensed-phase (Guzman et al., 2006b, Rincon et al., 2009), with mixtures containing inorganic salts, such [as] ammonium sulfate (Rincon et al., 2010), and at the air-ice interface (Guzman et al., 2006a, 2007) provided insight on the mechanism of formation of high molecular weight complex organic matter with similar optical properties to atmospheric HULIS." What was the mechanism? Were there differences between solution and ice?

As another example, consider p. 8892, lines 4-5: "There are very limited data in the literature from concurrent VOC and microbial snow measurements (Mortazavi et al., 2011)." What do these limited data show? There are other examples of this simple listing of paper topics in the manuscript. These should all be revised to at least move them into category "b".

(b) Describing the main results from studies (category "b") is very useful and for many studies this is as far as one can go. But there are some examples in the manuscript of missed opportunities to critically compare main results (i.e., to move the treatment to category "c"). For example, on page 8884 the discussion of the OH oxidation of organics in/on ice lists the main results (and interpretations) from several studies, but does not analyze the discrepancy of OH reactivity/non-reactivity. Work on bulk ice samples from several research groups (Abbatt, Klan, Anastasio) shows that OH can oxidize organics, but the surface-specific work from Donaldson's group shows no effect of OH on PAH degradation. What does this suggest? Is it solely a matter of low-solubility organics segregating from water-soluble H2O2? This does not seem to explain the Donaldson results since they can see the PAHs at the air-ice interface and, at least in

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

cc BY

some cases, H2O2 was doped from the gas phase.

As another example, how can we reconcile the cage effect results of Guzman (top of p. 8889), where there was no cage effect above 190 K, with the Ruzicka results in Fig. 4 (no escape from the cage at 190 K, 50% escape at 220 K)?

(c) There are several very nice examples of category “c” work in the manuscript as well, e.g., the p. 8878 discussion of the Fries et al. (2007) work. I thank the authors of these sections for this additional work and encourage others to bring their analyses up to this level if it is possible.

2. There needs to be more consistency in the discussion and definition of the “liquid-like areas” of ice. This is not a problem that is specific to this manuscript; rather, this is an unresolved issue in the field, but one that the current manuscript could address.

(a) At a minimum, this manuscript needs to have a consistent definition of what is meant by specific terms (e.g., QLL) and all authors need to use the terms in the same way. It would be even better if this paper could suggest and define a set of consistent terms for the various compartments in and on ice, as this is something missing from the current literature. This latter task might be done in the Bartels-Rausch et al. paper in preparation (“Influence of Snow and Ice Microstructure…”), but this paper is not yet available. Even if this upcoming paper does tackle this task, it would be good to at least summarize the consistent terms in the current manuscript.

(b) As an example of the term confusion, consider the introductory paragraphs of section 3.1. Here the quasi-liquid layer (QLL) is defined as the “nanoscale region of surface disorder [that] exists on pure ice near the melting temperature”, but at the end of this paragraph (p. 8869, lines 1 and 2), it is stated that the extent of the QLL increases with solutes. The next paragraph ends by saying that in the presence of sufficient solute there are liquid regions (“often called a brine”) at the air-ice interface or within ice grains (e.g., at grain boundaries). These definitions are a good reflection of the current uses of the terms in the literature. Unfortunately, as in the current literature, they are

cc BY

also “squishy” and qualitative. For example, at what point does a solute-containing, liquid-like region go from a QLL to a brine? What about internal regions containing the same solute composition as the QLL – are these not QLLs since they are not at the air-ice interface?

(c) The rest of the manuscript uses various terms, including QLL, liquid, quasi-liquid, micropockets, microveins, solid matrix, and grain boundaries, to refer to the liquid-like regions of ice samples. This proliferation of specific terms would be fine if we understood where solutes resided in a given sample and could distinguish between the various specific reservoirs. But, with the notable exception of the surface-specific studies of Donaldson and co-workers, we almost never know where solutes reside in laboratory samples. There is good evidence that in many studies solutes reside in liquid-like areas based on their chemical behavior, but we can rarely get more specific in our location determination. Thus I suggest the authors come up with a term (e.g., liquid-like areas), define it, and use it throughout the manuscript in place of the multitude of overly specific terms listed above. Of course in studies where the “air-ice interface” is specifically probed, this term (or something similar) should be used.

3. p. 8874 and Figure 2 discussion. (a) Are the Henry’s law constants (H) the physical or effective values (i.e., do they account for acid dissociation and carbonyl hydration)? It would be interesting to see the plot with both physical and effective values of H shown for the acids and carbonyls. (b) If effective values are used in the current plot, what pH value was assumed for the liquid-like regions in order to calculate H values for the carboxylic acids? The pH, of course, has an enormous impact on H. It would be useful to show the effect of pH on H values for the carboxylic acids in the plot, e.g., by considering a range of pHs. (c) The H values are all at 298 K. It would be more appropriate to show values at the ice temperature used for the free energy of adsorption measurements since H values for the species likely have different temperature dependencies.

4. p. 8876. To illustrate the points made in this subsection (titled “The effects of adsorption and desorption. . .”), it would be useful to have a figure or table that showed

CC BY

D(eff) values (and diffusion distances for a fixed time) for organics that span a range of K(LinC) values in several typical snowpacks.

5. p. 8881, last paragraph. (a) The results from Colussi and co-workers (Robinson et al., J. Phys. Chem B 2006, 110, 7613-7616; Cheng et al., J. Phys. Chem. Lett. 2010, 1, 374–378) should be incorporated into this discussion of the pH of liquid-like areas. (b) In the last sentence, it should be mentioned why the Workman-Reynolds freezing potential is important (e.g., in driving chemical reactions).

6. p. 8895, first line. “A comprehensive, accurate model of organic material in the cryosphere is needed. . .” This is an unrealistic goal given the complexity of the organic compounds in the cryosphere (e.g., Grannas’ measurements of 1000s of compounds with FT-ICR-MS). What is a more realistic expectation for the next decade? How do we, as a community, address the critical areas that need attention (e.g., those identified in the remainder of the Outlook section)?

7. Figure 1. The organic pools of the snowpack, and their connections, should be better described: (a) I have seen no evidence that snowpack VOCs make HULIS; certainly snowpack VOCs are not the major source of snowpack HULIS, as is suggested by the arrow going from VOCs to HULIS. This arrow should be deleted. (b) It is more likely that atmospheric deposition, and migration from underlying soil and vegetation, are the major sources of snowpack HULIS. These arrows are not shown in the figure but should be added. (c) The term “HULIS” is too narrow, as it does not include marine or terrestrial humic and fulvic acids, or other types of macromolecular, poorly defined, carbon. “Organic carbon” would be a better umbrella term, with “humic material and HULIS” as one of its subsets. Given that the focus of this manuscript is organic compounds, it would be good to give a more thorough depiction of the different classes of organics in the figure.

Minor Comments.

1. There are several sentences, or portions of sentences, that are awkward or run-

ons: (a) p. 8860, lines 14-19: “Organic impurities in snow. . .” (b) p. 8861, lines 13 – 15: “Since the discovery. . .” (c) p. 8866, lines 18 – 19: The phrase “snow and ice processed organic matter” is awkward. (d) p. 8870, lines 13-14: “. . .15 different small solutes organics and inorganics. . .” (e) p. 8889, lines 22 – 27: “Experiments at variable substrate concentration. . .” (f) p. 8894, lines 20 – 22: “This could serve. . .” The parenthetical phrases disrupt the sentence too much.

2. There are several places where the wording could be clarified or should be changed to be more accurate: (a) p. 8861, line 16. Rather than being “ambiguous” (i.e., vague and unclear), it’s more accurate to say that the role of snowpack is “complicated”. (b) p. 8862, lines 18-20: What are “free-cloud and free-precipitation conditions”? (c) p. 8864, lines 27 and 29: For the units of BrC, “ppb C” would be more accurate than simply “ppb”, which might be misconstrued. (d) p. 8865, line 20: “These optical measurements. . .” Which optical measurements? Neither the in-snow actinic fluxes nor the estimated photolysis constants in the previous sentence seem to be the correct answer. (e) p. 8872, lines 9 – 10: “. . .(assigned to the potential model used).” What does this mean? (f) p. 8891, lines 24-25: What is a biotic photochemical process? (g) p. 8893, line 12: “will be” should be replaced by “is”. (h) p. 8895, line 26 “. . .regarding the nature of the ice surface. . .” What does this mean? (i) p. 8896, line 10: “AICI” should be spelled out. (j) p. 8896, line 11: “. . .the role of the QLL or brine. . .” What does this mean?

3. p. 8865, lines 24 – 28: France et al. (2012) inferred a BC concentration in Barrow snow that is roughly 10 times higher than measured values from Barrow and surrounding areas. The current manuscript attributes this to enhanced absorption due to BC being included in ice grains, using Flanner et al. (2012) as the reference. But Flanner et al. modeled this effect to be much less significant, typically a factor of 2 increase in absorption for BC included in ice grains compared to “naked” BC. Given this, the proposed explanation in the text is unlikely. A more likely explanation is that the France et al. snow was contaminated from local sources at Barrow.

4. Typographical and spelling errors. (a) p. 8866, line 8: “autochtonous” (b) p. 8871, line 10: “. . .with another trace gases. . .” (c) p. 8873, lines 2-3: “. . .as pointed out by (Symington et al., 2010). . .” should be “. . .as pointed out by Symington et al. (2010). . .” (d) p. 8882, line 22: “peroxide” should be “peroxides” as both H2O2 and various organic hydroperoxides are important. (e) p. 8886, line 17: “acceptor” should be “acceptors”. (f) p. 8887, line 7: “acids” should be “acid” (g) p. 8889, line 12: the semicolon after (Kawamura et al., 2001) should be replaced with a comma. (h) p. 8889, line 24: missing “as” in the phrase “such ammonium” at the end of this line. (i) p. 8890, line 7: should be singular “rate constant”, with downstream changes in the sentence, i.e., “The rate constant at any given [O3(g)] was significantly faster than that. . .” (j) p. 8892, title of section 4 (“Impact of environmental ices. . .”): “cycle” should be plural. (k) Throughout the manuscript: “i.e.” and “e.g.” should both be followed by a comma.

5. p. 8866, lines 8 – 10: It would be helpful to define “autochthonous” and “allochthonous” in the text.

6. p. 8866, line 17: To say that these biochemical transformations of DOM are “specific to snow and ice” is an overstatement. Certainly very similar processes can occur in other media.

7. p. 8882, lines 23 – 24. It is not just the optical properties of organic compounds that determine their photochemical reactivity, but also their reaction efficiencies (i.e., quantum yields).

8. p. 8885, lines 13-14. It would be helpful to say why the authors proposed that the presence of contaminants other than benzene might affect the photolability of benzene.

9. p. 8886, line 8. This section refers to a “solid matrix”, but presumably the chemistry of pyruvic acid in/on ice is occurring in liquid-like regions (unless the temperature was very low). This should be clarified. If the chemistry is occurring in liquid-like regions then there is not a “fixed frame” for electron transfer, but rather a restricted region.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

10. p. 8886, lines 20-21. (a) What reducing agent donated the electron to NO2 to make nitrite? If it is the sensitizer then the resulting product should be the sensitizer cation. If not the sensitizer, what was the source of the electron? (b) My understanding is that nitrite does not undergo “acid-catalyzed hydrolysis” to form HONO, but rather is simply protonated.

11. p. 8893, lines 1-3. These chemical and biological processes occur not only at the air-ice and ice-sea interfaces, but also throughout the sea ice. See, for example, photochemical studies of J. France and M. King.

12. In the References section some of the entries have all title words capitalized, which is not the correct style.

Overall Assessment This is a nice piece of work that should be published after the comments above are addressed.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 8857, 2012.