

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

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We thank the reviewer for his or her positive overall assessment of the manuscript. We welcome the opportunity to improve the manuscript based on these comments and suggestions. Our responses to specific comments are in bold type below.

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

C6858

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.

We appreciate this comment. We have gone through the paper and elaborated on such statements where appropriate. More details are given below.

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?

This section has been expanded as per the reviewer’s suggestion and two schemes illustrating the mechanism have been added. The passage now reads: “The oligomerization of α -dicarbonylic compounds was demonstrated to form high molecular weight complex organic matter with similar optical properties to atmospheric HULIS in laboratory mimics of aqueous aerosol and environmental ices (Guzman et al., 2006b, 2007, Rincon et al., 2009, 2010). The radical mechanism is initiated via photoinduced electron transfer between triplet excited state and ground-state pyruvic acid to produce a bound radical ion pair (Scheme A).

C6859

The propagation steps (Scheme B) involve the addition of radicals X and Y to pyruvic acid and/or oligomer products, even in the presence of air because the oxyl radical Y is not scavenged by O₂. The same mechanism was operative in liquid and ice (Guzman et al., 2007). Beine et al. (2011) measured the absorbance of melted filtered snow in Barrow, Alaska and found that HULIS was the largest contributor to absorbance, even though they only represent 10 percent of DOC (Voisin et al., 2012).”

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”.

This example and others have been elaborated upon, following the reviewer’s suggestion. This passage now reads: “There are very limited data in the literature from concurrent VOC and microbial snow measurements. Mortazavi and coworkers (2012) found a significant amount of culturable bacteria and fungi in a variety of snow types and frost flowers in Barrow, AK during OASIS 2009. They also sampled and measured VOCs such as toluene, xylenes, and acetophenone. While anthropogenic influence cannot be ruled out, the apparent enrichment of acetophenone suggests a connection with biochemical activity. Further studies, for example, including isotopic probes, are required to shed light on mechanistic pathways of microbial biochemical interactions with VOCs in snow.”

(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

C6860

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 some cases, H₂O₂ was doped from the gas phase.

The passage referred to by the reviewer has been modified to now read: “In the only experiments to probe reactions between hydroxyl radicals and organic species directly in the DI, Kahan et al. (2010) reported significant suppression of reactivity compared to that measured in aqueous solution or in bulk ice samples. This was the case both when OH was formed through the photolysis of precursors such as H₂O₂, nitrate, or nitrite also present in the DI, and when OH was deposited from the gas phase. Although it could be that the OH and organics were present in different regions of the ice surface, the enhanced reaction rate at the ice surface as compared to the air-aqueous interface reported by the same authors using ozone as the oxidant (vide infra) suggests that this may not be the whole story. Molecular dynamics calculations of the fate of OH and its reactivity on an ice surface would certainly help to address this issue.”

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

The results of Guzman et al. (2006a) agree with those of Ruzicka et al. (Figure 4) up to 190 K, but above this temperature they differ because the initially formed radical ions do not retain their identity. Specifically, the radical cation, undergoes deprotonation followed by ultrafast decarboxylation, concomitantly with photon absorption, of the resulting acylcarbonyloxy radicals, rendering a

C6861

different species above 190 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.

We thank the reviewer for this positive feedback. In addition to the examples given above, we have added more critical analysis in sections II (discussion of BC absorption measurements in snow, see below) III A (discussion of experimental studies of physical interactions between organic gases and ice, discussion of the correlation between ΔG_{ads} and $\Delta G_{gas-liquid}$, H), section IV (ice and the carbon cycle) and Section V (outlook). Our discussion of the QLL and other compartments in ice is also more critical now, as described below.

2. There needs to be more consistency in the discussion and definition of the “liquidlike 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.

The definitions of the QLL and brine, as currently agreed upon by the AICI community, were stated on pages 8868-8869. As the reviewer correctly acknowledges, there is certainly some disconnect between these definitions and the language that has been used in the literature in the past. The reviewer is also

C6862

correct that the forthcoming review by Bartels-Rausch et al. in this special issue will delve into this topic in more detail. In response to the reviewer’s suggestion, we have included a definition of the other compartments mentioned in the paper (microveins, micropockets, grain boundaries) and have gone through the manuscript to improve self-consistency with the terminology. After further discussions within the AICI community we recommend the use of “disordered interface (DI)” to describe the surface disordering phenomenon (commonly referred to as QLL or premelting). The introduction to section III now reads:

“Ice in the environment may exist in the form of ice or snow at the Earth’s surface or frozen cloud particles in the troposphere or stratosphere. Impurities in snow can be molecules or ions adsorbed to or dissolved in crystals, aerosol particles which originated as a condensation nucleus (Parungo and Pueschel, 1973), gases and particles scavenged during precipitation (Lei and Wania, 2004), or species deposited onto snow on the ground (Domine et al., 2004). The amount and location of chemical species incorporated into growing ice crystals depends on the snow formation mechanism, i.e., whether the crystal forms by freezing supercooled water or by water vapor condensation. Once deposited on the surface, snow is a porous medium that continues to undergo morphological changes due to changes in ambient temperature and radiative heating (Domine et al., 2008). The void space of the snowpack consists of air which undergoes exchange with the ambient atmosphere and contains trace species which interact with the ice crystals (Domine and Shepson, 2002). Environmental ice and snow represent thus a complex matrix where physical exchanges, chemical reactivity and biological processes can occur in distinct, different local environments. The physical and chemical properties of these local environments (compartments) directly influence the overall reactivity, and vice versa. This has been reviewed in detail in a companion paper in this Special Issue (Bartels-Rausch et al. (2012)). In brief, and as evident from the history of snow described above, surface snow, sea-ice, and ice clouds may provide a variety of environments for interaction

C6863

with and reaction of organics, including: neat ice surfaces, grain boundaries, a neat ice crystal matrix, liquid phase, and water-insoluble solids. A nanoscale region of surface disorder exists on pure ice near the melting temperature, often referred to as a quasi-liquid layer (QLL). The QLL on pure ice is not a phase predicted by equilibrium thermodynamics. It is an interfacial medium thin enough that most molecules are affected by the nearest interface. Therefore, properties of molecules in a QLL are different from those in a liquid. For this reason, we recommend the use of the term disordered interface (DI). Affected properties include mobility, interaction with other molecules, and possibly reactivity. A key question is how chemical and physical processes on ice are influenced by the DI, and vice versa (Bartels-Rausch et al. (2012)). Grain boundaries containing relatively low impurity concentrations may share some of the characteristics of the DI, but little is known about this. When sufficient solute is present, the chemical potential of the interfacial layer increases sufficiently for an extra phase to form, as predicted by equilibrium thermodynamics. Down to a few tens of degrees below 0°C, this phase can exist in equilibrium with the ice and the gas phase, and is often called a brine (Cho et al., 2002; Kuo et al., 2011). The brine may exist at the gas-ice interface where it is available for reactions on short time scales, or be segregated inside the ice sample from where its solutes can only escape on long timescales (i.e., in grain boundaries, triple junctions, or inclusions within crystals). The presence of a brine changes the reactivity of environmental ices changes drastically. For more details on the influence of ice microphysics on air-ice chemical interactions please see Bartels-Rausch et al. (2012). Physical, chemical, and biological processes can affect the properties and cycling of organic materials in environmental ices. In the following sections we present an overview of these processes from field, laboratory and modeling perspectives.”

(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

C6864

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 also “squishy” and qualitative. For example, at what point does a solute-containing, liquid-like region go from a QLL to a brine?

We refer the reviewer to the work of Wettlaufer (1999) and Kuo et al. (2011) for a discussion of this interesting topic. It will also be covered in further detail in Bartels-Rausch et al. (2012).

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?

As described on page 8880, internal liquid regions (microveins/micropockets) are generally brines formed as a result of the freeze concentration effect. Grain boundaries containing relatively low impurity concentrations may share some characteristics of the DI but little is known about this. We now mention this in the manuscript when we introduce grain boundaries (see intro to section III, quoted above).

(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.,

C6865

liquidlike 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.

As described above, we have gone through the manuscript and improved self-consistency with the terminology. We recommend the use of “disordered interface (DI)” to describe the surface disordering phenomenon (commonly referred to as QLL or premelting). We have also expanded our description of the other compartments of ice (see intro to section III, quoted above).

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.

In response to points (a) and (b): Physical Henry’s Law constants are used. Note that the Effective Henry’s Law constant value for acetaldehyde was used in the original manuscript but this has been changed for consistency. The effective value for acetaldehyde will be somewhat higher, depending on ionic strength. The measurements for the organic acids were made under acidic conditions to inhibit ionization (Johnson, Betterton, and Craig, 1996). Acidic conditions are expected in environmental systems, with the possible exception of brines formed from sea ice freezing. Constructing a diagram using effective H values will necessitate an arbitrary choice of pH and ionic strength, so we will avoid this, but more discussion of this point has been added to the manuscript. Ulrich et al. re-

C6866

cently showed that KlinC for multiple acidic species was correlated with both H and pKa. In response to point (c): We appreciate the reviewer’s point, but experimental data do not exist for Henry’s Law constants at 228 K, and extrapolation of data to these low temperatures is necessarily uncertain, since this is below the freezing point of water. We note that ΔH_0 and ΔS_0 do not typically change much in going to low T, and so the quantity ΔG at 228 K is quite appropriate, i.e. most of the temperature dependence will arise from the changing T in $\Delta G = \Delta H - T \Delta S$.

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 D_{eff} values (and diffusion distances for a fixed time) for organics that span a range of $K(\text{LinC})$ values in several typical snowpacks.

A figure of this type was provided in the snow physics review by Domine et al. (2008), which is referenced in this section.

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).

The following material was added: “In a related study, Robinson et al. (2006) studied pH changes in brine remaining upon freezing of solutions using solid-state nuclear magic angle spinning (SS-MAS) NMR of the ^{19}F chemical shift (19δ) of 3-fluorobenzoic acid (3-FBA). It was observed that upon freezing a solution of 10 mM 3-FBA in 1.06 molal $(\text{NH}_4)_2\text{SO}_4$, the pH of the remaining liquidus in the brine decreases at lower temperatures. The increase in pH observed when freezing a 1 M NaCl solution at lower temperatures suggested that concentration effects were not the main factor controlling the acidity shift. The raise and drop in

C6867

pH observed at lower temperatures indicates that the observed process occurs in a fluid domain existent within the bulk solid phases. In agreement with the observations of Workman and Reynolds (1950) during the freezing of (NH₄)₂SO₄ and NaCl solutions, respectively, the sign of the acidity changes was related to the incorporation of ions to the ice phase. The preferential incorporation of NH₄⁺ and Cl⁻ into the ice matrix relative to their rejected counter-ions SO₄²⁻ and Na⁺ affects the transport of H⁺ and HO⁻ ions out of or into the ice. The finding was confirmed using a solution of a zwitterionic buffer, which did not change its acidity upon freezing (Robinson et al., 2006). Donaldson and coworkers compared the air-ice and air-water interfaces using Raman spectroscopy at glancing angle of the OH-stretch bands. The protonation of acridine, an organic fluorescent pH probe, at the air-ice interface was observed in the presence of HNO₃ or HCl deposited to the ice surface from vapors (Kahan et al., 2007; Wren and Donaldson, 2012). However, no enhancement in the proton concentration was observed at the interface upon freezing mildly acidic or neutral solutions. The authors concluded that dissociation of acids may occur within the DI. The release of hydroxide anion in the heterogeneous ozonation of bromide at sea-ice surfaces was also confirmed using harmine, another pH-sensitive fluorescent probe (Wren et al., 2010). Time-resolved confocal fluorescence microscopy showed that the morphology and composition of interstitial fluids in polycrystalline ice is affected by electrolytes as observed during the freezing of 4-(10-(dimethylamino)-3-oxo-3H-benzo-[c]xanthen-7-yl)isophthalic acid (a pH probe). The relatively thick (12 μm) glassy channels observed upon freezing the 10 μM probe in water became random inclusions with less than 1 μm diameter in the presence of 1 mM sodium chloride. The 30 μL frozen sample of 1 mM NaCl had an interstitial volume of 13.2 nL (or 0.044

The Workman-Reynolds freezing potential is mentioned in that section and defined in the following passage: “Upon freezing, the ice lattice incorporates more Cl⁻ than Na⁺ ions (Workman and Reynolds, 1950). The migration of H₃O⁺ ion

C6868

from the unfrozen solution to the ice allows the system to return to a charge-neutral state. The pH of the unfrozen portion, as a consequence, increases by 3 units and catalyzes the alkaline decomposition of gallic acid (Takenaka et al., 2006). The electrochemical potential which results between the ice and remaining unfrozen solution is known as the Workman-Reynolds freezing potential (Workman and Reynolds, 1950).”

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)?

We stated the need for a “comprehensive” and “accurate” model; we did not intend to imply that the model need be chemically detailed to the point of following the evolution of each organic species. We agree with the reviewer that this would be unrealistic. We have changed the language of this passage to hopefully avoid any misunderstanding on the part of the readers. We list other needs (such as improved analytical techniques) in the subsequent paragraphs of that 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.

We feel that sufficient evidence for VOCs as a source of HULIS exists to warrant keeping that pathway in the diagram. This topic is discussed in the text (Section III.B.5), and that discussion has been expanded in the revised manuscript.

(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

C6869

the figure but should be added.

The arrow indicating deposition of HULIS from SOA has been included. Other sources for OC in snowpack are now highlighted.

(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.

More detailed description of the different classes of organic carbon is now given.

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.

These sentences have been restructured for improved readability.

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”.

We have replaced “ambiguous” with “complex”

(b) p. 8862, lines 18-20: What are “free-cloud and free-precipitation conditions”?

C6870

This has been replaced with “cloud cover and precipitation”

(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.

The change has been made.

(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.

We have now specified “Measurements of light penetration into the snow, snowpack reflectance and density were recently associated to a coupled snow- atmosphere radiative-transfer model TUV-snow (Lee-Taylor and Madronich, 2002)”

(e) p. 8872, lines 9 – 10: “. . .(assigned to the potential model used).” What does this mean?

This has been rephrased to say “at 77 K and 239 K”

(f) p. 8891, lines 24-25: What is a biotic photochemical process?

This has been changed “biotic processes”

(g) p. 8893, line 12: “will be” should be replaced by “is”.

The replacement has been made.

(h) p. 8895, line 26 “. . .regarding the nature of the ice surface. . .” What does this mean?

“nature” has been replaced with “state” for improved clarity.

(i) p. 8896, line 10: “AICI” should be spelled out.

The change has been made.

(j) p. 8896, line 11: “. . .the role of the QLL or brine. . .” What does this mean?

C6871

This has been changed to “the influence of the DIL on the surface chemistry of ice”

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.

The reviewer raises a good point. However, any local sources of contamination in France’s study would likely have also been present during previous studies. Probably the biggest source of discrepancy arises from the very different analytical methods (chemical, physical, or optical) used between France’s and previous studies. BC measurements historically have been defined based on the amount of CO₂ evolved when a sample is burned at a given temperature. It is difficult to compare these results to France’s optical measurements. We have included this discussion in the manuscript.

4. Typographical and spelling errors.

(a) p. 8866, line 8: “autochthonous” (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

C6872

“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.

These errors have been corrected.

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

This has been done.

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.

This has been rephrased to say “biochemical transformations that may occur in ice and snow”

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).

This now reads ”For direct photochemical processes, the photochemical properties of organic compounds and the local illumination conditions in ice determine their photochemical reactivity”

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.

We have now added “. . . the presence of other contaminants may affect photochemical fates by altering the ice surface environment (c.f. Kahan et al. 2010a)”

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

C6873

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.

The experiments of Guzman et al. (2006) were performed at cryogenic temperatures, so “solid matrix” is correct in the case of that study. Liquid-like regions are more relevant for environmental ices. We have expanded this discussion to make this clear.

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.

This has been clarified and now reads: “The reaction between the organic material and the adsorbed NO₂ requires a light absorbing sensitizer (S) to promote the electron transfer from reduced (e.g., phenolic) moieties in humic acid to NO₂. Reactive excited state species S* and NO₂⁻ are generated, and the latter undergoes protonation to HONO.”

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.

This has been noted in the text.

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

Actually, ACP does not specify this in the Manuscript Preparation guide. We will work with the editorial office to ensure that the format is correct in the final version.

C6874

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

C6875