

## **The role of the global cryosphere in the fate of organic contaminants**

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Response to Reviewers

We appreciate the timely and detailed reviews of our manuscript submitted to Atmospheric Chemistry and Physics Discussions. The reviewers provided a number of helpful suggestions that have allowed us to improve the content and quality of this manuscript. We have made significant changes and hope that this revised version is now suitable for publication. Please find below detailed responses to reviewer comments, including line numbers in the current manuscript where we have made specific additions or changes. The comments of the reviewers are included below in black. Our responses follow each comment/set of comments in blue.

Reviewer #1 (Florent Domine):

1- How about a list of abbreviations at the start of the paper? Sure, we know what PCBs are, but some of the acronyms are much less common and are not even explained. How about LRAT: will all potential readers understand that?

We have added a list of abbreviations as a preface to the paper (lines 40-64).

2- I recommend discussing the possible location of contaminants in snow and sea ice at the beginning of the paper to make this point clear from the start. Partitioning between ice crystal surfaces and organic particles, solubility in brine in sea ice, etc; all this needs to be clarified at the very start.

We have added a paragraph in the introduction (lines 113-121) that briefly introduces these processes to the reader and refers to the specific sections where more detailed descriptions are included. The paper is organized around a discussion of the various “compartments” of the cryosphere, and the specific mechanistic details of contaminant uptake/partitioning is associated with each compartment description. Therefore, to avoid redundancy we did not add a new section that discusses the location of contaminants in snow and sea ice, as we felt it was important to keep these descriptions within the text of the particular section that describes that individual “compartment”.

3- P. 927, l. 6-8. Perhaps detail a bit more the feedbacks mentioned. Referring to AMAP does not suffice. One must be able to understand a paper without looking up references.

We have significantly revised the introduction. This particular reference to the hydrologic/cryospheric/organic carbon cycle is no longer present in the introduction. However, in the spirit of this suggestion, we have rewritten the introduction with an eye to better descriptions so that material is clear to the reader without reliance on other references.

4- P. 931, l. 10 ff. How about ice nuclei that also contain impurities?

This section has been significantly revised and now includes a more detailed description of scavenging processes, including incorporation of ice forming nuclei and particle scavenging by snow (lines 256-271).

5- Section 3.1. Processes taking place during the atmospheric phase of snow crystals should be clearly separated from those affecting deposited snow. It is not always clear what is being discussed. This needs to be better coordinated with section 3.3. Comparing scavenging by snow and rain needs to discuss the impact of the processes involved: adsorption (snow), dissolution (rain) and scavenging of particles. If solubility and adsorptivity are not discussed, how can the end result be discussed sensibly?

This section has been significantly revised and now includes a more detailed description of scavenging processes, including incorporation of ice forming nuclei and particle scavenging by snow as mentioned above. Current version Section 3.1 describes scavenging processes during deposition and more clearly discusses temperature dependence of this process. We have moved previous section 3.3. to section 3.2 which discusses the post-deposition physical processes that can lead to revolatilization of species from snowpack, and the variables that influence emission or retention of a species within the snow. For those chemicals that remain in the snowpack, Section 3.3 then discusses what may happen to these chemicals upon snowmelt. We have attempted to more clearly delineate processes affecting uptake during precipitation and processes affecting deposited snow (although in some instances this is not a clear delineation, as similar descriptions of partitioning equilibria are equally relevant to precipitating snow and deposited snow). We have also rewritten these sections to remove redundancy, and discuss the processes in a more linear fashion that should increase clarity for the reader, i.e. first we discuss what happens during precipitation, then what happens to the deposited snow/snowpack that influences revolatilization of contaminants, and finally what happens to the contaminants that remain in the snowpack as springtime snowmelt proceeds. We have added figure 2 in an effort to graphically tie these three sections together, given how these processes are interrelated.

6- P. 933, l. 17 ff. Discussing the effect of increased precipitation without discussing temperature effect is incomplete, especially since both effects are linked.

We have added more explicit discussion of temperature effects (lines 326-331).

7- P.935, Re. volatilization from snow. Perhaps consider discussing the paper of Jaffrezo et al. (1994), AE 28, 1139. This discusses long term decreases in contaminants in multi-year snow.

For this particular section, as we have rewritten it, we have tried to limit the discussion to snow scavenging processes, so the Jaffrezo et al (1994) reference would bring in an unrelated topic of volatilization from deposited snow.

8- P. 936, l. 11. Are organic particles not a phase involved here?

The particle phase is mentioned as a possible site for interaction (line 368), although this is important generally for dirty snow (i.e. urban snow). We have included also a statement based on conclusions of Roth et al (2004) that more work needs to be done to determine the role of particles in snow sorption processes (lines 398-400).

l. 19: why the factor 100?

The factor of 100 converts m into cm, so it is now written with its units “100 cm m<sup>-1</sup>”. We now also give the specific units for each value used in the equation so that the reader can follow the necessary units and apply them appropriately (lines 384-385).

I. 26. That MTC factor will surprise micrometeorologists. Is there any connection with air turbulence?

We have rewritten this section to more clearly define the MTC which applies to the transfer of mass within the snowpack and in the small surface layer (on order of millimeters) above the surface. We then discuss the atmospheric eddy diffusivity which would control the flux of species above the snowpack (lines 405-411), and how it is impacted by atmospheric stability.

9- P. 938. Last paragraph of section 3.3. Regarding PCB 28, Taillandier et al. (2006) had already concluded that subarctic snowpacks would take up much less of this compound than an arctic snowpack. Their conclusion was that in the subarctic, 71% of the PCB would be in the boundary layer whereas in the Arctic, only 6% would be in that atmospheric layer. The connection between the last sentence of the paragraph and the rest is not clear.

Taillandier et al. is now referenced and discussed (lines 441-445). The last sentence mentioned in the reviewer comment has been deleted from the revised manuscript to improve clarity.

10- Section 3.4.1. only includes vague general statements of little interest. It must be completely rewritten, and must include specific examples and a figure or table.

Sections 3.4.1, 3.4.2, and 3.4.3 have been rewritten and condensed into current section 3.3. We have tried to apply reviewer #2's suggestion of including a general statement, followed by specific examples. We believe that Table 2 (previously table 1) is adequate to visually aid the description of snowmelt processes (e.g. the different elution profiles), since we have condensed the previous sections.

11- Section 3.4.2. Perhaps Table 1 should be discussed half way down the section.

Table 2 (previously table 1) is now introduced much earlier in the section (at line 512, which is paragraph 4 of 13 in section 3.3). This section has been significantly revised, so we have attempted to link Table 2 (which discusses amplification processes) closely to where we introduce that concept.

12- Section 3.4.3. needs at least one figure with actual experimental curves. Table 1 is fine, but it should have been discussed earlier, and here we expect some hard data, not just theoretical considerations.

Table 2 (previously table 1) does actually represent experimental curves (not modeled) and this has been clarified in the text (lines 512-513) as well as in the table caption.

13- P; 945, top. How can type 5 of Table 1 not be explained and still be reproduced well by a snowpack melt model?

It does not state in the text that type 5 behavior cannot be explained. Rather the sentence states: "This release profile could only be explained by assuming that the strength of sorption of the compounds to the snow grain surface is declining during the snowmelt period, for reasons that are currently still unclear." In the snowpack melt model, the authors could reproduce this behavior by implementing a decline in the sorption coefficient to the snow grain surface during the melt period. It has only been observed to occur with intermediate chain length PFCAs, per Plassmann et al. 2011 laboratory experiments. This is described in the revision, lines 551-558.

14- Section 3.5. Fine section, clearly written, with a clear and totally adequate figure. If all sections were like this one, clear, concise, with adequate graphical support, the paper would take a quantum leap in quality. Watch for the size of the figures, however, and "glacier movement" is ambiguous. You mean the position of the front of the glacier, I guess.

We appreciate the positive comments regarding section 3.5 (now section 3.4). We have attempted to rewrite other sections in a similar manner, paying attention to clarity and conciseness. We have rephrased the term glacier movement to improve clarity (line 661).

15- Section 3.6 is good and interesting, but lacks clarity and many readers will miss several aspects. Should we know why different reservoirs have different enantiomeric ratios?

We have completely rewritten section 3.6 (now section 3.5) and, given the comments of reviewer #2, we now give more definitions and explanations of the chiral signature of pesticides and how the enantiomeric ratios might be expected to change under different conditions (e.g. lines 859-869).

Fig 3 is OK, but another one illustrating increases and decreases (both with long term trends kept and removed) of HCB would probably have been more useful.

We believe the reviewer is referring here to previous Figure 4. We have revised figure 4 (now figure 8) to include a longer term record, from 1993 to 2012. This illustrates better the initial decreases that occurred from 1993 – 2002, followed by increasing HCB trends more recently. The figure shows the individual measured HCB values, as well as seasonal and long term trends.

Is the purpose of the X axis of Figure 4 to confuse the reader? Having just years was too simple?

We have edited the revised figure (now Figure 8) to include axis labels of simply years.

This section illustrates difficulties in coordinating the paper. One would have liked to be explained that POPs partition to the ice surface and to organic particles, so that overall snow composition will affect contaminant location and reactivity. How do we know the actual location of contaminants (top of p. 953)? I recommend dividing this section into snow and ice subsections. Lastly, I suggest showing a table of saturating vapor pressures of POPs at -15\_C and referring to it to explain POP behavior.

We considered dividing this section into separate snow and ice discussions, but found this difficult in practice, as there are important interactions between the two. We have edited section 3.5 (formerly section 3.6) to include a more general introduction on the large scale role of sea ice on contaminant transport, followed by a section devoted to sea-ice formation and

brine processes (which also involve interactions with the overlying snowpack), followed by a section on the impact of sea ice on atmospheric concentrations of contaminants. Figure 4 has been added (replacing/improving previous Figure 7) to this section and is referred to much earlier in an effort to improve clarity.

Regarding the suggestion to include a table of vapor pressures, we have added Table 1 and provide references for physical chemical properties for POPs (which include vapor pressures), and interested readers can refer to these references. Since the studies discussed in Section 3.5 were done at different times of the year at different temperatures and at different locations, it is not possible to explain all observed behavior using saturating vapor pressures at -15C. (In fact, studies conducted by Jantunen and Wong during ice breakup were done at around 0C). As VP does not feature specifically in the paper we don't feel that including a standalone table with VP calculated for sub-zero temperatures (i.e. -15C) will serve a useful purpose, other than to show a significant (>order of magnitude) reduction relative to warmer temperate regions - which is intuitive anyway. We do however describe and discuss other physical chemical properties that are relevant to chemical partitioning in the cryosphere i.e. *K<sub>ia</sub>*.

16- Section 3.7 is vague and just general. We need actual examples with hard data and if possible a figure.

We have significantly revised section 3.7 and included more specific examples and quantitative aspects of the role of biovectors in contaminant transport and redistribution.

17- Section 3.9. Arguably, this is a difficult section to write. It is easy to guess who wrote it but I recommend that another coauthor critically evaluates it. All the experiments discussed here are good and interesting, but have severe limitations, as acknowledged by the authors. The impact of those limitations on our actual understanding of environmental processes must be stressed more. What is the impact of using ice mimics? What is the impact of the mode of formation of the ice on the location, and hence reactivity, of contaminants? Sure, there are fine papers on the suitability of ice mimics, but then are the arguments used still fully convincing? How could the presence of organic particles in actual snow affect reactivity? Can we extrapolate to natural snow the concentration effect and the presence of photoinitiators in lab experiments? By the way, snow is porous, snow crystals are not. It would be OK to conclude that today, we are far from understanding processes in actual snow. For example, have we tried to detect products such as those of Figure 8 in actual snow ? There needs to be a better coordination between section 3.9 and section 4.1.

We have significantly revised section 3.9, including a discussion of the limitations of laboratory ice mimics (lines, 1202-1229). This challenge is now also addressed explicitly in the revised section 4 (lines 1277-1286). The idea of detecting products identified in laboratory experiments is now addressed in section 4 (lines 1320-1324).

18- Section 4.2. This is a bit thin. For example, do not we need to know more about the interactions of POPs with organic particles ?

This is now addressed in section 4 (lines 1376-1379).

In conclusion, this is a potentially very good paper, but some sections definitely need improvements, sometimes complete rewriting, and the coordination between sections needs to be improved with great care and much attention to detail.

We have substantially revised major sections of the manuscript, aiming to improve clarity, better relate sections to one another, and remove redundancy.