

## ***Interactive comment on “Brief communication: Organochlorine pesticides in an archived firn core from Law Dome, East Antarctica” by M. Bigot et al.***

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Response to comments from Reviewer 2

The authors would like to thank the anonymous reviewer for their detailed comments and suggestions to improve this manuscript.

General comments:

- Reviewer wrote: "The conclusions are generally sound, although rewriting should be considered. Yes, the results are from as early as 70 years ago, but that results from

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inherent poor dating resolution of organic contaminants in ice cores."

This part of the conclusion has been revised as "Results show that legacy OCPs could have accumulated at Law Dome in deep firn dated from as early as 70 years ago. Our current understanding of organic contaminant retention, mobility and fate during aging of snow and formation of ice is poor. Apparent concentrations in glacial ice may not accurately indicate historical deposition. The analysis of ice or firn cores may nevertheless give us valuable information on the current OCP reservoir in polar regions."

- Reviewer wrote: "The quantitative difference between OCP amounts found the Antarctic and the Arctic are important, but the authors need to be much more precise in P6L30+ where they state that "deposition rates are orders of magnitude lower than those from Arctic regions". In that statement, they are suggesting that the Arctic is one uniform region with regard to OCP deposition rates, and the published literature shows that this is not true (some of the publications showing this are not included in the reference list)."

The reviewer is correct in that we had omitted to cite some key Arctic references (i.e. Hermanson et al. 2005 and Ruggirello et al. 2010) which are now included. These additional references were however considered in the initial version of this manuscript and in the statement that the reviewer has cited. We did not intend to suggest that the Arctic is one uniform region with regards to OCP deposition rates but simply wanted to point out the significantly lower concentrations and derived deposition rates that we are reporting in Antarctica compared to available Arctic literature. The sentence cited by the reviewer was modified to "OCP concentrations and deposition rates reported are orders of magnitude lower than those from sites with lower annual snow accumulation in the Arctic." This sentence was a conclusive statement based on previous discussion in the manuscript which was also extended to avoid possible confusion, see p5 lines 26-29 "Although the DSS site is characterised by higher snow deposition rates (0.68 m·yr<sup>-1</sup> weq) compared to the three other Arctic sites for which OCPs in glacial ice/firn cores

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were documented (from 0.36 to 0.52 m-yr<sup>-1</sup> weq), OCP results from the DSS site are 10 to 1000 fold lower than the reported Arctic levels (Hermanson et al., 2005; Isaksson et al., 2003; Ruggirello et al., 2010)."

- Reviewer wrote "Within the conclusions, I disagree with the use of the word "in-situ" with respect to melting techniques being supported by the references used. I am not certain that the referenced investigations used "in-situ" melting the way it was done for the current investigation because not all of the references specifically state melting at a field site."

Our ice-melting unit was designed based on Gustafsson et al. 2005 who performed "in-situ" sampling of sea-ice from a ship, using a similar device that could not be used without ship support and crane lifting capabilities. Given that no other studies performed "in-situ" melting as we mean it, we removed all other references cited in the conclusions to avoid confusion and modified the paragraph accordingly.

- Reviewer wrote: "The scientific methods and assumptions are clearly stated, along with some of the limitations. I am a bit concerned that limitations involved with using the KISP have not been identified, including long running times and short battery life. However, these are only a problem when using the KISP in the field, instead of in a laboratory."

The KISP model that we used requires connection to mains electrical power, therefore it would require a generator if used directly on-site. Other KISP models have been fitted with batteries by the manufacturer. All KISPs are generally very energy efficient, so we do not expect this to be a major limitation. Presently, the best option would be to collect samples on site and bring them back to the closest operational research station as stated on p4 lines 10-11, although powering the system (both KISP and water bath) using generators could be an alternative provided resources are available. This is now mentioned on p8 line 1 "The melting process can be performed in-situ provided powering resources are available, or locally at the closest research station."

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Increasing pumping rate is a possibility to reduce running times, however breakthrough of compounds would need to be investigated.

- Reviewer asked : "I have one question regarding the title: Is the DSS core really firm to a depth of 45.6 meters? There is no mention of the transition depth from firm to ice in this paper."

Yes, the section of the core that we used is firm as indicated by sample's densities between 0.63 and 0.74 g.cm<sup>-3</sup> (P3L29).

- Reviewer wrote "In the abstract, I do not understand what is meant by "nominal modern-use chemical contamination". How do deposition rates "orders of magnitude lower than those from Arctic regions" support validity? This is not standard QC procedure."

Our QC methods were limited by our inability to collect a "true field blank". We used modern-use chemicals (i.e. polybrominated diphenyl ethers, PBDEs) as an alternative to assess possible contamination of the core prior to the melting event. All information is documented in details in the method section of the manuscript. The abstract is only a brief summary of the content. The cited quote was modified to "nominal contamination by modern-use chemicals". The statement "orders of magnitude lower than those from Arctic regions" has been explained further in the body of the revised manuscript. See p5 lines 29-31 "This is consistent with the uneven distribution of the world's past usage (Voldner and Li 1995), with the Northern hemisphere having contributed larger emissions of OCPs than the Southern hemisphere, suggesting a larger pool of OCPs would have reached the Arctic in comparison to Antarctica." We believe it does not need expansion in the abstract due to word limits.

- C.E. is now defined in the abstract and main manuscript.

- Reviewer wrote: "Figures: Figure 1 needs additional information, including the dimensions of the unit. It would be useful to know the grade of N2 used and its circulation

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within the device, and not just that it is a “clean atmosphere”. "

N2 grade has been added to the figure. This figure is a 2D conceptual drawing, therefore our options to add technical information such as dimensions are limited. In an effort to address the reviewer's comment, the unit dimensions and mass have been added to the method section of the manuscript, see p4 lines 3-4. This unit could be reproduced to any dimensions depending on intended use.

- Reviewer wrote: "There is a significant issue with references used in the paper. Why is the Legrand et al. 1984 reference used for aerosols in a glacier? Why not Murozumi et al., 1969 (GCA, 1969, 33, 1247-)? Murozumi et al. also had data for contaminant lead both from Greenland and Antarctica, and was the first paper to identify contamination of ice cores by long-range transport of an anthropogenic substance. This issue takes on greater relevance with the earlier studies about organic contaminants in the Arctic used as references in this manuscript. One assumes that the Gregor et al. (1995) paper is used as a reference because it was the earliest study on PCB deposition in an Arctic glacier. This assumption arises because of absence of later reference to PCBs in glaciers. So again, why use Legrand et al., 1984, as a reference if it is not the earliest?"

Many thanks for bringing this older reference to our attention. Legrand et al. 1984 has been replaced by Murozumi et al. 1969

- Reviewer wrote: "There is no reason (or reference) given for the quantification of PBDEs as evidence of contamination. What is the rationale behind this?"

The reason is given p4 lines 29 et seq. "True blanks (i.e. similar volume of archive samples representative of a deposition period pre-OCP production) were not available. In order to evaluate possible contamination, modern usage POPs, namely polybrominated diphenyl ethers (PBDEs), were used as markers of contamination resulting from the sampling, processing and/or storage of firn cores. PBDEs are commercial flame retarding compounds widely produced since the 1970's." This is not a standard method

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and we only use PBDEs as “possible” indicators of contamination in an effort to address the absence of a true blank. We recognised that there is no direct link between PBDE contamination and OCP contamination in our discussion (see p5 line 21).

Specific comments & technical issues: - Reviewer wrote : "P1L26: Replace “hereby” with “thereby”. The statement made here, to “minimize the environmental and human health hazards that they pose” is overstated. Even though the compounds on the Stockholm list have been banned or restricted, they are still found in the environment. And they are still moving around. The only thing Stockholm can accomplish is prevent the mass of these contaminants now in the environment from becoming greater. P1L33: Again, Legrand et al., 1984 is not the best reference in this context. P2L5: The claim that “only one study has documented OCP concentrations in glacial ice/firn from the Arctic” is not correct. I can immediately think of 3 without looking. P3L4: This repeats P2L2. P3L19: C. E.? P4L27: The original results were not “corrected to estimate the mean deposition”. It is not a matter of correction, but calculation."

All above specific comments were addressed as suggested.

- Reviewer wrote: "P2L6: To say that there are no OCP studies in firn/ice cores from Antarctica is splitting hairs a bit too much for work like this. What about Kang et al., 2012, from the reference list? P5L9: Again, this limited selection of references is a bit surprising considering those not mentioned. Why are no comparisons offered between the results of Kang et al. 2012 and the results of this manuscript?"

We referenced Kang et al. 2012 in other places in this manuscript. In the specific statement (p2 line 5) we are referring to “firn/ice cores”. Kang et al. studied surface snow, therefore their study is not directly comparable. We however added a comparison of their HCH results on p6 lines 19-21 “Concentrations reported in this study are 19 and 22 pg·L<sup>-1</sup> for  $\alpha$ -HCH and 22 and 60 pg·L<sup>-1</sup> for  $\gamma$ -HCH, which are in the lower range of findings in surface snow collected more recently in Antarctica (Kang et al., 2012)."

- Reviewer wrote: "P3L13: Apparently it is true that Isaksson et al. (2003) never men-

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tion the diameter of the core used. The current manuscript also never mentions the diameter of the Law Dome core."

In this particular sentence, we are looking for volumes of ice analysed in the literature. Isaksson et al. 2003 does not indicate the sample volumes, only the length of the core, which is not sufficient to infer a volume. Nevertheless, we have now indicated the diameter of the DSS core (p3 line 9).

- Reviewer wrote: "P3L15: While it may be true that no earlier firn core studies are available to use as a guide for sample volume needed from Antarctica, the authors could have used Kang et al. study on surface snow as a guide."

We considered Kang et al., as well as other Antarctic studies on other matrices. They are all listed in this same paragraph (p3 line 20).

- Reviewer asked: "P3L26: Was the system shown in Figure 1 capable of holding 144 L of melt?"

The system would have been capable of holding 144L of liquid water but was not capable of holding the corresponding frozen volume. We melted cores in two successive batches for each sample. This was added p4 lines 4-5 "These were obtained through melting of two successive batches for each due to the limited capacity of the melting unit."

- Reviewer wrote: "P4L28: In my dictionary, "basal area" is defined as the area of total tree trunks (diamters) as a fraction of given land area where the trees are growing. That does not seem to apply here."

We replaced "basal area" by "surface area".

- Reviewer asked: "P4L31: What is meant by "dissolved fraction of the melt water"?"

The paragraph on the filtering materials p4 lines 14-17 was modified to describe and delineate dissolved and particle fractions.

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- Reviewer wrote: "P6L7: Reference to Stockholm for ban on Dieldrin is not very good. Dieldrin was banned under other regulations many years before 2004."

The Stockholm Convention is the official international treaty that banned dieldrin globally. Little detailed information is available about dieldrin restrictions for individual nations. Please note that in the same sentence we mention that its usage was restricted from the 1970s.

- Reviewer wrote: "P7L8: The authors need to do a better job describing "in situ"."

The paragraph was revised in an attempt to address this comment, see p7 lines 29 et seq. "The ice-melting unit used for the present work is designed to be transportable and represents a comprehensive tool offering a means of storage, transport, melting and pumping of large volumes of ice. It provides a cost-effective solution to the logistical challenges of transporting these volumes of ice back from Antarctica. It also reduces risks for contamination during storage and transport as well as minimising overall handling of the samples. The melting process can be performed in-situ provided appropriate power sources are available, or locally at the closest research station."

Please find revised manuscript in attachment.

Please also note the supplement to this comment:

<http://www.the-cryosphere-discuss.net/tc-2016-178/tc-2016-178-AC2-supplement.pdf>

Interactive comment on The Cryosphere Discuss., doi:10.5194/tc-2016-178, 2016.

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