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Title	"Brief communication: Organochlorine pesticides in an archived firn core from Law Dome, East Antarctica"

<u>Response to comments from Reviewer 1</u>

The authors would like to thank the anonymous reviewer for their very constructive comments.

The paper describes the methods used and the results from analyzing two bulk samples from the upper sections from an ice core from Law Dome for Organochlorine pesticides (OCPs). There has been no similar studies from Antarctica published before so therefore this is an important contribution to our knowledge about the fate of contaminants in the atmosphere. The paper is well written and its main focus in on the analytical methods; basically how to handle ice core samples that has been archived for a long time. Naturally, this is important knowledge as such studies described here will likely be on similar situations; i.e. left-over material after some of the fundamental sampling and analyses for dating and climate studies have been completed.

However, before the paper is accepted I would like the authors to provide more and accurate glaciological information about the ice coring site which is completely lacking and are of importance for any studies using material from ice cores.

- The position of Law Dome is likely not familiar to many readers and it is important to include information about where it is situated, altitude, annual accumulation rate and mean annual temperature. All these factors are likely to have an impact of the fate of contaminants during transport, deposition and post-deposition and thus on the concentration found.

> Site-specific information has been added from p2, line 26 to p3, line 2. "Law Dome is a small independent icecap located in Wilkes Land, East Antarctica and exposed to a maritime climate (Morgan et al., 1997). The DSS site is located near Law Dome summit, approximately 100 km from the coast and at 1370 m elevation (Morgan et al., 1997). This site was selected for its favourable bedrock topography and sufficiently low surface temperatures (mean annual average of - 21.8°C) which preclude summer melt (Morgan et al., 1997). The DSS site is characterised by a relatively high annual snow accumulation rate of 0.68 metres (water equivalent) (Roberts et al., 2015) facilitating the preservation of very clear seasonal cycles in glaciochemical species. This provided a means of accurate dating with monthly resolution in the upper portions of the core (van Ommen et al., 2004;Plummer et al., 2012;Roberts et al., 2015)."

- From glaciological perspective Law Dome is not part of the "East Antarctic Ice Shelf"; an expression that is used in this paper which is not correct. There are many ice shelves around the Antarctic continent but they are separate from each other and thus do not form a unit, which is implied here. Also, despite its coastal location Law Dome is not part of any ice shelf. It is a local ice dome with an altitude of close to 1400 m which is much higher that any ice shelf and therefore it is very confusing when melting ice shelves are referred to both in the "Introduction" and "Conclusions". Furthermore, it is not unlikely that the sources and

transport paths to Law Dome and lower elevation ice shelves are different and thus it is not a good idea to mix these things freely in the discussion.

> Thank you for the clarification. All references to the East Antarctic Ice Shelf have been removed from the manuscript.

p.5, line 3-4. "Both samples, however, also contained traces of our storage and handling contamination markers, PBDEs, indicating that sampling and/or storage conditions of the archived firn cores introduced organic contamination." I would like to see some more information/ideas around this aspect. For instance, is the type of plastic bags used important?

> We have further expanded on this point firstly on p5, lines 14-16 "These contaminants could have been introduced through various means such as the operator's personal clothing, storage in plastic bags, and the use of contaminated coring tools and inappropriate cleaning methods." Then on p7, line 28-29 "In particular, plastics should be avoided at all times as a general QA/QC measure for sampling and analysis of such compounds."

Finally, "polar regions" should not be capitalized as now is done through the manuscript.

> In the case of this manuscript, we purposely used capital letters for "Polar Regions" to distinguish "polar" from its other meanings in chemistry.

I recommend that the paper is accepted after these comments are considered.

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.

This paper documents the results of analysis of organochlorine pesticides in a firn/ice core from Law Dome, Antarctica. The core was drilled several years before analysis, and was kept in storage. There are few studies documenting the accumulation of organic contaminants in ice (of any kind) from Antarctica that were transported by the atmosphere. The reasons for so few studies are many, including the lack of available cores, which itself is related to the difficulty with drilling, retrieving and storing cores from Antarctica. Another issue is the expense involved with analytical work. The work of the authors in this regard is greatly appreciated.

This paper should be given consideration for publication after addressing the general and specific comments made below.

General comments:

In my opinion, the paper addresses a relevant issue within the scope of TCD. The idea presented and tools used in the research are not novel, but the data are new and are a *contribution to understanding levels of contamination found in the Law Dome area of Antarctica.*

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 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."

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 $m \cdot yr^{-1}$ weq) compared to the three other Arctic sites for which OCPs in glacial ice/firn cores were documented (from 0.36 to 0.52 $m \cdot yr^{-1}$ 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)."

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.

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

The results have not been over-interpreted, which is important. The results here are very limited, but are still significant.

It would likely not be possible to reproduce these results, which is a common issue with environmental work on this level. There is very little related work in Antarctica, and it appears that the authors have given credit to previous work.

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

> Yes, the section of the core that we used is firn as indicated by sample's densities between 0.63 and 0.74 $g \cdot cm^{-3}$ (P3L29).

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.

In general, the paper is well organized and carefully written, with the issues noted elsewhere. I note that the use of C. E. in the paper (including the abstract) is not define, requiring that the reader understand what this means. That may not be the case.

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

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

> N_2 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.

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-)? Murozomi 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

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 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:

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.

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 lines19-21 "Concentrations reported in this study are 19 and 22 pg·L^{-1} for α-HCH and 22 and 60 pg·L^{-1} for γ-HCH, which are in the lower range of findings in surface snow collected more recently in Antarctica (Kang et al., 2012)."

P3L13: Apparently it is true that Isaksson et al. (2003) never mention 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).

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).

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."

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".

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.

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.

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."

Response to comments from Reviewer 3

The authors would like to thank the anonymous reviewer for their thoughtful comments and suggestions.

In order to understand better the magnitude and to limit the environment's damage, it is clearly necessary to know about transportation, accumulation and concentration changes of organic pollutants through ages. One irreplaceable source to obtain some of this information is the investigation of chemical compounds in polar ice cores. Since snowflakes have the capacity to adsorb gas-phase chemical compounds, ice-sheets represent an archive of notions of the varying deposition of trace chemicals. From the stratigraphy of the ice cores, the ice-sheets can be temporally related, and every core can cover the chemical history of many decades. Antarctica's low temperatures during the whole year both reduce the speed of chemical reactions and allow the ice layering mentioned above. The paper, well written, describes the methods and the results from two bulk samples from the upper sections from an *“old” ice core from Law Dome for organochlorine pesticides: few studies have been published, so the paper is another small step towards knowledge about contaminants transport mechanism in the atmosphere.*

The ice core used in this study was drilled on Law Dome, a small ice cap with independent ice flow located on the edge of the main East Antarctic ice sheet (a map could be useful for many readers). The characteristics of Dome Summit South (DSS), include a high annual accumulation rate (0.7 m/yr ice equivalent), relatively low mean surface temperatures (-21.8 ◦C), and low wind speeds (8.3 m/s). These site characteristics lead to highly resolved records with clear annual cycles in most measured parameters, giving very robust chronological control. I did not find any of this information on the paper, and I have to find myself, in the literature, despite their fundamental importance.

> Thank you for your suggestions. Information on site-specific characteristics has been added to the revised manuscript as previously addressed in our response to Reviewer 1.
>
> We have added a map (see new Figure 1) which gives a better idea of the geographical location of Law Dome for readers who are not familiar with the region.

As RC1 wrote, it is also absolutely important to have more information around storage/handling contamination, but not only, the sampling conditions must absolutely be considered and described: was it a manual drilling or not? I think not, the ice-drilling was too deep (1196 m), this “modus operandi” can have influenced the results.

> Further information on handling/storage contamination was added in the revised manuscript in our response to reviewer 1.
> As requested, we added drilling information on p3, lines 8-9 “The sections of the core used in this work were extracted using thermal drilling (Morgan et al., 1997).”

The relationship between Arctic and Antarctic pollutants concentration amount may be taken into consideration, but cannot become the key to any conclusions.

> We agree with the reviewer, and it was our aim when writing this manuscript and its conclusions.

While it may be true that no earlier firn core studies are available to use as a guide for sample volume needed from Antarctica for OCPs, I think the volume used is really too big, a tenth could be enough for a more defined (in time) measurement.

> Selection of our target volume was based on multiple factors including our method detection limits, previous concentrations found in other Antarctic matrices and volumes used in previous studies. Some previous Antarctic studies had used from 500 mL in surface snow (for HCB and HCHs, Kang et al. 2012) up to 132L of sea-ice (for a slightly wider range of OCPs, Dickhut et al. 2005). We could have used lower volumes to detect the HCHs, but we were aiming at a wider range of OCPs.
>
> The following has however been added in the revised manuscript: p7, lines 11-12 “HCHs and dieldrin were found at the largest concentrations suggesting that they

> could be targeted in future Antarctic glacial ice investigations to obtain more refined measurements using much lower volumes..”

P3L19: C. E.?

> C.E. is now defined.

I recommend that the paper is accepted after these comments are considered.

> .

Brief communication: Organochlorine pesticides in an archived firn core from Law Dome, East Antarctica

Marie Bigot*[1], Mark A.J. Curran[2,3], Andrew D. Moy[2,3], Derek C.G. Muir[4], Darryl W. Hawker[5], Roger Cropp[5], Camilla F. Teixeira[4] and Susan Bengtson Nash[1]

[1] Environmental Futures Research Institute, Griffith University, 170 Kessels Rd, Nathan, QLD 4111, Australia
[2] Australian Antarctic Division**,** 203 Channel Highway, Kingston, TAS 7050, Australia
[3] Antarctic Climate and Ecosystems Cooperative Research Centre, University of Tasmania, Private Bag 80, Hobart TAS 7001, Australia.
[4] Aquatic Contaminants Research Division, Environment Canada, 867 Lakeshore Rd, Burlington ON, L7R 4A6 Canada
[5] School of Environment, Griffith University, 170 Kessels Rd, Nathan, QLD 4111, Australia

Correspondence to: Marie Bigot (~~marie.bigot@griffithuni.edu.au~~mbigot1@gmail.com)

Abstract. Organochlorine pesticides (OCPs) were, for the first time, quantified in archived firn cores from ~~the~~ East ~~Antarctic ice sheet~~Antarctica representative of 1945-1957 ~~C.E.~~ and 1958-1967 (current era, C.E~~.~~.). The core sections were melted under high purity nitrogen atmosphere and the melt water analysed. Methods allowed quantification of hexachlorocyclohexanes, heptachlor, *trans*-chlordane, dieldrin and endrin. While the core presented evidence of nominal ~~modern-use chemical~~ contamination by modern-use chemicals, indicating handling and/or storage contamination, legacy OCP concentrations and deposition rates reported are orders of magnitude lower than those from Arctic regions, lending support for their validity. The study further provides a description of equipment used and suggests ~~adapted~~ methods to overcome logistical challenges associated with trace organic contaminant detection in Polar Regions.

1 Introduction

Persistent Organic Pollutants (POPs) are ubiquitous, toxic, anthropogenic substances that have been widely used in agriculture and manufacturing industries since the 1930s. A variety of organochlorine pesticides (OCPs) have been listed as POPs under the Stockholm Convention, adopted by the United Nations Environment Program, to ban~~,~~ or severely restrict~~,~~ the use of these chemicals and ~~hereby minimise~~thereby prevent the environmental ~~and human health hazards that they pose.~~burden of these environmental contaminants from becoming greater. By definition, POPs are resistant to environmental degradation processes, allowing them to undergo long-range environmental transport to remote Polar Regions where cold conditions serve to restrict further movement.

Unlike seasonal sea-ice that persists for only limited periods of time, ice sheets are deposited over thousands of years. This makes them a rich archive for the study of past atmospheric composition and climate variations. Levels of inorganic chemical markers such as sodium, potassium, chloride, nitrate or sulphate have previously been successfully determined in glaciology studies ~~(Legrand et al., 1984).~~(Murozumi et al., 1969). Glacial ice cores also hold temporal information regarding historical organic pollution events, however their application for this purpose is far less prevalent in the documented literature. ~~Inherent incompatibilities exist between traditional glaciology research methods and the requirements for robust POP quantification in this environmental compartment.~~ Nevertheless, the work by Wang et al. (2008), for example, showed the potential of POPs in this regard by finding a strong correlation between historical usage of POPs in India and POP levels in ice cores of corresponding deposition ages from Mt Everest. ~~To our knowledge, only one study has determined OCP concentrations in glacial ice/firn from the Arctic (Isaksson et al., 2003)~~To our knowledge, few studies have determined OCP concentrations in glacial ice/firn from the Arctic (Isaksson et al., 2003;Hermanson et al., 2005;Ruggirello et al., 2010) while none, to date, exist from the Antarctic. Other studies in Polar Regions have focused on other chemicals of environmental interest (i.e. brominated flame retardants, polycyclic aromatic hydrocarbons, current use pesticides and polychlorinated biphenyls) and/or other frozen matrix (i.e. surface snow) (e.g. Fuoco et al., 2012;Gregor et al., 1995;Hermanson et al., 2010;Kang et al., 2012;Zhang et al., 2013;Peters et al., 1995).

In the current global climate context, accelerated melting and subsequent retreat of Antarctic ice shelves are frequently reported. As the ice compartment represents a reservoir of historically deposited POPs, quantification of concentrations in Antarctic continental ice is particularly relevant in order to predict the possible future POP re-emission into the atmosphere and oceans through ice-melt. This secondary input process has previously been demonstrated for melting alpine glaciers in Switzerland (Bogdal et al., 2009). Under this scenario, global efforts to moderate polar ecosystems' exposure to these potentially hazardous compounds would be compromised.

This work investigates the potential for a well-studied archived Antarctic firn core to elucidate historical deposition rates of OCPs. It was designed as a proof of concept to examine the implications of mismatched sampling priorities between classical glaciology programs and POP research, representing an important step for the assessment of the value of firn core archives world-wide for the progression of Polar contaminants research. Further, the work addresses some of the challenges associated with the sampling of this matrix for the trace levels of POPs generally observed in Antarctica and describes purpose built equipment for overcoming some of these challenges.

2 Materials and methods

2.1 Firn core sourcing

For this study, we accessed the historical firn core from a long-established glaciology study site located in East Antarctica: Dome Summit South (DSS), Law Dome~~. The 1196 m DSS ice core was collected in 1988-1993 and the entire records spans approximately 80 kyr B.P. (van Ommen et al., 2004). The DSS ice core chronology is derived from a combination of direct layer counting (van Ommen et al., 2004;Plummer et al., 2012;Roberts et al., 2015) and age ties to other records (van Ommen~~

~~et al., 2004). This ice core has provided a wealth of atmospheric circulation, ambient temperature, snow accumulation, and climate proxy records for climate reconstructions (Souney et al., 2002;Plummer et al., 2012;Roberts et al., 2015). Coring methods employed are presented elsewhere (Morgan et al., 1997). Following collection, the core was cut to one meter lengths on site, stored in double plastic bags at -18˚C, and archived in large cold storage facilities in Tasmania, Australia, until analysis.~~ (Figure 1). Law Dome is a small independent icecap located in Wilkes Land, East Antarctica and exposed to a maritime climate (Morgan et al., 1997). The DSS site is located near Law Dome summit, approximately 100 km from the coast and at 1370 m elevation (Morgan et al., 1997). This site was selected for its favourable bedrock topography and sufficiently low surface temperatures (mean annual average of - 21.8°C) which preclude summer melt (Morgan et al., 1997). The DSS site is characterised by a relatively high annual snow accumulation rate of 0.68 $m \cdot yr^{-1}$ water equivalent (weq) (Roberts et al., 2015) facilitating the preservation of very clear seasonal cycles in glaciochemical species. This provided a means of accurate dating with monthly resolution in the upper portions of the core (van Ommen et al., 2004;Plummer et al., 2012;Roberts et al., 2015).

The 1196 m DSS ice core was collected in 1988-1993 and the entire records spans approximately 80 kyr B.P. (van Ommen et al., 2004). Its chronology is derived from a combination of direct layer counting (van Ommen et al., 2004;Plummer et al., 2012;Roberts et al., 2015) and age ties to other records (van Ommen et al., 2004). This ice core has provided a wealth of atmospheric circulation, ambient temperature, snow accumulation, and climate proxy records for climate reconstructions (Souney et al., 2002;Plummer et al., 2012;Roberts et al., 2015). The sections of the core used in this work were extracted using thermal drilling (Morgan et al., 1997). Following collection, the 18 cm diameter core was cut to one meter lengths on site, stored in double plastic bags at -18˚C, and archived in large cold storage facilities in Tasmania, Australia, until analysis.

There is an inherent ~~mismatch~~incompatibility between standard glaciology and POP sampling procedures, particularly in terms of the volumes of matrix required for robust analysis, the type of materials used during sampling and long term storage requirements. Nevertheless, given the massive logistical investment to sample ice in remote Polar environments, and the rich source of ancillary information accompanying the well-studied DSS core, access to the remaining firn core represented an opportunity to examine the implications of method incompatibilities and assess whether useful information could be derived from this, and therefore similar valuable archives, world-wide.

Sample volumes recently used for determination of OCPs in other Antarctic frozen matrices such as continental surface snow (Kang et al., 2012) and sea-ice (Dickhut et al., 2005) were 500 mL and 95.5 to 132 L, respectively. In the Arctic, ~~Isaksson et al.~~Hermanson et al. (2005) and Ruggirello et al. (2010) used a minimum of 11 L of melted ice/firn core, while Isaksson et al. (2003) used a total of 48 metres of ~~glacial ice/firn~~a core (of unknown diameter) separated into nine individual samples. No other previous study on OCPs has been published for continental firn cores in Antarctica, hence the chemical burden and consequent volume of firn required for confident detection was largely unknown. We therefore adopted a conservative approach by utilising just two large volume samples from a known period as opposed to a higher number of samples of smaller volume. The DSS firn core was selected as it yielded large volumes for the relevant deposition time periods of interest, enabling guidance on chemical deposition rates for future investigations. It was separated into batches of approximately 10 metre length each, representing two early OCP deposition periods: 1945-1957 current era (C.E~~.~~.) (35.4 to 45.6 m depth, sample A) and 1958-1967 C.E. (26.3 to 35.4 m depth, sample B). Density of these firn sections had previously been estimated to be between 0.63 to 0.74 g·cm^{-3} (for core depth between 21.5 to 47.6 m) (Morgan et al., 1997) and dating had been ~~completed~~conducted by direct layer counting.

2.2 Sampling procedures

Firn core samples were minimally exposed to laboratory ambient air, and whole portions were melted together in a clean stainless steel unit~~,~~ purpose designed and built for POP analysis (Figure 2~~).~~, 125 cm (length) x 80 cm (height) x 40 cm (depth), approximately 70 kg empty). Melted sample volumes were 144 and 133 L for ~~sample~~samples A and B, respectively. ~~The ice~~ These were obtained through melting of two successive batches for each due to the limited capacity of the melting unit. This unit, derived from a design by Gustafsson et al. (2005), allowed complete isolation of the sample and melting under high purity nitrogen atmosphere (Figure 2). The unit was fitted with a drain connected to a modified Kiel in-situ Pump (KISP, Aimes GmbH, Germany), previously used for the purpose of trace organics sampling in water (Petrick et al., 1996). This set-up was designed to provide a means of *in-situ* sample extraction for field based snow, ice and water campaigns. The ice-melting unit is fully transportable for direct sample loading and sealing in the field. The unit can then be brought to the operational Polar research station for access to nitrogen gas, water and electrical power to complete sample extraction. Alternatively, it could be powered on site using generators for in-situ melting.

Melt-water was pumped directly from the melting unit through a pre-furnaced (12h at 450˚C) glass fiber filter (GFF, 142 mm, 0.7 µm, Whatman, England) ~~and~~collecting suspended particles followed by a stainless steel cartridge filled with approximately 150 mL of pre-cleaned Amberlite XAD-2 resin (Supelpak™-2, Sigma-Aldrich Co. LLC.) ~~in series at a~~collecting the dissolved fractions of the compounds. The flow rate of melt-water through the system was set at 150 mL·min^{-1}. Full sampling material preparation methods and analytical procedures for filters and XAD have been described elsewhere (Bigot et al., 2016). Sample extracts and blanks were analysed by Australian Laboratory Services (ALS Global, Burlington, ON, Canada) for OCPs using gas chromatography high resolution mass spectrometry (GC-HRMS) following standard protocols based on EPA method 1699.

2.3 Quality Assurance / Quality Control

The samples were handled in a clean room (positively pressured, high efficiency particulate and carbon filtered air) during extraction at Environment Canada (Canadian Centre for Inland Waters (CCIW), Burlington, ON, Canada). Three blanks

(XAD and filters) were treated in the same manner as the samples~~:~~, i.e. exposed to ambient air during changing of sampling materials in the laboratory, transported together, and extracted and analysed in parallel with samples. All sample values reported are blank corrected using the average of three blanks, providing a means of correcting for possible contamination during laboratory, storage and/or transport of the samples.

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. Their concentrations were determined in the final extracts using low resolution GC-MS at CCIW/Environment Canada.

Method detection limits (MDLs) were calculated for each compound as three times the standard deviation of the laboratory blanks. Recovery rates were evaluated via spiking sample materials with 200 µL of a solution containing δ-HCH and $^{13}C_8$ Mirex (10 $pg \cdot \mu L^{-1}$ each), and BDE-71 (9.6 $pg \cdot \mu L^{-1}$). XAD cartridges were spiked prior to sampling and filters were spiked prior to extraction. Labelled target analytes were also added by ALS Global and responses were used to correct for losses during clean-up and instrument drift. A list of recoveries for all surrogate standards is available in the supplementary information. Results originally expressed in $pg \cdot L^{-1}$ ~~were corrected to estimate the~~are presented as mean deposition per year ($pg \cdot cm^{-2} yr^{-1}$) calculated using the ~~basal~~surface area of the core as the deposition surface, thus allowing comparison of the two time periods studied.

3 Results and discussion

The relatively large volumes of firn analysed in this study enabled the quantification of the legacy OCPs α- and γ-HCH, heptachlor, trans-chlordane, dieldrin, and endrin in the dissolved fraction of the melt water of both samples (Figure). These compounds are likely to be deposited on snow after long range atmospheric transport from source regions within the Southern Hemisphere. Their presence have recently been reported in seawater and/or air close to the coast of East Antarctica (Bigot et al., 2016). Both samples, however, also contained traces of our storage and handling contamination markers, PBDEs, indicating that sampling and/or storage conditions of the archived firn cores introduced organic contamination. These contaminants could have been introduced through various means such as the operator's personal clothing, storage in plastic bags, and the use of contaminated coring tools and inappropriate cleaning methods.

While no direct link can be established between PBDE levels introduced and possible contamination of the firn core by legacy OCPs, the presence of the PBDE markers necessitate caution in the interpretation of results. Notwithstanding this, the firn deposition rates were below 0.8 $pg \cdot cm^{-2} \cdot yr^{-1}$ for α- and γ-HCH, heptachlor, trans-chlordane and endrin, while dieldrin had deposition rates of up to 4 pg·cm^{-2}·yr^{-1}. Previous studies reported data in melt-water concentrations rather than deposition rates. The OCP deposition rates that we report here are derived from melt-water concentrations of < 60~~.1~~ and 310 pg·L^{-1}, respectively~~,~~ (for detailed results see Supplementary Information, Table 2). Although the DSS site is characterised by higher snow deposition rates (0.68 m·yr^{-1} weq) compared to the three other Arctic sites for which OCPs in glacial ice/firn cores were documented (from 0.36 to 0.52 m·yr^{-1} weq), OCP results from the DSS site are 10 to 1000 fold lower than ~~corresponding OCP levels~~ the reported ~~for glacial ice/firn cores from~~ levels in the Arctic ~~(Hermanson et al., 2010;~~(Hermanson et al., 2005;Isaksson et al., 2003~~)~~;Ruggirello et al., 2010)~~.~~. This is consistent with the uneven distribution of the world's past usage of OCPs (Voldner and Li, 1995), with the Northern Hemisphere having contributed larger emissions than the Southern Hemisphere, suggesting a larger pool of OCPs would have reached the Arctic in comparison to Antarctica. Data previously reported from other environmental matrices, i.e. seawater and air, also show a 10 to 100 fold decrease between Arctic and Antarctic concentrations of HCHs, thus lending further support for the validity of the OCP results obtained.

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The relatively high sample volumes required for this analysis limit the temporal resolution of results and therefore the detail with which we are able to investigate accumulation history of OCPs. The samples represent firn from Law Dome over consecutive 13 and 10-year periods, respectively. Observed differences between the two time periods may reflect different usage patterns but may also be a function of the physicochemical properties of individual pesticides. Given OCPs are mainly transported to Polar Regions via atmospheric transport (Wania and Mackay, 1996), the Law Dome area would have been impacted by air originating from the Southern Hemisphere. Access to detailed historical usage of OCPs in this part of the world is limited, however~~,~~ most legacy OCPs were first used in the 1940's or early 1950's, e.g. in Australia and Africa (Harrison, 1997;Wandiga, 2001). The concentrations reported represent deposition of OCPs when their usage was at or near their maximum, before the first controls on the uses of these compounds were implemented in the 1970's. As a result, it gives an insight on possible maximum concentrations in Antarctic firn that may remobilise from melt water. Dieldrin and γ-HCH show a distinct increase in their concentrations in sample B, spanning the period (1958 to 1967 C.E.), compared to those in Sample A (1957 – 1945 C.E.) (Figure). This could reflect an increase in Southern Hemisphere usage of these two compounds between 1945 and 1967 C.E. Alternatively, the compounds may have started to deposit later than 1945, in which case sample A's results may be affected by dilution of the deposited burden by uncontaminated sections of the core.

HCHs are the most commonly studied OCPs in the abiotic Antarctic marine ~~abiotic~~ environment. Concentrations reported in this study are 19 and 22 pg·L^{-1} for α-HCH and 22 and 60 pg·L^{-1} for γ-HCH, which are in the lower range of findings in surface snow samples collected more recently in Antarctica (Kang et al., 2012). The relative contributions of each isomer (γ > α) observed in the continental firn samples from Law Dome are also consistent with reported Antarctic sea-ice and atmospheric profiles (Dickhut et al., 2005). All OCPs detected in this study have also been recently reported in atmospheric and oceanic samples in the same sector of Antarctica (Bigot et al., 2016). Some of these OCPs, heptachlor and dieldrin in particular, are currently found in Australian air samples at concentrations amongst the highest reported globally (Wang et al., 2015).

Dieldrin was detected at the highest levels in both dissolved and particulate fractions of the melted firn samples analysed in the present study. It is a versatile cyclodiene insecticide that has been largely used around the world for treatment of soil for plantations, as well as for control of various pests. Its usage was largely restricted ~~in~~from the 1970s, but its use was only fully banned ~~only~~internationally in 2004, under the Stockholm Convention. In the dissolved fraction, we report an average concentration of dieldrin of 222 and 310 $\mathrm{pg \cdot L^{-1}}$ in sample A and B, respectively. The dissolved fraction accumulated in firn cores may, if released due to rapid continental ice melting, be available for uptake by marine organisms, and present a toxicological threat to the Antarctic food web. ~~Dieldrin has only rarely been reported in Antarctica's marine environment (Bengtson Nash et al., 2008), yet it~~Dieldrin is currently one of the most prevalent OCPs found in this region (Bigot et al., 2016). Our findings indicate that ice-melt is likely to result in particularly high dieldrin enrichment compared to other OCPs found in the firn samples. Interestingly, it is also the only compound detected on particles contained in melt-water of the archived ice core at 3.~~81~~8 and 7.~~05~~1 $\mathrm{pg \cdot L^{-1}}$ for sample A and B, respectively, which suggests it may also be transported on atmospheric aerosols that could originate from wind eroded soils for example. Dieldrin was the only OCP compound detected on aerosols sampled in adjacent areas of the Southern Ocean (Bigot et al., 2016).

This proof of concept study determined OCP concentrations that reached ~~Antarctica's ice shelf~~Antarctica during their early usage. Melted water volumes of 144 and 133 L for each sample allowed quantification of legacy OCPs that have previously been reported in the vicinity of Antarctica, however results should be considered as maximum possible values given possible contamination introduced during sampling and/or storage. Results for other OCPs were below MDLs, although higher volumes may facilitate quantification. ~~It is important to note that the concentrations reported in this study may be representative of what is expected to be the highest deposition period and therefore volumes employed may be insufficient to detect lower concentrations in more recent parts of firn cores~~HCHs and dieldrin were found at the largest concentrations suggesting that they could be targeted in future Antarctic glacial ice investigations to obtain more refined measurements using much lower volumes.

4 Conclusion

Results show that legacy OCPs could have accumulated ~~in the East Antarctic ice shelf~~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. Although East Antarctica currently exhibits a slight positive ice mass balance~~ of its ice shelf~~ as opposed to the rest of the continent (Sasgen et al., 2013), driven by climate conditions in the Pacific (Meehl et al., 2016), the potential for OCPs to remobilise into the atmosphere and oceans raises the need for development of POP research in the cryosphere. While we found evidence of nominal PBDE contamination throughout the core, OCP concentrations and deposition rates reported are orders of magnitude lower than those from ~~Arctic regions.~~sites with lower annual snow accumulation in the Arctic. This appears realistic and therefore suggests that our results can be taken as first indications of OCP contamination at Law Dome, East Antarctica, through this time period.

Standard glaciology sampling procedures for inorganic analytes (e.g. metals), climate tracers and those for POPs are not necessarily compatible, particularly in terms of the volumes required for analysis, and methods used for collection~~, sampling~~ and storage. Given the potential value of POP quantification in the Polar cryosphere, we advocate pro-active sampling in collaboration with glaciology programs to ensure sufficient volumes of dedicated samples according to POP work QA/QC procedures. In particular, plastics should be avoided at all times as a general QA/QC measure for sampling, storage and analysis of such compounds. The ice-melting unit used for the present work ~~was~~is designed to be transportable and ~~offer~~represents a comprehensive tool offering a means of ~~in-situ~~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 ~~and also reduces risks for contamination during storage and transport. These in-situ melting techniques have previously been successful in the Arctic (Gustafsson et al., 2005;Isaksson et al., 2003) and should be implemented when dealing with trace POP analysis in Antarctica.~~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. A similar in-situ melting technique has previously been successful for the collection of sea-ice in the Arctic (Gustafsson et al., 2005). These methods should be implemented when dealing with trace POP analysis in Polar Regions. In lieu of such support, however, glaciology archives may provide useful indications for remote locations from which information is still lacking.

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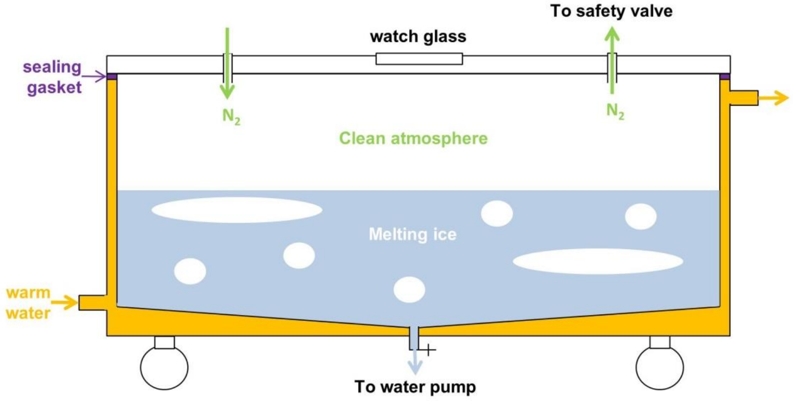

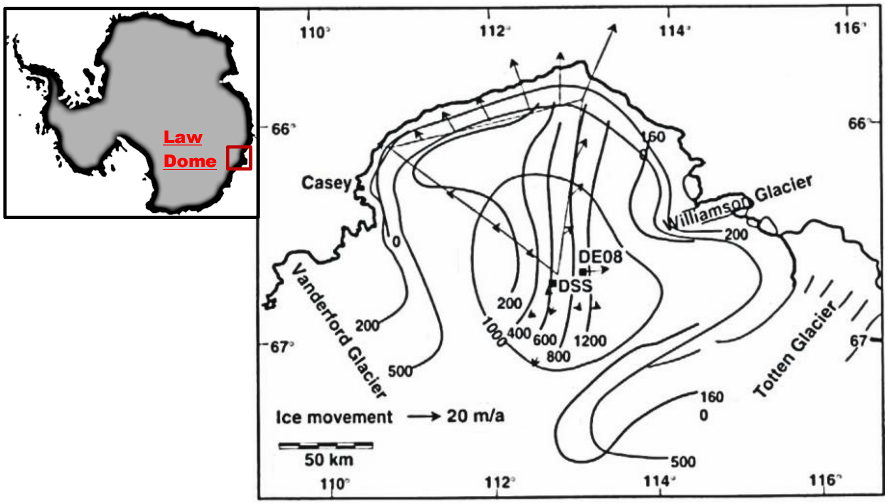

Figure 1~~: Cross section diagram of the ice-melting unit used for this work~~

~~Figure 2~~: Location of the Dome Summit South (DSS) coring site at Law Dome in East Antarctica. Elevation contours are represented using thinner lines compared to accumulation contours (expressed in $kg\cdot m^{-2}$) (right hand side map courtesy of Morgan et al., 1997, adapted from Xie et al., 1989).

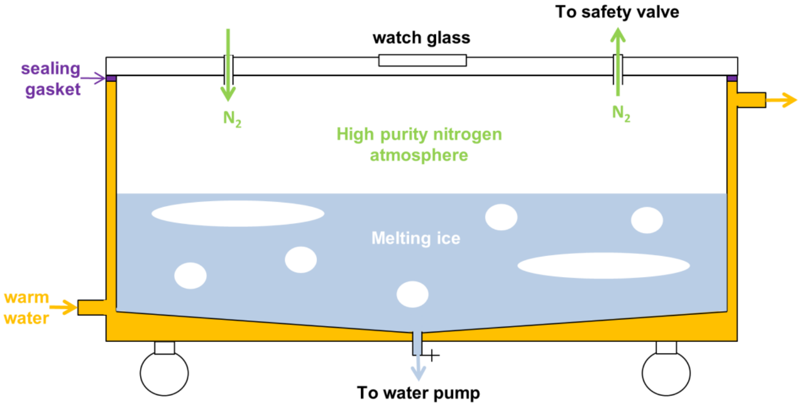

Figure 2: Conceptual cross sectional diagram of the ice-melting unit used in this work

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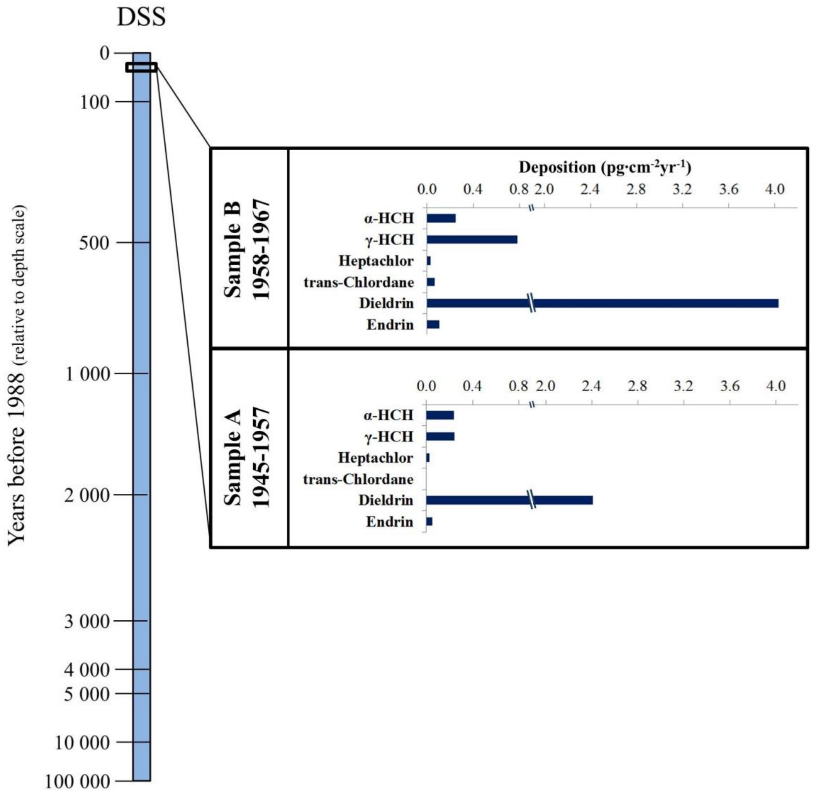

Figure 3: Deposition rates of 6 legacy OCPs at the Law Dome site in Antarctica between 1945 and 1957 (Sample A) and 1958 to 1967 (Sample B). Note: results should be considered as maximum possible values.

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