

## Current use and legacy pesticide deposition to ice caps on Svalbard, Norway

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[1] Transport and deposition of current use (CUP) and legacy pesticides (LP) and residual products to the Arctic have been documented in abiotic matrices. These observations show that some “low-persistence” pesticides with high OH· reaction rates are stable enough to accumulate in a polar environment. In 2005, we drilled an ice core on Holtedahlfonna, one of the major ice fields on Svalbard, Norway to measure the input of 47 CUPs and 17 LPs to a high-elevation abiotic environment with no local pesticide sources. Of these, 9 CUPs and 12 LPs were observed in at least one of 6 core segments dating to 1953: 15 of these were found in enough core segments to reveal time-related trends. CUPs often observed included chlorpyrifos, dacthal,  $\alpha$ - and  $\beta$ - endosulfan, endosulfan sulfate, trifluralin, and  $\gamma$ -HCH. LPs most often observed included methoxychlor,  $\alpha$ - and  $\gamma$ -chlordane, cis- and trans- nonachlor, endrin, dieldrin, and *p,p'*-DDE. In our comparison of core burdens at Holtedahlfonna and Austfonna (220 km ENE from Holtedahlfonna), we found twice as many CUPs at Austfonna along with greater amounts of dieldrin, methoxychlor,  $\alpha$ -endosulfan and chlorpyrifos suggesting different accumulation processes or sources. Air mass back trajectories over a 10-year period of comparison between sites (1986–1995) show air mass flow from Eurasia 74% of the time to Austfonna and 45% to Holtedahlfonna which may account for some of the differences.

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### 1. Introduction

[2] Since the introduction of DDT in the 1940s, synthesized pesticides have been credited with saving lives and extending food supplies by killing disease-carrying insects and plant pests [Curtis and Lines, 2000]. The persistence, bioaccumulation and toxicity of DDT and other organochlorine (OC) pesticides, that was discovered after their introductions, led to a series of regulations on many of them, most recently by the Stockholm Convention (chm.pops.int/). But the continuing need for pesticides resulted in development of alternative, or “current use” pesticides (CUPs)

which were intended to be less persistent, less bioaccumulative, and generally much more toxic [Walker and Nidiry, 2002].

[3] The appearance and accumulation of the now-banned OC legacy pesticides (LPs) and associated compounds in the Arctic, where they were never produced and not likely used, directed attention to investigation of processes that resulted in movement and accumulation of LPs in the polar regions. Two processes are most important: resistance to decomposition and transport geography. Resistance to decomposition focused on OH· because it represents the strongest oxidizer and most important decomposition process of organic compounds in the atmosphere [Unsworth *et al.*, 1999; Li *et al.*, 2008]. OH· can only be produced in the presence of ultraviolet radiation at wavelengths less than 330 nm, predominantly in the UV-B region [Matsumi *et al.*, 2002] and in the presence of precursors O<sub>3</sub> and H<sub>2</sub>O. As a result, OH· is not produced during periods of polar darkness or during the polar spring when concentrations of precursors are low [Brönnimann *et al.*, 2000; Eneroth *et al.*, 2007]. The resulting low level of contaminant oxidation apparently leads to a longer atmospheric lifetime and accumulation of LPs.

[4] The other important process is transport geography. Our earlier work at Austfonna [Hermanson *et al.*, 2005]

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**Figure 1.** Map of Svalbard showing the locations of the Holtedahlfonna and Austfonna ice core drilling sites.

showed that event-based long-range atmospheric transport (LRAT) from agricultural areas in northern Eurasia could account for the appearance of some pesticides on Svalbard. The transport of semi-volatile organic contaminants (SOCs) to the Arctic in general and accumulation in biotic and abiotic environments is well documented [Andersen *et al.*, 2001; Ballschmiter *et al.*, 2002; Muir *et al.*, 2004]. The impacts on both the biotic and abiotic environments on Svalbard are well known [Berg *et al.*, 2004; Fuglei *et al.*, 2007; Hermanson *et al.*, 2005; Oehme *et al.*, 1996; Wolkers *et al.*, 2008].

[5] Recent investigations of CUPs in the Arctic have also revealed accumulation of some of the “less persistent” compounds in Arctic sea ice, water and glaciers [Chernyak *et al.*, 1996; Hermanson *et al.*, 2005; Hoferkamp *et al.*, 2010; Muir *et al.*, 2004; Weber *et al.*, 2006], showing that persistence in the Arctic for these compounds is also different than defined elsewhere. Now that we can expect to see “non-persistent” compounds in the Arctic, we need more information about historic inputs, burdens and comparative transport in regions within the Arctic.

[6] Here we investigate the input history of 47 CUPs and 17 LPs to the Holtedahlfonna ice field on Svalbard, Norway (Figure 1). In addition, we provide a comparative study between two ice coring sites – Holtedahlfonna and Austfonna-

to distinguish different sources and burdens of LPs and CUPs. These two sites represent the Western-most and Eastern-most major ice caps on Svalbard, respectively. Additionally, the ice cores were collected at the highest elevation at each site to limit the effects of melting. Our results can support efforts to reevaluate persistence in the Arctic, which is an ongoing effort [Brown and Wania, 2008; Beyer *et al.*, 2000; Wania, 2003].

## 2. Methods

[7] In April 2005 we drilled a 105 mm diameter, 125 m deep ice core at Holtedahlfonna (79.13°N, 13.27°E at 1150 m above sea level (masl)) about 40 km northeast of Ny-Ålesund on the west coast of Spitsbergen, the largest island in Svalbard (Figure 1). The retrieved core sections were approximately 50–60 cm long. In the field they were packed in plastic bags and kept in insulated boxes at temperatures below freezing until transported to cold room facilities at the Norwegian Polar Institute (NPI), Tromsø, Norway. Estimated age of this core using glacial modeling is 400 years at 150 m – the maximum ice depth [Sjögren *et al.*, 2007]. Tritium analyses were performed on samples collected at 5 cm intervals and the 1963 peak level was identified at about 28.4 m core depth. Considering varying densities in

**Table 1.** Summary of Maximum Flux and Burden for Pesticides Found in the Holtedahlfonna Ice Core<sup>a</sup>

Chemical	CAS Number	Holtedahlfonna Peak Flux (pg cm <sup>-2</sup> yr <sup>-1</sup> )	Peak Years	Atmospheric Half-Life <sup>b</sup> (h)	Burden (ng), 1953–2005
<i>Legacy Organochlorines</i>					
α-HCH <sup>c</sup>	319846	295	1953–1962	2640	402
<i>p,p'</i> -DDT <sup>d</sup>	50293	2.93	1995–2005	120	5.4
<i>o,p'</i> -DDD	53190	11.5	1988–1995	96	22.4
γ-chlordane <sup>d</sup>	5566347	18.3	1988–1995	72	44.9
α-chlordane <sup>d</sup>	5103719	13.39	1988–1995	72	20.8
Endrin <sup>d</sup>	72208	16.3	1971–1980	48	24.9
<i>p,p'</i> -DDE	72559	1.14	1953–1962	48	2.9
Dieldrin <sup>d</sup>	60571	54.7	1953–1962	42	60.2
Trans-nonachlor	39765805	2.28	1971–1980	23	6.9
Cis-nonachlor	5103731	5.03	1971–1980	23	7.4
Endrin-ketone	53494705	13.6	1953–1962	17	17.6
Methoxychlor	72435	19.6	1971–1980	7	46.4
<i>Current Use Organochlorines</i>					
γ-HCH <sup>c</sup>	58899	369	1953–1962	1464	510
α-endosulfan <sup>c</sup>	959988	6.8	1995–2005	48	15.5
β-endosulfan <sup>c</sup>	33213659	2.8	1995–2005	48	13.8
Endosulfan sulfate <sup>c</sup>	1031078	2.81	1988–1995	48	4.2
<i>Organophosphorus Compounds</i>					
Methyl-parathion	298000	357	1988–1995	6.5	216
Chlorpyrifos	2921882	809	1995–2005	4.2	776
<i>Herbicides</i>					
Dacthal	1861321	12.7	1971–1980	864	33.5
Metribuzin	21087649	1.05	1971–1980	21	0.8
Trifluralin	1582098	2.32	1995–2005	16	3.6

<sup>a</sup>Pesticides are sorted within each category in order of estimated persistence based on the OH<sup>•</sup> reaction rate. See Table 2 for pesticides analyzed and not found at Holtedahlfonna.

<sup>b</sup>Data from CHEMFATE Chemical Database (Syracuse Research Corporation, available at <http://www.syrres.com/what-we-do/databaseforms.aspx?id=381>) and *Meylan and Howard* [1993] (as cited by TOXNET, <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>) based on the structure estimation method.

<sup>c</sup>To be added to Stockholm Convention August 2010.

<sup>d</sup>Stockholm Convention POPs 2004.

<sup>e</sup>Included in Stockholm Convention Annex F for possible future addition to the Convention.

the core, this gives an annual water equivalent (weq) accumulation rate of 0.52 m during the period 1963–2005, which compares well with the results from a core drilled at the same site in 1992 [*Kameda et al.*, 1994] showing that the 2005 core is representative of accumulation conditions in the area.

[8] Core sub-sampling for analysis of organic contaminants included gathering contiguous ice core segments into stainless steel cans and melting to a final temperature not >5°C. Liquid sample volume was 11–15 L. The core segments represented the upper 34 m of the core dating to 1953. Contaminants were separated from the melt by pumping 200–250 mL min<sup>-1</sup> through Teflon<sup>®</sup>-walled extraction columns filled with polymeric Amberlite<sup>®</sup> XAD-2 resin which adsorbed compounds of interest. The XAD-2 was precleaned by sequential solvent extraction and then packed into extraction columns in a clean room (positively pressured HEPA<sup>™</sup> and carbon filtered air) at the National Water Research Institute (NWRI), Burlington, ON, Canada [*Muir et al.*, 2004] (auxiliary material).<sup>1</sup> These XAD columns were then shipped to NPI in Tromsø, Norway, where the ice was melted and pumped.

[9] After sample pumping, the XAD columns were shipped back to the NWRI clean room laboratory where they were sequentially extracted in CH<sub>3</sub>OH and CH<sub>2</sub>Cl<sub>2</sub>. These extracts were combined and washed with 3% NaCl and dried on anhydrous Na<sub>2</sub>SO<sub>4</sub>. The extract was volume-reduced and added to a small column of 10% H<sub>2</sub>O-deactivated silica-gel and eluted with 10% CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub>, and then exchanged to CH<sub>3</sub>COCH<sub>3</sub>/C<sub>8</sub>H<sub>18</sub>. All CUPs were analyzed using gas chromatography-mass spectrometry (GC-MS, low resolution in electron capture negative ionization mode). A 1 μL aliquot of each extract was injected into a GC (pulsed splitless injection at 250°C) onto a capillary column (5% diphenyl-/95% dimethylsiloxane liquid phase (0.25 μm film thickness) 30 m long × 0.25 mm diameter) at an initial GC oven temperature of 80°C. LPs were analyzed by GC-electron capture detection using the same GC column and conditions [*Muir et al.*, 2004] (auxiliary material). All compounds were quantified using 4 point calibration curves based on authentic external standards. The analyte list (Tables 1 and 2) was selected based on high levels of use for the CUPs and known Arctic presence of the LPs.

[10] Quality control steps included the analysis of field blanks (XAD columns shipped to the laboratory where samples were pumped and analyzed with sample columns

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2010JD014005.

**Table 2.** Pesticides and Decomposition Products Analyzed but Not Detected at Holtedahlfonna<sup>a</sup>

	Peak Flux (pg cm <sup>-2</sup> yr <sup>-1</sup> ), Austfonna	Peak Flux (Years), Austfonna
Alachlor <sup>b</sup>	57	1979–82
Aldrin <sup>b,c</sup> (LP)	30,000	1992–98
Ametryn		
Atrazine <sup>d</sup>		
Butralin <sup>d</sup>		
Butylate		
Chlorthalonil		
Cycloate		
Desethyl atrazine <sup>b</sup>	144	1986–92
Diazinon <sup>b</sup>	1,410	1986–92
Diazinon-oxon		
Dimethenamid		
Dimethoate <sup>b</sup>	598	1986–92
Disulfoton <sup>b</sup>	447	1986–92
Dyfonate		
Ethalfuralin		
s-ethyl dipropylthiocarbamate (EPTC)		
Flutriafol <sup>b</sup>		
Heptachlor <sup>c</sup> (LP)	470	1992–98
Heptachlor epoxide <sup>b</sup> (LP)	1,580	1992–98
Imidan <sup>b</sup>	3,030	1986–92
Linuron		
Malathion		
Metolachlor <sup>b</sup>	450	1992–98
Mirex (LP)		
Myclobutanil		
Naled		
Napropamide		
Oxychlordane (LP)		
Pendamehalin <sup>b</sup>	890	1992–98
Pentachloronitrobenzene		
Phorate		
Phosalone		
Quizalfop ethyl		
Simazine		
Tebuconazol		
Tefluthrin		
Terbacil		
Terbufos <sup>b</sup>	530	1992–98
2,3,5,6-Tetrachloronitrobenzene		
TILT (Propiconazole)		
Trichlorfon <sup>c</sup>		
Triallate		

<sup>a</sup>All CUPs or decomposition products except as noted. Data from Austfonna are included.

<sup>b</sup>Found at Austfonna.

<sup>c</sup>Found < MDL at Holtedahlfonna (see Table S1).

<sup>d</sup>Analyzed but not found at Austfonna [Hermanson *et al.*, 2005].

and lab blanks). Method detection limit (MDL) was calculated as the sum of 3 standard deviations of the blank concentration (Table S1 in the auxiliary material). Spike recoveries are reported in Table S2 in the auxiliary material. Other QC results are in the auxiliary material.

[11] The contaminant analysis yielded results in ng l<sup>-1</sup>. These were converted to accumulation (net deposition) in pg cm<sup>-2</sup> yr<sup>-1</sup> by calculating the water deposition rate determined from liters of sample over the years represented, and the surface area of the core (86.6 cm<sup>2</sup>). Our average water input over the upper 6 core segments was 0.517 m yr<sup>-1</sup> water equivalent, in agreement with the 0.52 m yr<sup>-1</sup> water equivalent noted above. We calculated a contaminant burden for all segments of the core (in ng) as the product of the

concentration (ng l<sup>-1</sup>) and the number of liters. A similar calculation was used on data from Austfonna, 220 km to the ENE [Hermanson *et al.*, 2005]. This burden, along with the history of inputs, identifies which pesticides have had the greatest historic impact on Svalbard and which have a growing input up to 2005.

[12] To identify possible geographic differences in air mass movements (and therefore possible source regions of pesticides) to the two sites, we used back trajectories defined by the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) [Draxler and Hess, 2004]. We selected the 10-year period from 1986 to 95 which represented the most recent period of overlap between ice cores from the two sites. We used two sets of 5-day back trajectory data, ending at Holtedahlfonna and Austfonna locations and altitudes. NCEP/NCAR reanalysis fields were used for the calculation. The built-in clustering algorithm in the HYSPLIT-model was used to produce maps showing the mean trajectories for 5 clusters at each site.

### 3. Results

[13] Of the 64 pesticides analyzed in the Holtedahlfonna core, 47 were CUPs and 17 were LPs. Nine CUPs and 12 LPs were observed in at least one segment of the core. Seven of the CUPs (chlorpyrifos,  $\gamma$ -HCH,  $\alpha$ -endosulfan,  $\beta$ -endosulfan, endosulfan sulfate, dacthal and trifluralin) and eight LPs (methoxychlor, dieldrin, endrin, cis- and trans-nonachlor,  $\alpha$ - and  $\gamma$ -chlordane and *p,p'*-DDE) are observed in several core segments and show either a general historic trend or sporadic presence since the early 1950s. CUPs are shown in Figures 2–4 and LPs in Figures S1–S5 in the auxiliary material. Table 1 summarizes the maximum flux data and corresponding years for all detected compounds, and the estimated atmospheric persistence (half-life from OH-reaction rates) and the burden of each pesticide at Holtedahlfonna. The 43 compounds analyzed but not detected in any Holtedahlfonna core segment are listed in Table 2.

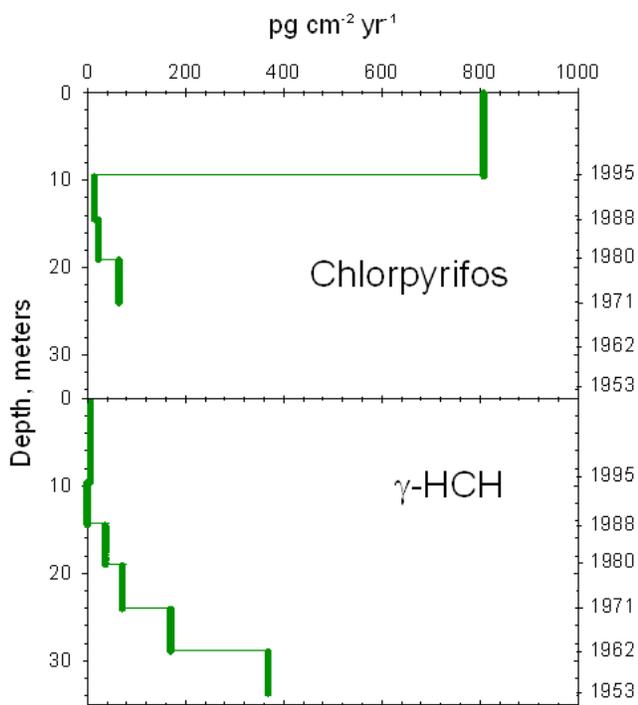
[14] Our discussion classifies each compound as current use organophosphorus (OP), current use organochlorine (OC), current use herbicide, or legacy OC. Within each category the pesticides are discussed in order of decreasing expected persistence based on atmospheric half-lives (Table 1).

#### 3.1. Current Use Pesticides

[15] Two analyzed CUPs, OP methyl parathion, and herbicide metribuzin, were detected in one core segment (1971–1980 and 1988–1995, respectively) and are included in Table 1, but not discussed further.

##### 3.1.1. Organophosphorus Compounds

[16] OP pesticides, while extremely toxic, are considered to be less persistent than predecessor OCs under midlatitude conditions where most pesticides are used. Chlorpyrifos was the only OP CUP detected continuously in the Holtedahlfonna ice core. It is a widely used, broad-spectrum organophosphorothioate insecticide first produced in 1962. At Holtedahlfonna, chlorpyrifos was first detected in 1971–1980 with a comparatively low input (64.8 pg cm<sup>-2</sup> yr<sup>-1</sup>), and a decreasing trend until 1995–2005 when the flux peaked at 808 pg cm<sup>-2</sup> yr<sup>-1</sup> (Figure 2). By comparison, a 2005 snow sample from the Devon Ice cap (Canada) showed an input <0.01 pg cm<sup>-2</sup> yr<sup>-1</sup> [Hoferkamp *et al.*, 2010]. Chlorpyrifos is



**Figure 2.** Flux trends at Holtedahlfonna over time for chlorpyrifos and  $\gamma$ -HCH.

a heavily used CUP ranking second in sales in the United States in the late 1990s and also widely used in Western Europe at that time [Kiely *et al.*, 2004]. Chlorpyrifos was the most widely used insecticide in the U.S. during 1997 (Pesticide National Synthesis Project, U.S. Geological Survey, available at <http://water.usgs.gov/nawqa/pnsp/>). However, restrictions on a number of uses in the USA in 2001 [U.S. Environmental Protection Agency, 2006] could influence global use. With a very short atmospheric half-life in midlatitude environments (4.2 h) (Hazardous Substance Data Bank (HSDB), TOXNET Toxicology Data Network, available at <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>), it should not be subject to LRAT. Contrary to this prediction, evidence of chlorpyrifos at Holtedahlfonna suggests that this pesticide is persistent in some Arctic conditions.

### 3.1.2. Organochlorine CUPs

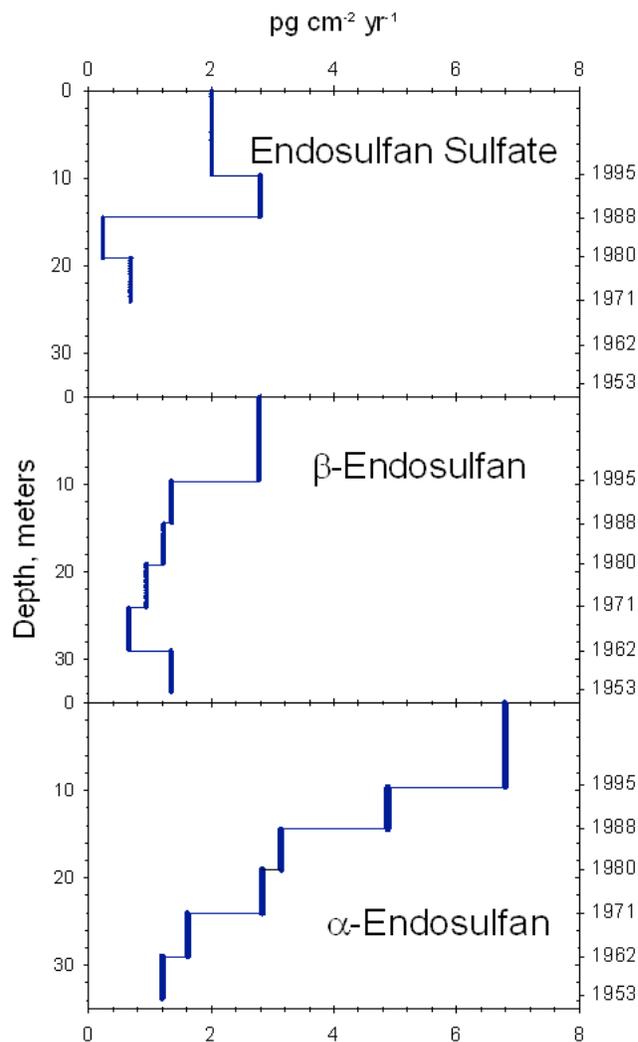
#### 3.1.2.1. Lindane ( $\gamma$ -HCH)

[17] Lindane (mostly  $\gamma$ -HCH) is an OC insecticide that replaced technical HCH (mostly  $\alpha$ -HCH). It was detected in all ice core segments from Holtedahlfonna with the peak input of  $369 \text{ pg cm}^{-2} \text{ yr}^{-1}$  in the oldest segment of the ice core (1953–1962), and a decreasing trend to 1995–2005, where the input was  $7.46 \text{ pg cm}^{-2} \text{ yr}^{-1}$  (Figure 2). This observation is >10 times greater than observed at the Devon Ice cap in 2005 ( $0.3\text{--}0.5 \text{ pg cm}^{-2} \text{ yr}^{-1}$ ) [Hoferkamp *et al.*, 2010]. Lindane is among the most persistent compounds that we analyzed, with a predicted atmospheric half-life of 1464 h or 61 days (TOXNET, <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>). The decline in accumulation observed at Holtedahlfonna is consistent with its use. Considering both the use of lindane and technical HCH, total global use of

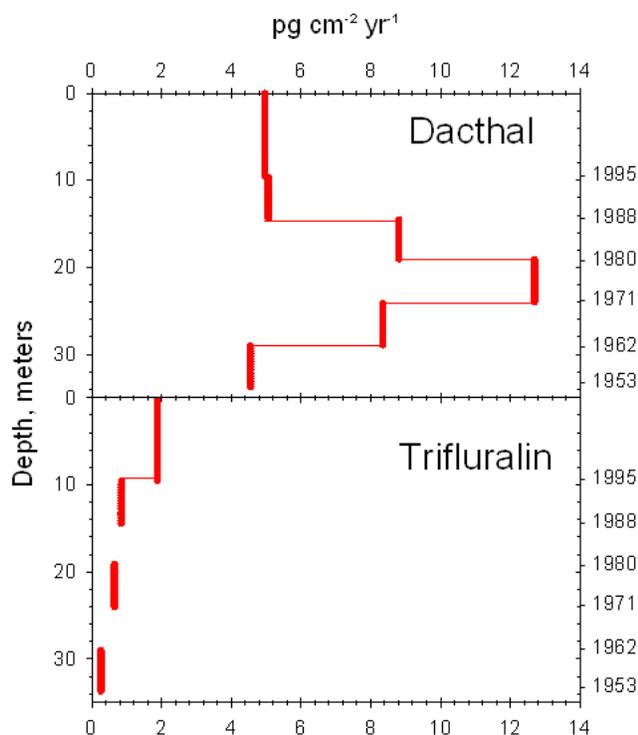
$\gamma$ -HCH was approximately 11,900 t (mt) in 1980 and 8,400 mt in 1990 [Li *et al.*, 1996], with a total of 720,000 mt used between 1970 and 1993 [Li and MacDonald, 2005]. Bans on use and production of technical HCH and the decline in use of lindane by China in the 1980s and Russia in the 1990s [Li *et al.*, 1996, 2004] as well as decline in use by Europe in the 1990s [Breivik *et al.*, 1999] may contribute to the declining inputs observed here.

#### 3.1.2.2. Endosulfans ( $\alpha$ -Endosulfan, $\beta$ -Endosulfan, and Endosulfan Sulfate)

[18] Endosulfans are a family of chlorinated cyclodiene insecticides first introduced in the 1950s. The endosulfan group presented a continuous but smaller flux than the other CUPs at Holtedahlfonna, with  $\alpha$ -endosulfan appearing first in the 1953–1962 core segment, with a general increasing trend to the surface layer ( $6.80 \text{ pg cm}^{-2} \text{ yr}^{-1}$ ) (Figure 3).  $\beta$ -endosulfan had a maximum accumulation rate of  $2.79 \text{ pg cm}^{-2} \text{ yr}^{-1}$  also in the surface layer (1995–2005) with continuous, increasing inputs after 1962. Endosulfan is predicted to be among the less persistent OC CUPs with a



**Figure 3.** Flux trends at Holtedahlfonna over time for endosulfan group compounds.



**Figure 4.** Flux trends at Holtedahlfonna for herbicides trifluralin and dacthal.

reported atmospheric half-life of 48 h (TOXNET, <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>) with a possible range of 31 to 84 h [Weber *et al.*, 2010] but trends observed here show sufficient persistence in the Arctic to have a continuous record over time. The increasing trend observed at Holtedahlfonna is consistent with global use of endosulfan which has increased continuously since the first year the pesticide was applied [Li and MacDonald, 2005]. Global use of endosulfan is estimated to be 10,500 mt from 1980 to 1989 increasing to 12,800 mt from 1990 to 1999 [Li and MacDonald, 2005], and dropping to about 11,000 mt by 2004 [Weber *et al.*, 2010]. Endosulfan sulfate, the metabolite of endosulfan, was detected in the ice core with lower flux than the parent compounds ( $2.81 \text{ pg cm}^{-2} \text{ yr}^{-1}$  in 1988–1995). Accumulation of endosulfan sulfate began in the 1971–1980 core segment; it apparently has similar persistence to the parent compounds.

[19] These findings for  $\alpha$ - and  $\beta$ -endosulfan are consistent with previous research in the Arctic. Weber *et al.* [2006] found that  $\alpha$ -endosulfan was one of the most abundant OC pesticides in the Arctic atmosphere with concentration trends showing no evidence of decline over time. Their research corroborates the increasing trend observed for  $\alpha$ -endosulfan at Holtedahlfonna. They also found that the  $\alpha/\beta$  ratio was  $\sim 25$  in Arctic air and  $\sim 2$  in Arctic seawater based on yearlong measurements taken in 1993; the ratio in the predominant technical mixture is  $\sim 2$  [Weber *et al.*, 2006]. Our observed range of  $\alpha/\beta$  ratios of 2.4 to 3.6 in all ice core segments since 1962 from Holtedahlfonna (Figure 3) falls

between what Weber *et al.* [2006] observed in air and seawater, and closer to the latter.

### 3.1.3. Herbicides

#### 3.1.3.1. Trifluralin

[20] The dinitroaniline herbicide trifluralin has a near-continuous profile in the ice core, but levels are apparently below the detection limit in two core segments (Figure 4). Its peak input was small, with a maximum accumulation of  $2.32 \text{ pg cm}^{-2} \text{ yr}^{-1}$  in the surface segment (1995–2005); it shows an increasing trend (with two segments below detection) over time since its first appearance in 1953–1962 ( $0.28 \text{ pg cm}^{-2} \text{ yr}^{-1}$ ). The lowest input occurs before its registration, suggesting some downward movement in the core, perhaps with seasonal melt. Trifluralin is widely used in the USA and UK [Kiely *et al.*, 2004; Pesticide Usage Survey Group, 1998; Colborn and Short, 1999] and has been observed in Arctic Canada on an event basis, with Eurasia considered to be the source [Welch *et al.*, 1991]. At the Devon Ice cap in Arctic Canada, the input in 2005 was  $0.016\text{--}0.022 \text{ pg cm}^{-2} \text{ yr}^{-1}$  [Hoferkamp *et al.*, 2010], less than 1% of the flux at Holtedahlfonna.

#### 3.1.3.2. Dacthal

[21] Dacthal, a preemergent phthalate herbicide [Yao *et al.*, 2007], was detected continuously at Holtedahlfonna from 1953 to 2005 (Figure 4). The accumulation of dacthal peaked at  $12.7 \text{ pg cm}^{-2} \text{ yr}^{-1}$  in 1971–1980 and then decreased in the surface layer to  $4.08 \text{ pg cm}^{-2} \text{ yr}^{-1}$ . At the Devon Ice cap in Arctic Canada, the 2005 input was found to be from  $0.006\text{--}0.027 \text{ pg cm}^{-2} \text{ yr}^{-1}$  [Hoferkamp *et al.*, 2010],  $<7\%$  of our peak value from 1995 to 2005. Dacthal is only registered for use as an herbicide in the UK, Canada (minor use), USA, New Zealand, and Australia [Yao *et al.*, 2007]. However, despite its apparent moderate use in North America, dacthal is found in many Arctic and Subarctic locations, including other Svalbard sites, the Passvik River (Russia) the Bering and Chukchi Seas, the Arctic Canadian atmosphere, and Alaskan and North American National Parks [Ackerman *et al.*, 2006; Chernyak *et al.*, 1996; Hermanson *et al.*, 2005; Yao *et al.*, 2007]. Dacthal has a predicted midlatitude half-life of 864 h [Muir *et al.*, 2004], second longest among CUPs found at Holtedahlfonna, confirming mobility and persistence which is probably related to its appearance far from areas of likely use. The comparatively low surface inputs to Holtedahlfonna relative to earlier observations suggest declining uses in source areas.

### 3.2. Legacy Pesticides

[22] Detection of legacy pesticides in remote regions has been well-documented [Andersen *et al.*, 2001; Berg *et al.*, 2004; Fuglei *et al.*, 2007; Hermanson *et al.*, 2005; Li and MacDonald, 2005; Oehme *et al.*, 1996; Welch *et al.*, 1991]. Consistent with past research, our data suggest that LPs continue to be transported to and persist in the Arctic.

[23] Four of the LP OC compounds or groups (dieldrin, endrin, DDT group and the chlordane group) found at Holtedahlfonna are among the organochlorine pesticides that are part of the “dirty dozen” compounds on the original Stockholm Convention list of POPs enacted in 2004 [chm.pops.int]. All were banned or the subject of phase-outs earlier in most western countries because they have extremely high persistence in the environment, can accu-

multate in food chains far from the original site of use after LRAT, and have toxic effects on non-target organisms [Muir *et al.*, 2004; de Wit *et al.*, 2004; Kaushik and Kaushik, 2007]. Methoxychlor, a DDT substitute, is also observed at Holtedahlfonna.

### 3.2.1. Dieldrin and Endrin

[24] Dieldrin and endrin are legacy cyclodiene insecticides detected in the core at low inputs ( $<20 \text{ pg cm}^{-2} \text{ yr}^{-1}$ , Figure S1 in the auxiliary material). The occurrence of dieldrin in the atmosphere could arise from the use of aldrin (which itself was  $< \text{LOD}$  at Holtedahlfonna), which can be converted to dieldrin in the environment [Poza *et al.*, 2006]. Dieldrin has a discontinuous record in the Holtedahlfonna core, but, overall, there are decreasing inputs from the 1950s to a surface flux of about  $5 \text{ pg cm}^{-2} \text{ yr}^{-1}$  (Figure S1 in the auxiliary material). Endrin is a stereoisomer of dieldrin. Its flux pattern has a somewhat similar pattern to dieldrin but does not appear after 1995.

[25] Dieldrin was used in agriculture from the 1950s to the 1970s, and from 1974 was used primarily against termites until 1987 when it was banned in the U. S. for all uses [Kanthasamy *et al.*, 2005]. The estimated dieldrin and endrin atmospheric half-lives (42 h and 48 h, respectively) (TOXNET, <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>) are relatively short, but long enough in the Arctic to accumulate in ice. Results from Holtedahlfonna also suggest that the bans on both compounds appear to have resulted in sharp input declines since the 1990s.

### 3.2.2. Chlordanes (Cis- and Trans-Nonachlor and $\alpha$ - and $\gamma$ -Chlordane)

[26] Chlordanes, first used in the 1940s, consist of many related chemicals; the major components that we analyzed were  $\gamma$ -chlordane,  $\alpha$ -chlordane, cis-nonachlor, trans-nonachlor and heptachlor (not detected). Cis- and trans-nonachlor and  $\alpha$ - and  $\gamma$ -chlordane were all detected almost continuously throughout the core (Figures S2 and S3 in the auxiliary material). All four species show a general flux increase in the core from 1953 but decreasing after 1995. The peak accumulation was  $2.28 \text{ pg cm}^{-2} \text{ yr}^{-1}$  for trans-nonachlor and  $5.03 \text{ pg cm}^{-2} \text{ yr}^{-1}$  for cis-nonachlor (both from 1971 to 1980) and  $18.3 \text{ pg cm}^{-2} \text{ yr}^{-1}$  for  $\gamma$ -chlordane,  $13.4 \text{ pg cm}^{-2} \text{ yr}^{-1}$  for  $\alpha$ -chlordane (both from 1988 to 1995). Regulations on the use and production of chlordane have led to a decrease in use of all four compounds, and may account for the non-detection of heptachlor and heptachlor epoxide. While cis-nonachlor and trans-nonachlor always had inputs smaller than the chlordane isomers, they also had earlier peak periods: Both  $\alpha$ - and  $\gamma$ -chlordane showed continuous input growth from 1962 to a peak input from 1988 to 1995. Following 1995, the input of chlordanes dropped by about half. The greater inputs of chlordanes probably reflect higher proportions in the pesticide product and perhaps greater persistence than the nonachlors. The trend with the chlordane isomers is consistent with a ban on technical chlordane in several countries after 1988. Both chlordane isomers are predicted to have a 72 h atmospheric half-life (Table 1), but the polar lifetime is long enough for them to appear at Holtedahlfonna.

### 3.2.3. DDT Group

[27] DDT was once widely used as an insecticide, and generally has been banned worldwide by the Stockholm Convention (although DDE and DDD are not), but con-

tinues to have limited use in controlling malaria. In the environment,  $p,p'$ -DDT, is converted to  $p,p'$ -DDE where and when metabolic activity is available. As expected,  $p,p'$ -DDE was the only DDT-group compound detected in most core segments at Holtedahlfonna (Figure S4 in the auxiliary material), although with low inputs (all  $<1.8 \text{ pg cm}^{-2} \text{ yr}^{-1}$ ) with a low surface peak input ( $0.95 \text{ pg cm}^{-2} \text{ yr}^{-1}$ ). The parent compound,  $p,p'$ -DDT was found discontinuously in the core, but peaked at  $2.9 \text{ pg cm}^{-2} \text{ yr}^{-1}$  in the surface layer, about 3 times greater than  $p,p'$ -DDE. A higher input of  $p,p'$ -DDT indicates recent use or lack of metabolic transformation before being transported to the Arctic.

### 3.2.4. Methoxychlor

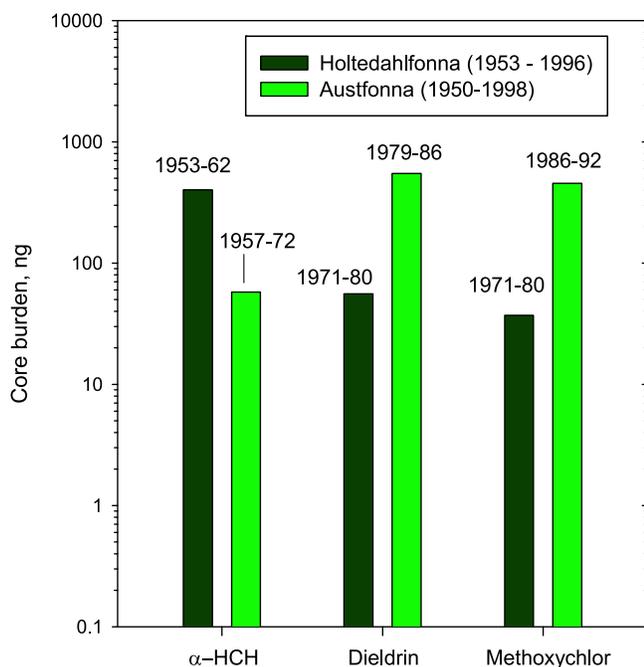
[28] Methoxychlor is an OC pesticide detected in all analyzed segments of the ice core beginning in 1953–1962 but with very inconsistent flux history (Figure S5 in the auxiliary material). The inputs grew to a peak value of  $19.6 \text{ pg cm}^{-2} \text{ yr}^{-1}$  in the core segment dated 1971–1980 and generally declined from there to the surface layer ( $10.7 \text{ pg cm}^{-2} \text{ yr}^{-1}$ ). After the U.S. DDT ban in 1972, use of methoxychlor – a DDT replacement – increased and this trend is indicated in the ice core (peak deposition in 1971–1980). While this pesticide is still registered for use in the U.S., production apparently has ended [Hoferkamp *et al.*, 2010], so it is considered to be an LP. It is unusual to see this compound at all because, if released to the atmosphere, its OH $\cdot$  reaction rate predicts a half-life of only 7 h (TOXNET, <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>). The record in the ice core at Holtedahlfonna indicates longer persistence but very irregular use or transport to the Arctic.

## 4. CUP and LP Burdens at Holtedahlfonna

[29] Table 1 shows total burden of individual pesticides to the Holtedahlfonna ice core. Seven of the 21 compounds in Table 1 are covered by the Stockholm Convention on POPs (as of August 2010). The top 4 compounds make up 85% of total core pesticide burden (2,235 ng) but only 2 of these compounds ( $\gamma$ -HCH and  $\alpha$ -HCH) are included on Stockholm. The two non-Stockholm CUPs, including OPs chlorpyrifos and methyl parathion, make up 44% of the total pesticide burden in the core. Of all 4 compounds, only chlorpyrifos shows a recently growing input (Figure 2). The only other compounds from Table 1 with growing inputs are  $\alpha$ - and  $\beta$ -endosulfan (Figure 3). They also have lower burdens than 8 of the legacy OCs, so their accumulation up to 2005 is comparatively minor. They are on Annex F of Stockholm, suggesting that they will be added to the Convention in the future. The suggestion is clear that the heaviest pesticide burdens at Holtedahlfonna are from LCs or older CUPs not showing growing inputs, with chlorpyrifos the important exception.

## 5. Differences in Pesticide Burdens Between Svalbard Sites

[30] An ice core drilled in 1998 from Austfonna (220 km ENE from Holtedahlfonna, Figure 1) was analyzed for some of the same compounds as the Holtedahlfonna core [Hermanson *et al.*, 2005]. We converted the Holtedahlfonna fluxes and the Austfonna concentration values from



**Figure 5.** Comparative ice core burdens and peak flux years of legacy pesticides in the Holtedahlfonna and Austfonna ice cores, shown by declining atmospheric half-life from left. Note the log scale for burden amounts.

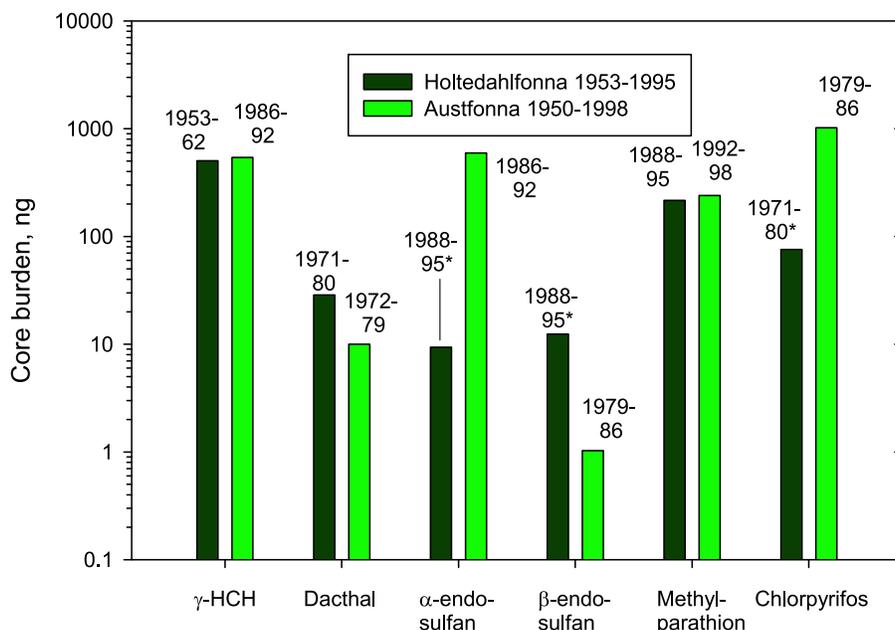
Hermanson *et al.* [2005] to core burdens (in ng, for the entire core) in order to compare the two sites. The major difference between sites is elevation: Austfonna is 740 masl while Holtedahlfonna is 1150 masl. Austfonna is expected to be warmer, however, average monthly air temperatures

are only slightly lower at Holtedahlfonna than Austfonna, and both are always  $<0^{\circ}\text{C}$  (Figure S6 in the auxiliary material) (T. V. Schuler, unpublished data, 2005). Snow deposition rate at Austfonna is  $0.45 \text{ weq yr}^{-1}$  [Isaksson *et al.*, 2003], about 12% lower than Holtedahlfonna. Another difference may be local atmospheric circulation to the sites: Different air mass geography, discussed below, may affect pesticide accumulation.

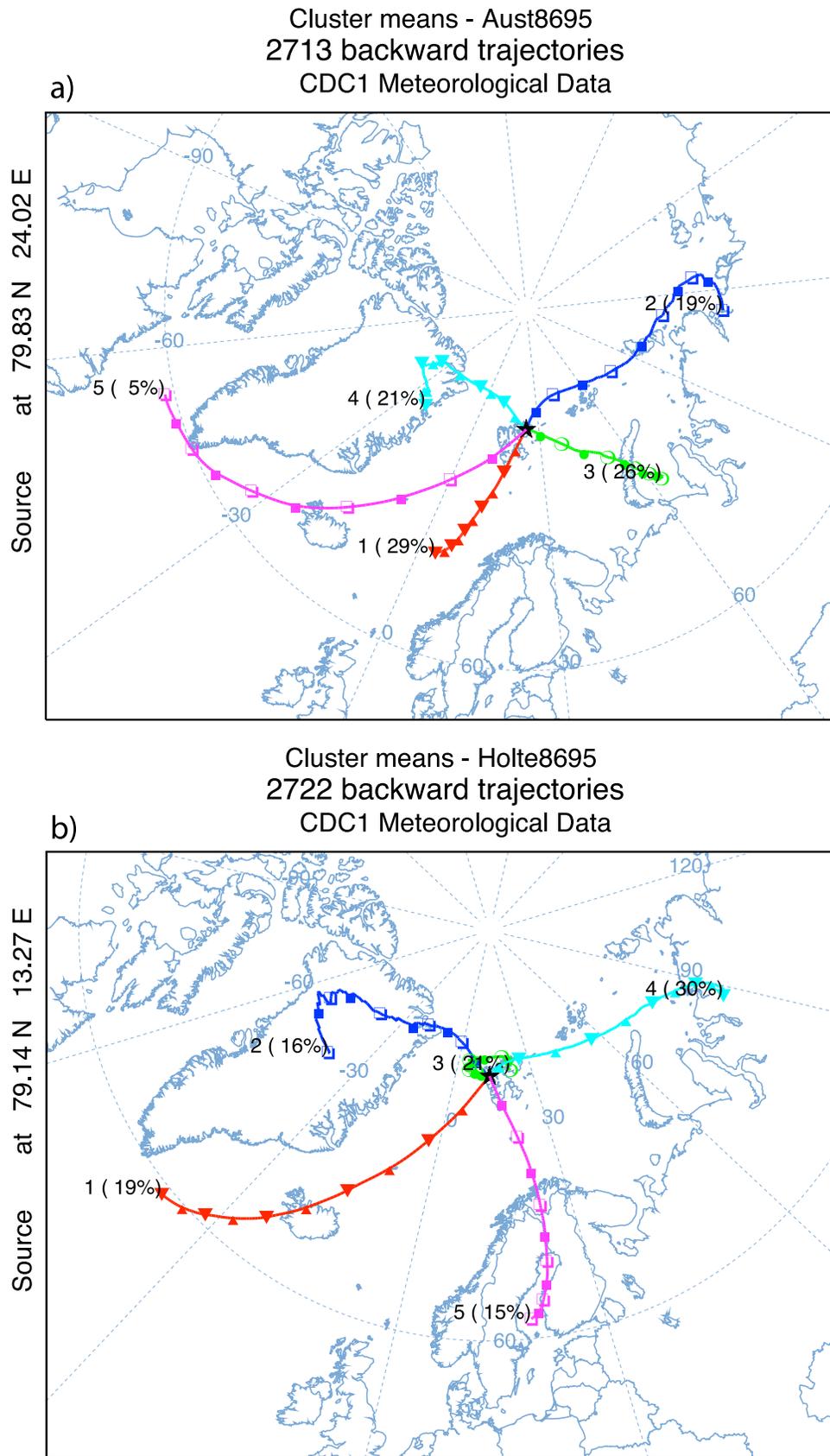
[31] The LPs detected at least once at both sites included  $\alpha$ -HCH, dieldrin and methoxychlor. The latter two have about a 10 times greater burden at Austfonna than Holtedahlfonna (Figure 5). The only higher LP burden at Holtedahlfonna, by a factor of about 9, is  $\alpha$ -HCH which had a maximum accumulation there during 1953–62. This period partially overlaps the peak  $\alpha$ -HCH accumulation time at Austfonna. The  $\alpha$ -HCH and  $\gamma$ -HCH peak inputs at Holtedahlfonna are earlier than any other LP or CUP at either site.

[32] The comparative data for CUPs (Figure 6) shows that  $\alpha$ -endosulfan and chlorpyrifos burdens at Austfonna are much higher by factors of about 60 and 13, respectively. The  $\beta$ -endosulfan burden has the opposite trend, being roughly 12 times greater at Holtedahlfonna. The burdens of methyl parathion are nearly the same, and occur at about the same time. For  $\gamma$ -HCH, the burdens are also nearly equal, but the Holtedahlfonna peak is 25–30 years earlier, suggesting different source regions to the sites. Dacthal burden at Holtedahlfonna is nearly three times greater than Austfonna, although the peak inputs occur over the same time periods.

[33] The divergence of burdens or peak input periods of these compounds between these sites suggests that the general sources of these pesticides is different at least part of the time, and that Austfonna generally receives the greater input.



**Figure 6.** Comparative ice core burdens and peak flux years of current use pesticides at Holtedahlfonna and Austfonna shown by declining atmospheric half-life from left. Note the log scale for burden amounts. Date ranges marked with asterisks indicate that the core peak input at Holtedahlfonna occurred from 1995 to 2005 which is not included in the burden.



**Figure 7.** Mean 5-cluster trajectories for (a) Austfonna and (b) Holtedahlfonna calculated from more than 5400 daily 5-day back trajectories over the period 1986–1995.

[34] Table 2 shows 43 compounds not detected at Høltedahlfonna. Of these, 9 CUPs and 3 LPs were found at Austfonna, also suggesting that Høltedahlfonna may be relatively less impacted by events that deposit contaminants at Austfonna, or may be influenced by different regional pesticide sources. The latter can be evaluated by 5-day air mass back trajectories covering a 10-year period (1986–1995) from the two sites (Figures 7a and 7b). These HYSPLIT trajectories show that during 1986–1995, corresponding approximately to the two surface segments of the Austfonna core and the next-to-surface segment of the Høltedahlfonna core, that Austfonna was dominated by flows from the south and east, including Europe and NW Asia, 74% of the time (Figure 7a), while Høltedahlfonna had flows from this area 45% of the time (Figure 7b). The greater Eurasian flow to Austfonna suggests that this region was responsible for the added number of pesticides found there. Our earlier results for Austfonna [Hermanson *et al.*, 2005] suggested that airflows over populated and agricultural regions in northern Eurasia might be the source of greater burdens of some pesticides used there.

## 6. Conclusion

[35] Our results from Høltedahlfonna confirm that many CUPs and LPs are persistent in the Arctic atmosphere and continue to reach high elevation sites on Svalbard. Some of the CUPs, including chlorpyrifos and the endosulfans, have growing inputs and burdens at the site. Other CUPs, including dacthal,  $\gamma$ -HCH and methyl parathion, like all other compounds with a record in the core, show little if any recent input. The observed LPs appear to be declining in most cases. Clearly, some of the more heavily used CUPs, developed to have lower persistence than legacy OC pesticides, are showing evidence of longer atmospheric lifetimes than predicted by OH $\cdot$  reaction rates.

[36] The comparison of CUP and LP burdens between the two sites shows that Austfonna receives more inputs of more pesticides than Høltedahlfonna. Ten-year cumulative 5-day air mass trajectories confirm that Austfonna has received more atmospheric flow from Eurasia than Høltedahlfonna. The result shown here is that atmospheric pesticide inputs can vary significantly on scales of  $\sim$ 200 km within parts of the Arctic having no direct human impact.

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