Current-Use and Legacy Pesticide History in the Austfonna Ice Cap, Svalbard, Norway

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The Svalbard archipelago in arctic Norway receives considerable semivolatile organic contaminant (SOC) inputs from the atmosphere. To measure the history of net SOC accumulation there, we analyzed the upper 40 m of an ice core from Austfonna, the largest ice cap in Eurasia, for several legacy organochlorine (OC) compounds and current-use pesticides (CUPs) including organophosphorus (OP), triazine, dinitroaniline, and chloroacetamide compounds. Five OP compounds (chlorpyrifos, terbufos, diazinon, methyl parathion, and fenitrothion), two OCs (methoxychlor and dieldrin), and metolachlor—an herbicide—had historical profiles in the core. The highest OC concentration observed was aldrin (69.0 ng L^{-1}) in the surface sample (1992–1998). The most concentrated OP was dimethoate (87.0 ng L^{-1}) between 1986 and 1992. The surface sample also had highest concentrations of pendimethalin (herbicide, 18.6 ng L^{-1}) and flutriafol, the lone observed fungicide (9.6 ng L^{-1}). The apparent atmospheric persistence of CUPs likely results from little or no oxidation by OH$^{•}$ during the dark polar winter and in spring. Long-range atmospheric pesticide transport to Svalbard from Eurasia is influenced by the positive state of the North Atlantic Oscillation Index since 1980 and also by occasional fast-moving summer air masses from northern Eurasian croplands.

Introduction

Pesticides are subject to long-range atmospheric transport (LRAT) from agricultural and urban areas to the Arctic where they may condense or be scavenged from air by precipitation or dry deposition (*1*). Transport pathways of organochlorine (OC) pesticides to the Arctic (*2*) and their burdens in indigenous peoples and wildlife are well documented (*3–7*). However, histories of LRAT inputs of OC compounds and the less persistent but more toxic current-use pesticides (CUPs) are largely unknown in the Arctic. Examination of ice core records can reveal historic patterns of net atmospheric inputs of both current-use and legacy products (*8*). We analyzed the historic concentration trends of 37 compounds in an ice core from Austfonna—the largest Eurasian polar ice cap—located on Svalbard, arctic Norway, where pesticides were never produced and likely were never used (Figure 1). The pesticide groups analyzed include OC and organophosphorus (OP) insecticides, and triazine, dinitroaniline, and chloroacetamide herbicides and fungicides, and some decomposition products. Most OCs have been banned; the other compounds are CUPs.

The present investigation follows earlier studies showing that some chemicals found on Svalbard are not used there and are transported through the atmosphere possibly from Eurasia or North America (*3, 9, 10*). Other investigations have observed OC pesticides in snow and ice from mountainous and arctic areas of North America and Russia (*11–13*). Previous research on OPs shows that they are distributed through the atmosphere to sites at considerable distances from areas of use (*14–17*), and are found in arctic sea ice, land ice, and lake water (*4, 12, 14*).

Many OP insecticides, herbicides, and fungicides or their degradation products are considered to be nonpersistent and not subject to LRAT because they are subject to oxidation. The atmospheric lifetimes of gaseous CUPs are generally defined by hydroxyl radical (OH$^{•}$) reaction rates, considered to be the most common atmospheric oxidation process for trace organics (*14, 16, 18*). Under conditions of low oxidation, the presence of CUPs and other organic compounds in the gas phase is a function of high vapor pressure (vp) and low water solubility (S_w). A lack of atmospheric moisture may influence the effect of S_w (*19*). The ratio of vp and S_w, when adjusted to common units, becomes K_{AW}, the air−water partition coefficient, which, when high, indicates a tendency to remain in the gas phase (*20*).

Experimental Section

In 1998, a field team from the National Institute of Polar Research (Japan) and the Norwegian Polar Institute drilled a 118-m ice core from the summit of Austfonna (79.48°N, 24°E, 740 meters above sea level (masl)) (*21*). The core was analyzed for density, δ^{18}O, major ions, conductivity, and ^{137}Cs which provided various dating reference horizons (*22*). The resulting accumulation rate is ~0.5 m (H$_2$O equivalent) yr^{-1}. The melt index for this core is 40−67%, suggesting that the summer melt penetrates no more than 5 years of the near-surface snow and firn (*23*): during warm summers the meltwater can penetrate through a few previous summer surfaces and introduce a disturbance to the annual layered records. Since our resolution is ~6−8 years, our results are not affected.

For our analysis, we combined contiguous sections of the core to accumulate a minimum of 11 L of H$_2$O per sample, resulting in 14 samples covering the period from 1906 (±5) to 1998, represented by the upper 70 m of the ice core. All of the blank corrected pesticide data of the core came from the upper 40 m dating from 1943 ± 5 to 1998: no blank-corrected values appeared below 40 m depth.

Ice core segments making up a sample were placed in a stainless steel can and melted to a final temperature not >5 °C. Contaminants were separated from melted ice by pumping 200−250 mL min^{-1} through Teflon-walled extraction columns filled with XAD-2 resin. The XAD-2 was precleaned by sequential solvent extraction (*14*) and then

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FIGURE 1. Map of Svalbard (with inset of the North Atlantic region) showing the Austfonna drill site.

packed into extraction columns in a clean room (positively pressured HEPA- and carbon-filtered air) at the National Water Research Institute (NWRI; Burlington, ON). The columns were then shipped to the Norwegian Polar Institute in Tromsø where the ice was melted and pumped. After sample pumping, the XAD columns were shipped back to the NWRI clean room laboratory where they were extracted in CH_3OH and CH_2Cl_2. The combined extracts were washed with 3% NaCl and dried on anhydrous Na_2SO_4. The extract was volume-reduced and added to a small column of 10% deactivated silica gel and eluted with 10% CH_3OH/CH_2Cl_2 and exchanged to CH_3COCH_3/C_8H_{18}. All pesticides were analyzed by a gas chromatograph−mass spectrometer (GC−MS) (low resolution in electron ionization mode). Extracts were injected into a GC (pulsed splitless at 250 °C) onto a Supelco MDN-5 column (30 m × 0.25 mm × 0.25 um film thickness) at an initial GC oven temperature of 80 °C. CUPs were quantified using 4-point calibration curves based on authentic external standards. The analyte list was selected based on high levels of use for the CUPs and known Arctic presence of the legacy OC pesticide compounds.

Quality assurance steps included pre-spiking with deuterated fenitrothion and atrazine to measure breakthrough, and the analysis of field blanks (XAD columns shipped to the laboratory where extractions were carried out and returned with sample columns). Details of the method are further described by Muir et al. (*14*).

Results

The results of the analysis can be generally classified three ways: compounds that were not detected, compounds detected in no more than two discontinuous core segments, and those that appeared in several continuous layers. Nine compounds were analyzed but not detected, including the DDT group (*p,p′*-DDT, *p,p′*-DDE, and *p,p′*-DDD), endrin, endosulfan-sulfate, chlorthalonil, pirimphos methyl, and oxons of chlorpyrifos and diazinon. They are not considered further. Twenty compounds were observed in discontinuous layers and include eight OCs (aldrin, α-endosulfan, β-endosulfan, endrin aldehyde, heptachlor, heptachlor epoxide, α-HCH, γ-HCH), seven OPs (dacthal, dimethoate, disulfoton, ethion, fonofos, guthion, and imidan), four herbicides and degradation products (alachlor, desethylatrazine, hexazinone,

and pendimethalin), and a fungicide (flutriafol). Their maximum concentrations are reported in Table 1 with dates of the ice core age segment where maximum values appeared. The third group comprises the eight compounds with continuous profiles in the core and includes OPs chlorpyrifos, terbufos, diazinon, methyl parathion, and fenitrothion, OCs methoxychlor and dieldrin, and metolachlor, an herbicide. They are also reported in Table 1 and their profiles appear in Figures 2 and 3.

We assume that pesticide concentrations observed in the ice core result from equilibrium between the atmosphere and the snow surface under the conditions present at the time of deposition. For the discontinuous group of 20 compounds, it is apparent that while their LRAT inputs to Austfonna are sporadic, the concentrations of many of them are often high. Seven of the ten most concentrated pesticides are in this group. Among these 7, there is no clear distinction in maximum concentrations between the OCs that were banned in the 1970s and 1980s and the current-use OPs (Table 1). Among the group of discontinuous compounds in the core, dimethoate (an OP) was the most concentrated (87 ng L^{-1} in 1986−1992), followed by aldrin (OC), 69 ng L^{-1} in 1992−1998, imidan/phosmet (OP), 44 ng L^{-1} in 1986−1992, and heptachlor epoxide (OC), 33 ng L^{-1} in 1992−1998. The concentrations of aldrin and heptachlor epoxide are high: they exceed the risk-based concentration for tap water established by USEPA Region 3 (*24*). Even though these levels are high by certain definitions, the concentrations in various Russian ice caps have been reported to be at least 3 times greater (*12*) as summarized in Table 1.

Of the compounds in the third group, shown in Figures 2 and 3, the concentrations are not high but their persistence, with some exceptions, suggests a continuing source to the atmosphere over Austfonna.

Trends over time for chlorpyrifos, terbufos, diazinon, and methyl parathion, four of the 10 most widely purchased OP pesticides in the USA (*27*) and in Russia (*28*) during the late 1990s, appear in Figure 2. Fenitrothion, while not among those 10 high-use pesticides, is included in Figure 2 because it has a time-trend in the core consistent with other compounds. With the exception of chlorpyrifos, all compounds in Figure 2 show generally increasing concentrations over time with fenitrothion showing the fastest growth and highest concentration of the group in surface layers of the ice core.

Chlorpyrifos first appears at Austfonna in 1972; its concentration peaked in the 1980s, began to decline in the 1990s, and was not found in the surface layer of the core (1992−1998). It is heavily used: It ranked number 2 in sales in the United States in the late 1990s (nearly 8600 metric tons of chlorpyrifos were sold in the U.S. in 1999 (*27*)) and was also widely used in western Europe in the late 1990s (*29*). These features would lead to the expectation that chlorphyrifos would be widely distributed through the global atmosphere. But its atmospheric lifetime based on reaction with OH•, which is measured in hours (in contrast to α-HCH which is probably >100 days), indicates that it would not be subject to LRAT (*30*). Since it is found at Austfonna, the actual OH• reaction rate apparently is much slower than predicted from the literature because OH• production is seasonal and often low in the Arctic (see Discussion, below). The departure from expected rates, which has also been observed in northern Canada (*14*), would affect all CUPs and some legacy OCs. The absence of chlorpyrifos from the surface sample does not suggest an oxidation loss: its oxon was not observed in any sample analyzed here.

Terbufos concentrations at Austfonna increase after 1979. It was the third most widely sold OP pesticide in the United States during the late 1990s (*27*) and widely used worldwide, particularly in Europe (*29*). But like chlorpyrifos, its atmo-

TABLE 1. Pesticides Analyzed in the Austfonna Ice Core and Found in Ice/Snow from Arctic Russia and Canada (Agassiz Ice Cap)

chemical	Austfonna peak amount (ng L^{-1})	Austfonna peak years[a]	Russian ice (ng L^{-1})[b]	Agassiz ice cap 1986 (ng L^{-1})[c]
Organochlorine Compounds (OCs)				
Aldrin	69.0	1992−1998	220−310	
Dieldrin	7.5	1979−1986		0.96−1.63
α-Endosulfan	10.7	1992−1998	40−240	0.95−1.34
β-Endosulfan	19.7	1979−1986	60−120	
Endrin-aldehyde	13.6	1986−1992	5.3−150	
Heptachlor	6.5	1986−1992	58−280	
Heptachlor-epoxide	32.8	1992−1998	11−98	0.27−0.41
α-HCH	1.1	1957−1972	200−1000	4.89−7.9
γ-HCH	7.7	1979−1986	20−170	2.98−4.55
Methoxychlor	4.7	1979−1986	72−2100	
Organophosphorus Compounds (OPs)				
Chlorpyrifos	16.2	1979−1986		
Dacthal	0.3	1979−1986		
Diazinon	20.5	1986−1992		
Dimethoate	87.0	1986−1992		
Disulfoton	6.5	1986−1992	5.8−8.5	
Ethion	3.1	1986−1992		
Fenitrothion	32.9	1992−1998	ND−320	
Fonofos	4.6	1979−1986		
Guthion	21.6	1964−1972		
Imidan	44.1	1986−1992		
Methyl-Parathion	7.4	1992−1998	ND−110	
Terbufos	11.1	1992−1998		
Herbicides				
Alachlor	1.2	1979−1986		
Desethyl-atrazine	2.1	1986−1992		
Hexazinone	1.5	1992−1998		
Metolachlor	9.3	1992−1998	24−110	
Pendimethalin	18.6	1992−1998	310−920	
Fungicides				
Flutriafol	9.8	1992−1998		

[a] Peak concentration in surface segments 1992−1998 or subsurface (pre-1992). Peak concentration for 1957−1972 represents two layers. [b] A range of values from several sites. Data from ref 12. ND = not detected. Missing values were not detected or not reported. [c] Data from ref 11. Missing values were not detected or not reported.

spheric lifetime is assumed to be hours in length under concentrations of OH• characteristic of the mid-latitudes. Again, however, lower OH• concentrations in the arctic atmosphere than in the mid-latitudes likely lead to longer atmospheric lifetimes for all CUPs.

Diazinon and methyl parathion were the 4th and 5th most widely purchased pesticides in the United States in the late 1990s (27). Both were used widely in Russia in the late 1990s in amounts ranging from 4 to 10 tonnes annually (28). Both are registered in the United States and in many developing countries. Diazinon is banned in most European countries, while methyl patathion is registered in the EU (29). Both are among the earliest developed OPs analyzed here: Methyl parathion, the oldest, was introduced in the late 1940s yet did not appear at Austfonna until the 1980s. Diazinon has the second-highest peak concentration among compounds in Figure 2. Its drop in concentration in the surface sample of the ice core may be related to its ban in Europe. As with other compounds in Figure 2, diazinon and methyl parathion show longer than expected atmospheric lifetimes.

Fenitrothion is the most concentrated of the group in Figure 2, but its concentrations before 1992 are consistent with observations for other OPs. Although some European countries have now banned its use, it is registered in the United States, Russia, and the U.K. (29) and was used well into the 1990s. It was found in snow in the French Alps at a concentration of 0.35 ng L^{-1}, about 100 times less than that found at Austfonna after 1992 (31).

Figure 3 shows results for two OC pesticides, methoxychlor and dieldrin, and metolachlor, an herbicide. Methoxychlor was first produced in the late 1940s as a nonpersistent substitute for p,p'-DDT. Its concentrations at Austfonna increase steadily after the 1950s to 5 ng L^{-1} in the early 1980s, then decline and do not appear in the surface sample dating between 1992 and 1998. This is consistent with its U. S. production, which fell sharply between the mid 1970s and early 1990s while still registered there and in Canada. It is no longer used in Europe (29). Its concentrations at Austfonna are low in comparison to results for Russian icecaps (Table 1): the methoxychlor concentrations observed there are the highest of any measured pesticide.

Dieldrin first appeared at Austfonna in the 1960s, peaked in the 1980s, and has declined since then, a pattern consistent with the banning of its use—and that of its precursor aldrin—in North America and Europe in the late 1970s. Its concentrations at Austfonna are greater than those observed in the Agassiz ice cap in the Canadian arctic (11).

Metolachlor was heavily used in North America, Germany, southern Europe, and Asia through the 1990s (29). At Austfonna, it first appears in the early 1970s, about the time of its introduction in 1973. The concentration was low in the 1990s (about 0.7 ng L^{-1}) then increased by a factor of ∼10. This may be related to the replacement of atrazine by metolachlor in corn (maize) production in Europe during the 1990s. Concentrations at Austfonna are less than one-half the amount in Russian ice (Table 1).

With the exception of α-HCH, all OC concentrations at Austfonna are greater than those observed in the Agassiz ice cap and elsewhere in snow and ice in Canada (11), but many are several times less concentrated than maximum amounts
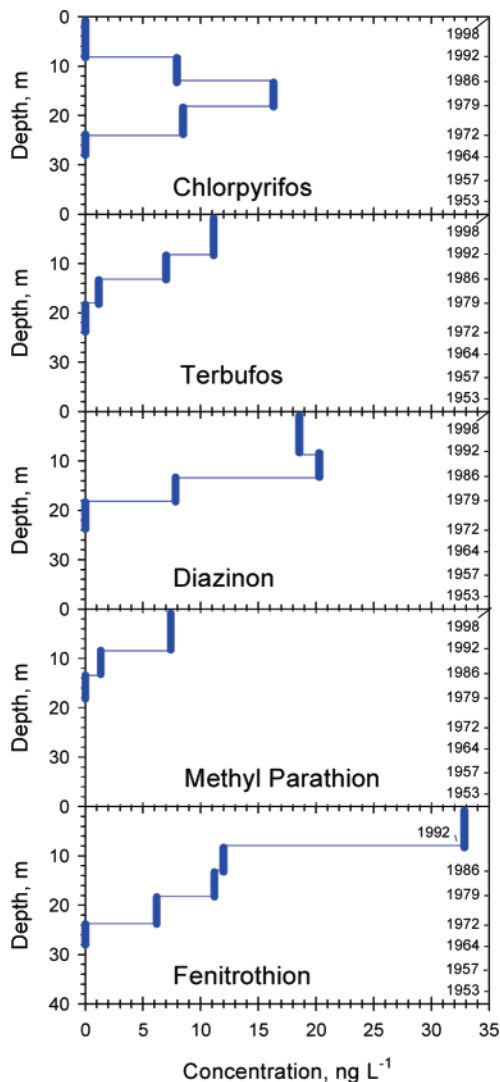
FIGURE 2. Concentration trends of five organophosphorus compounds at Austfonna. Chlorpyrifos, terbufos, diazinon, and methyl parathion ranked numbers 2, 3, 4, and 5, respectively, in sales in the United States in 1999. Data for methyl parathion are from ref 8.

FIGURE 3. Concentration trends of methoxychlor, dieldrin, and metolachlor. Data for dieldrin are from ref 8.

found in Russian ice caps (*12*) (Table 1). The α-HCH and γ-HCH concentrations at Austfonna (max 1.1 ng L^{-1} and 7.7 ng L^{-1}) and at Agassiz (range 4.9−7.9 and 3.0−4.6 ng L^{-1}) are close to or within the range of concentrations found in arctic Russian river and sea ice (ND to 5.1 ng L^{-1} and ND to 19.6 ng L^{-1}, respectively) (*13*). Where comparable data exist, Austfonna OP and herbicide concentrations are low in comparison to precipitation samples collected near areas of use (*25, 26*).

The only multiple CUPs investigation including comparable arctic and subarctic water results are from the lakes study by Muir et al. (*14*). While lakes represent a different freshwater environment than glaciers, in both cases the systems are influenced only by atmospheric inputs and provide a useful comparison of the influences of LRAT. Maximum concentrations at Austfonna are greater than those found in any of the Canadian arctic lakes, except for flutriafol. Mid-latitude Canadian lakes from the same study have higher concentrations of herbicides alachlor and metolachlor than Austfonna, but lower amounts of OPs chlorpyrifos, diazinon, and disulfoton. Agricultural and remote mid-latitude lakes in Canada had about the same maximum concentration of dacthal in 2000 (0.27 ng L^{-1}) as found at Austfonna (0.3 ng L^{-1}) in the early 1980s (*14*). In general, Austfonna pesticide
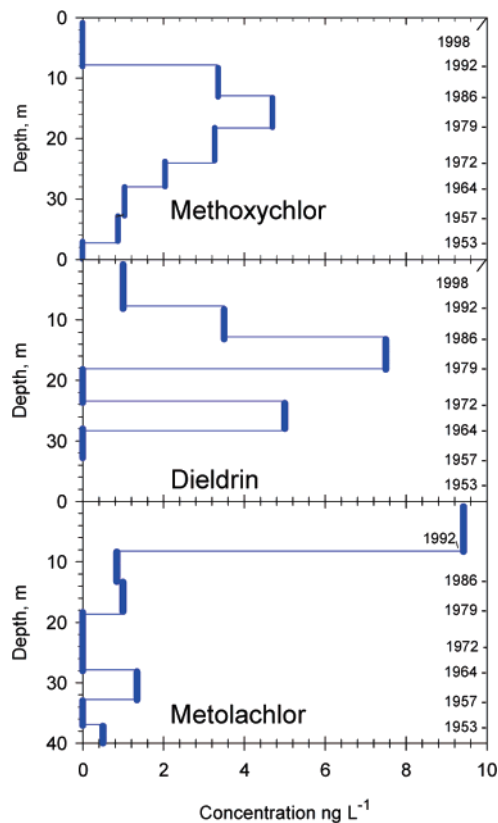
concentrations are higher than those likely found in the Canadian Arctic which is consistent with modeled results of atmospheric transport systems (see Discussion, below).

Discussion

The trends of the eight compounds in Figure 2 show that OP compounds move into the atmosphere and tend to persist there under conditions found in the regions that supply air to Austfonna. While vp and S_w are considered to be two critical factors in the prediction of pesticides being found in the atmosphere, both factors are variable among these compounds. Vapor pressures of all compounds in Table 1 range from a low of 7.1×10^{-9} Pa for flutriafol to 5.3×10^{-2} Pa for heptachlor (all at 25 °C), a variability > 6 orders of magnitude. But among the compounds with continuous records shown in Figure 2, the variability is much less, ~90. Three of the five vp values in Figure 2 (terbufos, diazinon, fenitrothion) are greater than those of α-HCH which is more volatile than many OCs and is found throughout the Arctic (*32*). The others (chlorpyrifos and methyl parathion) are roughly half as volatile as α-HCH. This comparatively narrow range of high vp values may account for continuous inputs of these compounds to Austfonna over decades.
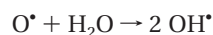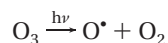
Water solubility for all compounds in Table 1 also varies over > 6 orders of magnitude between aldrin (0.0087 mg L^{-1}) and hexazinone (33,000 mg L^{-1}) (all at 25 °C). Among the compounds with continuous profiles in Figure 2, S_w varies much less, by a factor ~40. Within this range, only chlorpyrifos S_w is about half that of α-HCH, with other compounds 2−20 times greater. These high values have not prevented them from being transported to Austfonna through the atmosphere.

The atmospheric persistence and distribution of the 28 compounds observed here are functions of winter and spring processes characteristic of the Arctic. These include movement of the north polar meteorological front to the south, no or low production of OH•, low atmospheric moisture, and

low atmospheric O_3 content. The decades-long effect of the North Atlantic Oscillation (NAO) Index, which affects atmospheric circulation in the region, may also be important.

The north polar front extends far south during winter covering many potential pesticide source areas, including northern areas of America, Europe, and Russia. During this time, high atmospheric pressure over the continents channels pollutants northward (6, 33, 34). This is reflected in the high frequency of 850 hPa air mass back trajectories from likely contaminated sites in Eurasia during winter months (generally October through March) (10). Winter pollution events affecting Svalbard clearly appear in DDT and CO and hydrocarbon monitoring data from Ny-Ålesund (200 km WSW from Austfonna, Figure 1) (9, 35, 36). Another indicator that much of the winter contamination at Ny-Ålesund has Eurasian origins appears in modeled results of tropospheric circulation by Klonecki et al. (36) that show rapid poleward transport of Eurasian contaminants found in the lower troposphere. In the same model, North American contaminants are found in the upper tropospheric regions and are less likely to reach the surface (36). The estimated atmospheric lifetimes of CUPs are often measured in hours because of expected rapid oxidation by abundant OH• (30). But model concentrations of OH• that are characteristic of nonpolar regions are not typical in the Arctic: the absence of OH• production during polar darkness leads to longer atmospheric persistence of all organic compounds in the higher latitudes. The absence of chlorpyrifos and diazinon oxons in the Austfonna ice core suggests low level of oxidation of the parent compounds, which at times have been abundant in the atmosphere judging from Austfonna ice concentrations. CO is the most abundant contaminant gas on Svalbard and accounts for an estimated 50% of OH• consumption (37). Its presence is a clear indication of low oxidation during winter which leads to CO being effectively inert—with a long atmospheric lifetime (36). This is endorsed by observations of the CO mixing ratio at Ny-Ålesund which drops 75% between winter and summer (35, 38–40). During spring, a large amount of OH• can be produced in surface snow by photolysis of HCHO, HONO, and H_2O_2 as observed in Greenland and modeled elsewhere in the Arctic (41, 42). High OH• production from these processes would result in lower amounts of CUPs remaining in the gas phase. However, OH• production by these processes is not likely to occur in the Svalbard area to the extent observed on Greenland. The Svalbard archipelago has a small snow surface area in comparison to Greenland and is surrounded by the Barents Sea which is ice free—and snow free—from Svalbard to the Norwegian and Russian mainland between May and August, the time of year of greatest Eurasian pesticide application. During winter, the Barents Sea is ice-free in the southern half of that region.

Photolytic production of OH• may also be low in spring after the polar sunrise on Svalbard because tropospheric H_2O and O_3 concentrations there decline (43, 44) lowering the output of these typical OH• production reactions:

$$O_3 \xrightarrow{h\nu} O^{\bullet} + O_2$$

$$O^{\bullet} + H_2O \rightarrow 2\ OH^{\bullet}$$

The movement of European contaminants to the Arctic in general is enhanced by variations in the North Atlantic Oscillation. Eckhardt et al. (45) show that during high phases of the NAO index (NAO+), surface concentrations of trace gases in the Arctic originating in Europe and NW Russia are enhanced by about 70% while Asian sources are not affected. Since the 1980s, the NAO index has been mostly positive and may have influenced the movement of contaminants to
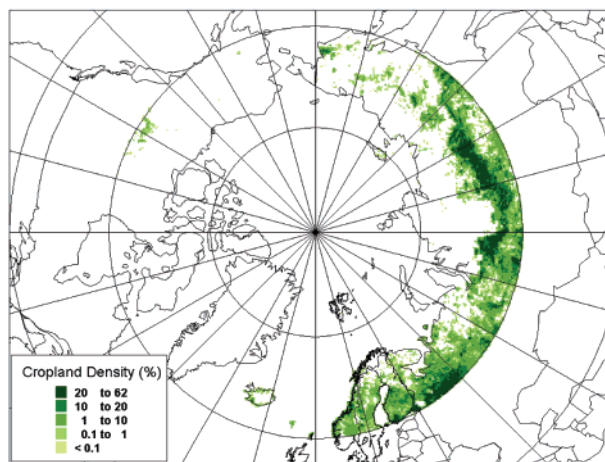

FIGURE 4. Map of cropland north from 60° N Latitude (ref 46).
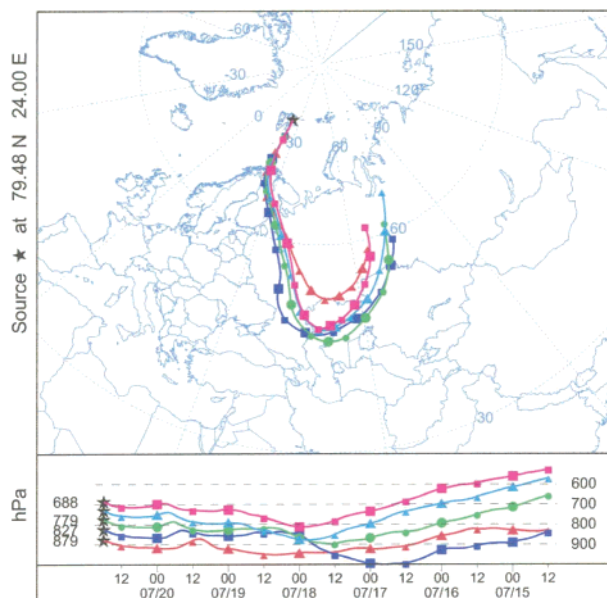

FIGURE 5. Summer HYSPLIT air mass back-trajectory (Global Final (FNL) meteorological data) covering 150 h from July 15–20, 2000. The near-surface trajectories show that summer air masses from agricultural areas of Russia and Finland from 60° N reach Svalbard at average speeds of >50 km hr^{-1}.

Austfonna: All but two of the compounds in Table 1 (α-HCH and guthion) reached peak concentrations after 1979 (45). This is of critical importance to distribution of contaminants to Svalbard because Russia now has more farmland north of 60°N than any other country, a region of likely high pesticide use (Figure 4) (46). Although most contaminant LRAT to Svalbard is expected in winter when pesticide application may be low, summer weather systems can also have major effects on air transport from Russian cropland and other areas, although less frequently (10). Occasional air masses can traverse the >2000 km distance from 60° N in Russia to Svalbard in 42 h, an average velocity >50 km hr^{-1}. An example is shown in a backward trajectory in Figure 5 calculated using the HYSPLIT 4 model and Global Final (FNL) data from July 2000 (47). In this example, trajectories at pressures from ~850 to ~500 hPA are fast-moving and vertically mixed (in this case up to ~3000 masl) over an area of high-density northern Russian cropland. The significant speed can deliver residues of recently applied pesticides, but significant mixing transfers some portion to higher altitudes—perhaps into the free troposphere—likely limiting deposition to the surface. Extensive vertical mixing is consistent with models for Eurasian

summer air masses and for North American winter air masses (*34*).

The rapid pesticide LRAT to Svalbard and subsequent accumulation of contaminants at Austfonna suggest that additional contaminant investigations in nearby regions will help further identify the magnitude of pesticide distribution by atmospheric conditions and processes of the North Atlantic region.

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