Chapter 2

Sources and Pathways of Persistent Organic Pollutants

The previous AMAP assessment summarized the pathways of pollutants in general (Gregor *et al.*, 1998), and POPs (de March *et al.*, 1998) specifically, as they were understood in the mid-1990s. Recent reviews have updated this information (Macdonald *et al.*, 2000; 2003). The general principles are briefly described in the following sections and the reader is referred to the above reviews for more details. In addition we also consider a novel pathway, biotic transport.

2.1. Pathways

For pristine regions like the Arctic, generally four possible pathways exist for the transport of POPs (Figure 2·1). The atmosphere, ocean currents, transpolar ice pack, and large Arctic rivers (Ob, Pechora, Yenisey, Lena, Mackenzie) are the main transport routes by which persistent organics enter Arctic ecosystems. The relative importance of each pathway depends on the chemical and physical properties of the substance and its emissions in the source region, which may vary over time. In addition to the above mentioned transport routes, POPs may also be transported into the Arctic via pelagic organisms (crustaceans, fish, marine mammals) and migratory birds, animals that migrate in large groups throughout different climate zones into the Arctic. These organisms can transfer the pollutants into higher-level organisms via the Arctic food web.

In general, present levels of most POPs cannot be related to known potential sources within the Arctic, and can therefore only be explained by long-range transport from lower latitudes (Hansen *et al.*, 1996; de March *et al.*, 1998; Macdonald *et al.*, 2000). However, there are sources of POPs within the Arctic that have local and possibly regional significance but are minor contributors from a circumpolar perspective. These include PCB emissions from military bases, harbors, and landfills, as well as PCDD/Fs and PAHs from smelters located in high latitudes (Section 2.3.2). Owing to increasing activities related to exploration and production of oil and gas, especially in the Russian and Norwegian Arctic, petroleum hydrocarbon releases are a potential local source of pollution for PAHs in ocean waters and sediments (Robertson, 1998; Hansen *et al.*, 1996). A future AMAP assessment of petroleum hydrocarbons will consider this particular source in more detail.
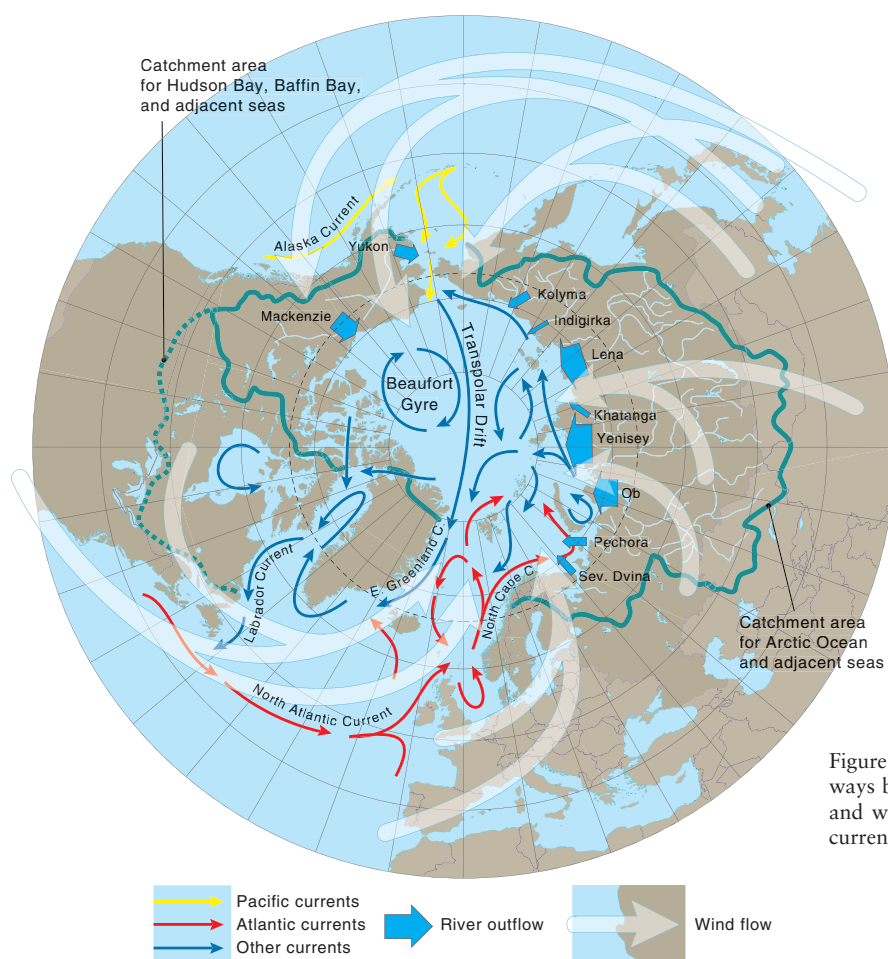

Figure 2·1. Illustration of the different physical pathways by which POPs enter the Arctic. Transport into, and within, the Arctic occurs via air currents, ocean currents, rivers, and transpolar ice movements.

2.1.1. Atmospheric transport and deposition of POPs

2.1.1.1. Meteorological conditions

Under favorable meteorological conditions, rapid air transport can take place in a few days or weeks, from the source regions into the Arctic. Almost twenty years ago, it was postulated that the global dispersion of semivolatile POPs occurred mainly via the atmosphere and was dependent on their vapour pressures (Ottar, 1981). Today, this is well documented and models developed show that atmospheric transport is probably the most important long-range transfer route for these compounds (Wania and Mackay, 1993; Strand and Hov, 1996; Wania and Mackay, 1996; Wania *et al.*, 1999a).

In winter, the lower tropospheric circulation is dominated by high pressures over the continents and low pressures over the northern Pacific (Aleutian Low) and Atlantic Oceans (Icelandic Low). The Siberian High tends to force air on its western side into the Arctic acting as an effective atmospheric conduit from industrialized regions of Siberia and eastern Europe into the high Arctic (Figure 2·1). The high-pressure ridge over North America then forces air southward giving a net transport out of Eurasia into the Arctic, across the Arctic and south over North America. The Icelandic Low produces westerly winds over the eastern North Atlantic and southerly winds over the Norwegian Sea providing a conduit for airborne contaminants from eastern North America and Europe to reach the Arctic rapidly. Finally, the Aleutian Low tends to steer air that has crossed the Pacific from Asia up into Alaska, the Yukon, and the Bering Sea (Bailey *et al.*, 2000; Li *et al.*, 2002; Wilkening *et al.*, 2000). During winter, these three routes into the Arctic – southerlies in the Norwegian Sea (40%), Eastern Europe/Siberia (15%), and Bering Sea (25%) account for about 80% of the annual south to north air transport (Iversen, 1996). Thus during winter, the polar front expands into an area encompassing southern regions of the northern hemisphere into central Europe, central U.S., Asia, the European part of Russia, Belarus, and the Ukraine. Eighty percent of the main source areas for persistent pollutants are situated in these regions. Therefore, during the winter season, the polar front is not limiting the atmospheric transport from these sources into the Arctic region.

Summer pressure fields and air-flow patterns are markedly different from those of winter. In summer, the continental high-pressure cells disappear and the oceanic low-pressure cells weaken with the result that northward transport from low latitudes weakens. During summer, the polar front is situated far north and creates a meteorological barrier often difficult to penetrate for air masses transported from southern regions. According to Iversen (1996), summer accounts for only 20% of the annual south to north air transport (southerlies in the Norwegian Sea (10%), eastern Europe/Siberia (5%), and Bering Sea (5%)). Prevailing winds provide a means to transport contaminants from industrialized North America and Europe to the North Atlantic but penetration into the Arctic weakens.

2.1.1.2. Light conditions

The polar night at 80° northern latitude lasts from October until March and then changes into the midnight sun period. These special seasonal light conditions have tremendous effects on the photochemical reactivity and degradation of some persistent pollutants. Lack of photochemical degradation processes may be the main reason why long-range transport of highly- and semivolatile organic compounds such as 2- and 3-ring PAHs is mainly observed during the winter. Photochemical processes during the 24-hour summer light period may quickly degrade chemicals that react rapidly with OH radicals or degrade by direct UV photolysis. In winter, on the other hand, air concentrations of these types of compounds are usually elevated by one or two orders of magnitude. Indications of a seasonally dependent photochemical degradation were also found for the persistent pesticide *trans*-chlordane. Seasonal shifts in the chlordane patterns have been found during year-round ambient air sampling campaigns at Ny-Ålesund (Svalbard, Norway) and at Alert (Ellesmere Island, Canada) (Oehme, 1991; Halsall *et al.*, 1998).

2.1.1.3. Precipitation inputs of POPs

Precipitation is a key factor in contaminant transport. Rain and snow scavenge aerosols and gasses from the atmosphere and deposit them at the Earth's surface (Gregor *et al.*, 1998; Macdonald *et al.*, 2000). Scavenging by precipitation may be relatively weak in the desert-like conditions of the High Arctic. For example, mean precipitation for the Arctic Ocean is estimated at about 25.2 cm/yr and evaporation is about 13.6 cm/yr for a net moisture flux to the ground of 11.9 cm/yr (Barry and Serreze, 2000). Precipitation over land in the Arctic drainage basins is greater, with the runoff yield (precipitation minus evaporation) being estimated at 21.2 cm/yr from the network of gauged discharge by rivers (Lammers *et al.*, 2001).

Due to the low annual average temperature, snow is the dominant form of precipitation in the Arctic. The influence of snow and ice on the fate and air–surface exchange of organic contaminants has been reviewed by Franz *et al.* (1997) and Wania *et al.* (1998). Wania *et al.* (1999b) demonstrated that falling snow serves as an extremely efficient scavenger of both vapour and particulate phase compounds, with vapour scavenging of lower chlorinated PCBs and 2- and 3-ring PAHs being a predominant process. Also the water–air partition coefficient and the ice–air sorption coefficient increase at low temperatures thus increasing the potential for vapour scavenging (Wania *et al.*, 1999b). In addition, a snow crystal possesses a large surface area and adsorbs particles and contaminants to its crystalline surface more efficiently than a water droplet (Franz and Eisenreich, 1998). Therefore snow precipitation transports contaminants more efficiently to the ground (soil, water surface) than rain droplets. In contrast to rainwater, the surface properties of snow crystals change during aging after deposition. The surface of a snow crystal diminishes dramatically after a short time on the ground because of the overall pressure of the surrounding snow, and the weather and climate conditions during the ageing process. Thus, due

to surface reduction, the adsorbed contaminants are either released into the ground, stay adsorbed to the snow crystal, or are re-evaporated into the atmosphere. These three possibilities are dependent on the vapour pressure of the respective contaminant and the ambient climatic conditions. Therefore, high POP levels can often be found in upper layers containing new snow surface whereas in aged snow, situated near the ground, the contaminants are already released into the soil.

2.1.1.4. Sea–air gas exchange

Gas absorption and volatilization of POPs are important pathways of deposition and removal in the Arctic Ocean. Evaluation of relative fugacities of PCBs and toxaphene in air and seawater, based on measurements in the mid-1990s, indicated that these compounds are still loading into the Arctic Ocean via the atmosphere, while α-HCH is volatilizing (Macdonald *et al.*, 2000). Verification of the sea–air exchange process for α-HCH was accomplished using the distribution of the enantiomers of this chiral pollutant as indicators (Falconer *et al.*, 1995; Jantunen and Bidleman, 1996; Jantunen and Bidleman, 1997). Enantiomeric ratios (ER) found in surface water and in high-volume ambient air samples were similar, implying a seawater source. A significant deviation from the racemic distribution (ER = 1) in environmental samples was also found. This deviation can only occur when biochemical transformation (microbiological or in higher organisms) takes place. Therefore, the authors concluded that α-HCH found in the ambient air had been subject to earlier microbiological degradation in the water column before being re-evaporated into the atmosphere. This finding represents the first evidence for water–air gas exchange of α-HCH using an experimental approach.

2.1.2. Ocean transport

POPs are also transported by ocean currents. Ocean circulation is driven by a combination of various forces and a particular force (e.g., tidal forces, wind stress, mixing of water masses) may dominate in a particular area. Within the Arctic Ocean, the main surface circulation features are the clockwise circulation of the Beaufort Gyre and the Transpolar Drift, which flows from Siberia (Russia), across the pole, and then southward, exiting as the East Greenland Current (Gregor *et al.*, 1998; Macdonald *et al.*, 2003). The major current systems whereby water is exchanged between the Arctic Ocean and other oceans, are found in Fram Strait. For example, the West Spitsbergen Current flows northward off the west coast of Spitsbergen (Svalbard, Norway), transporting Atlantic water from the Norwegian Sea into the Arctic Ocean (Gregor *et al.*, 1998). The transport via sea currents, however, may take years. Studies of the transport of radioactive isotopes released from the nuclear power plant in Sellafield (U.K.) indicates a four to five year transport over the 2200 km from southern Norway to northern Spitsbergen (Svalbard). Nevertheless, ocean transport is important for POPs with low HLCs such as β-HCH, which is selectively removed from the air by precipitation-scavenging as it heads northward and is enriched in seawater relative to other

HCH isomers (Li *et al.*, 2002). However, some degradation does occur in seawater. For example, α- and γ-HCH have recently been shown to undergo biotransformation in Arctic seawater with half-lives estimated to be 19 years for γ-HCH and 5.9 years for the + enantiomer of α-HCH (Harner *et al.*, 1999).

Prolonged half-lives in abiotic compartments, combined with efficient biomagnification and bioaccumulation in the Arctic food web due to lipophilicity and resistance to biological degradation, give rise to high concentrations of the long-range transported POPs in the higher trophic levels of the Arctic ecosystem, including indigenous people.

The low annual average temperature of the Arctic is the main reason why microbiological degradation of organic material slows to a minimum, especially in terrestrial and freshwater environments. This potentially extends the half-lives of many compounds in the Arctic relative to temperate regions.

2.1.3. Riverine inputs and sea-ice transport

Riverine input is considered to be another important source of contaminants to the Arctic Ocean (Barrie *et al.*, 1992; Pavlov and Pfirman, 1994; de March *et al.*, 1998; Gregor *et al.*, 1998) and can be considered as an important circumpolar source draining environmental pollutants into the Arctic Basin. Particles transported to the coast by large Russian Arctic rivers (e.g., Yenisey, Ob, Lena, and Pechora) during the melting period are contaminated with pollutants originating in the industrial areas of the northern Urals and western Siberia. As a result of various physical processes, the particles are incorporated in the coastal ice which may then carry large loads of contaminated sediments.

The general movement of sea ice from the coast of the Kara Sea is northward to join the Siberian branch of the Transpolar Drift between the Franz Josef Land and Severnaya Zemlya archipelagos. Ice-bound particles with possible contaminants may thus be carried out of the area and released in the main ice-melting areas east of Svalbard and in the Fram Strait (Figure 2·1). It is estimated that ice-rafted material forms up to 80% of the sediment on the ridges and upper slopes in the central Arctic Ocean (Darby *et al.*, 1989).

2.1.4. Biotic transport

Transport of pollutants, particularly POPs in migratory animals may also be a significant pathway in the Arctic, where many important species such as seabirds, cetaceans (beluga, bowhead whales, minke whales), pinnipeds (harp seals), salmon, and Atlantic cod are migratory. Some animals cover long distances, often crossing international boundaries and linking industrialized/agricultural and remote regions during their migration. Some species can be important prey of resident Arctic animals, for example, Barents Sea harp seals consumed by polar bear in eastern Svalbard and Franz Josef Land. A unique example is salmon entering Alaskan rivers to spawn and die. Ewald *et al.* (1998) described the entry of PCBs and DDT into the grayling population of the Copper River in Alaska by migrating sockeye salmon. The grayling in a salmon spawning lake had contami-

nant concentrations more than double those found in grayling from a nearby, but salmon-free lake.

Wania (1998) estimated that the amount of POPs transferred in and out of the Arctic via seabirds migrating annually from the Canadian Arctic to northwest Atlantic waters was in the range of grams to kilograms per year based on the fact that the populations involved are in the hundred thousands to millions of birds. Seabirds also leave behind guano which may contain significant quantities of persistent OC contaminants. Evenset *et al.*, (2002) have shown that elevated PCBs and other OCs in fish and sediments from Lake Ellasjøen on Bjørnøya (74°30'N, 19°E) are due to seabird guano (see Section 4.3.5). The seabirds at Bjørnøya are functioning as a transport link for POPs from the marine ecosystem to the freshwater ecosystem.

While many Arctic whales migrate regionally within the Arctic, the Eastern Pacific stock of gray whales (*Eschrichtius robustus*) spends the summer in the Bering and Chukchi Seas, and the winter off the Pacific coast of Mexico and California (Baker, 1978). Relatively reliable population estimates and recent contaminant concentrations in stranded individuals exist for this stock, allowing for an estimate of the amount of some POPs contained in these whales. Wania (1998) estimated that the total amount of PCBs and DDT contained in the gray whale population and therefore transported annually with gray whales is thus in the range of 20 to 150 kg PCBs, and 1 to 40 kg DDT. Of course only animals that die in the Arctic would leave the contaminants there. However, carcasses of dead or hunted whales are scavenged by Arctic fox and polar bears, thereby transferring contaminants from the temperate to the Arctic environment.

Considering all migratory whale populations, Wania (1998) concluded that the amount of PCBs and DDTs moved around in these whales is likely of the order of tens of tons per year. Especially for DDTs, these gross fluxes with whales may be comparable to those in air and ocean currents. On the other hand, for the more water soluble, more volatile, and less bioaccumulative HCHs the amounts in organisms are relatively low by comparison to the mass in the water column. Gross fluxes in migrating birds are much lower for PCBs, DDT or HCH than the transport rates in the physical media. The importance of biological transport media obviously increases with decreasing volatility and water solubility, and with increasing bioaccumulation potential of a chemical.

Ewald *et al.* (1998) pointed out that the pollutants in biological transport media are more readily available for bioaccumulation than those in abiotic media. In the case of the investigated Alaska freshwater system, they point out that the 'migrating salmon, the salmon roe, and the carcasses are fed upon directly by predators such as bald eagles, bears, and grayling, allowing the pollutants to be transferred to biota in a direct and efficient way'. Similarly, the studies on migrating salmonids in the Great Lakes (Scrudato and McDowell, 1989) concluded that resident fish in salmon-accessible tributaries derived their excess pollutant load by directly ingesting the contaminated salmon eggs. Ewald *et al.* (1998) even suggested that biotransport may provide a transport mode for POPs, whose physical chemical properties prevent them from long-range transport in atmospheric and water currents (extremely low volatility or water solubility, high atmospheric degradability, but resistance to metabolic degradation).

2.2. Modeling transport and distribution of POPs in the Arctic

2.2.1. Global fractionation

The most widely accepted hypothesis about atmospheric long-range transport and distribution of POPs is 'global fractionation' (Wania and Mackay, 1995; 1996) (Figure 2·2). The 'global fractionation hypothesis' explains atmospheric transport as a complex phenomenon depending on the physical-chemical properties of the transported contaminant (e.g., solubility, vapour pressure, molecule size). The physical-chemical properties of the substance are responsible for the atmospheric transport distance and the subsequent deposition via rain, fog or snow in the water column, sediment or soil. Relatively volatile hydrocarbons, characterized by a high vapour pressure, are taken directly into the gaseous phase and
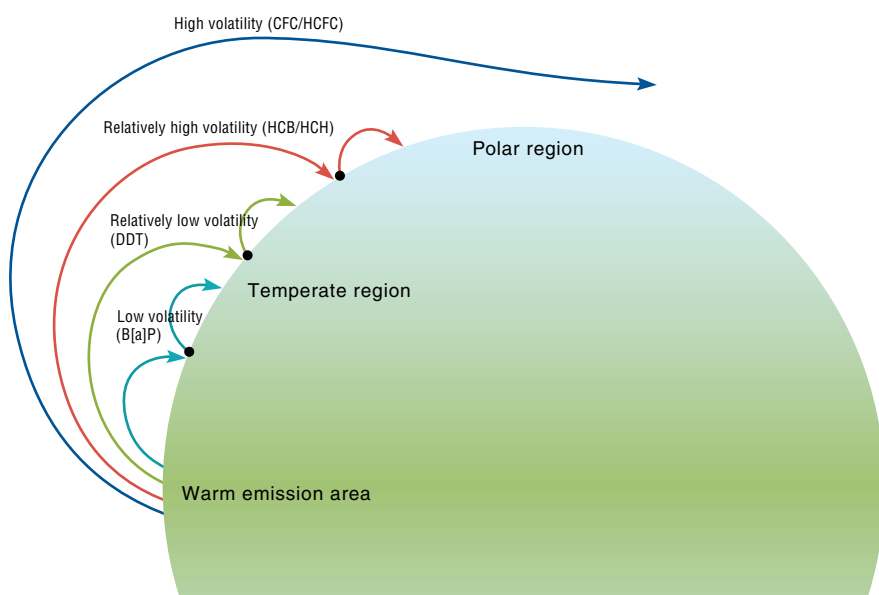

Figure 2·2. Schematic representation of the global fractionation hypothesis and the revolatilization (●) or 'grasshopper' effect. From Wania and Mackay (1996).

immediately transported into the deposition region as shown for lower chlorinated PCBs (CBs 8-99) and CBz. Semivolatile compounds such as lindane (γ-HCH) and chlordanes as well as some highly chlorinated PCBs (CBs 101-153), are distributed between airborne particles and the gaseous phase depending on temperature. These can be washed out via precipitation and temporarily deposited in seawater or soil and can absorb to water, plant and soil surfaces from the gaseous phase. During favorable warm weather conditions, these compounds evaporate again into the atmosphere and undergo further atmospheric transport. This remobilization is also called the 'grasshopper effect'. The role of stormy weather situations in remobilization of semivolatile compounds into the atmosphere is obvious but still scarcely investigated.

As a consequence of these processes, the levels of the more volatile POPs, such as HCHs and HCB, are found at comparable or even higher levels in Arctic biota compared to areas closer to source regions. However, the 'global fractionation hypothesis' and the 'grasshopper effect' are focused mainly on neutral, persistent organics transported via the atmosphere. At the present time, therefore, they are less useful for predicting levels of polar and water soluble persistent compounds that may be associated mainly with seawater.

2.2.2. Global transport modeling

A summary of the various modeling approaches for atmospheric and oceanic transport of contaminants in the Arctic was presented in the previous AMAP assessment report (de March *et al.*, 1998). Macdonald *et al.* (2000) also described box models of POP distribution and global transport of POPs using numerical models. The current state of knowledge on modeling the global fate and transport of POPs has recently been reviewed by Scheringer and Wania (2002).

2.2.2.1. Global scale box models

The basic approach for global box modeling is to use models that divide the global environment into a series of zonal bands, each of which is described by a series of well-mixed environmental compartments. This type of global model has seen further development and use during the past five years. In particular, the global distribution model by Wania and Mackay (1993; 1995), has seen further improvement, evaluation, and use, and a version of that model, named Globo-POP, is now available (Wania and Mackay, 2000). A new model of this type was also introduced by Scheringer *et al.* (2000). A detailed example of global modeling of POPs can be found in the recent study by Wania *et al.* (1999a), and Wania and Mackay (1999), on the global chemical fate of α-HCH. While α-HCH is no longer a significant POP, the detailed knowledge of its physical–chemical properties and use patterns enabled validation of the model predictions of prevailing and temporal trends of air and water concentrations over time, including contamination of the Arctic.

These global scale box models can be used in two different ways. They can be used to describe the fate of POPs using historical emission estimates, or they can be used in an evaluative fashion to understand global transport and accumulation processes without the availability of realistic emission scenarios. The first of these uses is primarily limited by the availability of suitable emission estimates, which need to be global in spatial scale and span decades in time. Such estimates only exist for α-HCH and PCBs at the present time (Section 2.3), and the Globo-POP model has been employed for simulation of the environmental fate of these two POPs (Section 4.2.1.4). The model has also been used to identify chemical property combinations that make a chemical susceptible to accumulation in remote polar regions (Wania *et al.*, 2001).

2.2.2.2. Three-dimensional global atmospheric transport models

Koziol and Pudykiewicz (2001) modeled the global transport of α- and γ-HCHs in 1993 and 1994 on a 2°×2° grid, using a three-dimensional global atmospheric transport model with high spatial resolution, and compared the measured and modeled air concentrations for several Arctic locations. The assumption of constant ocean water concentrations limits the model to fairly short time periods. The model also does not include particle-associated atmospheric transport, which may be important at the low temperatures of high altitudes and high latitudes.

A different modeling approach to quantifying the transport of POPs to the Arctic was used by Commoner *et al.* (2000). Using emission estimates for PCDDs for North America, in combination with air mass trajectories calculated with the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) air transport model, they derived source–receptor relationships for several communities in the Canadian High Arctic. The model estimated the amount of PCDD emitted by each of 44 000 sources that is deposited at each of eight receptor sites in Nunavut over a one-year period (1 July 1996-30 June 1997). A fairly limited number of North American sources outside of Nunavut were found to be responsible for almost all of the PCDDs deposited on that territory.

2.3. Global and circumpolar sources of POPs including emission inventories

2.3.1. Historical and current uses

The previous AMAP assessment report (de March *et al.*, 1998) gives an overview of sources of POPs in circumpolar countries. Since the preparation and completion of the first assessment report, several regional and global studies have been completed.

One important example is the European emission inventory of heavy metals and POPs for 1990 that has gained substantial interest (Berdowski *et al.*, 1997). This study was prepared based on submissions of emission data from the parties to the Oslo-Paris Commission (OSPARCOM), Helsinki Commission (HELCOM) and Convention on Long-Range Transboundary Air Pollution (LRTAP). For the countries where sources and compounds were lacking in officially submitted data, default emission estimates were prepared to make the inventory

Table 2·1. Estimates of the global historical usage or production of selected deliberately produced POPs, by-products, and potential POPs (thousands of tonnes) (modified after Macdonald *et al.*, 2000). For most chemicals, the major-use areas were, and are at present, the north temperate regions of Europe, North America, and Asia.

Chemical	Use	Production period	Estimated total global usage/ production (kt)*	Current annual global emissions (kt)**	Reference
Legacy organochlorine pesticides					
DDT	Insecticide	1950-present	2600	–	Voldner and Li, 1995
Toxaphene	Insecticide	1950-1993	1330	–	Voldner and Li, 1995
Technical HCH	Insecticide	1948-1997	10000	–	Li, 1999a
Chlordane	Insecticide	1945-1988	78	–	Barrie *et al.*, 1992
Aldrin	Insecticide	1950-1992	500	–	Barrie *et al.*, 1992
Dieldrin	Insecticide	1950-1992	34	–	Barrie *et al.*, 1992
Legacy industrial organochlorines and by-products					
PCBs	Various	1930-1992	1320	–	Breivik *et al.*, 2002a
CB 28			57	–	Breivik *et al.*, 2002a
CB 52			38	–	Breivik *et al.*, 2002a
CB 101			31	–	Breivik *et al.*, 2002a
CB 138			25	–	Breivik *et al.*, 2002a
CB 153			27	–	Breivik *et al.*, 2002a
CB 180			14	–	Breivik *et al.*, 2002a
By-products					
PCDD/Fs (as ITEQs)	By-products	1920-present	–	$0.8\text{-}3.6 \times 10^{-5}$	UNEP, 1999
Hexachlorobutadiene	Intermediate	1920-present	10	0.002-0.02	Van de Plassche, 2001a; Environment Canada, 2000
HCB	Pesticide by-product	1920-present	–	0.012-0.092	Bailey, 2001
Pentachlorobenzene	By-product and dielectric fluid	1920-present	15	0.001-0.005	Environment Canada, 1993
Octachlorostyrene	By-product	1920-present	–	0.0003-0.001	US EPA, 1999a
Polychlorinated naphthalenes	Flame retardants and by-products	1920-1980 (as products) 1920-present (as by-products)	200-400 0.01	– $<1 \times 10^{-4}$	Van de Plassche, 2001b Van de Plassche, 2001b
Currently produced organohalogens – potential POPs					
Short chain (C_{10}-C_{13}) chlorinated paraffins	Cutting oils and flame retardants	1945-present	500-700	50	Tomy *et al.*, 1998; Muir *et al.*, 2000a
Medium and long chain chlorinated paraffins (C_{14}-C_{30})	Flame retardant plasticizers	1930-present	2000-4000	250	OSPAR, 2000
TeBDE- and PeBDEs	Flame retardants	1960-present	70-120	8.5	BSEF, 2000
Octa- and Deca- bromodiphenyl ether	Flame retardant	1980-present	500-800	55	BSEF, 2000
Hexabromo- cyclododecane	Flame retardants	1980-present	100-200	16	BSEF, 2000
Tetrabromobisphenol-A	Flame retardants	1990-present	600-1000	121	BSEF, 2000
Perfluoroalkyl sulfonates	Surfactant and flame suppressant	1950-present	50 •	?	US EPA, 2000b
Perfluoroalkanoic acids	Surfactant and flame suppressant	1950-present	50 •	?	US EPA, 2000b
Current-use pesticides					
Lindane	Insecticide	1950- present	720	>2	Voldner and Li, 1995
Endosulfan	Insecticide	1956- present	57	1-2	Barrie *et al.*, 1992; USEPA, 2001
Butyltins					
Tributyltin	Algicide/fungicide	1960- present	100-500 •	<10	Hoch, 2001
Mono- and dibutyltin	Stabilizers	1960- present	200-1000 •	approx. 35	Hoch, 2001

* Estimated global use (to the late 1990s) as reported or inferred from published reports. Values with • are rough estimates assuming linear growth in production over the use period.

** Estimated annual emissions (kilotonnes) include use in consumer products and open applications as a pesticide. Volatilization losses (e.g., from treated soils) are not estimated; thus emissions of legacy OC pesticides are not given. Question mark indicates emissions are presently unknown.

complete. One of the major strengths of this study is thus the wide coverage of different priority substances as identified by OSPARCOM and HELCOM. This inventory covered a wide range of deliberately produced and accidentally formed POPs and related organic chemicals, including PAHs, PCBs, PCDD/Fs, HCB, several pesticides, and solvent chemicals. Another European emission inventory was recently presented by Pacyna (1999). This study focused on a subset of POPs, notably the PCBs, PCDD/Fs, HCHs, HCB, DDTs, and benzo[a]pyrene (B[a]P). One objective of this study was to estimate the historical trend in European emissions from 1970 to 1995 and to facilitate an analysis of the environmental response to changes in emissions. As individual constituents within groups of compounds (e.g., PCDD/Fs, PCBs, HCHs) may behave quite differently in the environment, a particular emphasis was on the emissions of individual isomers and congeners (Pacyna, 1999; Breivik *et al.*, 1999). Similar research efforts have been undertaken at the national level to estimate emissions of other POP constituents. In the United Kingdom, there have been studies on the national emissions for selected PCBs (Harrad *et al.*, 1994) and selected PCDD/Fs (Alcock *et al.*, 2001).

The best possibilities for deriving consistent and reliable source and emission estimates are for the deliberately produced POPs. Several databases have been established for the global production and usage of such compounds. Table 2·1 presents selected values compiled in a recent review (Macdonald *et al.*, 2000) along with updated figures for PCBs and 'new' chemicals of concern. Among the insecticides discussed below, most information is available for HCHs (technical HCH and lindane). The global estimates are described in a series of publications (Voldner and Li, 1995; Li *et al.*, 1996; Li *et al.*, 1998a; Li, 1999a; 1999b) and were recently utilized to model the global distribution and fate of α-HCH (Wania *et al.*, 1999a; Wania and Mackay, 1999).

PCBs

The estimates in Table 2·1 account for a reported historical global usage of approximately 1300 kt of PCBs of which more than 70% have been estimated as TrCBs, TeCBs, and PeCBs. The results further suggest that almost 97% of the global historical use of PCBs may have occurred in the northern hemisphere. Figure 2·3 shows the estimated cumulative global consumption pattern for total PCBs (Breivik *et al.*, 2002a). Most (approximately 86%) of the use (and thus emission to air) occurred in the industrialized, northern temperate latitudes, between 30-60°N. France, Germany, Italy, Japan, Spain, the U.K., and the U.S. were responsible for 68% of global PCB usage. The latitudinal distribution of
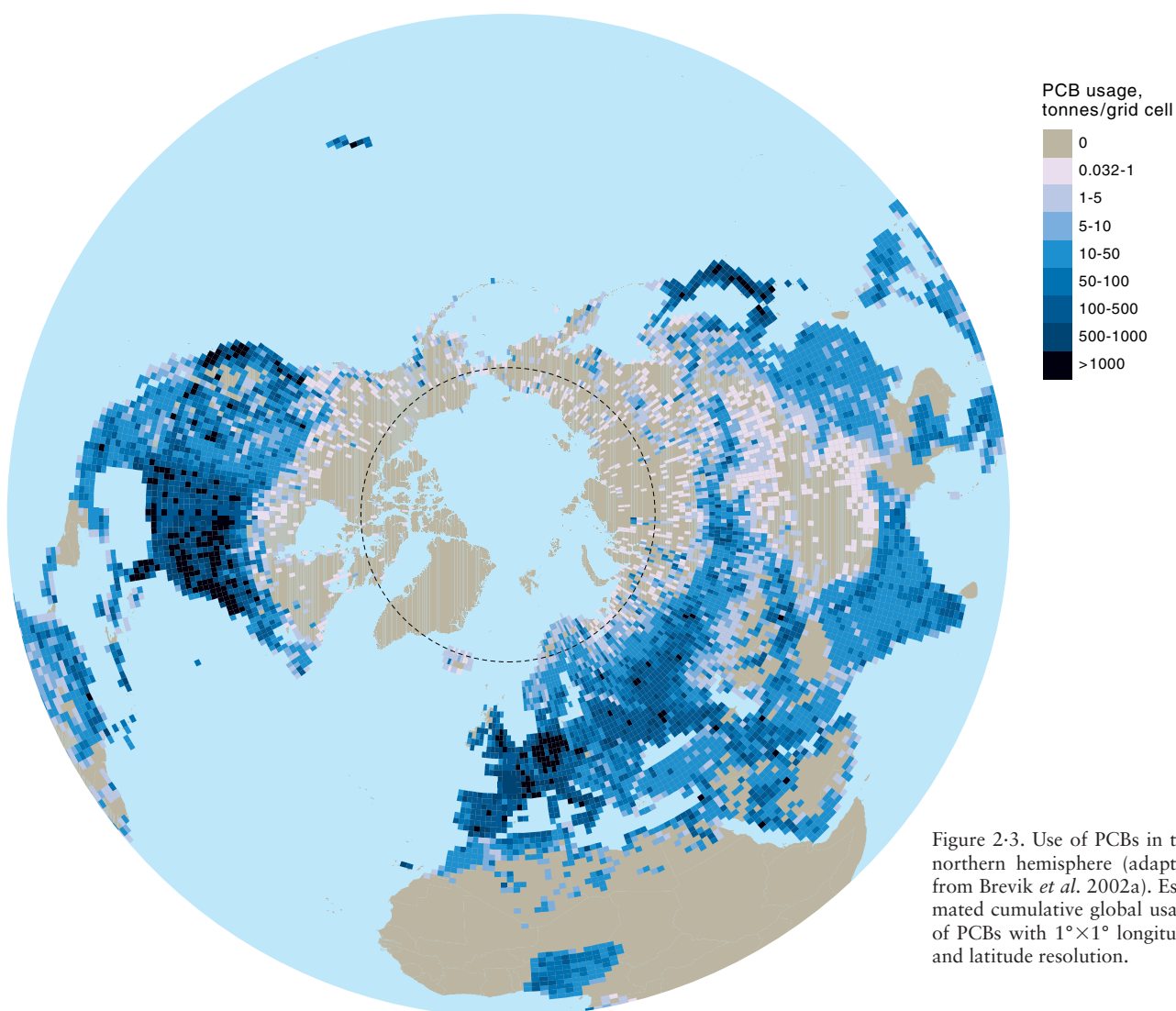

Figure 2·3. Use of PCBs in the northern hemisphere (adapted from Brevik *et al.* 2002a). Estimated cumulative global usage of PCBs with 1°×1° longitude and latitude resolution.
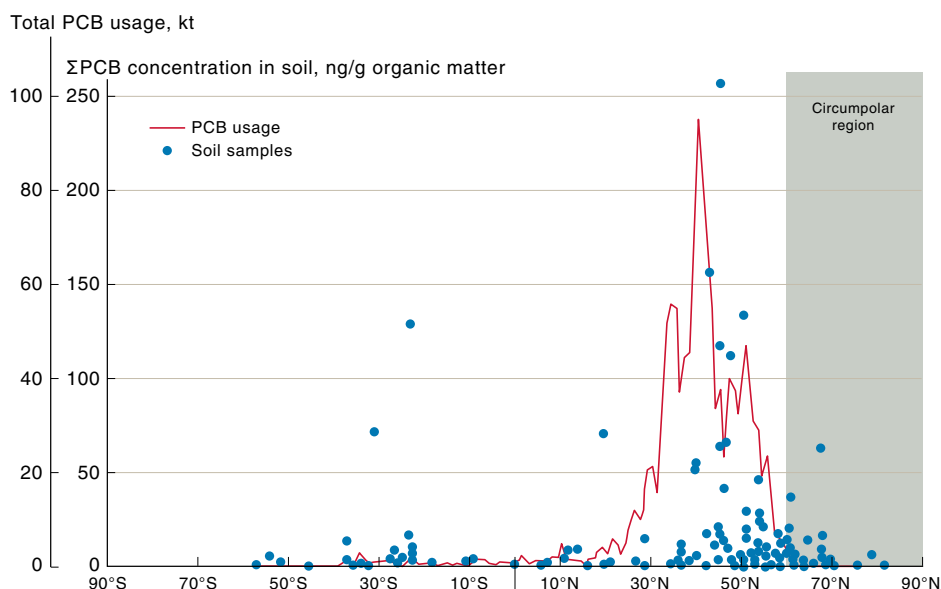
Total PCB usage, kt

Figure 2·4. The latitudinal distribution of global PCB usage and PCBs in surface soils from Ockenden *et al.* (2002) illustrating the large reservoir in soils of the north temperate zone (45-60°N latitude).

PCBs in surface soils derived from a global survey (Ockenden *et al.*, 2002) is shown in Figure 2·4 along with the latitudinal distribution of PCB usage.

Using the data from the global background soil survey and information on the latitudinal land surface area and soil organic matter content, Ockenden *et al.* (2002) estimated that 45 kt of PCBs were present in background surface (0-5 cm) soils globally. A further burden is present in the sub-surface (>5 cm depth) soils. Adding estimates of the burden in the sub-surface (5-20 cm; 22.5 kt) and urban (0.2 kt) soils increases the estimated burden in soils globally to approximately 67 kt. This is close to recent estimates of the total emissions of PCBs into the environment, of 82-100 kt (Wania, 1999; Axelman and Broman, 2001).

Russia discontinued production of PCB in 1992 (AMAP, 2000). In a recent Russian inventory, it was found that approximately 27 kt of PCB is currently still in circulation in PCB-containing equipment in Russia and therefore represents a source to the environment (AMAP, 2000). Current quantities of PCB wastes and amounts that have been released from equipment or spilled during dismantling were an additional 4.4 kt. The Arctic Council Action Plan against Pollution (ACAP) has initiated a cooperative project to assist Russia in phasing out PCBs and in dealing with PCB-contaminated waste.

Technical HCH and lindane
The use of a mixture of α-, β-, γ-, and δ-HCH isomers, known as technical HCH, began in 1943, and global consumption since then has been estimated to be about 10 000 kt (Li *et al.*, 1998a). Technical HCH use was banned in most western countries and Japan in the 1970s but continued in India, Russia and China. China is reported to have been the major world producer accounting for about 4500 kt between 1945 and 1983 (Li *et al.*, 1998b; Li, 1999a). In 1990, India banned the technical product for agricultural use but kept it for public health uses. The circumpolar use pattern for technical HCH in 1980 and 2000, adapted from Li (1999b), is shown in Figure 2·5.

Lindane, containing almost pure γ-HCH (the only insecticidally active isomer), replaced technical HCH in Canada, the U.S., and western Europe during the late-

1970s to early-1980s and in China in 1991. Worldwide, lindane usage between 1948 and 1993 was estimated to be 720 kt (Voldner and Li, 1995). Although lindane is still important on a global scale, many countries have restricted or eliminated its usage. Breivik *et al.* (1999) give the total lindane application in Europe as 81 kt between 1970 and 1996, and 2.2 kt in 1996. According to Centre International d'Études du Lindane (CIEL, 1998), the average lindane consumption in Europe was 2.1 kt/yr from 1992 to 1997. France was the major user of lindane in Europe and in the world during this period, with an annual average consumption of 1.6 kt (CIEL, 1998), more than 76% of total lindane usage in Europe. In July 1998, lindane usage was stopped in France (CIEL, 1998). Lindane use in Sweden, Finland and other countries bordering the Baltic Sea, except Russia, was approximately 0.001 kt in 1995 (HELCOM, 2001). Estimated lindane use in Russia was 0.019 kt in 1995, a decrease from 0.044 kt in 1990 and 0.657 kt in 1985 (HELCOM, 2001). Lindane use was severely restricted in Russia in 1987.

Lindane became one of the top ten insecticides used in Canada during the 1990s (Environment Canada, 1992). However, pesticide information from Canadian companies is proprietary; therefore, surrogate cropland information was used to estimate lindane usage for Canada (Li and Bidleman, 2003). Intensive use of lindane on croplands was concentrated in the prairie region of Canada including the provinces of Alberta, Saskatchewan, and Manitoba where it is used as a seed treatment on canola (Waite *et al.*, 2001). The other major use is as a seed treatment on corn in eastern Canada. Annual lindane applications in Canada to canola and corn seed are estimated to have increased from approximately 0.163 kt in 1970 to 0.477 kt in 2000, with a cumulative usage of about 9 kt over this time period.

Information on lindane use patterns in the U.S. is limited, especially in the case of quantities used for seed treatment (Li and Bidleman, 2003). Direct spray application of lindane to crops was estimated to be 28 kt/yr in the mid-1990s, with 81% on pecans grown in the southeastern U.S. (NCFAP, 2001). Based on the National Center for Food and Agricultural Policy (NCFAP) survey, it seems likely that use of lindane in Alaska during the 1990s was negligible.
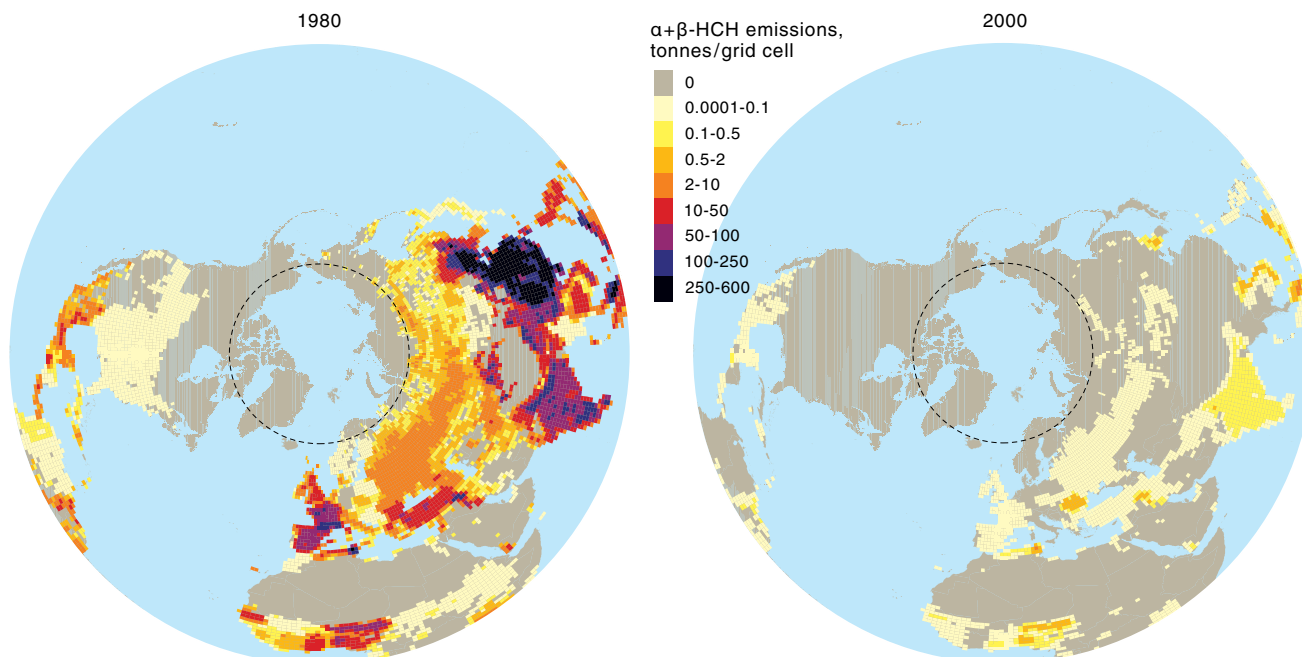
Figure 2·5. Use of technical-HCH in the northern hemisphere in 1980 and 2000 (adapted from Li and Bidleman, 2003).

Only 3.2 kt of lindane was applied in China between 1991 and 2000. The rest was exported or stockpiled. Consumption of lindane in China was 0.50 kt in 2000 (Li *et al.*, 2001a; Li and Bidleman, 2003).

DDT

Bans on the use of DDT were introduced in the U.S., Canada, and Japan and in most western European countries in the early-1970s. However, DDT production in China, India, Russia, and possibly other countries continued during the 1970s and 1980s. DDT production peaked in China during the late-1970s and was phased out in 1984 (Li *et al.*, 1999). DDT use in Russia continued until 1990 when 0.084 kt was reportedly used, down from 0.463 kt in 1980 (HELCOM, 2001). The total estimated global usage of DDT in agriculture from 1950 to 1993 is approximately 2600 kt (Voldner and Li, 1995). Between 1945 and 1972, the total cumulative production in the U.S. was 1340 kt, with domestic sales accounting for 645 kt and the rest exported. DDT production was discontinued in 1972 when some producers ceased operations. According to information provided to UNEP as part of the Stockholm Convention negotiations, DDT production continues in China and India, for use in fighting malaria and other insect-borne diseases in over 25 countries. The largest known current producer is India (approximately 0.007 kt/yr).

The gridded global annual usage of DDT on farmland for 1980 and 2000 is shown in Figure 2·6. Total global DDT usage in agriculture for 1980 was around 40 kt, and around 0.1 kt for 2000. Current uses for disease vector control in tropical countries are much larger
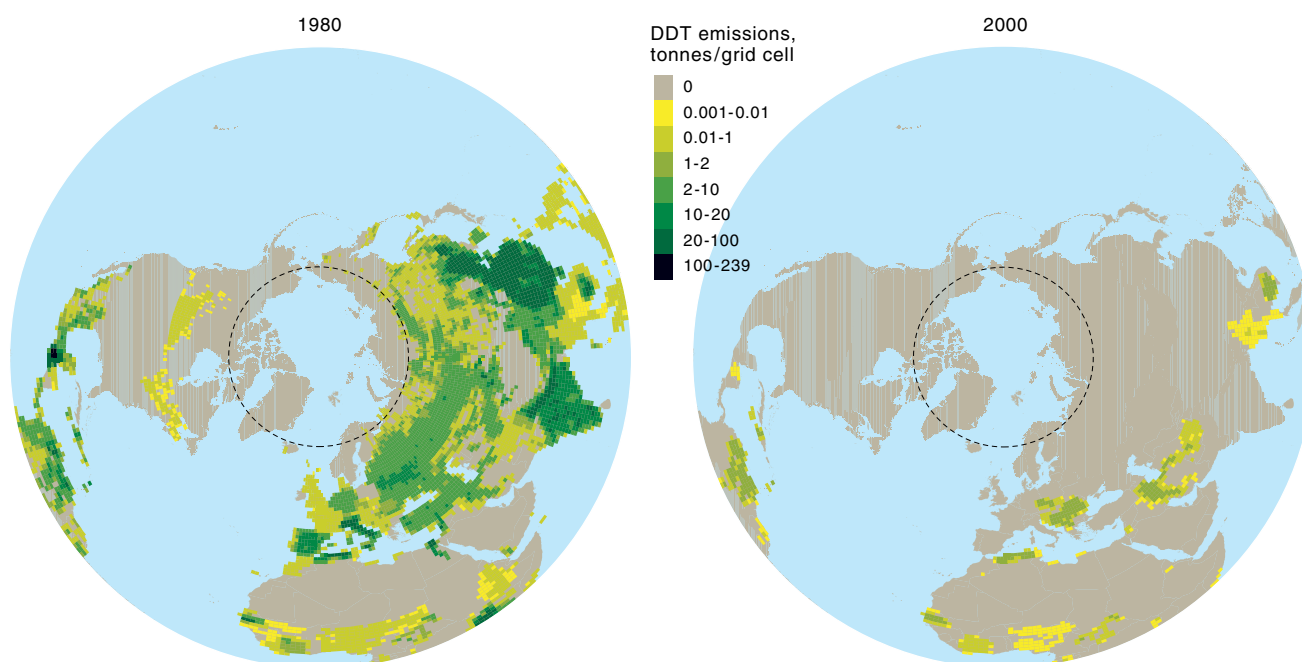

Figure 2·6. Use of DDT in the northern hemisphere in 1980 and 2000 (Li and Bidleman, 2003).

than agricultural uses; however, they are declining (UNEP, 2002). For example Mexico used about 1.80 kt of DDT in 1991. This was reduced to 0.497 kt in 1997 and further reductions are planned (UNEP, 2002). The trade publication *Europa Chemie*, gave India's cumulative DDT usage to 1989 as 280 kt for malaria control and 50 kt in agriculture (Li and Bidleman, 2003).

Polychlorobornanes and polychlorinated camphenes (toxaphene)

The major use region for toxaphene was the U.S. cotton belt, however, significant uses also occurred on other crop types. In 1983, toxaphene registration was canceled by the U.S. Environmental Protection Agency (EPA) and was banned in the U.S. in 1986. Use of toxaphene continued in Central America and Mexico until the early-1990s. Production for use in this region took place in Nicaragua until 1991. The total toxaphene residues left in agricultural soils in the U.S. at the beginning of 2000 are estimated to be about 29 kt. In 2000, almost 20 years after banning the use of this pesticide, approximately 0.360 kt of toxaphene was estimated to be emitted from agricultural soils in the U.S. (Li, 2001; Li *et al*., 2001b). Total use in the U.S. and Mexico/Central America was estimated to be 540 kt.

The former Soviet Union was also a significant producer and user of polychloroterpenes. This insecticide was introduced in the former Soviet Union in the 1950s and was still widely used in Russian agriculture at the end of the 1980s. The total toxaphene usage within the former Soviet Union was less than 100 kt (Voldner and Li, 1993; 1995) and was applied mostly in the Ukraine (Kundiev and Kagan, 1993). Toxaphene was still used to control sugar beet pests in 1993 (Kundiev and Kagan, 1993). As of 1992, toxaphene was categorized as a 'severely restricted' pesticide in Russia (Voldner and Li, 1993).

The former East Germany was a major producer and exporter of polychloroterpenes under the name 'Melipax' until 1990 (Heinisch *et al*., 1994).

China produced toxaphene between 1967 and 1972 with a maximum annual production of approximately 1 kt in 1970 and a total production around 3.6 kt (Li and Bidleman, 2003).

With the signing of the Stockholm Convention, toxaphene is likely to be consigned to the history books. Information supplied to UNEP as part of the Stockholm Convention negotiations suggests it is no longer produced.

Diene-organochlorine insecticides

Members of the large diene-organochlorine group (including chlordane/heptachlor, dieldrin/endrin/aldrin, mirex and chlordecone) were formerly used as insecticides and use-information was provided in the previous AMAP POPs assessment (de March *et al*., 1998). Chlordecone, mirex, aldrin, endrin and chlordane are included in the UN ECE POPs Protocol under the LRTAP Convention. Chlordecone has not been measured in Arctic biota or abiotic samples. This chemical was marketed in the U.S. as Kepone and pesticide registration was canceled in the U.S. in 1978 following widespread contamination of the James River in the eastern U.S. from factory releases. Mirex, formed by further chlorination of chlordecone, was more widely used as an insecticide, termiticide, and flame retardant. Total production in the U.S. was esti-

mated to be 1.5 kt, however, global production has not been estimated. The UNEP POPs survey indicated that there is no current mirex production. China, however, requested a production exemption for mirex for use as a termiticide and it is therefore likely that minor uses remain.

Chlordane

Technical grade chlordane is a mixture of at least 120 compounds, with the major constituents being *cis*- and *trans*-chlordane, heptachlor, *cis*- and *trans*-nonachlor, chlordene, and others (Dearth and Hites, 1991). Chlordane was released into the environment primarily from its application as a soil insecticide and termiticide. The U.S. was the major world producer and user of chlordane. However, there was limited use in western Europe, the former Soviet Union and tropical Asian countries. In the U.S., chlordane was used extensively prior to 1983, and from 1983 to 1988 it was registered for termite control. In 1997, the sole U.S. manufacturer of chlordane voluntarily ceased production at all of its national and international facilities. There are production facilities in Singapore and China, however.

Aldrin, dieldrin, endrin, and heptachlor

World sales of aldrin and dieldrin ceased in 1991 when the major manufacturer voluntarily stopped production. Endrin production ceased in the mid-1980s. Old stocks of these chemicals, particularly dieldrin, were, however, donated to African countries in the 1980s-90s for insect control, so emissions to the environment have continued (UNEP, 2002). Dieldrin was mainly used as a soil insecticide. In tropical countries it was used for the control of locusts and for disease vector control.

Endosulfan

Use of endosulfan in the U.S. has recently been estimated to be 0.64-0.95 kt per year (USEPA, 2001). Endosulfan is also used in Canada and Europe. Global use is thus estimated to be in the range of 1-2 kt per year. It is registered for use on a wide variety of speciality crops (pecans, pumpkins, squash). It is applied by boom sprayer and by aircraft, and thus, has the potential for significant dispersal in the environment.

Butyltins

TBT and other organotin compounds were initially used in agriculture. Subsequently, TBT has had wide application as a marine antifoulant starting in the 1960s. It has also been used as a wood preservative. TBT is found to provide effective protection for boat hulls at release rates of less than 4 μg/cm^2/day, and has been a popular antifoulant because it maintains its efficacy for up to five years compared to about three years for other conventional applications. TBT's most important entry route to the sea is directly from boats, aquaculture pens, moorings, and industrial cooling pipes to which products containing it have been applied. It may also enter ocean waters from municipal waste water and sewage sludge.

Organotin-stabilized PVC is used in a wide variety of applications including: pipes for drinking water, waste water, and drainage; packaging materials; and, window frames. The organotin constituents have been shown to leach from PVC and other materials leading to contami-

nation of food, drinking water, municipal water and, sewage sludge (Forsyth *et al*., 1992; 1994; Fent, 1996b; Forsyth and Jay, 1997). In a Japanese study, plastic products such as baking parchments of siliconized paper, polyurethane gloves, dish-washing sponges, and cellophane film for wrapping food bought from a supermarket, were found to contain MBT, DBT, and TBT (Takahashi *et al*., 1999). No information is available regarding leaching from PVC materials at dump sites, but this is a potential emission source to the environment in Arctic communities.

TBT is degraded by sequential debutylation to DBT, MBT and eventually to relatively non-toxic inorganic tin compounds, primarily by organisms. The breakdown of TBT is much slower in anaerobic sediments than in water (Clark *et al*., 1988), and therefore, contaminated sediments may act as an important environmental reservoir for TBT as well as MBT and DBT, long after their use has been curtailed.

Most circumpolar and northern European countries now partially regulate the use of TBT (France, 1982; U.S., 1986; U.K., 1987; Canada, 1989; Europe, 1991). Regulations vary, but generally, only controlled release formulations are permitted and TBT-based antifoulants are prohibited for boats smaller than 25 m. The U.N. International Maritime Organization (IMO) has agreed to a global ban on new use of TBT on ship hulls from 1 January, 2003. After 2008, TBT-based antifouling paints must be removed from ship hulls or encapsulated with an impermeable paint so no leakage to the environment can occur.

Global production of organotin compounds was estimated to be 50 kt in 1992 (Mercier *et al*., 1994). Biocides (primarily trialkyltins) make up approximately 20% of the total annual production (Bennett, 1996) with PVC stabilizers (primarily mono- and dialkyltins) being approximately 70% (Hoch, 2001). Total bis(tributyltin) oxide (TBTO) production in the Federal Republic of Germany, was estimated to be 2.0 kt, of which 70% was used in antifouling paints, 20% as a wood preservative, and 10% as a preservative in textiles, leather, and other materials (WHO, 1990). No estimates are available for current annual global consumption or for use patterns (Hoch 2001).

HCB and pentachlorobenzene (PeCBz)
HCB is produced as a by-product in the production of a large number of chlorinated compounds, particularly lower chlorinated benzenes, and in the production of several pesticides. In the 1960s, it had limited use as a fungicide. HCB is emitted to the atmosphere in flue gases generated by waste incineration facilities and metallurgical industries. Both HCB and PeCBz have previously been identified as by-products from production of chlorinated solvents (Environment Canada, 1993; USEPA, 1999c).

PeCBz was used in dielectric fluids in PCB-containing transformers. A Canadian survey found that up to 0.2 kt of PeCBz was in use in transformers in the early-1990s. However, this figure is now out of date due to the removal and destruction of most PCB-containing equipment. Nevertheless, it illustrates that older PCB containing devices in many circumpolar countries are potential sources of PeCBz. PeCBz is also an impurity in technical

HCB used in the manufacture of various substances such as pentachlorophenol, pentachlorothiophenol, and pyrotechnical products (HELCOM, 2001).

A recent assessment of global sources of HCB (Bailey, 2001) concluded that total current emissions could be around 0.023 kt/yr with a possible range between 0.012 and 0.092 kt/yr (Bailey, 2001). A substantial portion of the HCB measured in the atmosphere had unidentified sources and/or was due to revolatilization (i.e., currently known emissions could not account for prevailing global air concentrations). Russia was estimated to emit 0.011 kt/yr of HCB in 1995, with other countries bordering the Baltic Sea accounting for about 0.003 kt/yr (HELCOM, 2001).

OCS
Maximum emissions of OCS in the Great Lakes region of North America occurred in the 1960s (USEPA, 1999a), probably due to disposal of wastes related to chlorine manufacturing using graphite electrodes, a process abandoned in the 1970s. In Norway, emission of OCS and other chlorostyrenes was traced to production of magnesium using graphite electrodes (Lunde and Ofstad, 1976). Recent measurements have been made in Germany (Bester *et al*., 1998), however, in general, emissions and use of OCS are not well documented. Little is known about global emissions of OCS, however, magnesium production and chlorine manufacturing were historically important sources (USEPA, 1999a). Hydroxyheptachlorostyrene, a metabolite of OCS, was identified recently as a major hydroxylated metabolite in polar bear and human plasma in the Arctic (Sandau, 2000; Sandau *et al*., 2000).

PCDD/Fs
PCDD/Fs enter the environment as by-products of industrial processes. The most significant sources are low-temperature, incomplete incineration of chlorine-containing materials such as plastics. Other major sources include thermal processes, such as motor vehicle fuel combustion in countries where leaded fuel containing chlorine scavengers is still used, and metallurgical industries. Pulp and paper mills using chlorine in the bleaching process have been important sources for inputs to the aquatic environment. PCDD/Fs are also trace contaminants in chlorophenoxy herbicides, PCB formulations, and chlorophenol wood preservatives.

Few studies are available estimating circumpolar emissions of PCDD/Fs. Rough estimates of the global emissions of PCDD/Fs are available from Brzuzy and Hites (1996). In addition, an overview of the current status of national and regional emission inventories for PCDD/Fs globally can be found in UNEP (1999). This report includes estimates of PCDD/F emissions for northern Europe, Canada, the U.S., and Japan. Japan and the U.S. were considered the largest sources of PCDD/Fs (5300 g TEQ/yr and 2700 g TEQ/yr, respectively). Sweden, the only Nordic country in the survey, had very low annual estimated PCDD/F fluxes (22 g TEQ/yr) while Canadian emissions were estimated to be 290 g TEQ/yr.

PAHs
PAHs can be classified by their source type: petrogenic, biogenic, and pyrogenic. PAHs of petrogenic origin are

related to petroleum, including crude oil and its refined products. The presence of naphthalene and its alkyl-substituted homologues in sediments is characteristic of unweathered petroleum (Robertson, 1998). The naphthalene : phenanthrene ratio is much greater than 1.0 for most petroleum types. PAHs of petrogenic origin are also characterized by homologous families of related PAHs (naphthalenes, phenanthrenes and dibenzothiophenes), where the parent PAH for each family is less abundant than the alkylated homologues (Page *et al.*, 1999). PAHs of biogenic origin are generated by biological processes or by the early stages of diagenesis in marine sediments (e.g., perylene) (Venkatesan, 1988). PAHs with 4- to 6-ring hydrocarbons are generally of pyrogenic origin and are generated by the combustion of fossil fuels and recent organic material. The relative abundance of these PAHs to 2- to 3-ring hydrocarbons can be used to help distinguish between petrogenic and pyrogenic sources (Robertson, 1998). PAHs in the atmosphere are primarily from combustion of fossil fuels to produce electricity and heat, vehicular exhausts, forest fires, as well as industrial activities such as non-ferrous and ferrous metal production, and fertilizer production. PAHs detected in the Arctic atmosphere reflect contributions of emissions from middle and high latitudes in the circumpolar countries (Hoyau *et al.*, 1996; Halsall *et al.*, 1997; Masclet *et al.*, 2000).

PCNs

Until the 1970s, PCNs were high volume chemicals, with the worldwide production being approximately 9.0 kt/yr in the 1920s (Jakobsson and Asplund, 2000). Production of PCN decreased significantly after 1977. The production of PCNs in the U.S. stopped in 1980. Given the relatively high production volumes in the 1920-1930s, it seems likely that total PCN production was in the range of 200-400 kt. Crookes and Howe (1993) concluded that it was not possible to derive a global emission estimated for PCNs. Furthermore, Haglund *et al.* (1993) found that PCNs were contaminants in technical PCB formulations. Falandysz (1998) mentions technical PCBs as a potential source of PCNs and estimated a potential release of 0.1 kt based on the worldwide production of PCBs and a median value of 0.0067% PCNs in Aroclor and Clophen mixtures. A significant current source of PCNs is incineration (Crookes and Howe, 1993; Falandysz, 1998). Indeed, PCN congeners associated with combustion are elevated in Arctic air in winter (Harner *et al.*, 1998; Helm and Bidleman, 2003).

SCCPs

SCCPs are used mainly as extreme temperature additives in metal working fluids for a variety of engineering and metal working operations such as drilling, machining/cutting, drawing, and stamping (Environment Canada, 1993; Tomy *et al.*, 1998). They are also used in paints and sealants and have a minor but environmentally significant use as fat liquors in the leather working industry. Due to concerns about the toxicity, bioaccumulation, and persistence of SCCPs, use of these chemicals is declining as users switch to alternative products. Use since the 1940s, however, has been very high compared to most aliphatic chlorinated hydrocarbons of similar molecular weight (Table 2·1). Global manufacturing capacity is estimated to be 50 kt/yr.

MCCPs

MCCPs are mainly used as flame-retarding plasticizers in polyvinyl chloride plastics and releases to the environment are relatively small compared to production. MCCPs are large-volume production chemicals with global capacity estimated to be 0.25 kt/yr (Muir *et al.*, 2000a; OSPAR, 2000), and a steady production during the 1990s. Thus it is likely that over 5000 kt have been produced since the mid-1970s when production volumes were significantly increased. Annual releases of MCCPs to air and water in western Europe were estimated to be 1.87 kt in 1998, compared with production of 55 kt (OSPAR, 2000). There are, as yet, no reports on these compounds in the Arctic environment.

TeBDE and PeBDE

TeBDE and PeBDE compounds have been used since the 1970s as flame retardants in, among other things, polyurethane foams (de Boer *et al.*, 2000). The commercial PeBDE product is comprised mainly of pentabromodiphenyl ether with tetra- and hexabromodiphenyl ether impurities (Hardy, 2001; de Boer *et al.*, 2000). Annual worldwide production of PeBDE in 1990 was estimated to be 4.0 kt (Arias, 1992) and use increased during the 1990s. Global use in 1999 was 8.5 kt, of which >90% was in North America due to a phase-out of use in Europe (BSEF, 2000). Assuming a steady increase in production since the early-1980s, this implies a total production in the range of 70-120 kt. Environmental concentrations were increasing during the 1990s in the Canadian Arctic (See Section 5.4.6).

OcBDE and DeBDE

The main use of OcBDE and DeBDE technical products is in high impact polystyrene used to manufacture electrical enclosures (e.g., television sets). The major component of the OcBDE technical product is a heptaBDE as well as hexa-, octa- and nonaBDE impurities. Small amounts of octa- and nonaBDEs are found as impurities in DeBDE. A minor but important use of DeBDE is in flame-retarding of fabrics where it is applied as a fabric back coat encapsulated in latex (Hardy, 2001). Worldwide (i.e., mainly western Europe and North America) use of OcBDE and DeBDE technical products was 6.0 and 30 kt respectively in 1990 (Arias, 1992). Global demand for OcBDE and DeBDE was 3.8 kt and 54.8 kt, respectively, in 1999. Assuming a gradual increase in production since the early-1980s, this implies a cumulative production to date of 500-800 kt Oc- and DeBDEs. Most of this production was used in areas that are potential source regions for atmospheric transport to the Arctic, i.e., countries of the western Pacific/eastern Asia, North America and western Europe.

Other brominated flame retardants

Hexabromocyclododecane (HBCD) and TBBPA are other major brominated flame retardants. HBCD has replaced pentaBDEs in Europe, with 8.9 kt used in 1999 (BSEF, 2000). HBCD is produced by bromination of cyclododecane in a batch process and has been used for about 20 years. TBBPA is the major brominated flame retardant in current use primarily in electronic circuit boards (121 kt use globally in 1999; BSEF, 2000). TBBPA is covalently bonded into most materials but

some TBBPA is not bound (Sellström and Jansson, 1995), leading to some environmental releases, though probably minor compared to PBDEs.

Perfluoroalkyl sulfonates
Perfluorinated surfactants are employed for industrial and commercial applications and are used in lubricants, paints, polishes, food packaging, and fire-fighting foams (Hekster *et al.,* 2002; Key *et al.*, 1997). PFOS is an important perfluorinated surfactant as well as a precursor to other perfluorinated surfactants (Hekster *et al.,* 2002; Key *et al.*, 1997). In 2000, the estimated annual U.S. production of PFOS was 2.9 kt, but as a result of the 3M Company's phase-out, no PFOS production is anticipated in the U.S. in 2003. Total production of all fluorinated surfactants (anionics, cationics and neutrals) was 0.2 kt in the mid-1970s (Fielding, 1979), which suggests that a large increase in PFOS production occurred during the past 25 years. Assuming similar production volumes for the past ten years and smaller volumes since the introduction of these chemicals in the late- 1940s, it seems reasonable to estimate that at least 50 kt have been produced. Most of this production would have been released into the environment due to open uses as surface treatments. Production of PFOS, or its precursors, by other manufacturers outside of the U.S. or European Union may occur but is not presently documented. The properties of PFOS suggest that it is a poor candidate for long-range atmospheric transport. These facts have previously led to speculation that the global dissemination of PFOS must occur via an airborne neutral derivative that yields the free acid upon degradation (Renner, 2001). Long-range transport by ocean currents cannot be ruled out given the stability of PFOS.

Perfluoroalkanoic acids
Like PFOS, these compounds, particularly perfluorooctanoic acid (PFOA), are employed for industrial and commercial applications and are used in lubricants. PFOA has a unique application as a plasticizer in the fluorinated polymer Teflon®. PFOA was detected at low levels in a global survey of marine and freshwater biota, which included ringed seals (*Phoca hispida*) and polar bears, but results were not reported (K. Kannan, Michigan State University, pers. comm., 2002). No production information is publicly available on the perfluoroalkanoic acids.

2.3.2. **Local/regional sources within the Arctic**

Local sources of POPs are considered to be only minor contributors to contamination of the Arctic environment when considered on a continental or ocean-wide scale. On a local scale, however, household heating in settlements, burning of hydrocarbons for electricity and transport, and incineration and open burning of garbage, contribute significantly to the input of organic pollutants such as PAHs. Emissions of PCDD/Fs from these combustion sources may also be important in Nunavut (Canada) although considered very minor compared to heavily populated regions of North America (Commoner *et al.*, 2000). In several Arctic regions, mineral exploration, coal mining and heavy industry account for the highest input of persistent pollutants such as PAHs and PCBs.

Current and former military bases throughout the circumpolar Arctic, especially those with older radar equipment, have been previously identified as sources and were discussed in the previous AMAP POPs assessment (de March *et al.*, 1998). Many of these sites have undergone cleanup which include removal of contaminated equipment and soils. For example, the cleanup of 21 sites in the Canadian Arctic is scheduled for completion in 2008 (Canada DND, 2001) and there have been similar campaigns in Alaska, Greenland and Norway. The situation in the Russian Arctic regarding PCB use at military sites is unclear. The Russian Ministry of Defence did not take part in the inventory of PCBs or PCB-containing equipment in Russia because their position was that PCB-containing equipment was not in use anymore (AMAP, 2000). Thus no information is available on the disposal of PCBs and PCB-containing equipment from military sites in the Russian Arctic.

Svalbard
On Svalbard, local coal mining activities and settlements are the major primary sources of POPs (Kovacs, 1997), with coal-fired power plants located in five settlements being sources of PAHs to the atmosphere. Calculation of sulfur- and particle distribution as primary indicators of contaminant sources for the coal mines at Longyearbyen and Svea suggests that mining activities could be a major source of PAHs to the Svalbard environment (Holte *et al.*, 1996; dos Santos *et al.*, 1996). It is also suggested that the Russian coal mines at Barentsburg represent comparable sources. In a study of profiles of pyrogenic PAHs in lake sediments on Spitsbergen, Rose *et al.* (2003) found highest fluxes of PAHs in Tenndammen, a lake within 20 km of the coal mining towns of Barentsburg and Longyearbyen.

The major sources of PAHs in marine sediments are thought to be of natural petrogenic origin resulting from petrogenic seepage from the sea bed and erosion of coal seams (Akvaplan-niva, 1998). Higher ΣDDT concentrations (0.38 ng/g dw) were found at a deep site in Kongsfjorden relative to nearshore sites in eastern Svalbard (Lomfjorden, Erik Eriksen Strait) which had ΣDDT <0.2 ng/g dw. OC concentrations in sediments near the settlements in Svalbard were not assessed, however (Akvaplan-niva, 1998). Hop *et al.* (2001) found higher ΣPCB and PAH concentrations in macrobenthos sampled near the settlements of Billefjorden, Grønfjorden, Adventfjorden, and Kongsfjorden in Svalbard. PCB profiles from fjords with Russian settlements had a higher proportion of lower chlorinated congeners compared to fjords with Norwegian settlements, probably because of local pollution and the different PCB products used in each community.

Coastal Norway and western Russia
PCBs have been found in surface sediments from harbors in northern Norway (Harstad, Hammerfest, Tromsø, Honningsvåg) and Russia (Kola Bay, Guba Pechenga) (Dahle *et al.*, 2000) with relatively high (10-100 ng/g dw) levels found in comparison with background sites reported previously in the previous AMAP assessment (de March *et al.*, 1998). PCB levels and congener composition among harbors was similar (higher chlorinated PCBs predominated) except for Guba Pechenga, where lower chlorinated PCBs predominated for unknown rea-

sons. No large differences in OC concentrations were found between Norwegian and Russian harbors. Harbors probably constitute hotspots for PCBs in the Arctic marine environment with higher concentrations (up to 10 times) relative to non-harbor areas.

In a follow-up study in Kola Bay (1997), much higher concentrations of most OCs in question were found compared to a control location (Guba Zapadnaya Litsa) (Savinova *et al.*, 2000a). The stations with the highest levels of ΣPCBs, toxaphene and HCB were located close to the harbor of Polarnyy City, situated on Kola Bay, 20 km north of Murmansk. Concentrations of ΣPCB near Polarnyy City ranged from 650 to 8700 ng/g dw while levels were 24 ng/g dw in sediments in the outer reaches of Kola Bay. A surprising observation was the presence of relatively high levels of toxaphene in surface sediments in Kola Bay (3.5-680 ng/g dw) and in Guba Zapadnaya Litsa (19-85 ng/g dw). Although there are few other toxaphene measurements in marine sediments for comparison, the geometric mean levels in both Kola Bay and Guba Zapadnaya Litsa are higher than observed in freshwater surface sediments in the Great Lakes (Pearson *et al.*, 1998) or in northwestern Europe (Rose *et al.*, 2001). This suggests significant use of toxaphene in northern Russia, at least in the Kola Peninsula, possibly for insect control in urban areas or on ships.

Jan Mayen

On the island of Jan Mayen, elevated PCB levels were found in soil within and in the immediate proximity of a dump used between 1960 and 1995 (Gabrielsen *et al.*, 1997). The source of the PCBs was seven transformers, each containing approximately 200 L of oil, that were emptied into the dump in the late-1970s. Despite extensive sampling, it was only possible to estimate the amount of PCB in the dump as being between 10 and 2000 kg. There was no evidence of local PCB contamination extending from the dump into the freshwater lake or to other areas on the island. Up until 1989, 2000-3000 L of lubrication oil and other waste products (white spirits, paint) were also dumped. The dump is located 25 m from the edge of a coastal cliff of porous vulcanic rock, which is subject to erosion, primarily by seawater. Currently, the rate of erosion is unknown.

Greenland

The distribution of persistent halogenated organics was studied during 2000 near the western Greenland villages of Quaqortoq (3500 inhabitants), Igaliko (30 inhabitants) and Usuk (background site 3-5 km from Igaliko) (Christensen *et al.*, 2002; Vorkamp *et al.*, 2002). The animals analyzed were shorthorn sculpin (*Myoxocephalus scorpius*), Greenland cod (*Gadus ogac*), spotted wolffish (*Anarhichas minor*), starry ray (*Raja radiata*) and blue mussels (*Mytilus edulis*). All concentrations of persistent halogenated organics were low in mussels. The highest concentrations of ΣPCBs and PBDEs were observed in fish from Quaqortoq followed by Igaliko and Usuk. This trend was not as pronounced for chlorinated pesticides, which implied that there were local sources of PCBs and PBDEs, but not chlorinated pesticides. The levels of PBDEs were 15-24 times lower than PCB levels measured in the same individuals, except for shorthorn sculpin collected at Quaqortoq, where the level of ΣPCBs

was 40 times higher. The results suggest that villages are sources of legacy OCs such as PCBs, as well as currently used PBDEs, to the nearby marine environment.

Previous studies of scallops (*Chlamys islandicus*) and sediments have shown that Thule Air Base is a local source of PCBs to the marine environment (Kjølholt and Hansen, 1986).

Canada

From 1996 to 2001, additional studies and remediation of old military sites contaminated with PCBs were conducted in the Canadian Arctic. Detailed assessments of PCB contamination were conducted at two sites in the eastern Canadian Arctic, Saglek Bay (58°29'N, 62°40'W) in northern Labrador, and Resolution Island at the southeastern tip of Baffin Island.

At Saglek Bay, high levels of ΣPCBs (more than 50 μg/g dw in soils) were found at a former military radar site (ESG, 2002). The cleanup from 1997 to 1999 effectively removed the terrestrial sources of contamination to the surrounding land and to the marine environment of Saglek Bay. ΣPCB concentrations in sediment cores from lakes near the former radar facility declined with increasing distance from the site (Betts-Piper, 2001). Four of eight lakes within 5 km of the site had elevated levels (>100 ng/g dw) compared to background sites 30 km away (0.3-17 ng/g dw) or to other remote lakes in the Canadian Arctic (Muir *et al.*, 1996a). The PCB congener profile in both the near-site and remote lakes had a clear Aroclor 1260 profile similar to the product used at the radar facility. Bright *et al.* (1995a) and Duskenko *et al.* (1996) reported similar results from a study of 24 military radar sites in the Canadian Arctic. They concluded that the radar sites were acting as sources of contamination to nearby lakes via aerial redistribution. This was confirmed at Saglek Bay by the detailed study by Betts-Piper (2001).

Marine investigations were conducted to study PCB contamination in Saglek Bay over three seasons from 1997 to 1999. These studies delineated PCB-contaminated sediments and quantified PCB uptake in the marine food chain, including benthic invertebrates, bottom-feeding fish, pelagic fish, marine mammals, and seabirds. They indicated that the contaminated sediments represented a source of PCBs to local wildlife. Inputs of PCBs to the marine environment occurred from a contaminated beach area associated with the original station. Sediment ΣPCB concentrations near this beach were 500 ng/g to 130 000 ng/g dw in the intertidal sediment, and 600 ng/g to 6200 ng/g dw in the Saglek anchorage. Concentrations declined exponentially with distance, approaching background concentrations (<2 ng/g) within 6-10 km (ESG, 1999; 2002). PCBs were also present in deepwater sediments of the bay, particularly immediately offshore and west of the contaminated beach (Figure 2·7).

The samples of invertebrates collected from the immediate vicinity of the contaminated beach contained PCBs at high concentrations, consistent with the concentrations measured in the beach sediment (ESG, 1998). Snails and scuds from the intertidal area had ΣPCB concentrations of 8000 and 49 000 ng/g ww, respectively. The concentration in sea urchins from this area was slightly lower (5200 ng/g ww). Invertebrate tissue con-
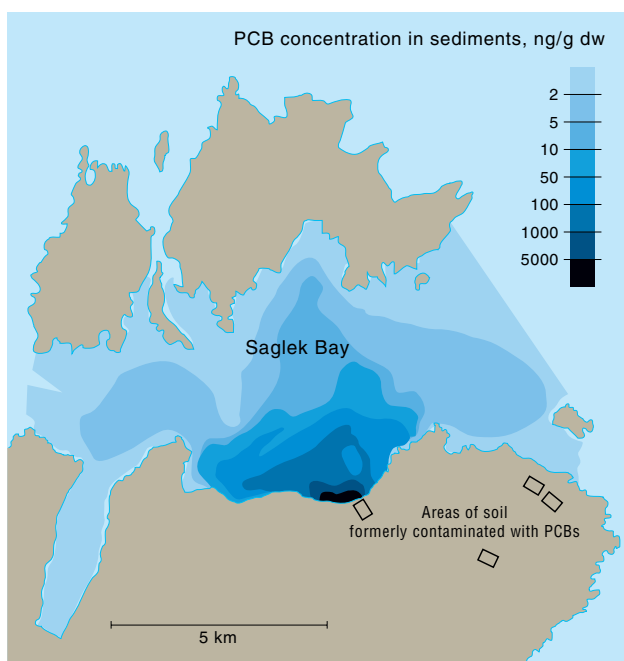
Figure 2·7. PCB contamination in marine sediments of Saglek Bay in northern Labrador based on 243 surface sediment sample results from 1997, 1998 and 1999 indicating the dispersion from a contaminated beach.

taminant concentrations generally return to near-background concentrations within 7-10 km of the formerly contaminated beach.

ΣPCB concentrations were relatively high in shorthorn sculpin sampled in the nearshore area close to the contaminated beach, exceeding 1000 ng/g ww (whole body minus liver, Aroclor equivalent) in two-thirds of the samples and exceeding 10 000 ng/g ww in a few samples. Concentrations also exceeded 1000 ng/g ww in some shorthorn sculpin samples collected at sites up to 1.5 km east and 3 km west of the beach. PCB concentrations in muscle and liver of Arctic char (*Salvelinus alpinu*s) did not vary with the proximity of the fish to the contaminated beach (ESG, 1998). PCB concentrations ranged from a low of 13 ng/g ww to a high of 66 ng/g ww (Aroclor equivalent), with both of these extremes measured in char collected at the Okak reference site (ESG, 1998). These were similar to results for PCBs in anadromous char from the Labrador coast (Muir *et al.* 1999c; 2000c) and are consistent with the largely pelagic feeding habits of char.

ΣPCB concentrations in seals from the Saglek Bay area varied over a wide range, from a low of 500 ng/g ww in the adipose tissue of one 11-year-old seal, to a high of 9400 ng/g ww in a 10-year-old seal. The result for this seal is exceptionally high, exceeding the results for the other seals by a factor of 4-6. It is also much higher than results reported for ringed seals from the community of Nain, further south on the Labrador coast, and elsewhere in the Arctic (Section 4.4.6.1).

Black guillemots (*Cepphus grylle*) in Saglek Bay, Labrador also had elevated ΣPCB concentrations due to marine sediment contamination around the former military site. ΣPCB concentrations in liver of nestlings ranged from 15 to 46 ng/g ww in a reference group, 24 to 150 ng/g ww in a group from moderately exposed islands, and 170 to 6200 ng/g ww in the highly exposed beach

group. Biomarker responses were dose-dependent and in some cases, sex-dependent (see Section 6.3.3.3).

Similar contamination by PCBs was investigated at Resolution Island (61°35'N, 60°40'W) at the southeastern tip of Baffin Island in the eastern Canadian Arctic (ASU, 1997; 2001). Initial assessment of the site in the early-1990s showed it to be highly contaminated with PCBs (ESG, 1994). The site contained at least twenty buildings requiring demolition, along with a large amount of visible debris, tanks, and many barrels. Buildings in the communications complex contained electrical equipment suspected of containing PCBs, and other buildings contained asbestos. The total volume of soil which was contaminated with ΣPCBs at concentrations above 50 000 ng/g (exceeding soil guidelines for PCBs under the *Canadian Environmental Protection Act*) was estimated to be 5000 m³ with about 20 000 m³ contaminated at the 1000-50 000 ng/g level. Site remediation initially involved building barriers composed of a variety of oil absorbent booms across PCB leachate pathways to prevent further PCB migration. PCB-containing components and liquids from transformers were removed from the main station to the registered PCB storage facility on the site. An environmental assessment of contaminant migration to the marine environment made the assumption that PCB movement was controlled by the barriers and aerial transport of PCBs was insignificant. The assessment concluded that the site does not present unacceptable contaminant exposure conditions to humans, or terrestrial and marine wildlife (Golder, 1997). Remediation work conducted from 1997 to 2001 involved excavation and removal of highly contaminated soils and debris from dump sites on the island (ASU, 2001). This material was stored in sealed containers on-site for future disposal.

In addition to PCBs, some former military sites received significant DDT applications. The bioavailability of this localized DDT contamination to the terrestrial Arctic environment was examined in a study at an abandoned Long Range Aid to Navigation (LORAN) station located at Kittigazuit, Northwest Territories (69°16'56"N, 133°54'32"W) in the western Canadian Arctic (Nirwal, 2001). The study site received applications of DDT between 1948 and 1950. Despite the passage of time, soil concentrations have remained high (maximum ΣDDT = 210 000 ng/g dw), and the composition of ΣDDT compounds in soil still resembled the original pesticide formulation (59% *p,p'*-DDT). In soils, loss and degradation of DDT was less pronounced when compared to temperate and tropical environments. Samples of soil, sediment, willow (*Salix* sp.), grass (*Elymus* sp.), and Arctic ground squirrel (*Spermophilus panyi*) were collected at the LORAN station and at a nearby reindeer herding camp. Concentrations of ΣDDT in soils at the station ranged from 62 to 210 000 ng/g dw. Highest concentrations were found within an area of approximately 4024 m², while a smaller area (386 m²) at the herding camp had elevated concentrations as well. Samples of *Elymus* sp. and *Salix* sp. collected from the station had a higher median ΣDDT concentration compared to the area near the herding camp or to background sites. Higher ΣDDT was found in *Salix* sp. (12-10 000 ng/g dw) compared to *Elymus* sp. (3.2-1500 ng/g dw). The concentration and composition of ΣDDT in Arctic

Table 2·2. Examples of sites in Alaska known to be sources of POPs. This does not represent a comprehensive assessment.

Site	POPs are a concern	Contaminated wildlife	Affected subsistence	Reference
Adak Island (Aleutian Islands)	Yes	Likely	Likely	Technical Memorandum, ADEC website [1, 3]
King Salmon Air Station	Yes (solvents)	Likely	Unknown	ADEC website [1, 3]
Pribilof Islands	Fuels, POPs possible	Likely	Likely	ADEC website [1, 3]
St. Lawrence Island	Yes	Potential	Likely	ADEC website [1, 3]
Cape Romanzof Long Range Radar Site	Yes	Yes		ADEC website [1, 3]
Umiat (former Air Force Base on Colville River)	Yes	Very Likely	Yes	Army COE website [2, 3]
Operable Unit D, Fort Richardson	Yes	Unknown	Unknown	ADEC website [1, 3]
Dutch Harbor, Unalaska	Yes	Possibly	Possibly	Army COE website [2, 3]
Yakutat Airport	Yes	Unknown	Unknown	Army COE website [2, 3]
Barter Island (Kaktovik)	Transformers (PCBs)	Unknown	Unknown	Army COE website [2, 3]
Wildwood AFS	Dioxins?	Unknown	Unknown	Army COE website [2, 3]

[1] www.state.ak.us/dec/dspar/csites
[2] www.poa.usace.army.mil/fuds
[3] www.akaction.net/pages/mapping

ground squirrel livers were clearly the result of contamination at the study site. Liver concentrations at contaminated areas (maximum ΣDDT = 4300 ng/g lw) declined to background levels (maximum ΣDDT = 4.5 ng/g lw) with increasing distance from contaminated areas. Estimated contaminant exposures were below no-observed effect levels, but a significant relationship between liver size and ΣDDT concentration was found. The concentrations in ground squirrels from background sites in this study were below concentrations reported for Arctic ground squirrels in Alaska (Allen-Gil *et al*., 1997).

The contribution of atmospheric DDT dispersal and transport at Kittigazuit was negligible because an abrupt transition existed between soil contaminant levels at the sites, and samples collected immediately off-site. For example, the median ΣDDT concentration was 1300 ng/g dw at the LORAN station, and 540 ng/g dw at the reindeer herding camp. In comparison, results for soil samples considered representative of background conditions (3-10 km off site) were below the analytical detection limit of 20 ng/g dw.

A scenario comparable to that at Kittigazuit was also studied in the vicinity of Fort Churchill, Manitoba, on the western coast of Hudson Bay. Three years after aerial spraying for mosquito control, sampling within treated areas showed that the livers of collared lemmings (*Dicrostonyx groenlandicus*) contained 5400-41 000 ng/g lw of ΣDDT and livers of red squirrels (*Tamiasciurus hudsonicus*) contained 7400-17 000 ng/g lw (Brown and Brown, 1970), indicating the persistence and bioavailability of DDT in other terrestrial Arctic environments.

Alaska
Abandoned sites formally operated by both military and private entities constitute hundreds of known or potential sources of contaminants in Alaska. While most of these sites involve oil-based hydrocarbons (e.g., fuel spills, abandoned wells, etc.), many involve PCBs and OC pesticides as well. Many reports and other informa-

tion on POPs in Arctic and subarctic Alaska exist, but they have not been peer-reviewed and are not generally available. They do serve, however, to describe reliably what contaminants have been detected at these sites of concern. Sources include citations in published manuscripts, reports from a variety of organizations, and websites. Hurwich and Chary (2000) recently outlined and mapped POPs-based research in Alaska and some of these local areas of concern.

Environmental contamination in Alaska is often considered from a general or statewide perspective (i.e., large-scale inputs). Much of the local public awareness of contaminants, however, stems from concern about local sites. Point sources are not typically addressed by researchers studying contaminants, which serves to increase the anxiety of community members. Examples of site-specific concerns in Alaska are the numerous military sites targeted by the *Installation Restoration Program (IRP)* and the *Formerly Used Defense Sites (FUDS)* cleanup programs, which fall under the auspices of the U.S. Department of Defense (Table 2·2).

Table 2·2 is based on a survey of non peer-reviewed documents and websites. Very little effort is made to publish (in scientific journals) the results of studies at these sites and to inform local communities. Examples of documents include *Technical Memorandum: Proposed Biomonitoring Plan for the Nearshore Marine Ecosystems at Adak Island, Alaska. Adak Naval Complex, Adak, Alaska* (Task Order 0204, February 1999) and the *Report of Findings: Cape Romanzof Long Range Radar Site Military Cleanup, USDOI, Memo to Refuge Manager, Yukon Delta National Wildlife Refuge* (January 17, 1991).

The U.S. EPA Superfund National Priority List sites in Alaska include Adak Naval Air Station, Ketchikan Pulp Company, Fort Richardson (U.S. Army), Elmendorf Air Force Base, Eielson Air Force Base, Fort Wainwright, Standard Steel and Metals Salvage Yard, Alaska Battery Enterprises, Arctic Surplus, and King Salmon (US EPA, 2002).