This chapter considers how the changes described in the previous chapters will affect specific groups of contaminants - heavy metals, radionuclides, organochlorine compounds (OCs), and hydrocarbons. For each group, the significance of the recent shift to high Arctic Oscillation (AO) index will be discussed and then consideration will be given to the more general, long-term changes thought likely. To avoid repetition, direct, unsupported statements are made for which the arguments and citations have been provided in previous chapters. Connections in the contaminant pathways (Figure 1.2) will be emphasized, such as: 1) mobilization from global primary or secondary contaminant sources and/or a change in delivery pathways to Arctic ecosystems; 2) entry into the base of the food web from water, snow pack, ice, soil, and runoff; 3) shifts in the relative importance of the source of primary productivity in aquatic systems (ice versus aquatic or coastal versus deep ocean); 4) change in food web structure affecting the degree of biomagnification (bottomup effects); 5) change in the feeding ecology of key higher order consumers (top-down effects); and 6) change in the age structure of higher trophic order populations where contaminant concentrations in tissue are agedependent.

6.1. Heavy metals6.1.1. Lead, cadmium, zinc

Lead (Pb), cadmium (Cd) and zinc (Zn) are commonly released to the atmosphere through high-temperature processes or, in even greater quantities, to water through runoff, municipal discharges and dumping (Pacyna et al., 1995). In addition, anthropogenic Pb has had a unique, predominant source in leaded gasoline combustion. Although leaded gasoline has been largely phased-out in North America and Europe, it is still used in other regions, including much of Russia. Due to the strong atmospheric connection in winter between Eurasia and the High Arctic (Figures 3.2 a and b), long recognized in events such as Arctic haze (Hileman, 1983) and brown snow (Welch et al., 1991), much attention has been focused on the atmosphere as a means of transporting contaminant metals to the Arctic (Akeredolu et al., 1994; AMAP, 1998; Boutron et al., 1995; Pacyna, 1995; Rosman et al., 1993; Sirois and Barrie, 1999; Sturges and Barrie, 1989). Based on back trajectories, models, and stable lead isotope composition, the sources of atmospheric metals have been established primarily as Eurasia, including the industrialized areas of Western and Eastern Europe and the Urals (in particular Norilsk), and secondly North America - each of which supplies air masses to the Arctic at particular times during the year (Figure 3.2). The shift between AO- and AO+ conditions alters mean wind fields thereby effecting change in the balance and timing of air movement from these various source regions, but the

connections remain intact. Air transport from eastern North America and Western Europe strengthens under strong AO⁺ conditions, especially in winter, due to the intensification and extension northward of the Icelandic Low. Air mass trajectory changes, while probably shifting the pathway and rate of transport between temperate sources and Arctic sinks, will probably not change the net delivery of airborne contaminants substantially. This hypothesis could be tested by running transport models (e.g., see Akeredolu *et al.*, 1994) under AO⁺ and AO⁻ conditions.

The greatest leverage for change with aerosol metals resides in the wet and dry removal processes within the Arctic for which present knowledge is relatively incomplete. Because the Arctic is a poor trap for atmospheric metals associated with aerosols and particulates, sequestering < 10% of the emissions that pass through it (Akeredolu et al., 1994; Pacyna, 1995), there is considerable scope to enhance the deposition of airborne contaminants to surfaces by altering location and intensity of precipitation (Figures 3.4 a and 3.4 b) and/or by changing the balance between snow and rain (see, for example, Sherrell et al., 2000). Under AO+ conditions, the atmospheric corridor from eastern North America and Western Europe will become a more efficient trap for particulates, raining them out in the Nordic Seas and in the southern portion of the Eurasian Basin. Particle scavenging will generally increase wherever higher precipitation prevails, such as over northern Europe and the Eurasian Basin in general. Contaminants deposited on the eastern side of the Nordic Seas will then enter the Barents Sea and the Eurasian Basin via ocean currents. Contaminants deposited to the west will be delivered back into the North Atlantic via the East Greenland Current. Given this scenario, it seems likely that under AO+ conditions, metal-contaminated aerosols entering the Arctic near the prime meridian will be subject to enhanced scavenging en route. Larger areas of open water (Figure 3.8) mean that scavenging will tend to place a greater proportion of these airborne contaminants directly into the surface ocean rather than on the sea ice. The decline of aerosol metal concentrations at Alert after about 1991, ascribed by Sirois and Barrie (1999) to the collapse of industry following the break-up of the former Soviet Union, could also be explained partly by changes in wind and precipitation patterns at the end of the 1980s (Figures 3.2 and 3.4). Enhanced loadings to sea-ice surfaces under AO⁺ conditions are most likely to occur over the southern Eurasian Basin and this ice would then be exported back into the Greenland Sea.

The focus on the atmosphere as a pathway for the transport of metals from anthropogenic sources to the Arctic has to some degree diverted attention from the ocean. Sediment cores collected along the margins of the Eurasian and Canadian Basins (Figure 6.1) suggest that a major route for contaminant Pb to the Arctic Ocean



Figure 6·1. The major sources of contaminant lead transported to the Arctic are indicated by the stable lead isotope composition of sediment cores as being either Western Europe (indicated by a ²⁰⁶Pb:²⁰⁷Pb ratio of 1.14) or Eurasia (indicated by a ²⁰⁶Pb:²⁰⁷Pb ratio of 1.18) (adapted from Gobeil *et al.*, 2001a).

has been the same ocean current that transports radionuclides northward from the European reprocessing plants (Gobeil et al., 2001a). The residence time of Pb in surface water, which is relatively short (< 5 years), is still long enough to permit transfer of contaminant Pb from the North Atlantic and Nordic Seas into the Arctic (Gobeil et al., 2001a). Under AO+ conditions an even more efficient transfer of metals may be expected from Western Europe to the Arctic either via rainout in the air transport corridor to the northwest of Europe (Figures 3.2 and 3.4) or via coastal discharges to the North or Baltic Seas. Lead comprises four stable isotopes: ²⁰⁴Pb (1.48%), ²⁰⁶Pb (23.6%), ²⁰⁷Pb (22.6%) and ²⁰⁸Pb (52.3%), with the composition varying between geological reservoirs (Sangster et al., 2000). This variation has provided an incisive means of determining the sources of contaminant Pb in global environmental media, including Arctic aerosols and ice (Rosman et al., 1993; Sturges and Barrie, 1989; Sturges et al., 1993). Accordingly, Gobeil et al. (2001a) were able to relate the contaminant Pb accumulating in sediments along the Barents Sea margin to a western European source (²⁰⁶Pb: 207 Pb ~ 1.14) with ocean currents acting as the major transporting mechanism (Figures 3.17 and 6.1). Anthropogenic Pb in sediments near the North Pole, however, had an Eastern European or Russian composition (²⁰⁶Pb:²⁰⁷Pb~1.18) (Figure 6·1). Based on the distribution of anthropogenic Pb in the Arctic sediments, these authors proposed a transport scheme wherein Pb from these source areas enters the Arctic Ocean via the Laptev Sea, either entrained in ice or, perhaps more likely, in water carried in the Transpolar Drift (TPD) (Gobeil et al., 2001a). The observation that anthropogenic Pb was conspicuous in the Eurasian Basin margins but not in the Canadian Basin, led these authors to conclude that ocean and ice transport pathways during the peak Pb emission years (~ the last 60 years) must have been predominantly those associated with AO- conditions. Under AO⁺ conditions, pathways for ice, ocean currents and runoff change dramatically (Figures 3.2, 3.5, 3.14) such that contaminant metals entering the Russian shelves (atmospherically or by runoff) would be diverted to the east into the Canada Basin and toward the Canadian Arctic Archipelago (Gobeil et al., 2001a; Mysak, 2001). The pathways indicated by Pb contamination are probably relevant for other particulate-bound contaminants - for example some of the more highly chlorinated polychlorinated biphenyls (PCBs).

Atmospheric aerosols of Cd and Zn will to some degree behave like Pb, except that the predominant source of anthropogenic Pb is leaded gasoline as opposed to metallurgical industries and stationary combustion for Cd and Zn. Time series of aerosol composition at Alert (Sirois and Barrie, 1999) and records from ice cores (Boutron *et al.*, 1991, 1995) and glacial snow (Sherrell *et al.*, 2000) reveal contamination due to industrial activity in Asia, Europe and North America. Like Pb, Cd and Zn are poorly captured within the Arctic (<15%; Akeredolu *et al.*, 1994; Pacyna, 1995) and changes in precipitation patterns probably have the greatest potential to change metal delivery to surfaces.

Of these three heavy metals, Cd provides the greatest risk to wildlife and human health, as a result of bioaccumulation and biomagnification (Figure 6.2), especially into liver and kidney of marine and terrestrial mammals (Braune et al., 1999; Muir et al., 1999). Observed high concentrations of Cd in Arctic biota, however, appear to be natural and not obviously related to human activities except, possibly, at locations close to sources (<100 km). In consequence, significant changes in Cd exposure are likely to occur through changes in the natural cycle of Cd and not by changes in anthropogenic Cd pathways. An exception to this rule may occur locally when Cd contamination is accompanied by, or followed by, system changes that alter Cd biogeochemistry. Croteau et al. (2002) provide a clear example of where reductions in Cd loadings to a contaminated lake were accompanied by increases in pH with the consequence that organisms actually exhibited increasing Cd uptake.

In the Arctic Ocean, natural cycles completely dominate Cd fluxes and budgets (Macdonald *et al.*, 2000a). Cadmium follows soft body parts in the marine biogeo-



Cadmium, biomagnification factors

Figure 6·2. Pathways and biomagnification factors for cadmium in the Arctic marine food web. Biomagnification factors are based on dry weight concentrations in whole organisms for biomagnification to invertebrates and fish, and on wet weight concentrations for fish to muscle in top predators (for polar bear, liver was used instead of muscle) (from Muir *et al.*, 1999). In the case of the biomagnification factors from ringed seal to polar bear, the lower value is for seal blubber to polar bear liver, and the higher value is for ringed seal liver to polar bear liver.

chemical cycle and exhibits a strong correlation with phosphate (Boyle, 1988; de Baar et al., 1994). The interaction between the biogeochemical cycle and circulation of the world ocean results in sub-surface water of the North Pacific containing naturally higher Cd concentrations than that of the North Atlantic (by a factor of about 5 - see Bruland and Franks, 1983) which in turn makes the Pacific inflow through Bering Strait by far the dominant source of Cd to surface waters of the Arctic Ocean (Macdonald et al., 2000a). Reduced Bering inflow since the 1960s (Figure 3.20 a) probably entails a similar (15%) reduction of the supply of Cd to the Arctic Ocean from that source. The encroachment of Atlantic water into the surface of the Makarov Basin, seen under recent AO+ conditions, will further reduce the domain of Cd-rich water within the Arctic (Figures 3.13 and 3.15). The accompanying increased stratification and recycled production in the smaller Pacific domain of the Canada Basin will, however, tend to maintain Cd from runoff or atmospheric deposition at the surface. It is noteworthy that the Canadian Arctic Archipelago is the downstream recipient of water from the Pacific Ocean and, therefore, the recipient of Cd and nutrients from that source.

Recent work on metal-impacted lakes near a coppersmelting center in Quebec, Canada, shows that metal loadings (Cd, Cu, Zn) can alter ecosystem structure, causing the demise of medium to large benthic invertebrates and producing fish populations shifted to smaller sizes (Sherwood *et al.*, 2000, 2001). This suggests the strong possibility that contamination by these heavy metals could interact with the accumulation and biomagnification of other contaminants like mercury (Hg) and OCs, potentially reducing concentrations of the latter in apex feeders.

6.1.2. Mercury

Due to its volatility and tendency to undergo biogeochemical transformation, Hg must be considered separately from other heavy metals (see, for example, Fitzgerald et al., 1998; Mason and Fitzgerald, 1996; Mason et al., 1994). Particular attention must be given to aquatic environments because it is there that Hg poses its greatest threat through biomagnification (Atwell et al., 1998; Evans and Lockhart, 1999; Muir et al., 1999). To a certain extent, processes leading to enhanced Hg concentration in the environment can be considered as either 'solvent switching' or 'solvent depletion' (Macdonald, et al., 2002c). In the former, Hg moves between phases such as air, water and particles based simply on partition coefficients, whereas in the latter Hg may achieve high fugacity through the loss of surfaces or through chemical reactions mediated by photons or microbes (see, for example, processes described by Lindberg et al., 2002; Malcolm and Keeler, 2002). The natural Hg cycle has been enhanced by human activities such that two to three times as much Hg is presently cycling through the atmosphere and upper ocean than before the rise of industry (Lamborg et al., 2002; Mason and Fitzgerald, 1996; Mason et al., 1994; Pacyna and Keeler, 1995). Because atmospheric Hg is almost entirely gaseous (Hg⁰), it is tempting to assume that the polar regions might be global sinks simply due to low tempera-



Figure 6-3. A schematic diagram illustrating how atmospheric mercury is scavenged after polar sunrise and subsequently enters surface waters.

ture and, accordingly, to make projections of the effects of climate change based on this fact alone. In fact, thermal forcing for Hg⁰ to Arctic aquatic systems, either by rain or by air-water exchange, is weak due to a relatively high Henry's Law constant (Macdonald et al., 2000a; Mason et al., 1994). Nevertheless, the Arctic may be especially vulnerable to Hg because of an extraordinary set of circumstances at polar sunrise that results in the deposition of reactive (and bioavailable) Hg to the surface (Figure 6.3; Lindberg et al., 2002; Lu et al., 2001; Schroeder et al., 1998). A relatively long residence time for Hg⁰ of one to two years in the atmosphere (Lamborg et al., 2002) ensures that winds can transport Hg to the Arctic from sources throughout the Northern Hemisphere. With the increase of UV radiation at polar sunrise, Hg⁰ is converted to reactive gaseous mercury (RGM) through reaction sequences in which bromine, chlorine and ozone, and compounds like BrO and ClO appear to have prominent roles (Figure 6.3 and see Lindberg et al., 2002; Lu et al., 2001). The RGM thus formed is very effectively removed from the atmosphere by particles/snow, with this process estimated to account for the deposition of ~ 50 t (>90% of the annual total) on the Arctic Ocean and Hudson Bay during spring (Lu et al., 2001) and perhaps as much as 150 to 300 t/yr (Lindberg et al., 2002). Using an air transport model, Christensen et al. (AMAP, 2003a) estimated Hg deposition north of the Arctic Circle at 180 t when mercury depletion event (MDE) chemistry was included in the model, as opposed to ca. 80 t in the absence of MDEs. Based on snow samples, and the BrO distribution as determined from satellite measurements, reactive or particulate Hg is probably deposited mainly in areas subject to marine influence (marine aerosol being the source of the bromine/chlorine compounds involved in MDEs). The marginal seas of the Arctic appear to be especially vulnerable, because it here that sea salt (and therefore bromine) can most easily interact with snow through aerosols or frost flower formation associated with flaw leads or first-year ice. With spring warming, about two-thirds of the Hg deposited in snow is estimated to re-volatilize (Brooks, pers. comm., 2001) with the remaining third entering aquatic environments through meltwater.

Before projecting the impact of global change on the Hg cycle in the Arctic, it is necessary to understand how the invasion of Hg to global aquatic reservoirs via wet and dry deposition of reactive forms is balanced by gaseous evasion of reduced forms of Hg such as Hg⁰ or methylmercury (MeHg) (Mason et al., 1994). Dissolved Hg or Hg associated with suspended particulates in meltwater and runoff can drain into surface water below the ice cover whereas the evasion of Hg⁰ is partly or completely blocked by ice cover. Indeed, this set of circumstances may provide the foundation for the elevated Hg levels which have been observed in Arctic biota (Evans and Lockhart, 1999; Macdonald et al., 2000a; Muir et al., 1999; Wagemann et al., 1995, 1996). Unfortunately, appropriate geochemical studies investigating the cycling of Hg in Arctic aquatic systems have not yet been conducted and this is only speculation at the present time.

The vulnerability of the Arctic to global Hg emissions, therefore, probably lies in the mismatch between invasion and evasion processes. Climate change can affect both the invasion and evasion routes for Hg. Springtime depletion of atmospheric Hg depends on the availability of sea salt, calm weather, a temperature inversion, the presence of sunlight and sub-zero temperatures (Lindberg *et al.*, 2002; Lu *et al.*, 2001). Initially with climate change, it is likely that increased amounts of firstyear ice around the polar margins will contribute to generally saltier ice and snow in spring which will enhance the production of BrO/CIO. Depending on what con-

The Effects of Climate Change on Contaminant Pathways

trols the rate of supply of Hg to the Arctic, increased BrO/ClO will either enhance scavenging or maintain it at present levels, possibly extending the area of springtime Hg depletion beyond that implied by recent satellite measurements of the distribution of BrO/ClO (see Lu et al., 2001). Considering that global emissions of Hg have generally decreased over the last 20 years, Lindberg et al. (2002) proposed that the recent increases observed in Hg levels in Arctic biota in some areas are, in fact, evidence that MDEs may be a recent phenomenon associated with change in sea-ice climate and atmospheric chemistry over the past decade or two. However, the entire Hg cycle must be considered before linking MDEs with Hg concentrations in apex aquatic feeders. Larger areas of open water in spring, either for ocean or lakes, will enhance exchange allowing gaseous forms of Hg to escape back into the atmosphere (Figure 6.3). With further warming, parts of the Arctic will become more temperate in character implying that atmospheric Hg depletion would decrease and evasion from the water increase leading eventually to lower Hg concentrations in water.

Aquatic food webs have strong leverage for change in Hg exposure in the Arctic because MeHg biomagnifies, exhibiting a concentration increase of about 1000to 3000-fold from particulate organic matter to apex predators (Figure 6.4; Atwell et al., 1998; Kidd et al., 1995a; Muir et al., 1999). Mercury concentration also increases with age/size in predatory fish, such that large, old fish often exceed thresholds considered safe for unrestricted human consumption (Lockhart and Evans, 2000), containing anywhere from two to five times the Hg concentration of smaller fish of the same species. Therefore, adding an extra step in the food web could reasonably be expected to enhance Hg concentrations in higher trophic levels by a factor of about five. Likewise, altering the population distribution of fish in a lake could produce a change rivaling or exceeding any change caused by alteration of physical pathways.

With warming (Figure 3.3) will come the loss of permafrost (Figure 3.24) causing altered hydrology, potentially more wetland, and enhanced fluxes of soil and organic carbon to rivers, lakes and estuaries. Warming of drainage basins in the Arctic, therefore, would appear to provide a widespread mechanism to increase Hg fluxes to northern aquatic environments and to the atmosphere. A recent study of the pathway of Hg from snowcovered land to streams in Vermont (Stanley et al., 2002) showed that Hg export from soils correlated with particulate organic carbon, and that Hg concentrations in runoff increased with flow - unlike most solutes (see also Bishop et al., 1995). These two factors together suggest that episodic, large releases of organically-bound Hg (of both anthropogenic and natural origin) may become a dominant feature accompanying permafrost degradation. Clearly, Arctic lakes would be most vulnerable to this process, but enhanced input of terrestrial carbon is projected to occur to Arctic seas as well (Kabat et al., 2001), suggesting that Hg loadings there may, similarly, be increased. In the ocean, Hudson Bay would seem especially vulnerable, partly due to its large drainage basin, already affected by reservoir flooding (Bodaly and Johnston, 1992), and partly due to the likelihood of permafrost melting within that drainage basin (Gough and Wolfe, 2001). It seems noteworthy that enhanced

Mercury, biomagnification factors







Figure 6-4. Biomagnification of mercury in Arctic food webs. This figure illustrates a) biomagnification factors for a simplified food web (based on dry weight concentrations in whole organisms (invertebrates and fish) and on a wet weight concentration for fish to muscle in top predators. For polar bear, liver was used instead of muscle) (Muir *et al.*, 1999) and b) biomagnification as a function of trophic level based on δ^{15} N measurements (adapted from Atwell *et al.*, 1998). In the case of the biomagnification factors from ringed seal to polar bear, the lower value is for seal blubber to polar bear liver.

concentrations of Hg in snow are observed generally in that region (Lu *et al.*, 2001) and that a recent increase in Hg flux to Hudson Bay sediments has, likewise, been observed (Lockhart *et al.*, 1995).

Historical records from dated sediment cores have been used to infer Hg fluxes increasing by factors of 3 to 7 in some Arctic lakes during the past two centuries (Bindler *et al.*, 2001; Landers *et al.*, 1995; Lockhart *et al.*, 1998). What is not so clear is whether such increases are due to increased atmospheric deposition or to alteration of processes that transfer Hg from wetlands to atmosphere or from the drainage basin into lakes or transfer Hg from the water to the sediments. In regard to the latter, Gajewski *et al.* (1997) have shown major increases in diatom fluxes to varved sediments from a lake on Devon Island which they attribute to climate change (i.e., longer, ice-free summers). Not only could such a mechanism explain enhanced Hg fluxes to Arctic lake sediments but it could also have the non-intuitive result of *reducing* the exposure of higher trophic levels to Hg through bloom dilution at the algal stage (Pickhardt *et al.*, 2002).

Mercury depletion events leading to the production of bioavailable Hg have been confirmed at Barrow, Alaska (Lindberg *et al.*, 2002). Given that this region receives airborne contaminants from Asia (Li *et al.*, 2002; Wilkening *et al.*, 2000), that China is increasing its reliance on coal for energy, and that coal is a leading source of anthropogenic Hg (Nriagu and Pacyna, 1988), it seems likely that the Bering/Chukchi Sea region may be especially vulnerable to further increased Hg loadings. In general, the pathways of anthropogenic Hg might be expected to change as a result of shifts in major sources, for example, as European and North American emissions decrease and Asian emissions increase.

6.1.3. Arsenic

The sediment geochemistry of arsenic (As) can, like Hg, be altered by changing the carbon cycle. Mining and smelting have been major sources of As to the environment (Nriagu, 1989), where it may accumulate in aquatic sediments (Martin and Pedersen, 2002). In the Arctic, it has also been suggested that underwater nuclear weapons testing may have provided a significant anthropogenic As source to the Pechora Sea (Loring *et al.*, 1995). Large natural surface sediment enrichment of As is often produced by diagenesis; solid-phase As(v) at depth in

sediments is remobilized through reduction to As(III), which then diffuses upward to re-precipitate through reactions with nitrate, oxides of manganese or oxygen (Figure 6.5). This natural redistribution of As in sediments makes it exceptionally precarious to infer contamination from sediment surface As enrichments (Loring *et al.*, 1995, 1998; Siegel *et al.*, 2001). However, strong sediment-surface enrichments serve as a warning that alteration of the organic geochemistry of aquatic sediments by enhanced organic carbon fluxes may have unanticipated consequences for As mobility (cf. Figures 6.5 a and b).

A geochemical study of a temperate, seasonally icecovered lake contaminated by As, Cu, nickel and Zn is especially instructive (Martin and Pedersen, 2002). When action was taken to reduce metal loadings, the lake's response was enhanced phytoplankton production which then invigorated carbon fluxes to sediments. Through metabolism in sediments, the enhanced carbon fluxes then reduced oxygen, thus mediating the conversion of solid-phase As(V) to dissolved-phase As(III) which then diffused back into the bottom water. The unanticipated result of decreasing metal loadings to the lake was to produce higher As concentrations. If one of the responses to change in Arctic aquatic environments is enhanced aquatic productivity or enhanced organic carbon loadings, release of solid-phase As, especially from sediments with high natural or anthropogenic contaminant burdens (e.g., see Loring et al., 1995, 1998; Siegel et al., 2001) is a likely response.

6.2. Radionuclides

Previous assessments have outlined the atmospheric and oceanic pathways that transport artificial radionuclides to the Arctic (AMAP, 1998; Macdonald, *et al.*, 2000). Atmospheric artificial radionuclides derive mainly from atmospheric weapons testing predating the mid 1960s, and the Chernobyl accident in 1986. Accordingly, predominant food web contamination from the atmosphere has occurred to terrestrial systems through fallout (AMAP, 1998) and there appears little opportunity for



Figure 6.5. A schematic diagram showing how arsenic cycles in sediments (modified from Sullivan and Aller, 1996). The solid-phase form of arsenic (As(V)) is released to pore water through reduction to As(III) which may then diffuse back out of sediments. Enhanced fluxes of organic carbon to sediments, shown in the right-hand panel, are reflected by enhanced diffusion of dissolved arsenic back into bottom waters.

present or future climate changes to have much impact on historical atmospheric sources which are decaying with half-lives of about 30 years (¹³⁷Cs and ⁹⁰Sr, predominantly). The distribution of fallout from Chernobyl was very much controlled by wind and rainfall patterns (see Figures 8.4 and 8.5 in AMAP, 1998), and these pathways are clearly subject to climate change. An important lesson to be learned from the Chernobyl accident is that climate patterns can predispose the Arctic in how it will receive contaminants from such accidents and, for example, wetter conditions in the Nordic Seas and Northern Europe during AO⁺ conditions (Figure 3·4 b) would favour deposition of ¹³⁷Cs fallout in that region.

In the ocean, the predominant artificial radionuclides $(^{137}Cs, ^{90}Sr, ^{239+240}Pu)$ do not biomagnify sufficiently (except perhaps for plutonium (Pu) in brown macroalgae; see Berrow *et al.*, 1998; Fisher *et al.*, 1999) to contribute significantly to the radiation dose for humans (Layton *et al.*, 1997; Macdonald and Bewers, 1996). This suggests that, in order to find pathway changes that might be cause for concern, it is the ice and surface water motion of the Arctic Ocean that must be considered, both of which exhibit variability resulting from the AO/NAO (Figures 3.9 and 3.14).

Clearly, the enhanced northward transport of water in the Nordic Seas under the AO⁺ conditions of the 1990s (Figure 3.15) strengthened the delivery to the Arctic of radionuclides discharged by the European nuclear reprocessing plants where they continued to spread into the surface waters of the Makarov Basin (Figures 3.13 and 3.15; Smith *et al.*, 1998).

The transport routes for radionuclides in the Nordic Seas are generally known (Figure 3.17). A shift in the climate regime toward increased NAO index and stronger wind fields will probably lead to radionuclides undergoing a faster transport closer to the Norwegian coast, with a larger proportion entering the Barents Sea. It is expected that other contaminants entering the North Sea and southern Norwegian Sea from sources in Europe will encounter similar change in their oceanic transport route as that proposed for radionuclides.

The enhanced coupling between release points for European reprocessing plant nuclear wastes and the Arctic Ocean will be more than offset by reduction in releases of the major radionuclides that have occurred since the 1970s (Macdonald et al., 2000a), and input of tracers such as ¹³⁷Cs to the Arctic Ocean should continue to decline. Recent increased discharges of technetium, however, provide a reminder that not all radionuclide discharges from European reprocessing plants are declining (AMAP, 2003c). Extensive data collection under the Arctic Nuclear Waste Assessment Program (ANWAP; Layton et al., 1997) and from icebreakers (Smith et al., 1998) has provided sufficient information on the distribution of artificial radionuclides in Arctic surface waters to show that they pose little risk to human or ecosystem health. The conclusion of the ANWAP assessment was that the largest radiation doses to individuals living on the Alaskan coast and consuming subsistence seafoods were, in order of importance, ²¹⁰Po (a natural radionuclide), followed by ¹³⁷Cs and ⁹⁰Sr from atmospheric fallout. It seems that the nuclear reprocessing radionuclides have made elegant tracers of water motion and, although they will reflect recent changes in that motion, they will continue to provide almost no risk to Arctic marine biota (Macdonald and Bewers, 1996).

The ice and surface water pathway changes forced by the AO (Figures 3.10 and 3.14) strongly suggest that radionuclides discharged to the Russian shelves may, under AO⁺ conditions, enter the Canadian Basin and subsequently find their way into the Canadian Arctic Archipelago. The estimated total release of radionuclides to the Kara Sea via river water (Ob, Yenisey) is about 1.1×1015 Bq (90Sr and 137Cs) (Paluszkiewicz et al., 2001), or about an order of magnitude less than the fallout and reprocessing plant sources to the Arctic Ocean (Aarkrog, 1994). It seems likely, therefore, that diversion of Russian river runoff from the Eurasian Basin to the Canadian Basin under AO+ conditions will be matched by a diversion of associated radionuclides (see Cooper et al., 1999) which, nevertheless, will provide little threat to ecosystems there.

Ice drift, the remaining transport pathway, provides a distinct, but difficult to quantify risk. Sediments from the Russian shelves, known to have been contaminated by weapons testing and accidental and deliberate radioactive waste discharges, have been found to be heavily contaminated at several locations (Josefsson, 1998; Matishov et al., 1999; Smith et al., 2000). Suspension freezing provides an efficient mechanism to entrain fine sediments into newly-formed ice in the Russian seas (Eicken et al., 2000) and ice has been shown to carry radioactive sediments (Dethleff et al., 2000a; Landa et al., 1998; Meese et al., 1997). High radioactivity has been found in ice-entrained sediments in the Canada Basin (>70 Bq/kg; Cooper et al., 1998) and in the Canadian Arctic Archipelago (Darby, pers comm., 2001) but the origin of the sediment in the ice, based on mineralogy, has not been assigned to Russian shelves. Given the very few samples together with their uncertain provenance, it is impossible to quantify risks to biota in the Canada Basin and the Canadian Arctic Archipelago from contaminated ice, except to say that the AO⁺ conditions of the early 1990s appear to produce ice transport pathways conducive to carrying sediment and surface water from the Russian shelves into the Archipelago.

Perhaps the most significant increase in radioactivity exposure to northern residents will come from the natural ²²⁶Ra decay series that supports ²²²Rn, ²¹⁰Pb and ²¹⁰Po. ²¹⁰Pb in aquatic systems derives partly from insitu production supported by ²²⁶Ra and partly from ²²²Rn which has diffused out of soils and, with a short (3.8 day) half-life, decays to ²¹⁰Pb which is scavenged by particles. This latter component, called excess ²¹⁰Pb, often exceeds the 'supported' ²¹⁰Pb in aquatic sediments. Presently, excess ²¹⁰Pb tends to be very low in the Arctic because ²²²Rn remains trapped in the soil by permafrost and snow/ice cover. With warming, ²²²Rn evasion will increase as will excess ²¹⁰Pb activity matched by the activity of ²¹⁰Po, its granddaughter. Since ²¹⁰Po and ²²²Rn together account for about 75% of the radiation dose to native northern residents (Layton et al., 1997; Macdonald and Bewers, 1996) any substantive increase in ²²²Rn evasion due to warming/permafrost melting would have a widespread and substantial (doubling or tripling) effect on the radiation dose.

6.3. Organochlorine compounds

Of all the contaminants, the organochlorines (OCs) provide the greatest challenge to predict consequences of change because they have been so widely released, comprise so many compounds and exhibit such a wide range of physical chemical properties. Furthermore, the important chemical properties - volatility, phase partitioning, and degradation kinetics - are all sensitive to temperature and hydrological change. Efforts to determine where in the environment these compounds end up have improved the understanding of global pathways enormously, but new surprises give an indication that intuition often fails due to an incomplete grasp of environmental processes (Macdonald et al., 2000b; Oreskes et al., 1994; Schindler, 1997). Recent OC budgets underscore the importance of the atmosphere-ocean coupling in the transfer of OCs to the Arctic from their temperate and tropical release points (Li et al., 2002; Macdonald et al., 2000a,b). These same budgets show that the relative importance of atmosphere versus ocean in transporting contaminants will vary widely among the OCs and over time. Therefore, change forced by the AO or by general global change will have a similarly varied impact depending on the particular OC and the time period in question. All the OCs of concern (DDT, toxaphene, chlordane, PCBs, hexachlorocyclohexanes (HCHs)) have transient emissions: that is, they were first released in the 1930s to 1940s, emissions peaked sometime in the 1970s to 1990s, after which they have generally declined or ceased. Continued declines, or possibly increases, will depend on bans, further controls, or new use following invigorated assaults by pests linked to climate change. As a general rule, particularly with transient releases of chemicals that partition strongly into water, the atmosphere is initially the dominant transporting medium, but as aquatic reservoirs (lakes, rivers, upper ocean) become loaded, these then contain the important if not dominant budget and flux terms (Li et al., 2002; Macdonald et al., 2000a,b) and it is dominant budget terms that posses the greatest leverage for change.

Before discussing how climate change is likely to impact upon OCs, it is important to understand the manner in which OCs become concentrated in the environment. Building on earlier perspectives developed by Wania (1999), Macdonald et al. (2002c) suggest there to be two fundamental concentrating processes which they termed solvent switching and solvent depletion. The distinction between these two processes is particularly important in the context of change. Solvent switching is a natural process wherein a particular contaminant distributes itself between various phases (solid, liquid, gas) according to well-described thermodynamic rules. This process can lead to elevated concentrations - for example, the partitioning of HCH into cold water will produce concentrations in the water that far exceed those in the air, and indeed this process alone can cause non-intuitive divergence of chemicals over large scales (Li et al., 2002). But this process cannot cause concentrations to exceed thermodynamic equilibrium (that is, solvent switching does not increase fugacity). Another very important solvent-switching process is the transfer of a POP from water to lipid at the bottom of the food web; again, this process enhances POP concentrations in phytoplankton or small zooplankton strictly according to thermodynamic forcing.

Solvent depletion, however, is a very different process in that it can lead to concentrations in selected media that exceed thermodynamic equilibrium (i.e., fugacity is increased), which requires a source of energy. Perhaps the clearest example of solvent depletion occurs in the food web where lipid transfers, going from one trophic level to a higher one, are inefficient. Metabolism effectively burns much of the lipid, leaving the contaminant to accumulate in a decreasing volume of stored fat. This process can lead to OC concentrations in aquatic apex feeders that are well above thermodynamic equilibrium with the water, and the situation can be exacerbated by starvation cycles during which individuals reduce their fat content further. Arctic and other cold environments offer several solvent depletion processes by which contaminants can be ramped up above thermodynamic equilibrium (Macdonald et al., 2002c). In particular, a POP can be scavenged by adsorption onto snow and thence transported to the ground. The initial large snow surface $(0.1 \text{ m}^2/\text{g})$ can be reduced by a factor of over 100 and, indeed, during melting, the snow surface can disappear entirely effectively removing the solvent (the snow's surface) from under the contaminant. The fugacity can be increased enormously during snow sintering/melt with the consequence that the OC is forced to diffuse back into the atmosphere, enter the meltwater or adsorb onto other particles. Similarly, fog water droplets can provide a temporarily large surface area which is thermodynamically attractive - upon coalescence, most of the surface is lost and contaminant fugacity increases in the remaining large water droplets. Finally, cryo-concentration may occur in shallow lakes or seas that form a thick ice cover. The withdrawal of water into the ice, leaving behind most of the POPs, can easily increase concentrations in the water beneath the ice to values that exceed thermodynamic equilibrium with the atmosphere by factors of 2 to 5. Due to the ice cover, diffusion back into the atmosphere is not an option.

Under change scenarios, the solvent-switching processes can be modeled by taking into account changes in partition coefficients and vapour pressures with temperature. However, changes in the solvent-depletion processes are much harder to project especially since the elevated fugacities imply transports that will be sensitive to time. For example, the effect of snow on contaminants entering an Arctic lake will depend on when the snow accumulates, how long it sinters, how porous and how deep the snow is, how and when snow melt occurs, and how quickly snow melt enters the lake. None of these transfer processes have been investigated in sufficient detail to provide guidance for modellers.

6.3.1. The influence of the Arctic Oscillation

There appear to be several consequential ways that physical pathways could change in response to the AO. In the Nordic Seas, especially under AO⁺ conditions, the atmospheric coupling of eastern North America and Western Europe with the Arctic becomes more intense, in particular during winter/spring (Figures 3.2 a and b) suggesting that spraying pesticides in these regions will, if anything, intensify 'events' such as those seen at Alert for α - and γ -HCH (see, for example, Figure 22 in Macdonald et al., 2000a). Furthermore, re-emission of old OC residues in soils and aquatic reservoirs of Europe or eastern North America will enter these same air pathways to be transported north. In this regard it is worth noting that the highest cumulative use of PCBs was in Western Europe and eastern North America (see Figure in AMAP 2003b) - both of which are source regions for air masses entering the Arctic between Greenland and Europe (Figures $3 \cdot 2 a$ and b). The higher precipitation in the Nordic Seas and southern Eurasian Basin (Figure 3.4) will provide more effective scavenging of particleassociated OCs (high molecular weight PCBs, for example) and for OCs with low Henry's Law constants (HLCs) that partition strongly into water (HCHs, toxaphene).

In the Bering Sea, gas exchange with the ocean or washout by rain can provide a mechanism to remove β -HCH selectively from the air as it moves northward, simply due to its exceptionally low HLC (Li et al., 2002). This process does not prevent the entry of this contaminant to the Arctic Ocean; rather, it switches the mode of delivery from winds to ocean currents and, as a consequence, slows the rate of transport from m/s to cm/s. Under AO⁺ conditions, therefore, a more rapid atmospheric transport of OCs into the Arctic from Western Europe is likely, with the delivery shifting toward the ocean pathway for OCs that partition strongly onto particles or have low HLCs. On the Pacific side, OCs will continue to enter the Arctic via the atmosphere and ocean currents (see, for example, Bailey et al., 2000), but the 15% reduction in Bering Sea inflow over the past several decades would effect a proportional reduction in this pathway. Variation in precipitation over the North Pacific and Bering Sea (Figure 3.20 b) will alter the balance between atmosphere and ocean as transport pathways to the Arctic.

Larger areas of open water under AO+ conditions or from general climate change (Figures 3.6, 3.7 and 3.8) will accelerate equilibrium between air and sea by an amount equivalent to the expanded open areas. Furthermore, increased numbers of polynyas in winter will enhance the production of fog over sea ice, acting to scavenge and deposit contaminants to surface (Chernyak et al., 1996) at locations known to be important for biota (Stirling, 1997). Due to the drastic reduction in atmospheric concentrations as a result of emission controls, α -HCH has become oversaturated in ice-covered areas of the Arctic Ocean (Jantunen and Bidleman, 1995; Macdonald et al., 2000b). The opening of the pack and seasonal clearance of shelves will, in this case, result in evasion and drawdown of HCH from the upper ocean. In contrast, PCBs and toxaphene are still loading into the Arctic Ocean via the atmosphere (Macdonald et al., 2000b) and, therefore, the same loss of ice cover will lead to increased loading of these substances in surface seawater. A PCB budget for the Arctic Ocean (Macdonald et al., 2000b) estimated a net gas exchange into the ocean of about 20 t/yr. The reduced ice cover evident in Figure 3.8might lead to as much as a doubling of the area of open water which would similarly double net exchange. Not only does change in ice cover alter the air-sea exchange of OC gases, but the consequent loading or unloading of the interior Arctic Ocean with such chemicals will later

Table 6.1. Russian river loadings for selected organochlorine compounds.

	Load, t/yr	Percent of Arctic Ocean input budget	Reference
α-HCH	25	13	Alexeeva <i>et al.</i> , 2001; Macdonald <i>et al.</i> , 2000a
γ-ΗCΗ	44	51	Alexeeva <i>et al.</i> , 2001; Macdonald <i>et al.</i> , 2000a
ΣPCBs	15	23	Macdonald et al., 2000b
ΣDDT	18		Alexeeva et al., 2001

be felt in the composition of water exiting the Arctic through the Canadian Arctic Archipelago and in the East Greenland Current and points farther downstream.

The diversion of Russian river inflow toward the east under AO⁺ conditions (Figure 3.14) will have a significant effect on OC pathways within the Arctic Ocean. Inherent with this diversion is a shift of all the OC loadings from these Russian rivers out of the Eurasian Basin and into the Canada Basin (Table 6.1, and see Macdonald et al., 2000a; Sericano et al., 2001). As the Canada Basin has a longer residence time (10 years, compared to 2 years in the TPD), there would be an added consequence of increased contaminant inventories for the Arctic Ocean in general and the Canada Basin in particular. Instead of tracking across the Eurasian Basin to exit into the East Greenland Current, OCs discharged by the Russian rivers might now exit via the Canadian Arctic Archipelago (see Figure 3.14). The changes here are consequential to budgets (Table 6.1) and to distribution within the water column, keeping in mind that the same river water that delivers contaminants also stratifies the ocean and potentially reduces new production and vertical particle flux, which together will act to maintain river-borne contaminants near the surface where they can partition into algae. Although there are few data from which to evaluate the relative importance of OC pathways in the ocean, the findings of Andersen et al. (2001) provide a strong warning that there are sources of PCBs in the region around the Kara Sea and Franz Josef Land, possibly as a consequence of riverine inputs.

Water in the Canadian Arctic Archipelago channels, supplied from surface water in the Arctic Ocean (~0-200 m), has the potential to undergo change in its OC content due to alterations in the distribution of water masses in the Canada or Eurasian Basins. As shown in several studies (Carmack et al., 1997; Li et al., 2002; Macdonald et al., 2000a,b), HCHs are not distributed uniformly within the Arctic Ocean and it is likely that other OCs are, likewise, not uniformly distributed. For example, α -HCH is highest near the surface, decreasing to very low concentrations in water deeper than several hundred meters, and the Canada Basin under the permanent pack ice exhibits much higher HCH concentrations than are observed in the Chukchi Sea or the Eurasian Basin surface waters. The redistribution of Pacific and Atlantic water masses in surface water of the Arctic Ocean (Figures 3.13 and 3.15) may therefore have been accompanied by change in the composition of water flowing into the Canadian Arctic Archipelago. Such change could occur in two ways, either by horizontal

Figure 6.6. Time series of organochlorine concentrations measured at Resolute (Canadian Arctic Archipelago) during 1993 at the surface and 50 m water depth for α - and γ -HCH, hexachlorobenzene and toxaphene (source: Hargrave *et al.*, 1997).

displacement of water mass domains or by vertical displacement of water properties. Although there are few data from which to evaluate how the water composition in the Archipelago channels might respond to the AO, an extraordinary set of data collected by Hargrave et al. (1997) illustrates clearly that change in upstream water composition can have important consequences for contaminant concentrations in water flowing through the Archipelago. Seasonal measurements of OCs made at Resolute in 1993 (Figure 6.6) reveal a coherence between the surface and 50 m water depth in contaminant trends. This coherence, together with patterns differing for the various OCs, argues strongly that the observed time trends at Resolute are produced by variation in the composition of upstream water drawn into the Archipelago from the Canada Basin. The concentration variations in this single season's data exceed a factor of two.

6.3.2. The effect of glacial melt back

Glacier ice-mass loss and snow melt back due to warming (cyclical or trend) can release archived contaminants accumulated during years of higher fluxes (Blais et al., 1998). Based on the total amount of glacial melt back (Figure 3.25) and the range in concentration of OC contaminants measured in ice and snow during the 1960s to 1990s for the Agassiz Ice Cap (Table 6.2) the maximum total inputs are expected to range from about 3 kg for PCBs to as much as 400 kg for Σ DDT. For 1993, the year exhibiting the most substantial melt back on record, the maximum inputs of PCBs and DDT were estimated at 0.5 kg and 74 kg, respectively. The HCH and PCB inputs are minuscule compared to Arctic Ocean budgets (Macdonald et al., 2000b) and are also relatively small compared to the flux of these contaminants through the Canadian Arctic Archipelago (Table 6.2). For DDT, however, glacial melt appears potentially to provide an important, climate-modulated source. For Arctic glaciers, most of the melt occurs in zones where old ice of pre-industrial age is emerging. This ice would contain little or no contaminant burden and, indeed, would act to dilute any contaminants released to aquatic environments. For smaller ice caps, more recent layers of snow and ice might be involved. Thus, glacial melt back appears to be of significance only for DDT, and even then is likely to be of only local and short-lived significance.

6.3.3. The effect of warming on organochlorine cycling in lakes

Arctic lakes presently tend to retain only a small fraction of the contaminants they receive, a fact which should indicate the potential for change. Studies and models (Helm et al., 2002; Macdonald et al., 2000a) show that the snowmelt and runoff cycle connects with the lake's hydrological cycle such that most of the contaminants deposited in the drainage basin throughout winter are transported across the lake surface in a low density layer under the ice to exit in out-flowing water. The lack of a strong particle flux due to oligotrophic conditions further decouples deep lake water from contaminants at the surface. Reduced ice cover and loss of permafrost, leading to greater mixing and stronger primary production, will enhance the ability of Arctic lakes to retain OCs. How this added retention will be expressed in the food web is less certain. Enhanced primary production and settling of ungrazed phytoplankton in early spring might draw down contaminant burdens in lake surface water and thereby reduce entry of contaminants into the food web or act so as to dilute the OC concentration in algae as has been shown for Hg (Pickhardt et al., 2002). How-

Table 6.2. Potential input of selected organochlorine compounds from glacial melt.

	Concen- tration, pg/L	Total glacial input, kg	Glacial input for 1993, kg/yr	Flux through the Canadian Arctic Archipelago ^a , kg/yr
α-HCH ^b	256	205	39	195 000
γ-HCH ^b	115	92	18	27 900
ΣDDT ^b	480	384	74	161
Chlordane ^b	35	28	5	96
HCB ^b	65	52	10	810
PCBs ^c	3.5	2.8	0.5	2700

^a Flux through the Canadian Arctic Archipelago was estimated assuming a mean flow of 54 000 km³/yr (Macdonald *et al.*, 2000a) and concentration data collected in the Archipelago during 1993 (HCH, HCB, Chlordane; Hargrave *et al.*, 1997) or Canada Basin in 1997–98 (PCB, DDT; Macdonald *et al.*, 2001);

^b Concentration data from Franz *et al.* (1997); samples collected for 1987, 1990 and 1992 in snow layers after first year loss;

^c Concentration data from Gregor *et al.* (1995); average concentration over a 30-year period from 1964/65 to 1992/93 (n=34).

Tal	bl	e 6·3.	Physical	parameters sensitive	e to temperature cl	nange.
-----	----	--------	----------	----------------------	---------------------	--------

	Unit	Description/application
Henry's Law Constant (HLC)	Pa m³/mol	Partitioning between air and water
Air–water partition coef- ficient (K _{AW})	unitless	K_{AW} = HLC/RT
Octanol-air partition coef- ficient (K _{OA})	unitless	Used as a proxy to model parti- tioning between air and organic phases such as vegetation, soil, sediment organic carbon, and particles in air and water
Vapour pressure (p ^o)	Pa	Describes the tendency of a chemical to volatilize
Particle-gas partition coef- ficient (K _{PG})	m³/µg	The ratio of chemical concentra- tion on atmospheric particles ng/µg) to concentration in the gas phase

ever, if a given lake has a very low sedimentation rate and most of the organic carbon depositing to sediments becomes metabolized, it is likely that OCs associated with the particle flux will be released to the bottom water and re-mixed within the lake as has been observed in Lake Superior (Jeremiason *et al.*, 1994). This process of drawdown and remineralization could slowly ramp up water column concentrations below the thermocline, especially if ice cover is sufficient to hinder exchange during lake turnover. It appears that climate change has the potential to cause substantive physical and biological changes in northern lakes that would alter OC pathways, but current knowledge is insufficient to predict what these changes might be.

6.3.4. The effect of warming on chemical partitioning and degradation

Physical–chemical properties sensitive to temperature include vapour pressure (p°), Henry's Law Constant (HLC; alternatively expressed as the air-water partition coefficient, K_{AW}), octanol-air partition coefficient (K_{OA}) and the octanol-water partition coefficient (K_{OW}) (Table 6·3). The particle-gas partition coefficient (K_{PG}), which depends on both particle composition and chemical composition, also varies with temperature.

The extent to which chemicals are associated with aerosols is fundamental to their atmospheric transport to the Arctic. Association with particles may, on the one hand, slow or reduce transport to the Arctic through temporary or permanent deposition to surfaces; while on the other hand, the association may protect a chemical from oxidation during transit to the Arctic. The potential for temperature to alter partitioning between gas and aerosol phases appears greatest for chemicals that exhibit log K_{OA} values in the range of 11 to 14 (Figure 6·7). For example, DDT varies from being over 70% particulate-bound in winter (-30°C) to occurring almost entirely in

Figure 6.7. The partitioning of selected persistent organic pollutants as a function of KOA. The figure shows changes in partitioning between winter (-30°C) and summer (0°C). Particulate fractions were calculated based on equations developed by Finizio et al. (1997) from field measurements of organochlorines. Calculations are based on measurements of particulate organic carbon in air at Alert during winter and summer 1998-1999 (Sharma et al., 2002). Temperature-adjusted K_{OA} values were taken from the literature (Harner and Bidleman, 1996, 1998; Harner and Shoeib, 2002; Harner et al., 2000; Shoeib and Harner, 2002).

Figure 6.8. Predicted percent changes in H, $1/K_{OA}$ and $1/K_{OW}$ associated with a 5°C increase in temperature for selected chemicals. 'High' and 'low' represent the upper and lower values reported for PCBs. Values are based on ΔH_{H} (enthalpy of phase change associated with transfer from water to air, kJ/mol), ΔH_{OA} (enthalpy of phase change from octanol to air), and ΔH_{OW} (enthalpy of phase change from octanol to water) (Bidleman *et al.*, 2003).

the gas phase in summer (0°C). Similar changes in partitioning are evident for many of the other OCs illustrated in Figure 6.7. Chemicals with K_{OA} values at -30° C of about 11 to 12, therefore, are most sensitive to change in atmospheric transport as a result of temperature rise.

At 0°C most of the chemicals shown in Figure 6.8occur in the gas phase, implying that they are easily advected by air but will be prone to photolytic degradation. Timing is important: the transport processes that produce Arctic haze in spring may alter substantially if warming comes earlier in the season, with consequent change to the particle-gas partitioning. Several of the higher molecular weight polybrominated diphenyl ethers (PBDEs) and polychlorinated dibenzo-p-dioxins (PCDDs) are appreciably associated with particles even at 0°C. Depending on their susceptibility to photolysis, particleassociation may actually protect these compounds during transport which might explain why the increase in PBDEs in the Arctic closely follows the production and usage to the south (Ikonomou et al., 2002) - which is not the case for the PCBs and other OCs which are mostly in the gas-phase during summer. Despite cold winter temperatures, many PCB, organochlorine pesticide (OCP) and polychlorinated naphthalene (PCN) compounds remain in the gas phase. Winter warming projected by climate models may therefore facilitate their transport during the period of year when reduced sunlight makes them less vulnerable to degradation.

Chemical partitioning between environmental media (air, water, soil, biota) can be described using three partition coefficients – K_{OA} , K_{AW} , and K_{OW} (Gouin *et al.*, 2000). K_{OW} , which is a ratio of two solubilities that both increase with temperature, tends to vary weakly with temperature, as shown by the modest 20% increase for hexachlorobenzene (HCB) in response to a 5°C increase (Figure 6·8; Bahadur *et al.*, 1997). A 5°C temperature rise produces a more substantive (60-100%) increase in $1/K_{OA}$, which will be manifest as an increase in volatility and greater potential for atmospheric transport. Under warming conditions, more chemical will partition out of surface soils and aerosols to enter the gas phase. Thus, if global warming occurs, cycling of chemicals through the atmosphere will increase. On the other hand, models suggest that temperature contrast between the equator and the pole will decrease (Figure 2.1) (Zwiers, 2002). Accordingly, kinetic processes will increase with temperature rise but the overall thermodynamic forcing toward polar regions will decrease with reduced global thermal contrast. KAW also increases significantly (40-70%) under warming conditions, which would favor evasion from surface waters. This would be particularly important for OCs such as the HCHs which are at, or in the case of α -HCH over, saturation in Arctic waters. The predicted increase in K_{AW} associated with a 5°C increase in water temperature corresponds to tonnes of HCHs that could be forced back into the atmosphere each year. However, temperature increases of 5°C are unlikely to occur in partially ice-covered regions where temperatures will be buffered by melting ice. Nevertheless, recent changes in the AO index (Figure 3.1) and model projections (Figures 2.1 and $2 \cdot 2$) indicate that a large number of lakes and major areas of Arctic shelves could be subject to such changes.

Loss of chemicals occurs during transport in the atmosphere through reactions with hydroxyl (OH) radicals, nitrate radicals (NO₃) or ozone (O₃), through photolytic oxidation and through sorptive partitioning to other phases (e.g., aerosols, precipitation, vegetation) with subsequent deposition. Although photolytic reactions do not have a strong dependence on temperature they will be affected by cloud cover which is predicted to increase with global warming (IPCC, 1995). Increased cloud cover will also result in lower OH radical concentrations and less chemical removed by this and other photolytic pathways.

The dominant removal processes in soil and water include hydrolysis, photolysis, redox reactions, microbial degradation and removal through soil-surface-air partitioning. Of these, only photolysis is not strongly dependent on temperature. The influence of temperature on the rate constant, *k*, is usually described using the Arrhenius expression,

$$k = Ae^{-E_a/RT}$$
 Eqn 1

where A is a constant, R is the gas constant, T is temperature, and E_a is the activation energy. Based on hydrolysis activation energies of 78 to 85 kJ/mol (Ngabe *et al.*, 1993) for α -HCH and γ -HCH respectively, a 5°C increase would increase removal rates by ~85 to 95%. The increase would be even greater if it is considered that the dissociation constant for water (K_W) (e.g., at pH = 8) increases with temperature, resulting in more OH⁻ ions. Activation energies associated with redox reactions are not reported for OCs but are usually assumed to be about 50 kJ/mol (Tratnyek and Macalady, 2000) which imply about a 50% increase in reaction rate with a 5°C rise in temperature.

Microbial degradation also follows the Arrhenius equation, but few studies report E_a . As a general rule, the biological activity in the mesophilic range (5-35°C) doubles for every 10 to 15°C temperature rise which implies an E_a of 30 to 45 kJ/mol (Viessman and Hammer, 1985). Arctic microbial populations exhibit a large diversity and abundance (Ravenschlag *et al.*, 2001; Sahm and Berninger, 1998) and are typically cold-adapted, being able to maintain efficient rates of organic degradation and mineralization down to the freezing point of

Figure 6.9. The marine food web observed during the Northwater Project. The panels show average concentrations of selected organochlorine compounds in air, water, and various trophic levels (see Fisk *et al.*, 2001a, 2001b; Hobson and Welch, 1992).

seawater $(-2^{\circ}C)$ (Arnosti, 1998; Sagemann *et al.*, 1998). This suggests that warming may be accompanied by consequences of adaptation or population change, but not necessarily that microbial degradation rates will increase. For example, reduced degradation of methyl dichlorprop was observed in experiments where field plots were warmed to a temperature of 5°C above normal for several years (Peterjohn, 1994).

Harner *et al.* (1999) found *in situ* microbial removal rates for α - and γ -HCH in cold Arctic Ocean waters to be surprisingly fast (t_{1/2} for (+) α -HCH, 5.9 yr; (-) α -HCH, 22.8 yr; γ -HCH, 18.8 yr). Assuming an E_a of 50 kJ/mol, a 2 to 5°C temperature rise in the upper Arctic Ocean would imply a reduction of these half-lives by 20 to 50%. Microbial degradation was estimated to account for over 30% of the removal of HCH suggesting that a small temperature rise could push this proportion to over 50%.

Aside from temperature, alterations in other environmental characteristics (e.g., soil moisture, soil and water pH, nutrient levels, vegetation cover and type) will be tied to global warming and will affect the composition and density of microbial populations. For instance Lewis et al. (1999) found differences in microbial preference for microbes inhabiting forested versus pasture soils. They also showed that the enantioselectivity (preference of the microbial population for a + or – enantiomer of a chiral compound, i.e., a compound exhibiting mirrorimage forms) changed with organic nutrient enrichment. Other studies have observed high rates of microbial degradation of HCHs in Arctic lakes (Law et al., 2001) and watersheds (Helm et al., 2000). Law et al. (2001) found that enantioselective degradation of α -HCH was greater in small, High Arctic lakes and streams compared to temperate lakes and wetlands. They concluded that low nutrient levels in the Arctic systems resulted in an adapted microbial population that was more capable of degrading organic contaminants. Thus biodegradation of chemical residues in soil and water will be altered as microbial populations adapt to changing climate. The complexity and uncertainty associated with these changes however, does not, at the present time, allow prediction of whether global warming will enhance or diminish chemical removal by this pathway.

Putting many of these concepts into a numerical model, McKone *et al.* (1996) investigated the effect of a 5°C temperature rise on the health risk from HCB. They found surprisingly little consequence from the projected 5°C temperature increase. Indeed, their results showed that warming would actually reduce exposure as it would enhance degradation and tend to force HCB out of water and into air. The critical step, controlled by the sensitivity of air–water partitioning to temperature, acts at the bottom of aquatic food webs which, due to biomagnification, are still of great significance for dietary exposure and related health risks.

6.3.5. The effect of altering food web structure

Biomagnification can concentrate fat-soluble compounds, such as the OCs, by factors as high as 10^5 to 10^9 from water to apex predators (Fisk *et al.*, 2001a; Kidd *et al.*, 1995b; Muir and Norstrom, 1994; Muir *et al.*, 1999). The distribution of contaminants in air, water, and the first step in the food web (phytoplankton, particulate organic carbon), can be predicted simply by applying appropriate partition coefficients (e.g., K_{AW} and K_{OW}) (Figure 6·8). Chemical partitioning, which is based solely on thermodynamics, provides a crucial platform upon which biomagnification can then operate (Figure 6·9). A chemical at equilibrium will have identical fugacity in the media in question (e.g., air, water, oil) and this makes it relatively simple to predict how temperature will alter its distribution.

Biomagnification, however, cannot be explained solely by thermodynamics, and it requires energetic processes to produce the elevated concentrations in top predators. These processes can be considered in part as a reduction of fat - the solvent containing OCs - through metabolism. The processes are complex and can lead to variability simply due to bio-energetics; the offloading of contaminants to offspring by nursing mammals is a classic example (Addison and Smith, 1998). It is not the intent here to conduct a thorough review of bioaccumulation and biomagnification except to state that the complexity of the process offers the opportunity for climate change to act in subtle ways. The data shown in the four panels of Figure 6.9 show an almost linear relationship between the log (contaminant burden) and trophic level. The slope of this relationship indicates the multiplication factor involved for each step in trophic level so that, for example, one step would multiply DDT concentration by perhaps as much as 6 (neglecting polar bears) whereas the other contaminants experience factors of 2 (Σ HCH), 3 (Σ PCB) and 4 (chlordane). The removal or addition of trophic levels in the food web mediated by climate change, therefore, will not have the same effect for all contaminants; for example, Figure 6.9 suggests that DDT will be the most sensitive to this kind of change.

Another way in which food web structure can effect change is by bifurcation. For instance, altering the coupling between pelagic and ice production and the benthos can change the relative proportions of organic carbon (and contaminant) that enter pelagic or benthic food webs. However, these changes in pathway do not alter the relationship between contaminant concentration and trophic level. In this context it can be seen that walrus (*Odobenus rosmarus*) feeding on a benthos enriched by strong coupling with primary production will be exposed to lower (by factors of 10 or more) OC concentrations than if they switch to predation on seals.

6.3.6. The epontic food web and changes in ice climate

The entry of contaminants to a stratifying surface layer from ice melt in spring offers a mechanism vulnerable to climate change. However, recent studies do not appear to show higher concentrations in epontic fauna than in zooplankton (Borgå et al., 2002). Organochlorine concentrations in epontic amphipods (Apherusa glacialis, Gammarus wilkitzkii, Onisimus spp.) and zooplankton (Calanus hyperboreus, Thysanoessa inermis, Parathemisto libellula, and Chaetognatha) from the marginal ice zone near Svalbard could mostly be explained by diet, with habitat (sea-ice underside versus the pelagic zone) accounting for a smaller part of the variance. Epontic amphipods had higher concentrations of HCB, γ - and α -HCH, while DDTs, PCBs and chlordanes did not differ between epontic and pelagic habitats. This pattern of uptake can be explained by the vertical distribution of OCs in the water column: higher concentrations of HCHs and HCB are found near the sea surface (Harner et al., 1999; Jantunen and Bidleman, 1998; Tanabe and Tatsukawa, 1983) whereas particle reactive compounds like DDTs and highly-chlorinated PCBs adsorb onto sinking particles to produce a more homogenous vertical distribution (Tanabe and Tatsukawa, 1983). Furthermore, most particles transported by sea ice are not available to epontic biota because they are released in the marginal ice zone when the ice melts (Ramseier *et al.*, 1999) and descend rapidly, carrying the adsorbed contaminants with them. For OCs that exhibit strong gradients in the upper ocean, the loss of ice and hence of epontic fauna can alter the dietary exposure of higher trophic levels like seabirds and seals.

6.3.7. Food deprivation or shifts in diet

Many of the Arctic top predators undergo periods of fasting forced by lack of food, seasonality of food, or inability to access food. Perhaps the best documented example is the stress to the Hudson Bay polar bear (Ursus *maritimus*) population deprived of their ability to hunt seals during spring due to change in the spring ice climate (see Figure 3.23 and Stirling, 2002; Stirling and Lunn, 1997; Stirling et al., 1999). The burning of stored fat through metabolism results in release of archived fatsoluble contaminants and, potentially, an increase of contaminant burden in the remaining fat reservoir. Longer periods of starvation due to change in ice or change in prey populations could lead to higher doses of OCs sequestered in fat – usually at a time when the animal can least afford it. Although the concern with nourishment-deprived polar bears has received much attention, similar circumstances probably apply to other species such as common eider (Somateria mollissima; Olafsdottir et al., 1998) and Arctic char (Salvelinus alpinus; AMAP, 2003b).

Species that have dietary flexibility may respond to ecosystem change by switching to alternate prey, again with consequences on their OC intake. For example, the large variation in OC concentrations in the livers of glaucous gulls (Larus hyperboreus) from the western Barents Sea correlates with nitrogen isotopic ($\delta^{15}N$) composition (AMAP, 2003b). Nitrogen isotopes provide a well-established, reliable chemical indicator of the trophic level of an animal's prey (Hobson and Welch, 1992) therefore implying that much of the variation in OC concentration in glaucous gull livers can be explained by the dietary choices the birds make - or are forced to make. Recent decreases in PCB concentrations in Svalbard minke whales (Balaenoptera acutorostrata) might superficially be ascribed to the banning of PCB manufacture during the 1970s. However, it seems more likely that this decline reflects a dietary switch from capelin (Mallotus villosus), whose stocks collapsed in 1992 to 1993, to krill which are lower down the food chain (AMAP, 2003b). Polar bears also display a range in prey that can explain regional variation in OC burdens. For example, Chukchi and Bering Sea bears feed more heavily on Pacific walrus which are less contaminated than ringed seals (*Phoca hispida*) because they are at a lower trophic level, whereas bears from Svalbard feed on more heavily contaminated harp seals (Phoca groenlandica). These latter results indicate that climate variables expressed through prey availability and biological condition can have a considerable influence on the exposure of apex feeders to OCs.

6.3.8. Altered migration pathways and invading species

Migratory species, including whales, fish, and birds, can obtain contaminant loadings in one location and release them in another, and migrating animals can be subject to varied exposure as they feed along their migration path. For one Alaskan lake, the loadings of OC contaminants returned by anadromous fish exceeded those entering the drainage basin from the atmosphere (Ewald et al., 1998). The recent expansion in the range of Pacific salmon (Oncorhynchus spp.) into rivers farther north in the Arctic (Babaluk et al., 2000) could, likewise, have an impact on contaminant budgets for the rivers or lakes that they enter. Certainly, these fish provide a new 'vector' for delivering contaminants to species that predate upon them or depend upon a food web supplied by their carcasses. Given the higher concentrations of β -HCH in the North Pacific Ocean than in the Arctic (Li et al., 2001) it seems likely that anadromous fish may provide an important, climate-sensitive vector for β -HCH into Arctic freshwater environments.

If the spatial distribution of contaminants is controlled by processes subject to climate change, then exposure during population migrations can also alter through climate change. An intriguing example of how such a process may operate has recently been described for the Bering/Beaufort bowhead whale (Balaena mysticetus) migration. The whales reflect in their body burdens the change in α - and β -HCH composition between the Bering and Beaufort Seas (Hoekstra et al., 2002). The ocean composition for the HCHs is probably controlled by large-scale physical processes (e.g., rainfall and air-sea partitioning - see Li et al., 2002) as are migratory routes (Dyke et al., 1996b; Moore et al., 1995), each of which is sensitive to climate change. Therefore, alteration in HCH loading of the ocean caused by change in winds, ice cover or rainfall pattern, or alteration in the feeding locations of the whales caused by change in ice distribution, will similarly alter the exposure to HCHs.

Finally, invasions of new species fostered by climate change, overfishing or by introduced exotic species also have the potential to re-structure food webs. An elegant example of how dramatic such change can be, both in trophic organization and contaminant pathways, was provided by the invasion of the zebra mussel (Dreissena polymorpha) into the Great Lakes (Morrison et al., 1998, 2000; Whittle et al., 2000). Following their invasion in 1988, zebra mussels have led to a decline in phytoplankton and rotifer densities, the water has become clearer (by the removal of particulates), and the deposition of nutrient-rich pseudofeces at the bottom has altered benthic habitat density and structure. In turn, the zebra mussels have become an important prey item altering the trophic structure within the lake as reflected by the stable isotopic composition of fish. In another example, devastating change in the Black Sea ecosystem has resulted from the population explosions of phytoplankton and jellyfish (Daskalov, 2002). In this case, top-down trophic change may have been initiated by overfishing of apex feeders. Clearly, the migration northward even of a humble filter feeder or jellyfish, potential products of changing water properties or organic carbon supply, could have unexpected impact on contaminant cycling in coastal seas.

6.3.9. Organochlorine compounds, disease, and epidemics

During the past decade or so, there has emerged much evidence that mass mortalities in marine mammals may occur as a result of a combination of factors including disease vectors, population stress and contaminants, each of which may be affected by climate change (see Lavigne and Schmitz, 1990; Ross, 2002). The complexity of this interaction provides fertile ground for surprises. Some disease outbreaks have been observed following migrations associated with large-scale ecological change, and some have derived from the introduction of viruses from domestic animals. But it is the addition of immunotoxic chemicals, such as many of the POPs, that may provide the trigger for disease to emerge (Ross et al., 2000; Vos and Luster, 1989). The widespread distribution of the canine distemper virus, or a closely related morbillivirus in seals from Greenland led Dietz et al. (1989) to speculate on the possibility that large-scale migration of harp seals from the Barents Sea to northern Europe in 1986 to 1987 might have provided a disease vector. The co-factors of a naïve marine mammal (seal) population in coastal Europe manifesting suppressed immune systems through high contaminant PCB burdens would then have provided the foundation for the epidemic (Heide-Jørgensen et al., 1992).

Within the Arctic, top predators would be at greatest risk due to their high exposure to contaminants, and marine mammals probably face the added stress of changes in ice climate. Accordingly, indications of immunosuppression have been found in polar bears, northern fur seals (Callorhinus ursinus) and glaucous gulls (AMAP, 2003b). In particular, the polar bears of the Kara Sea, Franz Josef Land, East Greenland and Svalbard would seem especially vulnerable. Firstly, these bears exhibit inordinately high contaminant burdens (Andersen et al., 2001; Norstrom et al., 1998) and these high burdens may well derive partly from the enhanced connection between this region and Europe/North America under the strong AO+/NAO+ conditions of the 1990s (Figures 3.2 and 3.17). Secondly, as previously discussed, change in ice climate and in marine ecosystems may have provided the added stress of malnourishment. Lastly, it seems that these bears already have sufficient contaminant burdens to exhibit health effects (Bernhoft et al., 2000; Skaare et al., 2001).

6.4. Hydrocarbons

Hydrocarbons in the Arctic derive from combustion and petrogenic sources (Yunker *et al.*, 1995). The pathways of these two sources of hydrocarbon differ substantially as will their sensitivity to climate change. Hydrocarbons of anthropogenic origin pose two kinds of problem; polyaromatic hydrocarbons (PAHs) and their oxidation products are toxic (Zedeck, 1980), and spilled oil has direct, well-known effects on biota, especially those that inhabit interfaces between water, air, ice and sediments. (Patin, 1999; Wolfe *et al.*, 1994).

6.4.1. Combustion PAHs

Combustion PAHs are well-known products of natural fires and human-related combustion processes (e.g., au-

Figure 6-10. Oil/gas-bearing regions and locations of oil/gas production together with the ice-drift field under a) AO⁻ conditions and b) AO⁺ conditions (ice motion based on Rigor *et al.* (2002) and oil data from Bakke *et al.* (1998)).

tomobiles, liquid and solid fuel burning, waste incineration, metallurgy, etc.). In the atmosphere, PAHs partition between the vapor phase and particulates (see for example Figures 14 and 15 in Macdonald et al., 2000a) and are detected at remote Arctic locations following transport over long distances (Halsall et al., 1997; Macdonald et al., 2000a; Patton et al., 1991). There is a strong seasonality in PAH concentrations in air at Alert (Ellesmere Island, Canada) with colder months (October-April) displaying concentrations about ten times higher than in warmer months (May-September). This suggests that the winter haze phenomenon that transports heavy metals across the pole from Eurasia also transports industrial combustion products. Therefore, much of what has been said about aerosol metals and climate change in section 6.1.1 relates directly to PAHs; altered wind patterns (Figure 3.2) and enhanced precipitation (Figure 3.4) have the potential to change pathways and to deposit PAH aerosols over parts of the Arctic Ocean especially toward the southern Eurasian Basin. Furthermore, temperature increases may shift the equilibrium from particulate to vapor phase for PAHs like pyrene, fluoranthene, phenanthrene and anthracene, which at Arctic temperatures are partially distributed between air and solid phase (Figure 6.7).

In addition to the strong seasonal signal of industrial PAHs observed in the Arctic, outliers (samples with abnormally high PAH concentrations) are also observed during summer months, particularly at Tagish (southwest Yukon, Canada), and these have been assigned to forest fires (Macdonald *et al.*, 2000a). Forest fires are projected to increase through climate change as a result of warmer continental temperatures (Figure 2·1) and less precipitation in continental interiors. A general increase in atmospheric PAHs in the Arctic deriving from such

biomass burning is thus likely, and this increase will probably have an impact on small rivers, e.g., in northern Canada, which already receive almost all their PAHs from combustion sources (Yunker *et al.*, 2002). Loss of permafrost and enhanced erosion of peat may also contribute enhanced amounts of relict PAHs to lakes and rivers (Yunker *et al.*, 1993).

6.4.2. Petrogenic hydrocarbons and oil

A leading concern for the Arctic is the risk of oil spills from both onshore and offshore exploration and production (Bakke *et al.*, 1998; Patin, 1999). Climate change that produces an ocean margin substantially clear of ice will undoubtedly encourage further offshore exploration, perhaps in more remote locations. Producing oil from the Arctic reserves, especially those on the remote shelves, has the associated problem of transporting produced oil to markets in the south, either by ship or pipeline.

It is clear that changes in the ice drift associated with changes in the AO index will have a dramatic influence on where spilled oil will go if it enters the ice pack (Figure 6.10). For example, in the Canadian and Alaskan sector of the Arctic Ocean during AO⁻ conditions, the oil will follow ice into the East Siberian Sea to traverse the Russian shelves and then exit to the Greenland Sea. During AO⁺ conditions, oil from the same location would tend to remain within the Beaufort Gyre potentially to return within a few years to where it was spilled.

Oil spilled over the Russian shelves, or entering their coastal seas from spills into rivers, would tend to track directly across the Arctic under AO⁻ conditions (Figure 6·10 a). However, oil spilled under AO⁺ conditions could move more to the east, with a slight chance that it might

reach the Canada Basin and then the Canadian Arctic Archipelago through which it would then have to pass. It is uncertain how viable this latter route might be for oil spilled in the Kara or Laptev Seas, but evidence from tree dendrology suggests that there have been periods during the Holocene when communication from Siberia to the Canadian Arctic Archipelago has been mediated by ice drift (Dyke and Savelle, 2000; Dyke *et al.*, 1997). Indeed, the transport of trees by Arctic sea ice and the change in that transport with time provides some of the best evidence of where oil spilled in Arctic coastal regions is likely to travel (see for example, Eggertsson, 1994a,b).

Pipelines transporting oil across land in the Arctic are vulnerable to enhanced permafrost degradation. Regions such as the Komi Republic, which experienced large oil spills onto the tundra in 1994, exemplify the difficulty. Warming and melting of frozen ground will put corroded pipelines, many working beyond their design life, at greater risk. Oil already spilled onto land within the Arctic drainage basin may become more mobile, entering water courses as the hydrological cycle becomes more vigorous.

Another connection between spilled oil and climate change derives from the projected increase in incident UV radiation (Weatherhead and Morseth, 1998) which could lead to an increase in photo-enhanced toxicity of spilled oil (see, for example Barron and Ka'aihue, 2001; Pelletier *et al.*, 1997). Toxicological assessments of oil made in the presence of UV light reveal a toxicity of up to 1000 times greater than that measured under the traditional fluorescent light. Furthermore, photo-enhanced toxicity of oil can occur at the intensities and wavelengths measured for UV in aquatic water columns suggesting that increased incident UV radiation projected for polar regions may, in addition to many other effects on ecosystems (Weatherhead and Morseth, 1998), enhance damage done by spilled oil.