# Chlorinated Hydrocarbon Contaminants in the Arctic Marine Environment

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## 1. Sources, Transport and Fate

Many different chlorinated hydrocarbon (CHC) compounds have been released to the environment. Among these are the pesticides chlordane and toxaphene (polychlorinated camphenes, PCCs) hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB) and DDT, and the industrial chemicals polychlorinated biphenyls (PCBs). These CHCs have been identified in air, snow, ocean water, and biota in the Arctic marine ecosystem[1),2),3)]. Most open uses of these chemicals have been severely curtailed in industrialized nations, but a considerable fraction of past production is probably still cycling in the ecosphere. For example, it has been estimated that 20 percent of the world production of PCBs, 230,000 tons, are present in the upper layers of the ocean, and 790 tons were in the open ocean atmosphere[4)]. Large quantities of CHC pesticides continue to be used in less developed countries, especially in the southern hemisphere[5)]. There is little quantitative information on production or release in the former USSR or China, but both areas undoubtedly are major contributors to the environmental burden of CHCs[1)]. Thus, despite over 20 years of controls in some cases, environmental concentrations of CHCs have decreased slowly, or even remained constant, in remote environments because of global recycling and slow removal processes.

CHCs can be remarkably resistant to environmental degradation by chemical and biological processes[6)]. They therefore tend to have long environmental half-lives. CHC pesticides and PCBs have sufficiently high vapour pressures that they readily volatilize when spread over a large surface area such as soil or water[7)]. Atmospheric residence time of PCBs has been estimated to be in the order of a few months[8)]. Pesticides such as toxaphene are released directly to the atmosphere by agricultural spraying, and PCBs continue to be released from electrical equipment and landfill sites. The CHCs listed above also have Henry's Law constants (0.1 to 50 $Pa.m^3/mol$), which are high enough to permit them to cycle back and forth between land or surface waters and air, and distributed globally in the troposphere[6),9)].

Wania and Mackay[7)] state that vapour pressure is the main factor governing organochlorine transport to the Arctic. Their view is that a negative gradient with increasing latitude for less volatile CHCs, such as DDTs and highly chlorinated PCBs, is in keeping with efficient removal close to sources at mid-latitudes. Ottar[10)] discussed the possibility of the Arctic becoming a "cold finger" sink for CHCs, that is, global distillation from warmer to colder areas. There is now some direct evidence for this effect in the research reported by Iwata et al.[11)]. They found that there was a net flux of PCBs and chlordanes from air to ocean surface water, and that

there was an increasing flux with increasing latitude as the air and water become colder. The sources, occurrence and pathways of CHCs (and other contaminants) in the Arctic have recently been reviewed[1),12)]

## 2. Concentrations in the Environment and Biota

Recent average concentrations of the major classes of CHC contaminants in the Arctic marine environment and ecosystem are given in Table 1. HCHs, HCB are the dominant CHCs in air, followed closely by PCCs. DDTs, Chlordane and PCBs are an order of magnitude lower. Because of its higher Henry's Law Constant, HCB becomes significantly less important in snow and seawater. The HCH levels in surface water in the Arctic Ocean are 4-5 ng/L[13], compared to levels of 2-3 ng/L in the Bering and Chukchi Seas[11),14),15)] and <2 ng/L in mid-latitude Pacific Ocean[11)]. The higher levels of HCH in Arctic Ocean water support the notion of distillation of HCH from warmer to colder environments. Higher levels of HCHs in Arctic water may also be related to the proximity of sources in Asia.

**Table 1**. Average levels of the major classes of organochlorine contaminants found in the Arctic marine environment and ecosystem. Levels are given as sums of total compound class, including metabolites such as DDE (in DDTs) and oxychlordane (in Chlordanes). Values are arithmetic means of all data, including both males and females in the case of mammals.

| Ref. No. | | HCHs | HCB | PCCs | DDTs | Chlordanes | PCBs |
|---|---|---|---|---|---|---|---|
| 16),17) | air, ng/m$^3$ | 0.58 | 0.19 | 0.044 | <0.001 | 0.006 | 0.014 |
| 16),17) | snow, ng/L | 1.72 | <0.002 | 0.085 | <0.01 | 0.06 | 0.086 |
| 16),17) | seawater (surf.), ng/L | 4.3 | 0.028 | 0.36 | <0.001 | 0.004 | 0.007 |
| 16),17) | seawater (deep), ng/L | 0.51 | 0.01 | 0.11 | <0.002 | 0.005 | <0.014 |
| 12) | zooplankton, $\mu$g/g lipid | 0.08 | 0.02 | 0.06 | 0.06 | 0.06 | 0.11 |
| 12) | amphipods*, $\mu$g/g lipid | 0.5 | 0.17 | NA | <0.35 | 0.43 | <0.44 |
| 2),18) | cod, $\mu$g/g lipid | 0.58 | 0.2 | 1.84 | 0.26 | 0.19 | 0.23 |
| 19) | beluga, $\mu$g/g lipid | 0.25 | 0.5 | 3.11 | 2.82 | 1.76 | 3.79 |
| 19) | ringed seal, $\mu$g/g lipid | 0.23 | 0.03 | 0.32 | 0.5 | 0.4 | 0.55 |
| 19) | polar bear, $\mu$g/g lipid | 0.51 | 0.27 | ~0.4** | 0.4 | 3.7 | 5.4 |
| 20) | human milk, $\mu$g/g lipid | NA | 0.14 | NA | 1.21 | na | 1.05 |

* pelagic, n = 1pooled sample
** estimated by ratio to total PCBs from Zhu et al.[21], n=1

The importance of DDTs, chlordanes and PCBs relative to the other CHCs increases going from water to zooplankton and amphipods, because their greater lipophilicity and lower water solubility (higher $K_{ow}$) enhances bioconcentration. Concentrations of CHCs on a lipid weight basis increase at each step in the food chain from plankton to amphipods/cod to beluga. Muir et al.[2)] in a comprehensive review of levels of the major classes of CHCs in the Arctic marine ecosystem estimated bioaccumulation factors of $10^7$ for HCH and PCCs and $10^9$ for PCBs from water to high trophic level predators. In spite of increases in concentration, there are few striking changes in the pattern among CHC compound classes between plankton and beluga, indicating that metabolism or selective excretion is a minor process in CHC bioaccumulation dynamics in this food chain. HCHs are an exception. Levels decrease markedly relative to

the other CHCs in the food chain above plankton. Bioconcentration of HCHs by plankton is less favoured due to lower $K_{ow}$. In the case of ringed seal, HCHs, HCB and PCCs are not biomagnified from amphipods/cod on a lipid weight basis, indicating faster excretion of these compounds than DDTs, chlordanes and PCBs, presumably by metabolism[19]. Polar bears accumulate mainly PCBs and Chlordanes (principally oxychlordane)[22].

In addition to selective accumulation of CHC classes in ringed seal and polar bear compared to the other species, considerable changes occur in the makeup of the compounds within the Chlordane and PCB classes due to metabolism. The ratio of the metabolite oxychlordane to one of its precursors, trans-nonachlor, can be used as an indicator of relative metabolic potential: arctic cod, 0.28; beluga, 0.55; ringed seal, 1.38; polar bear, 9.5[18),19]. Similarly, the ratio of the persistent PCB congener, CB-153 (2,4,5-2',4',5'-hexachlorobiphenyl), to total PCBs increases with metabolic potential as less persistent congeners are metabolized: arctic cod, 0.08; beluga, 0.06; ringed seal, 0.20; polar bear, 0.4[18,19].

The number of CHC classes investigated in humans potentially exposed to CHCs through ingestion of marine mammals has been limited largely to PCBs and DDTs. The most comprehensive study is on Inuit breast milk from northern Quebec in Canada[20]. Levels of PCBs (Table 1) were similar to those in beluga blubber from that area, and 6.7 times higher than in southern, Caucasian women. Although DDE was also higher in Inuit mother's milk, the ratio to levels in non-native women was less, 3.6.

### 3. Effect of Trophic Level on Bioaccumulation

Hobson and Welch[23] recently used stable nitrogen isotope ratios, $\delta$-$^{15}N$, to determine the trophic levels of a number of arctic marine species. Because biomagnification of a number of CHCs occurs at each step in the food chain, there ought to be some correlation between CHC concentrations and trophic level. This theory was tested with total chlordanes, total PCBs and CB-153 data for plankton, amphipods and ten arctic marine species. Data for zooplankton, arctic cod, amphipods, ringed seal, beluga and polar bear were taken from the same sources as indicated in Table 1. Narwhal data were from Muir et al.[24]. Walrus data were for Hall Beach and Igloolik in northern Foxe Basin[25]. Data for common eider, black guillemot, thick-billed murre and glaucous gull were Canadian Wildlife Service unpublished data (Birgit Braune, pers. comm.). In the case of amphipods and plankton, the CB-153 numbers were estimated from total PCBs assuming that the ratio of CB-153/total PCBs was the same as that in arctic cod[18]. DDT and PCB data for pelagic amphipods were assumed to be 0.5 X detection limit[13]. The trophic level of common eider was assumed to be the same as that of walrus because both are molluscivores. The trophic level of arctic cod was assumed to be an average of large and small fish.

The logarithm of the concentration of total chlordanes, total PCBs and CB-153 was linearly correlated to trophic level. All of the correlations were significant at the $p<0.01$ level or lower, the degree of significance being lowest for total Chlordanes ($r^2 = 0.6259$ $p<0.01$) and highest for CB-153 ($r^2 = 0.8818$ $p<0.0001$). Some of the variance in the total Chlordane and total PCB correlations may be due to differing metabolic capacity of the species. Susceptible compounds within the chlordane and PCB classes are metabolized by polar bears, seals, walrus and birds, which results in lower biomagnification factors. This tends to depress the slope of the log-linear relationship with trophic level. By contrast, CB-153 is probably not metabolized by any of the species, and is therefore a good marker compound for testing the relationship between

bioaccumulation and trophic level. Ringed seal had the greatest divergence from the linear model. This may be due to incorrect assignment of trophic level for the particular individuals which were chemically analyzed. Hobson and Welch[23] noted that trophic level of ringed seals may be age-, season- and site-specific because of diet shifts from invertebrates to fish.

Transforming the regression equations to exponential form, the concentrations in μg/g lipid are related to trophic level (TL) by the expressions: total Chlordanes = $0.0091 \cdot 10^{0.49TL}$; total PCBs = $0.0038 \cdot 10^{0.67TL}$; CB-153 = $0.00017 \cdot 10^{0.82TL}$ The exponent for CB-153 is probably close to the upper limit for biomagnification of CHCs in this ecosystem. The overall biomagnification factor between unit trophic levels in the Arctic marine ecosystem for non-metabolizable CHCs on a lipid weight basis can therefore defined as $10^{0.82(TL+1)}/10^{0.82TL} = 10^{0.82} = 6.6$. This value is close to that calculated directly for PCBs and chlordane biomagnification from ringed seal to polar bear[2], which are exactly one trophic level apart[23].

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