Bioaccumulation Factors for PCBs Revisited

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Bioaccumulation factors (BAFs) for individual polychlorinated biphenyl (PCB) congeners in Barents Sea and White Sea marine calanoid copepods were 1–3 orders of magnitude higher than BAFs in the same species in Canadian and Alaskan Arctic Ocean areas, and in freshwater plankton (Lake Ontario) reported from the mid- to early 1980s. The present study reviews variability in PCB BAFs from the North American Great Lakes and the Arctic Ocean, and discusses possible explanations for the large variation among different studies. BAFs are higher in recent arctic marine and Great Lakes studies than previously reported, and they are at least 10 times higher than those predicted from the octanol–water partition coefficient (KOW). If the recent high BAFs are realistic, it means that earlier reported BAFs are too low. This is likely due to earlier erroneously high quantification of water PCB concentrations, and it implies that bioaccumulation in zooplankton is more efficient than previously assumed. Evidence is presented supporting that also trophic transfer and biomagnification of PCBs in zooplankton leads to BAFs well above those predicted by simple equilibrium partitioning. Overall, miss-measurement of water PCB concentrations and biomagnification contribute significantly to variability in BAFs for PCBs within and among studies. This large variability of BAFs for PCBs in zooplankton illustrated in the present study is of importance for future assessments of potential new bioaccumulative chemicals that rely on measured BAFs, such as the European Union Registration, Evaluation and Authorization of Chemicals program (REACH).

Introduction

Bioaccumulation factors (BAF, L·kg⁻¹ lipid, eq 1) have been used for the past 25 years to describe the net increase of organic contaminants such as persistent organic pollutants (POPs) from water to biota due to uptake from all exposure routes (1, 2).

\[
\text{BAF} = \frac{\text{[POP in organism]}_{\text{LIPID CORRECTED}}}{\text{[POP in water]}_{\text{DISSOLVED}}} 
\]

The bioconcentration factor (BCF) is a special case of bioaccumulation seen in controlled laboratory experiments in which BCF is the equilibrium ratio between POPs in biota and the surrounding environment due to abiotic exposure; however, BAF and BCF are calculated the same way (eq 1). The Stockholm convention on POPs (3) and other chemical management programs categorize chemicals with BCF or BAF higher than 5000 (wet weight basis) as bioaccumulative. Although usually calculated on a wet weight basis (2, 4), BAFs and BCFs change depending on the lipid content of the organism. Therefore, lipid-normalized BAF and BCF values (eq 1) are more useful when comparing across animals, as the variation due to variable lipid content is eliminated.

BCF on a wet weight basis can be predicted from the chemical’s octanol–water partition coefficient (KOW), by models such as BCFWIN used by the U.S. Environmental Protection Agency (USEPA) (4). In absence of environmental measurements of a chemical in biota and water to calculate BAFs, BCFs predicted from KOWs are useful tools for exposure and risk assessments of new chemicals; however, for animals with dietary exposure and uptake of POPs they may be underpredicted. Programs such as Registration, Evaluation and Authorization of Chemicals (REACH) in the European Union (5), the Canadian Environmental Protection Act (CEPA)’s Domestic Substances List (DSL) (6), and the USEPA high production chemicals assessments (7) are screening large numbers of chemicals for bioaccumulation potential using predicted BCFs. Future candidate POPs will likely be chemicals with BCF or BAFs greater than 5000, and field evidence for this will probably be essential to develop a strong case for inclusion on the POPs list. Thus, a detailed understanding of the uncertainties of BCF and BAF measurements is needed.

The present study we have summarized data from arctic marine ecosystems and from the Great Lakes of North America to investigate uncertainties of field measurements of BAFs and factors affecting calculated values of BAFs. Factors influencing BAFs are those such as season or size-related characteristics of plankton (8–10), as well as differences in water sampling methods (such as filtration, sorbent material, on-board versus in situ sampling) that can affect estimates of dissolved POPs (11). Our focus is on water to zooplankton accumulation of polychlorinated biphenyls (PCB) for the following reasons. (i) PCBs are measured on a congener specific basis in many field programs, and their KOWs are known (e.g., 12). (ii) Although feeding on phytoplankton and other zooplankton, by virtue of their size and physiology, zooplankton are believed to accumulate a significant fraction of POPs from the dissolved phase in water and to rapidly reach equilibrium with water (2, 8, 13), thus they are more straightforward to model than fish and other top predators. (iii) Because zooplankton are typically one trophic level lower than most invertebrate-feeding fish in marine and freshwater food webs, BAFs of POPs in zooplankton are generally the lowest field BAFs that can be routinely measured, and they are thus conservative values.

The main objective of the present study was to revisit the issue of whether “true” BAFs could be established for PCBs dissolved in water to zooplankton in lakes and marine...
systems. In particular we wanted to understand whether BAFs for PCBs are in the range predicted by the congener’s $K_{ow}$.

**Materials and Methods**

**Comparison of BAFs.** Unfortunately, relatively few field studies include PCB measurements in both zooplankton and the operational dissolved phase in water. We selected studies which report both water and zooplankton PCB concentrations (9, 14–22) as well as other work in which water and zooplankton were collected in the same region or lake but analyzed by separate groups (23–29) (Tables 1 and 2). All water samples were filtered to separate particle-bound and dissolved PCBs in all studies, except Oliver and Niimi (16) and Morrison et al. (17) which were centrifuged (removing particles larger than 0.2 μm) (30). BAFs (eq 1) for PCBs were calculated for zooplankton from the Arctic Ocean and from the Laurentian Great Lakes (Figure 1) and compared to the calculated for zooplankton from the Arctic Ocean and from Morrison et al. (16) analyzed by separate groups (17) which report both water and zooplankton PCB concentrations

**Variation in PCB BAFs.** Both within and among studies, the PCB BAFs ranged widely around the 1:1 relationship with $K_{ow}$ (Figure 1) and decreased slightly with increasing $K_{ow}$ (n = 43, Pearson $R = 0.370$, $p = 0.015$; Spearman’s rank $R = 0.295$, $p = 0.054$). For the Great Lakes, differences between maximum and minimum BAF ranged from 0.002 to 4.01 for the individual congeners, and decreased slightly with increasing $K_{ow}$ (n = 86, Pearson $R = -0.231$, $p = 0.032$; Spearman’s rank $R = -0.155$, $p = 0.153$). Thus, the relationship between differences in observed freshwater log BAFs and log $K_{ow}$ was opposite to that of the marine studies, but note that neither the marine nor the freshwater nonparametric correlations were significant.

When the relationship between calculated BAFs and the measured water and zooplankton PCB concentrations was investigated, marine BAFs were not correlated with marine zooplankton PCB concentrations (Spearman’s rank: $\Sigma$PCB $r = 0.20$, $p = 0.704$; $\Sigma$10PCB $r = 0.25$, $p = 0.486$) (Figure 3). The lack of correlation between marine BAF and zooplankton PCB concentrations indicates that the PCBs in zooplankton were determined in a similar and comparable way among studies. Most of the marine zooplankton samples were comparable in that they were largely dominated by large calanoid copepods (14, 15, 19, 25). The quality of zooplankton PCB data is usually not considered problematic as lipids are relatively easy to separate and extract. Also, PCB levels in zooplankton are usually well above method detection limits, and interlaboratory comparisons for PCB quantification in marine biota suggest that between-laboratory accuracies of 15–20% can be achieved among experienced laboratories (32). Lake zooplankton PCB concentrations, however, were positively correlated with BAFs (Spearman’s rank: $\Sigma$PCB $r = 0.93$, $p = 0.0002$; $\Sigma$10PCB $r = 0.96$, $p = 0.0005$). The positive correlation may be due to either compromised PCB measurements, which seems unlikely given the elevated PCB levels in biota and the high extraction efficiency of lipids and associated PCBs, or it may be due to inclusion of a wide variety of zooplankton size fractions and trophic guilds in the different studies.

BAFs decreased with increasing seawater and lake PCB concentrations (seawater: Spearman’s rank $\Sigma$PCB $r = -0.72$, $p = 0.0427$; $\Sigma$10PCB $r = -0.81$, $p = 0.0041$; freshwater: $\Sigma$PCB $r = -0.75$, $p = 0.0199$; $\Sigma$10PCB $r = -0.79$, $p = 0.0362$) (Figure 3). The significant correlations between BAFs and water PCB concentrations suggest that either some PCB measurements were compromised or different sampling techniques (water collection, particle separation, volume extracted, extraction method) resulted in differences in fractionation of dissolved PCBs. Differences in water PCB measurements most likely explain the large variation in BAFs among the arctic marine studies, such as the Canadian Arctic and the Barents Sea, as PCB concentrations in similar zooplankton species did not differ between the studies (33), whereas the water concentrations differed widely (14, 23). When quantifying PCBs in water, water collection and contaminant extraction is the step associated with most uncertainties (34, 35). Passive respiratory uptake of contaminants from water is from the freely dissolved concentration, which should be used for BAF calculation to make them comparable among studies (2). Determination of the dissolved fraction of PCBs in water is challenging, and early work may not have thoroughly accounted for shipboard and laboratory contamination (36).

Several methodological advances during the late 1990s, including use of clean rooms on ships, solid-phase extraction, and in situ samplers, have led to significantly lower dissolved PCBs reported both in the Arctic and in the Great Lakes. Overestimated dissolved water PCB concentrations were also noted by Harding (37) when reviewing BAFs from the early 1970s. In the early 1980s, when the Great Lakes’ research was initiated, the general method used was to pump water onto the ship, centrifuge the water to separate out the
<table>
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<th>Year</th>
<th>Month</th>
<th>Method</th>
<th>Filters</th>
<th>Extraction</th>
<th>Volume</th>
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<th>S</th>
<th>A</th>
<th>Blank Corr.</th>
<th>∑PCBs</th>
<th>∑PCB10</th>
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<td>XAD-2</td>
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<td>submersible pump</td>
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<td>XAD-2</td>
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<td>-</td>
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<td>107 ± 12.6</td>
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<td>submersible pump</td>
<td>GF/F 293 μm</td>
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<td>-</td>
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<td></td>
<td>+</td>
<td>+</td>
<td>518</td>
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* S and A indicate whether clean room facilities were used during water extraction (S) and chemical analyses (A), respectively. * Infiltrex = AXYS Infiltrex II system in situ sampler; Seastar = Seastar in situ pump; AXYS Technologies, Sidney BC Canada; submersible pump = submersible pumping onto the ship (stainless steel system). * Blank corr indicates whether the results are blank-corrected. * Ref refers to reference list. See Table 1 in the supporting information for congeners included in the different studies.
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<th>biota</th>
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<td>VNH$^a$ (100 $\mu$m)</td>
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<td>Calanus glacialis</td>
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<td>zooplankton</td>
<td></td>
<td>3</td>
<td>2.1 ± 0.4</td>
<td>473 ± 46.2</td>
<td>21</td>
</tr>
<tr>
<td>Experimental Lake 110</td>
<td>1992/93</td>
<td>May/July</td>
<td>VNH (100 $\mu$m)</td>
<td>-</td>
<td>-</td>
<td>zooplankton</td>
<td></td>
<td>2</td>
<td>23.6 ± 0.6</td>
<td>194</td>
<td>71.2 ± 8.7</td>
</tr>
<tr>
<td>Experimental Lake 227</td>
<td>1992/93</td>
<td>May/July</td>
<td>VNH (100 $\mu$m)</td>
<td>-</td>
<td>-</td>
<td>zooplankton</td>
<td></td>
<td>2</td>
<td>28.0 ± 1.8</td>
<td>276</td>
<td>73.7 ± 9.9</td>
</tr>
</tbody>
</table>

$^a$ VNH = vertical net hauls (mesh size).
$^b$ S = field equipment was solvent-rinsed between samplings.
$^c$ Blank corr = whether measured values were blank-corrected.
$^d$ Lipid content is % of wet weight (except for Barrow, Lake Michigan and experimental lakes (ELA110 and ELA227), where they are % of dry weight, thus italicized).
$^e$ Ref refers to reference list. See Table 2 in the supporting information for congeners included in the different studies.
particles, and use dichloromethane extraction to recover the dissolved PCBs (e.g., \(16\)). This method however, can also accumulate PCBs shipboard and cause laboratory contamination, and was largely abandoned in favor of XAD-2 resin extraction (\(29, 38\)) or polyurethane foam (PUF), although in some laboratories with low PCB backgrounds dichloromethane extraction yielded results similar to those from XAD-2 resins (\(39\)).

Petrick et al. (\(34\)) estimated that 500–1000 L of water should be extracted to obtain reliable dissolved PCB concentrations without interference of analytical problems. In the reviewed studies, lower seawater dissolved PCB concentrations (fg \(\cdot \) L\(^{-1}\) range) were reported when 200–400 L was extracted using XAD-2 resins (\(9\)), and when more than 400 L was extracted using PUFs (\(23, 24\)) (Table 1). Higher seawater dissolved PCB concentrations (pg \(\cdot \) L\(^{-1}\) range) were reported when less than, or close to, 100 L was extracted using XAD-2 resins (\(14, 15\)). Thus, it appears that extraction by XAD-2 and PUFs yields different measurements of dissolved PCBs, and/or that extraction of low water volume may result in greater interference from background PCB contamination. Breakthrough of the cartridge in use by large volume sampling is considered negligible as extracting different high volumes of water resulted in comparable PCB concentrations (\(40\)).

Although all the studies considered in this analysis filtered or centrifuged water to remove particulate organic carbon (POC) and POC-associated PCBs, not all of the chemicals were freely dissolved as filtering and centrifugation are only operational definitions (\(30, 37\)). PCBs associated with dissolved organic carbon (DOC) will pass through the filter, and are not freely dissolved and bioavailable for passive uptake to lower trophic level biota. By adjusting for DOC, the freely dissolved concentration can be obtained, which is lower than the operationally dissolved, resulting in higher BAFs. Burkhard (\(41\)) suggest calculating the freely dissolved fraction by eq 2:

\[
f_d = 1/(1 + POC \times K_{OW} + DOC \times 0.08K_{OW})
\]

where \(f_d\) is the freely dissolved fraction, DOC is the average dissolved organic carbon concentration in the water column (kg of organic carbon \(\cdot\) L\(^{-1}\) of water), POC is the average particulate organic carbon concentration in the water column (kg of organic carbon \(\cdot\) L\(^{-1}\) of water), \(K_{OW}\) estimates the partition between POC and freely dissolved chemical, and \(0.08K_{OW}\) estimates the partition between DOC and freely dissolved chemical. Assuming POC is negligible for filtered or centrifuged water, the fraction dissolved is

\[
f_d = 1/(1 + DOC \times 0.08K_{OW})
\]

As more hydrophobic PCBs, usually with log \(K_{OW}\) higher than 6, have a larger proportion bound to or associated with dissolved organic carbon (\(2\)), the difference between BAFs based on operational and freely dissolved water PCB concentration is higher for these congeners. Likewise, the variability in measured BAFs would likely be higher with increasing \(K_{OW}\), as different collection techniques (in which some are more likely to have captured the freely dissolved concentrations) would be more influential on the more hydrophobic congeners. Some extraction devices, such as XAD-2 resins, do not capture DOC and associated contaminants unless the DOC concentrations are high (> 10 mg\(\cdot\)L\(^{-1}\)) (\(41\)), and DOC correction may therefore not be required. DOC values in Great Lakes waters ranged from 1 to 2 mg\(\cdot\)L\(^{-1}\) in Lake Superior, Michigan, Huron, and Ontario in water collected for PCB analysis in 1993 (\(42\)) and similar DOC concentrations were found in mid-lake sites in 1997 (\(27\)). Thus, \(f_d\) for a PCB congener with log \(K_{OW}\) of 7 is 99% after...
filtration, and no correction of BAFs for DOC sorption is necessary for oligotrophic freshwater systems, or for arctic marine waters where DOC concentrations are also low (0.5–1.5 mg L⁻¹, 43). An exception would be small inland lakes where DOC is higher. Jeremaison et al. (29) compared the PCB cycling in two ELA lakes, one (L227) that was eutrophic as a result of continuous nitrogen and phosphorus additions, and the other (L110) that was oligotrophic. Because of elevated DOC (7–13 mg L⁻¹), Jeremaison et al. (29) corrected dissolved PCB concentrations for DOC sorption leading to a reduction in 23PCB concentrations by 40% in both lakes. This would raise BAFs for ΣPCBs in zooplankton in those lakes by about a factor of 2. When the individual PCB congeners in L110 and L227 were DOC-corrected in the same way, the DOC-corrected BAFs were up to 20 times higher than the noncorrected ones, with largest difference for high $K_{OW}$ congeners (Figure 2f, g).

The present comparison of BAFs for PCBs is based on studies representing different areas, seasons, years, and zooplankton species, which may all contribute to variation in BAFs, in addition to variation caused by different water sampling and extraction methods. Both marine and freshwater BAFs vary seasonally due to variations in zooplankton’s lipid content as well as the suspended particulate matter concentrations which influence the chemical’s bioavailability (8, 9, 18, 21), but the seasonal variation in log BAFs for 23PCBs was less than 1 order of magnitude (Figure 4). Less than 1 order of magnitude in log BAFs due to seasonal variation was also seen for particulate organic matter in the Baltic Sea (10). Log BAFs for ΣPCBs varied with size fraction of marine zooplankton, but by less than 0.5 orders of magnitude (Figure 4a). Also, Barents Sea calanoid copepods species (C. glacialis and C. hyperboreus) with different body size showed different BAFs, however, usually less than 0.5 orders of magnitude (Figure 2). Thus, seasonal, zooplankton, or size specific BAF variation (8, 9, 21) was much lower than the BAF difference of 2–3 orders of magnitude observed between studies carried out at the same time of year including the same zooplankton species (C. hyperboreus) (14, 25) (Figure 2d, e).

Equilibrium Partitioning, Trophic Interactions, and BAFs. Several field studies with plankton have demonstrated a curvilinear relationship between log BAF and log $K_{OW}$ (e.g., 14, 15, 44). Higher BAFs than predicted by $K_{OW}$ and a curvilinear relationship between log BAF and log $K_{OW}$ suggest that PCB concentrations in zooplankton are not in equilibrium with water (2, 14, 25, 37). In some of the reviewed studies BAF for PCBs is close to $K_{OW}$ (e.g., 14, 15), however, as discussed above there is reason to believe that these BAFs are underestimated due to overestimated water PCB concentrations, as also discussed by Harding (37). The most challenging assumptions of a 1:1 linear relationship between BAF and $K_{OW}$ ($= equilibrium partitioning$) are that PCBs partition mainly into the neutral lipid pool of the organism, and that dietary PCB uptake leading to biomagnification is negligible so that the animal’s PCB level is in equilibrium with that in water (2, 17).

In organisms, hydrophobic contaminants may partition into other organic phases in addition to lipid (44–46). PCB partitioning into other organic phases could lead to linearity
between log BAF and log $K_{OW}$, but deviation from a 1:1 relationship, if the other organic phase is well described by $K_{OW}$. Several laboratory and field studies have reported BAFs (organic carbon normalized) higher than $K_{OW}$ (45, 47, 48), indicating greater partitioning of PCBs into organic carbon than octanol.

Biomagnification may occur between the lowest trophic levels of the food web (48–51), leading to higher BAFs than predicted from $K_{OW}$ (e.g., 17). One reason why this has often been overlooked may be erroneously high quantification of PCBs in water, as indicated by the negative relationship between BAFs and measured water PCB concentrations. To understand PCB dynamics in aquatic ecosystems it is important to understand energy and contaminant flux also under nonfeeding situations. Several bioaccumulation models have a nonequilibrium solution, taking into account not only partitioning uptake ($k_1$) and elimination ($k_2$) of POPs from the surrounding environment, but also uptake from diet ($k_D$) and elimination by fecal egestion ($k_F$), metabolism ($k_M$), and growth dilution ($k_G$) (e.g., 17). $k$ is the rate constant describing the respective uptake or elimination process. At steady state the animal’s POP concentration is:

$$[POP\text{ in organism}] = (k_1 \times [POP\text{ in water}]) \text{Dissolved} + k_D \times [POP\text{ in diet}]/(k_2 + k_E + k_M + k_G)$$

Of the elimination pathways, metabolism is often considered negligible in invertebrates (15, 17), whereas growth rates vary considerably (e.g., 57) and may greatly influence the bioaccumulation in the animal (e.g., 53). Elimination
through growth dilution is, however, often not considered when modeling contaminant bioaccumulation (e.g., 17). When a bioaccumulation model including growth dilution was parametrized for PCB bioaccumulation in the Barents Sea calanoid copepods, growth rate was indeed one of the most sensitive parameters (25). However, even by varying the growth rates in different bioaccumulation scenarios, resulting BAFs were not similar to those predicted by $K_{ow}$ (25).

The present study has demonstrated that BAFs for PCBs are greater in recent arctic marine and Great Lakes studies than previously reported in the same regions, and that they are at least 10 times higher than predicted from $K_{ow}$. It seems difficult to establish exact BAFs for PCBs in marine and freshwater zooplankton, as the variability of the system and the use of different PCB sampling and quantification methods results in BAFs that vary more than 1 order of magnitude. The BAF variation among studies is greater than can be accounted for by seasonal or size related differences. The negative dependence of BAFs to PCB exposure from water, in combination with the wide variety of methods used in water PCB measurements, suggest that earlier BAFs were too low due to overestimated water measurements. In addition, partitioning into other organic phases and dietary uptake of contaminants may lead to BAFs for PCBs above the ones predicted by $K_{ow}$. Whereas issues of water PCB measurements and partitioning medium do not require a process in addition to equilibrium partitioning to explain bioaccumulation in zooplankton, trophic transfer and bio-magnification of contaminants suggests that bioaccumulation in zooplankton exceeds what is predicted by equilibrium partitioning between water and lipids. All three contribute significantly to variability in PCBs BAFs both within and between studies, and may confound conclusions about zooplankton bioaccumulation and contaminant flux if assumed negligible.

The large variability of BAFs for PCBs in zooplankton illustrated in the present study needs to be considered in future assessments of potential new bioaccumulative chemicals that rely on laboratory or field measured BAFs, such as the European Union REACH program, the nomination of chemicals as future POPs under the Stockholm Convention, and other assessment programs. BAFs predicted from chemical structures and/or $K_{ow}$ may not give a sufficient estimate of bioaccumulation at the level of invertebrate communities, and overestimation of water concentrations due to contamination by candidate chemicals will need to be considered.

Acknowledgments

Colleagues attending the SETAC World Conference in Portland Oregon are thanked for valuable discussion and feedback. During the present study K.B. was supported by Norwegian Research Council’s project 159417/S30.

Supporting Information Available

Two tables showing congeners included in water and zooplankton data (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review February 23, 2005. Revised manuscript received March 29, 2005. Accepted March 30, 2005.

ES050376I