Bioaccumulation and differential partitioning of polychlorinated biphenyls in freshwater, planktonic food webs

Olof Berglund, Per Larsson, Göran Ewald, and Lennart Okla

Abstract: The planktonic food chain phytoplankton – zooplankton – young-of-the-year roach (*Rutilus rutilus*) was studied in 19 lakes in southern Sweden to investigate the bioaccumulation of polychlorinated biphenyls (PCBs). The ΣPCB concentrations did not steadily increase with increasing trophic level. The ΣPCB concentrations in zooplankton (400 ng·g lipid^{-1}) were lower than in both phytoplankton (660 ng·g lipid^{-1}) and fish (890 ng·g lipid^{-1}), which did not differ significantly. Lipid content explained 40% of the total variation in dry weight normalised ΣPCB concentrations in the samples. The PCBs were differentially partitioned between the trophic levels. The log BMFs (biomagnification factors, concentration in predator/concentration in prey) were a function of the $\log K_{ow}$ of the PCB congeners. The $\log \mathrm{BMF}_{zoo/phyto}$ values were < 0 for all PCB congeners on a lipid weight basis, and the $\log \mathrm{BMF}_{fish/zoo}$ values were < 0 for PCB congeners with $\log K_{ow} > 6$. We conclude that no PCBs had higher lipid-normalised concentrations in zooplankton than in phytoplankton and the most lipophilic PCBs had moderately higher concentrations in roach than in zooplankton. PCBs with $\log K_{ow} > 6$ decreased in concentration from phytoplankton to zooplankton to roach. We suggest that the concept of biomagnification did not apply to the planktonic food chain investigated in these lakes.

Résumé : Nous avons étudié la chaîne alimentaire planctonique phytoplancton – zooplancton – jeune gardon (*Rutilus rutilus*) dans 19 lacs du sud de la Suède afin d'analyser la bioaccumulation des polychlorobiphényles (PCB). Les concentrations de ΣPCB n'ont pas augmenté de façon constante avec l'augmentation du niveau trophique. Les concentrations de ΣPCB dans le zooplancton (400 ng·g lipides^{-1}) étaient plus faibles que dans le phytoplancton (660 ng·g lipides^{-1}) et chez les poissons (890 ng·g lipides^{-1}), concentrations qui ne différaient pas de façon significative. La teneur en lipides expliquait 40% de la variation totale des concentrations normalisées de ΣPCB en poids sec dans les échantillons. Les PCB étaient répartis de façon différentielle entre les niveaux trophiques. Le log FBA (facteurs de bioamplification, concentration chez le prédateur/concentration chez les proies) était une fonction du $\log K_{ow}$ des congénères de PCB. Le $\log \mathrm{FBA}_{zoo/phyto}$ était < 0 pour tous les congénères de PCB en fonction du poids en lipides, et le $\log \mathrm{FBA}_{poisson/zoo}$ était < 0 pour les congénères de PCB dont le $\log K_{ow} > 6$. Nous concluons qu'aucun PCB n'avait une concentration normalisée dans les lipides plus élevée chez le zooplancton que chez le phytoplancton, et que les concentrations de PCB les plus lipophiles étaient modérément plus élevées chez le gardon que chez le zooplancton. On observait une diminution de la concentration de PCB dont le $\log K_{ow} > 6$ en passant du phytoplancton au zooplancton puis au gardon. La notion de bioamplification ne semblait donc pas s'appliquer aux organismes de la chaîne alimentaire planctonique étudiés dans ces lacs.

[Traduit par la Rédaction]

Introduction

The concept of biomagnification of persistent organochlorines (OCs) has been investigated since high concentrations of dichlorodiphenyltrichloroethane (DDT) were observed in top predators five decades ago. Aquatic top predators were identified as especially vulnerable for biomagnification of OCs (Rudd 1964). This concentrative process was attributed to the presumed efficient transfer of OCs from one trophic level to the next, in combination with the reduction in biomass associated with each progressive trophic level, due to losses in the biomass conversion between trophic levels (Rudd 1964). This would yield greater concentrations (but not total amounts) of OCs associated with the next trophic level than those present in the previous trophic level. A consequence of the biomagnification process is that an increased number of trophic levels in a food chain will result in higher concentrations in the top predators.

There are indications of an efficient trophic transfer of OCs; 50–80% of polychlorinated biphenyls (PCB) have been estimated to transfer from food to lake trout (*Salvelinus namaycush*) in the Great Lakes (Madenjian et al. 1998). Biomagnification must result in concentrations in the predator that are higher than can be explained by passive diffusion from water. However, higher concentrations in predators than in prey can also be caused by processes other than biomagnification, such as elimination, growth dilution, or differences in age or exposure time. Accumulation of OCs via food rather than via water is necessary for biomagnification.

Received June 24, 1999. Accepted December 9, 1999. J15210

O. Berglund,[1] P. Larsson, G. Ewald, and L. Okla. Chemical Ecology and Ecotoxicology, Department of Ecology, Lund University, S-22362 Lund, Sweden.

[1]Author to whom all correspondence should be addressed. e-mail: olof.berglund@ecotox.lu.se

When in equilibrium between an organism and water, a chemical's bioconcentration factor (BCF), the ratio of the concentration in the organism to the concentration in water, is assumed to be a function of the octanol–water partitioning coefficient (K_{ow}) with a slope of unity (Mackay 1982). If organism BCFs are above that predicted from K_{ow}, the chemical is considered to have bioaccumulated via food (Oliver and Niimi 1988). However, as accumulation via food can be driven by passive diffusion over a fugacity gradient; food accumulation only is not evidence of biomagnification.

The biomagnification theory has been tested by examining OC concentrations at different trophic levels in aquatic food chains. Oliver and Niimi (1988) observed that PCB concentration increased with trophic level in a four-link food chain in Lake Ontario. Evans et al. (1991) similarly found increasing concentrations of PCB, dichlorodiphenyldichloroethylene (DDE), and toxaphene in a four-link food chain in Lake Michigan. Other, indirect approaches have also led to the conclusion that biomagnification of lipophilic chemicals via the food web is a major contributor to their accumulation in biota at higher trophic levels. Rasmussen et al. (1990) concluded that concentrations of PCB in top predators from different lakes increased with increasing length of the food chains, a result attributed to biomagnification. Russell et al. (1995) showed that concentrations of some PCBs were greater in white bass (*Morone chrysops*) than in their prey, emerald shiner (*Notropis atherinoides*), in Lake Erie, i.e., their biomagnification factors (BMFs) were > 1.

The concept of biomagnification has been questioned (LeBlanc 1995). Increasing concentrations of OCs with trophic level may instead be attributed to differences in lipid content (Bentzen et al. 1996; Kucklick and Baker 1998), depuration rates (LeBlanc 1995; Sijm and Van der Linde 1995), size (Bergner 1985), and exposure duration (Harding et al. 1997). LeBlanc (1995) argued that the apparent increase in lipid content with trophic levels would cause an increase in lipophilic OCs by bioconcentration alone, driven by passive diffusion over a fugacity gradient. Lipid content has been shown to explain a major part of the variation in OC accumulation by aquatic organisms (Larsson et al. 1996; Kucklick and Baker 1998). However, many studies show that even when lipid normalised, food web structure and trophic level may affect OC concentrations (Kiriluk et al. 1995; Bentzen et al. 1996; Kidd et al. 1998).

Most reports on biomagnification have focused on the transfer between planktivorous or benthivorous fish to piscivorous fish. Primary producers (phytoplankton and periphyton) are an important factor in controlling the fate and transport of OCs in natural waters. Settling algae acts as vectors for OCs from the water column to the sediment, and phytoplankton grazed by zooplankton transfer OCs into the pelagic food web (Stange and Swackhamer 1994). Despite the key role of this primary trophic level, to our knowledge, few studies have, in detail, examined the distribution of PCBs in the lower trophic levels of pelagic freshwater ecosystems (cf. Oliver and Niimi 1988; Harding et al. 1997).

Here, we examine the PCB distribution in the lower trophic levels in temperate lakes to determine whether PCBs may be biomagnified, i.e., if the concentration increases with trophic level in the food chain. We examined PCBs in the food chain phytoplankton – zooplankton – young-of-the-year (YOY) roach (*Rutilus rutilus*) in 19 lakes in southern Sweden. YOY roach were chosen for several reasons. Firstly, they are obligate pelagic planktivores (Persson 1997) and occupy the trophic level immediately above zooplankton. Secondly, we chose YOY fish to minimise variation in PCB concentrations due to age or size differences among the fish. Thirdly, we wanted to minimise age and size differences between the trophic levels. By choosing YOY fish, we also avoided differences in PCB concentrations between fish and plankton due to eventual differences in PCB exposure between seasons.

Methods

Study sites and sample collections

The 19 lakes included in this study are located in the southern part of Sweden (56°N, 14°E) within a 19 000-km^2 area and experience a similar climate. Limnological characteristics measured in the investigated lakes are presented in Table 1. For a detailed description of the methods of the limnological variables, see Berglund (1999).

All samples were collected in August 1997. We sampled plankton by towing three nets with 150-, 45-, and 10-μm mesh connected in series. This yielded three size-classes: macrozooplankton (>150 μm), microzooplankton (45–150 μm), and phytoplankton (10–45 μm). The 45–150 μm fraction consisted of ciliates, rotifers, and aggregated phytoplankton. Therefore, the plankton net setup operationally separated phytoplankton and macrozooplankton. As the 45–150 μm fraction contained more than one trophic level, only the 10–45 and >150 μm fractions were included in this study and will hereafter be referred to as phytoplankton and zooplankton, respectively. The compositions of the phytoplankton and zooplankton samples are described in more detail in Berglund (1999). Generally, phytoplankton samples consisted only of phytoplankton, and zooplankton samples only of zooplankton. The zooplankton communities were similar in all lakes. The dominating zooplankton in most lakes were the cladocerans *Daphnia galeata*, *Daphnia cristata*, and *Daphnia cuccullata* and calanoid and cyclopoid copepods. Other common species were the cladocerans *Chydorus*, *Diaphanosoma*, *Bosmina*, *Limnosida*, and *Holopedium*. YOY roach were collected with electrofishing. Fish were pooled into composite samples of 4–21 individuals. In two of the lakes, no YOY fish could be obtained. Plankton and fish were frozen after capture and later freeze-dried before analysis.

PCBs in water were sampled by collecting unfiltered water (50–100 L) just below the water surface and percolating it through two polyurethane columns (PUC) via a stainless steel funnel at a rate of 10–20 L·h^{-1} (Bremle et al. 1995).

PCB analyses

PCBs in plankton, fish, and PUCs were Soxhlet extracted with acetone–hexane according to Bremle et al. (1995) using octachloronaphtalene as an surrogate standard. The solvent was reduced in a vacuum centrifuge and the lipid amounts were determined gravimetrically. The sample was redissolved in hexane followed by an open column step as a cleanup. The column contained two layers of silica gel soaked in concentrated sulphuric acid and 1 M K_2CO_3. The solvent contained in the samples was evaporated in a vacuum centrifuge and was redissolved in isooctane prior to gas chromatographic analysis. For detailed information on preparation of the samples, see Bremle et al. (1995). For every 15 samples processed, a chemical blank was run. The average blank for ΣPCB (for included congeners, see Fig. 2) was 0.7 ng (concentration depends on sample size). PCB adsorption efficiencies on PUCs are given in Agrell et al. (1999). The average PUC

Table 1. Limnological characteristics of the studied lakes.

Lake	Area (km^2)	Maximum depth (m)	Total P ($\mu g \cdot L^{-1}$)	Chl *a* ($\mu g \cdot L^{-1}$)	Secci depth (m)	Biomass ($g \cdot m^{-3}$)	Total organic C ($mg \cdot L^{-1}$)
Krageholmsjön	2.1	10	153	38.7	1.1	1.45	7.2
Sövdesjön	2.8	12	80	105.7	0.5	1.78	11.7
Ringsjön	20	16	80	61.9	0.7	0.78	9.0
Vombsjön	12.8	16	80	15.8	1.1	1.92	6.1
Finjasjön	10	13	70	39.6	1.0	4.79	9.9
Åsnen	150	14	21	12.9	1.3	0.74	8.7
Västersjön	4.6	13	16	5.5	3.2	0.19	5.4
Vidöstern	48	35	15	5.9	2.8	0.18	7.9
Levrasjön	2.6	19	14	1.3	3.5	0.03	5.1
Kösen	11	22	12	4.9	3.5	0.20	8.2
Flåren	34	15	10	3.3	3.4	0.33	7.9
Ivösjön	54	50	10	3.0	2.5	0.23	6.7
Rottnen	33	18	10	4.0	3.2	0.19	9.2
Unnen	17	25	9	2.6	4.3	0.26	6.4
Immeln	24	28	9	3.8	3.0	0.19	6.2
Madkroken	12	21	8	5.9	3.1	0.27	7.2
Änghultasjön	4.4	28	8	6.4	3.4	0.24	8.4
Örken	23	38	7	2.6	5.2	0.24	11.9
Mien	20	39	7	2.6	5.0	0.08	7.5

field blank for ΣPCB was 2.2 ng (concentration depending on sample size). PUC field blank concentrations of domain 8 (IUPAC 16, 32) varied considerably (from below detection limits to 1.9 ng), so sample concentrations of this domain should be interpreted with caution. Sample concentrations were not corrected for blanks.

Gas chromatographic analysis

The samples were analysed for PCB by capillary gas chromatography – electron capture detection on a Varian Star 3400 cx equipped with an on-column injector. The chromatographic conditions and details are described in Bremle et al. (1995). The PCB components were identified and quantified according to Schulz et al. (1989). Thirty PCB domains were included in the analyses (see Fig. 2). PCB domains were identified and quantified on the basis of relative retention times and of response factors obtained for the chromatographic standard pentachlorobenzene. External standards of Clophen and Arochlor mixtures were run regularly to check performance. Extraction efficiencies for octachloronaphtalene were 83 ± 10% for plankton, 71 ± 11% for fish, and 64 ± 7% for PUCs. PCB concentrations in the different matrixes were not corrected for recovery.

Data analyses

Water concentrations of freely dissolved PCBs were calculated using the equations from Burkhard (1998):

$$(1) \qquad f_{fd} = 1/(1 + 0.1 \times DOC \times K_{oc} + POC \times K_{oc})$$

$$(2) \qquad C_w^{fd} = C_w^t f_{fd}$$

where f_{fd} is the fraction of the chemical that is freely dissolved in the water, DOC is the concentration of dissolved organic carbon, POC is the concentration of particulate organic carbon, K_{oc} is the organic carbon – water (freely dissolved basis) partitioning coefficient for the chemical, C_w^t is the total concentration of the chemical in the water, and C_w^{fd} is the freely dissolved concentration of the chemical in the water. Values for K_{oc} were estimated from the chemical's K_{ow} using the relationship from Karickhoff (1981):

$$(3) \qquad K_{oc} = 0.41 K_{ow}.$$

The K_{ow}s for the different PCB congeners were obtained from Hawker and Connell (1988). The K_{ow}s for coeluting congeners were calculated according to the relative composition of the congeners in the commercial Clophen A60 mixture (Schulz et al. 1989). Bioaccumulation factors (BAFs) were calculated by dividing the concentration of PCB in organisms (nanograms per kilogram of lipid or nanograms per kilogram dry weight) by the concentration of freely dissolved PCB in water (nanograms per litre). BMFs were calculated by dividing the concentration of PCB in predators (nanograms per kilogram of lipid or nanograms per kilogram dry weight) by the concentration of PCB in prey (nanograms per kilogram of lipid or nanograms per kilogram dry weight).

Prior to statistical analysis, concentration data were $\log_{10}$ transformed owing to their skewed distributions. *F* tests were performed to investigate homogeneity of variance between the groups (trophic levels). Analysis of variance (ANOVA) was used to investigate the effects of group (trophic level) on BAFs, PCB concentrations, and lipid contents. Sheffe's *F* post hoc test was used after ANOVA to examine which group means were significantly different from each other. Analysis of covariance (ANCOVA) was performed to confirm differences between slopes of regressions by the significant interaction terms. Statistics were carried out using Stat View® (Abacus Concepts, Inc.) and SYSTAT.

Results

Among-lake differences in ΣPCB concentrations in water or in biota on a lipid basis were not correlated with trophic status or any of the lake characteristics measured in this study (Table 1; also see Berglund 1999). The between-lake variance of lipid contents, logBAFs, and ΣPCB concentrations were homogenous in the three trophic levels. The *F* tests for homogeneity of variance showed that the variance ratios were not different from 1 ($p > 0.1$) except in one case, between ΣPCB concentrations (dry weight) in phytoplankton and zooplankton ($p = 0.02$). Therefore, we concluded that lipid and PCB data from all lakes could be compared.

The concentration of ΣPCB freely dissolved in water averaged 13 $pg \cdot L^{-1}$, ranging from 3.1 to 86 $pg \cdot L^{-1}$. We found

Table 2. Mean values (minimum–maximum in parentheses) of lipid content (% of dry weight), ΣPCB_{DW} concentrations (ng·g dry weight^{-1}), and ΣPCB_{LW} concentrations (ng·g extractable lipid^{-1}) in three trophic levels from 19 Swedish lakes.

	Phytoplankton	Zooplankton	Fish	*p*
Lipids	5.4[b] (0.7–13.6)	8.8[a] (1.6–14.4)	6.6 (2.9–10.8)	<0.01
ΣPCB_{DW}	28[c] (4.8–57)	33 (16–70)	55[a] (32–260)	<0.01
ΣPCB_{LW}	660[b] (250–1700)	400[a,c] (190–1000)	890[b] (460–2600)	<0.01

Note: Means for PCB concentrations are geometrical. ANOVA *p* values are given.
[a]Significantly different from phytoplankton (Sheffe's *F*, $p < 0.05$).
[b]Significantly different from zooplankton (Sheffe's *F*, $p < 0.05$).
[c]Significantly different from fish (Sheffe's *F*, $p < 0.05$).

that dry weight normalised ΣPCB concentrations differed significantly between the three trophic levels (Table 2). Concentrations of ΣPCB in the fish (55 ng·g dry weight^{-1}) were higher than in the phytoplankton (28 ng·g dry weight^{-1}) but not significantly different from those in the zooplankton (33 ng·g dry weight^{-1}). The plankton fractions did not differ in dry weight normalised ΣPCB concentration. Lipid content (percentage of dry weight) differed significantly between trophic levels. The zooplankton lipid content (8.8 ± 2.9%) was significantly higher than the phytoplankton lipid content (5.4 ± 3.3%). No difference in lipid content was found between the phytoplankton and the fish (6.6 ± 2.4%) or between the zooplankton and the fish. On a lipid weight basis, the zooplankton ΣPCB concentrations (400 ng·g lipid^{-1}) were lower than both the phytoplankton (660 ng·g lipid^{-1}) and the fish (890 ng·g lipid^{-1}) ΣPCB concentrations. No difference in lipid normalised ΣPCB concentrations was found between the phytoplankton and the fish (Table 2)

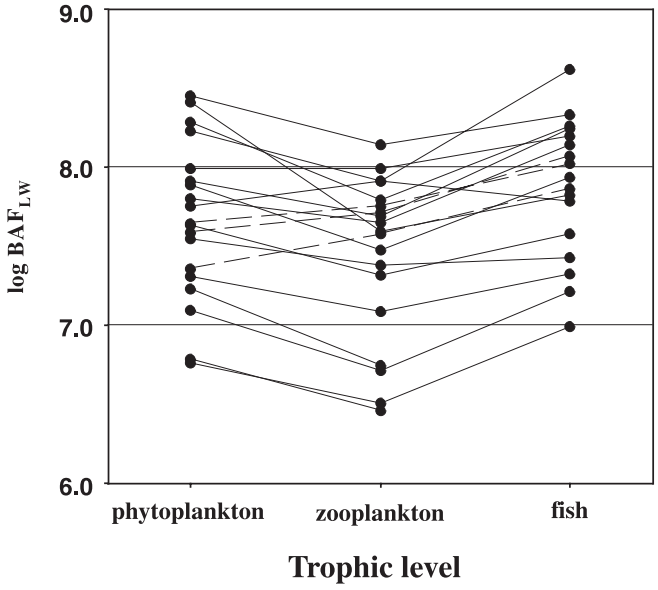
BAFs, calculated from concentration in biota/freely dissolved concentration in water, for ΣPCB did not differ between trophic levels when calculated on a dry weight basis (BAF_{DW}) (ANOVA, $p > 0.05$), although the fish logBAFs were higher than the phytoplankton logBAFs (Sheffe's *F*, significance level 5%). On a lipid weight basis, $\log BAF_{LW}$s differed between trophic levels (ANOVA, $p = 0.026$, Sheffe's *F*, significance level 5%) in that the fish logBAFs were higher than the zooplankton logBAFs. This pattern was consistent in all lakes but three (Fig. 1).

Lipid content explained 40% of the total variation in ΣPCB concentrations (nanograms per gram dry weight) in all plankton and fish samples (simple regression, $p < 0.01$, $r^2 = 0.40$). We found no trends in degree of explanation or slopes with lipophilicity (K_{ow}) of the individual PCB domains.

The relative compositions of individual PCBs, expressed as a percentage of ΣPCB, are shown in Fig. 2. The $\log BAF_{LW}$s for the individual PCB congeners in the three trophic levels were positively related to $\log K_{ow}$ (simple regression, $p < 0.01$, $r^2 = 0.61$, 0.83, and 0.84 for the phytoplankton, zooplankton, and fish, respectively) (Fig. 3). The slopes for the logBAF versus K_{ow} relationships were significantly different between phytoplankton, zooplankton, and roach as determined from the trophic level × $\log K_{ow}$ interaction term in ANCOVA ($p < 0.01$). The absolute values of lipid-normalised BAF_{LW}s were 1–1.5 orders of magnitude greater than K_{ow}. On a dry weight basis, BAF_{DW}s were of the same order of magnitude as K_{ow} and the slopes were significantly different (ANCOVA, $p < 0.01$).

The logBMFs for zooplankton/phytoplankton ($BMF_{zoo/phyto}$) and fish/zooplankton ($BMF_{fish/zoo}$) were positively related to $\log K_{ow}$, on both a lipid and a dry weight basis (Figs. 4 and 5) (simple regression, $p < 0.01$, $r^2 = 0.44$, 0.72 and 0.32, 0.69, respectively). The $\log BMF_{LWzoo/phyto}$ values were < 0 for all PCBs. The $\log BMF_{LWfish/zoo}$ values were < 0 for PCBs with $\log K_{ow} < 6$ and > 0 for PCBs with $\log K_{ow} > 6$.

Fig. 1. BAFs (nanograms PCB per kilogram lipid in biota/nanograms freely dissolved PCB per litre of water) for the three trophic levels: phytoplankton (10–45 μm), zooplankton (>150 μm), and fish (YOY roach). Solid lines connect the BAFs for each individual lake. Broken lines connect the three lakes in which BAF increased with trophic level.



Discussion

The theory of biomagnification predicts that due to more efficient transfer of OCs than energy between trophic levels, OC concentrations will increase in the food chain (Rudd 1964). We could not find an increase in lipid-normalised PCB concentrations from phytoplankton to zooplankton. We found higher concentrations of the most lipophilic PCBs in roach than in zooplankton, but PCBs with $\log K_{ow} < 6$ decreased in concentration from phytoplankton to zooplankton to roach. Hence, PCBs were not biomagnified from the primary trophic level to the secondary trophic level. Several studies have failed to find evidence of biomagnification in aquatic ecosystems, especially when investigating planktonic

Fig. 2. Composition of PCB domains in the investigated compartments (*a*) freely dissolved in water, (*b*) phytoplankton (10–45 μm), (*c*) zooplankton (>150 μm), and (*d*) fish. The relative frequencies (% of ΣPCB) are plotted for the 30 different domains (D) (from left to right: D8 (IUPAC Nos. 16, 32), D13 (31, 28), D14 (20, 33, 53), D20 (49), D21 (47, 48, 75), D23 (44), D25 (41, 64), D32 (66, 95), D36 (92), D38 (90, 101), D39 (99), D42 (97), D47 (82, 151), D50 (123, 149, 118), D53 (146), D54 (132, 153, 105), D58 (160, 138, 158), D59 (129, 126, 178), D61 (187), D62 (183), D63 (128), D65 (185), D66 (174), D67 (177), D68 (202, 171, 156), D70 (172), D72 (180), D77 (170, 190), D79 (199), and D84 (194).

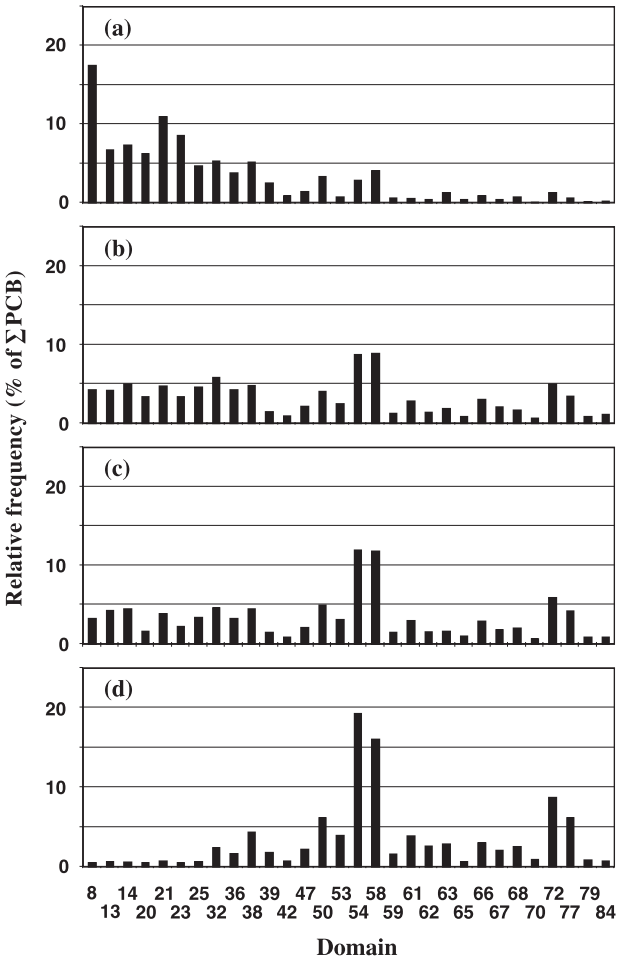
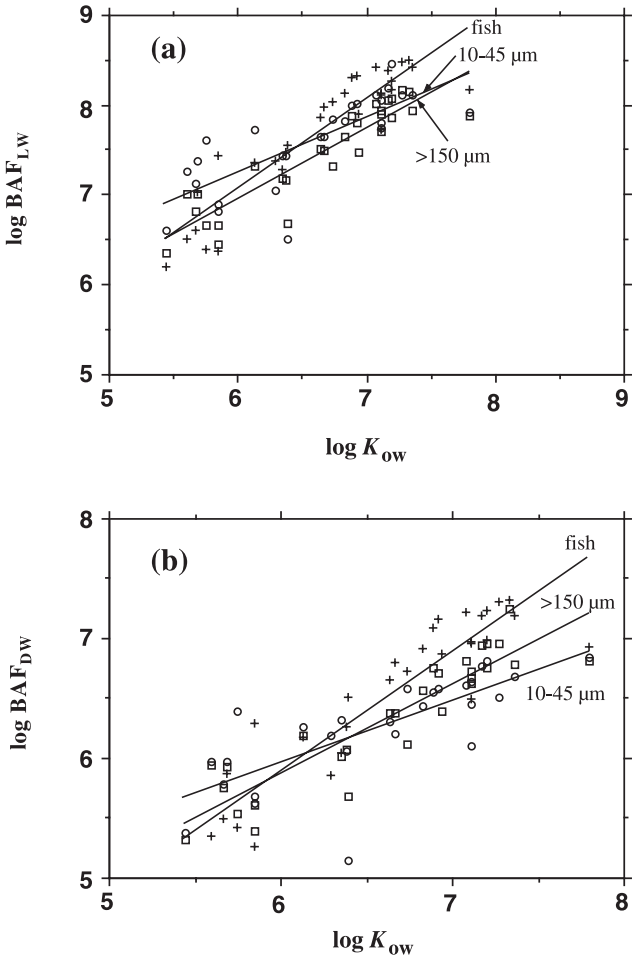


Fig. 3. Relationships between (*a*) BAF_{LW} and (*b*) BAF_{DW} and K_{ow} for the three trophic levels phytoplankton (10–45 μm, circles), zooplankton (>150 μm, squares), and YOY roach (fish, plus signs). Linear regression analysis gave the following relationships. Phytoplankton: $\log BAF_{LW} = 0.62 \log K_{ow} + 3.54$ ($r^2 = 0.61$); zooplankton: $\log BAF_{LW} = 0.78 \log K_{ow} + 2.30$ ($r^2 = 0.83$); fish: $\log BAF_{LW} = 1.02 \log K_{ow} + 0.97$ ($r^2 = 0.84$); phytoplankton: $\log BAF_{DW} = 0.52 \log K_{ow} + 2.87$ ($r^2 = 0.57$); zooplankton: $\log BAF_{DW} = 0.75 \log K_{ow} + 1.36$ ($r^2 = 0.83$); fish: $\log BAF_{DW} = 1.00 \log K_{ow} - 0.10$ ($r^2 = 0.83$).



food webs (Harding et al. 1997; Paterson et al. 1998). Kucklick and Baker (1998) concluded that the main influence of trophic position on PCB concentrations in Lake Superior's food web was due to the concurrent increase in lipid content with trophic position.

Daphnia spp. and copepods dominated the zooplankton samples in all lakes. *Daphnia* are generalist herbivorous filter-feeders that feed on a variety of algal taxa. They feed unselectively over a broad range of particle sizes and are unable to handle and reject poor-quality particles individually (DeMott 1995; Repka 1997). Copepods also feed on algae, but cyclopoid copepods are potential omnivores and feed on both algae and invertebrates (Adrian and Frost 1993). However, the *Daphnia* dominated by volume and weight in the zooplankton samples due to the small size of copepods. Therefore, the phytoplankton samples may be representative of the diet of the dominating *Daphnia* in the zooplankton samples. In a gut content analysis, Persson (1997) found that the diet of YOY roach from southern Sweden consisted exclusively of pelagic zooplankton species such as *Daphnia* spp., *Bosmina* spp., *Chydorus sphaericus*, *Leptodora kindtii*, and copepods, species that dominated in the zooplankton samples in this study. Thus, although we did not perform any diet analyses in this study, we feel that the phytoplankton samples and the zooplankton samples may be representative of the diets of the zooplankton samples and roach samples, respectively.

In an expanded analysis of the data used by Rasmussen et al. (1990), Bentzen et al. (1996) found that PCB concentrations in lake trout (*Salvelinus namaycush*) from different lakes were a function of lipid content, but the intercepts of the regressions differed between lakes. This was attributed to

Fig. 4. Relationships between (*a*) lipid-normalised $BMF_{zoo/phyto}$ and (*b*) $BMF_{fish/zoo}$ and K_{ow} for the different PCBs.

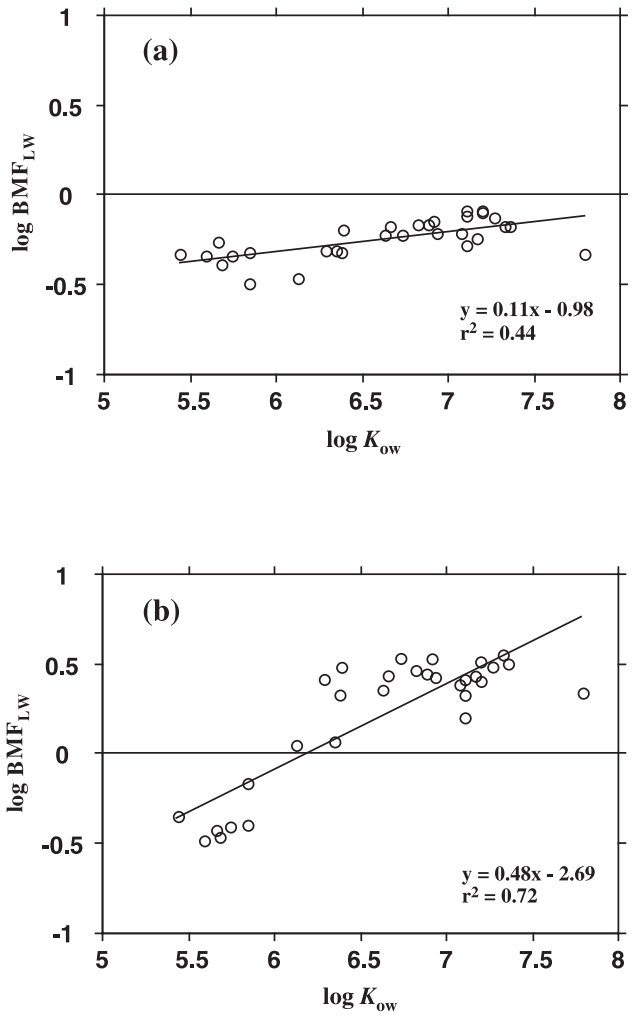
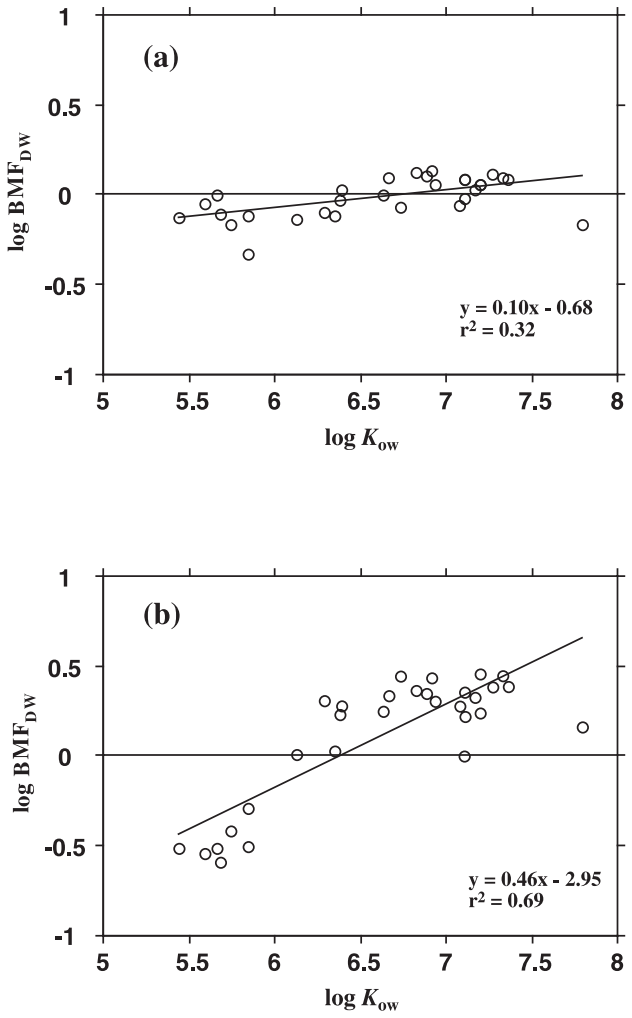


Fig. 5. Relationships between (*a*) dry weight normalised $BMF_{zoo/phyto}$ and (*b*) $BMF_{fish/zoo}$ and K_{ow} for the different PCBs.



food chain effects and (or) different loading of PCB. In our study, the relationship between BAF and trophic level showed the same behaviour in 14 of 17 investigated lakes. The phytoplankton and the fish BAFs were similar, but the zooplankton BAFs were lower. This pattern was exhibited for the majority of lakes despite a nearly two orders of magnitude difference between lakes in PCB concentration at each trophic level. It is unlikely that there existed any difference in the investigated food chain length between the lakes in our study. In all lakes, our pelagic food chain consisted of primary producers (phytoplankton), herbivore/planktivores (zooplankton), and obligate planktivores (YOY roach) at the very base of the pelagic food chain; therefore, there is no room for additional trophic levels. Hence, food chain differences seem unlikely to be responsible for the among-lake differences in the BAFs of the food chains, i.e., the intercepts for the BAF versus trophic level functions. Differences in loading of PCB to the lakes may affect the results but should be compensated for when comparing BAF rather than concentration in the organisms. The among-lake differences are, therefore, more likely attributable to differences in other processes.

The BAFs for the three trophic levels were positively related to K_{ow}. On a lipid basis, BAFs were 1–1.5 orders of magnitude higher than K_{ow} for all three trophic levels. Swackhamer and Skoglund (1993) found similar results for phytoplankton in natural waters. They suggested that normalisation to POC may be more appropriate than to lipids. When expressed on a dry weight basis, we found that BAFs were of the same magnitude as K_{ow} for all three trophic levels, a result similar to what Swackhamer and Skoglund (1993) obtained for phytoplankton. The slopes of the BAF function of K_{ow} in our study were not affected by normalisation of BAF. The slopes increased with trophic level, i.e., the relative amount of PCBs with low K_{ow} decreased in the organisms, compared with water, with trophic level: phytoplankton > zooplankton > fish. When OCs are in thermodynamic equilibrium between the dissolved phase in water and biota, the BCF should be a linear function of K_{ow} with a slope of 1 (Mackay 1982). We found that the slope for fish was approximately 1, for zooplankton was 0.8, and for phytoplankton was 0.6. Hence, the slopes indicated that the PCBs in fish were in equilibrium or steady state with the dissolved phase in water. The most lipophilic PCBs did not seem to be in steady state between water and zooplankton and even further from steady state between water and phyto-

plankton. The slopes of the BAF function of K_{ow} for the three trophic levels in this study are comparable with those observed by Oliver and Niimi (1988) in Lake Ontario in 1984. The slopes in their food chain were 0.7 for plankton (dominated by phytoplankton), 0.8 for mysids (*Mysis relicta*), and 0.9 for small rainbow smelt (*Osmerus mordax*). Although seldom tested, small planktonic organisms are often considered to be in equilibrium with dissolved water concentrations (Campfens and Mackay 1997). As the BAFs were above the 1:1 line between log BAF and log K_{ow}, the ΣPCB concentrations in phytoplankton, zooplankton, and fish all seemed to exceed equilibrium with water. There may be several explanations as to why the measured BAFs were not identical to the corresponding K_{ow}s for the PCB congeners. Exposure time of organisms to the PCBs may affect the BAFs. The organism PCB concentrations represent integrated measures of contamination over a period of time, and water measures are instantaneous. Therefore, changes in water concentrations may not be reflected in organism concentrations due to a lag period for equilibrium to be reached. Analytical and modelling procedures may also affect the BAF measures. The model used here to estimate freely dissolved water concentrations only provides an approximation, and the influence of POC and DOC on the freely dissolved concentrations may vary considerably. We cannot, therefore, exclude the possibility that we may have underestimated the freely dissolved concentrations and thereby overestimated the BAFs. Also, different methods of lipid extraction can vary in efficiency for different lipid classes (Ewald et al. 1998), which may affect lipid-normalised BAFs. Lipid composition in itself may also affect the relationship between BAF and K_{ow}. Different lipid classes have different affinity for PCBs, and it may not be appropriate to make direct, quantitative comparisons between lipids and octanol as solvents for PCBs.

The phytoplankton concentrations of PCB should only be affected by equilibrium partitioning with the water phase. However, for zooplankton, we found that the PCB pattern was different from that for phytoplankton in that the average lipophilicity increased and the concentrations were lower. Therefore, we believe that some processes other than biomagnification, differing from the phytoplankton–water partitioning, may be responsible for the PCB matrix observed in zooplankton. Thus, although we found strong relationships between log BAF and log K_{ow} for the PCB congeners, care should be taken when assuming equilibrium partitioning with the water phase, based on K_{ow} relationships, when modelling OC concentrations in small aquatic organisms.

If PCBs are biomagnified from prey to predator (Evans et al. 1991), the log BMF (predator/prey) should be > 0. In our study, on a lipid weight basis, no PCB congeners were biomagnified from phytoplankton to zooplankton, as all $BMF_{zoo/phyto}$ values were < 0. The $\log BMF_{zoo/phyto}$ values were positively related to log K_{ow}, i.e., PCBs with high log K_{ow} were relatively more abundant in zooplankton than in phytoplankton. Kucklick et al. (1996) suggested that the positive relationship between log BMF (predator/prey) and log K_{ow} found in Lake Baikal could be accounted for by a depuration rate inversely related to log K_{ow}, and lower in the predator than in the prey as suggested by LeBlanc (1995). The $\log BMF_{fish/zoo}$ showed the same pattern, but PCB congeners with log K_{ow} > 6 all had $\log BMF_{fish/zoo} > 0$, on both a lipid and a dry weight basis, concentrations being two to three times greater in fish than in zooplankton. Here also, PCBs with log K_{ow} < 6 had $BMF_{fish/zoo} < 0$, i.e., concentrations were lower in predator than in prey. In our study, the fractionation of the most lipophilic PCBs seemed to cease in the zooplankton to fish step, but the less lipophilic PCBs continued to be fractionated. Oliver and Niimi (1988) concluded that most of the differential PCB fractionation seemed to occur at the lower end of the food chain: in their study, the transfer from water to plankton to mysid. At the higher end of the food chain (mysid to rainbow smelt to adult salmonid), the PCBs seemed to be distributed as a uniform composition mixture. Thus, the concentrations of PCBs with log K_{ow} < 6 decreased with increasing trophic level: phytoplankton > zooplankton > fish. Oliver and Niimi (1988) concluded that there was a typical stepwise increase in PCB concentration as they moved up the food chain constituting plankton – mysids – rainbow smelt – salmonids. However, when regarding lipid content at the different trophic levels, it appears as if they also observed decreasing concentrations of trichlorobiphenyls from plankton to mysids to rainbow smelt and decreasing tetrachlorobiphenyl concentrations from plankton to mysids or rainbow smelt. As expected, the PCB pattern in water was skewed towards the low-chlorinated or less lipophilic congeners compared with plankton and fish, reflecting the decreasing water solubility with increasing chlorination of the PCB congeners.

The concentrations of the most lipophilic PCBs were approximately the same in phytoplankton and zooplankton but increased two to three times in fish. It has been shown that factors other than food uptake influence bioaccumulation of OCs and may explain the apparent increase in OC concentrations with trophic level. As mentioned above, lipid content strongly affects OC accumulation. Other factors that influence OC accumulation are elimination and lipid quality and composition. LeBlanc (1995) suggested that because of the sequestration of lipophilic OCs, within the body, in compartments distant from the site of elimination and the reduced ratio of elimination sites to body mass, elimination rates for OCs would be expected to decrease with increasing body mass. Zooplankton eliminate xenobiotics 10–100 times more rapidly than fish, and depuration rates of both fish and zooplankton are inversely related to the lipophilicity of the compound (LeBlanc 1995). The depuration of OCs has also been shown to decrease with increasing size of fish (Sijm and Van der Linde 1995; Fisk et al. 1998). The differences in depuration rates between zooplankton and fish increase with increasing lipophilicity of the xenobiotic (LeBlanc 1995). This would account for the differential partitioning of PCBs between phytoplankton, zooplankton, and phytoplankton in our study. Kucklick et al. (1996) also found positive relationships between BMF (predator/prey) and K_{ow} in the Lake Baikal trophic food chain. Their results indicated that in Lake Baikal, all PCBs were partitioned differentially between trophic levels 3 and 2 (amphipod–netplankton) and between levels 4 and 3 (sculpin–amphipod).

The observed relationship between $BMF_{zoo/phyto}$ and K_{ow} may be caused by increased differences in depuration rate with increased lipophilicity of the compound. Elimination of extremely hydrophobic chemicals is observed in small fish,

but elimination rates decrease with fish size (Sijm and Van der Linde 1995; Fisk et al. 1998). The more lipophilic OCs have longer elimination half-lives in biota than the less lipophilic compounds (Sijm et al. 1992). Therefore, the former accumulate to higher concentrations in an organism's tissues and bioaccumulate to a greater extent through the food chain (Oliver and Niimi 1988).

The lipid composition of aquatic organisms has been shown to affect uptake of lipophilic compounds. Ewald and Larsson (1994) demonstrated that nonpolar triglycerides accumulated more 2,2′,4,4′-tetrachlorobiphenyl than polar phospholipids. Lipid composition differs between phytoplankton, zooplankton, and fish. The polar to nonpolar lipid ratio increases from phytoplankton to zooplankton to fish (Wainman et al. 1993; Ewald and Larsson 1994; Stange and Swackhamer 1994; Napolitano et al. 1996). The higher content of nonpolar lipids, and consequently the higher OC accumulation capacity, in fish compared with zooplankton and phytoplankton may, therefore, be partly responsible for the reported higher concentrations of OCs in fish than in zooplankton and phytoplankton, independent of biomagnification processes.

In conclusion, lipid-normalised ΣPCB concentrations in zooplankton were lower than in both phytoplankton and fish, which did not differ in concentrations. No PCB domains were biomagnified from phytoplankton to zooplankton in the studied lakes. However, the concentrations of the most lipophilic PCBs were higher in fish than in zooplankton. PCB domains were differentially fractionated in all the links of the food chain; the average lipophilicity of the PCBs increased from water to fish. Concentrations of PCBs with $\log K_{ow} < 6$ decreased from phytoplankton to zooplankton to fish. We suggest that this may be an effect of a decreasing depuration rate of the most lipophilic PCBs with increasing size or trophic level.

Acknowledgements

This study was funded by the National Swedish Environmental Protection Agency (the EUCON project area), Swedish Association of Graduate Engineers, and Oscar and Lili Lamm's Memorial Foundation. Thanks to Cecilia Agrell for statistical guidance.

References

Adrian, R., and Frost, T.M. 1993. Omnivory in cyclopoid copepods — comparisons of algae and invertebrates as food for 3 differently sized species. J. Plankton Res. **15**: 643–658.

Agrell, C., Okla, L., Larsson, P., Backe, C., and Wania, F. 1999. Evidence of latitudinal fractionation of polychlorinated biphenyl congeners along the Baltic Sea region. Environ. Sci. Technol. **33**: 1149–1156.

Bentzen, E., Lean, D.R.S., Taylor, W.D., and Mackay, D. 1996. Role of food web structure on lipid and bioaccumulation on organic contaminants by lake trout (*Salvelinus namaycush*). Can. J. Fish. Aquat. Sci. **53**: 2397–2407.

Berglund, O. 1999. The influence of ecological processes on the accumulation of persistent organochlorines in aquatic ecosystems. Ph.D. thesis, Department of Ecology, Lund University, Lund, Sweden.

Bergner, P.-E.E. 1985. On relations between bioaccumulation and weight of organisms. Ecol. Model. **27**: 207–220.

Bremle, G., Okla, L., and Larsson, P. 1995. Uptake of PCB in fish in a contaminated river system: bioconcentration factors measured in the field. Environ. Sci. Technol. **29**: 2010–2015.

Burkhard, L.P. 1998. Comparison of two models for predicting bioaccumulation of hydrophobic organic chemicals in a Great Lakes food web. Environ. Toxicol. Chem. **17**: 383–393.

Campfens, J., and Mackay, D. 1997. Fugacity-based model of PCB bioaccumulation in complex aquatic food webs. Environ. Sci. Technol. **31**: 577–583.

DeMott, W.R. 1995. Effect of prey hardness on size-selective feeding by *Daphnia*. Hydrobiologia, **307**: 127–138.

Evans, M.S., Noguchi, G.E., and Rice, C.P. 1991. The biomagnification of polychlorinated biphenyls, toxaphene, and DDT compounds in a Lake Michigan offshore food web. Arch. Environ. Contam. Toxicol. **20**: 87–93.

Ewald, G., and Larsson, P. 1994. Partitioning of ^{14}C-labelled 2,2′,4,4′- tetrachlorobiphenyl between water and fish lipids. Environ. Toxicol. Chem. **13**: 1577–1580.

Ewald, G., Bremle, G., and Karlsson, A. 1998. Differences between Bligh and Dyer and Soxhlet extractions of PCBs and lipids from fat and lean fish muscle: implications for data evaluation. Mar. Pollut. Bull. **36**: 222–230.

Fisk, A.T., Norstrom, R.J., Cymbalisty, C.D., and Muir, D.C.G. 1998. Dietary accumulation and depuration of hydrophobic organochlorines: bioaccumulation parameters and their relationship with the octanol/water partition coefficient. Environ. Toxicol. Chem. **17**: 951–961.

Harding, G.C., LeBlanc, R.J., Vass, W.P., Addison, R.F., Hargrave, B.T., Pearre, S., Jr., Dupuis, A., and Brodie, P.F. 1997. Bioaccumulation of polychlorinated biphenyls (PCBs) in the marine pelagic food web, based on a seasonal study in the southern Gulf of St. Lawrence, 1976–1977. Mar. Chem. **56**: 145–179.

Hawker, D.W., and Connell, D.W. 1988. Octanol–water partitioning coefficients of polychlorinated biphenyl congeners. Environ. Sci. Technol. **22**: 382–387.

Karickhoff, S.W. 1981. Semi-emperical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere, **10**: 833–846.

Kidd, K.A., Schindler, D.W., Hesslein, R.H., and Muir, D.C.G. 1998. Effects of trophic position and lipid on organochlorine concentrations in fishes from subarctic lakes in Yukon Territory. Can. J. Fish. Aquat. Sci. **55**: 869–881.

Kiriluk, R.M., Servos, M.R., Whittle, D.M., Cabana, G., and Rasmussen, J.B. 1995. Using ratios of stable nitrogen and carbon isotopes to characterize the biomagnification of DDE, mirex, and PCB in a Lake Ontario pelagic food web. Can. J. Fish. Aquat. Sci. **52**: 2660–2674.

Kucklick, J.R., and Baker, J.E. 1998. Organochlorines in Lake Superior's food web. Environ. Sci. Technol. **32**: 1192–1198.

Kucklick, J.R., Harvey, H.R., Ostrom, P.H., Ostrom, N.E., and Baker, J.E. 1996. Organochlorine dynamics in the pelagic food web of Lake Baikal. Environ. Toxicol. Chem. **15**: 1388–1400.

Larsson, P., Backe, C., Bremle, G., Eklöv, A., and Okla, L. 1996. Persistent pollutants in a salmon population (*Salmo salar*) of the southern Baltic Sea. Can. J. Fish. Aquat. Sci. **53**: 62–69.

LeBlanc, G.A. 1995. Trophic-level differences in the bioconcentration of chemicals: implications in assessing environmental biomagnification. Environ. Sci. Technol. **29**: 154–160.

Mackay, D. 1982. Correlation of bioconcentration factors. Environ. Sci. Technol. **16**: 274–278.

Madenjian, C.P., Hesselberg, R.J., Desorcie, T.J., Schmidt, L.J., Stedman, R.M., Quintal, R.T., Begnoche, L.J., and Passino-

Reader, D.R. 1998. Estimate of net trophic transfer efficiency of PCBs to Lake Michigan lake trout from their prey. Environ. Sci. Technol. **32**: 886–891.

Napolitano, G.E., Shantha, N.C., Hill, W.R., and Luttrell, A.E. 1996. Lipid and fatty acid compositions of stream periphyton and stoneroller minnows (*Campostoma anomalum*): trophic and environmental implications. Arch. Hydrobiol. **137**: 211–225.

Oliver, B.G., and Niimi, A.J. 1988. Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecoystem. Environ. Sci. Technol. **22**: 388–397.

Paterson, M.J., Muir, D.C.G., Rosenberg, B., Fee, E.J., Anema, C., and Franzin, W. 1998. Does lake size affect concentrations of atmospherically derived polychlorinated biphenyls in water, sediment, zooplankton, and fish? Can. J. Fish. Aquat. Sci. **55**: 544–553.

Persson, A. 1997. Fish excretion in relation to internal and external load in a eutrophic lake. Limnol. Oceanogr. **42**: 577–583.

Rasmussen, J.B., Rowan, D.J., Lean, D.R.S., and Carey, J.H. 1990. Food chain structure in Ontario lakes determines PCB levels in lake trout (*Salvelinus namaycush*) and other pelagic fish. Can. J. Fish. Aquat. Sci. **47**: 2030–2038.

Repka, S. 1997. Effects of food type on the life history of *Daphnia* clones from lakes differing in trophic state. I. *Daphnia galeata* feeding on *Scenedesmus* and *Oscillatoria*. Freshwater Biol. **37**: 675–683.

Rudd, R.L. 1964. Biocider och den levande naturen. Wahlström & Widstrand, Stockholm, Sweden.

Russell, R.W., Lazar, R., and Haffner, G.C. 1995. Biomagnification of organochlorines in Lake Eire white bass. Environ. Toxicol. Chem. **14**: 719–724.

Schulz, D.E., Petrick, G., and Duinker, J.C. 1989. Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography – electron capture detection. Environ. Sci. Technol. **23**: 852–859.

Sijm, D.T.H.M., and Van der Linde, A. 1995. Size-dependent bioconcentration kinetics of hydrophobic organic chemicals in fish based on diffusive mass tranfer and allometric relationships. Environ. Sci. Technol. **29**: 2769–2777.

Sijm, D.T.H.M., Seinen, W., and Opperhuizen, A. 1992. Life-cycle biomagnification study in fish. Environ. Sci. Technol. **26**: 2162–2174.

Stange, K., and Swackhamer, D.L. 1994. Factors affecting phytoplankton species-specific differences in accumulation of 40 polychlorinated biphenyls (PCBs). Environ. Toxicol. Chem. **13**: 1849–1860.

Swackhamer, D.L., and Skoglund, R.S. 1993. Bioaccumulation of PCBs by algae: kinetics versus equilibrium. Environ. Toxicol. Chem. **12**: 831–838.

Wainman, B.C., McQueen, D.J., and Lean, D.R.S. 1993. Seasonal trends in zooplankton lipid concentration and class in freshwater lakes. J. Plankton Res. **15**: 1319–1332.