

Seasonal PCB Bioaccumulation in an Arctic Marine Ecosystem: A Model Analysis Incorporating Lipid Dynamics, Food-Web Productivity and Migration

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Received September 2, 2009. Revised manuscript received
November 16, 2009. Accepted November 16, 2009.

Primary production and species' lipid contents in Arctic ecosystems are notoriously seasonal. Additionally, seasonal migration patterns of fish may alter prey availability and thus diet. Taking the southern Barents Sea as a study region and PCBs as model contaminants, we examined to what extent each of these factors cause bioaccumulation in fish to change throughout the year. Data on physiology and standing stocks of multiple trophic levels were used to estimate season-specific carbon budgets and by inference also corresponding values for food ingestion and production of cod, capelin, and herring. When combining these values with Arctic lipid dynamics for bioaccumulation model parameter setting, we predicted bioaccumulation factors (BAFs) that were in good agreement with BAFs for cod and capelin observed between 1998 and 2008. BAFs in all fish were 10 times lower in summer than in spring and fall/winter and were mainly driven by lipid dynamics. Trophic magnification factors (TMFs: increase in BAF per unit increase in trophic level as derived from our carbon budgets) were highest for PCB 153 during spring (2.3–2.4) and lowest for PCB 52 in summer and fall/winter (1.5–1.6) and were driven by seasonal shifts in trophic level and lipid dynamics.

Introduction

Increasing our insight into the bioaccumulation of hydrophobic chemicals such as polychlorinated biphenyls (PCBs), chlorinated pesticides, and polycyclic aromatic hydrocarbons is one of the challenges in contemporary environmental science (1). This is especially true for the European and north American Arctic which functions as a sink for these substances (2, 3).

Arctic ecosystems exhibit a strong seasonal variability in primary production that is driven by extreme variations in

light, temperature, and water advection and mixing (4). Spring and summer are characterized by day lengths of up to 24 h, water temperatures >2 °C, and net particulate primary production rates in the range of grams of C m⁻² d⁻¹. In winter, day lengths are short (as low as 0 h), water temperatures may be below freezing, and primary production is decimated. Arctic species have adapted to these conditions by storing body fat during spring and summer (5) or by reducing metabolism to survive winter (6). Additionally, fish may opportunistically migrate to areas with higher food abundance during some periods of the year (4), thus altering food-web topology.

Based on the food-web paradigm, one could suspect seasonal changes in primary production to result in fluctuating food availability and thus fluctuating ingestion and production rates of higher trophic levels as well. Also, seasonal changes in food-web topology may cause diet shifts for species depending on migrating prey. Because food source and ingestion rate codetermine dietary uptake of chemicals and because production rates determine chemical dilution (7), seasonality in bioaccumulation can be suspected. Lastly, annual patterns of lipid build-up and loss may decrease and increase the chemical concentrations in lipid-rich organs and tissues through dilution and concentration, respectively.

Bioaccumulation in Arctic ecosystems has been studied extensively (as reviewed in refs 8 and 9), yet never during a complete annual cycle, often because of logistic limitations in seasonally ice-covered regions (8). Here, we assembled all freely available ecological and chemical data to study a full annual cycle of PCB bioaccumulation in the main fish stocks in the southern Barents Sea. To do so, season-specific carbon budgets were reconstructed taking into account migratory behavior of fish. From these budgets, season-specific rates of ingestion and production of cod, capelin, and young herring were estimated. Together with seasonal lipid dynamics of fish, invertebrates, and phytoplankton these estimates were used as input of a bioaccumulation model (10) to predict annual dynamics of PCB concentrations in these fish species. Predictions were compared to an independent data set containing PCB concentrations in cod and capelin caught between 1998 and 2008 in the southern Barents Sea (ref 11 and this paper). The Barents Sea is an ecologically and economically relevant study region as it is the largest among the pan-Arctic shelf seas, accounts for nearly 50% of the regional primary production (12), is essential to Arctic Ocean biogeochemical cycling (4), and supports one of the world's largest fisheries (13). The southern Barents Sea region in particular was chosen because its permanently ice-free waters allow year-round sampling and thus offer a high data availability, while it still exhibits the features of a typical high-latitude ecosystem (4). PCBs were chosen as contaminants because of data availability and because they are highly accumulative, persistent, toxic, and ubiquitous (1).

Experimental Section

Bioaccumulation Modeling. The rate of change of the concentration of a polychlorinated biphenyl (PCB) in a fish individual was calculated with the OMEGA model (10) and a matrix notation was used to represent a community of *m* interacting species as in Campfens and MacKay (14) and De Laender et al. (15):

$$\dot{c} = K_{\text{up,food}} \cdot c + K_{\text{up,water}} \cdot c_{\text{water}} + K_{\text{out+dil}} \cdot c \quad (1)$$

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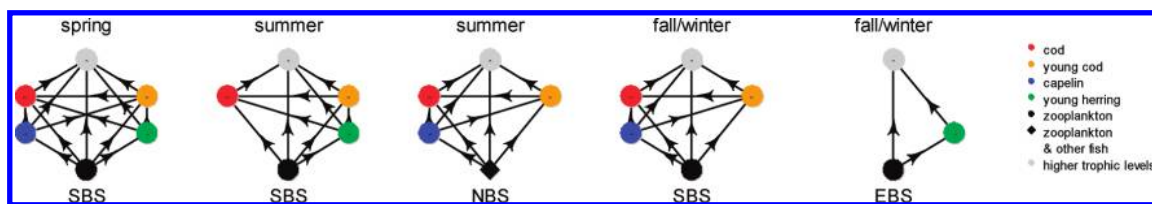


FIGURE 1. Trophic relationships among the fish species in the five bioaccumulation models for the southern, northern, and eastern Barents Sea (SBS, NBS, and EBS, respectively). Complete food-web topology for the SBS is given elsewhere (26).

where $\dot{c}$ is the rate of change of the internal concentration vector c , $K_{up,food}$ is a $m \times m$ matrix containing the uptake rate constants through feeding ($k_{up,food,j \rightarrow i}$; d^{-1}), $K_{up,water}$ is a column vector with uptake rate constants through water ($k_{up,water,i}$; $L \text{ kg}^{-1} d^{-1}$), and $K_{out+dil}$ is a $m \times m$ diagonal matrix with summed egestion, production and excretion rates ($k_{out,eg,i}$, $k_{dil,pr,i}$, and $k_{out,water,i}$; all d^{-1}). $K_{up,food}$ depends on the number of food-web constituents and predator–prey interactions and thus on food-web topology. $K_{up,food}$ and $K_{out+dil}$ depend on the organisms' ingestion rates ($f_s^{ingestion}$; $\text{kg prey kg predator}^{-1} d^{-1}$) and production rates ($f_s^{production}$; d^{-1}), respectively (Supporting Information (SI) Table S1) and thus on food-web productivity. By using a recently developed approach that combines inverse modeling with the OMEGA model, uncertainty on food-web productivity was used to derive uncertainty on $f_s^{ingestion}$ and $f_s^{production}$ (15). The sorbing matrix in fish was the lipid phase and consequently the octanol–water partitioning coefficient K_{OW} described partitioning between lipids and water (SI Table S1). Biotransformation of PCBs was assumed negligible, given the low water temperatures and high K_{OW} s of the considered chemicals (but see refs 16 and 17). Predicted concentrations c_i were lipid normalized and divided by c_{water} to calculate the bioaccumulation factors (BAFs). In that sense, the exact value chosen for c_{water} was unimportant, as predicted internal concentrations change linearly with c_{water} . Based on evidence from literature (18, 19), internal concentrations in Barents Sea zooplankton and lower trophic levels were assumed to be in rapid equilibrium with the water phase, and their BAFs were calculated using organic carbon as the sorbing matrix, i.e., as $OC \cdot K_{OC}$ (20), where OC represents their organic carbon content (–), and K_{OC} the organic carbon–water partition coefficient ($L \text{ kg}^{-1}$), calculated as $\alpha_{oc-o} \cdot K_{OW}$, with α_{oc-o} the organic carbon–octanol proportionality constant ($L \text{ octanol} \cdot \text{kg OC}^{-1}$). Model implementation was done in R (21).

Incorporation of Seasonality in Bioaccumulation Modeling. Following the modeling approach described above, three season-specific bioaccumulation models were constructed that differed in food-web topology, food-web productivity, and lipid contents. Because of data limitations for fall (see below), one bioaccumulation model was constructed for fall and winter.

Food-Web Topology. Key fish species in the southern Barents Sea (SBS) are cod (*Gadus morhua*), young herring (*Clupea harengus*), and capelin (*Mallotus villosus*) (22), and season-specific topologies within the fish community are given in Figure 1. During summer, capelin leaves the SBS to migrate up north to the Northern Barents Sea (NBS) where food is abundant (23). It is to some extent followed by cod and young cod (approximately one-half of both stocks remains in the SBS (24)). During winter, young herring leaves the SBS as it migrates to the eastern Barents Sea (EBS) (25). Topology of the remaining food-web (including zooplankton and microbial compartments) did not vary seasonally. Complete food-web topology for the southern Barents Sea, i.e., not including migration areas, is given elsewhere (26).

Food-Web Productivity. The implications of seasonal differences in primary production for food-web productivity and eventually for ingestion rates $f_s^{ingestion}$ and production

rates $f_s^{production}$ of fish in the SBS were examined by calculating season-specific carbon budgets using linear inverse models (LIMs) that relied on the food-web topologies in Figure 1. A full description of these carbon budget estimations and the underlying data (26), as well as more information on inverse modeling (27–29) can be found elsewhere. In first instance, LIMs were only constructed for the species remaining in the SBS: one for spring, one for summer, and one for fall/winter. For every LIM, i.e., for every season, a Markov Chain Monte Carlo procedure (ref 30; 1000 iterations) was used to estimate $f_s^{ingestion}$ and $f_s^{production}$ and associated uncertainty for each fish compartment as shown previously (15). To estimate $f_s^{ingestion}$ and $f_s^{production}$ for migrating fish, two additional, but simplified, LIMs were constructed: one for the EBS during fall/winter (including herring, zooplankton, and higher trophic levels) and one for the NBS during summer (including capelin, cod, young cod, zooplankton, and higher trophic levels). The complete topologies of these simplified LIMs are in Figure 1. The constraints used to construct these two additional LIMs were those of the corresponding original LIMs (26), yet setting no limits on zooplankton production, i.e., carbon input for fish, in absence of site specific information. Obtained rates were derived for the included fish stocks and assumed to be representative for individual fish within these stocks.

Lipid Content. The dynamic behavior of lipids throughout the season (5, 23) was used as a forcing function of the dynamic bioaccumulation model (see also SI Tables S1 and S2) and is shown in SI Figure S1. Annual patterns and peak lipid contents were taken from Falk-Petersen et al. (5), except for capelin which has a 5 times higher peak lipid content (10% of wet weight) than other fish (31).

Bioaccumulation Model Solution. We used Runge–Kutta integration from the R package “deSolve” (32) to solve the bioaccumulation models dynamically for spring (days 1–90), summer (days 91–180), and fall/winter (days 181–360). Initial concentrations for the summer and fall/winter models were set to the final concentrations of the spring and summer models, respectively. For cod and young cod, two bioaccumulation models were run for summer, as half of this species' stock migrates to the NBS, whereas the other half remains in the SBS. For both models, initial internal concentrations were set to the final spring concentrations. Predicted dynamics of the migrating cod and of remaining cod were averaged to represent average summer dynamics of PCBs in this species as only aggregate data were available. Initial internal concentrations in spring were set arbitrarily to $100 \mu\text{g kg}^{-1}$ wet weight and consecutive model solutions were repeated for multiple years until the annual dynamics of PCBs in fish stabilized, which was after one year. Changing initial concentrations (we tried 10 and $1000 \mu\text{g kg}^{-1}$ wet weight) did not influence stabilized annual dynamics. During all simulations, season-specific lipid contents, $f_s^{ingestion}$ and $f_s^{production}$ entered the equations in SI Table S1. The uncertainty associated with $f_s^{ingestion}$ and $f_s^{production}$ (represented by 1000 values per rate: see the Food-Web Productivity section) was propagated through the bioaccumulation model using a Monte Carlo approach (consequently 1000 iterations) to obtain the uncertainty associated with the predicted BAF

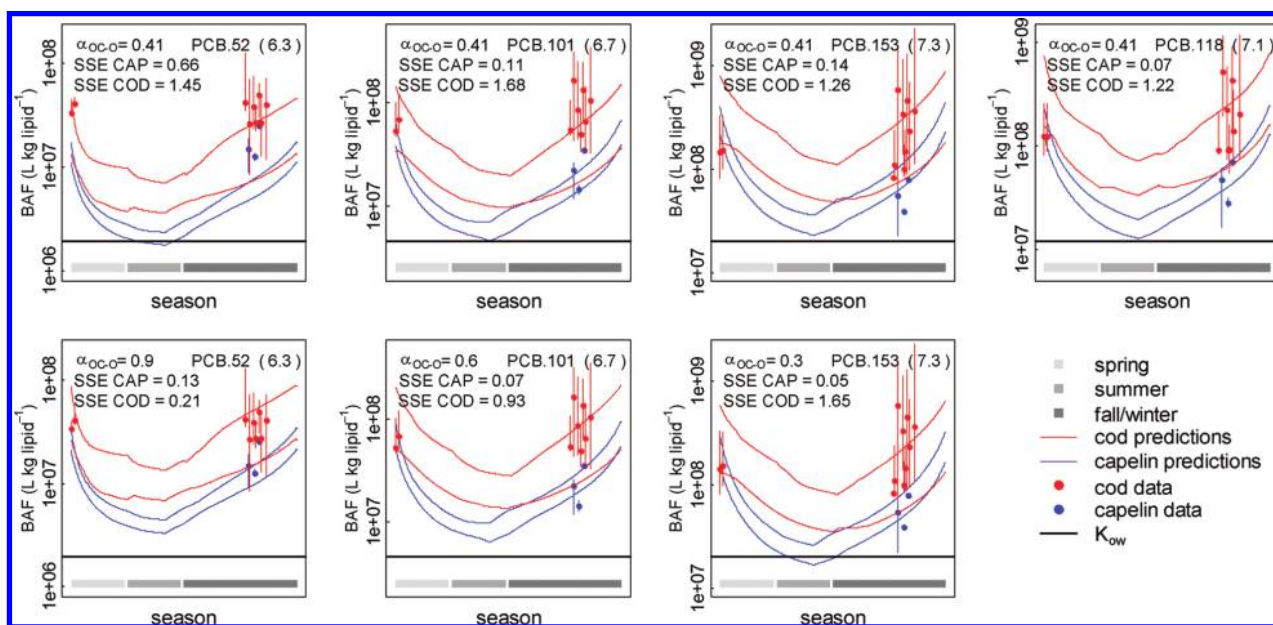


FIGURE 2. Predicted and observed bioaccumulation factors (BAFs) for three PCB congeners ($\log K_{ow}$) in adult cod and capelin. Two lines indicate 5% and 95% percentiles of the predictions. In the upper row, predictions with a default value for α_{OC-O} are given; in the lower row, α_{OC-O} was optimized (see text). The optimized α_{OC-O} equaled the default value of 0.41 for PCB 118. SSE COD and SSE CAP are the sum of squared errors, i.e., a measure for differences between median model predictions and median observations for cod and capelin, respectively.

dynamics. Finally, predicted BAFs were divided by the lipid dynamics in SI Figure S1 for lipid normalization.

Based on availability of measured concentrations in fish and water (see further on), PCB congeners 52, 101, 118, and 153 were selected for model analysis. Their octanol–water partition coefficients K_{ow} —a bioaccumulation model parameter (SI Tables S1 and S2)—were gathered from Li et al. (33) and corrected for Arctic temperatures (SI Table S2). An overview of all parameter values used in all bioaccumulation models is given in SI Table S2.

Measurements and Data Treatment. PCB concentrations in adult cod (filets and liver) and capelin (whole fish) measured during fall/winter and spring in the SBS (see SI between 1998 and 2002 (11) and 2006–2008 (this paper) were divided by water concentrations to derive observed BAFs so that bioaccumulation model performance could be examined. Because seawater concentrations of PCBs are heavily influenced by the adopted method (reviewed and discussed in ref 34) and are crucial for accurate BAF calculation (35), we assembled measured seawater concentrations from four different sources (19, 36–38), shown as blue bars in SI Figure S2. Additionally, they were estimated from air concentrations at the site “Pallas” in northern Finland (2) by us (black bars in SI Figure S2) and by Borga and Di Guardo (34) from air concentrations measured in the Svalbard and Eastern Arctic Ocean region (2, 39) (gray bars in SI Figure S2). To do so, air–water partition coefficients (K_{AW}) were applied, after correction for Barents sea temperature using the van’t Hoff equation as in Li et al. (ref 33 and SI).

Results and Discussion

Seasonality in Bioaccumulation Model Input. In winter, carbon uptake and production by phytoplankton was 5–10 times lower than in spring or summer (SI Figure S3). These seasonal changes gradually decreased with increasing trophic level (from left to right in SI Figure S3) and were reduced to changes <10% at the highest trophic levels considered (SI Figure S3). Only cod remaining in the southern Barents Sea (SBS) during summer fed 50–400% less than in spring or in fall/winter and this difference was compensated by adult

cod migrating north that had grazing rates comparable to those of adult cod in spring, which agrees well with reports on cod stomach content (40, 41). The lower feeding rate of adult cod remaining in the SBS in summer did not result from changes in primary production but from the exceptionally low krill stock ($<0.01 \text{ g C m}^{-2}$ in (42)) used to infer carbon budgets (26). In summer, krill is an important prey item for cod in absence of migrating capelin (22) and a food limitation of cod during summer because of low krill biomass has been previously observed (43) providing further evidence that cod ingestion rate may be lower in summer.

Seasonality in Bioaccumulation Model Output. Predicted bioaccumulation factors (BAFs) for PCB 118 in cod and capelin were in good agreement with the experimentally derived BAFs (Figure 2 upper right panel), attaining an accuracy comparable to other bioaccumulation modeling exercises (14, 44). However, for PCBs 52, 101, and 153, predicted BAFs were less consistent with the data. To improve model performance, we evaluated model sensitivity to changes in parameters that were nonspecific to the Barents Sea case and were thus most likely to cause deviations between predictions and data. Predicted log BAFs changed less than 2% upon varying layer permeation resistances ($\rho_{H_2O,O}$, ρ_{H_2O} and ρ_{CH_2}) or the water absorption–excretion coefficient (γ_o) within their uncertainty ranges (10). However, by changing the organic carbon–octanol proportionality constant (α_{OC-O} ; $\text{L octanol kg OC}^{-1}$) from its default value (0.41) to one of its empirically derived limits (0.1 and 0.9, ref 45), log BAF predictions changed up to a factor of 10. Therefore, we repeated bioaccumulation model calculations for all four PCBs at nine values for α_{OC-O} (0.1–0.9 in steps of 0.1) and evaluated the corresponding sum of squared errors based on the date-specific median predictions and data ($\text{SSE} = \sum [\log \text{BAF}_{\text{observed}} - \log \text{BAF}_{\text{predicted}}]^2$) (SI Figure S5). The values for α_{OC-O} that resulted in an optimal fit were not always the same for capelin and for cod (SI Figure S5). In Figure 2 we show simulations with optimal values for capelin because model fit for this species was more sensitive for changes in α_{OC-O} (SI Figure S5). Optimized α_{OC-O} values were lower for congeners with higher K_{ow} (SI Figure S5 and lower row and

upper right panel of Figure 2), a trend which agrees with available correlations between K_{OC} and K_{OW} (SI Figure S6 46, 47). Additionally, data on PCB descriptors compiled by Seth et al. (45) also suggested such a decreasing trend, although it was not significant. The fact that, even after optimization, observed BAFs in spring were often still on the lower side of predictions may be due to underestimation of the observed BAFs due to overestimation of seawater concentration in spring. Indeed, intense primary production in spring most probably decreased dissolved concentrations in spring (48), whereas here we had to assume that water concentrations remain constant throughout the year upon derivation of observed BAFs (SI Figure S2) in absence of SBS-specific seasonal data. The higher uncertainty on the observed BAFs than on predicted BAFs suggests additional sources of uncertainty that were not included in the model such as uncertain lipid content, body weight, and shape factor. Lastly, an increasing uncertainty of the BAFs with increasing K_{OW} was noted for the observed (e.g., 1 and 1.4 log units for PCBs 52 and 153 in summer) as well as for the predicted BAFs (e.g., 0.5 and 0.6 log units for PCBs 52 and 153 in summer). The reason for this trend to be more apparent in the data than in the predictions is in line with the higher uncertainty on the former than on the latter.

The bioaccumulation model predicted lower BAFs in summer and the start of fall than in spring or in winter, and this for all fish species (SI Figure S4 upper row). The differences between summer/fall and spring/winter BAFs increased with the hydrophobicity of the PCB congener (a factor 2 for PCB 52 with a log K_{OW} of 6.3; an order of magnitude for PCB 153 with a log K_{OW} of 7.3). Because our inverse analyses did not reveal any major seasonal differences in ingestion or production rates for fish (SI Figure S3), the observed seasonality in PCB bioaccumulation was largely driven by the lipid dynamics shown in SI Figure S1. To demonstrate this, we performed additional simulations in which lipid contents of all species was kept constant throughout the year (SI Figure S7) and only food-web productivity and topology was allowed to vary. These simulations did not reflect the seasonality of BAFs that was predicted in Figure 2 and compared less well to the observed BAFs (SSEs 2–5 times higher). Although our primary data set did not contain summer BAFs for fish in the SBS and none were found in the literature, the incorporation of lipid dynamics as a forcing function for the bioaccumulation model resulted both in summer/early fall BAF minima and markedly improved predictions. This underscores the importance of lipid dynamics for accurate BAF prediction and adds credence to the predicted BAFs in summer and early fall, although the latter certainly need confirmation by field data. The influence of lipid dynamics is supported by Fisk et al. (49) who found the Σ PCB (77 congeners) concentrations on a lipid basis—but not on a dry weight basis—in the copepod *Calanus* sp. to be lower in summer than in early spring in the Northwater Polynya. Hargrave et al. (50) made similar conclusions for organochlorines in mixed zooplankton samples from Lancaster Sound in the Canadian Arctic.

Next to seasonality in BAFs, our model also indicated that relationships among the BAFs of the different fish species in the SBS vary seasonally. To illustrate this, the trophic levels (TLs) of the SBS species were calculated and plotted against time-averaged BAFs for the three considered periods (spring, summer and fall/winter). Linear regression to lipid normalized BAFs vs TL ($\log \text{BAF} = a + b \times \text{TL} + \text{error}$) yielded trophic magnification factors ($\text{TMFs} = 10^b$), i.e., the average increase of log BAF per unit increase in TL (51). Such relationships are normally established by combining trophic level estimates based on stable isotopes with contaminant data (e.g., refs 51 and 52). Here, we used the carbon budgets for the SBS as estimated by our inverse modeling approach

to calculate TLs of fish using the R package “NetIndices” (53, 54). Note that migrating species were not included in this regression analysis, as TL calculus was impossible for these species due to food-web simplification. TMFs in spring were higher than in other seasons and for PCBs 118 and 153 (SI Figure S8) these were 1.2–2 times lower than those determined for the same congeners in northern Barents Sea poikilotherms in spring by Hop et al. (55). This observation is counterintuitive because piscivorous adult cod (TL between 4 and 4.5 in spring) was included in our study, whereas the highest TL among the poikilotherms considered by Hop et al. was 2.8–3.5 for young cod which is primarily a plankton feeder (40). A higher maximum TL in this study than in Hop et al. was thus not accompanied by a higher maximal log BAF, implying a limited influence of the TL in the BAF prediction in this study. This reflects what was already noted in SI Figure S7, i.e., seasonality in predicted BAFs was not driven by food-web productivity or topology but by the dynamic lipid behavior. The TLs of all fish species were higher in spring than in the rest of the year (SI Figure S8). This can be understood from the proportions of different prey items in the diet of the four considered fish compartments (SI Table S3). Relying mainly on capelin (88%), adult cod was piscivorous in spring, whereas in summer it shifted to krill (72%) upon capelin migration and to a 50:50 mixture of capelin and krill in fall/winter. The higher TL for herring and capelin in spring than in the rest of the year is explained by copepod-feeding chaetognaths (TL = 3; SI Figure S8) making up 30–50% of their diets in spring, whereas in summer/fall/winter this was maximally 15% when both fish species predominantly ate copepods (TL = 2; SI Figure S8). Also the seasonality of the TL of young cod reflected its diet: feeding mainly on copepods in summer (and thus TL approaching 3) and on a diet containing fish in the other seasons (and thus TL between 3 and 4).

The present study shows that the addition of quantitative food-web studies may be used to inspect if and how seasonal trends in food-web productivity and topology combine with lipid dynamics to form seasonal patterns in internal PCB concentrations in fish. Because of the importance of lipid dynamics found here, a mechanistic and process driven incorporation of lipid transfer between trophic levels may be a promising refinement in future bioaccumulation models.

Acknowledgments

F.D.L. and D.V.O. are supported by the CORAMM project (<http://www.irccm.org/coramm/CORAMM.htm>) which is funded by StatoilHydro. We thank four anonymous reviewers for their constructive feedback and useful insights.

Supporting Information Available

A description of the collection, preparation, and analysis of fish samples; the conversion of air to water concentrations; lipid dynamics (Figure S1); assembled seawater concentrations (Figure S2); uptake and production rates in different seasons by all food-web constituents (Figure S3); predicted bioaccumulation factors (BAFs) for all considered fish species (Figure S4), model fit as a function of the organic carbon-octanol proportionality constant α_{OC-O} (Figure S5); relationships between log K_{OW} and log K_{OC} derived here and obtained from literature (Figure S6); BAF predictions for two PCBs when using annual mean lipid contents (Figure S7); predicted increase in the bioaccumulation factor (BAF) per unit of trophic level (TL) (Figure S8); rate constant equations for the bioaccumulation models (Table S1) and their parameters (Table S2); and results from diet analysis (Table S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ES902625U