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ARTICLE

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Combining Monitoring Data and Modeling Identifies PAHs as Emerging Contaminants in the Arctic

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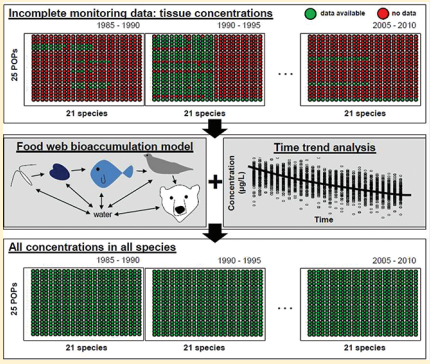
Supporting Information

ABSTRACT: Protecting Arctic ecosystems against potential adverse effects from anthropogenic activities is recognized as a top priority. In particular, understanding the accumulation and effects of persistent organic pollutants (POPs) in these otherwise pristine ecosystems remains a scientific challenge. Here, we combine more than 20 000 tissue concentrations, a food web bioaccumulation model, and time trend analyses to demonstrate that the concentrations of legacy-POPs in the Barents/Norwegian Sea fauna decreased 10-fold between 1985 and 2010, which reflects regulatory efforts to restrict these substances. In contrast, concentrations of fossil fuel derived PAHs in lower trophic levels (invertebrates and fish) increased 10 to 30 fold over the past 25 years and now dominate the summed POP burden (25 POPs, including 11 PAHs) in these biota. Before 2000, PCBs dominated the summed POP burden in top predators. Our findings indicate that the debate on the environmental impacts of fossil fuel burning should move beyond the expected seawater temperature increase and examine the possible environmental impact of fossil fuel derived PAHs.



INTRODUCTION

Protecting the health of Arctic ecosystems is a global concern,[1] as direct [2] and indirect changes [3] due to global warming are expected to be most pronounced in these regions. An often overlooked potential source of stress for these ecosystems is the exposure to persistent organic pollutants (POPs), i.e., chemical compounds that are resistant to environmental biodegradation, bioaccumulate in lipid tissues and negatively affect human and environmental health.[4,5] In recognition of these issues, legislative actions in the 1970s and 1980s banned the production and/or use of the most toxic and bioaccumulative POPs such as PCBs and DDTs.[6,7] Despite these efforts, multiple POPs are still present in many ecosystems today, including remote regions such as the Arctic where they have been found in biota [8] as well as in humans.[9] Northward air and sea currents have been identified as transport vectors of (semi-) volatile POPs from temperate regions to the colder Arctic environment where they condense.[10] Field studies relating measurements of POPs in biota to observed adverse effects highlight that environmental concentrations of these pollutants have the potential to negatively affect humans [11] as well as the local fauna.[12,13]

The Arctic Monitoring and Assessment Programme (AMAP) has been documenting tissue concentrations of POPs in Arctic biota over the past 25 years; the data produced by these monitoring campaigns are freely accessible (http://ecosystemdata.ices.dk/). However, a typical feature of these data is that they are fragmentary, i.e., not all POPs have been measured in all species. This limitation in data availability is problematic if the status of Arctic ecosystems as a whole is to be assessed as information on certain species may be lacking. Bioaccumulation models have demonstrated their capacity to predict tissue concentrations based on water concentrations and easily inferable characteristics of the chemical and the species [14−16] and therefore at first seem suitable to fill in crucial data gaps. However, measured water concentrations of POPs —the input of bioaccumulation models—are scarce and are only available for a few points in time which makes it difficult to study temporal trends in Arctic ecosystem health.[17] Also, the chemical biotransformation rate in other species than fish remains a poorly known parameter in these models,[18−20] thus increasing the uncertainty on internal concentrations predicted by bioaccumulation models for these species.

In this paper, we combine monitored tissue concentrations, a bioaccumulation model and time trend analyses to reconstruct concentrations of the 4 legacy POP classes (PCBs, DDTs,

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HCHs, and HCB) and of PAHs in 21 species occupying various trophic levels (from mussels to Polar bears) in the Barents/Norwegian Sea food web between 1985 and 2010. The strategy we introduce uses a bioaccumulation model to infer seawater concentrations from concentrations in fish, i.e., species for which biotransformation rates are relatively well-known and for which decadal-scale tissue concentration data are available. Next, statistical modeling is performed to quantify temporal trends in these inferred seawater concentrations. These trends are then used as an input for a bioaccumulation model to estimate concentrations of all 5 POP classes in all 21 species between 1985 and 2010. In addition, we investigate the capacity of the model to accurately predict an independent set of monitoring data under various assumptions on the biotransformation rates in other species than fish.

EXPERIMENTAL SECTION

Measured Tissue Concentration and Sediment Data. Concentrations of 92 POPs from 5 classes (PCBs, PAHs, HCHs, HCB, and DDTs, see Table S1, Supporting Information, SI, for a list) measured in various tissues (Table S2 of the SI) from 21 different species (Table S3 of the SI) were downloaded from the database of the International Council for the Exploration of the Sea (ICES: http://ecosystemdata.ices.dk/). Only data from the Barents and Norwegian Sea were considered. The tissue concentrations were standardized to lipid content using appropriate lipid contents of the tissue matrix (Table S2 of the SI).

Bioaccumulation Modeling. A bioaccumulation model [15] was used to estimate bioaccumulation factors (BAFs) for all 21 species for which tissue concentrations were available. The model estimates a BAF (L kg^{-1} wet weight) of a species at a given trophic level (BAF_{TL}), i.e., the ratio of the tissue concentration (C_{tissue} $\mu g\ kg^{-1}$ wet weight) and the water concentration (C_{water} $\mu g\ L^{-1}$), using the pollutant's octanol−water partition coefficient (K_{ow}), the species' weight (kg) and lipid content and the bioaccumulation factor of a representative prey species ($BAF_{TL\text{-}1}$):

$$BAF_{TL} = \frac{C_{tissue}}{C_{water}} = \frac{k_{0,x,in} + (k_{1,x,in} \cdot BAF_{TL\text{-}1})}{k_{0,x,out} + k_{1,x,out} + k_{2,x,out} + k_{3,x,out}} \quad (1)$$

with $k_{0,x,in}$ the pollutant absorption rate from water (L kg^{-1} d^{-1}), $k_{1,x,in}$ the pollutant assimilation rate from ingested food (d^{-1}), $k_{0,x,out}$ the pollutant excretion rate to the water (d^{-1}), $k_{1,x,out}$ the pollutant loss rate via faeces (d^{-1}), $k_{2,x,out}$ the dilution rate of the pollutant in the body caused by growth or reproduction (d^{-1}) and $k_{3,x,out}$ the rate of biotransformation (d^{-1}). Equations of all rate constants (eqs S1−S5 of the SI) and the numerical solution procedure are described in the SI.

Inferring Water Concentrations from Tissue and Sediment Concentrations. We used BAFs for fish, as predicted by the bioaccumulation model, to infer seawater concentrations C_{water} from tissue concentrations C_{tissue} in fish. Fish were chosen because biotransformation rates $k_{3,x,out}$, and therefore the modeled BAFs that rely on it, are most certain for fish. For PCBs, DDTs, HCHs, and HCB, 22284 tissue concentrations were available for fish. For PAHs, insufficient concentrations in fish tissue were available, forcing us to use tissue concentrations in mussels (2877 data points) and our modeled BAFs for mussels to obtain C_{water}. The water concentrations we inferred from (fish and mussel) tissue concentrations were compared to seawater concentrations that we inferred from an independent set of sediment concentrations using the following formula:

$$C_{water} = C_{sediment} \cdot (K_{oc} \cdot OC)^{-1} \quad (2)$$

with K_{oc} the organic carbon−water partitioning coefficient (eq S6 of the SI) and OC the organic carbon content of the sediment, which is about 2%.[21] Concentrations of POPs in sediments $C_{sediment}$ (μg kg wet $sediment^{-1}$) from the Norwegian and Barents Sea region were also downloaded from the ICES Web site. We only considered data from the top layer (<10 mm), containing sediment deposited about 10 years before the listed sampling date, based on Barents Sea sedimentation rates [22] of 1 mm y^{-1}. Reported concentrations in the sediment (μg kg dry $sediment^{-1}$) were converted to wet weight basis (μg kg wet $sediment^{-1}$) assuming a 90% water content of sediment.[21]

Time Trend Analysis of Mussel and Fish-Inferred Water Concentrations. For 67 pollutants, either the inferred seawater concentrations were available for less than 10 different years, the measurements spanned a period shorter than 15 years, or the K_{ow} was higher than the maximum K_{ow} for which the bioaccumulation model was calibrated, i.e., $10^{8.5}$.[15] For these pollutants, no time trend analysis was pursued. For the other 25 pollutants, additive models (*ams*) were fitted to the log-transformed water concentrations (10 base logarithm) as follows:

$$E[\log10(C_{water})] = \text{intercept} + f(\text{time}) + \varepsilon \quad (3)$$

where $E[\log10(C_{water})]$ is the expected value of $\log10(C_{water})$, which was assumed to be normally distributed, as was the error ε, with mean 0 and σ as a standard deviation, i.e., $\varepsilon \sim N(0,\sigma)$. The smoothing function f is a non parametric relationship between the predictor (time) and the effect this predictor has on the response variable ($\log10(C_{water})$). Additive models replace multivariate regression by so-called "additive approximation", which has a number of statistical advantages over the former, as discussed in detail elsewhere.[23] All dates in the database were converted to real numbers between 1985 and 2010. By fitting the model (eq 3) to the data ($\log10(C_{water})$ and time) estimates of f were obtained, together with the corresponding p-value for these estimates. A cutoff p-value of 0.05 was chosen. Additive models were chosen because they make no assumptions about the shape of the resulting time trend f. Absence of autocorrelation was confirmed (p was always >0.05) by likelihood ratio testing of the *ams* against corresponding additive mixed models (*amms*) that extended the residual term of eq 3 with an autocorrelation structure Δ, making $\varepsilon \sim N(0,\Delta\sigma)$. Because sampling intervals were irregular, a corCAR1 structure was chosen.[23] Model fits were performed using the R-functions *gam* and *gamm* from the *mgcv* package.[23] The resulting time trend models for water concentrations of POPs were checked for normality of the residuals (Figure S1 of the SI).

Tissue Concentrations of All POPs in All Species and Validation. The time trends for water concentrations of the 25 POPs and the associated residuals were multiplied by the modeled bioaccumulation factors (BAF) of the 21 species that were representative for the aquatic Arctic food web. In this way, tissue concentrations were obtained for all 25 POPs in 21 species of the Arctic food web. There were 6866 observed tissue concentrations in the database that were not used to infer seawater concentrations, i.e., concentrations of PCBs, DDTs, HCHs, and

HCB in other species than fish, and PAH concentrations in other species than mussels. These were used to validate the bioaccumulation model predictions. Predicted tissue concentrations were compared to the corresponding observations and the sum of squared errors (SSE) was calculated.

Biotransformation (BT) Rates in Other Species than Fish. Measured BT rates of all 25 POPs in all 21 species are unavailable. Our default assumption on BT rates was therefore that all species had BT rates equal to BT rates for fish estimated from.[19] However, we repeated our analysis (from the BAF modeling to the tissue concentration modeling and validation against 6866 observations) in 5 additional scenarios, each time making an alternative assumption on the BT rates, including a scenario in which absence of BT in all species was assumed (scenario 1). Other scenarios were as follows: 2: BT only in fish; 3: BT only in fish and benthos at rates for fish; 4: BT only in fish and mammals at rates for fish; 5: BT in all species at rates for fish (the default assumption). In a sixth scenario, we assumed that BT rates in mammals were faster than in fish, acknowledging that the BT capacity of mammalian cells has been found to be higher than in cells from in poikilotherms.[24,25] In absence of compound- and species-specific BT rates, and following earlier modeling exercises,[26] we assumed BT rates in mammals to be 5 times those for fish in this sixth scenario. All computational details are provided in the SI, as are the calculated BT rates for fish (Figure S2A&B, SI).

RESULTS AND DISCUSSION

Inferred Seawater Concentrations. By combining tissue concentrations of PCBs, DDTs, HCHs, and HCB in fish and of PAHs in mussels with a bioaccumulation model, we inferred time trends of dissolved seawater concentrations for these 5 pollutant classes in the Arctic region between 1985 and 2010. The seawater concentrations we inferred corresponded well with the seawater concentrations we independently inferred from sediment concentrations using chemical equilibrium modeling (Figure 1). Note that the uncertainty of the dating of these sediment-inferred concentrations is high because POP concentrations were only available for the whole top layer of the sediment (10 mm), containing sediment deposited 0 to 10 years before the listed sampling date.[22] The time trend analyses showed that the most inferred water concentrations significantly ($p < 0.05$) decreased following bans on production and/or use and our results comply with the decreasing trends found in seabirds and marine mammals from the Canadian Arctic.[27] This is shown in Figure 1 for selected POPs; results for other POPs are shown in Figure S3 of the SI. Decreases were apparent for most PCBs (Figure 1a), for the two analyzed DDT breakdown products (Figure 1b, Figure S3i of the SI) and HCHs (Figure 1d,e) and for HCB (Figure 1f). For these POPs, water concentrations in 1985 were 10 times higher than current-day concentrations. For the water concentrations of the PCB congeners with higher molecular weights (e.g., PCB 156, Figure S3g of the SI), a decrease was only apparent after 1995. A possible cause for this delay between the legislative action and the observed decrease might be the slower movement toward the poles and the higher environmental persistence of heavier congeners than of the lighter congeners.[28] In contrast, HCHs and HCB are transported relatively quickly to higher latitudes due to their volatility and are also less persistent than heavy congener PCBs,[29] which explains why the time trend of these POPs follow legislative actions more closely (Figure 1d−f).

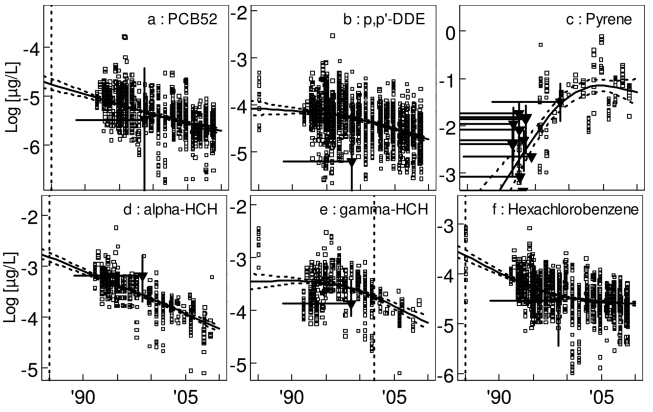

Figure 1. Water concentrations as inferred from measured concentrations in fish and Blue mussel, the estimated time trend (solid line) and its point-wise 95% confidence interval (dotted lines, calculated as +−1.96 • se). Triangles represent water concentrations inferred from measured sediment concentrations. Horizontal lines indicate the time window over which these values average (min−max); vertical lines are the mean +−1 standard deviation. Dashed vertical lines indicate the start of pollutant regulation. DDT was banned before 1985.

For gamma HCH, a clear decrease was only noted after 2000 (Figure 1e), i.e., following the ban by the U.S. in 2002 and by the EU in 2004. A decrease of α-HCH (Figure 1d) and HCB (Figure 1f) from 1985 on reflects European and U.S. bans on the production and use of these pollutants in the 1980s already.

For 9 of the 11 PAHs for which a time trend analysis was possible, a 10- to 30-fold increase of the mussel-inferred water concentration over time was found between 1990 and today (Figure 1c and Figure S3j−s of the SI). Note that modeled PAH concentrations prior to 1990 are uncertain because they exceed the period for which inferred water concentrations were available. In general, PAH concentrations were at least 100× higher than the concentrations we obtained for the legacy POPs. We only found one other published data set containing both water concentrations of PAHs and of legacy POPs in the Norwegian/Barents Sea region.[30] This data set confirmed the higher concentrations of PAHs than of legacy POPs, although the dissolved PAH concentrations it contained were an order of magnitude lower than those found by us.

The observed increase in water concentrations of most PAHs was not an artifact from the approach we followed to infer water concentrations from tissue concentrations. The same trend can be observed from the original tissue concentration data for PAHs in mussels (symbols in Figure 2c), from which the water concentrations were inferred. Eight of the 9 PAHs that increased over time have been shown to originate at least partly from fuel combustion:[31] benzo[ghi]perylene, benzo[a]pyrene, benzo[a]anthrancene, antracene, pyrene, phenanthrene, fluoranthene, and benzo[e]pyrene. The two PAHs for which the inferred water concentrations did not increase over time (fluorene, acenaphtylene) are PAHs that are generally not produced by fossil fuel burning but are used in chemical synthesis, e.g., as a precursor of pharmaceuticals.

Tissue Concentrations. Our approach yielded predictions of 25 POPs in 21 species, i.e., 525 POP-species combinations. Here, we only show predictions for three species that are representative for various tropic levels (TL) of the Norwegian/Barents Sea food web: the Blue mussel (TL = 3), North East Arctic cod (TL = 4), and Polar bear (TL = 6), as well as the original tissue concentrations

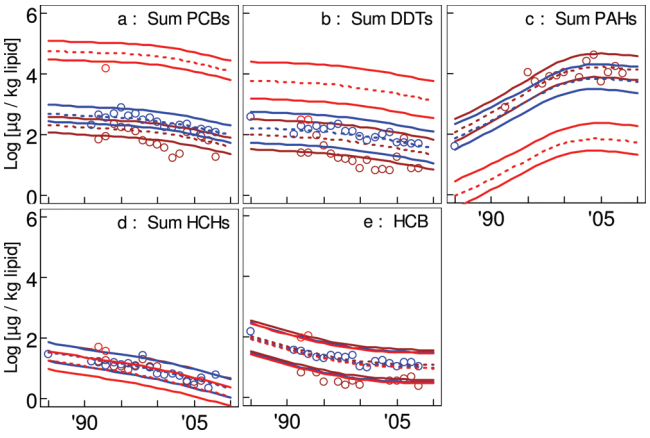

Figure 2. Observed (dots) and modeled tissue concentrations (median: dotted lines; 95% uncertainty interval: solid lines) of 5 pollutant classes in North East Arctic cod (*Gadus morhua*, blue), Blue mussel (*Mytilus edulis*, brown) and Polar bear (*Ursus maritimus*, red). Sum PCBs includes congeners 28, 52, 101, 105, 118, 138, 153, 156, and 180. Sum DDT includes *p,p'*-DDE and *p,p'*-TDE. Sum PAHs includes benzo[ghi]perylene, benzo[a]pyrene, benzo[a]anthrancene, antracene, pyrene, phenanthrene, fluoranthene, benzo[e]pyrene, fluorene, acenaphtylene, and indeno[1,2,3-cd]pyrene. Sum HCHs is α-HCH and γ-HCH.

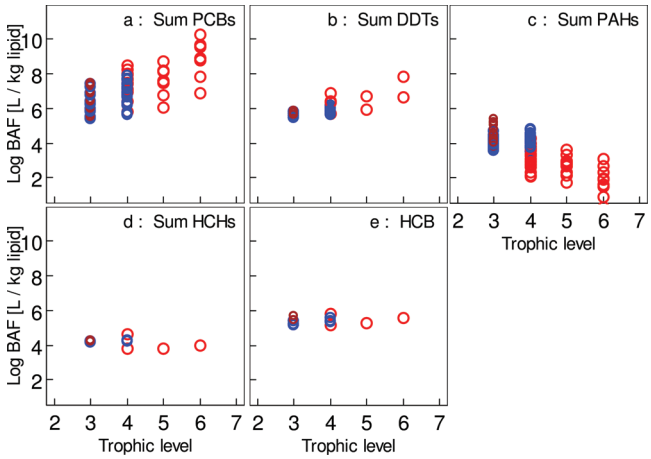

Figure 3. Log 10, transformed bioaccumulation factors (BAFs) of 5 chemical classes as a function of the trophic level of the 21 included species, including fish (blue), benthos (brown), and mammals (red).

in these three species (Figure 2). Predicted lipid normalized bioaccumulation factors for benthos, fish, and mammals as a function of trophic level are summarized in Figure 3 for the 5 POP classes. Predicted and observed lipid normalized concentrations that are not shown in Figure 2 are shown in Figures S4−S6 of the SI. Because the inferred water concentrations served as an input for the predictions of tissue concentrations, the temporal trends of the latter are the same as those of the former.

The strategy we propose here—converting available tissue concentrations to time trends of seawater concentrations—considerably expanded the current information on POP concentrations in the Arctic food web. For the 21 species and 25 POPs we considered here, the original database contained data on 2 to 25 POPs per species (median = 14 POPs). Our approach yielded tissue data on all 25 POPs for all 21 species and this for the whole period 1985−2010. Interestingly, also predictions were obtained for species-chemical combinations for which data were already available in the original database. The data that were not used to infer seawater concentrations (PAHs in other species than mussels, other POPs in other species than fish) were independent from our predictions and could thus be used for validation. This validation exercise showed that our predicted tissue concentrations differed less than a factor 5 from the observed concentrations in 87% of the species- pollutant combinations (Figure S7 of the SI), which is comparable to earlier validation efforts of bioaccumulation models [16] indicating that we can confidently use the predicted tissue concentrations of POPs in species for which no data are available. Our scenario analysis in which we made alternative assumptions on the biotransformation (BT) rates always had a higher sum of squared errors, i.e., a lower accuracy, than the default scenario in which all species had BT rates equal to those of fish (scenario 5) (Figure S8 of the SI). Scenario 4, in which it was hypothesized that BT occurs only in fish and mammals—and not in benthos such as mussels—yielded the same SSE as our default assumption. Interestingly, scenario 6, which was identical to scenario 5 but with mammals having BT rates that were five times higher than fish, was less accurate than our default scenario 5. The rest of this paper will therefore further discuss the results of the default scenario 5.

The bioaccumulation model suggested that concentrations of PCBs and DDTs were 10−1000 times higher at the top (Polar bear) than at the base of the food web (Blue mussel), indicating biomagnification of these pollutants in the Arctic food web (Figure 2a,b). This can also be seen from the increase of the modeled bioaccumulation factor (BAF) with increasing trophic level (Figure 3a,b), which agrees with earlier findings for these pollutants.[32−34] Modeled concentrations of HCHs and HCB did not increase with the trophic level (Figure 2d,e), again also illustrated by the modeled BAFs (Figure 3d,e). For PAHs, modeled concentrations decreased with increasing trophic level, a process that is referred to as "biodilution" (Figures 2c and 3c) and has been reported in other marine food webs as well, e.g., the Baltic sea,[35] Bohai bay China [36] and Tokio Bay.[37] Interestingly, these studies often assume that biodilution of PAHs is caused by an alleged increase in BT rate with trophic level. Although inferred BT capacities have been found to be higher in mammals than in cold-blooded animals,[24,25] it is uncertain to what extent this results in higher BT rates for Arctic mammals than for lower trophic levels.[15] In our default scenario 5, BT in all species was set to rates for fish and simulation results still displayed biodilution for PAHs (Figure 3c). This implies that no trophic increase of the BT rate is needed for biodilution to occur. Our simulations show that the smaller chemical loss rates in higher trophic levels—a typical allometric effect[38]—combined with quasi invariant BT rates makes the proportion of the chemical that is lost by BT higher at higher trophic levels, as is illustrated for pyrene in Blue mussel and Polar bear in the SI (Figure S9 of the SI).

Ecological Risks. Tissue concentrations measured in the field have been compared with laboratory-derived toxicity thresholds to assess the health status of Arctic residents.[39] Often, the heterogeneity among the species and end points (e.g., biomarker vs individual-level) for which the available toxicity thresholds are valid has made it difficult to interpret the results of such comparisons, let alone to estimate much needed measures of mixture toxicity.[17,39] One approach would be to compare the

sum of all POPs in one species with a threshold for a well-defined end point with a direct relation to the population-level. MacLeod et al.[40] have compared hydrocarbon burdens to a whole-body "critical body residue" (CBR) for lethal effects of nonspecific acting narcotics, to assess ecological risks. However, because of the heterogeneity of substances and species included here, and thus possibly various modes of toxic action at play, we refrained from such an exercise. In addition, there are a number of additional reasons why such an approach applied to the data at hand may underestimate toxicity. First, from the initially considered 92 POPs, only 25 were amenable to time trend analysis and 67 had to be excluded. Possible effects of these 67 chemicals would therefore not be accounted for. Second, a range of new POPs have been found in Arctic biota,[12,41] many of which have an unknown mode of action.

The legislative actions to ban the production and use of PCBs, that were triggered by measured concentrations in mammals, appear to have been successful as concentrations at the top of the Arctic food web have dropped substantially over time. In contrast, concentrations at the base of the Arctic food web after 2000 seem to be dominated by PAHs. However, these concentrations seem to be stabilizing during the last 5 years (Figure 2c), which may be explained by the search for and use of alternative energy sources that are independent of fossil fuels,[42] the continuous efforts to increase the efficiency of engines,[43] or depleting oil reserves.[44] Typically, the main consequences for the Arctic environment of fossil fuel burning are often stated to be an increase in atmospheric CO_2 concentrations, an increase in seawater temperatures and sea ice melting.[45] Our results, which highlight a substantial increase of PAHs in lower trophic levels during the past 25 years, show that an additional dimension should be added to the debate on the consequences of human reliance on fossil fuels.

■ ASSOCIATED CONTENT

Supporting Information. Tables S1−S4 and Figures S1−S10. This material is available free of charge via the Internet at http://pubs.acs.org.

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