

Regional Contamination versus Regional Dietary Differences: Understanding Geographic Variation in Brominated and Chlorinated Contaminant Levels in Polar Bears

MELISSA A. MCKINNEY,^{*,†,‡}
 ROBERT J. LETCHER,^{*,†,‡} JON AARS,[§]
 ERIK W. BORN,^{||} MARSHA BRANIGAN,[⊥]
 RUNE DIETZ,[#] THOMAS J. EVANS,[∇]
 GEIR W. GABRIELSEN,[§]
 DEREK C. G. MUIR,[○]
 ELIZABETH PEACOCK,^{¶,♦} AND
 CHRISTIAN SONNE[#]

Ecotoxicology and Wildlife Health Division, Science and Technology Branch, Environment Canada, Ottawa, Ontario K1A 0H3, Canada, Department of Chemistry, Carleton University, Ottawa, Ontario K1S 5B6, Canada, Norwegian Polar Institute, Tromsø NO-9 296, Norway, Greenland Institute of Natural Resources, Nuuk DK-3900, Greenland, Department of Environment and Natural Resources, Government of the Northwest Territories, Inuvik, Northwest Territories X0E 0T0, Canada, Aarhus University, National Environmental Research Institute, Department of Arctic Environment, Roskilde DK-4000, Denmark, United States Fish and Wildlife Service, Anchorage, Alaska 99503, United States, National Water Research Institute, Environment Canada, Burlington, Ontario L7R 4A6, Canada, and Department of Environment, Government of Nunavut, Igloolik, Nunavut X0A 0L0, Canada

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The relative contribution of regional contamination versus dietary differences to geographic variation in polar bear (*Ursus maritimus*) contaminant levels is unknown. Dietary variation between Alaska, Canada, East Greenland, and Svalbard subpopulations was assessed by muscle nitrogen and carbon stable isotope ($\delta^{15}\text{N}$, $\delta^{13}\text{C}$) and adipose fatty acid (FA) signatures relative to their main prey (ringed seals). Western and southern Hudson Bay signatures were characterized by depleted $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$, lower proportions of C_{20} and C_{22} monounsaturated FAs and higher proportions of C_{18} and longer chain polyunsaturated FAs. East Greenland and Svalbard signatures were reversed relative to Hudson Bay. Alaskan

and Canadian Arctic signatures were intermediate. Between-subpopulation dietary differences predominated over inter-annual, seasonal, sex, or age variation. Among various brominated and chlorinated contaminants, diet signatures significantly explained variation in adipose levels of polybrominated diphenyl ether (PBDE) flame retardants (14–15%) and legacy PCBs (18–21%). However, dietary influence was contaminant class-specific, since only low or nonsignificant proportions of variation in organochlorine pesticide (e.g., chlordane) levels were explained by diet. Hudson Bay diet signatures were associated with lower PCB and PBDE levels, whereas East Greenland and Svalbard signatures were associated with higher levels. Understanding diet/food web factors is important to accurately interpret contaminant trends, particularly in a changing Arctic.

Introduction

Studies have found associations between high levels of legacy chlorinated contaminants in certain polar bear (*Ursus maritimus*) subpopulations and biomarkers of toxic effects on, for example, endocrine, immune, and reproductive function (1). Levels of PCBs, organochlorine pesticides (OCPs), and brominated flame retardants, like polybrominated diphenyl ethers (PBDEs), continue to be of concern to bear health, although levels and patterns vary widely within and among subpopulations across the Arctic (2). To improve reliability of reported contaminant trends, studies have considered confounding biological variation related to adipose tissue lipid content, sex, age, season, and habitat use (3–5). Contaminant trends have additionally been discussed in relation to variation in source inputs, distances from source regions, and physicochemical behavior dictating the fate and transport of individual contaminants to and within the Arctic. However, these specific biological and abiotic factors may not fully explain geographic concentration differences among subpopulations. Other ecological factors like feeding ecology and food web composition may also contribute to differences in contaminant levels, as has been observed within individual regions (6–8).

General information on polar bear diets from prey kill observations has consistently shown that ringed seals (*Pusa hispida*) are the predominant prey, followed by bearded seals (*Erignathus barbatus*) (9, 10). Yet, polar bears are opportunistic consumers, whose feeding ecology is influenced by spatiotemporal variability in prey abundance and accessibility. Predation or scavenging on other species includes harp seals (*Phoca groenlandica*), Atlantic and Pacific walrus (*Odobenus rosmarus*), narwhals (*Monodon monoceros*), beluga (*Delphinapterus leucas*), bowhead (*Balaena mysticetus*), and sperm whales (*Physeter macrocephalus*) (refs 9–11 and references therein). Size differences between prey imply that prey larger than ringed seals, but less frequently consumed, may still represent important dietary items on a biomass basis. Contaminant levels and patterns among prey species may vary due to differences in trophic positions, fasting periods, foraging strategies, biotransformation capacities, and other biological factors (1, 12, 13). Thus, it has been hypothesized that large-scale spatial variation in polar bear contaminant levels and patterns is, in part, affected by regional food web and/or diet differences (4).

Nitrogen and carbon stable isotope (SI) ratios ($\delta^{15}\text{N}$, $\delta^{13}\text{C}$) and fatty acid (FA) composition are increasingly used as chemical tracers of food web pathways and structure. Recently, these tracers have provided inferences regarding

* Address correspondence to either author. Phone: 613-998-6696 (R.J.L.). Fax: 613-998-0458. E-mail: melissaamckinney@gmail.com (M.A.M.); robert.letcher@ec.gc.ca (R.J.L.).

[†] Science and Technology Branch, Environment Canada.

[‡] Carleton University.

[§] Norwegian Polar Institute.

^{||} Greenland Institute of Natural Resources.

[⊥] Government of the Northwest Territories.

[#] Aarhus University.

[∇] United States Fish and Wildlife Service.

[○] National Water Research Institute, Environment Canada.

[♦] Government of Nunavut.

[¶] Current address: USGS Alaska Science Center, Anchorage, Alaska 99508, United States.

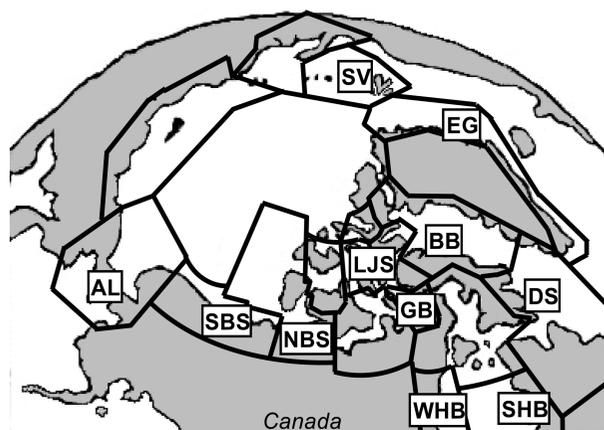


FIGURE 1. Polar bear subpopulations located throughout the circumpolar basin. Labeled subpopulations denote those examined in this study and are abbreviated as follows: Alaska–Bering–Chukchi Sea (AL), southern Beaufort Sea (SBS), northern Beaufort Sea (NBS), Lancaster/Jones Sound (LJS), Gulf of Boothia (GB), western Hudson Bay (WHB), southern Hudson Bay (SHB), Baffin Bay (BB), Davis Strait (DS), East Greenland (EG), and Svalbard–Barents Sea (SV).

the time-integrated diets of individual bears (11, 14). Relative trophic positions of species within food webs have been estimated using $\delta^{15}\text{N}$, whereas $\delta^{13}\text{C}$ differentiates feeding strategies, for example, nearshore/offshore, benthic/pelagic, freshwater/marine, terrestrial/freshwater, and terrestrial/marine (13, 15–19). Patterns of FAs have also proven useful in distinguishing feeding patterns including terrestrial/freshwater and freshwater/marine (16, 19). Many higher trophic level organisms are not able to produce sufficient amounts of specific FAs and must therefore obtain these FAs from dietary sources. The profile of FAs of carbon chain length ≥ 14 in a predator reflects that of its prey, with some predictable and correctable difference due to biosynthesis and metabolism (20). Distinct FA signatures in several marine mammal species were recently used to estimate prey species composition in diets of Canadian polar bear subpopulations (11, 21, 22). In the present study, we first hypothesized that polar bear diets, inferred from SI and FA signatures, vary spatially in subpopulations from Alaska, Canada, East Greenland, and Svalbard. Second, we hypothesized that dietary variation contributes in part to spatial variation in chlorinated and brominated contaminant levels between subpopulations.

Experimental Methods

Sample Details. Adipose and muscle tissues were collected in 2005–2008 from 11 polar bear subpopulations: Alaska (AL), S. Beaufort Sea (SBS), N. Beaufort Sea (NBS), Gulf of Boothia (GB), Lancaster/Jones Sound (LJS), Baffin Bay (BB), Davis Strait (DS), W. Hudson Bay (WHB), S. Hudson Bay (SHB), E. Greenland (EG), and Svalbard (SV) (Figure 1, Supporting Information Table S1). Samples were collected during native subsistence hunts, except in SV, where adipose biopsies were collected from live sampled bears. After sampling and during shipment, samples were kept frozen and then stored at -40°C until further processing. Ringed seal blubber samples were collected at similar locations/time periods ($n \geq 10/\text{location}$; 2004–2006) for FA analysis. Ringed seal muscle samples were collected in East Greenland for SI analysis, and remaining ringed seal muscle SI data was available from published studies. Ringed seals were of both sexes and various ages.

Contaminant and Diet Analysis and Quality Control. Brominated and chlorinated contaminant analysis of these adipose samples was carried out in the Letcher Laboratories at the National Wildlife Research Centre (NWRC) in Ottawa.

Contaminant concentrations were calculated on a lipid weight basis.

FA analysis on polar bear adipose and ringed seal blubber tissues is described elsewhere (8). Here, we considered only FAs that were detected in all samples, present in the external standard and resulted primarily or solely from dietary accumulation, the “dietary” FAs (20). The final 12 FAs, calculated as the mass % of total dietary FAs (calculated using FAME values), included linoleic acid (18:2n-6), γ -linolenic acid (18:3n-6), *cis*-11-eicosenoic acid (20:1n-9), α -linolenic acid (ALA; 18:3n-3), *cis*-11,14-eicosadienoic acid (20:2n-6), *cis*-8,11,14-eicosatrienoic acid (20:3n-6), erucic acid (22:1n-9), *cis*-11,14,17-eicosatrienoic acid (ETA; 20:3n-3), arachidonic acid (ARA; 20:4n-6), *cis*-5,8,11,14,17-eicosapentaenoic acid (EPA; 20:5n-3), *cis*-7,10,13,16,19-docosapentaenoic acid (DPA; 22:5n-3), and *cis*-4,7,10,13,16,19-docosahexaenoic acid (DHA; 22:6n-3).

For SI analysis, polar bear muscle tissues were homogenized, lipid-removed and prepared for analysis by standard protocols (e.g., ref 23). For comparability with published ringed seal muscle SI data, in which lipids were not removed, East Greenland ringed seal samples were not lipid-removed prior to SI analysis. Carbon and nitrogen SIs were determined with an elemental analyzer coupled to a continuous flow isotope ratio mass spectrometer (Environmental Isotope Laboratory (EIL), University of Waterloo, Waterloo, ON, Canada; see Supporting Information). Quality control and assurance details for contaminant, SI and FA analyses are provided in the Supporting Information.

Data Analysis. Polar bear SI and FA signatures not only reflect their food web, which includes their diet (e.g., marine mammal prey species) and the lower food web (e.g., phytoplankton, zooplankton, fish species), but also region-specific baseline tracer values. Primary producer SI values, especially $\delta^{15}\text{N}$, vary across systems and over time (18). Phytoplankton FA composition at the base of the food web also varies widely interannually and between organisms (24). Therefore, comparison of raw polar bear FA and SI (Supporting Information Table S2, Figure S1, S2a,b) was not a valid indicator of polar bear food webs without considering region-specific and temporally comparable SI and FA values for an appropriate baseline organism. Since such baseline tracers were not available, we generated and/or used published region-specific SI and FA values from ringed seals collected in similar years as a pseudo-baseline. We used ringed seal tracer data collected within the appropriate polar bear subpopulation region or within the closest adjacent region, since FA signatures among Canadian Arctic ringed seals are most similar between adjacent locations (22) (Supporting Information Table S1). Since muscle samples were not available for SV, this subpopulation was excluded from analyses involving SI data.

A modified trophic level (TL) equation was used to adjust polar bear $\delta^{15}\text{N}$ values (23). We used a trophic enrichment factor, $\Delta\delta^{15}\text{N}$, of 3.8‰ reported for the Lancaster/Jones Sound marine food web (17) and the modification of the tertiary consumer ringed seal to adjust for baseline variation among sites. For an individual bear from a given subpopulation

$$\text{TL} = 4 + \left[\frac{(\delta^{15}\text{N}_{\text{bear}} - \delta^{15}\text{N}_{\text{seal}})}{3.8} \right] \quad (1)$$

assuming ringed seal at $\text{TL} = 4$ and where $\delta^{15}\text{N}_{\text{seal}}$ was the mean $\delta^{15}\text{N}$ value of ringed seal collected within that polar bear subpopulation region (or adjacent region). Polar bear TLs could be slightly higher than estimated here, as the assumption that ringed seal occupy TL 4 may be an underestimate (25). Analogously, for a bear from a given subpopulation

$$\delta^{13}\text{C}_{\text{adj}} = \delta^{13}\text{C}_{\text{bear}} + [\delta^{13}\text{C}_{\text{seal-allregions}} - \delta^{13}\text{C}_{\text{seal}}] \quad (2)$$

where $\delta^{13}\text{C}_{\text{seal}}$ was the mean $\delta^{13}\text{C}$ value of ringed seal collected within that polar bear subpopulation region (or adjacent region) and $\delta^{13}\text{C}_{\text{seal-allregions}}$ was the mean of all $\delta^{13}\text{C}_{\text{seal}}$. Similar to the TL calculation, this equation adjusted $\delta^{13}\text{C}_{\text{bear}}$ to account for any spatial $\delta^{13}\text{C}$ variation among ringed seals, and thus $\delta^{13}\text{C}_{\text{adj}}$ was used to compare regional differences in polar bear feeding (Supporting Information Figure S2c). For each FA, FA_{adj} was similarly calculated as per eq 2, but based on polar bear and ringed seal FA values instead of $\delta^{13}\text{C}$ values. This adjustment normalizes variation in tracer signatures due to variation in the phytoplankton-to-ring-ed seal portion of the food web. Therefore, adjusted values were more representative of tracer variation due to polar bear diets and not overall food webs. We acknowledge that this is less ideal than comparisons of overall food web differences across regions in terms of understanding contaminant accumulation. Based on these calculations, polar bears with exclusively ringed seal diets would occupy TL 5. As $\Delta\delta^{13}\text{C}$ changes are minimal within food webs (18), bears feeding only on ringed seals would be expected to have a $\delta^{13}\text{C}_{\text{adj}}$ nearly equal to that of ringed seal. However, we observed an increase in $\delta^{13}\text{C}$ from seals to bears, likely because lipids were extracted from the bear samples, but not the seal samples, before SI analysis. Lipids are more depleted in ^{13}C than proteins (18). Thus, we could not reliably estimate a $\delta^{13}\text{C}_{\text{adj}}$ for polar bears feeding exclusively on ringed seals and subsequently could not compare polar bear $\delta^{13}\text{C}_{\text{adj}}$ values relative to a solely ringed seal based diet.

Overall geographic variation in polar bear dietary tracers was visualized by hierarchical cluster analysis (HCA) and discriminant function analysis (DFA) using TL, $\delta^{13}\text{C}_{\text{adj}}$ and FA_{adj} (11). All tracer values were used in HCA as variable means are used for each group. Only six tracers (TL, $\delta^{13}\text{C}_{\text{adj}}$, and the highest proportion and most variable FA_{adj} : 18:2n-6, 20:1n-9, 22:5n-3, and 22:6n-3) were used in DFA to meet the statistical assumption that the sample number in the smallest group exceeds the number of variables (11). Principal components analysis (PCA) was performed on the correlation matrix of FA_{adj} values. The first PC accounted for 41% of the variation and PC1 factor scores were considered the overall FA_{adj} -Index (Supporting Information Figure S2d). Subpopulation variation in TL, $\delta^{13}\text{C}_{\text{adj}}$, and FA_{adj} -Index were examined to infer geographic differences in polar bear diets. A second PCA was performed on TL, $\delta^{13}\text{C}_{\text{adj}}$ and FA_{adj} -Index to generate an overall Diet-Index (PC1, which accounted for 60% of the variation). This approach for creating an overall Diet-Index using SI and FA data was adopted from Hebert et al. (16). The influence of age, sex, subpopulation, and all available first-order interactions on TL, $\delta^{13}\text{C}_{\text{adj}}$, FA_{adj} -Index, and Diet-Index was determined by GLM (Type III). Sex \times subpopulation could not be tested as only one sex was sampled in DS and SV. However, this term was not significant when the model was run excluding these two subpopulations.

We studied contaminants known to be recalcitrant and to biomagnify in polar bears or their prey and thus most likely influenced by dietary factors (6, 8): ΣPCB , ΣCHL , ΣDDT , ΣPBDE , CB153, CB180, oxychlordan, *p,p'*-DDE, BDE47, BDE153, α -HCH, and β -HCH. Detailed contaminant concentration and pattern trends were reported in a separate paper (2). Contaminant concentrations were $\log(x + 1)$ -transformed to approximate normal distribution (Shapiro-Wilks *W* test) in each subpopulation. The best subset of variables to model each contaminant was selected by Akaike's Information Criteria (AIC) generated from the variables: subpopulation, Diet-Index, sex, age, and all first-order interactions. The resulting best subset model was tested by GLM (Type III). Finally, for selected contaminants, we compared subpopulation differences in contaminant con-

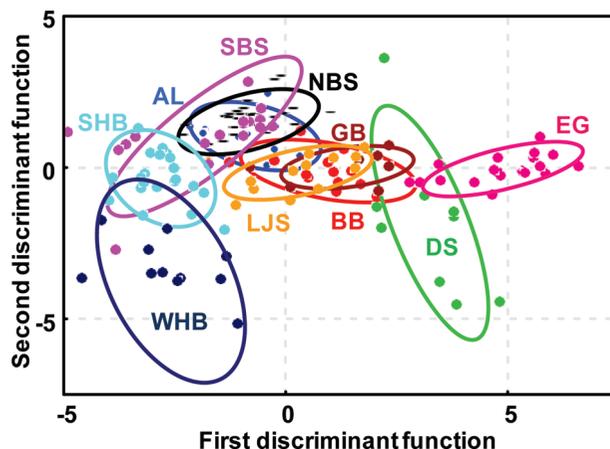


FIGURE 2. Discriminant function analysis (ellipses enclose 95% data ranges) of TL, $\delta^{13}\text{C}_{\text{adj}}$, and 4 dietary FA_{adj} in 10 polar bear subpopulations. The first two discriminant functions accounted for 81% of the total variance. Polar bears were 79% correctly classified by subpopulation. Subpopulation abbreviations: Alaska (AL), S. Beaufort Sea (SBS), N. Beaufort Sea (NBS), Gulf of Boothia (GB), Lancaster/Jones Sound (LJS), Baffin Bay (BB), Davis Strait (DS), W. Hudson Bay (WHB), S. Hudson Bay (SHB), and E. Greenland (EG).

centrations before and after adjusting for the influence of Diet-Index. Statistical differences in the adjusted least-squares subpopulation means were compared *post hoc* using Bonferroni correction. All inferential statistics were assessed with Statistica 6.0 (Statsoft, Tulsa, OK).

Results and Discussion

Geographic Variation in Polar Bear Diets. Taken together, SI and FA signatures indicated dietary differences among polar bear subpopulations (Figure 2, Supporting Information Figure S3). Discriminant function analysis and hierarchical cluster analysis showed that neighboring subpopulation diet signatures were more similar than geographically distant subpopulations. On average, subarctic WHB and SHB as well as eastern Arctic DS and EG had the most distinct signatures. Signatures were most similar among central and western Canadian Arctic subpopulations. Discriminant analysis classified 79% of bears to the correct subpopulation (Figure 2). The only individual subpopulations in which less than 70% of bears were classified correctly were AL (67%) and SBS (29%), most frequently misclassified as NBS. These findings are in good agreement with previous FA analyses of Canadian Arctic subpopulations (11).

TL varied significantly by polar bear subpopulation (partial $\eta^2 = 0.24$, $F_{9,132} = 4.57$, $p < 0.001$), but not by age, sex or interaction terms (p -values > 0.29). Age ($\eta^2 = 0.08$, $F_{1,132} = 11.43$, $p < 0.001$) and age \times sex ($\eta^2 = 0.03$, $F_{1,132} = 4.33$, $p = 0.04$) explained a significant but small amount of $\delta^{13}\text{C}_{\text{adj}}$ variation, whereas the effect of subpopulation predominated ($\eta^2 = 0.43$, $F_{9,132} = 11.21$, $p < 0.001$). Significant but small age ($\eta^2 = 0.03$, $F_{1,139} = 4.47$, $p = 0.04$) and age \times subpopulation ($\eta^2 = 0.14$, $F_{10,139} = 2.17$, $p = 0.02$) effects were also found for FA_{adj} -Index, with a larger effect of subpopulation ($\eta^2 = 0.35$, $F_{10,139} = 7.61$, $p < 0.001$). Sex and age-related variation in feeding has been suggested from previous FA studies, and even from parasite prevalence (11, 26). Overall, though, the current results suggested that persistent regional dietary differences were more important for SI and FA signatures than sex, age, and likely interannual or seasonal variation.

Individual examination of TL, $\delta^{13}\text{C}_{\text{adj}}$ and FA_{adj} -Index provided insight into the types of feeding differences between subpopulations (Figure 3). Polar bears are considered top trophic marine predators across their circumpolar distribu-

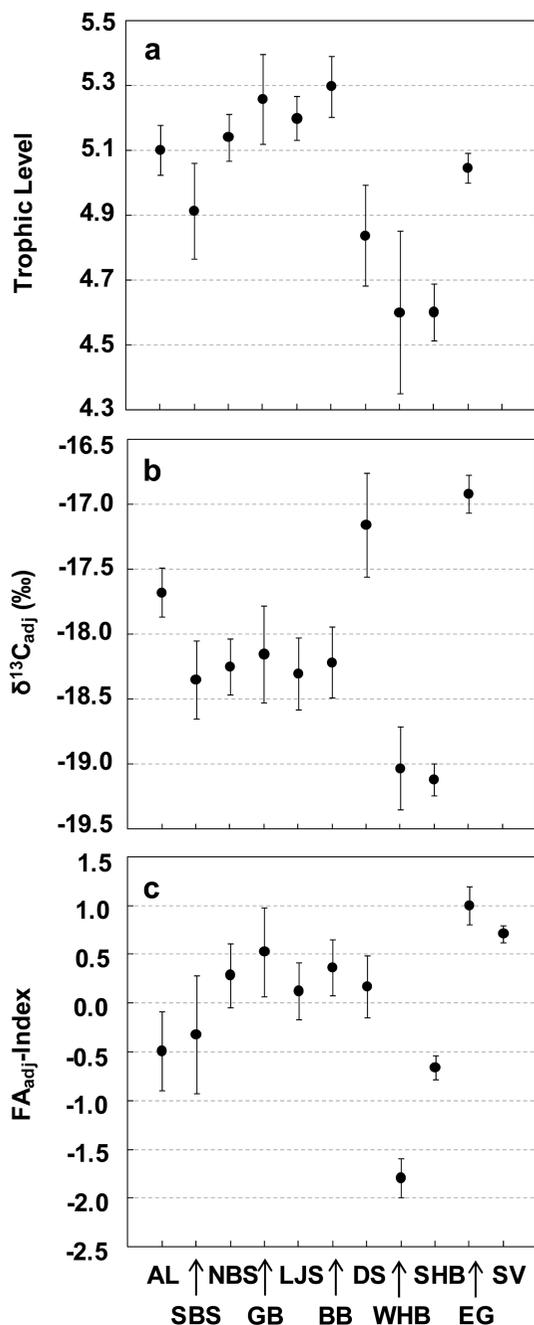


FIGURE 3. Mean ($\pm 95\%$ CI) (a) trophic level (TL), (b) $\delta^{13}\text{C}_{\text{adj}}$, and (c) FA_{adj}-Index signatures in 11 polar bear subpopulations. TL and $\delta^{13}\text{C}_{\text{adj}}$ were not available in SV. Subpopulation abbreviations: Alaska (AL), S. Beaufort Sea (SBS), N. Beaufort Sea (NBS), Gulf of Boothia (GB), Lancaster/Jones Sound (LJS), Baffin Bay (BB), Davis Strait (DS), W. Hudson Bay (WHB), S. Hudson Bay (SHB), E. Greenland (EG), and Svalbard (SV).

tion. In agreement, we found that subpopulation mean TLs straddled those estimated for an entirely ringed seal based diet (TL 5). Relatively narrow ranges were observed of 0.70 TL units (or 2.66‰ in $\delta^{15}\text{N}$) and 2.20‰ in $\delta^{13}\text{C}_{\text{adj}}$. Yet, there were clear subpopulation differences in TL and $\delta^{13}\text{C}_{\text{adj}}$ and also relative to a ringed seal diet (based on TL). Elevated proportions of higher TL prey (relative to ringed seal) were suggested in GB, LJS and BB (TLs 5.20–5.30) (Figure 3a). The identities of such prey were uncertain since other potential marine mammal prey species feed at TLs similar to or lower than ringed seals (13, 17). Elevated TLs could be related to body condition or cannibalism/scavenging on other bear carcasses. Trophic enrichment of $\delta^{15}\text{N}$ also occurs in nursing

seal pups, on which polar bears feed heavily (27, 28). In contrast, elevated proportions of lower TL prey could be inferred for WHB and SHB (TL 4.60), and perhaps also in SBS and DS (TLs 4.84–4.91). This interpretation was consistent with greater availability and/or consumption of lower TL prey in the latter subpopulations, including scavenged bowhead whales in SBS and Atlantic walrus in DS (14, 21). Surprisingly, one-third of WHB TLs were actually closer to TL 4 than 5. SHB and WHB mean $\delta^{13}\text{C}_{\text{adj}}$ signatures (-19.12 to -19.03%) were also more depleted than other subpopulations (Figure 3b). Since ringed seals are mainly pelagic foragers (21), the TL and $\delta^{13}\text{C}_{\text{adj}}$ findings together suggested elevated proportions of lower TL, more freshwater or terrestrially associated prey in SHB and WHB than in other subpopulations. However, significant terrestrial feeding has consistently been discounted in WHB, despite long ice-free periods in Hudson Bay during which the bears are forced on land (29). The unknown prey could be ringed seals from other regions within the ranges of these polar bear subpopulations that forage closer to freshwater inputs within the Bay than the ringed seals used as a reference in this study. Progressively lower marine contributions (depleted $\delta^{13}\text{C}$) have been found in Hudson Bay sediments with proximity to shore and from north to south, related to riverine inputs (30). Indeed, other studies have reported more depleted $\delta^{13}\text{C}$ values in Hudson Bay ringed seals than the values we used (e.g., ref 31), supporting spatial or temporal variation in freshwater-associated inputs within Hudson Bay. Consumption of harbor seals in Hudson Bay could also contribute to depleted $\delta^{13}\text{C}$ in the bears, as these seals inhabit rivers and areas of fresh (and tidal) flowing waters (32). Hudson Bay food web studies should be initiated, particularly given recent reports of sea ice-associated ecosystem change (8, 33).

Enriched mean $\delta^{13}\text{C}_{\text{adj}}$ signatures in EG (-17.68%) and DS (-17.15%) implied higher proportions of primarily benthic foraging prey compared to other subpopulations (Figure 3b), possibly bearded seals and/or walruses (27). The SV bears had similar diets to adjacent EG bears based on FA_{adj}-Index signatures (Figure 3c), and previous reports estimated 55% (biomass) bearded seal consumption in SV (10). Somewhat elevated $\delta^{13}\text{C}_{\text{adj}}$ signatures in AL may have been related to availability of a wider variety of prey items within the Chukchi–Bering Seas; however, AL variation could have been associated with baseline differences. Our use of Barrow ringed seal to adjust AL SI signatures may not have been adequate, given spatial heterogeneity in baseline SI ratios from the Bering Sea northeast to the eastern Beaufort Sea (14, 34). Western and central Canadian Arctic subpopulations had similar $\delta^{13}\text{C}_{\text{adj}}$ signatures. Although unequivocal prey identification and quantification of prey proportions were not possible from polar bear SI signatures, subpopulation variation likely represented substantial diet differences. For example, since bearded seal $\delta^{13}\text{C}$ signatures are around 1‰ enriched cf. ringed seal (17, 27), the $>1\%$ higher $\delta^{13}\text{C}_{\text{adj}}$ in EG than in central Canadian Arctic subpopulations likely reflected ecologically significant feeding differences.

Mean FA_{adj}-Index separated subpopulations by proportions of C_{20} and C_{22} monounsaturated FAs (MUFAs) versus proportions of C_{18} polyunsaturated FAs (PUFAs) and longer chain PUFAs (Supporting Information Figure S1). That is, 20:1n-9 and 22:1n-9 MUFAs loaded positively on FA_{adj}-Index, whereas 18:2n-6, 18:3n-6, 20:4n-6, 20:5n-3, and 22:5n-3 PUFAs loaded negatively. Higher proportions of C_{18} PUFAs and 20:4n-6 as well as lower proportions of C_{20} and C_{22} MUFAs are typical of freshwater feeding mammals compared to marine feeding mammals (e.g., ref 19). Consistent with $\delta^{13}\text{C}_{\text{adj}}$, this FA signature implied higher proportions of prey items foraging near or within freshwater in SHB and WHB (Figure 3c). Among marine mammals sampled in 1992–2004 and

TABLE 1. General Linear Model Results Testing Subpopulation, Diet-Index, Sex and Age Effects on Brominated and Chlorinated Contaminant Concentrations in Polar Bear Adipose from 10 Subpopulations from Alaska, Canada and East Greenland^a

contaminant ^b	whole model r^2 , p	independent variables ^c partial η^2 , p			
		subpopulation	Diet-Index	age	sex \times age
Σ PCB	0.52, < 0.001	0.49, < 0.001	0.21, < 0.001		
CB153	0.45, < 0.001	0.42, < 0.001	0.18, < 0.001		
CB180	0.57, < 0.001	0.53, < 0.001	0.18, < 0.001		0.04, 0.02
Σ CHL	0.48, < 0.001	0.31, < 0.001	0.06, 0.003	0.24, < 0.001	0.24, < 0.001
oxychlordane	0.51, < 0.001	0.30, < 0.001	0.05, 0.01	0.29, < 0.001	0.28, < 0.001
Σ DDT	0.40, < 0.001	0.39, < 0.001	0.04, 0.01		
<i>p,p'</i> -DDE	0.41, < 0.001	0.41, < 0.001			
Σ PBDE	0.85, < 0.001	0.84, < 0.001	0.15, < 0.001	0.04, 0.02	
BDE47	0.77, < 0.001	0.77, < 0.001		0.04, 0.02	
BDE153	0.81, < 0.001	0.79, < 0.001	0.14, < 0.001		
β -HCH	0.60, < 0.001	0.58, < 0.001	0.10, < 0.001	0.08, < 0.001	0.08, < 0.001
α -HCH	0.64, < 0.001	0.63, < 0.001			

^a For each contaminant, the best subset from the possible variables subpopulation, sex, age, Diet-Index, and all testable first-order interactions was selected for inclusion in the model using the lowest Akaike's Information Criterion (AIC) value.

^b Considered as $\log(x+1)$ -transformed lipid weight concentrations. ^c Partial η^2 ($SS_{\text{effect}}/SS_{\text{effect}} + SS_{\text{error}}$) is a measure of the effect size for each independent variable. Blank cells indicated variables not selected by AIC or not significant in the GLM ($p > 0.05$).

that range within Hudson Bay, lowest proportions of 20:1n-9 and 22:1n-9 and highest proportions of 18:2n-6 and 18:3n-6 were found in harbor seals; yet, lower proportions of 20:1n-9 and 22:1n-9 were also found in Hudson Bay ringed seals compared to ringed seals in Canadian Arctic locations (21, 22). Consistent with kill observations in adjacent SV and with FA-based diet estimations in adjacent DS (10, 11), the reversed FA pattern in EG and to a lesser extent SV may in part have reflected significant harp seal consumption, which was not apparent from SI signatures alone. Highest proportions of C₂₀ and C₂₂ MUFAs have been found in harp seals relative to other potential marine mammal prey (21). Similar to ringed seal, harp seal abundance is very high compared to other arctic marine mammals. However, harp seals are highly migratory and their distribution is concentrated in the North Atlantic and adjacent arctic waters including Davis Strait, Greenland Sea, and Barents Sea, which overlap the currently studied bear subpopulations of DS, EG, and SV (35). Similar and intermediate FA_{adj}-Index signatures in Canadian Arctic and AL subpopulations were consistent with their more similar and intermediate SI signatures relative to Hudson Bay and eastern Arctic subpopulations. The exception was DS, wherein intermediate FA_{adj}-Index signatures were unexpected given divergent SI signatures compared to most Canadian subpopulations. These findings suggest a more varied diet in DS (consistent with ref 11) that on average resulted in similar FA signatures to other subpopulations. Variety in the dietary basket may also be suggested by variance around individual subpopulation mean dietary tracer values (e.g., high variation in TL and $\delta^{13}\text{C}_{\text{adj}}$ in DS; Figure 3), but could also be related to sex/age composition of the samples (e.g., low FA_{adj}-Index variation in the all-female SV samples).

Influence of Diet on Contaminant Concentrations. We investigated the relationship between diet and contaminant levels by combining TL, $\delta^{13}\text{C}_{\text{adj}}$ and FA_{adj}-Index into an overall Diet-Index. FA_{adj}-Index was positively correlated with TL ($r = 0.72$, $p = 0.02$) and $\delta^{13}\text{C}_{\text{adj}}$ ($r = 0.69$, $p = 0.03$) (Supporting Information Figure S4). So, decreasing Diet-Index reflected increasing TL, $\delta^{13}\text{C}_{\text{adj}}$, C₂₀ and C₂₂ MUFAs and decreasing C₁₈ and longer chain PUFAs. Diet-Index varied significantly by subpopulation ($\eta^2 = 0.43$, $p < 0.001$), but not by age, sex, or interaction terms (p -values > 0.37).

As hypothesized, Diet-Index significantly explained variation in polar bear contaminant levels (Table 1). Contaminant concentrations increased with TL, $\delta^{13}\text{C}_{\text{adj}}$ and proportions of C₂₀ and C₂₂ MUFAs and decreased with proportions of C₁₈ and longer chain PUFAs. Considering all variables, effect

sizes were largest for subpopulation, followed by Diet-Index. Age and sex effects were low or nonsignificant, except for Σ CHL and oxychlordane levels (discussed elsewhere: ref 2). With larger sample sizes than in this study, variation associated with age/sex would likely be detected. Additionally, measurements of rump fat thickness as an indicator of body condition were collected for 29% of bears, but within this sample subset did not significantly explain contaminant concentrations. The effect of Diet-Index was largest for PCBs, accounting by itself for 21%, 18%, and 18% of the overall variance in Σ PCB, CB153 and CB180 concentrations, respectively (Table 1, Supporting Information Figure S5). Levels of Σ PBDE and BDE153 (but not BDE47) were also significantly explained by Diet-Index (14–15%), but not as strongly as for PCBs. Although Diet-Index explained 10% of variation in β -HCH levels, the effect was low or nonsignificant ($\leq 6\%$) for all other OCPs. In a study on SBS bears, the influence of TL (as $\delta^{15}\text{N}$) on chlorinated contaminant level variation was previously found to be highest for PCBs and low or nonsignificant for CHL, HCH, and DDT compounds (6). Differences in Diet-Index effects for individual congeners/isomers within a single compound class (e.g., significant for β -HCH but not α -HCH, significant for BDE153 but not BDE47) implies the importance of dietary factors in contaminant patterns as well, though a comprehensive analysis of contaminant patterns in relation to diet was outside the scope of the current study. Sea ice-associated dietary changes in WHB bears similarly had a higher impact over time (1991–2007) on Σ PCB and Σ PBDE than on Σ CHL, α -HCH, and β -HCH levels (8). Although regional differences in dietary exposure may occur for various contaminants, exceptional biotransformation abilities of polar bears may also be a substantial factor influencing the levels of the less recalcitrant OCPs (6). Therefore, for certain contaminants, polar bear burdens may not fully describe a spatiotemporally variable relationship between food web structure and arctic marine food web contamination. Contaminant studies within changing arctic ecosystems should consider the idiosyncratic nature of monitoring individual species, and would likely benefit from adopting a more holistic food web approach.

Influence of Diet on Geographic Contaminant Trends. We calculated polar bear subpopulation contaminant levels adjusting for Diet-Index (adjusted to mean of zero) and compared the levels to those we reported previously (2), to investigate the effect of dietary variation on geographic contaminant trends. We focused on Σ PCB and Σ PBDE, since these contaminants were most strongly associated with Diet-

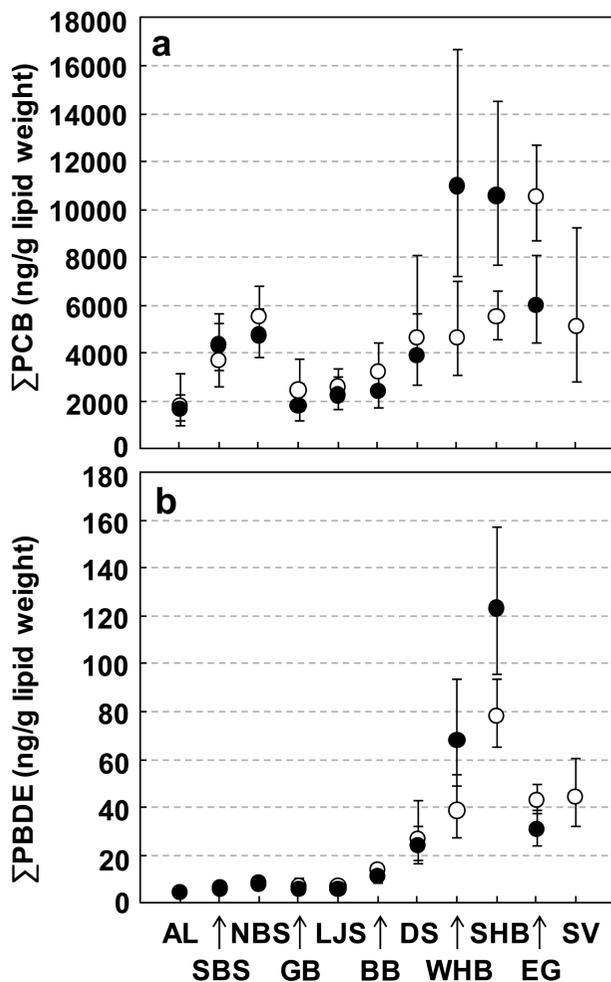


FIGURE 4. Mean ($\pm 95\%$ CI) (a) Σ PCB and (b) Σ PBDE levels before (\circ) and after (\bullet) adjusting for the influence of Diet-Index in 11 polar bear subpopulations from Alaska east to Svalbard. Adjusted levels were not available for SV. Subpopulation abbreviations: Alaska (AL), S. Beaufort Sea (SBS), N. Beaufort Sea (NBS), Gulf of Boothia (GB), Lancaster/Jones Sound (LJS), Baffin Bay (BB), Davis Strait (DS), W. Hudson Bay (WHB), S. Hudson Bay (SHB), E. Greenland (EG), and Svalbard (SV).

Index. Not surprisingly, Diet-Index adjustment had the largest effects on EG, SHB, and WHB levels (Figure 4), as these subpopulations had the most divergent SI and FA signatures. Prior to adjustment, EG polar bears had the highest Σ PCB concentrations and WHB and SHB bears had intermediate Σ PCB concentrations. After adjustment, Σ PCB levels were 76% lower in EG and 137% and 91% higher in WHB and SHB bears, respectively, resulting in higher levels in WHB and SHB than in all other subpopulations ($p < 0.001$) except EG ($p = 0.03$ and 0.02 , respectively). Σ PBDE levels were higher in EG, WHB, and particularly SHB than in most other subpopulations prior to diet adjustment. After adjustment, Σ PBDE levels were 76% and 57% higher still in WHB and SHB, respectively, and 40% lower in EG bears. That is, diet-controlled Σ PBDE levels were statistically higher in WHB and SHB than in all other subpopulations including EG ($p < 0.001$). Diet effects could not be quantified in SV bears in the absence of SI values, although their Diet-Index may be similar to EG based on FA_{adj} -Index. Diet-adjusted Σ PCB and Σ PBDE levels in SV bears are thus hypothesized to be lower than unadjusted values but less so than in EG bears. These results provide the first preliminary evidence that, relative to circumpolar subpopulations excluding SHB and WHB, higher PCB contamination in EG and SV subpopulations are

influenced not just by proximity to sources but also by dietary differences. Based on the FA_{adj} -Index, this finding may be partly related to consumption of harp seals, and although only suggestive, is consistent with the hypothesis that harp seals are a vector for transport of contaminants to these polar bear subpopulations (7). More research into eastern Canadian Arctic, Greenland, and Svalbard polar bear reliance on very (seasonally) abundant harp seal populations and the potential impact on contaminant exposure is warranted.

In contrast to EG, diet may actually have mitigated contaminant exposure for SHB and particularly WHB polar bears relative to other subpopulations, as adjusting for diet showed higher levels (Figure 4). The currently divergent dietary tracer signature in WHB bears relative to other subpopulations (except SHB) could be a result of recent sea ice-associated dietary and/or food web changes (8). We tested this using PCA to compare dietary FAs from the various subpopulations to those in WHB from years between 1991–2007 (8) (Supporting Information Figure S6). There were clear interyear differences in WHB FA signatures, but in all years, WHB was distinguished from the other subpopulations. Separation along PC1 was between 20:1n-9 and 22:1n-9 loading positively and 18:2n-6, 18:3n-6, 20:5n-3, and 22:5n-3 loading negatively. Thus, currently divergent WHB FA signatures relative to other subpopulations were not simply due to recent changes. Continued monitoring of dietary tracers in these apex arctic predators would contribute to understanding spatiotemporal variation in arctic marine food web structure and how it influences contaminant levels and patterns.

Although spatial variation in baseline SI values has been “mapped” over limited Arctic marine regions, there has been no circumpolar characterization nor a definitive understanding of why such variation occurs, for example, nutrient variation, growth rates, freshwater inputs (34). As shown in the present study, from a contaminant perspective, Hudson Bay appears most influenced by dietary factors, and would thus be an ideal ecosystem to “map” food webs using chemical tracers to better understand their influences on contaminant levels. Application of these tracers to the study of spatiotemporal variation in marine food webs and contaminant pathways remains a challenge and comprehensive food web research is necessary, particularly under changing temperatures, sea ice conditions and ecosystem structures in the Arctic (33).

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Supporting Information Available

Polar bear subpopulation biological data, mean SI ratios, FA composition, HCA results, TL, $\delta^{13}\text{C}_{\text{adj}}$, and FA_{adj}-Index correlations, subpopulation ΣPCB153 and Diet-Index correlations, comparison of FA signatures in spatial subpopulations to 1991–2007 WHB. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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