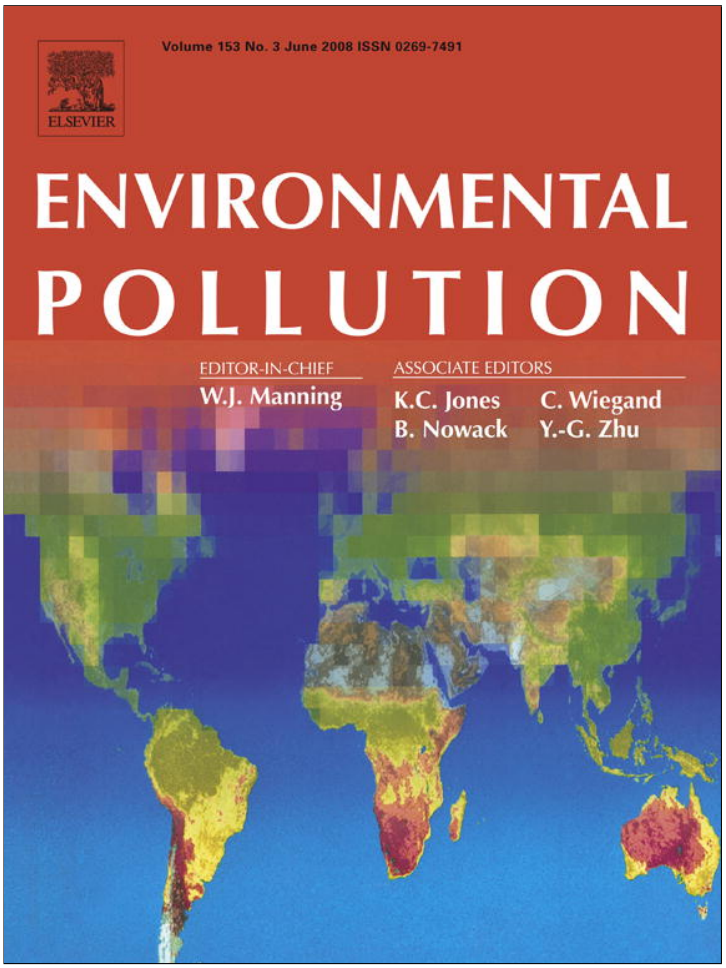

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Geographic distribution of selected elements in the livers of polar bears from Greenland, Canada and the United States

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Geographical trends were observed for a number of elements in livers, including mercury, of polar bears collected across Alaska, Canada and Greenland and were similar to those observed in the early 1980s.

Abstract

To assess geographic distributions of elements in the Arctic we compared essential and non-essential elements in the livers of polar bears (*Ursus maritimus*) collected from five regions within Canada in 2002, in Alaska between 1994 and 1999 and from the northwest and east coasts of Greenland between 1988 and 2000. As, Hg, Pb and Se varied with age, and Co and Zn with gender, which limited spatial comparisons across all populations to Cd, which was highest in Greenland bears. Collectively, geographic relationships appeared similar to past studies with little change in concentration over time in Canada and Greenland for most elements; Hg and Se were higher in some Canadian populations in 2002 as compared to 1982 and 1984. Concentrations of most elements in the polar bears did not exceed toxicity thresholds, although Cd and Hg exceeded levels correlated with the formation of hepatic lesions in laboratory animals.

Keywords: Contaminants; Regional differences; *Ursus maritimus*; Arctic; Metals

1. Introduction

Although many elements/metals occur naturally, concentrations of some elements within the Arctic have been augmented by increased resource extraction and atmospheric transport of elements from lower-latitudes (Dietz et al., 1998) and may manifest in localized contaminant problems in the Arctic (Gamberg et al., 2005). While substantial efforts have been made to monitor contaminant loads within the Arctic, proper assessment requires continued collection of data through time and across wide geographic areas (Dietz et al., 1998).

Polar bears (*Ursus maritimus*) are large, long-lived, trans-Arctic, mammalian predators that exist at the top of their food web and are excellent sentinels of contaminants in this environment (Norstrom et al., 1986). Polar bears feed almost exclusively on two species of seals: the ringed seal (*Phoca hispida*) and bearded seal (*Erignathus barbatus*) (Derocher et al., 2002), of which ringed seal is the dominant prey (Hammill and Smith, 1991). Because of these characteristics and their large

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home ranges, polar bears are excellent sentinels of a wide array of contaminants in the Arctic (Norstrom et al., 1986; Kucklick et al., 2002; Verreault et al., 2005). Additionally, information on historic element concentrations in polar bears is available for assessment of both temporal and spatial trends (e.g., Norstrom et al., 1986; Braune et al., 1991).

Previous research has shown that the accumulation of organohalogen contaminants, primarily PCBs, could be affecting polar bears through functions such as reproductive success (Dahl et al., 2003) and immune response (Lie et al., 2004; Bernhoft et al., 2000). Additionally, past analysis of element concentrations in the livers of polar bears has suggested that concentrations of some elements may by high enough to disrupt normal physiological function (Norstrom et al., 1986; Derome et al., 2002). Thus contaminant burdens may pose an additional stress on polar bears already facing potential population declines attributable to such factors as global warming (Wiig, 2005).

In an effort to continue the monitoring of temporal and spatial trends of elements in the Arctic, and assess current concentrations, we present concentrations of elements in polar bear livers collected across the Canadian arctic in 2002 and compare these data with older data collected in Alaska (1994–1999) and Greenland (1983–2000).

2. Methods

2.1. Sampling

Liver tissue samples were taken from polar bears collected by hunters within Canada, Greenland and the United States (Alaska) (Fig. 1). Details of the tissue sampling procedures are given in Norstrom et al. (1986). Tissue samples collected within each of the three countries were grouped according to management areas (hereafter referred to as populations) based on polar bear sub-populations: two areas in Greenland, one area in Alaska and five areas within Canada. Livers from Greenland ($n = 128$) were collected over the period 1983–2000, from Alaska ($n = 6$) from 1994 to 1999, and from Canada ($n = 60$) in 2002. Polar bears ranged in age from 2 to 24 years old while the year in which samples were collected varied by population (Table 1). Gender of the bears was recorded and age was determined by histological sectioning of a tooth (Stirling and Archibald, 1977) if the jaw was provided. Unfortunately, age and sex data were lacking for a number of samples (sex: 10 bears from Canada; age: 28 bears from Canada).

2.2. Chemical analysis

A total of 21 elements were assessed in livers of polar bears collected in Canada (essential elements: As, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Se, V and Zn; and non-essential elements: Ag, Ba, Ga, La, Pb, Rb, Sr, Hg and Pt; as defined in Pais and Jones, 1997). Ten elements (Cr, Cu, Mo, Se, V, Zn, Ag, Cd, Hg and Sr) were analyzed in Alaska bears, and four elements (Se, Zn, Cd and Hg) in samples from Greenland.

Samples of polar bear livers collected in Canada were analyzed at the National Laboratory for Environmental Testing (NLET) at National Water Research Institute in Burlington, Ontario. Total mercury in liver tissue (NLET Method 02-2802) was analyzed by cold vapor atomic absorption spectrometry (CVAAS). Twenty-two elements in liver (NLET Method 02-2705) were analyzed by inductively coupled plasma-Sector Field spectrometry (ICP-SFMS), with 20 elements analyzed at low resolution (Ag, Ba, Cd, Co, Cr, Cu, Ga, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sr, Tl, U, V and Zn) and the rest at high resolution (As and Se). The instrumental detection limits for most elements were 0.001 μg/g, except for Sr (0.05 μg/g), Pt (0.01 μg/g), Pb (0.1 μg/g), Li (0.1 μg/g) and Sb (0.01 μg/g).

Analysis of liver samples from Alaskan polar bears was performed by Research Triangle Institute in Research Triangle Park, North Carolina. Samples were analyzed for Al, Ag, As, Ba, Be, Ca, Cr, Cu, Fe, Pb, Hg, Mg, Mn, Mo, Ni, Se, Sr, V and Zn. All samples were homogenized and then freeze dried for determination of percent moisture. Each sample (0.25–0.5 g) was digested in 5 ml of Baker Instra-Analyzed nitric acid in a CEM microwave for 3 min each at 120, 300 and 450 W. The final residue was then diluted to 50 ml with laboratory pure water. Concentrations of As, Se and Ag were analyzed using graphite furnace atomic absorption (GFAA) and a Perkin–Elmer Zeeman 3030 or 4100ZL atomic absorption spectrometer. Mercury concentrations were determined using CVAAS analysis with a tin chloride ($SnCl_4$) reduction. Concentrations of Hg were determined on a Leeman PS200 Hg Analyzer using CVAAS and $SnCl_4$ as a reducing agent. All remaining elements were measured using inductively coupled/plasma spectroscopy with a Leeman Labs Plasma Spec 1 sequential or ES2000 simultaneous spectrometer.

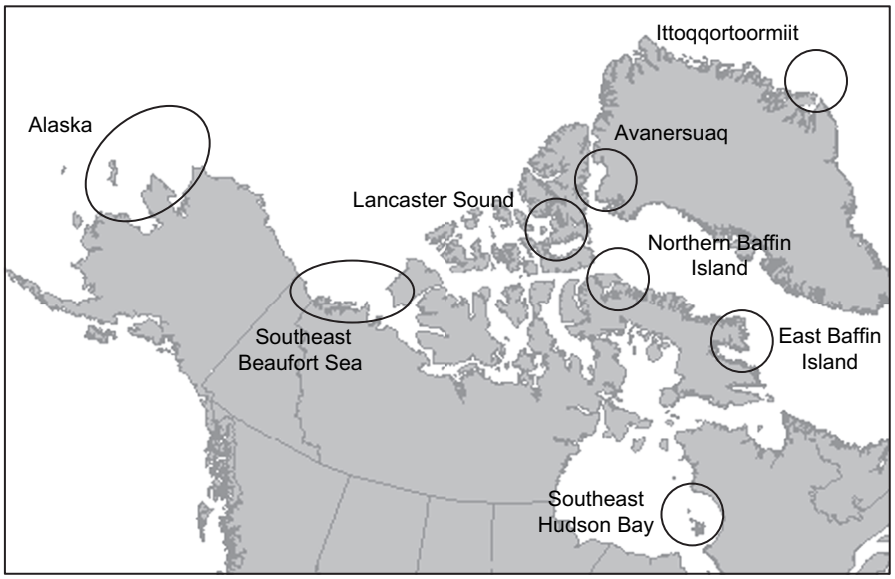

Fig. 1. Locations of polar bear sample populations.

Table 1
Essential and non-essential element levels and standardized ratios of Se:Hg in the livers of polar bears from Canada, Alaska and Greenland (mean ± 1 SE, ww, mg/kg)

Element	Canada					Alaska	Greenland	
	East Baffin Island	Lancaster Sound	Northern Baffin Island	Southeast Beaufort Sea	Southeast Hudson Bay		Avanersuaq	Ittoqqortoormiit
n	13	13	12	11	11	6	46	82
Male:female	5:7	3:1	7:5	8:3	5:6	0:6	19:27	40:42
Age range	2–18: 7[a]	5–14: 6[a]	5–13: 7[a]	3–24: 1[a]	3–7: 7[a]	5–19: 0[a]	1–16:29[a]	2–23:46[a]
Years	2002	2002	2002	2002	2002	1994–1999	1988–1990	1983–2000
Essential								
As^{+}	0.22 ± 0.04	0.32 ± 0.05	0.37 ± 0.05	0.46 ± 0.05	0.17 ± 0.05	–	–	–
Co	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	–	–	–
Cr	0.04 ± 1.49	0.09 ± 1.36	0.06 ± 1.49	0.13 ± 1.56	0.09 ± 1.38	–	–	–
Cu	35.61 ± 8.07	38.2 ± 8.07	37.92 ± 8.18	32.84 ± 8.3	52.26 ± 8.3	50.5 ± 6.68	–	–
Li	0.01 ± 0.00	0.01 ± 0.00	–	0.01 ± 0.00	0.01 ± 0.00	–	–	–
Mn	3.58 ± 0.51	4.96 ± 0.51	3.7 ± 0.52	3.89 ± 0.53	4.1 ± 0.53	–	–	–
Mo	0.46 ± 0.08	0.67 ± 0.08	0.67 ± 0.08	0.73 ± 0.08	0.55 ± 0.08	0.67 ± 0.07	–	–
Ni	0.05 ± 0.03	0.05 ± 0.04	0.04 ± 0.04	0.1 ± 0.05	0.06 ± 0.05	–	–	–
Se^{+}	9.16 ± 3.75	14.38 ± 3.75	11.63 ± 3.8	21.82 ± 3.85	3.31 ± 3.85	4.98 ± 3.09	5.61 ± 3.67	4.85 ± 3.37
V	0.08 ± 0.05	0.06 ± 0.05	0.07 ± 0.05	0.11 ± 0.05	0.22 ± 0.047	0.21 ± 0.04	–	–
Zn	63.32 ± 7.85	74.72 ± 7.85	66.37 ± 7.95	62.76 ± 8.07	58.74 ± 8.07	55.92 ± 6.49	57.85 ± 7.68	54.77 ± 7.06
Non-essential								
Ag	0.13 ± 0.11	0.28 ± 0.11	0.21 ± 0.11	0.13 ± 0.11	0.26 ± 0.11	0.16 ± 0.1	–	–
Ba	0.02 ± 0.01	0.03 ± 0.001	0.02 ± 0.01	0.02 ± 0.01	0.04 ± 0.01	–	–	–
Cd	0.62 ± 0.4	0.87 ± 0.4	1.02 ± 0.41	0.35 ± 0.42	1.06 ± 0.42	0.51 ± 0.33	1.59 ± 0.36	1.15 ± 0.35
Ga	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	–	–	–
Hg^{+}	28.43 ± 11.05	45.24 ± 11.05	32.48 ± 11.2	62.49 ± 11.37	7.34 ± 11.37	10.36 ± 9.14	13.00 ± 9.14	11.43 ± 9.94
La	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	–	–	–
Pb	0.69 ± 0.2	0.23 ± 0.28	0.26 ± 0.28	0.06 ± 0.29	0.12 ± 0.29	–	–	–
Pt	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	–	–	–
Rb	5.29 ± 0.5	4.86 ± 0.71	5.29 ± 0.73	3.72 ± 0.74	5.84 ± 0.74	–	–	–
Sr	0.17 ± 0.06	0.11 ± 0.06	0.08 ± 0.06	0.12 ± 0.66	0.22 ± 0.06	0.06 ± 1.24	–	–
Molar ratios								
Se:Hg	1.01	1.12	0.94	0.89	1.21	1.54	1.20	1.18

Element levels not corrected for age or sex are indicated with a "+".
[a] Number of individuals of unknown age within sample.

Analysis for polar bear samples collected in Greenland was carried out at the National Environmental Research Institute, Denmark. After removal from the freezer the tissue samples were lightly thawed and the outer exposed tissue layer was cut away to minimise possible contamination and changes in water content due to handling and storage. Stainless steel scalpels, polyethylene gloves, and cutting boards were used. Approximately 0.5 g of tissue was transferred to the tarred Teflon liner of a Berghof stainless steel bomb. After the addition of 3 ml of 65% HNO_3 (Merck Suprapur®), the bombs were closed and incubated for 12 h at 120–150 °C. Following a cooling period, the digests were transferred quantitatively to 50-ml screw-cap polyethylene bottles and adjusted to approximately 25 g weight using metal-free, deionized water (Millipore®). Approximately 8% HNO_3 was used for all further dilutions. Mercury (Hg) analysis was performed using hydride generation and the amalgam technique, as described by e.g. Dietz et al. (2000). The detection limit for laboratory analyses was 0.005 μg/g ww of mercury. The analytical quality was checked by repeating analyses, and by the frequent use of various reference standards; especially Tort-1 lobster hepatopancreas supplied by the National Research Council of Canada, Marine Analytical Chemistry Standards Program and the dried tuna internal standard of National Food Agency of Denmark. The DAE laboratory participates in the international intercalibration exercises conducted by the International Council for the Exploration of the Sea (ICES), EEC (QUASIMEME), National Research Council, Canada and by the Department of Fisheries and Oceans, Winnipeg, Canada (Asmund and Cleemann, 2000).

2.3. Statistical analysis

All element concentration data were expressed on a wet weight basis prior to statistical analysis. Several elements (Cr, La, Li, Pt, Sb, Tl and U) had incomplete data sets or levels below detection limits and thus were not included in statistical analyses. Tests for normality revealed that the data were not uniformly distributed and thus all element data were logarithmically transformed to meet this assumption before further statistical analysis.

2.4. Influence of age and sex on element concentrations

The influence and interaction of age and sex on element concentration were assessed by linear models using the GLM (General Linear Model) procedure and Type III sums of squares in the statistical package R (3.1: R Development Core Team, 2004) ($n = 25$, Canadian data set only). Since sample sizes differed significantly between populations we assumed an unequal sample variance and used a pooled standard deviation in the model. We used Tukey's multiple comparison tests (HSD) to assess differences in mean element concentration between geographic regions. When element concentrations were identified to be influenced by the age of the bear sampled we treated age as a continuous variable and applied an analysis of covariance (ANCOVA) to assess regional differences in mean element concentrations.

2.5. Spatial trends of elements

The elements Ag, Cd, Cu, Mo, Sr, V, Zn, Ba, Cr, Li, Mn, Ni and Rb were not influenced by age, sex or their interaction and thus, where measured, were compared between populations in Alaska, Greenland and Canada without consideration for age or sex. For this analysis we used linear models (single-factor ANOVAs) with element concentration as the dependent variable and population as the independent variable. Differences between populations were assessed by comparing the statistical significance of the estimated mean for each element between sample populations.

2.6. Spatial trends of elements in Canadian polar bears

To analyze spatial differences in the behavior of essential versus non-essential elements, the Canadian polar bear data set was analyzed using multivariate ordination (CANOCO 4.5 for Windows, ter Braak and Šmilauer, 2002). Only the 15 elements Ag, As, Ba, Cd, Cu, Ga, Hg, Mn, Mo, Pb, Rb, Se, Sr, V and Zn were included in the analyses, as Cr, Li, Ni, Tl, U, Sb, Pd, Pt, Co and La were below detection limit in more than 20% of the samples. For elements with fewer than 20% non-detections, the missing values were replaced by random numbers generated by Excel, using 0.5 × DL as the mean. Both element concentrations and element pattern ([element]/[∑elements]) were analyzed, identifying the behavior of the two element groups across the Canadian populations. As univariate analyses showed that gender influenced the concentration of some of the elements, the first ordination was performed on only gender-known Canadian samples ($n = 50$), using Monte Carlo permutation test to analyze the significance of gender on the concentrations of elements. This preliminary ordination analyses showed that gender was not influential in explaining underlying structure in the variance of the 15 element concentrations among the samples ($p = 0.172$, $F = 1.53$). Therefore, a principal component analysis (PCA) was performed on the complete Canadian data set ($n = 60$) without adjusting for gender. The replacement of random numbers resulted in artificially low numbers for three samples, that appeared as outliers, and were therefore removed from the final PCA.

3. Results

3.1. Influence of sex and age

When compared across populations in Canada the essential element As (slope = 0.021, $F_{1,30} = 19.89$, $p < 0.001$), and for Canada and Greenland Se (slope = 1.91, $F_{1,30} = 37.7$, $p < 0.001$), showed positive relationships with the age of the bear sampled. Females had higher levels of Co than males ($F_{2,57} = 6.509$, $p = 0.003$), while males had higher levels of Zn than females ($F_{2,57} = 3.962$, $p = 0.024$). A similar analysis of the non-essential elements (Ag, Cd, Ga, Hg, La, Pb, Pt, Rb and Sr) and their interactions indicated that Hg concentration increased with the age of the bear sampled ($F_{1,30} = 9.06$, $p < 0.005$). After adjusting for age we found mean concentrations of Se were higher for the Southeast Beaufort Sea population than at East Baffin Island ($t = -3.8$, df = 7, $p = 0.007$) and Southeast Hudson Bay ($t = -5.29$, df = 7, $p < 0.001$). Similarly, we found concentrations of the Hg differed significantly between Southeast Hudson Bay and the Southeast Beaufort Sea populations ($t = -4.81$, df = 7, $p < 0.001$) and Southeast Hudson Bay and Northern Baffin Island ($t = -3.44$, df = 7, $p = 0.02$). While for Greenland, mean concentrations of Hg and Se appeared higher for Avanersuaq (Table 2) after adjusting for age we did not find Hg or Se differed significantly among sample populations. All other elements showed no significant relationship with either the age or sex of the bear sampled.

Levels of Co, Zn and As were not found to differ among Canadian populations. Results of a single-factor ANOVA identified Mo, Pb and V varied significantly between populations sampled in Canada and Alaska. Concentrations of Mo were significantly higher for the Southeast Beaufort Sea population than elsewhere in Canada ($F_{1,64} = 5.66$, $p = 0.023$) and the highest levels of Ag were found for samples collected in Lancaster Sound, concentrations significantly greater than those found for the East Baffin Island ($t = -3.70$, df = 4, $p = 0.004$) or Southeast Beaufort Sea populations ($t = -3.44$, df = 4, $p = 0.01$). Hepatic concentrations of Pb were higher among polar bears sampled from the Southeast Beaufort Sea population than at Northern Baffin Island ($t = 3.60$, df = 4, $p = 0.006$) and while concentrations of V were significantly higher at Southeast Hudson Bay, they did not significantly differ from

Table 2
Temporal comparison of Hg, Se and As concentrations (mg/kg, ww) in polar bear livers, age-adjusted to 6.9 years, for populations in Canada and Greenland

Year	1980–1985		1986–1990		1994–2000		2002	
Location	Hg	Se	Hg	Se	Hg	Se	Hg	Se
Canada								
East Baffin Island	16.65	6.07	–	–	–	–	24.66	7.84
Lancaster Sound	22.01	8.19	–	–	–	–	45.84	14.83
Northern Baffin Island	25.09	7.93	–	–	–	–	31.69	11.5
Southeast Beaufort Sea	53.04	23.43	–	–	–	–	69.75	24.53
Southeast Hudson Bay	6.54[a]	1.54[a]	–	–	–	–	4.16	2.32
Alaska	–	–	–	–	5.243	1.13	–	–
Greenland								
Avanersuaq	–	–	17.84	7.66	–	–	–	–
Ittoqqortoormiit	9.649	4.09	9.56	3.62	9.663	4.79	–	–

Data for bears sampled in Canada between 1980 and 1985 are from Braune et al. (1991).
[a] While several populations may exist within Hudson Bay these populations likely share similar trophic relationships and share similar exposure. On the basis of similar feeding patterns we have drawn comparison with concentrations measured for Southwest Hudson Bay (Braune et al., 1991).

concentrations identified for samples collected from the Southeast Beaufort Sea ($t = 2.91$, df = 5, $p = 0.056$) or Alaskan populations ($t = 0.16$, df = 5, $p = 0.873$).

Cadmium (Cd), measured in bears from all three countries was not influenced by gender or age, had the highest concentrations in polar bears from Avanersuaq and Ittoqqortoormiit, Greenland (Table 1).

3.2. Element concentrations and patterns among Canadian polar bears

When simultaneously analyzing the 15 elements found in more than 80% of the Canadian polar bears (Ag, As, Ba, Cd, Cu, Ga, Hg, Mn, Mo, Pb, Rb, Se, Sr, V and Zn), the essential and non-essential elements showed no clear difference in behavior in terms of separating the different polar bear populations (Fig. 2). Due to the large variability in element concentration with each population sampled, the polar bear populations were not distinctively separated on the PCA plots. However, the samples were separated along PC1 accounting for 37.5% of the variation, due to lower concentrations of As, Hg and Se, and higher concentrations of V and Mn in polar bears from Southeast Hudson Bay compared to the other populations (Fig. 2A). Likewise, the samples were separated along PC2 accounting for 19% of the variation, due to higher Mo concentrations in polar bears from the Southeast Beaufort Sea population compared to East and Northern Baffin Island, and Lancaster Sound. Of the five populations, East and Northern Baffin Island, and Lancaster Sound were the most similar, especially the two latter, with highly overlapping individual scores. North Baffin Island and Lancaster Sound were adjacent populations. Polar bears from Southeast Hudson Bay and Southeast Beaufort Sea populations expressed the greatest dissimilarity among all Canadian sample sites.

Additionally, the patterns of elements showed a high degree of variation within each population sampled, and greatly overlapping scores among the samples. The structure in the element variance did not differ between the essential and non-essential elements. The low concentration of Hg and Se in Southeast Hudson Bay also affected this pattern, whereas these samples were separated from the other populations due to lower relative contribution of Hg and Se compared with other elements (Fig. 2B). This separation is along PC1, which accounts for 74.6% of the variation in element pattern among the samples. The Southeast Hudson Bay polar bears were also separated from the other populations due to higher relative contribution of Cu. As with the concentration data, the element pattern in the polar bears from Southeast Hudson Bay and Northwest territories represents the greatest difference, whereas concentrations among the other populations fall between these endpoints.

4. Discussion

Concentrations of a number of essential and non-essential elements in polar bear livers showed geographic variation across the western hemisphere of the Arctic. Age and sex were also found to influence concentrations of a number of elements in Canadian polar bears. Single-element analyses of Canadian and Alaskan polar bear identified that most of the non-essential elements differed in concentration among the populations, whereas a limited number of the essential elements varied between populations. Multivariate element analyses of Canadian polar bears revealed that the variance associated with the essential and non-essential element concentrations could not be clearly determined by the element's physiological function.

4.1. Essential elements

Accumulation of essential elements is regulated by organisms, and thus differences across populations of the same species should be minimal (Borgå et al., 2006). Comparison of element concentrations between our samples and those of Norstrom et al. (1986) and Braune et al. (1991) suggests lower levels of Cu and Mn in our study. While the earlier studies report higher concentrations of Cu across all sample populations we found significantly higher concentrations among the Southeast Beaufort Sea polar bear population, a result similar

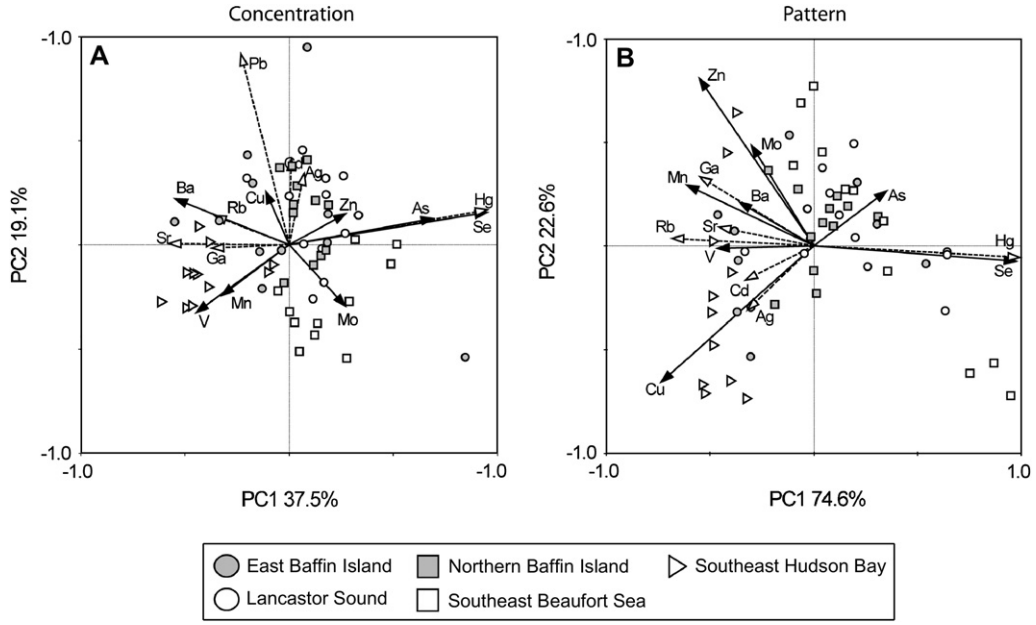

Fig. 2. Biplot of Canadian polar bear mean scores (circles) by region on the principal components (PC) extracted by principal component analyses (PCA) and the element loadings on the PCs. Absolute element concentrations (A) (mg/kg) and standardized element concentrations (B) (pattern) in liver of polar bears collected from five regions in Canada (EB – East Baffin Island; LC – Lancaster Sound; NB – Northern Baffin Island; SBS – Southeast Beaufort Sea; SHB – Southeast Hudson Bay). Direction and length of arrows indicate respective element strength and increasing value of loading.

to the trend identified by Norstrom et al. (1986). Additionally, like these two earlier studies and those of Woshner et al. (2001) we found concentrations of Cu in the livers of western polar bears exceeded those of ringed seals collected within the geographical area (Dehn et al., 2005). Despite these differences there is no supportive evidence that hepatic concentrations of Cu in the polar bears exceed their normal physiological range for this element.

After accounting for age, levels of Se were found to be higher in polar bears from the Southeast Beaufort Sea population than the Southeast Hudson Bay population. Comparison of Se levels normalized to an age of 6.9 (Table 2) showed that Se in Greenland polar bears was lower than that for the Canadian polar bears with the exception of the Southeast Hudson Bay population. Similar to the results of Norstrom et al. (1986) and Dietz et al. (2000), we found a strong correlation between Se and Hg, both in terms of absolute and standardized concentrations.

Arsenic (As) concentrations were found to be higher for the Southeast Beaufort Sea and North Baffin Island populations than for any other population within Canada. Cadmium levels were highest among all sample sites in Greenland at Avanersuaq and Ittoqqortoormiit and in Canada, at Southeast Hudson Bay and Northern Baffin Island. A similar geographic relationship has been identified in polar bears collected in 1982 and 1984 by Braune et al. (1991) and for other species including ringed seals (Wagemann et al., 1996), which has been attributed to geological differences between the collection sites. Concentrations of V were highest in Alaska and within Canada at Southeast Hudson Bay. Our finding of significant positive correlations between Ag, Cd, Cu and Zn is in agreement with the findings of Braune et al. (1991) for polar bears. Braune et al. (1991) and Woshner et al. (2001) attributed this to a positive association in the concentrations of these elements in polar bear tissues to their common binding to the protein metallothionein (MTH).

4.2. Non-essential elements

Non-essential elements, unlike essential elements, are not physiologically regulated to specific levels (Pillet et al., 2002; Viarengo et al., 2000). Thus, differences in non-essential elements between populations of a species likely reflect difference in exposure due to geographical differences in concentrations or differences in the feeding ecology of the populations (Borgå et al., 2006). For example, Braune et al. (1991) suggest that some non-essential element concentrations in polar bears from the Canadian Arctic may track differences in mining intensity. Regional differences in geology may also influence observed concentrations of elements in the abiotic and biotic environment (Dietz et al., 1998). As well, a number of non-essential elements, Hg, Rb and sometimes Cd, have been shown to biomagnify in food webs (Campbell et al., 2005; Atwell et al., 1998), and may be explained by differences in feeding ecology among polar bear populations (Braune et al., 1991) whereas Riget et al. (2005) suggested that high levels of Hg among ringed seals sampled near the Southeast Beaufort Sea may be best explained by geological differences.

For polar bear populations within Canada we found levels of Hg were highest in the Southeast Beaufort Sea population and in general from more northerly populations. The most southerly population sampled, Southeast Hudson Bay, had the lowest Hg concentrations of all populations, corroborating previous results for liver (e.g. Lentfer and Galster, 1987;

Norstrom et al., 1986; Braune et al., 1991; Dietz et al., 1995, 1998) and hair (Eaton and Farant, 1982; Renzoni and Norstrom, 1990; Born et al., 1991; Dietz et al., 1998). However, Renzoni and Norstrom (1990) did not find strong correlations between concentrations in hair and liver providing the suggestion that concentrations in liver represent shorter-term storage than hair and may be a less reliable means of determining geographic of temporal trends of Hg in the environment.

While underlying geology may lead to differences among element concentrations, geographically differing levels of atmospheric deposition must also be considered as models pointing towards higher atmospheric deposition of Hg within more northern latitudes (Ariya et al., 2004). In addition to latitudinal trends, several studies of Hg concentration among marine mammals have identified higher concentration of Hg in the central and western Canadian Arctic (Lockhart et al., 2005; Riget et al., 2005; Dietz et al., 1998). These patterns may reflect land use and geologic processes or, as suggested by Norstrom et al. (1986) differences in trophic relationships among populations. Stirling and Archibald (1977) found bearded seals comprise a higher proportion of polar bear diet in the western than eastern Arctic.

After normalizing to an age of 6.9 years comparison of the mean concentrations of Hg found for polar bear populations sampled in Canada (2002) and Greenland (sampled between 1980 and 2000) as part of our study with data collected from similar locations in 1982 (Norstrom et al., 1986) and 1984 (Braune et al., 1991) suggested element concentrations may have increased slightly in some Canadian populations over this period (Table 2). However, we caution against using these results to infer long-term trends as the number of years involved in this analysis was limited and information on food web structure is not available. In the central Canadian Arctic several studies have shown an increase in Hg, whereas in the other regions of the arctic Hg seems to be decreasing. In Northwest Greenland, polar bear hair showed a significant positive 2.1% increase per year in Hg concentrations from the period 1920 to 1991 (Dietz et al., 2006a). Results for ringed seals from Canada do not provide a clear picture. Of eight regions sampled between 1972 and 2001 increases, decreases and fluctuating trends were detected (Braune et al., 2005). Three age groups of ringed seals in Northwest Greenland showed a significantly increasing trend of Hg (and decrease in Cd) from 1984 to 1998 (Riget et al., 2004). Whether the changes reflect anthropogenic input, changes in seal feeding behavior or other environmental factors are unknown. In a later study Riget et al. (2005) added more data and stable isotope analysis which showed that the observed increase was no longer significant when corrected for trophic position. In another investigation, Hg increases were found in seven out of eight comparisons of West Greenland gyrfalcons, peregrine falcons and white-tailed eagle populations from 1850 to 2004 (Dietz et al., 2006b). Similarly, a study of Hg in American (*Falco peregrinus anatum*) and Arctic (*Falco peregrinus tundrius*) peregrine falcon eggs from Alaska found a recent increase of Hg (Ambrose et al., 2000). In other arctic regions Hg concentrations have been decreasing (e.g. East Greenland polar bear hair (Dietz et al., 2006a) and in human deciduous teeth from Norway (Tvinnereim et al., 1997 cited in Braune et al., 2005a)).

Highest concentrations of Pb were found among polar bears sampled in Northern Baffin Island, East Baffin Island and Lancaster Sound. Similar trends have been observed in other marine mammals and may reflect underlying geological differences and/or the intensity of regional mining activity (Gamberg et al., 2005; Muir et al., 1999; Norheim et al., 1992; Braune et al., 1991). A trend was identified in the ordination of the sites based on our PCA analysis. The more eastern sites of East Baffin Island and Southeast Hudson Bay showed greater similarity than populations further to the west: Lancaster Sound, Northern Baffin Island and the Southeast Beaufort Sea. In addition, the neighbouring sites of North Baffin Island and Lancaster Sound showed the greatest similarity in ordination. Lead and Ag followed a similar pattern with highest concentrations of Pb found in bears from Northern Baffin Island and for Ag, bears from both Northern Baffin Island and Lancaster Sound had the highest concentrations. Riget et al. (2005) suggest geological differences between the eastern and western Canadian Arctic may lead to contaminant differences among some marine mammals. These geographical differences may explain Pb levels among the populations of bears sampled but at the scale provided by this study they do not provide a strong explanation for differences in Hg concentrations.

4.3. Toxicological significance of element concentrations

While we did find significant geographic differences in the concentrations of some essential and non-essential elements among polar bears it is unknown whether these burdens pose a significant health risk for this species. While we expected that the essential elements would not differ greatly between geographic regions, the finding of differences among populations of bears may suggest that concentrations are somewhat dependent on exposure as well as physiological requirements, and may be within the normal range for this species. While we did find differences in the concentrations of several non-essential elements the potential physiological impacts of these concentrations remain unknown. Dietz et al. (1995) suggested that for terrestrial mammals liver-based concentrations of Se above 7 μg/g ww may lead to hepatic lesions. The present levels in polar bears sampled from all Canadian regions, except Southeast Hudson Bay, are above or close to this threshold, which may render them susceptible to potential liver damage. Mean concentrations of Hg in liver in three of eight populations exceeded 30 μg/g ww which is considered lethal or harmful in terrestrial mammals based on concentrations in liver and kidney (Thompson, 1996) but lower than the threshold of 60 μg/g ww associated with liver damage in marine mammals (Law, 1996). According to Dietz et al. (2000) the concentrations of Hg are higher in kidneys than in liver, and as the threshold limit is the same for the two organs the kidneys may be the primary target organ. However, a 1:1 molar ratio of Se:Hg has been suggested to mitigate toxicity of Hg,

and is commonly observed in marine mammals with very high Hg concentrations (above approximately 2.0 μg/g ww) (Braune et al., 1991; Dietz et al., 2000). Se:Hg molar ratios for the polar bears in this study were close to 1 (Table 1), and similar to values reported previously for polar bears (Dietz et al., 2000), suggesting that potential toxicity associated with the high Hg and Se concentrations in the polar bears may be mitigated by Se:Hg complex. Concentrations of Pb and Cd were well below levels associated with effects of these metals (Derome et al., 2002). Whether Canadian polar bears are experiencing these or similar ailments as a result of specific elemental contaminants needs further exploration (Derome et al., 2002).

While we believe that element and other contaminant issues may potentially pose a long-term threat to polar bear populations we also believe that short-term climatic changes present a much greater concern. For example, Stirling (2000) suggested changing ice conditions, as a product of global warming can affect recruitment, and population characteristics of polar bears. However, global warming and changing climatic conditions can also lead to increased deposition or mobilization of both essential and non-essential elements and other physical changes within the Arctic system (ACIA, 2005; Oechel et al., 1997) and continued monitoring of elements in arctic organisms is warranted and encouraged.

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