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PAPER

Spatial and temporal trends of selected trace elements in liver tissue from polar bears (*Ursus maritimus*) from Alaska, Canada and Greenland

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Spatial trends and comparative changes in time of selected trace elements were studied in liver tissue from polar bears from ten different subpopulation locations in Alaska, Canadian Arctic and East Greenland. For nine of the trace elements (As, Cd, Cu, Hg, Mn, Pb, Rb, Se and Zn) spatial trends were investigated in 136 specimens sampled during 2005–2008 from bears from these ten subpopulations. Concentrations of Hg, Se and As were highest in the (northern and southern) Beaufort Sea area and lowest in (western and southern) Hudson Bay area and Chukchi/Bering Sea. In contrast, concentrations of Cd showed an increasing trend from east to west. Minor or no spatial trends were observed for Cu, Mn, Rb and Zn. Spatial trends were in agreement with previous studies, possibly explained by natural phenomena. To assess temporal changes of Cd, Hg, Se and Zn concentrations during the last decades, we compared our results to previously published data. These time comparisons suggested recent Hg increase in East Greenland polar bears. This may be related to Hg emissions and/or climate-induced changes in Hg cycles or changes in the polar bear food web related to global warming. Also, Hg : Se molar ratio has increased in East Greenland polar bears, which suggests there may be an increased risk for Hg^{2+}-mediated toxicity. Since the underlying reasons for spatial trends or changes in time of trace elements in the Arctic are still largely unknown, future studies should focus on the role of changing climate and trace metal emissions on geographical and temporal trends of trace elements.

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Environmental impact

Polar bears (*Ursus maritimus*) are a sentinel species for monitoring the state of circumpolar arctic marine ecosystem contamination by persistent organic pollutants (POPs) and trace elements. We report on the most recent (2005–2008) spatial trends and comparative changes in time of trace elements known to accumulate in polar bears (arsenic (As), cadmium (Cd), copper (Cu), total Hg, manganese (Mn), lead (Pb), rubidium (Rb), selenium (Se), zinc (Zn) and total mercury (Hg)) in liver tissue from polar bears from ten different subpopulation locations across Alaska, Canadian Arctic and East Greenland. Concentrations of total Hg, Se and As were subpopulation dependent. For example, the highest concentrations of Hg, Se and As are found in the Beaufort Sea and lowest in Hudson Bay and Chukchi/Bering Sea (Alaska) areas. Time comparisons with previously published data suggested recent total Hg increase in East Greenland polar bears, which may be related to Hg emissions and/or climate-induced (Arctic warming) changes in Hg cycles or changes in the polar bear food web. This work contributes to an improved knowledge of environmental processes and important factors (*e.g.*, time) on bear subpopulation exposure to important bioaccumulative metals in the Arctic.

Introduction

Trace elements are widely distributed in the environment and have both natural and anthropogenic origin.[1] Significant quantities of trace elements have been introduced and redistributed in the environment by human activities including fossil fuel combustion, non-ferrous metal production, and waste incineration.[1] Trace elements are transported to the Arctic *via* atmospheric pathways and ocean and river currents.[2–4] For several trace elements, anthropogenic emissions to the Arctic have been postulated to be more important than natural emissions.[1] The man-made contribution of the present mercury (Hg) concentrations in Arctic wildlife has been estimated to be above 92%.[5,6] An order-of-magnitude increase of Hg concentrations has been observed in hard tissues of Arctic mammals and birds since mid- to late-19th century.[5,7–10] Also, the concentrations of cadmium (Cd) and lead (Pb) in ice cores from Greenland have increased tenfold from preindustrial concentrations by the early 1900s due to coal burning in Europe and North America.[11] Although Cd concentrations in ice cores have decreased since 1940s, the concentrations are still 2.5 times higher compared to preindustrial times.[11] Also lead concentrations in precipitation at the ice core sites have decreased since 1970s, but they are still 2.5 times higher compared to the concentrations measured before 1860s.[11]

The emissions of Hg, Pb and Cd are expected to increase in the next few decades due to the rapid growth of coal-driven economy in Asia.[11,12] Worldwide Hg emissions have increased since 1996, and the global yearly emission in 2050 compared to 2006 is predicted to increase by an additional 100% unless the expensive Hg sorbent technologies are put into commercial use as such as activated carbon injection in the combustion of coal.[12] In addition, climate change may alter natural cycles and long-range transport of metals.[13] In fact, the Arctic is likely to become a more effective trap of Pb, Cd and zinc (Zn) because precipitation is likely to increase,[13] and the complex cycle of Hg may be altered by climate change.[4,13,14] Increased Hg concentrations in burbot (*Lota lota*) from Canadian Arctic have been related to warming temperatures and reduced sea ice cover.[15] The length of the ice free season has also been related to Hg concentrations in ringed seals (*Phoca hispida*) from the Canadian Arctic.[16]

The polar bear (*Ursus maritimus*) is the apex predator of the arctic marine ecosystem. Polar bears are distributed throughout the circumpolar region, and thus are an ideal sentinel species for contaminants in the Arctic. Trace elements, including Hg, Zn and rubidium (Rb), have been shown to biomagnify in arctic marine food webs.[17–21] Some trace elements, *e.g.* Hg and Cd, have been detected at relatively high concentrations in arctic marine mammals.[21,22] In polar bears, concentrations of Hg are among the highest observed in the Arctic due to its position at the top of the marine food web.[22] Dietz *et al.*[6] recently reported on the temporal trends (1892–2008) of total Hg in polar bear subpopulation from Northwest Greenland using archived hair samples. Hg concentrations showed significant annual increases of 1.6 to 1.7% from 1892 to 2008. The toxic effects of these elements, including Cd and Hg, have been of interest in arctic wildlife including polar bears.[23–28]

Circumpolar trends of trace elements in polar bears were last studied in samples collected in 2002 and the concentrations of many trace elements, and especially the major trace element contaminants Cd and Hg, varied among different regions of the Canadian Arctic.[29] To our knowledge, recent temporal trends or time point comparisons of trace elements in polar bears for circumpolar Arctic subpopulations have received minor attention.

Increasing emissions of certain trace elements and the effects of climate change (Arctic warming) on trace element concentrations in the Arctic environment raise a need to assess the most recent spatiotemporal trends of trace elements in a circumpolar top predator, namely polar bear. In the present study, we investigated spatial trends of trace elements in polar bear liver tissue sampled in 2005–2008 from Alaska (United States), Canada, and Greenland. In addition, we assessed the comparative temporal changes of trace element concentrations in polar bears from Alaska, Canada and Greenland over the last few decades.

Materials and methods

Sample collection

Polar bear samples from ten subpopulations/management zones in Alaska (Chukchi/Bering Sea) in the United States, Canada and East Greenland were collected during 2005–2008 (n = 136 individual bears) from the native subsistence hunts (Table 1; Fig. 1). Polar bears were of both sexes and their age ranged from 2 to 29 years (Table 1). The complete detailed information on sampling and biometric measurements of all of the bears has been described elsewhere.[30]

Trace element analysis and QA/QC

As we reported in Rush *et al.* (2008) in our previous assessments of metals and elements in polar bear (liver) from Canadian bears collected in 2001–2002, metals/elements that were detected and at a high enough frequency in samples were As, Cd, Cu, Mn, Pb, Rb, Se, Zn and total Hg. Thus, we focused on these 9 metals/elements in the present study.

All trace element analysis of the present polar bear liver samples was carried out at the National Wildlife Research Centre (NWRC), Environment Canada, Carleton University. Liver samples were thawed, homogenized and then refrozen immediately at −20 °C. A thoroughly validated method used extensively at NWRC was used for total Hg determination in the liver samples. Briefly, freeze-dried and homogenized liver samples were analyzed for total Hg using DMA-80 Direct Mercury Analyzer (Milestone, Shelton, CT).

The certified reference materials (CRMs) used for total Hg were Dolt-3 and Tort-2 (*lobster hepatopancreas*) from the National Research Council (NRC) of Canada and Oyster Tissue 1566b from National Institute of Standards Technology (NIST). To check for the homogeneity of total Hg in the samples, 22 random liver samples were analyzed in replicate. Replicates of the CRMs, Oyster Tissue 1566b, Dolt-3 and Tort-2 were also analyzed to check calibration of the instrument, the within-run precision and the reproducibility of the method. Recoveries of Total Hg for the daily calibration check standards (CRMs Dolt-3, Tort-2 and Oyster Tissue 1566b) ranged from 83.0 to 111.4%. Values obtained were within the acceptable limits. Standard deviations for all replicate readings for CRM samples were below

Table 1 Sampling area, year, number of individuals, and median age of polar bears investigated for spatial trends and time point comparisons. M: male; F: female; U: Unknown

	Chukchi/Bering Sea (CB)	N. Beaufort Sea (NB)	S. Beaufort Sea (SB)	Gulf of Boothia (GB)	Lancaster/Jones Sound (LJS)	W. Hudson Bay (WHB)	S. Hudson Bay (SHB)	Baffin Bay—N.E. Baffin Island (BB)	Davis Strait—S.E. Baffin Island (DS)	E. Greenland/Scoresby Sound (EG)
Year	2005–07	2007	2007	2007	2007–08	2007–08	2007–08	2007–08	2008	2006
n(M:F:U)	12(7:5:0)	11(7:4:0)	27(18:9:0)	6(4:2:0)	13(11:2:0)	11(8:3:0)	14(10:4:0)	14(11:3:0)	8(8:0:0)	20(14:6:0)
Age (range):U	8(2–22):0	6(4–24):1	9(3–20):1	9(3–24):0	6(3–11):1	7(3–29):0	9(3–22):2	5(2–10):4	5(3–6):1	7(3–19):0
Year			2002[a]		2002[a]		2002[a]	2002[a]	2002[a]	1999–2000[a]
n(M:F:U)			11(8:3:0)		13(3:1:9)		11(5:6:0)	12(7:5:0)	13(7:5:1)	22(9:13:0)
Age (range):U			3(0–25):1		9(5–14):6		4(3–7):7	7(5–13):7	7(2–18):7	6(3–23):9
Year	1994–99									1987–90[a]
n(M:F:U)	6(0:6:0)									29(16:13:0)
Age (range):U	12(5–19):0									4(2–18):19
Year		1982[b]	1982[b]		1982[b]	1984[b]		1984[b]	1984[b]	1983–86[a]
n(M:F:U)		7(6:1:0)	7(4:3:0)		22(16:6:0)	10(7:3:0)		8(3:5:0)	11(7:4:0)	24(13:11:0)
Age (range):U		U(4–14):2	U(4–20):3		U(2–14):2	U(1–18):1		U(4–19):0	U(2–21):0	6(2–10):14

[a] Ref. 29. [b] Ref. 32.

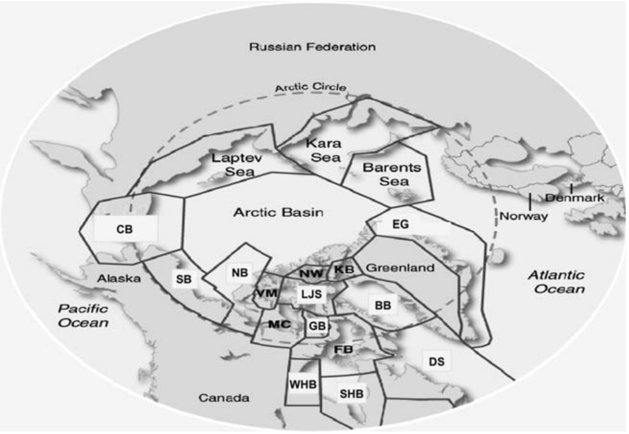

Fig. 1 Polar bear subpopulations located throughout the circumpolar basin. Subpopulations that were part of the present study included: Chukchi/Bering Sea (CB), southern Beaufort Sea (SB), northern Beaufort Sea (NB), Lancaster/Jones Sound (LJS), Gulf of Boothia (GB), western Hudson Bay (WHB), southern Hudson Bay (SHB), Baffin Bay (BB), Davis Strait (DS) and East Greenland (EG). Adaption of source: IUCN/SSC Polar Bear Specialist Group (2006).

10%. Standard deviations for replicate readings for random liver samples were from 1.1 to 11.2%. Standard deviation between results for solid, directly analyzed and digested samples were between 1.9 and 11.3%.

As, Cd, Cu, Mn, Pb, Rb, Se and Zn were analyzed in liver samples using EPA Method 200.8 with modifications for biological samples. Briefly, each sample was digested in 0.5 mL of ROP (Reverse Osmosis Purified) water and 1.0 mL of 70% nitric acid overnight at room temperature. The sample was then heated at 100 °C for 4 hours and diluted with ROP water to 4 mL. Before analysis, the original digestives were diluted 10 and 40 times with ROP water, and internal standard was added to all solutions including calibration blanks and standards, samples and quality control samples and standards. Concentrations of elements were measured in samples using ELAN 9000, inductively coupled plasma mass spectrometry from Perkin Elmer (Waltham, MA).

The CRMs used for As, Cd, Cu, Mn, Pb, Rb, Se and Zn were Dolt-3 and Tort-2 from NRC and Oyster Tissue 1566b, Bovine Liver 1577a, Bovine Muscle 8414 and Mussel Tissue 2976 from NIST. Replicates of the CRMs were also analyzed to check calibration of the instrument, the within-run precision and the reproducibility of the method. Average recoveries of analyzed metals/elements for the daily calibration check standards (CRMs) ranged from 80.9% for copper to 103.5% for Se. Values obtained were within the acceptable limits. To check for the homogeneity of As, Cd, Cu, Mn, Pb, Rb, Se and Zn in the samples, 7 random liver samples were analyzed in duplicate. Standard deviations between results for random liver samples are below 10% for Cd, Cu, Mn, Rb, Se and Zn. Standard deviation for As in duplicate samples ranged from 1.3 to 18.6%. Standard deviation for Pb ranged from 0.9 to 13.9%. Standard deviations for replicate readings for CRM samples: Tort-2, Dolt-3, Bovine Liver 1577a, Bovine Muscle 8414 and Oyster Tissue 1566b were from 0.1 to 17.7% with values below 10%. Standard deviations in CRM Mussel Tissue 2976 were between 3.6 and 17.7% with most values >10%.

NWRC (Environment Canada) participates annually in an inter-lab QA/QC exercise by the Northern Contaminants Program (NCP; Indian and Northern Affairs Canada). In the most recent QA/QC exercise (NCP III—Phase 5) in 2010, for all trace elements under study (total Hg, Cd, Cu, Mn, Pb, Rb, Se and Zn), of twelve participating labs, NWRC had the best quantitative performance with 88% compliance of measured concentrations being within ±20% of the overall study median values. This exceptional compliancy was based on several CRMs including NIST SRM 1947 (Lake Michigan Fish Tissue homogenate).

The practical detection limit (PDL; $\mu g\ L^{-1}$) is based on a trace element response that is 5 times the theoretical detection limit (TDL). The TDL ($\mu g\ L^{-1}$) is a response that is based on 3 times the standard deviation of the analysis noise. The PDLs for total Hg, As, Cu, Cd, Hg, Mn, Rb, Se, and Zn ranged from 0.005 (Cd) to 5.5 (Zn) $\mu g\ L^{-1}$. The TDLs for total Hg, As, Cu, Cd, Hg, Mn, Rb, Se, and Zn ranged from 0.001 (Cd) to 1.1 (Zn) $\mu g\ L^{-1}$. Concentrations for all analyzed liver samples were above the PDL for total Hg, As, Cu, Cd, Hg, Mn, Rb, Se, and Zn. Concentration of Pb in liver samples was below the TDL (0.02 $\mu g\ g^{-1}$ dry weight) in 14 liver samples, between the TDL and PDL (0.02 and 0.1 $\mu g\ g^{-1}$ dry weight) in 47 samples and above PDL in 75 samples, respectively. For Pb, the samples with concentration of below TDL were replaced by randomly generated normally distributed data, assuming half of the detection limit as the mean and with 40% variance.

Data analysis

Statistical analyses were carried out using R version 2.11.1.[31] Pair-wise differences between geographical areas were tested using a one-way ANOVA followed by a Tukey's *post hoc* test. Level of significance was set to $p \leq 0.05$. Prior to *post hoc* tests trace element concentrations were adjusted according to the most parsimonious model for the element in question. The most parsimonious models were selected using likelihood ratio tests *i. e.* full models (including area, sex, age and their interaction as explanatory variables) were simplified by eliminating interaction terms and variables if their removal did not result in a significant increase in deviance. All the trace element concentrations were ln-transformed to meet model assumptions, *i.e.*, most importantly homogeneity of the variance of the data distribution between groups.

In order to investigate qualitative temporal trends, concentrations of total Hg, Se, Zn and Cd in the seven polar bear subpopulations were compared to previously published datasets.[29,32,33] Including data from the present study, data for a three-point temporal comparison (*i.e.*, 1982–1984, 2002 and 2006–2008) were available for bears from the Beaufort Sea (combined southern and northern Beaufort Sea), Lancaster/Jones Sound and Davis Strait (Table 1). Based on the available data, time point comparisons of trace elements in bears from Hudson Bay and Chukchi/Bering Sea were investigated using two-point comparisons (western Hudson Bay: 1984 and 2007–2008; southern Hudson Bay: 2002 and 2007–2008; Chukchi/Bering Sea: 1994–1999 and 2005–2007) (Table 1). Comparative time changes of trace element concentrations in bears from East Greenland were studied in animals sampled from four periods (1983–1986, 1987–1990, 1999–2000 and 2006) (Table 1). Concentrations of Hg, Se and Zn in the bears from the Canadian Arctic sampled in 1982–1984 were age-adjusted to 6.9 years.[32] Element concentrations in bears sampled from Chukchi/Bering Sea, Canada in 2002–2008 and East Greenland in 1983–2006 were not age-adjusted, because age adjustments did not result in any changes in qualitative time point comparisons. However, due to unknown ages for some bears, age-adjustments decreased the number of individuals from 156 to 116, and from 95 to 53, for the Canadian Arctic and East Greenland, respectively.

Results and discussion

Geographical trends

Concentrations of Hg in bears from the northern and southern Beaufort Sea subpopulations were higher than in any other populations ($p \leq 0.036$) except the adjacent areas of Lancaster/Jones Sound and the Gulf of Boothia ($0.43 \leq p \leq 0.93$) (Fig. 2). Bears from western and southern Hudson Bay had lower concentrations of Hg compared to the other areas ($p < 0.001$) except the Davis Strait and Chukchi/Bering Sea ($0.25 \leq p \leq 0.63$). Similarly, previous studies in polar bears from the Canadian Arctic have reported total Hg concentrations being highest in the Beaufort Sea and lowest in the western Hudson Bay.[29,32,34] In ringed seals, which is the main prey of polar bears, total Hg concentrations have also been found to be higher in the western Canadian Arctic compared to the eastern Canadian Arctic.[35] In addition, higher levels of Hg have been reported in ringed seals from the Canadian Arctic compared to ringed seals from Alaska or Greenland.[36] In contrast, Hg analysis in beluga whales (*Delphinapterus leucas*) suggested that such regional differences within the Canadian Arctic have diminished and are no longer statistically significant.[37]

The observed subpopulation dependence on the total Hg distribution in the present polar bears may be related to both abiotic and biotic factors. The high concentrations of Hg in marine mammals from Beaufort Sea are potentially a consequence of the Hg input by the Mackenzie River.[38,39] Geographical patterns in Hg concentrations in belugas, narwhals (*Monodon monoceros*) and ringed seals have been related to geological formations.[35,36] However, time trend analysis in polar bear hair has shown an increase by up to 20 since the onset of industrial revolution indicating that geological signals in polar bear tissue may be of minor importance.[6,9] Furthermore, recent studies have pointed to the importance of food web structure on Hg concentrations in polar bears[40,41] and other marine mammals including beluga whales[42] and various seal species.[43]

Despite being an essential element, Se concentrations, similar to Hg, were higher in Beaufort Sea polar bears compared to the subpopulations from Chukchi/Bering Sea, Hudson Bay, Davis Strait and East Greenland ($p < 0.001$). The lowest Se concentrations were found in bears from Chukchi/Bering Sea and Hudson Bay ($p \leq 0.041$). However, Se concentrations in bears from southern Hudson Bay did not differ from those from Davis Strait ($p = 0.60$) and East Greenland ($p = 0.15$). Also, previous studies have reported strong correlations and thus similar geographical trends between Hg and Se in polar bears from the Canadian Arctic.[29,32,34] The molar ratio of Hg : Se has been found to be 1 : 1 in tissues of marine mammals with high Hg concentrations suggesting that Hg and Se are complexed in those species.[44,45] Se may reduce the toxicity of Hg by forming a stable equimolar tiaminite complex that binds to several proteins.[46,47] Interestingly, the molar ratio of Hg : Se was approximately 1.5 in the bears from Gulf of Boothia and East Greenland, and close to one in the other areas (Fig. 2). Because Hg concentrations were only moderate in the bears from Gulf of Boothia and East Greenland, the high Hg : Se ratios in these populations may be due to limited intake of Se. This excess of total Hg concentration relative to Se suggests that the bears from Gulf of Boothia and East Greenland may be at greater risk from exposure to Hg and any mediated effects.

Concentrations of Cd were lower in Chukchi/Bering Sea population compared to all other populations ($p \leq 0.047$) except Lancaster/Jones sound ($p = 0.57$) and southern Beaufort Sea ($p = 0.091$) (Fig. 2). Concentrations of Cd were higher in East Greenland bears compared to bears from the (northern and southern) Beaufort Sea ($p = 0.012$ and 0.019, respectively) and Lancaster/Jones sound ($p < 0.001$). The increase of Cd concentrations from western to eastern Arctic has previously been reported in polar bears, ringed seals and belugas.[29,32,34,35] Relatively high concentrations of Cd in arctic marine biota[21,27] have been suggested to be mainly natural in origin.[10,48] The spatial trends in Cd concentrations in polar bears for the different subpopulations could be a function of the differences in the bear diets (*e.g.* ringed seals *versus* other seal species) and/or may be related to differences at lower trophic levels in polar bear food web. A complementary study showed the influence of diet difference for bears among these subpopulations was contaminant-specific for various chlorinated and brominated POPs, *e.g.*, PCBs and PBDEs.[49] Regardless, any interpretation of bear diet–food web influence on trace element spatial trends is beyond the scope of the present study. However, a carnivorous plankton species *Parathemisto libellula*, which is an important dietary item to ringed seals, has been reported to accumulate several times higher concentrations of Cd compared to other plankton or fish species.[50]

Concentrations of Pb were in general low compared to the other trace elements under study. The concentrations were higher in polar bears from East Greenland compared to those from Lancaster/Jones Sound ($p = 0.019$), Beaufort Sea ($0.025 \leq p \leq 0.030$) and Chukchi/Bering Sea ($p < 0.001$). In addition, Pb concentrations in bears from Chukchi/Bering Sea were lower compared to those from Gulf of Boothia ($p = 0.040$), western Hudson Bay ($p = 0.049$), Baffin Bay ($p = 0.002$) and Davis Strait ($p = 0.004$). However, the geographical trends of Pb concentrations in the present polar bears should be interpreted with caution, because 40% of the polar bear liver samples showed Pb concentrations below the practical detection limit.

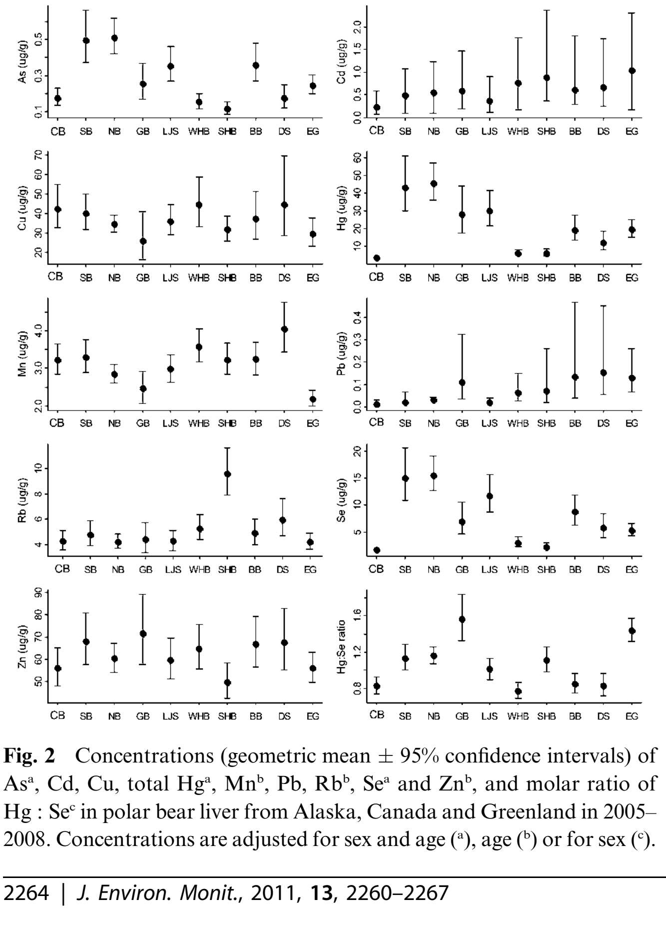

Fig. 2 Concentrations (geometric mean ± 95% confidence intervals) of As[a], Cd, Cu, total Hg[a], Mn[b], Pb, Rb[b], Se[a] and Zn[b], and molar ratio of Hg : Se[c] in polar bear liver from Alaska, Canada and Greenland in 2005–2008. Concentrations are adjusted for sex and age ([a]), age ([b]) or for sex ([c]).

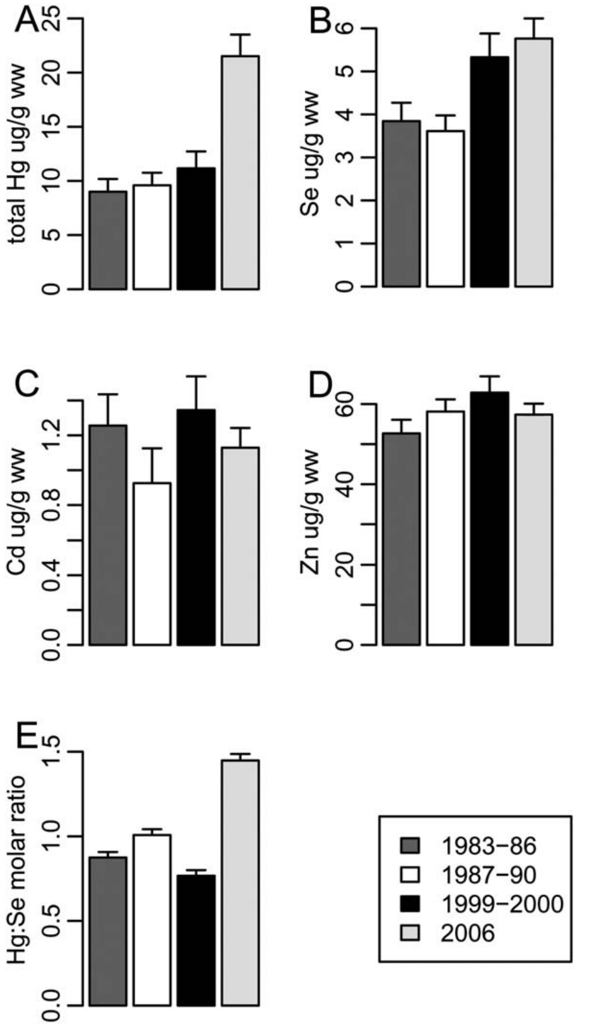

Fig. 3 Concentrations (mean ± SE) of total Hg (A), Se (B), Cd (C) and Zn (D) and molar ratio of Hg : Se (E) in polar bear liver from East Greenland in 1983–2006.

Concentrations of As were higher in the Beaufort Sea compared to Chukchi/Bering Sea, Hudson Bay, Davis Strait and East Greenland ($p \leq 0.004$) (Fig. 2). Southern and western Hudson Bay bears showed lower concentrations of As compared to those from Lancaster/Jones Sound and Baffin Bay ($p < 0.002$). The high concentrations of As in polar bears from the Beaufort Sea are in agreement with previous findings.[29] Concentrations of As followed similar spatial trends to Hg and Se, which may be explained by Se forming an equimolar complex with As.[51]

Bears from western Hudson Bay showed the highest concentrations of Rb in relation to any other bear population ($p < 0.001$) except Davis Strait ($p = 0.079$). Otherwise, no geographical trends in Rb concentrations were observed ($p \geq 0.25$), which is similar to previous results.[29]

Minor geographical trends were observed for Mn concentrations in polar bears (Fig. 2). Mn concentrations in bears from East Greenland were lower compared to those from Canadian Arctic ($p \leq 0.005$) or Chukchi/Bering Sea ($p < 0.001$) except the bears from Gulf of Boothia ($p = 0.97$). Within the Canadian Arctic, Mn concentrations in Davis Strait were higher compared to those from northern Beaufort Sea ($p = 0.007$), which is in accordance with the generally lower concentrations of Mn in polar bears from the western Canadian Arctic compared to those from the eastern Canadian Arctic.[32] No geographical trends were observed for Zn ($p \geq 0.18$) or Cu concentrations ($p \geq 0.17$) (Fig. 2).

Temporal trends

Concentrations of total Hg in polar bear livers from East Greenland and sampled in 2006 were substantially higher than those sampled over the period of 1999–2000 (Fig. 3). This is similar to an increase of total Hg concentrations in ringed seal teeth from Central East Greenland between 1994 and 2006[52] and ringed seal liver from central western Greenland during 1999–2004.[53] In contrast, total Hg concentrations in polar bear hair from East Greenland decreased significantly during 1973–2001; however, an increase since 2001 has been detected.[54] Other studies based on soft tissues of polar bears, ringed seals, harp seal (*Phagophilus groenlandicus*), hooded seal (*Cystophora cristata*), Atlantic walruses (*Odobenus rosmarus*) and shorthorn sculpins (*Myoxycephalus scorpius*) from different locations in Greenland have not shown any clear time trends during the last decades of 20th century.[7,29,53,55,56] In bears from the Beaufort Sea an increasing trend in Hg concentrations was observed between 1980s and 2002[29] (Fig. 4A). The result of the present study suggests that no changes in Hg concentrations were observed between 2002 and 2007–2008 in the bears from the Beaufort Sea (Fig. 4A). Temporal trends were neither observed in ringed seals sampled from the Beaufort Sea in 1973–2007.[16]

The results of the present study suggest that the total Hg concentrations in polar bears from Canadian Arctic, other than from the Beaufort Sea, are similar to the concentrations reported from 1980s (Fig. 4A). Similarly, temporal trends in Hg concentrations were not observed in arctic char (*Salvelinus alpinus*) from north-eastern Canadian Arctic[57] or in ringed seals from several locations in the Canadian Arctic.[58] Increasing Hg concentrations in ringed seals have only been observed in ringed seals from Pond Inlet (Baffin Bay).[58] Also Hg concentrations in eggs of northern fulmars and thick-billed murres increased in the Lancaster Sound area during 1975–2003.[59] Hg concentrations in polar bears from Chukchi/Bering Sea showed a decreasing trend (Fig. 4A). However, these two-point temporal trends should be interpreted with caution, because data from 1994–99 included only six individuals (all males) (Table 1).

The recent increase in Hg concentrations in the East Greenland polar bears is consistent with global changes of Hg emissions, which have increased from 2128 to 2480 mg per year

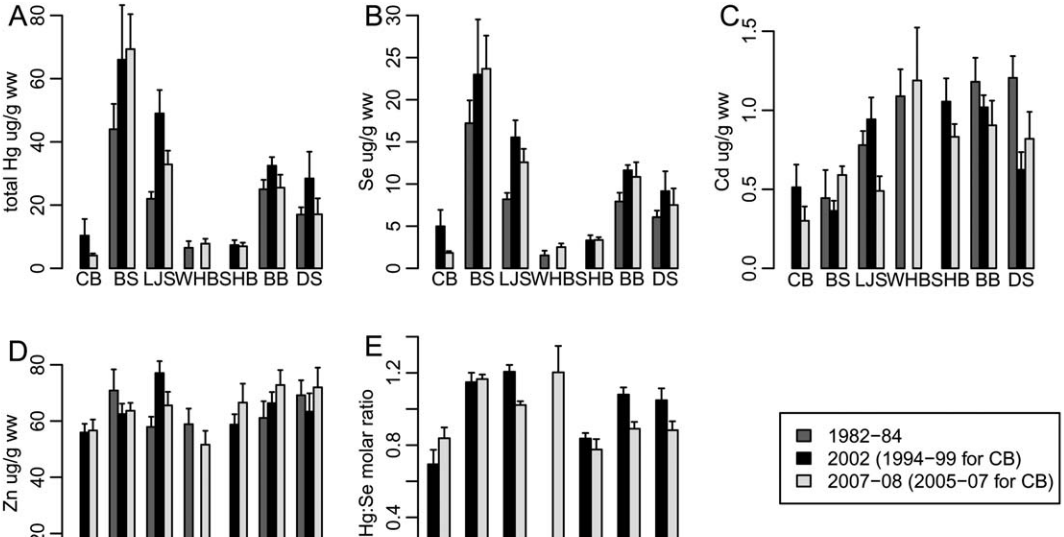

Fig. 4 Concentrations (geometric mean ± standard error) of total Hg (A), Se (B), Cd (C) and Zn (D), and molar ratio of Hg : Se (E) in polar bear liver from Alaska in 1994–2007 and Canada in 1982–2008. CB: Chukchi/Bering Sea; BS: Beaufort Sea; LJS: Lancaster/Jones Sound; WHB: western Hudson Bay; SHB: southern Hudson Bay; Baffin Bay (BB), DS: Davis Strait.

between 1996 and 2006.[12] Increased Hg concentrations in ringed seal teeth from Greenland were also attributed to global changes in environmental Hg concentrations.[52] Furthermore, a mass balance of Hg in the Arctic Ocean is likely to be associated with climate warming.[4] Climate change including the reduction of ice cover, changes in first- and multiyear ice and timing of ice melt, melting of permafrost and increased coastal erosion, may lead to changes of Hg cycle in the Arctic Ocean,[4,14] which may further alter Hg concentrations in species of the Arctic marine food web. In addition, melting of multi-year ice may have a major impact on Hg uptake in Arctic marine ecosystems.[60] A recent study on burbot from Mackenzie River suggests that warming temperatures and reduced ice cover may lead to increased exposure to Hg in high trophic level Arctic biota.[15] Recent changes in Hg concentrations in arctic biota have also been proposed to depend on top-down processes *i.e.* the rate of uptake and trophic transfer of Hg by marine food webs.[4] The increase of Hg concentrations in ringed seals from central western Greenland during 1999–2004 was explained by changes in feeding behavior measured by δ^{15}N.[53] Also, temporal trends of brominated and chlorinated contaminants in polar bears from western Hudson Bay were suggested to be related to dietary changes.[61,62]

Concentrations of Se did not increase in concert with Hg in East Greenland polar bears (Fig. 3B) resulting in an increased molar ratio of Hg : Se (Fig. 3E). In contrast, the increase in Hg concentrations in the bears of the present study from the Beaufort Sea was consistent with the increase of Se (Fig. 4B), leading to stable Hg : Se molar ratio over time in this subpopulation (Fig. 4E).[32]

Cd concentrations in polar bears showed a decreasing trend in Lancaster/Jones Sound and Davis Strait since 1980s (Fig. 4C). These results are parallel with generally stable or declining concentrations of Cd in abiotic and biotic arctic environment.[63,64]

Conclusions

The present study indicates that different trace elements have different trends across the Arctic. In general, the concentrations of total Hg, Se and As were highest in the Beaufort Sea area and lowest in (southern and western) Hudson Bay area and Chukchi/Bering Sea. In contrast, concentrations of Cd increased from east to west. Minor or no spatial trends were observed for Cu, Mn, Rb and Zn. The geographical trends of trace elements observed in the present study may be related to river output of trace elements, local differences in geology or in the food webs of polar bears. Time point comparisons suggest that total Hg concentrations in East Greenland polar bears have recently increased. This increase may be related to changes in Hg emissions or climate-induced changes in Hg cycle or changes in polar bear food web. The increase of Hg : Se molar ratio in concert with Hg concentrations may suggest enhanced Hg-mediated toxicity in the East Greenland population. Since the underlying reasons for spatiotemporal trends of trace elements in the Arctic are unknown, future studies should focus on the role of changing climate and trace metal emissions on geographical and temporal trends of trace elements.

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