Science of the Total Environment 408 (2010) 5613–5618

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Short Communication

A screening of persistent organohalogenated contaminants in hair of East Greenland polar bears

Veerle L.B. Jaspers [a,*], Rune Dietz [b], Christian Sonne [b], Robert J. Letcher [c], Marcel Eens [a], Hugo Neels [d], Erik W. Born [e], Adrian Covaci [a,d]

[a] Department of Biology, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium
[b] Aarhus University, National Environmental Research Institute, Department of Arctic Environment, Frederiksborgvej 399, P.O. Box 358, DK-4000 Roskilde, Denmark
[c] Wildlife and Landscape Science Directorate, Science and Technology Branch, Environment Canada, Carleton University, National Wildlife Research Centre, Raven Road, Ottawa, K1A 0H3, ON, Canada
[d] Toxicological Centre, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium
[e] Greenland Institute of Natural Resources, P.O. Box 570, DK-3900 Nuuk, Greenland, Denmark

ARTICLE INFO

Article history:
Received 26 March 2010
Received in revised form 20 July 2010
Accepted 22 July 2010
Available online 30 August 2010

Keywords:
Polar bear
Ursus maritimus
Hair
Adipose
Blood
Brain
Liver
Persistent organohalogenated contaminants
Polychlorinated biphenyls
PCBs
BDE 47
p,p′-DDE

ABSTRACT

In this pilot study, we report on levels of persistent organohalogenated contaminants (OHCs) in hair of polar bears (*Ursus maritimus*) from East Greenland sampled between 1999 and 2001. To our knowledge, this is the first study on the validation of polar bear hair as a non-invasive matrix representative of concentrations and profiles in internal organs and blood plasma. Because of low sample weights (13–140 mg), only major bioaccumulative OHCs were detected above the limit of quantification: five polychlorinated biphenyl (PCB) congeners (CB 99, 138, 153, 170 and 180), one polybrominated diphenyl ether (PBDE) congener (BDE 47), oxychlordane, *trans*-nonachlor and β-hexachlorocyclohexane. The PCB profile in hair was similar to that of internal tissues (i.e. adipose, liver, brain and blood), with CB 153 and 180 as the major congeners in all matrices. A gender difference was found for concentrations in hair relative to concentrations in internal tissues. Females (n = 6) were found to display negative correlations, while males (n = 5) showed positive correlations, although p-values were not found significant. These negative correlations in females may reflect seasonal OHC mobilisation from periphery adipose tissue due to, for example, lactation and fasting. The lack of significance in most correlations may be due to small sample sizes and seasonal variability of concentrations in soft tissues. Further research with larger sample weights and sizes is therefore necessary to draw more definitive conclusions on the usefulness of hair for biomonitoring OHCs in polar bears and other fur mammals.

1. Introduction

It has been hypothesized that in some areas the long term viability of polar bear (*Ursus maritimus*) subpopulations is being threatened by pollution reaching the Arctic (Sonne, 2010). Persistent organohalogenated contaminants (OHCs) may be released into the environment through intentional application of pesticides, as by-products of chemical processes or through unintentional leaching from consumer products and electrical appliances (Hoffman et al., 2001). Because of their high persistence and lipophilic nature, OHCs biomagnify in animals at the top of food webs. In addition, OHCs have been able to reach the remote Arctic areas following long-range transport through air and water currents (Braune et al., 2005; de Wit et al., 2004).

Polar bears are top predators in the Arctic marine food web and as such they are exposed to high levels of OHCs relative to other Arctic species (Braune et al., 2005; Letcher et al., 2010). Their diet is of a high fat-content, with the ringed seal (*Phoca hispida*) and bearded seal (*Erignatus barbatus*) as the primary prey (Kingsley, 1998; Stirling and McEwan, 1975; Thiemann et al., 2008). In particular, polar bears from East Greenland have been documented to accumulate high levels of OHCs (Dietz et al., 2004, 2007, 2008; Letcher et al., 2010). However, the load of OHCs in polar bears is highly dependent on the age, sex and season of the year (Dietz et al., 2004; Polischuk et al., 2002). Furthermore, the levels and temporal trends of OHCs, such as polychlorinated biphenyls (PCBs), organochlorine pesticides and polybrominated diphenyl ethers (PBDE), in polar bears from western Hudson Bay in Canada have been shown to be linked to Arctic warming, sea-ice conditions and shifting seal diets (McKinney et al., 2009). Polar bears mate in March–May (Rosing-Asvid et al., 2002), but the active gestation period is delayed until September–October at the start of the hibernation period (Wiig et al., 1992). During this

* Corresponding author. Tel.: +32 3 265 22 85; fax: +32 3 265 22 71.
E-mail address: veerle.jaspers@ua.ac.be (V.L.B. Jaspers).

0048-9697/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2010.07.059

hibernation period (October–March) the female is fasting and is relying on fat reserves as energy source. As a result, OHCs that have been stored in adipose tissue are released into the blood stream and may cause adverse effects to the offspring during the pre- and postnatal periods (Letcher et al., 2010; Sonne, 2010). In addition, the cubs will also be exposed to high levels of OHCs during lactation (Bernhoft et al., 1997), as the milk has a high load of OHCs associated with a high mean lipid-content of 33% (Jenness et al., 1972). Furthermore, polar bears may also experience periods when food is scarce leading to a reduction of their adipose tissue from 50% to 10% of their total body mass (Atkinson and Ramsay, 1995). The highest seasonal exposure is however linked to the periods when the bears have access to the ringed seals as observed from year-round monitoring of bears from central East Greenland (Dietz et al., 2004, 2007).

Given that the polar bear is a protected species and its population is declining, samples are not readily available. Monitoring of OHCs in polar bears has mostly been conducted on adipose tissue and to a lesser extent on full blood or plasma, which can both be obtained during tagging operations of live polar bears. Recently, studies have been performed on the tissue distribution of OHCs obtained from the Inuit subsistence hunting (Gebbink et al., 2008a, b; Letcher et al., 2009). However, the impact of these pollutants on polar bears has been difficult to assess because it is logistically difficult to take many and repeated samples of blood or tissue from live polar bears. To our knowledge, there are no studies investigating the use of hair in assessing the concentrations of OHCs in polar bears. Keratinous tissues, such as hair and feathers in other species, have recently been proven useful as non-destructive and non-invasive biomonitors for OHCs (Schramm, 1997; Dauberschmidt and Wennig, 1998; D'Havé et al., 2005; Jaspers et al., 2006). Hair can easily be sampled without harming individuals (e.g. during tagging operations) and access to historical hair samples may shed light on populations and periods from which other tissue samples cannot be obtained (Dietz et al., 2006, 2009). Moreover, hair can simply be stored in envelopes or plastic bags and can be transported over large distances with Inter CITES Institutional permits and thus minimizing logistical difficulties. Conversely, OHC concentrations are rather low in hair, because of its low lipid-content (D'Havé et al., 2005), which makes the analysis of OHCs in hair a challenging task. Unlike human hair, polar bear hair is growing at a specific time of the year, i.e. September (Born et al., 1991), and is therefore reflecting blood concentrations at that time only (as is also the case for feathers, e.g. Jaspers et al., 2006). This is in contrast with the seasonal variation seen in other tissues (Dietz et al., 2004, 2007) and concentrations in polar bear hair may therefore be easier to compare among studies.

This pilot study investigates OHC concentrations in hair of polar bears and assesses the usefulness of hair as a non-destructive biomonitoring matrix. It also examines the correlation between OHC levels in hair with concentrations in internal tissues reported earlier from the same polar bear specimens (Gebbink et al., 2008a, b; Letcher et al., 2009). Furthermore, the study also explores gender related differences in OHC levels.

2. Materials and methods

Hair samples were pulled out from 15 individual polar bears (8 females, 7 males) previously included in studies on OHC tissue distribution of polar bears (Gebbink et al., 2008a, b; Letcher et al., 2009). Samples from these polar bears were collected by local subsistence hunters educated for that purpose in the Ittoqqortoormiit/Scoresby Sound area in central East Greenland (69°00′N–74°00′N) during 1999–2001. More information on the sampling procedures and age estimations can be found in Gebbink et al. (2008a).

In all samples, 37 polychlorinated biphenyl (PCB) congeners (CB 18, 28, 31, 47, 49, 52, 74, 87, 95, 99, 101, 105, 110, 118, 128, 138, 146, 149, 153, 156, 158, 170, 171, 172, 174, 177, 180, 183, 187, 194, 195, 196/203, 199, 205, 206 and 209), 8 polybrominated diphenyl ethers (PBDE) congeners (BDE 28, 47, 49, 99, 100, 153, 154 and 183), dichlorodiphenyltrichloroethane (*p,p′*-DDT and *o,p′*-DDT) and metabolites (*p,p′*-DDE, *p,p′*-DDD, *o,p′*-DDE and *o,p′*-DDD), hexachlorocyclohexanes (HCHs; α-, β- and γ-HCH), chlordanes (CHLs; *cis*-chlordane (CC), *trans*-chlordane (TC), *trans*-nonachlor (TN) and oxychlordane (OxC)) and hexachlorobenzene (HCB) were analysed.

The hair samples were washed with distilled water, dried at room temperature and cut in small pieces. An amount between 13 and 140 mg hair was weighed, internal standards (CB 143, BDE 77 and e-HCH) were added and incubated overnight at 40 °C with 5 mL of HCl (4 M) and 5 mL of a mixture of hexane/dichloromethane (4:1, *v:v*). After liquid extraction with additional 5 mL hexane/dichloromethane (4:1, *v:v*), the organic phase was cleaned-up on acidified silica (Covaci and Schepens, 2001).

For PBDEs, CHLs, and HCHs, analysis was done using an Agilent 6890-5973 GC–MS operated in electron capture negative ionization (ECNI) mode and equipped with a 30 m × 0.25 mm × 0.25 μm DB-5 capillary column. The ion source, quadrupole and interface temperatures were set at 250, 150 and 300 °C, respectively. Helium was used as carrier gas at constant flow (1.0 mL/min), while methane was used as moderating gas. The electron multiplier voltage was set at 2200 V. One microliter of the extract was injected in solvent vent mode (initial injector temperature at 90 °C, stay 0.03 min, then heated at 700 °C/min to 300 °C, vent time 0.03 min, vent flow 75 mL/min, splitless time 1.50 min). The temperature of the DB-5 column was programmed from 90 °C (1.50 min) to 230 °C at a rate of 15 °C/min and then to 300 °C at a rate of 5 °C/min, holding 10 min. The MS was used in the selected ion-monitoring (SIM) mode with 2 ions monitored for each OCP and the bromine isotope ions (*m/z* 79 and 81) for PBDEs.

PCBs, DDTs, and HCB were analysed using an Agilent 6890-5973 GC–MS system operated in electron ionization (EI) mode and equipped with a 25 m × 0.22 mm × 0.25 μm HT-8 capillary column. The ion source, quadrupole and interface temperatures were set at 230, 150 and 300 °C, respectively. One microliter of the cleaned extract was injected in cold pulsed splitless mode (injector temperature 90 °C (0.03 min) rising to 300 °C with 700 °C/min), pressure pulse 25 psi and pulse time 1.50 min. The splitless time was 1.50 min. Helium was used as carrier gas at constant flow (1.0 mL/min). The temperature of the HT-8 column was kept at 90 °C for 1.50 min, then increased to 180 °C at a rate of 15 °C/min (kept for 2.0 min), further increased to 280 °C at a rate of 5 °C/min and finally raised to 300 °C at a rate of 40 °C/min, kept for 12 min. The MS was used in SIM mode with 2 ions monitored for each OCP and PCB homologue group.

Quantification was done using internal standards. Procedural blanks and a certified reference material (CRM 397: human hair) were analysed for supporting quality control. Values of OCPs and PCBs obtained in the CRM 397 did not deviate with more than 10% from the indicative values established by Gill et al. (2004). For each analyte, the average blank value was subtracted from the measured value. The limit of quantification (LOQ) was fixed on 3 × SD of the procedural blanks. For pollutants not detectable in the blanks, the LOQ was calculated from S/N ratio of 10. LOQs for the analysed pollutants varied from 0.5 to 3.0 ng/g wet weight. Method recoveries ranged between 85 and 105% (RSD < 12%) (Covaci and Schepens, 2001).

Analyses of OHCs in internal tissues were performed in Letcher's Research Lab at the National Wildlife Research Centre in Ottawa, Canada. Details on the procedures of analysis and data of the internal tissue OHCs concentrations can be found in Gebbink et al. (2008a). These results have been used in the present study in order to link hair concentrations to internal tissue concentrations of the polar bears and to investigate differences in the OHC accumulation profiles.

All statistical analyses were performed using STATISTICA 7.0 (StatSoft Inc. 1984–2004). Samples with levels below the LOQ were assigned a value of f × LOQ, with "f" the proportion of measurements