



TEMPORAL AND SPATIAL TRENDS IN ORGANIC AND METAL
CONTAMINANTS IN CANADIAN POLAR BEARS: 2006-2007 NCP PROJECT
SUMMARY REPORT

Robert Letcher¹

¹National Wildlife Research Centre, Wildlife and Landscape Science Directorate,
Science and Technology Branch, Environment Canada, Carleton University,
Ottawa, ON

2007

Interim Wildlife Report, No. 14

Letcher, Robert, et al. 2007. Temporal and spatial trends of organic and metal contaminants in Canadian polar bears: 2006-2007 NCP project summary report. Government of Nunavut, Department of Environment, Interim Wildlife report: 14, Iqaluit, 15 pp.

Temporal and Spatial Trends of Organic and Metal Contaminants in Canadian Polar Bears: 2006-2007 NCP Project Summary Report

Project Leaders

Robert Letcher, National Wildlife Research Centre, Wildlife and Landscape Science Directorate, Science and Technology Branch, Environment Canada, Carleton University, Ottawa, ON, Ph: (613) 998-6696, Fax (613) 998-0458, E-mail: robert.letcher@ec.gc.ca

Project Team Members

a: Polar bears and food chain:

Conservation officers, Hunters and Trappers Associations (HTAs) and hunters in Nunavut and NWT (participating communities); Nunavut Conservation Officers (seven PB management zones):

Southern Hudson Bay (SH) – Paul Prefontaine, P.O. Box 191, Sanikiluaq X0A 0W0
Gulf of Boothia (GB) – Remi Krikort, Box 86, Kuugaruk, X0B 1K0
Dustin Fredlund, Box 6, Taloyoak, X0B 1B0
Lancaster Sound (LS) – Teema Palluq, Box 99, Arctic Bay, X0A 0A0
Jeffrey Qaunaq, Box 71, Grise Fiord, X0A 0J0
Tabitha Mullin, Box 217, Resolute Bay, X0A 0V0
Baffin Bay (BB) – George Koonoo, Box 400, Pond Inlet, X0A 0S0
Bruce Hainnu, Box 90, Clyde River, X0A 0E0
Davis Strait (DS) – Alden Williams, Box 1000, Stn 1370, Iqaluit, X0A 0H0
Russell Brandon, Box 36, Kimmirut, X0A 0N0
Foxe Basin (FB) – Chad Harden, Box 99, Coral Harbour X0C 0C0,
western Hudson Bay (WH) – Joe Savikataaq, Box 120, Arviat, X0C 0E0
Johanne Coutu-Autut, Bag 002, Rankin Inlet, X0C 0A0
Issatik HTA, Box 119, Whale Cove, X0C 0J0

Elizabeth Peacock and Markus Dyck (Nunavut, polar bear samples):

Department of Environment, Government of Nunavut, Igloolik, NU

Marsha Branigan (NWT, polar bear samples):

Dept. of Resources, Wildlife and Economic Development, Government of the Northwest Territories, Inuvik, NWT, Canada

Derek Muir (ringed seal samples and chemical analysis):

Water Science and Technology Directorate, Science and Technology Branch,
Environment Canada, Burlington, ON

Martyn Obbard (polar bear samples):

Ontario Ministry of Natural Resources, Government of Ontario, Peterborough, ON,
Canada

Ian Stirling and Nick Lunn (polar bear samples, western Hudson Bay, data interpretation and consulting):

Canadian Wildlife Service, Environment Canada, Edmonton, AB, Canada

Andrew Derocher (data interpretation and consulting):

Dept. of Zoology, University of Alberta, Edmonton, AB, Canada

b: Chemical, fatty acid and stable isotope analysis and sample archiving:

EC-NWRC (Carleton University students and postdoctoral fellows):

Melissa McKinney (PhD student, Carleton University, supervised by R.J. Letcher)

Dr. Shaogang Chu (Postdoctoral Fellow, Carleton University, supervised by R.J. Letcher)

EC-NWRC staff:

Bryan Wakeford (Lab Services; metals and fatty acid analysis), Francois Cyr (Lab Services, CH-03; GC-HRMS analyte identification), Luke Periard (Organics Research Group, EG-04; sample analysis), Gau Savard and Rosalyn McNeil (sample storage and archiving)

Michael Kwan (QA/QC, metals):

Nunavik Research Centre, Makivik Corp., Kuujjuaq QC

Paul Middlestead (C and N stable isotopes analysis):

G.G. Hatch Stable Isotope Laboratory, University of Ottawa, Ottawa, ON

Abstract

The polar bear (*Ursus maritimus*) is the apex predator of the Arctic marine ecosystem and an integral component of Inuit culture. Due to its position at the top of the marine food web, levels of persistent organic pollutant (POP) and metal contaminants in polar bears are among the highest observed in the Arctic. The last circumpolar spatial/temporal trends assessment of contaminants in polar bears (from populations spanning the western hemispheric Arctic in Alaska, Canada, Greenland and Svalbard (Norway)) was based on tissue samples collected in 2000-2001. This 2001-2002 assessment updated on the trends of legacy POPs (PCBs, OC pesticides and methyl sulfonyl-PCB metabolites (MeSO₂-PCBs)) and metals (e.g., Hg, Se, Rb, Sr, Ba and Mn). However, several novel and emerging classes and congeners of POPs of environmental concern were also identified for the first time in polar bear, e.g., the brominated flame retardants (BFRs) polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), perfluoroalkyl compounds (PFCs; e.g., perfluorooctane sulfonates (PFOS)) and several hydroxylated (OH) brominated and chlorinated compounds. Until these 2001-2002 studies there was no published data on spatial and temporal trends of any BFR or PFC contaminants in polar bears, a core NCP monitoring species. With the exception of major bioaccumulative PFCs studied in one Canadian population (northern Baffin Bay) assessed in 6 years spanning 1972 to 2002, there is currently no geographically-specific, temporal trends information for any BFR or PFA in polar bears from any circumpolar population.

In the present, ongoing study, liver, fat and in some cases muscle tissue samples were collected from bears harvested in late winter/early spring 2007 from locations encompassed within the seven Canadian polar bear management zones. Although not a mandate of NCP directly, similar bear sample sets were also collected and obtained from East Greenland, Svalbard and Alaskan zones. The bear samples collected attempted to adhere as closely as possible to an optimal study design, although sampling was dependent on the bears hunted as part of community harvests, as a result of opportunism in the field, and within the collection quotas permissible for each community. If at all possible, the collected bears adhered to the design to minimize age, reproductive and nutritional variation and thus minimize the effects of these parameters on contaminants, e.g., the bears were adult females between the ages of 5 and 15, and from bear harvests in the late winter/early spring and nearing the end of the hyperphasic period.

Expected results include the first circumpolar temporal trend and spatial change assessments in polar bears for emerging POPs such as PBDEs, HBCDs and PFCs in fat or liver tissue. Samples have been obtained for stable carbon and nitrogen isotopes (SIs; muscle) and a profile of fatty acids (FAs; fat) to be used as ecological tracers of trophic level and diet, respectively, and will be used to assess variations in the ringed seal-polar bear dietary relationships as a function of populations, which may be a variable affecting contaminant trend data.

Key Project Messages

- Tissue samples were collected in 2007 from bears from several Nunavut and NWT populations, and spatial and temporal trend investigations were begun on known POPs such as PCB and OC pesticides, as well as emerging POPs such as PBDEs, other BFRs and PFCs.
- Relevant to contaminant exposures in Canadian polar bears was the finding of numerous emerging and newly detected brominated flame retardant and other brominated substances in East Greenland bears collected in 2001-2002.
- Relevant to increasing our understanding of contaminant exposure implications in Canadian polar bears, and in collaboration with scientists from Denmark and Greenland, were findings showing relationships between various POP concentrations, including PBDE flame retardants, and immune, endocrine and physiological (e.g., sex organ size and renal lesions) health biomarkers in bears from East Greenland that were collected in 2001-2002..

Project Objectives

- To determine and monitor the spatial and temporal trends (e.g., concentrations and congener patterns), bioavailability, fate, and toxicokinetics (e.g., biotransformation and tissue distribution) of legacy and “new” persistent organic pollutants (POPs; chlorinated, brominated and fluorinated), their persistent degradation products as well as metal and other elements in polar bears from the seven Canadian Arctic management zones, as well as in bears from other circumpolar Arctic regions (Alaska (U.S.), Svalbard (Norway), Greenland (Denmark) and Russia).
- To assess population- and time-dependent variations, and corresponding influence on contaminant trends, in trophic level and dietary relationships between polar bears and seals using stable carbon and nitrogen isotope and fatty acid profiles, respectively as ecological tracers.
- Archive the remaining polar bear tissue samples that were collected as part of this project, in Environment Canada’s Wildlife Specimen Bank (EC-WSB) located at the NWRC, Carleton University, Ottawa.
- Provide information in a timely manner to each Inuit community participating in the study, on the levels and temporal trends of these contaminants in polar bear. This would include translation of documentation and deliverables into Inuktitut.

Introduction

Like humans, polar bears (*Ursus maritimus*) are at the top of the Arctic marine food web, circumpolarly distributed, and thus are an ideal sentinel/monitoring species for contaminants in the Arctic. Through the process of biomagnification the polar bear achieves some of the highest contaminant concentrations of any arctic species or any species on the planet (Braune et al.

2005), with potential effects ramifications in exposed bears and the human consumers who eat them or their prey items such as ringed seals (Fisk et al. 2005).

A comprehensive examination of the spatial trends of legacy organochlorine (OC) contaminants such as PCBs, methyl sulfone (MeSO₂) PCB metabolites and OC pesticides was last carried out for Canadian bear populations and other circumpolar populations on samples collected 1996 but mostly on 2001-2002 samples (Verreault et al. 2005a). Levels of legacy organochlorine contaminants, such as PCBs and chlordane pesticides, have been monitored in the western Hudson Bay polar bear population consistently through the 1980s into the 1990s (Norstrom et al. 1998; Norstrom 2001). Recently we reported on PCBs and OC pesticides in western Hudson Bay bears on samples collected in 2001-2002 (Verreault et al. 2005a). In this study, we carried out two-point temporal comparisons (1989-1993 relative to 2001-2002) on PCBs and OC pesticides for in bears from six Canadian management zones including western Hudson Bay (Norstrom et al. 1998; Verreault et al. 2005). The results showed a general decrease for age-adjusted mean concentrations of Σ CHL, *p,p'*-DDE, Σ_{42} PCB, Σ MeSO₂-PCB and 3-MeSO₂-*p,p'*-DDE over a period of approximately 10 years. Comparisons of present 2001-2002 concentrations in fat of female polar bears from western Hudson Bay showed great consistency with temporal trends (1991-1999) previously reported for the same region, i.e. the apparent non-decreasing trend of Σ CHL, β -HCH, Σ HCH and dieldrin, and the apparent declining trend for Σ PCB (Norstrom 2001). However, 2001-2002 concentrations of α -HCH and Σ CBz were elevated, and Σ DDT was notably lower in western Hudson Bay samples compared to the last measurements in fat samples collected in 1999, which was not in accord with reported temporal trends for this region. Clearly, continued temporal and spatial monitoring of bears from western Hudson Bay and other Canadian zones is warranted.

We showed in the last monitoring cycle that several emerging POPs such as PFCs (e.g., perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA)) accumulated in the liver of bears spanning the Canadian arctic (Smithwick et al. 2005a, 2005b). There is only one known study on the temporal trends of PFAs in polar bears for any circumpolar populations. In liver samples of bears collected in 6 years between 1972 and 2002 from one Canadian location (Northern Baffin Island) and Barrow, Alaska, concentrations of PFOS and PFCAs with carbon chain lengths from C₉ to C₁₁ were reported to be exponentially increasing at both locations with doubling times ranging from 3.6 ± 0.9 years for perfluorononanoic acid in the eastern group to 13.1 ± 4.0 years for PFOS in the western group. PFOSA showed decreasing concentrations over time at both locations, while the remaining PFCs showed no significant trends or were not detected in any sample (Smithwick et al. 2006). The emergence of PFAs as ubiquitous environmental contaminants is recent (Houde et al. 2006). Moreover, Butt et al. (2007) very recently reported on the temporal trends in PFCs in liver samples from two ringed seal (*Phoca hispida*) populations in the Canadian Arctic, Arviat (western Hudson Bay) (1992, 1998, 2004, 2005) and Resolute Bay (Lancaster Sound) (1972, 1993, 2000, 2004, 2005). C₉-C₁₅ PFCAs showed statistically significant increasing concentrations during 1992-2005 and during 1993-2005 at Arviat and Resolute Bay, respectively. PFOS and PFOSA concentrations showed maximum concentrations during 1998 and 2000 at Arviat and Resolute Bay, with statistically significant decreases from 2000 to 2005. PFOS disappearance half-lives for seals at Arviat and Resolute Bay were 3.2 and 4.6 years. These results demonstrated that ringed seals and their food web are rapidly responding to the phase out of perfluorooctane sulfonyl fluoride based

compounds by 3M in 2001. Given the PFC changes reported in Canadian arctic ringed seal, that there has been a pan-Canadian spatial assessment for one time point, and that there has been a temporal assessment (up until 2002) for only one Canadian population, further spatial/temporal assessments of PFCs in polar bears are highly warranted.

We have also reported on PBDEs in the fat of bears collected in 2001-2002 from all Canadian (Nunavut and NWT) management zones (Muir et al. 2006). PBDEs have also been reported in Arctic biota with increasing frequency; however the focus has generally been on Br₄ to Br₈ PBDE congeners, which largely comprise the PentaBDE and OctaBDE technical mixtures, and continue to be phased out from commercial use. Much less is known about in Arctic biota about higher brominated PBDEs, and especially BDE-209, which is the major constituent of the unregulated DecaBDE technical mixture (Braune et al., 2005). Very recently, Verreault et al. (2005b) reported on PBDEs in plasma of Svalbard polar bear although BDE-209 was not detectable. Other important and bioaccumulative brominated flame retardants (BFRs) such as hexabromocyclododecane (HBCD; total and not isomer-specific) have yet to be determined in Canadian polar bears. Although with fat samples collected in 2001-2002 we did report on total-HBCD in Alaskan, East Greenland and Svalbard bears, and levels were high and comparable to ΣPBDE concentrations (Muir et al. 2006). Clearly more spatial and temporal studies on HBCDs are necessary for Canadian bears. Furthermore, there are other numerous and current-use non-PBDE BFRs that may also be of environmental relevance to the Arctic and present in polar bears. For example, in other top predators, very recently in herring gulls from the Great Lakes numerous non-PBDE BFRs such as hexabromobenzene (HBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), pentabromoethylbenzene (PBEB) and pentabromotoluene (PBT) were reported in eggs collected from sites spanning the Great Lakes (Gauthier et al. 2007a) as well as in male and female plasma and egg yolk of Svalbard glaucous gulls (Verreault et al. 2007). BDE-209 and other highly brominated PBDE congeners were also detected in the eggs of these Great Lakes herring gulls and Svalbard glaucous gulls.

There is presently a dearth of temporal data for BFRs in polar bears and other marine mammals from the circumpolar Arctic (Braune et al. 2005; Muir et al. 2006). Ikonomou et al. (2002) reported exponential increases of PBDEs in Canadian arctic biota from measured in samples from 1981 to 2000. PBDEs have been shown to be increasing significantly in ringed seals at Holman (Muir et al. 2006). The only report of PBDEs in Canadian polar bear tissues was by Muir et al. (2006) on fat samples collected in 2001-2002. The PBDE congener pattern was dominated by BDE-47. However, there may be shifts in the PBDE congener patterns due to recent phase-outs of PentaBDE and Octa-BDE technical formation, and the rise in the use of DecaBDE formulations. In temporal studies on PBDEs in the eggs of Great Lakes herring gulls, it was recently reported the post-2000 PentaBDE-derived congeners are not increasing and appear to be on the decline, whereas BDE-209 and other highly brominated (and BDE-209 degradation product) congeners were only detectable in the mid-1990s and large increases were observed in the mid-2000s (Gauthier et al. 2007b, unpublished data).

The occurrence of retained OH-PCB and persistent MeSO₂-PCB metabolites in wildlife tissues has been of bioaccumulative and toxicological concern from some time (Letcher et al. 2000). In polar bears, MeSO₂-PCB and/or OH-PCBs (mainly in blood) have been reported in whole blood, plasma, fat and/or liver of East Greenland, central Canadian arctic and Svalbard polar bears

(Letcher et al. 1998, 2005; Norstrom 2001; Sandala et al. 2004; Sandau et al. 2000). MeSO₂-PCB and 3-MeSO₂-*p,p'*-DDE have similar bioaccumulative properties as PCBs, and circumpolar trends in polar bears were last assessed in 2001-2002 for bears from Canadian, East Greenland, Svalbard and Alaskan populations (Verreault et al., 2005a).

The last study that examined spatial trends of metals in Canadian polar bears was carried out in 2001-2002 (Letcher et al. 2005; Rush et al. 2007). These studies showed that the levels of many metals, and especially the major metal contaminants Cd, Hg and Se varied between different regions of the Canadian Arctic. For example, polar bears collected from the western Canadian Arctic had lower concentrations of Cd but higher concentrations of Hg and Se than those collected from other regions. In light of the evidence of increasing Hg concentration in Arctic biota and the lack of temporal trend metal data for polar bears there is a need to assess the current levels of metals.

Activities in 2006-2007

a) NCP-Supported Projects

Sample collections: Samples from polar bears from all management zones (populations) in the Canadian arctic are routinely collected by Nunavut and Northwest Territories agencies and governments. We have obtained fat, liver and/or muscle samples from a number of polar bears collected in the late winter/early spring 2007 harvests of participating community HTOs, hunters and Nunavut and NWT collaborators encompassed within the seven Canadian polar bear management zones. We have also received or are receiving fat, liver and/or muscle samples (and in the case of Svalbard whole blood samples) via international collaborators of polar bears from East Greenland, Alaska and Svalbard. As the requisite samples arrived for bears from the Canadian (and other circumpolar) populations, various contaminant determinations have proceeded.

Contaminant Determinations

Chemical analysis

PBDEs/BFRs: We completed an exhaustive search for new and current-use BFRs reported in the scientific literature in the environment, produced in high commercial/industrial volumes, described as replacements of PBDE technical formulations, and/or the commercial availability of analytical standards. Among the BFRs found were 2,3,4,5,6-pentabromoethylbenzene (PBEB), 1,4-bis(pentabromophenoxy)-tetrabromobenzene, 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl ethane (DBDPE), hexabromobenzene (HBB), pentabromobenzyl acrylate (PBBA), pentabromobenzyl bromide (PBBB), pentabromotoluene (PBT), tetrabromo-*p*-xylene and 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane. McKinney has optimized analytical methodologies for PBDE/BFR determinations, as well as for PCBs, OC pesticides and MeSO₂-PCBs/*p,p'*-DDE in polar bear fat samples.

PFCs: Progress was made at NWRC in implementing and validating a HPLC-MS-MS-based methodology for the determination of a suite of PFCs in polar bear liver samples. The methodology currently being utilized is the same as was used in the previous monitoring study for PFCs in polar bears, where we had adapted and successfully applied such a PFC method for polar bear liver (Smithwick et al. 2005a, 2005b; Smithwick et al. 2006) and ringed seal liver (Butt et al. 2007). The methodology being implemented will monitor for a suite of 10 saturated

and linear, C₆-C₁₅ perfluorinated carboxylic acids (PFCAs, including PFOA), 4 saturated and linear (C₄, C₆, C₈ and C₁₀) perfluorinated sulfonic acids (including PFOS), perfluorooctane sulfonamide (PFOSA), and the precursor PFCs 8:2 and 10:2 fluorotelomer alcohols, and 8:2 and 10:2 fluorotelomer unsaturated alcohols.

FAs: Over the course of 2006-2007 at NWRC we successfully set-up a method for the determination of a profile of fatty acids (FAs) (i.e., a suite of 37 saturated and polyunsaturated, C₆-C₂₄ fatty acids) in herring gull egg, to be used as an ecological tracer of dietary changes and differences, and complement the use of SIs as indicators of trophic level. In a given sample FAs are derivatized to their methyl ester analogues as fatty acid methyl esters (FAMES), which are subsequently separated and quantified by gas chromatography-flame ionization detection (GC-FID). A similar methodology was recently applied to in the determination of a profile of FAs in polar bear fat.

b) non-NCP funded projects

Additional research had been conducted and completed using samples obtained via or in relation to the NCP II, 2001-2002 polar bear monitoring assessment. For example, initiatives were completed on the screening, tissue distribution (plasma, fat, brain and liver) and bioaccumulation (from ringed seal blubber) of legacy and emerging contaminants in a sub-set of 20 individual adult bears (10 males and 10 females) from East Greenland population collected in 1999-2001 (Gebbinck et al. 2007a, 2007b, 2007c). This sub-project was the basis of the thesis research project of Mr. Wouter Gebbinck (Carleton University, under the supervision of R. Letcher) that was entitled, “*Bioaccumulation and Toxicokinetics and Brominated and Chlorinated Contaminants in East Greenland Polar Bears (Ursus maritimus)*”.

In 2006-2007 a number of other non-NCP funded projects were ongoing or completed on the spatial and temporal trends and effects on contaminants in polar bears, and several papers were published. Sonne et al. (2006a) reported on the relationships between tissue levels (fat) of potentially xenoendocrine organohalogenes and the possible implication of reduced size of sexual organs in East Greenland polar bears. In Sonne et al. (2006b) we also reported on the relationships between organohalogen contaminant levels and the potential co-factor involvement in the development of renal lesions in East Greenland polar bears. Again in East Greenland polar bears, we also reported on the seasonal trends and bioaccumulation of PBDEs (Dietz et al. 2007). Finally, in polar bears in the vicinity of Resolute Bay in the Canadian high arctic, we reported on the composition of PCBs and OC pesticides and degradation products among major and metabolically active adipose tissue depots of polar bear (Verreault et al. 2007).

Results

a) NCP-Supported Projects

Despite only receiving NCP funding for the 2006-2007 fiscal year in November 2006, much progress has been made in 2006-2007. In Sept. 2006 a new PhD, Melissa McKinney, began her studies under the supervision of R. Letcher (Department of Chemistry, Carleton University). In the latter part of 2006 McKinney has been focusing her energies on 1) arranging Canadian, as well as Alaskan, Svalbard and East Greenland polar bear sampling and samples, 2) preparing a PhD thesis research proposal, 3) setting up and optimizing analytical methodologies for PBDE/BFR determinations, as well as for PCBs, OC pesticides and MeSO₂-PCBs/-*p,p'*-DDE in

polar bear fat samples, and 4) initiating processes for FA (fat) and SIA (muscle) determinations for available polar bear and ringed seal (in collaboration with D.C.G. Muir) samples. Including the NCP-supported component, the title of McKinney's PhD thesis project is, "*Relationship of Diet and Body Condition to Organohalogen Accumulation and Toxicokinetics in Circumpolar Polar Bear Populations Assessed on Both Spatial and Temporal Scales*".

As a functional analytical methodology has been set-up at NWRC (post-doctoral fellow Dr. Shaogang Chu), PFC analyses have commenced on available polar bear liver samples. However, there is insufficient data at the moment to report on an temporal or spatial trends in Canadian bears. Such data is expected over the course of 2007-2008, and trend assessments will result from comparisons with PFC levels and compound patterns found as part of 2002 and earlier surveys (Smithwick 2005a, 2005b, 2006).

Major findings on chlorinated and brominated POP in Canadian polar bears were.....

b) non-NCP funded projects

In studies on the tissue- (liver, fat and brain) and blood-specific composition of chlorinated and brominated compounds and metabolites in East Greenland polar bears (Gebbink et al. 2007a), the PCB congener patterns were similar in the three tissues and blood, and the pattern was dominated by five congeners: CB-99, -138, -153, -170/-190 and -180, which made up 79-95% of Σ PCB (Figure 1, Table 1). However, PCB congener patterns were variable among the tissues and blood. the trend for P-PCB concentrations was adipose tissue > liver > brain > blood (Table 1) (Gebbink et al. 2007b). In the adipose tissue, the OH-PCB congener to Σ OH-PCB concentration ratios showed significant differences relative to the other tissues ($p < 0.04$) (Figure 1), and trend for mean Σ OH-PCB concentrations follows blood >> liver > adipose tissue > brain (Table 1)

A total of 13 BDE congeners were detected in the polar bear tissues (Figure 1) (Gebbink et al. 2007a). The total percent composition among the tissues of the congeners BDE-47, -99, -100, -153, and -154 was 86 to 91% of Σ PBDE concentration (Table 1). Among the BDE-47, -99, -100, -153 and -154 congeners the trend showed a significant brain localization preference for BDE-47 ($p < 0.03$), a significant preference of BDE-99 to accumulate in the liver ($p < 0.001$), and a significant accumulation preference of BDE-153 in the subcutaneous adipose tissue ($p < 0.001$). The trend for P-PBDE concentrations follows adipose > liver > blood > brain (Gebbink et al. 2007b). We unexpectedly detected three unknown, brominated phenolic contaminants in the present bears, which we identified as OH-PBBs (Gebbink et al. 2007a).

We also reported on the comparative bioaccumulation, biotransformation and/or biomagnification of various classes and congeners of contaminants and metabolic by-products, *i.e.*, PCBs, CHLs, MeSO₂-PCBs, PBDEs, OH-PBDEs, OH-PCBs, MeO-PBDEs and OH-PBBs, *p,p'*-DDE, 3-MeSO₂-*p,p'*-DDE, PCP, 4-OH-HpCS, BB-101 and total-(α)-HBCD, from East Greenland ringed seal blubber (*Phoca hispida*) to polar bear tissues (periphery adipose, liver, brain) (Gebbink et al. 2007c). For the entire brominated and chlorinated compounds under study, only OH-PCB congeners and 4-OH-HpCS were not detected in the ringed seal blubber. The tissue-specific biomagnification factors (BMFs) demonstrated biomagnifications and/or preferential tissue localization in bear relative to seal. In polar bear liver all the detectable organohalogen had biomagnification factors (BMFs) >1, with BMFs ranging from 2.4 to 570. In

the brain, the mean BMFs were around 1 with the exception of OH-PBBs (mean BMF = 93 ± 54). Unlike the OH-PCB metabolites, which were mainly in the blood, OH-PBDEs bioaccumulated in the bear tissues from the seal blubber. In a hepatic microsomal *in vitro* assay for the polar bears, a slow rate of oxidative metabolism of PBDE congeners corroborated seal accumulation as a source of OH-PBDEs in the bear tissues.

Discussion and Conclusions

The difference in PCB congener pattern in brain and liver of East Greenland polar bears (Figure 1) could be a result of biochemical processes, biotransformation in the liver and the congener-specific discrimination by the BBB. The Σ OH-PCB concentrations clearly showed a preference for localization in the blood (Figure 1, Table 1), which means that OH-PCBs are likely more protein associated rather than lipid associated as is the case with POPs in general (Gebbinck et al., 2007b). However, OH-PCBs were present in adipose tissue indicating that these PCB metabolites possess some bioaccumulation potential. Our findings are consistent with other polar bear studies where BDE-47 and -153 were the dominant congeners and BDE-154 a minor in adipose tissue samples (Muir et al., 2006; Sørmo et al., 2006).

To our knowledge, this is the first comparative report of PCB, PBDE, OH-PCB, MeSO₂-PCB, OH-PBDE and MeO-PBDE metabolite/degradation product, congener patterns among polar bear tissues, and specifically including the brain. Our findings show that tissue composition of congener pattern varies as a function of the multiple congener class in question. The pattern composition differences for PCBs, OH-PCBs, MeSO₂-PCBs, PBDEs and OH-PBBs indicate that there are congener-specific mechanisms into or out of the brain, liver, adipose tissue and blood. Clearly, our findings suggest that exposures with respect to congener patterns may elicit target tissue-specific effects in East Greenland polar bears. In a separate report, we provide an in-depth examination of the tissue composition and body burdens of the individual or sum concentrations of classes with multiple congeners, of a wide variety of chlorinated and brominated contaminants of contrasting physico-chemical properties (e.g., polarity and lipophilicity) (Gebbinck et al., 2007b).

In further investigations on the comparative bioaccumulation, biotransformation and/or biomagnification of various PCBs, CHLs, MeSO₂-PCBs, PBDEs, OH-PBDEs, OH-PCBs, MeO-PBDEs and OH-PBBs, *p,p'*-DDE, 3-MeSO₂-*p,p'*-DDE, PCP, 4-OH-HpCS, BB-101 and total-(α)-HBCD, from East Greenland ringed seal blubber (*Phoca hispida*) to polar bear tissues (periphery adipose, liver, brain) were revealing. Unlike the OH-PCB metabolites, which were mainly in the blood, OH-PBDEs bioaccumulated in the bear tissues from the seal blubber. Our findings demonstrated that organohalogen biotransformation and bioaccumulation in polar bears originating from a ringed seal diet are the main sources depending on the organohalogen type and the tissue in question.

Expected Project Completion Date

All aspects of the project is expected to be completed by March 31, 2010.

Acknowledgments

The project leaders and team members thank all individuals (e.g. northern peoples, field biologists and students) and agencies that participated in this project. The collection of polar bear

tissues in Nunavut for contaminant analysis was initiated and carried out by the Department of Environment (Government of Nunavut), which was included as part of the normal sampling of all polar bear that are collected as part of the traditional hunt by northern peoples. All appropriate permits were obtained (Nunavut Wildlife Research Permit). The collection of polar bear tissues in Northwest Territories was carried out by the Department of Resources, Wildlife and Economic Development, Government of the Northwest Territories. Appropriate permits and community approval were approved and granted by the Inuvialuit Game Council and appropriate Hunters and Trappers Committees. Collection of samples was carried out exclusively by hunters in the NWT and Nunavut communities. The project therefore relies heavily on the knowledge and experience of these hunters for its samples and for the ecological information on behavior, condition and population numbers they provide to wildlife officers and biologists.

References

- Braune, B., D.C.G. Muir, G. Stern, P.F. Hoekstra, R. Dietz, M. Kwan, F.A.C. Gobas, R. Kelly, R.J. Letcher, R.J. Norstrom, N. Burgess, Z.Z. Kuyuk and P. Outridge. 2005. Spatial and temporal trends of mercury and POPs in Canadian arctic biota. *Sci. Total Environ.* 351-352: 4-56.
- Butt, C.M., D.C.G. Muir, I. Stirling, M. Kwan and S.A. Mabury. 2007. Rapid response of arctic ringed seals to changes in perfluoroalkyl production *Environ. Sci. Technol.* 41(1): 42-49.
- de March, B. *et al.* 1998. AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway, xii+859 pp.
- Dietz, R., F.F. Rigét, C. Sonne, R.J. Letcher, S. Backus, E.W. Born, M. Kirkegaard, D.C.G. Muir. 2007. Age and seasonal variability of polybrominated diphenyl ethers in free-ranging East Greenland polar bears (*Ursus maritimus*). *Environ. Pollut.* 146(1):166-173.
- Fisk, A.T., C.A. de Wit, M. Wayland, Z.Z. Kuzyk, N. Burgess, R.J. Letcher, B. Braune, R.J. Norstrom, S. Polischuk-Blum, C.D. Sandau, E. Lie, H. Jørgen, S. Larsen, J.-U Skaare and D.C.G. Muir. 2005. An assessment of the toxicological significance of anthropogenic contaminants in Canadian arctic wildlife. *Sci. Total Environ.* 351-352: 57-93.
- Gauthier, L.T., C.E. Hebert, D.V. Chip Weseloh and R.J. Letcher. 2007a. Current-use flame retardants in the eggs of herring gulls (*Larus argentatus*) from the Laurentian Great Lakes. *Environ. Sci. Technol.* 41(13): 4561-4567.
- Gauthier, L.T., C.E. Hebert, D.V. Chip Weseloh and R.J. Letcher. 2007b. Emergence and temporal trends of decabromodiphenyl ether flame retardant and lower brominated congeners in herring gull eggs from the Laurentian Great Lakes. *Environ. Sci. Technol.* Submitted August 2007.
- Gebbink, W.A., C. Sonne, R. Dietz, M. Kirkegaard, F.F. Rigét, E.W. Born, D.C.G. Muir and R.J. Letcher. 2007a. Tissue-specific congener composition of organohalogen and metabolite contaminants in East Greenland Polar Bears (*Ursus maritimus*). *Environ. Pollut.* In press.
- Gebbink, W.A., C. Sonne, R. Dietz, M. Kirkegaard, E.W. Born, D.C.G. Muir and R.J. Letcher. 2007b. Target tissue selectivity and burdens of diverse classes of brominated and chlorinated contaminants in polar bears (*Ursus maritimus*) from East Greenland. *Environ. Sci. Technol.* Submitted Aug. 2007.
- Gebbink, W.A., C. Sonne, R. Dietz, M. Kirkegaard, E.W. Born and R.J. Letcher. 2007c. Biomagnification and biotransformation of brominated and chlorinated contaminants and their Metabolites in East Greenland ringed seals (*Phoca hispida*) and polar bears (*Ursus maritimus*). *Environ. Toxicol. Chem.* In prep.

- Houde, M., J.W. Martin, R.J. Letcher, K.R. Solomon, D.C.G. Muir. 2006. Environmental and biological monitoring of polyfluoroalkyl compounds: A critical review. *Environ. Sci. Technol.* 40:3463-3473.
- Ikonomou, M.G., S. Rayne and R.F. Addison. 2002. Exponential increases of the brominated flame retardants, polybrominated diphenyl ethers, in the Canadian arctic from 1981 to 2000. *Environ. Sci. Technol.* 36(9): 1886-1892.
- Letcher, R.J., E. Klasson-Wehler and Å Bergman. 2000a. Methyl sulfone and hydroxylated metabolites of polychlorinated biphenyls. In: J. Paasivirta (ed.), *Anthropogenic Compounds: New Types of Persistent Halogenated Compounds*, Heidelberg, Germany: Springer-Verlag Publishers. pp. 315-359.
- Letcher, R.J., D.C.G. Muir, A.T. Fisk. 2005. Temporal and spatial trends of contaminants in Canadian polar bears: Part II. In: S. L. Smith and J. Stow (eds.), *Synopsis of research conducted under the 2004/2005 Northern Contaminants Program*. Ottawa: Indian and Northern Affairs Canada. pp. 140–154.
- Muir, D.C.G., S. Backus, A.E. Derocher, R. Dietz, T.J. Evans, G.W. Gabrielsen, J. Nagy, R.J. Norstrom, C. Sonne, I. Stirling, M.K. Taylor, R.J. Letcher. 2006. Brominated flame retardants in polar bears (*Ursus maritimus*) from Alaska, the Canadian Arctic, Greenland and Svalbard. *Environ. Sci. Technol.* 40:449-455.
- Muir, D. C. G., M. Kwan, M. Evans, C. Butt, S. Mabury, S. Moore, E. Sverko, W. M. and X. Wang. 2006. Temporal trends of persistent organic pollutants and metals in ringed seals from the Canadian Arctic. In: S.L. Smith and J. Stow (eds.), *Synopsis of research conducted under the 2005/2006, Northern Contaminants Program*. Ottawa: Indian and Northern Affairs Canada. Ottawa, pp. 162-169.
- Norstrom, R.J., S.E. Belikov, E.W. Born, G.W. Garner, B. Malone, S. Olpinski, M. A. Ramsay, S. Schliebe, I. Stirling, M.S. Stishov, M.K. Taylor and O. Wiig. 1998. Chlorinated hydrocarbon contaminants in polar bears from eastern Russia, North America, Greenland and Svalbard: biomonitoring of Arctic pollution. *Arch. Environ. Contam. Toxicol.* 35:354-367.
- Norstrom, R. 2001. Effects and trends of POPs on polar bears. NCP In: S. Kalkok (Ed.) *Synopsis of Research Conducted Under the 2000-2001 Northern Contaminants Program*, pp. 215-226. 371p.
- Rush, S.A., K. Borgå, R. Dietz, T. Evans, D.C.G. Muir, R.J. Letcher, R.J. Norstrom and A.T. Fisk. 2007. Geographic distribution of select elements in the livers of polar bears (*Ursus maritimus*) from Greenland, Canada and the United States. *Arch. Environ. Contam. Toxicol.* Submitted June 2007.
- Smithwick, M.M., D.C.G. Muir, S. Mabury, K.R. Solomon, J.W. Martin, C. Sonne, E.W. Born, R.J. Letcher and R. Dietz. 2005a. Perfluoroalkyl contaminants in liver tissue from East Greenland polar bears (*Ursus maritimus*). *Environ. Toxicol. Chem.* 24(4): 981–986.
- Smithwick, M.M., S.A. Mabury, K.R. Solomon, C. Sonne, J.W. Martin, E.W. Born, R. Dietz, A.E. Derocher, R.J. Letcher, T.J. Evans, G.W. Gabrielsen, J. Nagy, I. Stirling, M.K. Taylor and D.C. G. Muir. 2005b. A circumpolar study of perfluoroalkyl contaminants in polar bears (*Ursus maritimus*). *Environ. Sci. Technol.* 39(15):5517-5523.
- Smithwick, M.M., R.J. Norstrom, S.A. Mabury, K.R. Solomon, T.J. Evans, I. Stirling, M.K. Taylor and D.C.G. Muir. 2006. Temporal trends of perfluoroalkyl contaminants in polar bears (*Ursus maritimus*) from two locations in the North American Arctic, 1972-2002. *Environ. Sci. Technol.* 40: 1139-1143.

- Sonne, C., R. Dietz, P. S. Leifsson, E. W. Born, M. Kirkegaard, R.J. Letcher, D.C.G. Muir, F.F. Riget and L. Hyldstrup. 2006a. Are organohalogen contaminants a co-factor in the development of renal lesions in East Greenland polar bears (*Ursus maritimus*)? *Environ. Toxicol. Chem.* 25(6): 1551-1557.
- Sonne, C., P.S. Leifsson, R. Dietz, E.W. Born, R.J. Letcher, L. Hyldstrup, F.F. Riget, M. Kirkegaard and D.C.G. Muir. 2006b. Xenoendocrine pollutants may reduce size of sexual organs in East Greenland polar bears (*Ursus maritimus*) *Environ. Sci. Technol.* 40: 5668-5674.
- Sørmo, E.G., M.P. Salmer, B.M. Jenssen, H. Hop, K. Bæk, K.M. Kovacs, C. Lydersen, S. Falk-Petersen, G.W. Gabrielsen, E. Lie and J.U. Skaare. 2006. Biomagnification of brominated flame retardants in the polar bear food chain in Svalbard, Norway. *Environ. Toxicol. Chem.* 25: 2502-2511.
- Verreault, J., G.W. Gabrielsen, S.-G. Chu, D.C.G. Muir, M. Andersen, A. Hamaed, and R.J. Letcher. 2005a. Brominated flame retardants and methoxylated and hydroxylated PBDEs in top-predator species from the Norwegian Arctic: Glaucous gulls (*Larus hyperboreus*) and polar bears (*Ursus maritimus*). *Environ. Sci. Technol.* 39: 6021-6028.
- Verreault, J., D.C.G. Muir, R.J. Norstrom, I. Stirling, A.T. Fisk, G.W. Gabrielsen, A.E. Derocher, T.J. Evans, R. Dietz, C. Sonne, G.M. Sandala, W. Gebbink, E.W. Born, F.F. Riget, M.K. Taylor, J. Nagy and R.J. Letcher. 2005b. Chlorinated hydrocarbon contaminants and metabolites in polar bears (*Ursus maritimus*) from Alaska, Canada, East Greenland, and Svalbard: 1996–2002. *Sci. Total Environ.* 351-352: 369-390.
- Verreault, J., R.J. Norstrom, M.A. Ramsay, M. Mulvihill, R.J. Letcher. 2006. Composition of chlorinated hydrocarbon contaminants among major adipose tissue depots of polar bear (*Ursus Maritimus*) from the Canadian High Arctic. *Sci. Total Environ.* 370: 580–587.
- Verreault, J., W.A. Gebbink, L.T. Gauthier, G.W. Gabrielsen and R.J. Letcher. 2007. Brominated flame retardants in glaucous gulls from the Norwegian Arctic: More than just an issue of polybrominated diphenyl ethers. *Environ. Sci. Technol.* 41(14): 4925-4931.

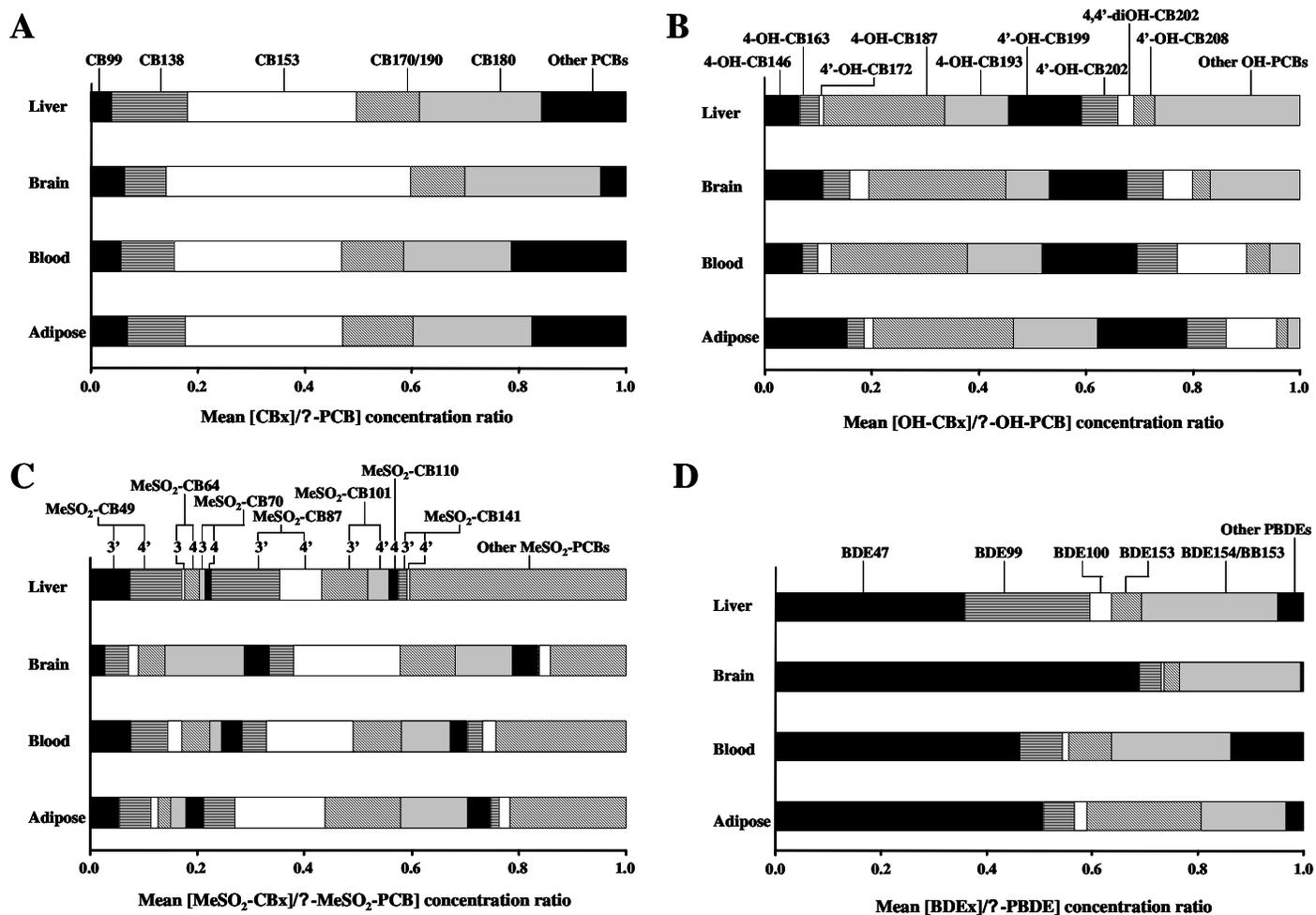


Figure 1. The mean concentration ratio (relative to the sum concentrations of each class) of major congeners of (A) PCBs, (B) OH-PCBs, (C) MeSO₂-PCBs and (D) PBDEs in adipose, brain and liver tissue and whole blood of polar bears (n=20) from East Greenland.

Table 1. The arithmetic mean (\pm SE) of concentrations (ng/g wet wt) of classes of neutral and phenolic organohalogen compounds in the tissues of female and male polar bears from East Greenland (n=20).

Analyte	Adipose		Blood		Brain		Liver	
	Mean (\pm SE)	Range	Mean (\pm SE)	Range	Mean (\pm SE)	Range	Mean (\pm SE)	Range
Lipid (%)	90 \pm 4	28 – 120	1.3 \pm 0.1	0.88 - 1.9	21 \pm 1	13 - 29	11 \pm 1	5.1 - 19
Σ -PCB ^a	5 387 \pm 606	887 - 12 262	40 \pm 9	7 - 204	148 \pm 23	31 - 459	3 125 \pm 372	1 412 - 7 443
Σ -MeSO ₂ -PCB ^b	455 \pm 123	61 - 2 648	7 \pm 2	1 - 52	12 \pm 1	9 - 23	225 \pm 61	31 - 1 268
Σ -OH-PCB ^b	60 \pm 8	20 – 173	1 020 \pm 132	385 - 2 888	18 \pm 3	4.8 - 51	355 \pm 36	176 - 714
Σ -PBDE ^d	83 \pm 19	24 – 422	1.2 \pm 0.1	0.5 - 1.9	2.9 \pm 0.4	<0.5 - 7.6	40 \pm 4	14 - 103
Σ -OH-PBDE ^e	0.9 \pm 0.5	<0.3 – 10	2.9 \pm 1.0	<0.5 - 13	n.d.	<0.2	n.d.	<0.5
Σ -MeO-PBDE ^f	4.3 \pm 1.7	<0.3 – 25	0.16 \pm 0.06	<0.5 - 0.78	n.d.	<0.5	n.d.	<0.5

n.d. – not detected.

^a Σ -PCB: CB-28/31, -42, -44, -49, -52, -60, -64/71, -66/95, -70, -74, -84/101, -87, -97, -99, -105, -110, -118, -128, -129/178, -138, -141, -146, -149, -151, -153, -156/171/202, -158, -170/190, -172, -174, -177, -179, -180, -182/187, -183, -194, -195, -196/203, -200, -201, -206.

^b Σ -MeSO₂-PCB: 3'/4'-MeSO₂-CB49, 3/4-MeSO₂-CB52, 3/4-MeSO₂-CB64, 3/4-MeSO₂-CB70, 3'/4'-MeSO₂-CB87, 3/4-MeSO₂-CB91, 3'/4'-MeSO₂-CB101, 3/4-MeSO₂-CB110, 3'/4'-MeSO₂-CB132, 3'/4'-MeSO₂-CB141, 3/4-MeSO₂-CB149, 3/4-MeSO₂-CB174.

^c Σ -OH-PCB: 4'-OH-CB79, 4-OH-CB97, 4'-OH-CB101/4-OH-CB134, 4-OH-CB107/4'-OH-CB108, 2'-OH-CB114, 3-OH-CB118, 4'-OH-CB120, 4'-OH-CB127, 4'-OH-CB130, 3'-OH-CB138, 4-OH-CB146, 4'-OH-CB159, 4-OH-CB162, 4-OH-CB163, 4'-OH-CB172, 4'-OH-CB177, 4-OH-CB178, 3'-OH-CB180, 3'-OH-CB182, 3'-OH-CB183, 3'-OH-CB184, 4-OH-CB187, 4-OH-CB193, 4'-OH-CB199, 4'-OH-CB200, 4'-OH-CB201, 4'-OH-CB202, 4,4'-diOH-CB202, 3'-OH-CB203/4'-OH-CB198, 4'-OH-CB208.

^d Σ -PBDE: BDE-17, 28, -47, -66, -85, -99, -100, -138, -153, -154, -183, -190, -209.

^e Σ -OH-PBDE: 6'-OH-BDE17, 6'-OH-BDE17, 6'-OH-BDE49, 2'-OH-BDE68, 6-OH-BDE47, 3-OH-BDE47, 5-OH-BDE47, 4'-OH-BDE49, 4-OH-BDE42, 6-OH-BDE90, 6-OH-BDE99, 2-OH-BDE123, 6-OH-BDE85, 6-OH-BDE137.

^f Σ -MeO-PBDE: 4'-MeO-BDE17, 6'-MeO-BDE17, 2'-MeO-BDE28, 4-MeO-BDE42, 3-MeO-BDE47, 5-MeO-BDE47, 6-MeO-BDE47, 4'-MeO-BDE49, 6'-MeO-BDE49, 2'-MeO-BDE68, 6-MeO-BDE85, 6-MeO-BDE90, 6-MeO-BDE99, 2-MeO-BDE123, 6-MeO-BDE137.