POLYBROMINATED DIPHENYL ETHER FLAME RETARDANTS IN THE ANTARCTIC ENVIRONMENT

A Dissertation

by

GILVAN TAKESHI YOGUI

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

August 2008

Major Subject: Oceanography

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ABSTRACT

Polybrominated Diphenyl Ether Flame Retardants in the Antarctic Environment.

(August 2008)

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Polybrominated diphenyl ethers (PBDEs) are anthropogenic chemicals whose environmental behavior is similar to the well-known polychlorinated biphenyls (PCBs). Few studies have quantified the amount and distribution of PBDEs in the southern hemisphere and Antarctica. The analyses reported in this dissertation document the levels of PBDEs in lichens, mosses and seabird eggs collected at King George Island, Antarctic Peninsula. The analyses were carried out using Gas Chromatography/Electron Impact-Mass Spectrometry (GC/EI-MS). Employing the ion stacking technique lowered detection limits and ensured instrument selectivity and sensitivity to the compounds of interest.

Lichens and mosses absorb PBDEs directly from the atmosphere and their contamination indicates that long-range transport is the primary source of these chemicals to King George Island. The congener patterns of PBDEs in plants indicate that commercial mixtures of Penta-BDE and Octa-BDE have reached Antarctica. Differences in the levels of PBDEs observed in lichens and mosses are probably due to factors that

govern the uptake of PBDEs from the atmosphere. Contamination in lichens showed a positive correlation with local precipitation. Conversely, absorption of PBDEs in mosses appears to be controlled by other plant-specific factors. Marine phytoplankton-derived aerosols are hypothesized to play an important role in the atmospheric transport of PBDEs to the Antarctic environment.

PBDEs in south polar skua eggs revealed much higher concentration than in penguin eggs. This is likely associated with the northward migration of these seabirds during the non-breeding season. While penguins reside year-round in Antarctica, south polar skuas migrate northward and can be seen in boreal oceans during the austral winter. Distribution of PBDEs in penguin eggs matches the pattern found in local vegetation suggesting a common source for the chemicals. In contrast, the congener pattern of south polar skuas suggests that birds breeding at King George Island are wintering in the northwestern Pacific Ocean. A potential metabolism of PBDEs in penguin eggs during the incubation period seems to be limited. Most congeners were unaltered from source material in the eggs of chinstrap and gentoo penguins. Low levels of PBDEs, short incubation periods and energy constraints may explain these observations.

DEDICATION

To my beloved mother Izilda, father Gilberto and sister Gilvana.

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First of all I thank God for giving me perseverance, peace and health to finish this important step of my professional and academic education. My deepest appreciation goes to my family in Brazil for their infinite and unconditional love, encouragement, support and prayers. I LOVE YOU!

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I greatly appreciate Dr. Rosalinda Montone for the opportunity to participate in the Antarctic expeditions. My two field trips to collect samples in Antarctica were financially supported by the Brazilian Antarctic Program and the College of Geosciences (through the Pipes Endowed Fellowship). Chemical analyses were financially supported by GERG funds.

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NOMENCLATURE

α	critical value of a statistical test used to reject the null hypothesis
ANOVA	Analysis of Variance
BDE	Brominated Diphenyl Ether
BFR	Brominated Flame Retardant
DC	Direct Current
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
df	degrees of freedom
DMS	Dimethylsulfide
dw	dry weight
GC	Gas Chromatography (or Gas Chromatograph)
GERG	Geochemical and Environmental Research Group
GPC	Gel Permeation Chromatography
ECNI	Electron Capture Negative Ionization
EI	Electron Ionization (or Electron Impact)
F	*F*-test Statistic
H	Kruskal-Wallis Test Statistic
HBCD	Hexabromocyclododecane
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane

HPLC	High Performance Liquid Chromatography
id	inner diameter
IUPAC	International Union of Pure and Applied Chemistry
K_{OA}	octanol-air partition coefficient
K_{OW}	octanol-water partition coefficient
LOEL	Low-Observed-Effect-Level
LOQ	Limit of Quantification
m/z	mass-to-charge ratio
MDL	Method Detection Limit
MS	Mass Spectrometry (or Mass Spectrometer)
MSA	Methanesulfonic Acid
n	number of samples
nd	not detected
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
p	level of significance of the statistical test (aka *p*-value)
PBB	Polybrominated Biphenyl
PBDE	Polybrominated Diphenyl Ether
PCB	Polychlorinated Biphenyl
PCDD	Polychlorinated Dibenzo-*p*-dioxin
PCDF	Polychlorinated Dibenzofuran
POP	Persistent Organic Pollutant

QA	Quality Assurance
QC	Quality Control
r	Pearson's product-moment correlation coefficient
r_s	Spearman's rank order correlation coefficient
RPD	Relative Percent Difference
SD	Standard Deviation
SIM	Selected Ion Monitoring
S/N	Signal-to-Noise Ratio
SOC	Semivolatile Organic Compound
SRM	Standard Reference Material
TEQ	2,3,7,8-tetrachlorodibenzo-*p*-dioxin Toxic Equivalent
TBBPA	Tetrabromobisphenol A
TIC	Total Ion Chromatogram
ww	wet weight

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

1.1. Brominated flame retardants

Flame retardants are chemicals used in numerous combustible materials in order to reduce the risk of fire and meet fire safety regulations (Alaee et al., 2003). Currently, there are over 175 compounds or groups of compounds with known flame retardant properties. They are generally divided into four classes: inorganic, halogenated organic, nitrogen-containing and phosphorus-containing compounds (Birnbaum and Staskal, 2004). Among halogenated flame retardants, brominated compounds represent the largest market because of their lower decomposing temperatures, higher performance efficiency and low cost (Alaee et al., 2003; Birnbaum and Staskal, 2004). Thus, brominated flame retardants (BFRs) have been extensively used to improve the fire resistance of materials such as plastics, textiles, furniture foam, and electronic circuitry (Rahman et al., 2001). Around 38% of total global production of bromine is currently used in the manufacturing of BFRs (Alaee et al., 2003).

Based on their use in the chemical industry, BFRs can be classified as either reactive or additive. Reactive BFRs such as the tetrabromobisphenol A (TBBPA) are

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This dissertation follows the style of Marine Pollution Bulletin.

covalently bound into the polymer matrix. Conversely, additive BFRs are dissolved in the matrix and therefore weakly bound to the polymer. The additive BFRs are more likely to be released into the environment as they tend to leach out of a product much more easily than their reactive BFRs counterparts. Examples of additive BFRs include polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), and hexabromocyclododecane (HBCD). Production of PBBs in the U.S. was phased-out in the 1970s after a contamination of farm products incident in Michigan (Alaee et al., 2003). Conversely, production of PBDEs has increased peaking in the mid-1990s (Alcock et al., 2003).

Brine wells in Arkansas are the main source of bromine in the United States. Considering bromine's reactivity and toxicity, manufacturing of BFRs including PBDEs occurs near production sites to avoid long distance transportation (Alaee et al., 2003). The two major companies producing BFRs in the U.S. are Albemarle Corporation and Great Lakes Chemical Corporation. There are three PBDE technical formulations used in industry: Penta-BDE, Octa-BDE and Deca-BDE. They are named according to the predominant homolog groups in the mixture (Table 1). Penta-BDE is mostly used in polyurethane foams while Octa-BDE is mainly used in rigid plastics such as ABS and high-impact polystyrene. Deca-BDE formulation is a flame retardant used in a wide range of polymers including textiles, resins and rigid plastics (Table 2). According to Hale et al. (2003), the U.S. leads North American demand for PBDEs representing approximately 50% of the total global demand and almost 95% of the most environmentally problematic Penta-BDE (Table 3).

Table 1

Percent distribution of homolog brominated diphenyl ether (BDE) groups in the three technical products used in industrial processes. After de Wit (2002).

Homolog Groups	Technical Product		
	Penta-BDE	Octa-BDE	Deca-BDE
mono-BDEs			
di-BDEs			
tri-BDEs			
tetra-BDEs	24-38%		
penta-BDEs	50-60%		
hexa-BDEs	4-8%	10-12%	
hepta-BDEs		44%	
octa-BDEs		31-35%	
nona-BDEs		10-11%	< 3%
deca-BDE		< 1%	97-98%

Table 2

Application and common usage of the three commercially available polybrominated diphenyl ether (PBDE) mixtures in different types of polymeric materials. Source: www.bsef.com

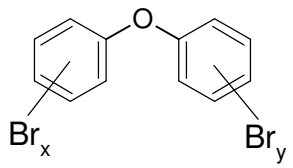
Formulation	Polymer Type	Common Usage
Penta-BDE	phenolic resins	printed circuit boards
	polyvinylchloride (PVC)	cable sheets
	polyurethane (PUR)	cushioning materials, packaging, padding
	unsaturated (Thermoset) polyester (UPE)	circuit boards, coatings
	rubber	transportation
	textiles, paints/lacquers	coatings
Octa-BDE	acrylonitrile-butadiene-styrene (ABS)	moulded parts
	polyamide (PA)	electrical connectors, automotive interior parts
	polybutylene terephthalate (PBT)	electrical connectors and components
	polystyrene (PS), high-impact PS (HIPS)	TV cabinets and back covers, electrical appliance housings
Deca-BDE	epoxy-resins	circuit boards, protective coatings
	phenolic resins	printed circuit boards
	polyacrylonitrile (PAN)	panels, electrical components
	polyamide (PA)	electrical connectors, automotive interior parts
	polybutylene terephthalate (PBT)	electrical connectors and components
	polyethylene (PE), cross-linked PE (XPE)	cross-linked wire and cable, foam tubing, weather protection and moisture barriers
	polyethylene terephthalate (PET)	electrical components
	polypropylene (PP)	conduits, electronic devices
	polystyrene (PS), high-impact PS (HIPS)	TV cabinets and back covers, electrical appliance housings
	polyvinylchloride (PVC)	cable sheets
	unsaturated (Thermoset) polyester (UPE)	circuit boards, coatings
	rubber	transportation
	textiles, paints/lacquers	coatings

Table 3

Estimated regional and global demand of the three polybrominated diphenyl ether (PBDE) technical products in 2001. Source: www.bsef.com

Technical	Americas		Europe		Asia		Others		Global Demand
Product	(metric tons)	(%)	(metric tons)	(%)	(metric tons)	(%)	(metric tons)	(%)	(metric tons)
Penta-BDE	7,100	94.7	150	2.0	150	2.0	100	1.3	7,500
Octa-BDE	1,500	39.6	610	16.1	1,500	39.6	180	4.7	3,790
Deca-BDE	24,500	43.6	7,600	13.5	23,000	41.0	1,050	1.9	56,150

PBDEs are structurally similar to the well-known polychlorinated biphenyls (PCBs). In addition to the bromine substitution, the major difference between them lies in the presence of an ether group linking the two phenyl rings (Fig. 1). PBDEs comprise a group of 209 isomers and congeners theoretically possible through bromination of the phenyl rings. However, reaction conditions for the bromination of the two rings are not disclosed by the manufacturers (Alaee et al., 2003). PBDEs are numbered according to the same IUPAC system used for numbering PCBs.



$x + y = 10 - H$

Fig. 1. General chemical structure of polybrominated diphenyl ethers (PBDEs).

1.2. PBDEs in the environment

PBDEs were first detected in the environment in the 1970s (DeCarlo, 1979; Andersson and Blomkvist, 1981). The environmental occurrence of PBDEs has been of increasing concern to scientists and policy makers since the 1990s. Sediment cores from the Baltic Sea exhibited an exponential increase of PBDEs since the late 1970s (Nylund et al., 1992). In contrast, the historical record of dioxins, PCBs and DDTs in the same cores showed a decreasing trend. At present, PBDEs are recognized as a worldwide pollution problem since they have reached remote areas such as the deep ocean, the Arctic and Antarctica (de Boer et al., 1998; Alaee et al., 1999; Chiuchiolo et al., 2004; de Wit et al., 2006). The environment and human populations in North America are considerably more contaminated than those in Europe (Hites, 2004). This is most likely due to the aforementioned higher demand in North America for Penta-BDE commercial mixtures (see Table 3).

Industrial plants manufacturing technical products along with facilities incorporating PBDEs into polymers are major point sources of these chemicals to the environment (Hale et al., 2003). Recently, electronic waste recycling facilities were highlighted as point sources of PBDEs (Wang et al., 2005). Sewage treatment plants (STPs) and landfills are also considered point sources since contaminants are concentrated in them from a variety of sources. High concentrations of PBDEs have been detected in both the effluent and sludge from STPs (Hale et al., 2003; North, 2004). Osako et al. (2004) also detected high PBDE concentrations in the raw leachate from

several landfills. On the other hand, wear and tear of products containing PBDEs constitutes a diffuse, non-point source of PBDEs. Experiments conducted by Hale et al. (2002) suggested that fragments from the disintegration of polyurethane foam may be a mechanism by which PBDEs diffuse into the atmosphere.

PBDEs tend to be stable and persistent in nature. These chemicals are often associated with soils and sediments due to their high hydrophobicity and relatively low volatility. However, air and water particulate phases constitute important transport media for the dispersion of these contaminants on local, regional and global scales. According to Watanabe and Sakai (2003), the lower brominated PBDEs are more volatile, water soluble and bioaccumulate more than higher brominated PBDEs. Many congeners have been found to accumulate in living organisms and biomagnify in food chains. Moreover, higher concentrations have been detected in marine biota as compared to terrestrial biota (de Wit, 2002).

There is only limited data available on the effects of PBDEs in living organisms. Darnerud (2003) presented a comprehensive summary of the knowledge based on tests with laboratory animals. According to this author, critical effects of the Penta-BDE formulation include neurobehavioral development disorders and thyroid hormone level alterations. Octa-BDE adverse effects include fetal toxicity and teratogenicity while the Deca-BDE negatively affects thyroid, liver and kidney morphology. Laboratory tests have shown that the Penta-BDE product is the most toxic among the three technical formulations, with Deca-BDE exhibiting the lowest toxicity. Studies on effects of

PBDEs in fish species have revealed changes in hematocrit and blood glucose as well as reduction in spawning success (see de Wit, 2002 and references therein).

1.3. PBDEs in the U.S. marine environment

Despite half of the global demand coming from North America (Table 3), the number of investigations addressing the cycling and fate of PBDEs in the U.S. environment is limited. Moreover, few data have been published on the distribution of PBDEs in U.S. marine environments. The first report was published by Kuehl et al. (1991) and is associated with a mass mortality of marine mammals. Table 4 shows a summary of the distribution of PBDE flame retardants in several U.S. marine matrices including water, sediment and biota (shellfish, finfish, birds and mammals). Whenever possible, concentrations published in different papers were converted between wet, dry and lipid weight (based on information provided by the authors) in order to facilitate comparisons. These data are discussed in the following sections.

Table 4

Average concentration of total polybrominated diphenyl ethers (PBDEs) in various U.S. marine compartments.

Sample Type	Location	Survey Years	Tissue	*n*	Σ PBDE (ng g^{-1})	Additional Information	Reference
abiotic matrices					**dry wt.**		
water	San Francisco Bay	2002		33	103[a]		Oros et al. (2005)
sediment	San Francisco Bay	2002		48	9.63		Oros et al. (2005)
invertebrates					**dry wt.**		
bivalves	Gulf of Mexico	1999	soft tissue	38	5.26		Sericano et al. (2003b)
bivalves	Pacific coast	1999	soft tissue	30	22.4		Sericano et al. (2003b)
bivalves	Atlantic coast	1999	soft tissue	52	37.8		Sericano et al. (2003b)
blue mussel (*Mytilus edulis*)	Massachusetts Bay	1999	soft tissue	2	46		Yogui and Sericano (in prep.)
blue mussel (*Mytilus edulis*)	Boston Harbor	1999	soft tissue	4	212		Yogui and Sericano (in prep.)
California mussel (*Mytilus californianus*)	San Francisco Bay	2002	soft tissue	7	29	transplant	Oros et al. (2005)
Pacific oyster (*Crassostrea gigas*)	San Francisco Bay	2002	soft tissue	5	40	transplant	Oros et al. (2005)
Asian clam (*Corbicula fluminea*)	San Francisco Bay	2002	soft tissue	2	95		Oros et al. (2005)
teleost fishes					**wet wt.**		
chum salmon (*Oncorhynchus keta*)	coast of Alaska	2000	whole body	1	0.039		Easton et al. (2002)
Chinook salmon (*Oncorhynchus tshawytscha*)	coast of Alaska	2000	whole body	1	0.485		Easton et al. (2002)
jacksmelt (*Atherinopsis californiensis*)	San Francisco Bay	2002	edible parts	3	5.70		Holden et al. (2003)
halibut	San Francisco Bay	2002	edible parts	4	14.1		Holden et al. (2003)
striped bass (*Morone saxatilis*)	San Francisco Bay	2002	edible parts	4	18.0		Holden et al. (2003)
perch	San Francisco Bay	2002	edible parts	6	21.5		Holden et al. (2003)
king fish	San Francisco Bay	2002	edible parts	4	44.1		Holden et al. (2003)
pink salmon (*Oncorhynchus gorbuscha*)	Kodiak (AK)	2001-2002	muscle + skin	3	0.049		Hites et al. (2004)
pink salmon (*Oncorhynchus gorbuscha*)	Southeast Alaska	2001-2002	muscle + skin	3	0.056		Hites et al. (2004)
chum salmon (*Oncorhynchus keta*)	Kodiak (AK)	2001-2002	muscle + skin	3	0.055		Hites et al. (2004)
chum salmon (*Oncorhynchus keta*)	Southeast Alaska	2001-2002	muscle + skin	3	0.098		Hites et al. (2004)
sockeye salmon (*Oncorhynchus nerka*)	Kodiak (AK)	2001-2002	muscle + skin	3	0.064		Hites et al. (2004)
sockeye salmon (*Oncorhynchus nerka*)	Southeast Alaska	2001-2002	muscle + skin	3	0.108		Hites et al. (2004)
coho salmon (*Oncorhynchus kisutch*)	Kodiak (AK)	2001-2002	muscle + skin	3	0.087		Hites et al. (2004)
coho salmon (*Oncorhynchus kisutch*)	southeast Alaska	2001-2002	muscle + skin	3	0.112		Hites et al. (2004)
Chinook salmon (*Oncorhynchus tshawytscha*)	southeast Alaska	2001-2002	muscle + skin	3	0.490		Hites et al. (2004)
Chinook salmon (*Oncorhynchus tshawytscha*)	coast of Oregon	2001-2002	muscle + skin	3	2.11		Hites et al. (2004)
silver perch (*Bairdiella chrysoura*)	eastern coast of Florida	2004	muscle	6	0.064		Johnson-Restrepo et al. (2005)
striped mullet (*Mugil cephalus*)	eastern coast of Florida	2004	muscle	6	0.140		Johnson-Restrepo et al. (2005)
spotted seatrout (*Cynoscion nebulosus*)	eastern coast of Florida	2004	muscle	7	0.109		Johnson-Restrepo et al. (2005)
red drum (*Sciaenops ocellatus*)	eastern coast of Florida	2004	muscle	11	0.156		Johnson-Restrepo et al. (2005)
hardhead catfish (*Arius felis*)	eastern coast of Florida	2004	muscle	8	0.788		Johnson-Restrepo et al. (2005)
speckled sanddab (*Citharichthys stigmaeus*)	coast of California	2001	muscle + skin	1	0.042		Brown et al. (2006)

Table 4 (continued)

Sample Type	Location	Survey Years	Tissue	*n*	Σ PBDE (ng g^{-1})	Additional Information	Reference
teleost fishes					**wet wt.**		
kelp rockfish (*Sebastes atrovirens*)	coast of California	2001	muscle	1	0.198		Brown et al. (2006)
rainbow surf perch	coast of California	2001	muscle + skin	1	0.349		Brown et al. (2006)
black rockfish (*Sebastes melanops*)	coast of California	2001	edible parts	1	0.894		Brown et al. (2006)
white surf perch	coast of California	2001	muscle + skin	3	1.67		Brown et al. (2006)
canary rockfish (*Sebastes pinniger*)	coast of California	2001	muscle	1	2.28		Brown et al. (2006)
kelp bass (*Paralabrax clathratus*)	coast of California	2001	muscle	1	3.79		Brown et al. (2006)
striped bass (*Morone saxatilis*)	coast of California	2000	muscle	4	4.15		Brown et al. (2006)
Pacific mackerel (*Scomber japonicus*)	coast of California	2001	muscle	1	5.06		Brown et al. (2006)
spotted sand bass (*Paralabrax maculatofasciatus*)	coast of California	2001	muscle	3	5.68		Brown et al. (2006)
shiner surf perch (*Cymatogaster aggregata*)	coast of California	2000-2001	edible parts	16	6.22		Brown et al. (2006)
jacksmelt (*Atherinopsis californiensis*)	coast of California	2000-2001	edible parts	2	6.24		Brown et al. (2006)
white croaker (*Genyonemus lineatus*)	coast of California	2000-2001	muscle + skin	6	7.14		Brown et al. (2006)
cartilaginous fishes					**wet wt.**		
leopard shark (*Triakis semifasciata*)	San Francisco Bay	2002	edible parts	1	1.42		Holden et al. (2003)
Atlantic stingray (*Dasyatis sabina*)	eastern coast of Florida	2004	muscle	7	0.208		Johnson-Restrepo et al. (2005)
spiny dogfish (*Squalus acanthias*)	eastern coast of Florida	2004	muscle	5	3.78		Johnson-Restrepo et al. (2005)
Atlantic sharpnose shark (*Rhizoprionodon terraenovae*)	eastern coast of Florida	2004	muscle	5	2.36		Johnson-Restrepo et al. (2005)
bull shark (*Carcharhinus leucas*)	eastern coast of Florida	1993-2004	muscle	13	3.49		Johnson-Restrepo et al. (2005)
fish-eating birds					**lipid wt.**		
Caspian tern (*Sterna caspia*)	Grays Bay, WA	2002	egg	20	4870		She et al. (2003)
Caspian tern (*Sterna caspia*)	San Francisco Bay	2002	egg	14	5730		She et al. (2003)
California least tern (*Sterna antillarum browni*)	San Francisco Bay	2002	egg	6	4570		She et al. (2003)
Forster's tern (*Sterna forsteri*)	San Francisco Bay	2002	egg	29	7590		She et al. (2003)
Caspian tern (*Sterna caspia*)	San Francisco Bay	2003	egg	20	6760		She et al. (2004)
California least tern (*Sterna antillarum browni*)	San Francisco Bay	2003	egg	5	5870		She et al. (2004)
Forster's tern (*Sterna forsteri*)	San Francisco Bay	2003	egg	20	9420		She et al. (2004)
osprey (*Pandion haliaetus*)	South River, Chesapeake Bay	2000	egg	15	176[b]	reference site	Rattner et al. (2004)
osprey (*Pandion haliaetus*)	Baltimore Harbor, Chesapeake Bay	2000	egg	14	320[b]		Rattner et al. (2004)
osprey (*Pandion haliaetus*)	Potomac River, Chesapeake Bay	2000	egg	16	725[b]		Rattner et al. (2004)
osprey (*Pandion haliaetus*)	South River, Chesapeake Bay	2001	egg	15	253[b]	reference site	Rattner et al. (2004)
osprey (*Pandion haliaetus*)	Elizabeth River, Chesapeake Bay	2001	egg	15	195[b]		Rattner et al. (2004)
osprey (*Pandion haliaetus*)	coast of Delaware	2002	egg	2	82.2[b]		Toschik et al. (2005)
osprey (*Pandion haliaetus*)	Delaware Bay	2002	egg	6	206[b]		Toschik et al. (2005)
osprey (*Pandion haliaetus*)	Delaware Estuary	2002	egg	6	572[b]		Toschik et al. (2005)

Table 4 (continued)

Sample Type	Location	Survey Years	Tissue	*n*	Σ PBDE (ng g^{-1})	Additional Information	Reference
mammals (Order Carnivora)					**lipid wt.**		
harbor seal (*Phoca vitulina*)	San Francisco Bay	1992	blubber	1	430	fetus	She et al. (2002)
harbor seal (*Phoca vitulina*)	San Francisco Bay	1989-1998	blubber	4	449	adult (F)	She et al. (2002)
harbor seal (*Phoca vitulina*)	San Francisco Bay	1989-1998	blubber	6	2584	adult (M)	She et al. (2002)
harbor seal (*Phoca vitulina*)	San Francisco Bay	2001-2002	blood	33	760		Neale et al. (2005)
polar bear (*Ursus maritimus*)	northern Alaska	1993-2000	liver	8	11.9	adult (M/F)	Kannan et al. (2005)
polar bear (*Ursus maritimus*)	western Alaska	1994-2002	liver	27	11.2	all ages (M/F)	Kannan et al. (2005)
polar bear (*Ursus maritimus*)	northwestern Alaska	1994-2002	fat	8	6.71	F	Muir et al. (2006)
polar bear (*Ursus maritimus*)	northwestern Alaska	1994-2002	fat	7	6.84	M	Muir et al. (2006)
California sea lion (*Zalophus californianus*)	coast of California	1993-2003	blubber	25	5036	M	Stapleton et al. (2006)
spotted seal (*Phoca largha*)	Bristol Bay (AK)	2000-2001	blood	5	0.280	F	Neale et al. (2007)
spotted seal (*Phoca largha*)	Bristol Bay (AK)	2000-2001	blood	2	0.456	M	Neale et al. (2007)
bearded seal (*Erignathus barbatus*)	Bering Sea (AK)	2003	blubber	5	3.42	M/F	Quakenbush (2007)
ringed seal (*Phoca hispida*)	Bering Sea (AK)	2003	blubber	6	5.85	M/F	Quakenbush (2007)
spotted seal (*Phoca largha*)	Bering Sea (AK)	2003	blubber	3	12.4	M/F	Quakenbush (2007)
ribbon seal (*Phoca fasciata*)	Bering Sea (AK)	2003	blubber	6	16.5	M/F	Quakenbush (2007)
California sea otter (*Enhydra lutris nereis*)	coast of California	1992-2002	liver	80	2170	adult (F)	Kannan et al. (2007)
Alaskan sea otter (*Enhydra lutris kenyoni*)	Aleutians (AK)	1996	liver	2	329	adult (F)	Kannan et al. (2008)
Alaskan sea otter (*Enhydra lutris kenyoni*)	Prince William Sound (AK)	1996-1998	liver	3	785	adult (M/F)	Kannan et al. (2008)
Alaskan sea otter (*Enhydra lutris kenyoni*)	coast of Washington	1995-1998	liver	6	941	adult (M/F)	Kannan et al. (2008)
California sea otter (*Enhydra lutris nereis*)	Monterrey Bay (CA)	1995-1998	liver	6	2240	adult (M/F)	Kannan et al. (2008)
mammals (Order Cetacea)					**lipid wt.**		
bottlenose dolphin (*Tursiops truncatus*)	Atlantic coast (VA)	1987	blubber	3	200	adult (F)	Kuehl et al. (1991)
bottlenose dolphin (*Tursiops truncatus*)	Gulf of Mexico (TX)	1990-1991	blubber	2	115	fetus	Kuehl and Haebler (1995)
bottlenose dolphin (*Tursiops truncatus*)	Gulf of Mexico (TX)	1990	blubber	5	313	suckling (M/F)	Kuehl and Haebler (1995)
bottlenose dolphin (*Tursiops truncatus*)	Gulf of Mexico (TX)	1990	blubber	5	1900	juvenile (M/F)	Kuehl and Haebler (1995)
bottlenose dolphin (*Tursiops truncatus*)	Gulf of Mexico (TX)	1990-1991	blubber	5	190	adult (F)	Kuehl and Haebler (1995)
bottlenose dolphin (*Tursiops truncatus*)	Gulf of Mexico (TX, AL)	1990	blubber	8	3110	adult (M)	Kuehl and Haebler (1995)
killer whale (*Orcinus orca*)	Pacific coast (AK)	1993	blubber	8	415	northern resident; F	Rayne et al. (2004)
killer whale (*Orcinus orca*)	Pacific coast (AK)	1993-1994	blubber	13	203	northern resident; M	Rayne et al. (2004)
killer whale (*Orcinus orca*)	Pacific coast (WA)	1993-1995	blubber	5	942	southern resident; M	Rayne et al. (2004)
killer whale (*Orcinus orca*)	Pacific coast (WA, AK)	1993-1997	blubber	7	885	transient; F	Rayne et al. (2004)
killer whale (*Orcinus orca*)	Pacific coast (WA, AK)	1993-1996	blubber	6	1014	transient; M	Rayne et al. (2004)
Atlantic white-sided dolphin (*Lagenorhynchus acutus*)	Atlantic coast (MA)	1993-2000	blubber	23	2410[b]	juvenile (M/F)	Tuerk et al. (2005a)
Atlantic white-sided dolphin (*Lagenorhynchus acutus*)	Atlantic coast (MA)	1993-2000	blubber	9	609[b]	adult (F)	Tuerk et al. (2005a)
Atlantic white-sided dolphin (*Lagenorhynchus acutus*)	Atlantic coast (MA)	1993-2000	blubber	15	1820[b]	adult (M)	Tuerk et al. (2005a)
rough-toothed dolphin (*Steno bredanensis*)	Gulf of Mexico (FL)	1997	blubber	7	1360[b]	juvenile (M/F)	Tuerk et al. (2005a)
rough-toothed dolphin (*Steno bredanensis*)	Gulf of Mexico (FL)	1997	blubber	6	510[b]	adult (F)	Tuerk et al. (2005a)

Table 4 (continued)

Sample Type	Location	Survey Years	Tissue	*n*	Σ PBDE (ng g^{-1})	Additional Information	Reference
mammals (Order Cetacea)					**lipid wt.**		
striped dolphin (*Stenella coeruleoalba*)	Gulf of Mexico (FL)	1994	blubber	1	660	adult (F)	Johnson-Restrepo et al. (2005)
bottlenose dolphin (*Tursiops truncatus*)	Gulf of Mexico (FL)	1991-2001	blubber	14	817	all ages	Johnson-Restrepo et al. (2005)
bottlenose dolphin (*Tursiops truncatus*)	Atlantic coast (FL)	2001-2004	blubber	6	1130	all ages	Johnson-Restrepo et al. (2005)
bottlenose dolphin (*Tursiops truncatus*)	Atlantic coast (FL)	2002-2004	blubber	6	21[b]	adult (F)	Litz et al. (2007)[c]
bottlenose dolphin (*Tursiops truncatus*)	Atlantic coast (FL)	2002-2004	blubber	31	394[b]	adult (M), juvenile (M/F)	Litz et al. (2007)[c]
bottlenose dolphin (*Tursiops truncatus*)	Atlantic coast (FL)	2003-2004	blubber	16	718	adult (F)	Fair et al. (2007)
bottlenose dolphin (*Tursiops truncatus*)	Atlantic coast (FL)	2003-2004	blubber	25	1690	adult (M)	Fair et al. (2007)
bottlenose dolphin (*Tursiops truncatus*)	Atlantic coast (FL)	2003-2004	blubber	11	979	juvenile (M)	Fair et al. (2007)
bottlenose dolphin (*Tursiops truncatus*)	Atlantic coast (SC)	2003-2004	blubber	9	1153	adult (F)	Fair et al. (2007)
bottlenose dolphin (*Tursiops truncatus*)	Atlantic coast (SC)	2003-2004	blubber	31	6830	adult (M)	Fair et al. (2007)
bottlenose dolphin (*Tursiops truncatus*)	Atlantic coast (SC)	2003-2004	blubber	13	7055	juvenile (M/F)	Fair et al. (2007)
killer whale (*Orcinus orca*)	Pacific coast (AK)	2003-2004	blubber	40	76	northern resident; adult (M)	Krahn et al. (2007b)
killer whale (*Orcinus orca*)	Pacific coast (AK)	2003-2004	blubber	4	3300	offshore; adult (M)	Krahn et al. (2007b)
killer whale (*Orcinus orca*)	Pacific coast (CA, AK)	2003-2004	blubber	16	6695	transient; adult (M)	Krahn et al. (2007b)
killer whale (*Orcinus orca*)	Pacific coast (WA)	2006	blubber	1	7500	southern resident; F	Krahn et al. (2007a)
killer whale (*Orcinus orca*)	Pacific coast (WA)	2004-2006	blubber	8	5275	southern resident; M	Krahn et al. (2007a)

[a] concentration expressed as pg L^{-1}

[b] concentration in wet weight

[c] geometric mean

1.3.1. Water, sediment and bivalves

Considering the limited number of publications on PBDEs concentration in matrices from U.S. coastal waters, San Francisco Bay is comparatively well studied with regard to PBDEs contamination. North (2004) tracked PBDE releases from a tertiary wastewater treatment plant in Palo Alto, CA and estimated that the treated effluent discharges about 0.9 kilogram of PBDEs into San Francisco Bay every year. Over 70% of that load was comprised of BDE-47 plus BDE-99 which are the major congeners in the Penta-BDE commercial mixture. Conversely, BDE-209 which is the principal congener in the Deca-BDE mixture (see Table 1) represented only 5% of total PBDEs. BDE-209 has low water solubility (log $K_{OW} \approx 10$) and in discharged effluents it is likely associated with suspended particles remaining in the effluent after treatment (North, 2004). If similar introduction rates apply to all wastewater treatment plants in the vicinity of San Francisco Bay, annual PBDE amounts entering the estuary would be an order of magnitude higher than for PCBs (Oros et al., 2005). Such findings highlight that sewage treatment plants are significant point sources of PBDEs in some coastal waters (North, 2004).

Oros et al. (2005) investigated PBDEs in the water, sediments and bivalves of San Francisco Bay. Concentrations in water ranged from 3 to 513 pg L^{-1} (mean: 103 pg L^{-1}). The highest values were found in the highly urbanized southern portion of the bay (103-513 pg L^{-1}) while the lowest values were in non-urbanized areas such as the mouth of the Sacramento and San Joaquin rivers (3-43 pg L^{-1}). Over 78% of PBDEs in water

was associated with the particulate phase (Oros et al., 2005). Average concentrations in sediments were 9.63 ng g^{-1} dry weight (dw) (range: nd-212 ng g^{-1} dw). According to the authors, these concentrations are higher than concentrations observed in the coastal environments of Europe. Mean levels of PBDEs found in California mussels (*Mytilus californianus*), Pacific oysters (*Crassostrea gigas*) and Asian clams (*Corbicula fluminea*) were 29 ng g^{-1} dw (range: 13-47 ng g^{-1} dw), 40 ng g^{-1} dw (range: 9-64 ng g^{-1} dw) and 95 ng g^{-1} dw (range: 85-106 ng g^{-1} dw), respectively. Mussels and oysters were transplanted from uncontaminated sites to San Francisco Bay, whereas clams were resident organisms. Thus, the higher levels observed in clams may be due to extended periods of exposure (i.e., greater than 90 days) (Oros et al., 2005). Of 22 PBDEs investigated, only 18, 5 and 3 individual congeners were detected in water, sediment and bivalves, respectively. This suggests that not all congeners are readily bioavailable since only BDEs 47, 99 and 100 were found in bivalves tissues.

Yogui and Sericano (in preparation) analyzed PBDEs in blue mussels (*Mytilus edulis*) from Massachusetts Bay and Boston Harbor. Average concentrations in the former and latter sites were 46 ng g^{-1} dw (range: 33-59 ng g^{-1} dw) and 212 ng g^{-1} dw (range: 103-366 ng g^{-1} dw), respectively. These levels are comparable to those detected in bivalves from San Francisco Bay and are as much as three orders of magnitude higher than detected in mussels from Europe, Asia and Greenland (Yogui and Sericano, in preparation). Sericano et al. (2003b) investigated PBDEs in bivalves from coastal environments along the three U.S. coasts. Mean concentrations in the Gulf of Mexico, Pacific coast and Atlantic coast were 5.26 ng g^{-1} dw (range: 0.61-366 ng g^{-1} dw), 22.4 ng

g^{-1} dw (range: nd-52.5 ng g^{-1} dw) and 37.8 ng g^{-1} dw (range: nd-145 ng g^{-1} dw), respectively. The highest levels were detected in two of the most developed coastal areas of the U.S. namely Boston, MA on the Atlantic coast and San Francisco, CA on the Pacific coast. In the Gulf of Mexico, Galveston Bay, TX and Tampa Bay, FL exhibited the highest contamination with PBDEs although the levels were well below those reported for Boston Harbor and San Francisco Bay.

1.3.2. Teleost and cartilaginous fishes

Easton et al. (2002) investigated PBDEs in wild salmon from Alaska. Concentration levels in chum and Chinook salmon were 0.039 ng g^{-1} wet weight (ww) and 0.485 ng g^{-1} ww, respectively. Similarly, Hites et al. (2004) analyzed PBDEs in five wild salmon species caught in the waters of Alaska and Oregon. Average contamination in coho (*Oncorhynchus kisutch*), chum (*O. keta*), pink (*O. gorbuscha*) and sockeye (*O. nerka*) caught in Alaskan waters ranged from 0.049 ng g^{-1} ww to 0.112 ng g^{-1} ww. In contrast, average concentrations in Chinook (*O. tshawytscha*) from Alaska and Oregon were 0.490 ng g^{-1} ww and 2.11 ng g^{-1} ww, respectively. These two independent studies found differences between Chinook and the other four salmon species that are likely due to differences in feeding habits (Hites et al., 2004). Coho, chum, pink and sockeye salmon diets are based on zooplankton and invertebrates while Chinook salmon tends to feed on higher trophic level organisms. In addition, Chinook salmon caught in coastal

waters of the highly urbanized continental U.S. (i.e., Oregon) exhibited higher PBDE levels than the same fish species from less urbanized areas in Alaska.

Johnson-Restrepo et al. (2005) analyzed PBDEs in teleost and cartilaginous fishes from the eastern coast of Florida. Average contaminant levels in the muscle tissue of teleost fishes ranged from 0.064 ng g^{-1} ww (in silver perch, *Bairdiella chrysoura*) to 0.788 ng g^{-1} ww (in hardhead catfish, *Arius felis*). In cartilaginous fish, mean concentrations ranged from 0.208 ng g^{-1} ww (in Atlantic stingray, *Dasyatis sabina*) to 3.78 ng g^{-1} ww (in spiny dogfish, *Squalus acanthias*). The wide range of values was attributed to differences in feeding habits and trophic level (Johnson-Restrepo et al., 2005). Interestingly, BDE-47 was the major congener detected in bony fish while BDE-209 was the most abundant in sharks. According to the authors, high levels of BDE-209 in all shark species suggest exposure to the Deca-BDE formulation and lack of metabolism of the fully brominated congener.

Brown et al. (2006) measured organohalogenated compounds in edible parts of several bony fish caught along the California coast. Average concentration of PBDEs ranged from 0.042 ng g^{-1} ww (in speckled sanddab, *Citharichthys stigmaeus*) to 7.14 ng g^{-1} ww (in white croaker, *Genyonemus lineatus*). The highest PBDE levels were found in areas of highest population density such as San Francisco Bay, Los Angeles and San Diego Bay (Brown et al., 2006). This is consistent with the idea that PBDEs are a legacy of urban, modern societies. Holden et al. (2003) quantified PBDEs in whole fish (minus head, tail and guts) collected from San Francisco Bay in 2002. Contamination in bony fish ranged from 5.70 ng g^{-1} ww in jacksmelt to 44.1 ng g^{-1} ww in king fish.

Additionally, a specimen of leopard shark (*Triakis semifasciata*) contained total PBDEs of 1.42 ng g^{-1} ww. Although these samples were collected from highly contaminated areas of San Francisco Bay, PBDE levels found by Holden et al. (2003) are among the highest ever measured in fish species.

1.3.3. Fish-eating birds

Osprey (*Pandion haliaetus*) is a fish-eating bird that has been recognized as an excellent sentinel of environmental contamination in estuarine systems (Golden and Rattner, 2003). In 2000-2001, Rattner et al. (2004) monitored PBDEs in eggs of osprey nesting at Chesapeake Bay. Mean PBDEs concentration in reference sites ranged from 176 ng g^{-1} ww to 253 ng g^{-1} ww, whereas average contamination in regions of concern ranged from 195 ng g^{-1} ww to 725 ng g^{-1} ww. According to the authors, sites such as Anacostia and middle Potomac rivers are statistically more impacted by PBDEs than reference sites. Nevertheless, this study was inconclusive about whether contaminant levels were affecting the reproductive success of ospreys in Chesapeake Bay. Similarly, Toschik et al. (2005) investigated PBDEs in ospreys breeding at Delaware Bay. Average concentration of PBDEs in eggs was 82.2 ng g^{-1} ww (range: 70.9-93.5 ng g^{-1} ww) along the coast of Delaware, 206 ng g^{-1} ww (range: 141-429 ng g^{-1} ww) in Delaware Bay and 572 ng g^{-1} ww (range: 442-820 ng g^{-1} ww) in the Delaware estuary. These results documented a decrease in contamination towards the open ocean and reflect distance from pollution sources as well as differences in congener mobility (Toschik et al., 2005).

BDE-47 appears to be the most bioavailable congener since it is the predominant congener in samples representing 31% to 69% of the total PBDEs present. Furthermore, BDE-47 is at higher proportion in osprey eggs collected along the coast of Delaware (i.e., farther from pollution sources) suggesting that its higher volatility and higher water solubility make it more mobile and recalcitrant once released to the environment (Toschik et al., 2005).

In 2002, She et al. (2003) investigated PBDEs in seabird eggs collected from nesting sites at San Francisco Bay, CA and Grays Bay, WA. Eggs of Caspian tern (*Sterna caspia*) contained higher average contamination at the former site (5,730 ng g^{-1} lipid) than in the latter (4,870 ng g^{-1} lipid). Additionally, mean PBDEs concentrations in California least tern (*Sterna antillarum browni*) and Forster's tern (*Sterna forsteri*) from San Francisco Bay were 4,570 ng g^{-1} lipid and 7,590 ng g^{-1} lipid, respectively. In the following breeding season (i.e., 2003), total PBDEs increased in all three tern species nesting near San Francisco Bay. Average contaminant levels were 6,760 ng g^{-1} lipid in Caspian tern, 5,870 ng g^{-1} lipid in California least tern and 9,420 ng g^{-1} lipid in Forster's tern (She et al., 2004). Furthermore, a concentration of 63,300 ng g^{-1} lipid was found in one of the Forster's tern eggs. According to the authors, this value is the highest PBDE level ever reported in wildlife or humans tissues (She et al., 2004).

1.3.4. Mammals: pinnipeds, sea otters and polar bears

The polar bear (*Ursus maritimus*) is a key species of the Arctic marine ecosystem that has been threatened by both climate change and persistent organic pollutants (POPs). Muir et al. (2006) investigated PBDEs in adipose tissue of polar bears from several Arctic regions. Average concentration in individuals from Alaska was 6.71 ng g^{-1} lipid (range: 4.64-11.3 ng g^{-1} lipid) in females and 6.84 ng g^{-1} lipid (range: 2.91-16.6 ng g^{-1} lipid) in males. These values were comparable to those found in polar bears from Canada, but significantly lower than individuals from East Greenland and Svalbard (Muir et al., 2006). This suggests that the North American Arctic may be less impacted than the European Arctic reflecting the greater proximity of the latter to sources of pollution. Kannan et al. (2005) measured PBDEs in liver tissues of two subpopulations of polar bear from Alaska. Mean concentration in the northern and western subpopulations were respectively 11.9 ng g^{-1} lipid and 11.2 ng g^{-1} lipid. No statistical difference was found in levels of PBDEs between the two groups. In addition, PBDEs were not correlated with age in either gender (Kannan et al., 2005). Interestingly, these authors targeted eight major congeners (i.e., IUPAC Nos. 28, 30, 47, 85, 99, 100, 153 and 154) but only BDE-47 was detected in the liver of polar bears.

Sea otters have been considered suitable indicators of local pollution by organic contaminants because of their sedentary behavior and diet mainly comprised of benthic invertebrates (Bacon et al., 1999). Kannan et al. (2008) measured PBDEs in the liver of two sea otter subspecies from California, Washington and Alaska. Mean contamination

in Alaskan sea otters (*Enhydra lutris kenyoni*) was 557 ng g^{-1} lipid and 941 ng g^{-1} lipid in samples collected at Alaska and Washington, respectively. Conversely, concentration in California sea otters (*Enhydra lutris nereis*) was more than two-fold higher, averaging 2,240 ng g^{-1} lipid. Interestingly, levels of PBDEs in sea otters were positively correlated with human population density in the study areas (Kannan et al., 2008). Kannan et al. (2007) assessed the occurrence of organohalogenated contaminants and infectious diseases in sea otters from the California coast. Concentration of PBDEs in liver tissues ranged from 10 ng g^{-1} lipid to 26,800 ng g^{-1} lipid (mean: 2,170 ng g^{-1} lipid). Despite PBDEs being lower in well-nourished animals, no significant association was found between concentration of PBDEs and the health status of sea otters (Kannan et al., 2007).

Stapleton et al. (2006) determined PBDEs in archived blubber of 25 male California sea lions (*Zalophus californianus*) and found an average concentration of 5,036 ng g^{-1} lipid (range: 570-24,240 ng g^{-1} lipid). According to the authors, the levels of PBDE found in sea lions from the California coast are among the highest ever reported for marine mammals. BDE-100 was generally detected at higher concentration than BDE-99 in this species. Considering that the opposite is true in the Penta-BDE technical formulation, it indicates that California sea lions metabolize BDE-99 to some extent (Stapleton et al., 2006). Quakenbush (2007) determined PBDE baseline levels in the blubber of four seal species harvested by Arctic natives in the Bering Sea, AK. Average concentrations of PBDEs were as follows: 3.42 ng g^{-1} ww in bearded seal (*Erignathus barbatus*), 5.85 ng g^{-1} ww in ringed seal (*Phoca hispida*), 12.4 ng g^{-1} ww in spotted seal

(*Phoca largha*) and 16.5 ng g^{-1} ww in ribbon seal (*Phoca fasciata*). Only 11 out of 38 investigated congeners were detected in the animals. Surprisingly, IUPAC Nos. 2 and 30 were the dominant congeners in the four species while penta- through hexa-BDEs were not detected in any sample, including BDEs 99, 100 and 153 (Quakenbush, 2007). BDE-47 was detected only in the spotted seal which forages at the highest trophic level among the four species studied (Quakenbush, 2007).

Harbor seal (*Phoca vitulina*) is a non-migratory species in San Francisco Bay and has been considered an excellent indicator of the health of this estuarine system (Kopec and Harvey, 1995). She et al. (2002) investigated PBDEs in archived blubber of harbor seals from San Francisco Bay. Contamination levels ranging from 88 to 8,325 ng g^{-1} lipid are among the highest reported for this species. Average concentrations in adult male and female were 2,584 ng g^{-1} lipid and 449 ng g^{-1} lipid, respectively. Differences in PBDE concentrations between sexes suggest that females transfer part of their load to offspring during gestation and lactation as observed for other persistent organic pollutants in marine mammal species (e.g., Borrell et al., 1995). Indeed, She et al. (2002) analyzed samples from a mother-fetus pair and suggested that lower brominated diphenyl ethers are more likely to be transferred than higher brominated congeners.

Neale et al. (2005) analyzed BDEs 47, 99 and 153 in blood samples from 33 harbor seals living in San Francisco Bay. Mean contamination was 760 ng g^{-1} lipid. According to the authors, PBDEs were significantly positively correlated with leukocyte counts and negatively correlated with red blood cell counts. Though PBDE levels are not necessarily pathologic, such responses might be used as proxies for contaminant-induced

changes in harbor seals (Neale et al., 2005). In Alaska, the spotted seal is strongly associated with sea-ice and can be found in coastal areas only during summers. Neale et al. (2007) investigated BDEs 47, 99 and 153 in blood of clinically healthy, free-ranging spotted seals captured at Bristol Bay, AK. Only BDEs 47 and 99 were detected in the animals. Average concentration of PBDEs was 0.456 ng g^{-1} lipid and 0.280 ng g^{-1} lipid in males and females, respectively. Such levels are three orders of magnitude lower than harbor seals from San Francisco Bay (see Neale et al., 2005), reflecting the more pristine environment in Alaska.

1.3.5. Mammals: cetaceans

Bottlenose dolphins (*Tursiops truncatus*) are the most common small cetacean in coastal waters of the southeastern U.S., and are one of the best studied species. Kuehl et al. (1991) investigated anthropogenic organic contaminants in carcasses of bottlenose dolphins stranded during a mass mortality event between June 1987 and March 1988. Over this period, more than 740 dead animals were found along Atlantic coast beaches from New Jersey to Florida. Although chemical contamination was not identified as a cause for the mass mortality, high concentrations of organic contaminants were found in the recovered carcasses. Average PBDEs in the blubber of three adult female dolphins was 200 ng g^{-1} lipid (range: 180-220 ng g^{-1} lipid). A second mortality event occurred in the Gulf of Mexico in 1990 (Kuehl and Haebler, 1995). In the first three months of that year, 293 bottlenose dolphins were found dead along beaches of the five Gulf States.

Mean PBDE concentrations in the blubber of adult male and female were 3,110 ng g^{-1} lipid and 190 ng g^{-1} lipid, respectively. Average PBDE levels in pooled (i.e., male and female) fetus, suckling and juvenile animals were 115 ng g^{-1} lipid, 313 ng g^{-1} lipid and 1,900 ng g^{-1} lipid, respectively. However, an adult female contained a maximum concentration of 20,000 ng g^{-1} lipid.

Litz et al. (2007) studied fine-scale spatial variation of POPs in bottlenose dolphins from Biscayne Bay, FL. Dart biopsy samples were collected from animals that live year-round in the estuarine waters of the bay. Average concentrations of PBDEs were 21 ng g^{-1} ww in adult females and 394 ng g^{-1} ww in all other pooled dolphins (i.e., adult males and juveniles of both genders). Contamination was significantly higher in males and juveniles than in females. In addition, PBDEs were higher in dolphins from the northern portion of Biscayne Bay when compared to animals that occupy the southern areas of the bay. Such a fine-scale spatial heterogeneity is likely associated with the greater urbanization and industrialization around the city of Miami which is located in the northern part of the bay (Litz et al., 2007). In contrast, Johnson-Restrepo et al. (2005) did not find statistical differences in the levels of PBDE between bottlenose dolphins from the east and west coasts of Florida. Concentrations of PBDEs averaged 817 ng g^{-1} lipid and 1,130 ng g^{-1} lipid in the blubber of animals from the west (Gulf of Mexico) and east (Atlantic Ocean) coasts, respectively. These values are higher than the level of 660 ng g^{-1} lipid found in the blubber of an adult female striped dolphin (*Stenella coeruleoalba*) from the west coast of Florida (Johnson-Restrepo et al., 2005). Fair et al. (2007) conducted capture-release studies with free-ranging bottlenose dolphins from

Charleston Harbor, SC and Indian River Lagoon, FL. Mean PBDEs in dolphins from the Charleston Harbor estuary were as follows: 1,153 ng g^{-1} lipid in adult females, 6,830 ng g^{-1} lipid in adult males and 7,055 ng g^{-1} lipid in pooled juveniles. Conversely, contamination in the blubber of animals from the Indian River Lagoon was 718 ng g^{-1} lipid in adult females, 1,690 ng g^{-1} lipid in adult males and 979 ng g^{-1} lipid in juvenile males. Higher levels in dolphins from South Carolina were attributed to higher population densities as well as effluent inputs from wastewater treatment facilities in the Charleston Harbor estuary (Fair et al., 2007).

Tuerk et al. (2005a) assessed PBDEs in carcasses of Atlantic white-sided dolphins (*Lagenorhynchus acutus*) and rough-toothed dolphins (*Steno bredanensis*) from stranding events along the Massachusetts coast and west coast of Florida, respectively. Mean contaminant levels in the Atlantic white-sided dolphin were as follows: 609 ng g^{-1} ww in adult females, 1,820 ng g^{-1} ww in adult males and 2,410 ng g^{-1} ww in pooled juveniles. Average concentrations in the rough-toothed dolphin were 510 ng g^{-1} ww in adult females and 1,360 ng g^{-1} ww in pooled juveniles, respectively. In both species, concentration of PBDEs was statistically lower in adult females than in adult males and juveniles (Tuerk et al., 2005a). The burden of PBDEs significantly decreased with length in males of Atlantic white-sided dolphin which might suggest metabolic elimination of contaminants (Tuerk et al., 2005b). Alternatively, this might be associated with contaminant dilution due to growth of male dolphins, a phenomenon known as growth dilution.

In the northeastern Pacific Ocean there are three ecotypes of killer whale (*Orcinus orca*) that inhabit the coastal waters of the U.S. and Canada: resident, transient and offshore (Ford et al., 2000; Krahn et al., 2007b). The distribution range of transient and offshore killer whales extends from Alaska to California. However, they differ in several biological and ecological aspects (see Krahn et al., 2007b and references therein). In the U.S., the resident ecotype can be further separated into northern and southern residents which occupy protected waters of Alaska and Washington States, respectively (Rayne et al., 2004). In the 1990s, Rayne et al. (2004) analyzed PBDEs in 39 killer whales belonging to three distinct communities. Average contamination levels in the northern residents were 203 ng g^{-1} lipid (range: 26.8-758 ng g^{-1} lipid) and 415 ng g^{-1} lipid (range: 23.4-2,828 ng g^{-1} lipid) for males and females, respectively. Mean total PBDE in male southern residents was 942 ng g^{-1} lipid (range: 242-1,812 ng g^{-1} lipid), whereas mean concentrations in the transient community were 1,014 ng g^{-1} lipid (range: 492-2,250 ng g^{-1} lipid) in males and 885 ng g^{-1} lipid (range: 162-2,896 ng g^{-1} lipid) in females. In 2003-2004, Krahn et al. (2007b) studied PBDEs in adult males belonging to distinct killer whale ecotypes from the northeastern Pacific. Average concentrations were as follows: 76 ng g^{-1} lipid (range: <LOQ-270 ng g^{-1} lipid) in northern residents, 6,695 ng g^{-1} lipid (range: 93-12,600 ng g^{-1} lipid) in transients and 3,300 ng g^{-1} lipid (range: 2,200-4,400 ng g^{-1} lipid) in offshore animals. In comparison to the study conducted by Rayne et al. (2004), PBDE levels were 6.5 times higher in transients and 2.5 times lower in northern residents. In 2004/2006, Krahn et al. (2007a) measured PBDEs in southern resident killer whales from Puget Sound, WA. Total PBDEs

averaged 7,500 ng g^{-1} lipid in females and 5,275 ng g^{-1} lipid in males. These values are an order of magnitude higher than those found ten years earlier by Rayne et al. (2004) in the same community. Overall, contamination seems to be stable or decreasing in the northern residents from Alaska while it is increasing in the transients and southern residents from Puget Sound, WA. Northern residents also appear to be the least contaminated community. This may be associated with the consumption of less contaminated prey items as well as differences in feeding habits (Rayne et al., 2004). Comparing northern and southern residents, the former community inhabits relatively pristine coastal waters while the latter spends more time in the urbanized Puget Sound, WA. In Alaska, northern residents have a diet that consists of fish (especially salmonids), whereas it is known that both transient and offshore whales feed on higher trophic levels (e.g., marine mammals) (Ford et al., 1998; Krahn et al., 2007b). Additionally, the distribution of offshore and transients extends southward to the highly urbanized California coast which also explains part of their contamination.

1.3.6. Temporal trends

In general, investigations of temporal trends have revealed that PBDEs are increasing in North America and decreasing in Europe and Japan (Hale et al., 2003 and references therein). She et al. (2002) investigated PBDEs in archived harbor seals from San Francisco Bay between 1989 and 1998. According to the authors, concentrations in harbor seal blubber increased almost two orders of magnitude during that period.

Preliminary results reported by Holden et al. (2003) also suggest that levels of PBDE doubled in bony fishes from San Francisco Bay between 1997 and 2002. Johnson-Restrepo et al. (2005) observed exponential increase of PBDEs in both sharks and dolphins from Florida. The doubling time of PBDEs was estimated to be 2-3 years for bull sharks and 3-4 years for bottlenose dolphins in the period 1991-2004 (Johnson-Restrepo et al., 2005). These findings are in concert with other studies in aquatic environments of the Great Lakes (Luross et al., 2000; Zhu and Hites, 2004). Yogui and Sericano (in preparation) analyzed PBDEs in archived blue mussels collected in Boston Harbor and Massachusetts Bay between 1990 and 1999. These samples were part of the NOAA National Status and Trends Mussel Watch Program. They found a significant increase in contamination at Deer Island, Boston Harbor. Conversely, no trends with time were distinguishable at five other sites in the same area. The authors postulate that such findings may be associated with a comprehensive clean-up program initiated in the Boston Harbor in the early 1990s. Tuerk et al. (2005a) investigated time trends of PBDEs in juvenile Atlantic white-sided dolphins stranded near Cape Cod, MA between 1993 and 2000. Similar to most sites in Boston Harbor and Massachusetts Bay, contamination of PBDEs in the blubber of juvenile dolphins did not exhibit a significant temporal trend. Stapleton et al. (2006) measured PBDEs in California sea lions stranded between 1993 and 2003. They did not observe temporal trends in the concentration of either total PBDEs or individual congeners. Kannan et al. (2007) also found no significant trends in PBDE over time in sea otters from coastal California. In summary, the studies above suggest that temporal trends of PBDEs in the U.S. coastal environment

are site-specific and linked with the history of contamination at the site and in some cases with remediation efforts. However, it is important to emphasize that these investigations did not detect a temporal decrease in contaminant concentrations, indicating that PBDEs will continue to be an issue of concern in the future.

1.4. PBDEs in Antarctica

Few researchers have investigated the distribution of flame retardants in Antarctica. Chiuchiolo et al. (2004) measured PBDEs at the base of the marine food web of the western Antarctic Peninsula. Concentration of PBDEs in sea ice particulate matter (mainly algae growing on ice) was 13,920 ng g^{-1} lipid. Contamination in plankton samples (mainly diatoms of the genus *Thalassiosira*) averaged 49.7 ng g^{-1} lipid. According to the authors, detection of PBDEs in primary producers of Antarctica indicates retention of long-range transported contaminants at the ocean surface and subsequent uptake by marine phytoplankton. Juvenile and adult krill exhibited mean concentrations of 1,318 ng g^{-1} lipid and 5.0 ng g^{-1} lipid, respectively. Several causes might explain these differences such as dilution of contaminants due to growth of juvenile krill and accumulation of lipid reserves in adult krill (Chiuchiolo et al., 2004). In addition, juvenile krill feeds on more contaminated sea ice algae while adult krill forages on phytoplankton living in the water column. No biomagnification of PBDEs was observed from plankton to krill (Chiuchiolo et al., 2004).

In the Ross Sea, Corsolini et al. (2006) investigated POPs in krill (*Euphausia superba*), fish (emerald rockcod, *Trematomus bernacchii*) and eggs of Adélie penguin (*Pygoscelis adeliae*). Concentration of PBDEs in krill averaged 5.60 ng g^{-1} lipid. This is in good agreement with levels found in adult krill of the western Antarctic Peninsula (Chiuchiolo et al., 2004). PBDEs in emerald rockcod caught in the Ross Sea exhibited similar concentrations in muscle (5.81 ng g^{-1} lipid) and whole body homogenate (4.57 ng g^{-1} lipid). Eggs of Adélie penguin had an average contamination of 3.06 ng g^{-1} lipid. BDE-47 was the most abundant congener in all tissues, constituting 50% to 73% of the total PBDEs (Corsolini et al., 2006). In the Ross Sea food web, PBDE congeners were not biomagnified from krill to fish which might suggest metabolic elimination in the emerald rockcod (Corsolini et al., 2006).

Corsolini et al. (2007) collected blood samples for analysis of POPs in three species of penguin breeding sympatrically at King George Island, Antarctic Peninsula. Average concentration of PBDEs was 0.291 ng g^{-1} ww (range: 0.002-1.73 ng g^{-1} ww), 0.108 ng g^{-1} ww (range: 0.002-0.278 ng g^{-1} ww) and 0.117 ng g^{-1} ww (range: 0.004-0.307 ng g^{-1} ww) in Adélie (*Pygoscelis adeliae*), chinstrap (*Pygoscelis antarctica*) and gentoo (*Pygoscelis papua*) penguins, respectively. PBDEs represented approximately 1% of the total POPs residue while *p,p'*-DDE, HCB and PCBs were the dominant contaminants in blood samples (Corsolini et al., 2007). Sericano et al. (2003a) analyzed PBDEs in archived adipose tissues of seabirds collected at King George Island. Mean concentration of PBDEs in brown skua (*Catharacta antarctica lonnbergi*) was 259 ng g^{-1} lipid (range: 91.2-551 ng g^{-1} lipid). In contrast, BDE-47 was the only congener detected

at low levels (range: nd-7.80 ng g^{-1} lipid) in a few individuals of Adélie penguin, chinstrap penguin, gentoo penguin, Antarctic tern (*Sterna vittata*), snowy sheathbill (*Chionis alba*) and blue-eyed shag (*Phalacrocorax atriceps*). It is interesting to note that Sericano et al. (2003a) collected penguins in 1997-1998 and detected only 1 out of 39 congeners analyzed in fat samples. Conversely, Corsolini et al. (2007) collected samples in 2004 and found 15 di- through hexa-BDEs in blood samples. The differences between these two studies might suggest that some PBDE congeners are transformed in the blood of penguins. In addition, the occurrence of higher brominated diphenyl ethers in Antarctic penguins could be a recent event.

Hale et al. (2008) investigated local sources of flame retardants to the Antarctic environment. Indoor dust obtained at McMurdo Station (USA) and Scott Base (New Zealand) exhibited total PBDE concentrations of 9,560 ng g^{-1} dw and 2,240 ng g^{-1} dw, respectively. BDE-209 was the dominant congener in dust from McMurdo and Scott bases, accounting for 43.5% and 73.7% of the total PBDEs (Hale et al., 2008). Wastewater sludge from treatment plants of both stations contained 4,690 ng g^{-1} dw at McMurdo and 637 ng g^{-1} dw at Scott. The authors pointed out that concentration of PBDEs in the McMurdo sludge was among the highest ever reported. Effluent of the McMurdo treatment plant had PBDEs concentration of 347 ng L^{-1} which is comparable to values reported for wastewater effluents from major U.S. cities (Hale et al., 2008). PBDEs were also detected in sediments, bottom-dwelling organisms and fish collected at different distances from the McMurdo outfall. In general, levels of PBDEs in these matrices decreased with increasing distances from the outfall suggesting local source of

contamination. The results evidence that even modern wastewater treatment plants such as the one at McMurdo Station can release PBDEs in the environment (Hale et al., 2008).

1.5. Summary

Coastal environments such as estuaries are preferred areas for the settlement of human populations. These areas shelter important trade harbors and cities as well as industrial complexes. In addition, estuaries are depositional environments that accumulate sediment and are critical habitat for numerous fish and shellfish species of commercial value. Along the U.S. coast major cities (including Boston, Houston and San Francisco) are potential sources of anthropogenic contaminants (e.g., PBDEs) to the marine system. Concerns with regard to PBDEs as environmental contaminants have increased in the past 15 years. This review of studies has shown that PBDEs are ubiquitous in virtually all marine matrices collected along the three coasts of the continental U.S. as well as Alaska. Contamination is higher in urbanized regions such as Boston on the Atlantic coast and San Francisco on the Pacific coast. In numerous cases, concentrations of PBDEs in U.S. marine matrices are among the highest in the world (e.g., Holden et al., 2003; She et al., 2004; Stapleton et al., 2006; Fair et al., 2007; Kannan et al., 2007). Moreover, the highest level ever detected in wildlife (63,300 ng g^{-1} lipid) was found in the egg of a Forster's tern from San Francisco Bay, CA (She et al., 2004). These findings are in concert with a critical analysis elaborated by Hites (2004) in

which the author concluded that the environment as well as human populations of North America are considerably more contaminated with PBDEs than those from Europe. High PBDE contamination levels in the U.S. marine environment reflect that over 90% of the Penta-BDE global production is utilized in the United States. This commercial mixture is an environmental concern since it is more than 70% BDE-47 and BDE-99 which are congeners known to bioaccumulate (Alcock et al., 2003; Hale et al., 2003).

In the U.S. marine environment, BDEs 28, 47, 49, 66, 99, 100, 153, 154 and 155 were detected in more than 75% of the studies in which these congeners were analyzed for. BDEs 47, 99 and 100 typically dominate the PBDEs composition in all samples and exhibit high concentrations in several matrices. BDEs 17, 28, 33, 49, 153, 154 and 155 are also of concern since they are known to be present in the Penta-BDE products (see La Guardia et al., 2006). Interestingly, mono- through tri-BDEs such as IUPAC Nos. 2, 8, 15 and 30 have been detected in samples from U.S. marine organisms (e.g., Quakenbush, 2007) even though these congeners do not occur at detectable levels in commercial formulations. This strongly suggests that the degradation of higher brominated diphenyl ethers into less brominated compounds is occurring and that mono- through tri-BDEs should be monitored in future studies. Conversely, BDEs 206, 207, 208 and 209 which occur in Deca-BDE products do not appear to accumulate in most marine organisms. Sharks are an exception as they have been found to contain high levels of BDE-209 (see Johnson-Restrepo et al., 2005). Highly brominated congeners have been detected in water and sediment samples from U.S. coastal environments. Further investigations on nona-BDEs and deca-BDE are warranted as they are known to

undergo photochemical debromination (e.g., Hua et al., 2003; Eriksson et al., 2004; Soderstrom et al., 2004).

Production of Penta-BDE and Octa-BDE mixtures in the U.S. was voluntarily ended by manufacturers on December, 2004. However, there is still no regulation (i.e., acute and chronic thresholds) addressing PBDEs contamination in the U.S. aquatic environments at the State or Federal level. This is possibly a consequence of the limited number of studies on this new class of anthropogenic contaminants. Thus, efforts to understand the cycling of PBDEs in the environment as well as the toxic effects of both individual congeners and commercial mixtures in biota are needed to support the development of environmental quality criteria. Information gathered from the Bromine Science and Environmental Forum (BSEF, www.bsef.com) provides insights on the regulation of PBDEs in the United States. Goods containing Penta-BDE and Octa-BDE formulations have recently been prohibited in ten states including the coastal States of Maine, Rhode Island, New York, Maryland, California, Oregon, Washington and Hawaii. In addition, partial restrictions on the use of the Deca-BDE formulation have been approved in Maine and Washington.

According to Ballschmiter et al. (2002), POPs are defined as “organic substances that possess toxic characteristics in a broad sense, are persistent, bioaccumulate, are prone to long-range transboundary atmospheric transport and deposition, and are likely to cause significant adverse human health or environmental effects near to and distant from their sources”. Modeling studies have demonstrated that several polybrominated diphenyl ethers (including BDEs 47, 99 and 100) are of environmental concern,

bioaccumulate and may be subject to long-range transport (e.g., Palm et al., 2002; Wania and Dugani, 2003). Monitoring data have also shown that various congeners are persistent in the environment, accumulate in living organisms and can be found in remote areas far away from pollution sources (e.g., de Boer et al., 1998; Alaee and Wenning, 2002; de Wit, 2002; Ikonomou et al., 2002 and this Chapter). Limited data are available on the toxicity of individual PBDE congeners. However, they have been proven to be endocrine disruptors effecting thyroid hormones in experimental systems (both *in vitro* and *in vivo*) (Darnerud, 2008). Additionally, commercial products (especially the Penta-BDE) have been demonstrated to cause adverse effects in laboratory animals (e.g., McDonald, 2002; Darnerud, 2003). This scientific evidence suggests that at least some PBDE congeners fulfill the criteria to be recognized as POPs. Other congeners (e.g., BDE-209) that do not fit the criteria may be debrominated into more toxic congeners that have the potential to be transported long distances. Taking these facts into account, PBDEs should be considered for addition to the list of POPs established by the United Nations Stockholm Convention.

CHAPTER II

RATIONALE AND OBJECTIVES

2.1. Study area

King George is the largest island in the South Shetlands archipelago and is located approximately 120 km north of the Antarctic Peninsula (Fig. 2). Over 90% of its 1300 km^2 is ice-covered (Rakusa-Suszczewski, 1980). Admiralty Bay is the largest fjord-like embayment on King George Island encompassing a surface area of 122 km^2 (Rakusa-Suszczewski et al., 1993). The shoreline of Admiralty Bay is fairly irregular alternating between gravel/sandy beaches, rocky shores and glaciers along its *ca.* 84 km long coast (Rakusa-Suszczewski, 1995). The geographical setting is comprised of three inlets (Ezcurra, Mackellar and Martel) and a main outlet that flows southward into the Bransfield Strait.

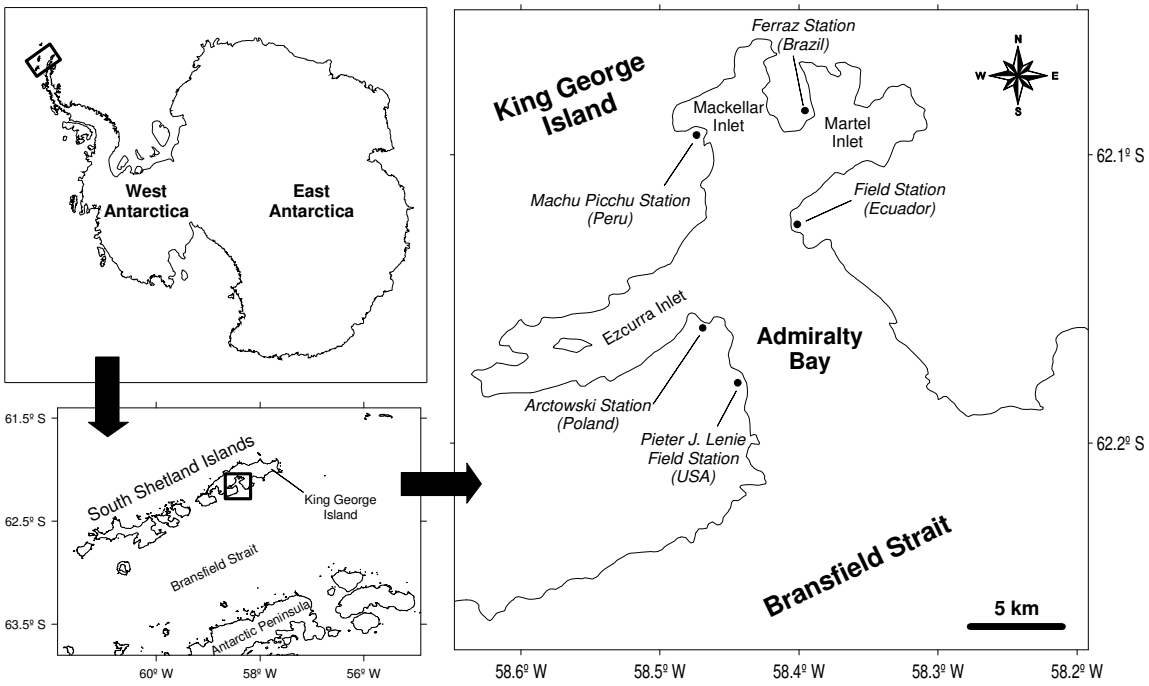


Fig. 2. Geographical setting and location of Admiralty Bay, King George Island, Antarctica.

There are three medium-sized scientific stations along Admiralty Bay: Arctowski (Poland), Ferraz (Brazil) and Machu Picchu (Peru). In addition, there are two small field stations (USA and Ecuador) that are only occupied during the summer months. Human activities have led Admiralty Bay to be designated an Antarctic Specially Managed Area (ASMA) in accordance with the Protocol on Environmental Protection to the Antarctic Treaty (*aka* the Madrid Protocol).

The ice-free areas of King George Island support a significant diversity of living organisms including extensive lichen and moss beds as well as colonies of seabirds and pinnipeds. The western shore of Admiralty Bay, in particular, has an exceptionally rich

fauna and flora which has led to the designation of this area as an Antarctic Specially Protected Area (ASPA).

Olech et al. (1998) has proposed continuous efforts to monitor pollution levels in the Antarctic environment. Several studies in Admiralty Bay have revealed pollution sources related to human activities. Local sources of petroleum hydrocarbons and heavy metals are wastewater, fuel handling and fossil fuel combustion (Bícego et al., 1996; Martins et al., 2004; Santos et al., 2005). However, the contamination is limited to small areas in the vicinity of scientific stations and does not appear to threaten local wildlife (Martins et al., 2002; Santos et al., 2006).

Persistent organic pollutants (POPs) such as DDTs and PCBs have also been studied in Admiralty Bay. However, no significant local input of POPs has been detected and long-range atmospheric transport is assumed to be the primary source of these chemicals to Admiralty Bay (Montone et al., 2003; Montone et al., 2005). Chlorinated hydrocarbons biomagnify in the local food chain and are detectable at higher concentrations in top predators (Montone et al., 1998). PBDEs have been recently detected in seabirds breeding at King George Island (Sericano et al. 2003a; Corsolini et al., 2007).

2.2. Transport of POPs to Antarctica

Wania and Mackay (1993) proposed that semivolatile organic compounds (SOCs) are transported from low to high latitudes/altitudes through a phenomenon they

defined as cold condensation – more recently termed "cold trapping" by Wania and Su (2004). This phenomenon is the transfer of SOCs from the gas to condensed phase in response to a decrease in temperature. Over time, a series of deposition/volatilization events (i.e., hopping effect) eventually trap these chemicals in the polar regions. Cousins and Gouin (2003) further hypothesized that the fraction of SOCs available for re-volatilization back to the atmosphere in vegetated areas is greater than in non-vegetated areas. This is because plant leaves decrease the chemical's tendency to remain on immobile surface media boosting the "grass-hopper" effect (Gouin and Harner, 2003). The importance of the role of vegetation in the global transport and fate of SOCs has been demonstrated by several authors (e.g., Calamari et al., 1991; Simonich and Hites, 1994).

2.3. Vegetation as pollution monitors

Plants can absorb pollutants from soil (via roots) or the atmosphere (via above ground parts, especially leaves). In the case of SOCs, which are generally highly hydrophobic, the former route of entry tends to be negligible in comparison with the latter (see Simonich and Hites, 1995; Barber et al., 2004). So the main uptake mechanism is from the surrounding air to the leaf surface through either gas or particle deposition. In addition, SOCs can enter the leaf through the cuticle or the stomata (Paterson et al., 1990; Barber et al., 2004). Atmosphere-vegetation partitioning is controlled by a number of physical-chemical parameters of the compound (e.g., vapor

pressure, octanol-air partition coefficient, air-water partition coefficient), environmental factors (e.g., temperature, wind speed, rainfall) and plant properties (e.g., species, lipid content, leaf morphology) (see Paterson et al., 1990; Simonich and Hites, 1995; Smith and Jones, 2000; Barber et al., 2004).

Vegetation has been used to monitor organic pollution since the early 1980s (see Buckley, 1982). It is a convenient biomonitor for atmospheric pollution since plants integrate contamination over time and are easier to collect than air samples, particularly in remote areas away from pollution sources (Simonich and Hites, 1995). Several authors have found a good correlation between levels of SOCs in plants and their concentration in the surrounding atmosphere (e.g., Nakajima et al., 1995). Morosini et al. (1993) calculated the atmospheric concentration of SOCs based on measurements in plants. This must be done with caution. According to Simonich and Hites (1995), vegetation may be used as an indicator of SOC atmospheric concentrations provided that the mechanism of accumulation is taken into consideration. McLachlan (1999) developed a framework to identify the primary accumulation process for interpreting SOC levels in plants (see detailed discussion below).

Monitoring studies using lichens and mosses in the western Antarctic Peninsula have investigated trace metals, radioactive elements and chlorinated hydrocarbons (Bacci et al., 1986; Poblet et al., 1997; Godoy et al., 1998; Olech et al., 1998; Mietelski et al., 2000; Schuller et al., 2002; Osyczka et al., 2007). However, there appears to be no data published on PBDEs in Antarctic vegetation.

2.4. Antarctic vegetation

The distribution of terrestrial vegetation in Antarctica is limited to ice-free areas which are primarily found along the mainland coast and adjacent islands. Plant species have been recorded throughout Antarctica from its northernmost limit (60º S, according to the Antarctic Treaty) poleward to the Transantarctic mountains at latitude of 86º S (Peat et al., 2007). Plant communities are dominated by lower plants (predominantly lichens and mosses) and biodiversity tends to decline with increasing latitude. Peat et al. (2007) divided the Antarctic flora into three major provinces namely northern maritime, southern maritime and continental. Species richness is highest in the northern maritime Antarctica and is characterized by approximately 350 lichens, 115 mosses, 27 liverworts and 2 phanerogams (Peat et al., 2007).

The lichens *Usnea antarctica* Du Rietz and *Usnea aurantiaco-atra* (Jacq.) Bory along with the moss *Sanionia uncinata* (Hedw.) Loeske are commonly found in the Antarctic tundra (Osyczka et al., 2007). *U. antarctica* has a circumpolar distribution with greatest abundances along the Antarctic Peninsula. *U. aurantiaco-atra* is less ubiquitous than its counterpart and is restricted to the South Orkney Islands, South Shetland Islands and the Antarctic Peninsula. The moss *S. uncinata* is a bipolar species and has widespread distribution along the western Antarctic Peninsula (Smith, 1996; Øvstedal and Lewis-Smith, 2001; Shaw, 2001). These three species have been used as bioindicators of atmospheric pollution in Antarctica because of their dominant

occurrence in ice-free areas and ease of sampling (e.g., Mietelski et al., 2000; Osyczka et al., 2007).

2.5. Antarctic seabirds in this study

Seabirds occupy high trophic levels in Antarctic food webs, harvesting significant Southern Ocean biomass. Some species are endemic and live year round south of the Antarctic Convergence. Others are migratory and can be observed in Antarctica only during the breeding season (i.e., austral summer). In this context, the south polar skua (*Catharacta maccormicki* Saunders, 1893) is a migratory seabird while both chinstrap (*Pygoscelis antarctica* Forster, 1781) and gentoo (*Pygoscelis papua* Forster, 1781) penguins are endemic species. The south polar skua is one of the few Antarctic seabirds that undertake trans-equatorial migration. This species is well adapted to the extreme polar weather conditions and breeds all around Antarctica (Devillers, 1977; Ritz et al., 2006). After the breeding season, it migrates northward, crosses the Antarctic Convergence, and can be seen in boreal oceans as far north as 66º N (Devillers, 1977; Shirihai, 2002). The chinstrap penguin is mainly distributed in the Atlantic sector of the Southern Ocean (i.e., islands of the Scotia Arc and the Antarctic Peninsula), also breeding in a few other islands of the maritime Antarctica (Lynch, 2007). The gentoo penguin has circumpolar distribution and breeds on most of the subantarctic islands as well as the Antarctic Peninsula south to 65º S (Bost and Jouventin, 1990). While gentoo penguins reside near their breeding colony year-round,

chinstrap penguins migrate as far as 1500 km during the winter months (Tanton et al., 2004; Trivelpiece et al., 2007). At King George Island (South Shetland Islands, Antarctic Peninsula), all three species share breeding grounds and forage on marine resources (Volkman et al., 1980; Trivelpiece and Volkman, 1982).

2.6. Transformation of PBDEs in the environment

Despite their persistency, PBDEs may undergo transformation in the environment. As a general rule, higher brominated congeners debrominate at faster rates than lower brominated congeners. For example, Eriksson et al. (2004) observed reaction rate differences around 700 times between BDE-77 (tetrabrominated) and BDE-209 (decabrominated). Photolysis of PBDEs in abiotic media has been investigated since the 1980s (see Watanabe and Tatsukawa, 1987). Recently, researchers started to focus on the metabolism of PBDEs by living organisms. Most of these ecologically relevant studies have been carried out on fish (e.g., Stapleton et al., 2004; Tomy et al., 2004; Isosaari et al., 2005), whereas there is limited information on metabolism of PBDEs by avian species (see Pirard and De Pauw, 2007; Van den Steen et al., 2007). Pirard and De Pauw (2007) fed domestic chickens a diet contaminated by PBDEs for 98 days. Their experimental results suggested a reductive debromination of PBDEs in the chicken's digestive tract. Van den Steen et al. (2007) used silastic tube implants in order to expose a terrestrial songbird species (European starling, *Sturnus vulgaris*) to an environmentally relevant concentration of BDE-209. After a period of 76 days, they detected octa- and

nona-BDEs (e.g., IUPAC Nos. 196, 197, 206, 207 and 208) in muscle and liver tissues of the exposed birds. The authors attributed these findings to biotransformation of BDE-209 in the European starling.

It is known that a female bird can transfer PBDEs to eggs during the laying period (see Verreault et al., 2006; Pirard and De Pauw, 2007). Penguins constitute approximately 80% of the seabird biomass in the Southern Ocean and adjacent Antarctic continent (Tanton et al., 2004 and references therein). Chinstrap and gentoo penguins – whose population estimates are about 7,490,000 and 314,000 breeding pairs, respectively – are among the most abundant seabird species southward of the Antarctic Convergence (Lynch, 2007). Taking this into consideration, it is important to identify possible metabolic pathways of man-made chemicals in these seabirds.

2.7. Objectives

The review presented in Chapter I showed that a limited number of researchers have investigated PBDEs in U.S. marine environments. Even fewer studies have addressed PBDEs in Antarctica. Many questions remain to be answered and several gaps need to be filled to understand the global cycle of PBDEs. The objectives of this dissertation are four-fold:

- Evaluate the concentration of PBDEs in Antarctic lichens and mosses;
- Investigate the transfer mechanisms of PBDEs from the atmosphere to Antarctic vegetation;

- Compare the levels of PBDEs in eggs of migratory and endemic seabirds breeding in Antarctica; and
- Study the potential for metabolism of PBDE congeners during incubation of penguin eggs.

CHAPTER III

FIELD AND LABORATORY METHODS

3.1. Field methods

Antarctic vegetation was collected along the shore of Admiralty Bay, King George Island (Fig. 3). A total of 44 samples were collected over two consecutive austral summer expeditions (2004-05 and 2005-06). Plants were identified as lichens (*Usnea antarctica* and *Usnea aurantiaco-atra*), mosses (*Sanionia uncinata*, *Syntrichia princeps* and *Brachythecium* sp.) and a phanerogam (*Colobanthus quitensis*). Samples were collected by hand and thoroughly shaken to remove extraneous material such as animal-related debris and soil particles. All samples were stored in clean glass jars and frozen at -20 ºC as soon as possible.

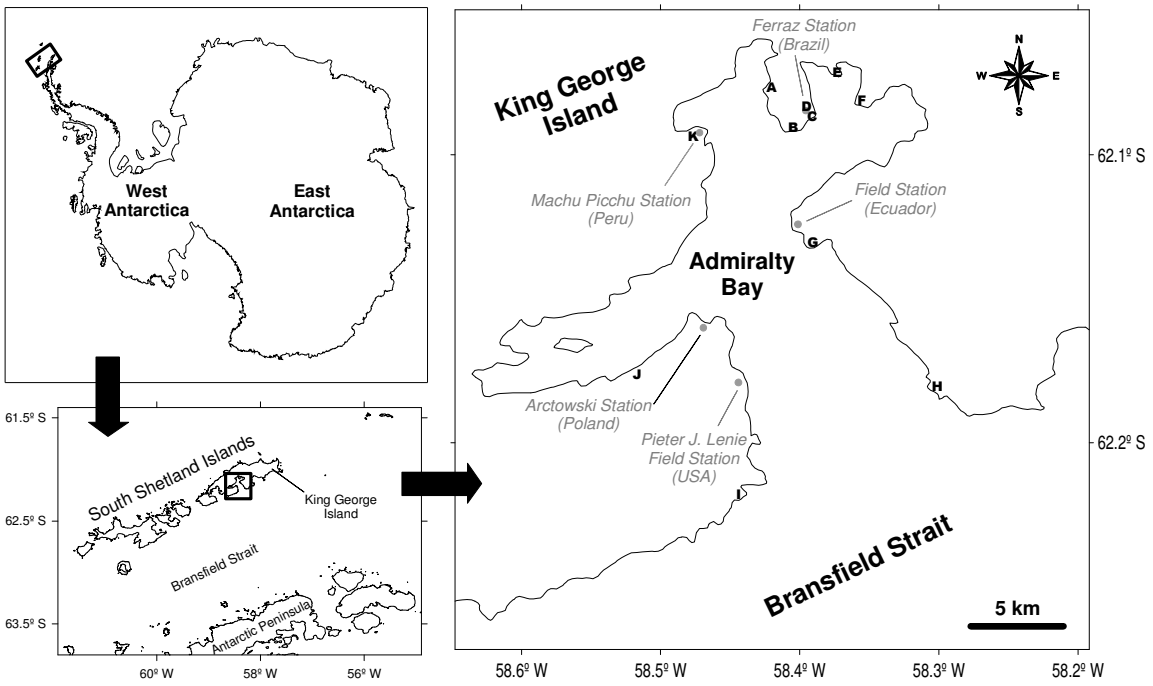


Fig. 3. Location of the vegetation sampling sites along the shore of Admiralty Bay, King George Island.

Seabird eggs were collected from breeding colonies located at Admiralty Bay, King George Island (Fig. 4). Eggs of chinstrap penguin and south polar skua were collected in the breeding season 2004-2005. Another set of chinstrap penguin eggs was collected in the following year (2005-2006) along with eggs of gentoo penguin. In the second sampling season, 11 gentoo and 28 chinstrap eggs were weighed out using a semi-analytical balance. Only non-viable eggs were collected so as not to interfere with the birds breeding success. All eggs found cold and outside the nest were assumed to be non-viable. Samples were carefully transported to the laboratory where the whole egg content (including yolk, albumen and embryo) was transferred to clean glass jars and frozen at -20 ºC as soon as possible.

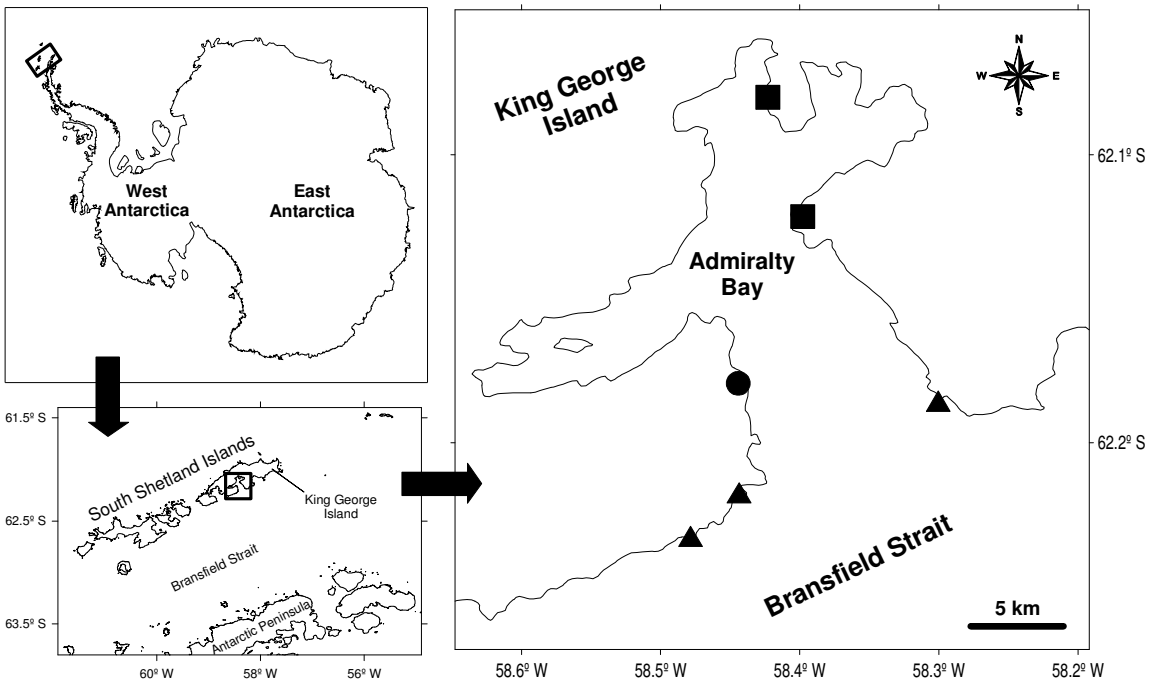


Fig. 4. Location of the breeding sites where eggs of south polar skua (*Catharacta maccormicki*, squares), chinstrap penguin (*Pygoscelis antarctica*, triangles) and gentoo penguin (*Pygoscelis papua*, circle) were collected at King George Island.

3.2. Laboratory methods

3.2.1. Chemical analyses

All tissue samples (i.e., lichens, mosses and eggs) were homogenized in the laboratory prior to analysis. Extraction and clean-up followed standard procedures routinely used at the Geochemical and Environmental Research Group (GERG) and published elsewhere (e.g., Lauenstein and Cantillo, 1998). Labeled PBDEs (i.e., ^{13}C-BDEs 3, 15, 28, 47, 99, 100, 118, 153 and 183) were used as surrogate standards and

added to all samples before extraction. Approximately 10 g of wet plant tissue (or 5 g of wet egg tissue) was mixed with 40 g of anhydrous sodium sulfate and extracted with 100 mL of dichloromethane for 3 min using a tissumizer (PRO Scientific Inc., model PRO250). This procedure was repeated three times to ensure complete extraction. Each of the three extraction steps was filtered through anhydrous sodium sulfate, combined into a single flask, concentrated to near dryness, and solvent exchanged to approximately 2 mL of *n*-hexane. At this point, the plant extracts were extensively cleaned up with sulfuric acid (concentration: >51%) to oxidize organic matter. Then, all extracts (i.e., plant and egg tissues) were eluted with 200 mL of *n*-pentane:dichloromethane (1:1, v/v) through silica/alumina chromatographic columns (300 mm length × 10 mm inner diameter). Columns were packed from bottom to top as follows: a piece of glass wool, 1 cm of combusted sand, 10 g of alumina (1% deactivated with HPLC grade water), 20 g of silica gel (5% deactivated with HPLC grade water), 2 cm of anhydrous sodium sulfate, and 1 cm of activated copper. The copper was added to egg extracts in order to remove sulfur. The eluates were concentrated in a water bath to approximately 1.5 mL for further purification by gel permeation chromatography/high performance liquid chromatography (GPC/HPLC). In this step the extracts were eluted through two Phenogel™ columns connected in series. The columns specifications are as follows: 300 mm length × 21.2 mm diameter, 10 μm particle size, 100Å pore size. Labeled internal standards (i.e., ^{13}C-BDEs 77 and 126) were added to the purified extracts which were then concentrated to approximately 25 μL, and stored in freezer until injection in the GC/MS.

Dry and lipid weights were gravimetrically determined using an analytical balance following standard procedures used at the GERG facilities. Dry weight percent was calculated based on the weight difference of a known aliquot of wet tissue dried to a constant weight for at least 24 h at 50-60 ºC. Lipid weight percent was similarly calculated after removing a known aliquot of the extracted tissue. Before weighing, the extract was filtered to retain non-lipophilic materials and the organic solvent was evaporated. It is important to note that throughout this dissertation the term lipid is operationally defined as the fraction of organic matter extractable using dichloromethane as a solvent. Other solvent systems may produce different results.

3.2.2. Instrumental parameters

Sample extracts were injected into a gas chromatograph (Agilent Technologies, model 6890N) coupled to a mass selective detector (Agilent Technologies, model 5975C) in the selected ion monitoring (SIM) mode. A HP-5ms capillary column (30 m length × 0.25 mm id × 0.25 μm film thickness) was used for separation of compounds. Splitless injections of 2 μL (purge off time: 2 min) were done using an autosampler. Helium was used as carrier gas under constant flow (0.8 mL min^{-1}) into the column while the purge flow rate was adjusted to 20 mL min^{-1}. The injector temperature was set at 270 ºC. The oven temperature was programmed as follows: 130 ºC for 1 min, ramped at 12 ºC min^{-1} to 154 ºC, ramped at 2 ºC min^{-1} to 210 ºC, and ramped at 3 ºC min^{-1} to 300 ºC with a final hold time of 5 min (total run time: 66 min). The mass spectrometer was

operated in electron ionization (EI) mode. The interface, ion source and quadrupole temperatures were set at 290 ºC, 230 ºC and 150 ºC, respectively. The electron energy was 70 eV (emission current: 300 µA).

A suite of 36 di- through hepta-BDEs were investigated including the following congeners: 7, 8, 10, 11, 12, 13, 15, 17, 25, 28, 30, 32, 33, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 153, 154, 155, 166, 181, 183, and 190 (numeration according to the same IUPAC system used for PCBs). Three ions representing a typical bromine cluster were monitored for each target analyte (Table 5). The primary *m/z* for di-, tri-, tetra-, penta-, hexa-, and hepta-BDEs were respectively 327.9, 405.8, 485.7, 563.6, 643.5, and 721.4. The ion stacking technique was employed to increase the GC/MS sensitivity so that ultra-trace analyte concentrations could be detected (see discussion below). This technique consists of recording the intensity of a particular ion several times during a single scan cycle of the MS detector. The SIM parameters were optimized based on instrument and software capabilities in order to maximize analyte detector response. The dwell time was set at 10 ms for all ions. The SIM run was divided into seven functions where each *m/z* was recorded 6-12 times per scan cycle (see Table 6). In function 1, for example, five *m/z* ions (325.9, 327.9 and 329.9 for di-BDEs; 337.9 and 339.9 for ^{13}C labeled di-BDEs) were recorded six times (i.e., stacks) in every scan cycle of the MS detector.

Table 5

Ions monitored for analysis of polybrominated diphenyl ethers by GC/EI-MS. Ions in bold face represent the primary *m/z* of each homolog group.

Homolog group	Monitored *m/z* ions					Congeners
	M	M+2	M+4	M+6	M+8	
di-BDEs	325.9	**327.9**	329.9			7, 8, 10, 11, 12, 13, 15
tri-BDEs		**405.8**	407.8	409.8		17, 25, 28, 30, 32, 33, 35, 37
tetra-BDEs		483.7	**485.7**	487.7		47, 49, 66, 71, 75, 77
penta-BDEs		561.6	**563.6**	565.6		85, 99, 100, 116, 118, 119, 126
hexa-BDEs			641.5	**643.5**	645.5	138, 153, 154, 155, 166
hepta-BDEs			719.4	**721.4**	723.4	181, 183, 190

Table 6

Selected ion monitoring (SIM) parameters used in the analysis of polybrominated diphenyl ethers by GC/EI-MS. The last column contains details of the ion stacking technique.

Function	Start time (min)	Dwell time (ms)	Homolog groups	Records per scan cycle (ions × stacks = total)
1	5.0	10	di-BDEs	5 × 6 = 30
2	24.0	10	tri-BDEs	5 × 12 = 60
3	36.0	10	tetra-BDEs	5 × 12 = 60
4	45.0	10	penta-BDEs	5 × 12 = 60
5	50.0	10	penta- and hexa-BDEs	6 × 10 = 60
6	53.0	10	hexa-BDEs	5 × 12 = 60
7	58.0	10	hepta-BDEs	5 × 12 = 60

3.2.3. Quality control

Quality control criteria were based on EPA (2003) and Lauenstein and Cantillo (1998). Quantitation of the target analytes used isotope dilution and internal standard techniques. Acceptable recovery of surrogates was between 25% and 150% based on the ultra-trace amounts spiked into the samples. The average recovery of surrogate standards

was 82 ± 1.8% (95% level of confidence). In each analytical batch, two matrices were spiked with PBDEs and analyzed in duplicate. For these samples, acceptable recovery was between 40% and 120% while the relative percent difference (RPD) cutoff was 25%. The accuracy and precision criteria applied to 80% of the PBDEs whose concentration in the spike was equal to or greater than the concentration in the original sample (i.e., valid spike). The mean recovery of PBDE standards in the spiked matrices was 95 ± 2.1% (95% level of confidence). The RPD between the spiked duplicates was 15 ± 2% (95% level of confidence). The NIST SRM 1945 (organics in whale blubber) was also analyzed with analytical batches of seabird eggs. Acceptable values for 80% of the congeners was within 35% of the certified range published by Stapleton et al. (2007).

The mass spectrometer was appropriately tuned up before injection of each analytical batch. Laboratory check solutions were routinely injected into the GC/MS system to confirm instrument accuracy and precision. Calibration of the instrument was performed using a six level calibration curve. The limits of detection were compound- and sample-specific taking into consideration the lowest calibration level of a particular analyte and the amount of sample extracted. In vegetation, the mean limits of detection for selected major PBDEs were 1.0 pg g^{-1} dry weight (BDEs 15, 47 and 49), 1.5 pg g^{-1} dry weight (BDEs 99 and 100), and 1.3 pg g^{-1} dry weight (BDEs 153 and 154). In seabird eggs, the average limits of detection for selected major congeners were 0.02 ng g^{-1} lipid weight (BDE-47), 0.03 ng g^{-1} lipid weight (BDEs 99 and 100) and 0.04 ng g^{-1} lipid weight (BDEs 153, 154 and 183).

3.2.4. Statistical analyses

The analysis of variance (ANOVA) is a robust, parametric test used to infer statistically significant differences between two or more population means. Assumptions of the test are: (1) data are independent and continuous; (2) data are approximately normally distributed; and (3) data set variances are homogeneous (Dytham, 2003). The assumption of normality was tested using the Kolmogorov-Smirnov test (critical level of significance typically set at 0.05). Data normality was also checked using normal probability and normal Q-Q plots. The assumption of equal variances was tested using the Levene's test ($\alpha = 0.05$) and visually inspected using box-and-whisker plots. Distribution of organic contaminants in biological tissues is generally skewed. So, whenever needed, the data sets were transformed using natural logarithm to meet the assumptions of the ANOVA. This is a valid alternative as long as all data points are systematically converted using the same procedure (Ott and Longnecker, 2001). In this dissertation, single factor ANOVA and two-factor ANOVA (Model I, fixed effects) were performed to compare population means. *Post hoc* tests (i.e., multiple comparisons) were done using the Bonferroni procedure (overall $\alpha = 0.05$) in order to further investigate pairwise differences between factor levels. When a suitable transformation could not be found to normalize data distributions, the non-parametric Kruskal-Wallis test ($\alpha = 0.05$) was used to compare population medians.

The degree of association (and its significance) between two variables can be assessed using correlation analyses. The Pearson's product-moment correlation analysis

is a parametric test whose assumptions are: (1) independent samples and continuous bivariate data; (2) linear relationship between the two variables; and (3) normally distributed data sets (Ott and Longnecker, 2001; Dytham, 2003). Similarly to the ANOVA, the normality assumption was checked using the Kolmogorov-Smirnov test ($\alpha = 0.05$) as well as normal Q-Q plots. Data were natural log transformed whenever necessary. In some cases, a suitable transformation could not be found to ensure the data fit a normal distribution. Then, the non-parametric Spearman's rank order correlation analysis was performed to determine the significance and strength of correlation between two data sets. The critical level of significance was set at 0.05 in all analyses.

3.3. Analytical issues

3.3.1. Ion stacking

The ion stacking methodology and its validity as an analytical technique was discussed with the mass spectrometer manufacturer (Agilent Technologies) technical support staff who confirmed that ion stacking is a valid analytical approach. A series of tests with two different GC/MS instruments showed the utility of the procedure. Instrument response gain using the ion stacking technique is illustrated in Fig. 5. The response for all analytes is about four times greater when the same *m/z* ions are recorded twice per scan cycle (i.e., two stacks of ions), whereas it is approximately ten times greater when the monitored ions are recorded three times (i.e., three stacks of ions).

Total ion chromatograms (TICs) of the same neat solution injected with and without ion stacking are illustrated in Fig. 6. Concentrations of PBDEs in this illustration range from 500 to 1500 ng mL^{-1}, representing the highest level GC/MS calibration standard. In both injections, all instrument parameters are held constant other than the stacking of ions in the SIM mode. The intensity of peaks in the TIC is substantially improved when ion stacking is employed to record data (see Fig. 6).

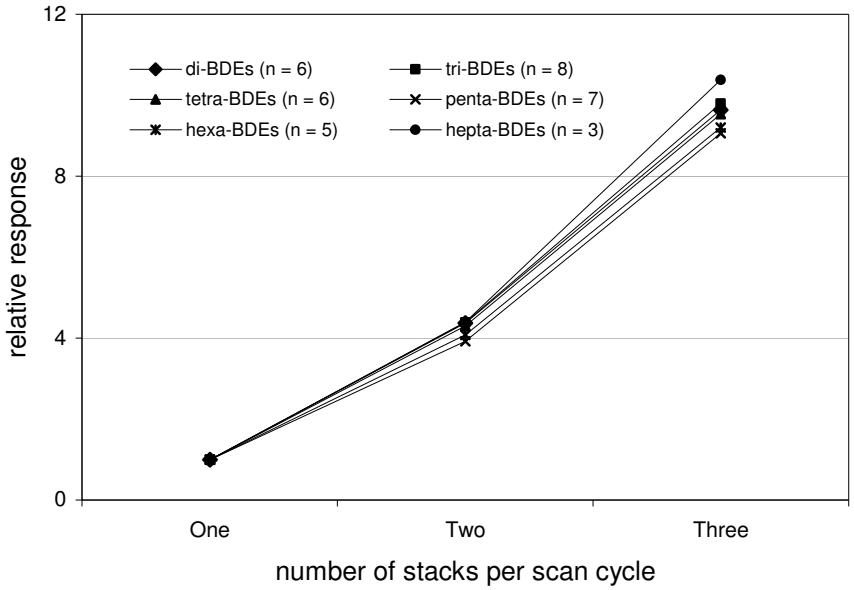


Fig. 5. Average relative response of PBDE homolog groups using techniques with distinct number of stacks per scan cycle. All responses are relative to the run with no stacking of ions which was assigned a relative response of 1.

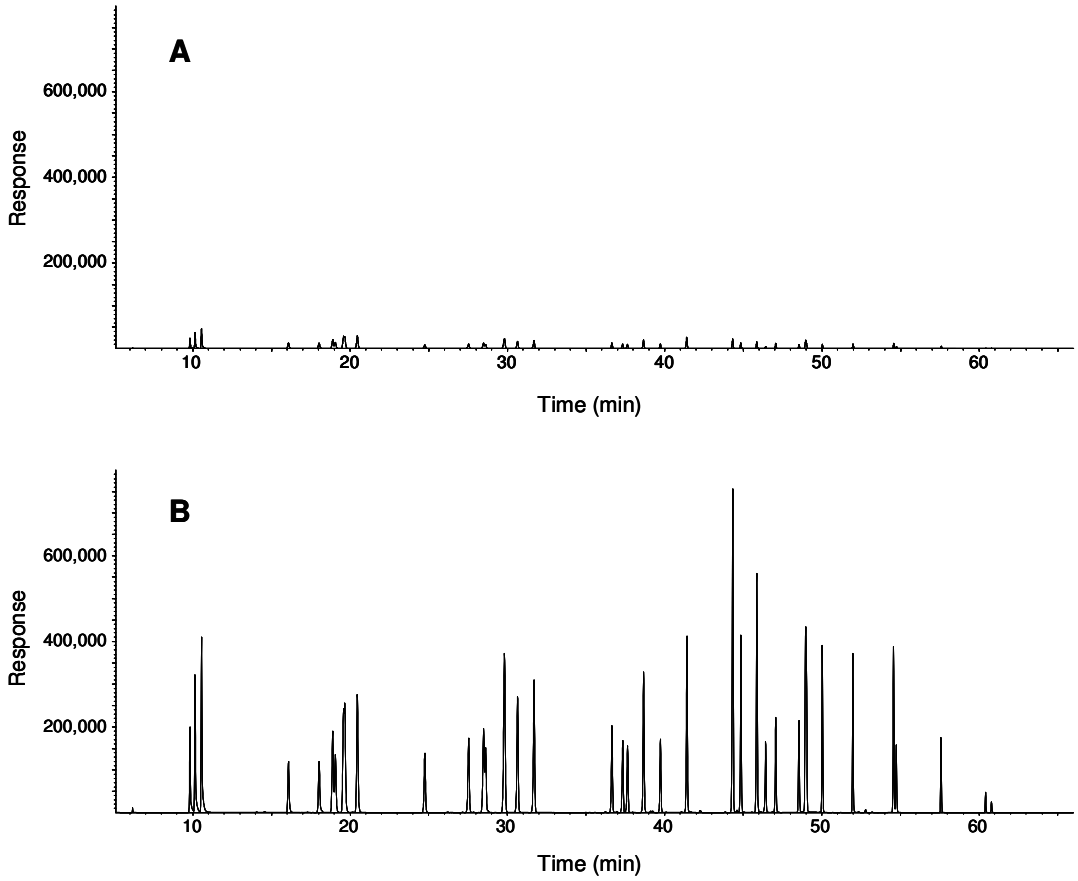


Fig. 6. Total ion chromatogram (TIC) of the same PBDE calibration standard (500-1500 ng mL^{-1}) injected without ion stacking (A) and with ion stacking (B).

The enlargement of peaks using ion stacking allows the detection of lower analyte amounts. The signal-to-noise (S/N) ratio of several PBDE homolog groups in the lowest calibration standard are shown in Table 7. Concentrations of individual congeners in this solution range from 0.2 to 0.6 ng mL^{-1}. The injection of 2 µL resulted in mean S/N ratios between 1.7 and 8.7. All di- through penta-BDE congeners produced S/N ratios above the threshold of 3 – typically used as minimum acceptable level for positive identification of target analytes. In contrast, some individual hexa-BDEs (IUPAC Nos.

138, 154 and 166) and all hepta-BDEs (IUPAC Nos. 183, 181 and 190) produced S/N ratios below 3. Lower S/N ratio for higher brominated diphenyl ethers is attributed to the high-mass discrimination effect. Such a phenomenon is typically observed in MS instruments equipped with quadrupole mass analyzers, and is caused by direct current (DC) fringe fields at the entrance to the quadrupole (Watson and Sparkman, 2007). These electrical fields tend to divert high-mass, low speed ions toward the quadrupole rods where they are disintegrated upon collision (Watson and Sparkman, 2007).

Table 7

Signal-to-noise (S/N) ratio in the lowest calibration standard (0.2-0.6 ng mL^{-1}) injected using the ion stacking technique.

Homolog group	Mass injected (pg)	S/N ratio[a]	n
di-BDEs	0.4	5.4 ± 1.5	7
tri-BDEs	0.4	3.6 ± 0.6	7
tetra-BDEs	0.4	7.8 ± 3.7	6
penta-BDEs	0.6	8.7 ± 6.8	7
hexa-BDEs	0.8	3.5 ± 2.1	5
hepta-BDEs	1.0	1.7 ± 0.3	3

[a] mean ± standard deviation

Standard reference materials (SRMs) are useful for validating the reliability, accuracy and reproducibility of analytical methods (Wise et al., 2006). The analysis of two different SRMs from the National Institute of Standards and Technology (NIST) confirmed the effectiveness of the ion stacking technique. In general, the calculated concentrations of PBDEs are in good agreement with those published by Zhu and Hites (2003) and Stapleton et al. (2007) (see Tables 8 and 9). Most congeners in the SRM

1945 (organics in whale blubber) are within the uncertainty range of the NIST certificate of analysis while all analytes in the SRM 1974b (organics in mussel tissue) match the certificate values. Additionally, several non-certified PBDEs concentrations agree with those published by Zhu and Hites (2003). The two most common sources of ionization used in mass spectrometers for the analysis of halogenated compounds are electron impact (EI) and electron capture negative ionization (ECNI). The former is generally regarded to be more selective while the latter is said to be more sensitive (Stapleton, 2006). Results from the analysis of SRM 1974b demonstrate that EI-MS can be not only selective but also very sensitive when the ion stacking technique is employed to measure PBDEs at low levels (under 1 ng g^{-1}). Therefore, the combination of EI-MS and ion stacking provides an excellent choice in terms of cost, selectivity, and sensitivity for the analysis of trace halogenated contaminants in environmental matrices.

Table 8

Concentration of selected PBDE congeners measured in the NIST SRM 1945 (organics in whale blubber) using three different methods. The data published by Stapleton et al. (2007) correspond to the values in the certificate of analysis.

Congener	Zhu and Hites (2003)[a] (ng g^{-1} wet weight)	This Study[b] (ng g^{-1} wet weight)	Stapleton et al. (2007)[c] (ng g^{-1} wet weight)	Notes
BDE-17	0.21 ± 0.06	0.16 ± 0.03		
BDE-28/33	1.53 ± 0.30	1.77 ± 0.29	2.66 ± 0.37	reference
BDE-47	46.6 ± 2.0	39.6 ± 5.5	39.6 ± 0.2	certified
BDE-49	2.57 ± 0.11	2.44 ± 0.36		
BDE-66	1.53 ± 0.13	1.49 ± 0.21		
BDE-99	23.0 ± 1.9	20.6 ± 2.8	18.9 ± 2.3	certified
BDE-100	11.8 ± 0.9	10.7 ± 1.4	10.3 ± 1.1	certified
BDE-153	10.1 ± 1.1	10.0 ± 1.2	8.34 ± 0.55	certified
BDE-154	20.8 ± 3.0	20.5 ± 2.6	13.3 ± 1.7	certified
BDE-155		5.64 ± 0.80	4.75 ± 0.93	reference
BDE-183	2.27 ± 0.18	2.23 ± 0.08		

[a] n = 6; mean ± standard deviation

[b] n = 4; mean ± standard deviation

[c] certified value ± uncertainty

Table 9

Concentration of selected PBDE congeners measured in the NIST SRM 1974b (organics in mussel tissue) using three different methods. The data published by Stapleton et al. (2007) correspond to the values in the certificate of analysis.

Congener	Zhu and Hites (2003)[a] (ng g^{-1} wet weight)	This Study[b] (ng g^{-1} wet weight)	Stapleton et al. (2007)[c] (ng g^{-1} wet weight)	Notes
BDE-17	0.30 ± 0.06	0.27 ± 0.04		
BDE-28/33	0.11 ± 0.02	0.13 ± 0.03	0.13 ± 0.03	reference
BDE-47	3.53 ± 0.20	3.20 ± 0.08	3.41 ± 0.21	certified
BDE-49	0.76 ± 0.02	0.71 ± 0.02	0.75 ± 0.06	certified
BDE-66	0.10 ± 0.01	0.11 ± 0.02	0.11 ± 0.02	certified
BDE-99	1.73 ± 0.05	1.45 ± 0.10	1.50 ± 0.18	certified
BDE-100	1.01 ± 0.05	0.91 ± 0.07	0.93 ± 0.07	certified
BDE-153	0.09 ± 0.01	< 0.10	0.08 ± 0.01	reference
BDE-154	0.11 ± 0.01	< 0.10	0.10 ± 0.02	reference

[a] n = 5; mean ± standard deviation

[b] n = 3; mean ± standard deviation

[c] certified value ± uncertainty

3.3.2. Blank contamination

Laboratory blanks were consistently contaminated with several PBDE congeners. Several analytical steps were thoroughly examined in order to identify sources and minimize blank contamination. Possible sources of PBDEs to the blank could be organic solvents and dust in the laboratory environment. In order to address the first alternative, approximately 400 mL of dichloromethane – the most used solvent for extraction and clean-up of samples – was concentrated in the laboratory for injection in the GC/MS. The dry deposition investigation consisted of uncovered beakers placed in the laboratory and exposed to airborne contaminants for 19 h. The selected sites were counters in the extraction room, water bath room and HPLC room along with the fume hood used for running silica/alumina columns. Each beaker initially contained 50 mL of dichloromethane. At the end of the exposure period, three beakers contained around 10-15 mL due to evaporation of solvent. The fourth beaker was dry because it was intentionally placed below an air conditioning vent. All of the beakers were rinsed with 10 mL of dichloromethane and concentrated for injection into the GC/MS.

In addition to these experiments, dust particles were sampled from four places in the laboratory. The first sample was collected from the top of the analytical balance. The second was collected from the countertop in the water bath room. The other two samples came from dust accumulated in different air conditioning filters located below fume hoods in the water bath room. All dust samples were weighed and extracted with 20 mL

of dichloromethane (i.e., shaking for 3 min). The extracts were then concentrated and prepared for injection in the GC/MS system.

The mean contaminations in the experiments described above are summarized in Table 10 as well as the average contamination in blanks from all analytical batches used in this study. The results show that dichloromethane and passive dry deposition of airborne contaminants are unlikely sources of PBDEs in laboratory analytical blanks. Residues detected in both experiments are two orders of magnitude lower than those in the blanks (see Table 10). Organic solvents used at GERG are pesticide grade and this experiment demonstrated that dichloromethane is also suitable for BFR analysis. Regarding the dry deposition experiment, a visual inspection of the beakers at the end of the exposure period did not reveal the presence of any dust particles.

In contrast, the pattern of congeners found in the analytical blanks is similar to those found in laboratory dust samples (see Table 10). The mean level of PBDEs in blanks and countertop dust are on the same order of magnitude (2.32 vs. 5.38), whereas dust from the air conditioning filters is roughly ten times higher (42.9). The higher average level in the latter is probably a consequence of both airborne contaminants and dust particles being trapped and concentrated in air conditioning filters. In conclusion, laboratory dust seems to be a source of PBDEs to the analytical blanks. However, the actual contamination mechanism still remains unknown.

Table 10

Comparison of average contamination between analytical blanks and potential PBDE sources in the laboratory. Note that all values were normalized to the same nominal weight (i.e., 1 g) in order to make them comparable.

	Average Contamination (ng)				
	Blank (n = 12)	Solvent (n = 3)	Dry Deposition (n = 4)	Lab Dust (n = 2)	A/C Filter (n = 2)
BDE-7	nd	nd	nd	nd	nd
BDE-8	0.003	nd	nd	nd	nd
BDE-10	nd	nd	nd	nd	nd
BDE-11	nd	nd	nd	nd	nd
BDE-12	nd	nd	nd	nd	nd
BDE-13	nd	nd	nd	nd	nd
BDE-15	0.010	nd	nd	0.003	0.015
BDE-17	0.003	nd	nd	0.010	0.046
BDE-25	nd	nd	nd	nd	0.024
BDE-30	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd
BDE-33/28	0.027	nd	nd	0.054	0.222
BDE-35	nd	nd	nd	nd	0.006
BDE-37	0.003	nd	nd	0.001	0.014
BDE-47	0.822	0.027	0.016	2.85	18.7
BDE-49	0.025	nd	nd	0.060	0.358
BDE-66	0.017	nd	nd	0.051	0.265
BDE-71	0.002	nd	nd	0.004	0.045
BDE-75	nd	nd	nd	nd	0.014
BDE-77	0.001	nd	nd	nd	0.002
BDE-85	0.041	nd	nd	0.050	0.536
BDE-99	0.893	0.027	0.015	1.62	15.5
BDE-100	0.192	0.004	0.003	0.427	3.42
BDE-116	nd	nd	nd	nd	nd
BDE-118	0.005	nd	nd	0.007	0.030
BDE-119	0.011	nd	nd	nd	0.012
BDE-126	0.005	nd	nd	nd	nd
BDE-138	0.027	nd	nd	0.016	0.176
BDE-153	0.107	nd	nd	0.089	1.25
BDE-154	0.084	nd	nd	0.095	1.10
BDE-155	0.010	nd	nd	0.006	0.061
BDE-166	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	0.103
BDE-183	0.031	nd	nd	0.025	0.917
BDE-190	nd	nd	nd	nd	0.129
di-BDEs	0.013	nd	nd	0.003	0.015
tri-BDEs	0.034	nd	nd	0.065	0.313
tetra-BDEs	0.867	0.027	0.016	2.97	19.4
penta-BDEs	1.15	0.031	0.018	2.11	19.5
hexa-BDEs	0.229	nd	nd	0.207	2.58
hepta-BDEs	0.031	nd	nd	0.025	1.15
Total PBDEs	**2.32**	**0.058**	**0.034**	**5.38**	**42.9**

Harrad et al. (2008) investigated PBDEs in domestic indoor dust from all over the world. Average concentration (i.e., tri- through hexa-BDEs) in several countries was as follows: 98 ng g^{-1} in the UK, 160 ng g^{-1} in New Zealand, 1100 ng g^{-1} in Canada and 3000 ng g^{-1} in the USA. The sum of di- through hepta-BDEs in indoor dust from GERG ranged from 81 ng g^{-1} to 3196 ng g^{-1}, with the highest levels detected in air conditioning filters. Hazrati and Harrad (2006) also found intra-building variability of airborne PBDEs in both domestic and office settings. Concentration of PBDEs in indoor air may be an order of magnitude higher than in outdoor air (Harrad et al., 2006). PBDEs have been detected in cars, homes, offices, and public indoor environments (Hazrati and Harrad, 2006). In a review on the pitfalls of BFR analysis, de Boer and Wells (2006) emphasized the importance of keeping the laboratory as clean as possible to avoid dust contamination of samples.

Intriguingly, the pattern of blank contamination did not repeat in the samples. In some cases, congeners detected in the blank were not found in samples of the same analytical batch. In others instances, analytes were quantified in the sample at much lower levels when compared to the blank. Additionally, QC samples (e.g., SRMs and spiked matrices) often did not pass the quality criteria if the blank contamination was subtracted from them. A non-parametric statistical test was performed to evaluate the effect of the blank on the concentration of PBDEs in samples. The data set consisted of 30 penguin eggs extracted across three distinct analytical batches. These eggs belonged to the same species (*Pygoscelis antarctica*) and were collected at the same colony (Chabrier Rock) on the same day (January 6, 2005). Thus, it might be expected that all

eggs had about the same contamination levels. According to the Kruskal-Wallis test, concentration of PBDEs in eggs was not significantly different among the three analytical batches when the blank contamination was ignored and not subtracted from the samples ($H = 4.47$, $df = 2$, $p = 0.107$). However, PBDEs in penguin eggs did differ among batches if the blank residue was subtracted from the samples (Kruskal-Wallis test, $H = 17.4$, $df = 2$, $p < 0.0001$). This statistical evidence supports the idea that contamination of analytical blanks did not affect samples. Based on all indicators above, analytical blanks were not subtracted from sample results. The quality of the analyses was judged based on recovery of surrogates, spikes and SRM analytes.

CHAPTER IV

RESULTS AND DISCUSSION

4.1. PBDEs in Antarctic vegetation

Among 36 di- through hepta-BDEs, only BDEs 15, 28, 33, 47, 49, 66, 85, 99, 100, 153, 154, and 183 were detected above the method detection limits in Antarctic vegetation. It is important to note that hexa-BDEs (IUPAC Nos. 138, 153, 154, 155 and 166) could not be identified and quantified in the phanerogam and mosses because of interfering peaks that remained in the extracts after extensive purification.

An analysis of variance revealed no significant difference between PBDEs in the lichens *Usnea antarctica* and *Usnea aurantiaco-atra* ($F = 1.67$, $df = 1$, $p = 0.229$). Poblet et al. (1997) also did not find a statistical difference in the accumulation of metals (Fe, Zn, Pb and Cd) by *U. antarctica* and *U. aurantiaco-atra* collected at King George Island. Genetic and morphological investigations have revealed a very close relationship between these two species, supporting the hypotheses that they might be a single species, or alternatively constitute a species pair where *U. antarctica* would be the sterile form and *U. aurantiaco-atra* the fertile form (Walker, 1985; Seymour et al., 2007). Based on these reports and the statistical results, both lichen species are pooled as a single species for purposes of comparison with mosses of the species *S. uncinata*.

Concentrations of total PBDEs in Antarctic vegetation collected at King George Island are shown in Table 11. A two-factor model I (fixed effects) ANOVA was

performed to determine the effects of sampling year (2004-05 vs. 2005-06) and plant species (*Usnea* spp. vs. *Sanionia uncinata*) on concentration of PBDEs. In this analysis, the genus *Usnea* was pooled as a single species (see discussion above). The phanerogam and two other mosses were not statistically meaningful (i.e., n = 1) and were excluded from the analyses. The ANOVA indicated that PBDE levels were not influenced by interaction (year*species) of the main factors ($F = 2.08$, $df = 1$, $p = 0.157$). It also revealed a significant difference between sampling years ($F = 10.6$, $df = 1$, $p = 0.002$). PBDE levels in the Antarctic vegetation were significantly higher in 2004-05 (580 pg g^{-1} dry weight) when compared to 2005-06 (493 pg g^{-1} dry weight) (see detailed discussion in the next section). The mean total PBDEs in the moss *S. uncinata* (904 pg g^{-1} dry weight) were significantly higher than in lichens of the genus *Usnea* (213 pg g^{-1} dry weight) ($F = 173$, $df = 1$, $p < 0.0001$).

Table 11

Concentration of PBDEs (pg g^{-1} dry weight) in Antarctic vegetation collected along the shore of Admiralty Bay, King George Island, maritime Antarctica.

Year	Plant Group	Species	n	Σ PBDEs (pg g^{-1} dw)
2004-05	lichen	*Usnea antarctica*	4	220 ± 76.8[a]
		Usnea aurantiaco-atra	5	262 ± 48.7
		Usnea sp.	2	326 ± 32.3
	moss	*Sanionia uncinata*	8	1022 ± 348
		Syntrichia princeps	1	718
		Brachythecium sp.	1	276
	phanerogam	*Colobanthus quitensis*	1	328
2005-06	lichen	*Usnea antarctica*	6	192 ± 93.9
		Usnea aurantiaco-atra	5	139 ± 33.6
	moss	*Sanionia uncinata*	11	818 ± 270

[a] mean ± standard deviation

Other pollution monitoring studies in the western Antarctic Peninsula have observed differential contaminant accumulation in lichens and mosses. Osyczka et al. (2007) found greater concentration of trace elements in the moss *S. uncinata* when compared to lichens *U. antarctica* and *U. aurantiaco-atra*. Mietelski et al. (2000) observed fractionation of radionuclides between mosses and lichens. While *S. uncinata* is non-selective with regard to ^{137}Cs and ^{241}Am from atmospheric fallout, these radioactive elements seem to be leached out of *U. antarctica* and *U. aurantiaco-atra*. Godoy et al. (1998) also observed greater accumulation of ^{137}Cs in several moss species in comparison with lichens from the South Shetland Islands.

Along the shore of Admiralty Bay, there are three scientific stations (Arctowski, Poland; Ferraz, Brazil; and Machu Picchu, Peru) and two field stations (USA and Ecuador). Arctowski and Ferraz are occupied year-round while the others' activities are limited to summer (and are often unoccupied even in the summer in the case of Peru and Ecuador). Considering that Ferraz is the largest station in Admiralty Bay, it is reasonable to assume that it will cause the greatest human impact in the area. An analysis of variance was performed in plants collected in 2005-06 to determine the effects of human presence on concentration of PBDEs. Plants were grouped as sampling sites close to (sites A-F) and distant from (sites G-K) the Brazilian scientific station (see Fig. 3). ANOVA analysis revealed no significant difference in contamination levels close to (443 pg g^{-1} dry weight) and distant from (553 pg g^{-1} dry weight) Ferraz station ($F = 3.10$, $df = 1$, $p > 0.05$), suggesting that station activities are not a significant source of PBDEs to the local environment. Indeed, no significant local input of POPs (e.g., PCBs) has

been detected in the area and long-range atmospheric transport is believed to be the primary source of these chemicals to Admiralty Bay (Montone et al., 2003; Montone et al., 2005). In contrast, a recent study found high PBDE levels in indoor dust and wastewater sludge from McMurdo (USA) and Scott (New Zealand) research bases, showing that human activities may be a local source of PBDEs to the Antarctic environment (Hale et al., 2008). McMurdo and Scott bases – located within 3 km from each other – host over 1000 people during the summer. This far exceeds human occupation at the Brazilian station which hosts approximately 50 people each summer.

The average percent distribution of PBDEs in lichens and mosses was similar (Fig. 7). Tetra-BDEs represented 38% of the total PBDEs in both lichens and mosses, whereas penta-BDEs averaged 47% in lichens and 58% in mosses. This is similar to commercial formulations of Penta-BDE which are 24-38% tetra-BDEs, 50-60% penta-BDEs and 4-8% hexa-BDEs (de Wit, 2002). Congener pattern similarities between Antarctic vegetation and the Penta-BDE mixture suggest that PBDEs do not undergo major fractionation during transport to Antarctica. IUPAC Nos. 47, 99 and 100 were the three major congeners detected in all samples, accounting for more than 75% of total PBDEs. This agrees with other studies (see de Wit, 2002).

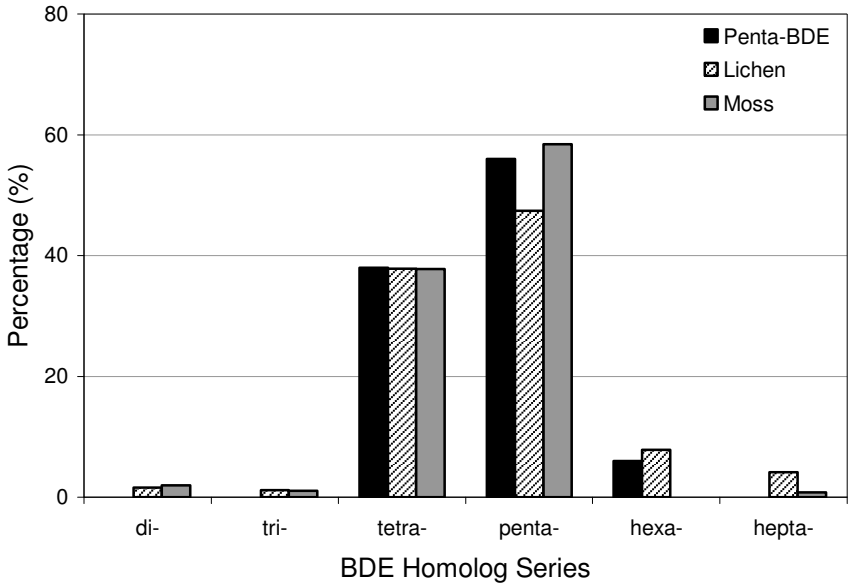


Fig. 7. Percent distribution of PBDE homologs in the commercial Penta-BDE formulation compared to lichens and mosses collected along the shore of Admiralty Bay, King George Island, Antarctica.

Di and tri-BDEs occur in trace amounts in Penta-BDE formulations (La Guardia et al., 2006). Minor proportions of BDE-15 and BDE-28/33 (co-eluted) in the Antarctic samples may be explained by either global fractionation or degradation of more highly brominated congeners. Global fractionation preferentially transports more volatile chemicals to sites farther away from their emission areas as compared to less volatile organic compounds (Wania and Mackay, 1993). It has also been reported that PBDEs undergo photochemical debromination (e.g., Eriksson et al., 2004; Keum and Li, 2005; Ahn et al., 2006; Rayne et al., 2006). Thus, it is reasonable to assume that transformation processes alter PBDE mixtures during long-range atmospheric transport to Antarctica. In

addition, degradation might also take place at the plant surface as suggested by Simonich and Hites (1995). Detection of the heptabrominated BDE-183 in lichens and mosses implies that technical mixtures other than the Penta-BDE formulation have reached the Antarctic environment. BDE-183 is a major congener present in the Octa-BDE product (La Guardia et al., 2006). According to Bezares-Cruz et al. (2004), BDE-183 may also be a degradation product of BDE-209 which is the dominant congener in the Deca-BDE formulation – the most widely produced PBDE commercial mixture.

Simonich and Hites (1995) recommended that concentration of organic pollutants in vegetation be normalized to lipid basis when comparing different species. This approach accounts for some of the variability due to biochemical differences in plants. In this study, the lipid-normalized PBDE concentrations in lichens and mosses were 9.11 ± 3.62 ng g^{-1} lipid and 97.3 ± 42.7 ng g^{-1} lipid, respectively (mean ± SD). Lipid-normalized contamination levels in mosses remain significantly higher than in lichens (ANOVA, $F = 166$, $df = 1$, $p < 0.0001$). Such differences are most likely associated with processes responsible for PBDEs uptake from the atmosphere which are complex and may be governed by a number of chemical, environmental and plant parameters. Hexa-BDEs (i.e., BDEs 153 and 154) represented approximately 8% of the total PBDEs in lichens. Taking into consideration that these congeners could not be measured in mosses and are usually detected in environmental samples, it is reasonable to suggest that PBDEs concentrations in mosses are somewhat higher than the reported values. This confirms the differences observed in the ANOVA that higher levels of PBDEs occur in mosses when compared to lichens.

There are few data published on PBDEs in lichens and mosses. A comprehensive study in northern Russia collected plants (including lichens and mosses) from several sites (AMAP, 2004). However, BDEs 47 and 99 were not found above the limit of detection (0.2 ng g^{-1} dry weight) in any sample (AMAP, 2004). Moss samples from two locations in Norway revealed total PBDE concentrations of 149 pg g^{-1} wet weight and 328 pg g^{-1} wet weight (de Wit et al., 2006 and a reference therein). These levels are similar to those reported here. On a wet basis, the mean total PBDEs in mosses collected at King George Island was 363 pg g^{-1} wet weight (range: 108-729 pg g^{-1} wet weight). In the 1980s, Bacci et al. (1986) investigated chlorinated hydrocarbons in mosses and lichens of the western Antarctic Peninsula. Levels of HCB, α-HCH, γ-HCH, *p*,*p*'-DDT and *p*,*p*'-DDE at that time are comparable to levels of PBDEs reported in this study (carried out 20 years later). However, the concentration of PCBs measured in the 1980s is an order of magnitude higher than the PBDEs contamination in this study (Bacci et al., 1986).

4.2. Long-range transport and transfer of PBDEs to Antarctic vegetation

Lichens and mosses lack root-like structures and thus absorb SOCs solely from the atmosphere. According to McLachlan (1999), the three primary processes involved in the atmospheric uptake of SOCs by plants are: (1) gaseous equilibrium partitioning between vegetation and the surrounding air, (2) kinetically limited dry gaseous deposition, and (3) dry/wet particle-bound deposition (Fig. 8). These three mechanisms

are intrinsically related to the octanol-air partition coefficient (K_{OA}) of a chemical. Thus, high volatility SOCs (i.e., low K_{OA}) are absorbed mainly through equilibrium partitioning between gas phase and plant surface (mechanism 1). Several authors have found this partitioning to be a function of K_{OA} (e.g., Bacci et al., 1990; Su et al., 2007). Intermediate volatility SOCs (i.e., intermediate K_{OA} values) are also chiefly absorbed from the gas phase. However, the uptake is controlled by the rate at which the chemical is deposited on the plant surface (mechanism 2). Low volatility SOCs (i.e., high K_{OA}) are absorbed through either dry or wet particle-bound deposition which is dependent upon the amount of particles in the atmosphere and their deposition rate on plant surfaces (mechanism 3). Experimental data have shown that the critical log K_{OA} between mechanisms 1 and 2 is around 10, whereas mechanism 3 is dominant for SOCs with log K_{OA} greater than 12 (Horstmann and McLachlan, 1998; Su et al., 2007).

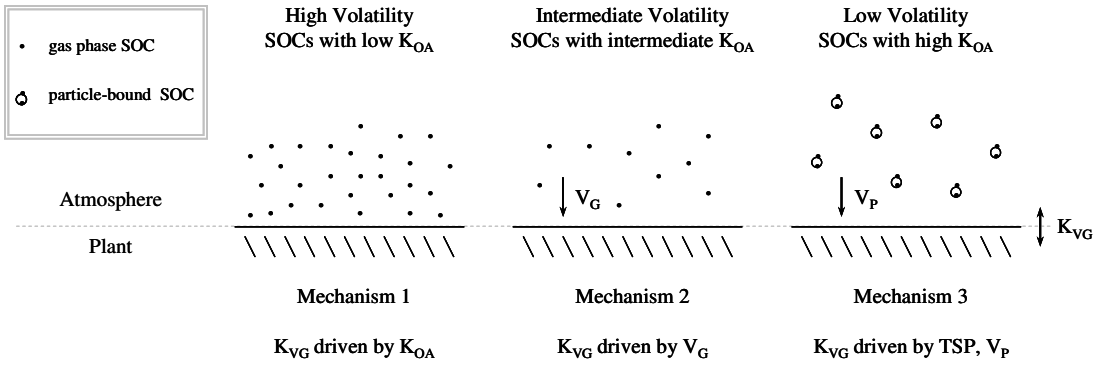


Fig. 8. Three primary processes associated with vegetation uptake of SOCs from the atmosphere according to the framework developed by McLachlan (1999). Acronyms: SOC = semivolatile organic compound; K_{VG} = vegetation-atmosphere partition coefficient; K_{OA} = octanol-air partition coefficient; V_G = dry gaseous deposition rate; V_P = dry/wet particle-bound deposition rate; TSP = total suspended particles.

The partitioning of a SOC between gaseous and particle-bound phases is strongly correlated with temperature and can be described using the Langmuir adsorption concept (see Yamasaki et al., 1982). Several authors have further demonstrated that log K_{OA} varies linearly with the inverse absolute temperature (e.g., Harner and Mackay, 1995; Harner and Shoeib, 2002), following the general equation:

$$\log K_{OA} = A + \frac{B}{T} \tag{1}$$

where *A* and *B* are regression coefficients. Harner and Shoeib (2002) experimentally derived equations to calculate the K_{OA} for 13 PBDEs at different temperatures. In addition, they also present a semi-empirical method to estimate the K_{OA} of additional PBDEs using the equation:

$$\log K_{OA} = a' + b' t_R \tag{2}$$

where t_R is the relative retention time of PBDEs reported by Sjödin et al. (1998). The regression coefficients *a*' and *b*' are corrected for the absolute temperature as follows:

$$a' = \frac{2187.9}{T} - 2.020 \tag{3}$$

$$b' = \frac{4003.7}{T} - 5.2425 \tag{4}$$

In this study, equation 1 was used to calculate the temperature-adjusted K_{OA} for BDEs 28, 47, 66, 85, 99, 100, 153, 154 and 183 while equations 2-4 were used to calculate the K_{OA} for BDE-15 (see Appendix A for examples of calculation). The K_{OA} of BDE-49 could not be estimated due to lack of retention time information in the literature. The ambient air temperature was averaged over five days prior to the collection of vegetation. This time frame is supposed to account for most of the short term responses in the uptake of SOCs by plants (see Hauk et al., 1994). The other equation parameters were obtained from Sjödin et al. (1998) and Harner and Shoeib (2002). The log K_{OA} of PBDEs adjusted to typical summer temperatures at King George Island are summarized in Table 12. The air temperature during the period of study ranged from -0.20 ºC to 4.32 ºC, with a mean of 1.43 ºC. The log K_{OA} of PBDEs show little variation over the observed temperature range (see standard deviations in Table 4.2). Therefore, average values were used to make inferences about the uptake of PBDEs by Antarctic plants.

Table 12

Calculated log K_{OA} of PBDEs according to the ambient air temperature at each sampling date. The air temperature is averaged over five days prior to the actual collection of vegetation. Air temperature data retrieved from the following source on the internet: http://www.cptec.inpe.br/prod_antartica/weatherdata.shtml.

Sampling	Temperature	log K_{OA}									
Date	(ºC)	BDE-15	BDE-28	BDE-47	BDE-66	BDE-85	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183
22-Nov-2004	1.67	9.90	10.61	11.97	12.41	13.18	12.67	12.68	13.28	13.32	13.29
23-Nov-2004	1.55	9.90	10.62	11.98	12.42	13.19	12.68	12.69	13.29	13.33	13.30
24-Nov-2004	1.52	9.90	10.62	11.98	12.42	13.19	12.68	12.69	13.29	13.33	13.30
1-Dec-2004	0.86	9.94	10.65	12.03	12.47	13.24	12.72	12.74	13.34	13.38	13.34
3-Dec-2004	1.31	9.91	10.63	12.00	12.44	13.20	12.69	12.71	13.30	13.35	13.31
4-Dec-2004	1.37	9.91	10.63	11.99	12.43	13.20	12.69	12.71	13.30	13.34	13.31
5-Dec-2004	1.06	9.93	10.64	12.01	12.45	13.22	12.71	12.73	13.32	13.36	13.33
20-Dec-2004	-0.20	9.99	10.71	12.10	12.55	13.31	12.79	12.82	13.41	13.45	13.41
24-Dec-2004	0.64	9.95	10.66	12.04	12.49	13.25	12.73	12.76	13.35	13.39	13.35
2-Jan-2005	1.63	9.90	10.61	11.97	12.41	13.18	12.67	12.69	13.28	13.33	13.29
3-Jan-2005	1.65	9.90	10.61	11.97	12.41	13.18	12.67	12.69	13.28	13.32	13.29
7-Jan-2005	3.86	9.78	10.50	11.83	12.25	13.02	12.53	12.53	13.13	13.18	13.16
11-Jan-2005	2.53	9.85	10.57	11.91	12.35	13.12	12.62	12.62	13.22	13.27	13.24
13-Jan-2005	1.90	9.88	10.60	11.96	12.39	13.16	12.66	12.67	13.26	13.31	13.28
15-Dec-2005	2.12	9.87	10.59	11.94	12.38	13.15	12.64	12.65	13.25	13.29	13.26
17-Dec-2005	1.07	9.93	10.64	12.01	12.45	13.22	12.71	12.73	13.32	13.36	13.33
21-Dec-2005	-0.53	10.01	10.73	12.12	12.57	13.33	12.81	12.84	13.43	13.47	13.43
23-Dec-2005	-0.70	10.02	10.73	12.13	12.59	13.35	12.82	12.86	13.44	13.48	13.44
27-Dec-2005	0.47	9.96	10.67	12.05	12.50	13.26	12.75	12.77	13.36	13.40	13.36
6-Jan-2006	4.32	9.76	10.48	11.80	12.22	12.99	12.50	12.49	13.10	13.15	13.13
11-Jan-2006	2.05	9.88	10.59	11.95	12.38	13.15	12.65	12.66	13.25	13.30	13.27
Mean	**1.43**	**9.91**	**10.62**	**11.99**	**12.43**	**13.20**	**12.68**	**12.70**	**13.30**	**13.34**	**13.31**
SD	**1.22**	**0.06**	**0.06**	**0.08**	**0.09**	**0.09**	**0.08**	**0.09**	**0.08**	**0.08**	**0.08**

Based on the framework developed by McLachlan (1999), BDE-15 (log K_{OA} = 9.91) will directly partition from the atmosphere onto plants surface at King George Island (mechanism 1). BDE-28 (log K_{OA} = 10.62) is mainly in the gas phase but its uptake by Antarctic plants will be controlled by dry deposition rates (mechanism 2). These two congeners are volatile and less brominated diphenyl ethers (di- and tri-BDEs, respectively). All other congeners (tetra- through hepta-BDEs) will be mostly bound to atmospheric particles. Consequently, plant uptake will be mainly driven by dry/wet particle deposition rates (mechanism 3). Overall, particle settling is the primary

mechanism controlling the uptake of PBDEs by Antarctic vegetation since major congeners such as BDEs 47, 99 and 100 are mostly bound to atmospheric aerosols.

In view of the discussion on the primary mechanisms of pollutant accumulation in Antarctic plants, the observed distributions can be explained. One explanation of differences observed in PBDE levels between the two sampling years may be attributed to meteorological conditions. Rainfall and snowfall were much higher in the austral summer 2004-05 when compared to 2005-06. Total precipitation during the study was 152 mm in 2004-05 and 34 mm in 2005-06 (Table 13). Thus, higher concentration of PBDEs in plants collected in 2004-05 may be associated with more efficient washout of particle-bound contaminants from the atmosphere. Lei and Wania (2004) pointed out that wet deposition becomes progressively more important toward the poles. In addition, snow scavenging ratios tend to be higher than rain scavenging ratios as air temperature decreases.

Table 13

Total precipitation (sum of rainfall and snowfall) in the austral summers 2004-05 and 2005-06 at Admiralty Bay, King George Island, Antarctica. Meteorological data retrieved from http://www.cptec.inpe.br/prod_antartica/weatherdata.shtml.

Month	Precipitation (mm)	
	2004-05	2005-06
November	59	14
December	61	10
January	32	11
Total	152	34

In support of the wet deposition mechanism, concentration of BDEs 28, 47, 99, 100, 153 and 154 showed a moderate, positive correlation with the total precipitation over the five days before collection of lichens of the genus *Usnea* (see Table 14). The correlation coefficient increased from tri- through hexa-BDEs (see r_s in Table 14). This is consistent with the stronger partition of higher brominated diphenyl ethers onto atmospheric aerosols. The significant correlation between BDE-28 and precipitation might suggest that both rain and snow efficiently scavenge gas phase tri-BDEs from the atmosphere although McLachlan's mechanism 2 (i.e., driven by gaseous deposition rate) is supposed to be the primary process for BDE-28 uptake by lichens. On the other hand, concentration of BDE-15 (di-BDE) in lichens did not significantly correlate with precipitation (Spearman's rank order correlation analysis, $r_s = 0.231$, $n = 22$, $p = 0.301$). This field evidence supports McLachlan's interpretations since BDE-15 is directly absorbed through air-plant equilibrium partitioning (mechanism 1) which is independent of dry/wet deposition rates. It was not possible to perform a correlation analysis for BDE-183 because this congener was detected in few lichen samples.

Table 14

Output statistics of the Spearman's rank order correlation analysis. The correlated variables are atmospheric precipitation and concentration of individual PBDE congeners in lichens of the genus *Usnea*. Acronyms: n = number of samples; r_s = correlation coefficient; p = level of significance of the test.

Homolog	Congener	n	r_s	p
tri-BDE	28	22	0.553	0.008
tetra-BDE	47	22	0.588	0.004
penta-BDE	99	22	0.620	0.002
penta-BDE	100	22	0.618	0.002
hexa-BDE	153	22	0.627	0.002
hexa-BDE	154	22	0.637	0.001

In contrast to lichens, concentration of BDEs 15, 28, 47, 99 and 100 in the moss *S. uncinata* showed no correlation with atmospheric precipitation (Spearman's rank order correlation analysis, $r_s < 0.010$, n = 19, $p > 0.75$). This suggests that other factors such as species-specific parameters might control the uptake of PBDEs by *S. uncinata*. For example, the morphology of both species is very different. While the fruticose lichen *Usnea* spp. looks like a tiny shrub, the moss *S. uncinata* looks like a mat over the ground. Such morphological differences might play an important role in trapping PBDE-containing atmospheric aerosols. The different pollutant accumulation capacity of both species is confirmed by the ANOVA results that indicate a significantly higher contamination of the moss *S. uncinata* compared to the lichens of the genus *Usnea*.

The PBDEs partitioning to aerosols in the Antarctic atmosphere can be estimated using expressions published in the literature. According to Harner and Shoeib (2002), the partitioning of PBDEs between atmospheric aerosols and the gaseous phase is calculated using the expression:

$$\log K_P = \log K_{OA} + \log f_{OM} - 11.91 \quad (5)$$

where K_P is the particle-gas partition coefficient and f_{OM} is the mass fraction of organic matter in the total suspended particles. The percent fraction (Φ) of PBDEs bound to atmospheric particles is calculated as follows:

$$\Phi = \frac{100 \times TSP \times K_P}{(TSP \times K_P) + 1} \quad (6)$$

where TSP is the concentration of suspended particulate matter in the atmosphere. Equations 5 and 6 were used to estimate the percent fraction of PBDE congeners bound to aerosols in the Antarctic atmosphere (see Appendix A for examples of calculation). Typical summer values of TSP and f_{OM} at an Antarctic coastal site are 2343 ng m^{-3} and 1.5%, respectively (Minikin et al., 1998; Wagenbach et al., 1998). According to Table 15, virtually all tetra- through hepta-BDEs will be bound to aerosols' organic phase in the Antarctic atmosphere. Conversely, most of BDE-15 (di-BDE) will be in the gas phase while approximately 65% of BDE-28 (tri-BDE) will be adsorbed on aerosols. These estimates are in concert with the above discussion on the primary uptake mechanisms of PBDE congeners by Antarctic vegetation.

Table 15

Calculated percent fraction (Φ) of PBDE congeners bound to atmospheric aerosols in the Antarctic summer. Acronyms: K_{OA} = octanol-air partition coefficient; K_p = particle-gas partition coefficient; Φ = contaminant fraction onto atmospheric aerosols.

Homolog	Congener	log K_{OA}	log K_P	Φ (%)
di-BDE	15	9.91	-3.81	26.5
tri-BDE	28	10.62	-3.10	65.2
tetra-BDE	47	11.99	-1.73	97.7
tetra-BDE	66	12.43	-1.29	99.2
penta-BDE	85	13.20	-0.53	99.9
penta-BDE	99	12.68	-1.04	99.5
penta-BDE	100	12.70	-1.02	99.6
hexa-BDE	153	13.30	-0.42	99.9
hexa-BDE	154	13.34	-0.38	99.9
hepta-BDE	183	13.31	-0.42	99.9

Marine inputs dominate the chemical composition of Antarctic aerosol which basically consists of sea salt (primary component) and biogenic emissions (secondary component) (Wolff et al., 1998 and references therein). The organic fraction of Antarctic aerosols is in the submicron size range and is mostly methanesulfonic acid (MSA) which peaks during the austral summer (Rankin and Wolff, 2003; Fattori et al., 2005). Thus, PBDEs in the Antarctic atmosphere are most likely associated with MSA submicron particles. Studies in the northern hemisphere confirm that SOCs are primarily associated with atmospheric particles in the submicron size range (e.g., Kaupp et al., 1994; Schnelle et al., 1996; Kaupp and McLachlan, 1999). MSA is an oxidation product of dimethylsulfide (DMS) which in turn is released to the atmosphere by microalgae. It is hypothesized that marine phytoplankton play a role in the long-range atmospheric transport of less volatile SOCs such as PBDEs to the Antarctic environment. When travelling to the southern hemisphere, more highly brominated diphenyl ethers gradually

partition from the gaseous to the particle phase as atmospheric temperature decreases poleward. In this partitioning they are coupled to phytoplankton-derived MSA and may be eventually deposited on land and plant surfaces. Wet deposition processes (i.e., rain and snowfall) remove these chemicals from the atmosphere, eventually boosting their partitioning to and accumulation in vegetation.

4.3. PBDEs in eggs of Antarctic seabirds

The average concentration of PBDEs in seabird eggs was 6.78 ng g^{-1} lipid (range: 3.13-33.0 ng g^{-1} lipid) for chinstrap penguin, 8.12 ng g^{-1} lipid (range: 3.03-22.7 ng g^{-1} lipid) for gentoo penguin and 146 ng g^{-1} lipid (range: 19.0-558 ng g^{-1} lipid) for south polar skua (Table 16). Few congeners were detected in the samples above the MDL: 8 in gentoo penguin, 11 in chinstrap penguin and 16 in south polar skua (Table 17).

Table 16

Percent dry weight, percent lipid and concentration of PBDEs (ng g^{-1} lipid) in seabird eggs collected from nesting sites at King George Island, Antarctic Peninsula. Values are mean ± standard deviation.

Species	n	Dry Weight (%)	Lipid (%)	BDE-47	BDE-99	BDE-100	Σ PBDEs
				(ng g^{-1} lipid)			
Chinstrap Penguin	35	23.1 ± 2.37	6.1 ± 1.3	2.60 ± 2.89	2.55 ± 2.42	0.695 ± 0.726	6.78 ± 6.42
Gentoo Penguin	17	23.2 ± 2.29	5.1 ± 1.0	2.90 ± 1.68	3.42 ± 2.50	0.795 ± 0.550	8.12 ± 5.32
South Polar Skua	13	23.3 ± 2.65	6.4 ± 1.7	53.1 ± 72.2	14.0 ± 14.3	29.4 ± 42.5	146 ± 164

Table 17

Diversity of PBDE congeners detected in seabird eggs collected from nesting sites in Antarctica. Congeners in bold were detected in more than 90% of the samples. Congeners underlined were detected in less than 10% of the samples.

Species	PBDE Congeners Detected (IUPAC No.)
Chinstrap Penguin	33/28[a], **47**, 49, 66, **99**, **100**, **153**, **154**, 155 and 183
Gentoo Penguin	33/28[a], **47**, 49, **99**, **100**, **153** and **154**
South Polar Skua	**33/28**[a], **47**, **49**, 66, 71, **99**, **100**, 118, 119, 126, 138, **153**, **154**, **155** and 183

[a] These congeners co-eluted in the chromatograms

An analysis of variance showed that concentrations of PBDEs differed among the three seabird species ($F = 60.6$, $df = 2$, $p < 0.0001$). PBDEs in skua eggs are approximately 20 times higher than in penguin eggs. There was no difference in PBDEs concentrations between the two penguin species (Bonferroni test, $p = 0.569$). These results illustrate the difference in contamination exposures of endemic versus migratory seabirds in Antarctica. During the breeding season at King George Island, penguins and south polar skuas forage exclusively on marine resources although they do not occupy the same trophic level. The diet of both chinstrap and gentoo penguins is primarily krill (*Euphausia superba*) which represents respectively 99.6% and 84.5% of their stomach contents (Volkman et al., 1980). Gentoo penguins also feed on fish (*Pleuragramma antarcticum*) – 15.4% of the diet (Volkman et al., 1980). South polar skuas, in turn, forage almost solely on fish (*P. antarcticum*) (Hemmings, 1984). Thus, south polar skuas occupy a higher trophic level when compared to chinstrap penguins since the nototheniid fish *P. antarcticum* is a zooplankton feeder that forages on krill (DeWitt and Hopkins, 1977). Gentoo penguins occupy an intermediate trophic position closer to

chinstrap penguins. The level of PBDEs in eggs of the three species is not exclusively explained by their diets during the breeding season. If PBDE contamination was due to local sources, gentoo eggs would be expected to exhibit intermediate concentrations significantly higher than those of chinstrap eggs. The higher contamination levels in south polar skuas probably result from exposure during the non-breeding season when they migrate northward to waters of the northern hemisphere. Unfortunately, little is known about the winter distribution and habits of the south polar skuas that breed at King George Island. Alternatively, part of the differences among the three species could be explained by different contaminant transfer rates from female to egg. Verreault et al. (2006) observed different patterns of PBDEs in female plasma and eggs of glaucous gulls (*Larus hyperboreus*) breeding in the Arctic, suggesting selective maternal transfer. Conversely, Tanabe et al. (1986) did not find significant differences in the pattern of PCBs in a pair mother-egg of Adélie penguin (*Pygoscelis adeliae*).

The distribution of PBDE homolog groups in seabirds is compared with a commercial mixture of Penta-BDE in Fig. 9. The composition of brominated homologs in penguin eggs is similar to the technical formulation. Furthermore, it resembles the PBDEs found in local lichens which integrate atmospheric contamination over time (see discussion above). In contrast, south polar skuas PBDE contamination is depleted in pentabrominated congeners and is almost five times as high in hexabrominated diphenyl ethers when compared with commercial products. This suggests that south polar skuas are exposed to contaminated food stuffs that have accumulated PBDE formulations other

than Penta-BDE mixtures (e.g., Octa-BDE and/or Deca-BDE). This exposure most likely occurs north of the Antarctic Convergence.

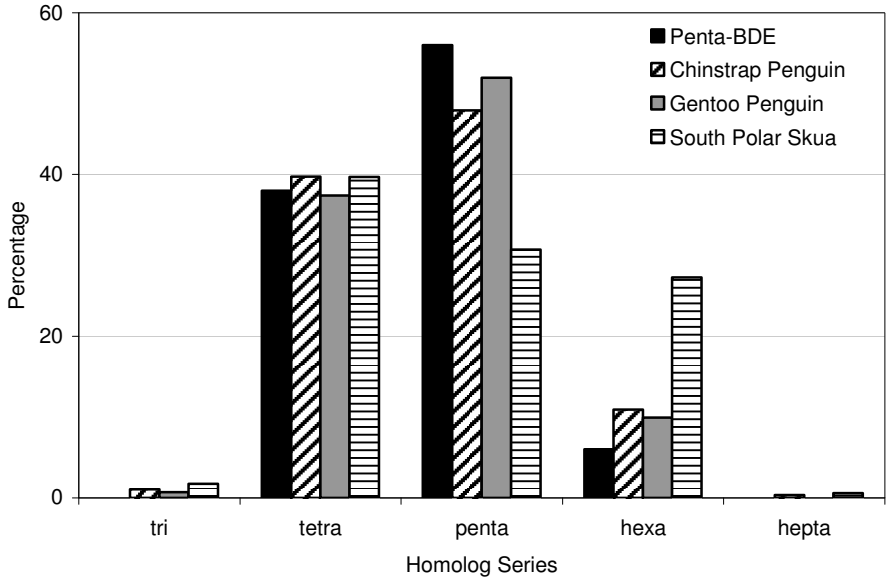


Fig. 9. Percent distribution of PBDE homologs in the commercial Penta-BDE formulation and seabird eggs collected from nesting sites at King George Island, Antarctic Peninsula.

A more detailed examination of the individual congeners present in the bird eggs reveals interesting patterns. The percent distribution of congeners is similar in chinstrap and gentoo eggs (see Fig. 10). The per cent of BDE-47 in the mixture is also comparable in all three species. However, south polar skuas have relatively more BDEs 100, 153 and 154 than penguins while the opposite is true for BDE-99. IUPAC No. 155 concentrations also showed a noteworthy difference between migrating and endemic species. This

congener was detected in a single sample of penguins, whereas it was found in all south polar skua eggs at ~5% of total PBDEs. The sum of BDEs 47, 99 and 100 represented over 85% of the total PBDEs in both chinstrap and gentoo penguins. Such a percentage is comparable to that found in lichens and mosses of King George Island suggesting a common contaminant source. Conversely, the same congeners represented only 66% of south polar skua egg contamination which is in good agreement with PBDE mixtures found in seabirds from the northwestern Pacific Ocean (see Watanabe et al., 2004; Wan et al., 2008). Moreover, congeners such as IUPAC Nos. 71, 118, 119 and 138 were also detected in south polar skua eggs at King George Island (see Table 17) and seabirds inhabiting the coasts of China and Japan (Watanabe et al., 2004; Wan et al., 2008). Generally, these PBDE congeners have not been found in the wildlife of North America and Europe (see reviews by de Wit, 2002; Hale et al., 2003; de Wit et al., 2006). These findings suggest that south polar skuas breeding at King George Island may be wintering in the northwestern Pacific Ocean.

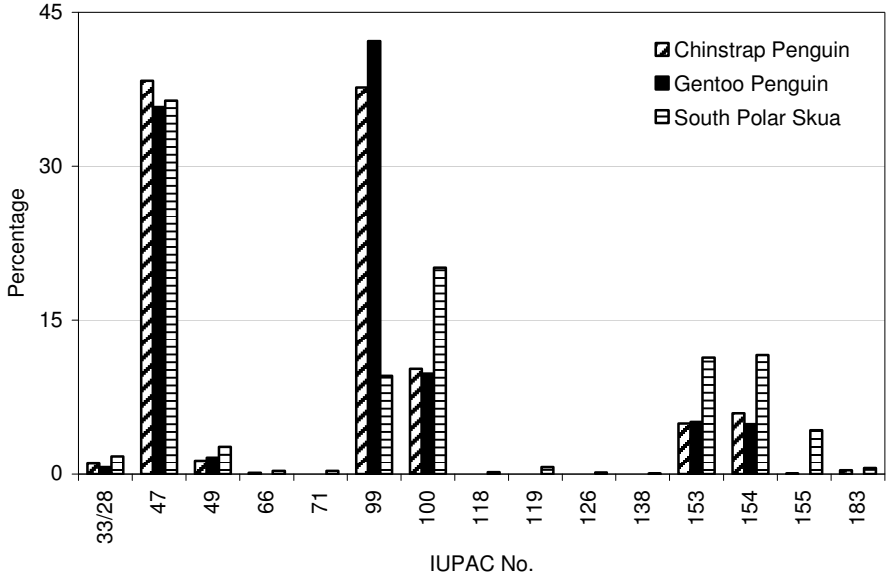


Fig. 10. Percent distribution of PBDE congeners in seabird eggs collected from nesting sites at King George Island, Antarctic Peninsula.

Antarctic penguins eggs are the least contaminated in the world regarding PBDEs (see Table 18). In the Ross Sea (East Antarctica), Corsolini et al. (2006) found concentration of PBDEs in eggs of Adélie penguin (*Pygoscelis adeliae*) similar to those detected in chinstrap and gentoo penguin eggs from King George Island (West Antarctica). These low levels are related to the endemism of pygoscelid penguins. Eggs of black guillemots (*Cepphus grylle*) from the Arctic had PBDE concentrations at least three times as high as penguins from Antarctica (Vorkamp et al., 2004). Such a difference may be attributed to the Arctic proximity to the sources of PBDEs. Low levels of brominated flame retardants were also detected in eggs of northern fulmars (*Fulmarus glacialis*) from the Faroe Islands, North Atlantic (Fangstrom et al., 2005; Karlsson et al.,

2006). Seabird eggs from more industrialized areas such as North America, Europe and Asia exhibit contamination an order of magnitude higher or more than penguin eggs from Antarctica. For example, eggs of Leach's storm petrel (*Oceanodroma leucorhoa*) from Canada and guillemot (*Uria aalge*) from Sweden had total PBDE concentrations of 67.6 ng g^{-1} lipid and 77.4 ng g^{-1} lipid, respectively (Elliott et al., 2005; Lundstedt-Enkel et al., 2006). Even higher PBDE levels (mean = 1400 ng g^{-1} lipid) were found in the eggs of great cormorants (*Phalacrocorax carbo*) from the densely populated and highly industrialized Tokyo Bay, Japan (Watanabe et al., 2004). The eggs of south polar skua exhibited high levels of contamination when compared to the eggs of other seabird species around the world (see Table 18). The average concentration of 146 ng g^{-1} lipid in south polar skua eggs from King George Island is higher than PBDE levels found in seabird eggs from the Baltic Sea and the Pacific coast of Canada. This confirms the interpretation that exposure of these migratory species to PBDEs occurs north of the Antarctic Convergence during the non-breeding season (probably in the northern hemisphere).

Table 18

Concentration of PBDEs in seabird eggs collected from different nesting sites all over the world.

Species	Location	Year	n	Σ PBDE (ng g^{-1} lipid)	Reference
Adélie Penguin (*Pygoscelis adeliae*)	Ross Sea, Antarctica	1995-96	6	3.06[b]	Corsolini et al. (2006)
Chinstrap Penguin (*Pygoscelis antarctica*)	Antarctic Peninsula	2004-05	35	6.78[c]	this study
Gentoo Penguin (*Pygoscelis papua*)	Antarctic Peninsula	2005-06	17	8.12[d]	this study
Northern Fulmar (*Fulmarus glacialis*)	Faroe Islands, North Atlantic	2003	9	11.7[e]	Karlsson et al. (2006)
Northern Fulmar (*Fulmarus glacialis*)	Faroe Islands, North Atlantic	2000-01	19	21[f]	Fangstrom et al. (2005)
Black Guillemot (*Cepphus grylle*)	Qeqertarsuaq, West Greenland	2001	7	24.2[g]	Vorkamp et al. (2004)
Leach's Storm Petrel (*Oceanodroma leucorhoa*)	British Columbia, Canada	2002	1[a]	67.6[h]	Elliott et al. (2005)
Guillemot (*Uria aalge*)	Baltic Sea, Sweden	2000-02	30	77.4[i]	Lundstedt-Enkel et al. (2006)
South Polar Skua (*Catharacta maccormicki*)	Antarctic Peninsula	2004-05	13	146[j]	this study
Great Cormorant (*Phalacrocorax carbo*)	Tokyo Bay, Japan	1998	10	1400[k]	Watanabe et al. (2004)

[a] Homogenate from several eggs

[b] Sum of BDEs 28, 47, 99 and 100

[c] Sum of BDEs 28, 33, 47, 49, 66, 99, 100, 153, 154, 155 and 183

[d] Sum of BDEs 28, 33, 47, 49, 99, 100, 153 and 154

[e] Sum of BDEs 47, 99, 100, 153, 183 and 209

[f] Geometric mean. Sum of BDEs 47, 99, 100, 153 and 154

[g] Sum of BDEs 28, 47, 99, 100, 153 and 154

[h] Conversion from wet weight assuming 5% lipid. Sum of BDEs 47, 49, 99, 100, 153 and 154

[i] Geometric mean. Sum of BDEs 47, 99, 100, 153 and 154

[j] Sum of BDEs 28, 33, 47, 49, 66, 71, 99, 100, 118, 119, 126, 138, 153, 154, 155 and 183

[k] Sum of BDEs 28, 47, 99, 100, 119, 153, 154 and 183

According to Corsolini et al. (2007), PBDEs are a small percentage (~1%) of the total POPs burden in the blood of three species of penguins breeding at King George Island (the same nesting sites as this study). They found that PCBs, HCB and *p*,*p*'-DDE dominated POPs in penguin blood. Likewise, PBDEs in gentoo eggs analyzed in this study are about 1.5% of the total organohalogenated compounds (Fig. 11). When compared to PBDEs (5.68 ng g^{-1} lipid), concentration of PCBs, HCB and DDTs (162 ng g^{-1} lipid, 117 ng g^{-1} lipid and 39.4 ng g^{-1} lipid, respectively) are at much higher levels in the same samples (Cipro, 2007). Corsolini et al. (2006) detected concentrations of HCB

and DDTs two orders of magnitude higher than PBDEs in eggs of Adélie penguin from the Ross Sea.

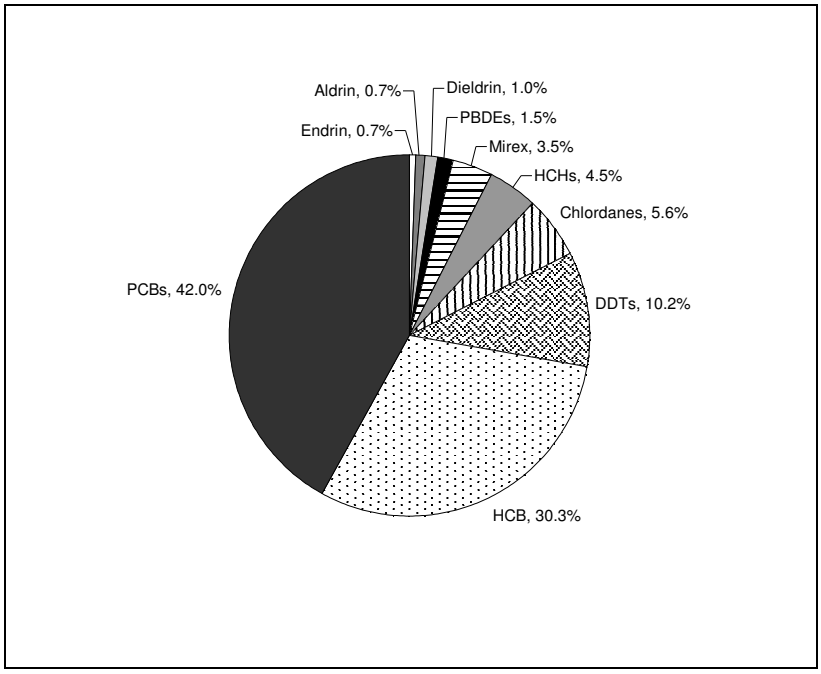


Fig. 11. Percent contribution of different classes of organohalogenated compounds to the total contamination of gentoo penguin (*Pygoscelis papua*) eggs collected at King George Island (Antarctic Peninsula) during the austral summer 2005-2006. Organochlorine data from Cipro (2007). Percent distribution calculated from concentrations in ng g^{-1} lipid (n = 9).

Several authors have found higher levels of organochlorines in skuas when compared to penguins. Court et al. (1997) investigated chlorinated compounds in eggs of sympatric Adélie penguin and south polar skua that breed in the Ross Sea region. Concentrations of PCBs, DDTs and HCB were approximately an order of magnitude higher in south polar skua eggs as compared to penguin eggs. Weichbrodt et al. (1999)

analyzed organochlorines in eggs of two species of skua (south polar skua and brown skua – *Catharacta antarctica lonnbergi*) and three species of penguin (chinstrap, gentoo and Adélie) collected at Potter Peninsula, King George Island. Concentrations of PCBs were two orders of magnitude higher in skuas than in penguins, whereas DDTs along with chlordanes were an order of magnitude higher in skuas. Kumar et al. (2002) assessed the toxicity of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like PCBs in eggs of south polar skua and Adélie penguin collected at Terra Nova Bay, East Antarctica. Average 2,3,7,8-tetrachlorodibenzo-*p*-dioxin toxic equivalents (TEQs) in penguin and skua were 5.9 pg g^{-1} wet weight and 32 pg g^{-1} wet weight, respectively. Although both concentrations are below the low-observed-effect-level (LOEL), the authors pointed out that the mean TEQ in eggs of south polar skua was close to those that might cause adverse effects in some bird species. Bustnes et al. (2007) examined a series of variables to compare the reproductive performance of south polar skuas and their levels of chlorinated hydrocarbons. They found no association between POPs and the occurrence of non-viable eggs. Also, POPs did not seem to affect the survival of adult individuals. Conversely, the authors found that organochlorine contaminants might delay reproduction and reduce fetal growth in the investigated birds.

4.4. Potential metabolism of PBDEs in penguin eggs

Although persistent in the environment, PBDEs are subject to slow transformation due to metabolic activities (e.g., Stapleton et al., 2004; Van den Steen et al., 2007). A female bird transfers some of her body burden of PBDEs to eggs (see Verreault et al., 2006; Pirard and De Pauw, 2007). The incubation period in pygoscelid penguins lasts about five weeks (Volkman and Trivelpiece, 1980). It can be hypothesized that the incubation period in penguins is short enough that significant metabolization of PBDE congeners does not occur. In order to address this hypothesis, the following assumptions are made: (1) the burden of PBDEs in freshly laid eggs is approximately uniform throughout the studied population of chinstrap or gentoo penguins and (2) there are no losses of PBDEs due to gas exchange through the eggshell during the incubation period. The validity of these assumptions is discussed below.

Pygoscelid penguins typically lay a two-egg clutch. So one might argue that the female would maximize her energy investment in the first egg and thus she would transfer more PBDEs to that egg. However, several authors have found that the cost of egg production in penguins is low (e.g., Astheimer and Grau, 1985; Davis et al., 1989; Williams, 1990; Adams, 1992). For instance, the daily cost of egg production for a gentoo female is 5.4% of the basal metabolic rate for the two-egg clutch (Adams, 1992). Bost and Jouventin (1991) also did not find significant differences in egg mass between first and second clutches in gentoo penguins. Furthermore, eventual differences in egg mass within clutches of pygoscelid penguins have been attributed to reduced albumen

content while yolk mass remains relatively constant (Astheimer and Grau, 1985). Nosek et al. (1992) investigated the distribution of labeled 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in eggs of ring-necked pheasants (*Phasianus colchicus*) and found that all TCDD is confined to the yolk. These findings support the assumption that the variability of PBDEs within a two-egg clutch will be comparable to that between clutches.

Eggs of avian species lose mass during the incubation period (Sotherland and Rahn, 1987). The mass loss is primarily represented by exchange of gases such as water vapor, carbon dioxide and oxygen through the eggshell (Ar, 1991; Paganelli, 1991). The net diffusive flux of water vapor and carbon dioxide goes toward the egg exterior while the oxygen flux goes into the egg. The octanol-air coefficient (K_{OA}) is a good descriptor of how organic compounds such as PBDEs will partition between air and organic matter. The K_{OA} of PBDEs is very high on the order of 10^9-10^{12} at ambient temperature (Harner and Shoeib, 2002). This means PBDEs will strongly partition to the yolk in the egg environment. So it is reasonable to assume that penguin eggs form a closed system with regard to PBDEs and that any losses through the eggshell will be negligible during incubation.

All eggs collected for this investigation were weighed in the laboratory with the shell on. So it is necessary to estimate the egg content from data published in the literature. Some authors have found that eggshell of king penguin (*Aptenodytes patagonicus*) and Adélie penguin (*Pygoscelis adeliae*) represent 11% and 13% of the initial fresh egg mass, respectively (Astheimer and Grau, 1985; Handrich, 1989). The eggshell also gets thinner during incubation since it serves as a source of calcium for the

developing embryo (Handrich, 1989). Groscolas et al. (2003) measured a decrease by 10% of the initial egg mass throughout the incubation period in king penguins. Based on these data, it was assumed that the eggshell in both chinstrap and gentoo penguin eggs represents 12% of the initial fresh egg mass and that it decreases linearly by 10% in mass during incubation. Thus, weight of eggshell for all samples was estimated using a linear regression between the lightest and heaviest eggs (see Fig. 12).

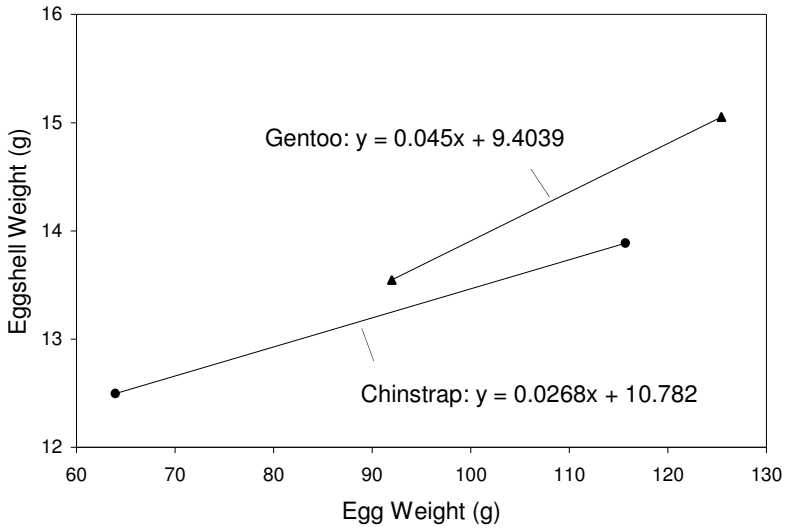


Fig. 12. Linear regression used to estimate eggshell mass loss during incubation of chinstrap (*Pygoscelis antarctica*) and gentoo (*Pygoscelis papua*) penguin eggs.

Several authors have found mass differences between freshly laid and pre-hatched (i.e., pipping phase) eggs ranging from 13% to 20% in penguins (Astheimer and Grau, 1985; Bucher et al., 1986; Yom-Tov et al., 1986; Handrich, 1989; Groscolas et al., 2003). In this study, the mass difference between the heaviest and the lightest eggs was

49% and 29% for chinstrap and gentoo penguins, respectively (Tables 19 and 20). This is somewhat higher than values reported in the literature and might suggest that eggs pushed out of the nest by the parents lose water at a faster rate than eggs being incubated in the nest. Consequently, some calculations of eggshell mass may be slight underestimates.

Yolk mass also decreases during incubation as the embryo utilizes energy and nutrient reserves (Sotherland and Rahn, 1987; Adams, 1992). Groscolas et al. (2003) found that fatty acids in the yolk of king penguin eggs decrease by 72% of the initial mass. In this study, lipids decreased by 65% (from 7.7 % to 2.7%) and 52% (from 7.6% to 3.6%) in eggs of chinstrap and gentoo penguins, respectively (Table 19 and 20). The lower percentage of oxidized lipids in gentoo eggs suggests that the collected set does not represent the entire incubation period (only one of the eggs was found with an embryo). Conversely, the chinstrap values are close to the total percent of lipid oxidized during incubation, indicating that samples of this species represent different stages in the incubation period. This set of eggs contained several embryos at distinct developmental stages including a hatchling that died in the pipping phase. Thus, the lipid content of eggs can be used to investigate the transformation of PBDEs during incubation as an approximation of the egg mass.

Table 19

Biological and chemical parameters of the chinstrap eggs collected at Admiralty Bay (King George Island, Antarctic Peninsula) in the austral summer 2005-2006.

ID	Whole Egg (g)	Eggshell (g)	Content (g)	Moisture (%)	Lipid (g)	Lipid (%)	Notes
GY0102	82.0	13.0	69.0	76.4	3.8	5.5	
GY0103	89.6	13.2	76.4	76.9	5.0	6.5	
GY0104	98.2	13.4	84.8	80.1	4.7	5.6	embryo
GY0105	86.3	13.1	73.2	75.3	4.6	6.3	
GY0106	92.0	13.2	78.7	71.1	6.1	7.7	
GY0107	84.5	13.0	71.4	73.7	5.5	7.7	
GY0108	66.2	12.6	53.6	75.9	3.6	6.7	
GY0109	64.0	12.5	51.5	73.3	3.4	6.7	
GY0110	100.1	13.5	86.6	76.0	5.7	6.6	
GY0111	99.8	13.5	86.4	77.1	4.8	5.6	
GY0112	91.3	13.2	78.1	74.5	5.0	6.4	
GY0113	100.2	13.5	86.7	73.7	6.7	7.7	
GY0114	115.7	13.9	101.8	78.3	5.1	5.0	
GY0115	76.2	12.8	63.3	76.3	3.1	5.0	
GY0116	104.0	13.6	90.4	78.9	4.7	5.2	
GY0117	66.5	12.6	53.9	73.0	4.0	7.5	
GY0118	78.9	12.9	66.0	81.3	1.8	2.7	embryo
GY0119	79.1	12.9	66.2	79.4	2.7	4.1	embryo
GY0120	88.0	13.1	74.9	80.1	2.7	3.6	
GY0121	87.6	13.1	74.5	81.3	2.8	3.8	embryo
GY0122	87.3	13.1	74.1	75.7	4.4	6.0	
GY0123	77.2	12.9	64.4	75.4	4.7	7.3	
GY0124	96.8	13.4	83.4	76.9	4.9	5.9	
GY0125	85.5	13.1	72.4	76.9	4.4	6.1	embryo
GY0126	76.6	12.8	63.8	77.2	3.0	4.6	embryo
GY0127	94.6	13.3	81.3	75.9	5.9	7.3	
GY0128	84.4	13.0	71.4	75.1	3.9	5.5	
GY0129	83.8	13.0	70.8	77.9	3.7	5.2	
Max	**115.7**	**13.9**	**101.8**	**81.3**	**6.7**	**7.7**	
Min	**64.0**	**12.5**	**51.5**	**71.1**	**1.8**	**2.7**	

Table 20

Biological and chemical parameters of the gentoo eggs collected at Admiralty Bay (King George Island, Antarctic Peninsula) in the austral summer 2005-2006.

ID	Whole Egg (g)	Eggshell (g)	Content (g)	Moisture (%)	Lipid (g)	Lipid (%)	Notes
GY0136	105.2	14.1	91.0	77.5	4.4	4.8	
GY0137	107.9	14.3	93.7	81.9	3.4	3.6	embryo
GY0138	106.2	14.2	92.0	75.2	4.9	5.3	
GY0139	105.1	14.1	91.0	77.1	4.5	4.9	
GY0140	105.5	14.2	91.4	76.7	4.7	5.2	
GY0141	105.2	14.1	91.1	76.5	5.2	5.7	
GY0142	125.4	15.1	110.4	76.3	5.9	5.4	
GY0143	94.0	13.6	80.4	75.4	4.0	5.0	
GY0144	96.0	13.7	82.3	76.1	4.0	4.9	
GY0145	106.0	14.2	91.8	80.9	4.2	4.6	
GY0146	92.0	13.5	78.5	73.5	5.9	7.6	
Max	**125.4**	**15.1**	**110.4**	**81.9**	**5.9**	**7.6**	
Min	**92.0**	**13.5**	**78.5**	**73.5**	**3.4**	**3.6**	

According to the Pearson's product-moment correlation analysis, in almost all cases there is no significant correlation between the total lipid content and total burden of PBDE congeners in penguin eggs (see Table 21). The only exception is a significant correlation between total lipid and total BDE-33/28 in chinstrap eggs ($r = 0.675$, $n = 9$, $p < 0.05$). Bearing in mind that lipids are oxidized during incubation, they may be used as a proxy for time of incubation: the lower the lipid content, the longer the time of incubation. If the burden of contaminant in the egg remains constant over the incubation period, this is a sign that no transformation has occurred. Thus, the positive significant correlation between lipids and BDE-33/28 in chinstrap eggs might suggest metabolism of these congeners during incubation (Fig. 13a) while the lack of significant correlation for all other congeners suggests no metabolism (Fig. 13b). One might argue that the

limited number of data points used in the BDE-33/28 correlation (n = 9) could invalidate the significance of the statistical test. However, the Pearson's correlation analysis using the same nine data points for the other congeners still reveals no significant statistical correlation between lipids and PBDEs ($r < 0.40$, $p > 0.30$).

Table 21

Correlation parameters between total lipid content and total burden of PBDE congeners in penguin eggs collected at Admiralty Bay (King George Island, Antarctic Peninsula). Acronyms: r = Pearson's product-moment correlation coefficient; p = level of significance of the test; n = number of samples.

	Chinstrap Penguin			Gentoo Penguin		
	r	p	n	r	p	n
BDE-33/28	0.675	0.046	9	-0.397	0.378	7
BDE-47	0.159	0.419	28	0.104	0.761	11
BDE-49	0.370	0.109	20	0.394	0.294	9
BDE-99	0.049	0.803	28	0.014	0.968	11
BDE-100	0.050	0.799	28	0.030	0.930	11
BDE-153	0.165	0.420	26	0.157	0.645	11
BDE-154	0.156	0.427	28	0.159	0.640	11
Σ PBDEs	0.109	0.581	28	0.064	0.851	11

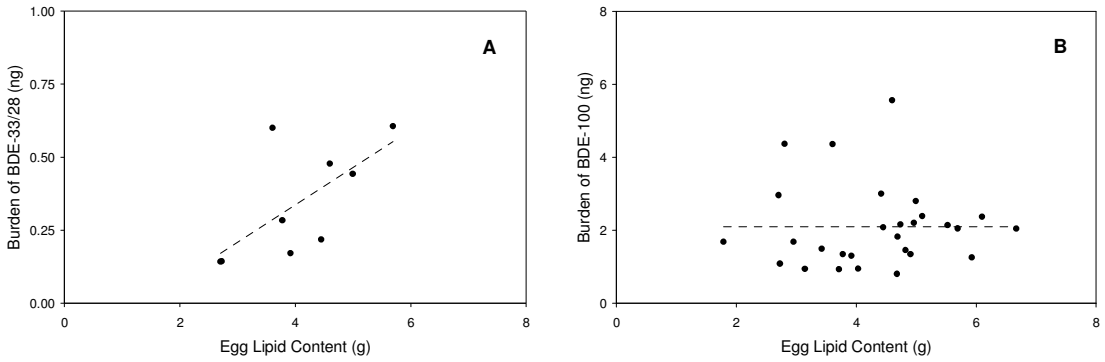


Fig. 13. Comparison of a significant (BDE-33/28) and a non-significant (BDE-100) correlation between lipids and PBDE congeners in chinstrap eggs. The dotted lines depict data point tendency.

It is important to note that the lack of correlation between lipids and most PBDEs does not completely rule out the lack of potential metabolism during incubation. The low residues of BDE-33/28 in chinstrap eggs might have contributed to their decreasing trend since these two co-eluted compounds were detected at the lowest concentration of all congeners. For example, the average burden of BDEs 47, 99 and 100 in chinstrap eggs is about an order of magnitude higher than BDE-33/28. If the metabolization capacity of PBDEs in eggs is limited, tiny amounts will be degraded during incubation. Consequently, it would be much easier to detect variations in the burden of contaminants at the lower end. This might be the case of BDE-33/28 in chinstrap eggs. The fact that no significant correlation was found between lipids and BDE-33/28 in gentoo eggs might be related to the lack of representativeness of the collected set as discussed above.

Avian eggs are laid with a limited amount of available resources that must be used to complete embryo development. So it is likely that all metabolic processes are

optimized and directed toward the most relevant functions such as synthesis of new embryonic tissues. In this context, metabolization of xenobiotics would be of minor relevance in eggs unless the level of contaminants is high enough to negatively effect the embryo development. Metabolism of xenobiotics in birds is mediated by enzymes of the superfamily cytochrome P450. Blus et al. (1998) investigated the activity of these enzymes in tern eggs collected from nesting colonies in the USA. They concluded that low levels of POPs seem not to activate the cytochrome P450 enzymes in embryos of both Forster's tern (*Sterna forsteri*) and Caspian tern (*Sterna caspia*). This might also be the case of total PBDEs in penguin eggs. A significant correlation between lipid content and burden of Σ PBDEs in eggs of both species was not observed (see Table 21).

In addition to the restricted energy budget, time might also be an issue for metabolization of xenobiotics in eggs. The incubation period of both chinstrap and gentoo penguin lasts approximately 35 days (Conroy et al., 1975; Adams, 1992). However, the most intense growth of pygoscelid embryos (i.e., highest metabolic activity) occurs in the last 14 days of incubation (Bucher et al., 1986). The chorioallantoic membrane is suggested to be the first line of defense of avian embryos against xenobiotics, but cytochrome P450 enzymes are highest in the liver which takes some time to fully develop (Noble, 1987; Annas et al., 1999). Therefore, the relatively short time of incubation may restrict any significant metabolism of PBDEs in penguin eggs.

In several studies carried out with avian and reptile species, the level of POPs has also been similar between freshly laid eggs and hatchlings. Rattner et al. (1996)

investigated the burden of *p*,*p*'-DDE and total PCBs in siblings of black-crowned night-herons (*Nycticorax nycticorax*) from a contaminated site in Wisconsin, USA. The authors found no significant statistical differences in the high contaminant burdens (~30 μg for PCBs and ~300 μg for *p*,*p*'-DDE) of fresh eggs and pipping embryos. Custer et al. (1997) carried out a similar study with double-crested cormorants (*Phalacrocorax auritus*). A comparison of the burden of individual organochlorines (including 13 PCB congeners) revealed no statistical difference between fresh eggs and sibling embryos. Analogous results have been found in hens (*Gallus gallus*), herring gulls (*Larus argentatus*) and common snapping turtles (*Chelydra serpentina serpentina*) (Gilman et al., 1978; Brunstrom et al., 1982; Bishop et al., 1995). In contrast, Berny et al. (2002) detected age-related variations (i.e., lower levels in eggs near hatching when compared to freshly laid ones) in PCBs in eggs of little egrets (*Egretta garzetta*) nesting in wetlands of the Mediterranean Sea. Interestingly, the same trends were not observed for *p*,*p*'-DDE and γ-HCH.

In summary, metabolism of organohalogenated compounds in eggs appears to be both species- and compound-specific (e.g., Rattner et al., 1996; Custer et al., 1997; Berny et al., 2002). The only congener that might possibly be metabolized in this study was BDE-33/28 in the eggs of chinstrap penguins. This is the first study of individual PBDE compounds in avian species exhibiting low contaminant burden (i.e., on the order of nanograms). The short incubation period of penguins (~35 days) may be a factor in limiting transformation of PBDE congeners in eggs, especially considering that the most intense metabolic activity takes place in the last two weeks of embryo development. In

addition, the restricted amount of energy in eggs may be preferentially directed towards the synthesis and maintenance of embryonic tissues rather than metabolization of xenobiotics at low levels such as PBDEs.

CHAPTER V

SUMMARY, FUTURE STUDIES AND CONCLUSION

5.1. Summary

In the past 15 years, increasing concerns have been expressed about growing worldwide contamination by PBDEs. It can be argued that PBDEs should be added to the list of POPs since scientific evidence has demonstrated long-range atmospheric transport, persistency in the environment, accumulation in living organisms, and potential to cause adverse effects in humans and wildlife. Although PBDEs are ubiquitous, their global biogeochemical cycle is poorly understood. Few studies have investigated PBDEs in the southern hemisphere including Antarctica. This dissertation adds to the knowledge of the distribution of PBDEs in Antarctica and the processes that control the observed patterns. The objectives of the study were: (1) evaluate the concentration of PBDEs in Antarctic lichens and mosses; (2) investigate the transfer mechanisms of PBDEs from the atmosphere to Antarctic vegetation; (3) compare the levels of PBDEs in eggs of migratory and endemic seabirds breeding in Antarctica; and (4) study the metabolism of PBDEs during the incubation of penguin eggs. Use of an ion-stacking technique in GC/EI-MS analyses lowered limits of detection while maintaining analytical selectivity and sensitivity.

The data presented here are the first report on PBDEs in Antarctic vegetation. PBDEs were detected at low levels (i.e., pg g^{-1}) in all lichen and moss samples analyzed.

These plants take up chemicals directly from the atmosphere serving as proxies for the global atmospheric transport of chemicals. Contaminant levels were not statistically different at sites close to and distant from human facilities. Long-range atmospheric transport is believed to be the primary source of PBDEs to King George Island, Antarctica but local sources cannot be completely ruled out. The pattern of congeners in plants resembles those found in commercial mixtures of Penta-BDE. In addition, the presence of BDE-183 in lichens and mosses implies that other technical BFR formulations (e.g., Octa-BDE and Deca-BDE) have reached Antarctica. Mosses contained higher contaminant levels than lichens. This difference is most likely due to the differing mechanisms of PBDEs uptake from the atmosphere which are controlled by a number of chemical, environmental and plant variables.

Concentrations of PBDEs in Antarctic vegetation were significantly higher in 2004-05 compared to 2005-06. Precipitation at King George Island was also higher in 2004-05 than in 2005-06. In Antarctica, airborne PBDEs mostly partition onto atmospheric aerosols. The transfer of congeners to vegetation is at least partially controlled by local dry/wet particle washout. Concentration of PBDEs in lichens collected at King George Island showed a significant, positive correlation with the local precipitation patterns. In contrast, PBDEs in mosses exhibit no significant correlation with atmospheric precipitation, suggesting that other factors such as plant-specific parameters (e.g., morphology) control the uptake of PBDEs by mosses.

Marine inputs dominate the chemical composition of Antarctic aerosols which consist of sea salt and biogenic components such as methanesulfonic acid (MSA).

PBDEs in the Antarctic atmosphere are likely associated with organic MSA particles – a byproduct of phytoplanktonic releases to the atmosphere. Marine phytoplankton may play a role in the long-range atmospheric transport of PBDEs to the Antarctic environment by providing the aerosols that transport the chemicals to the land surface. Higher brominated diphenyl ethers gradually partition from the gaseous to particle phase as atmospheric temperatures decrease poleward. In this partitioning they are coupled to phytoplankton-derived MSA and eventually reach the Antarctic environment. Finally, wet deposition (i.e., rain and snowfall) removes the chemical-laden particles from the atmosphere facilitating partition to and accumulation in Antarctic vegetation.

Penguins are endemic species to the Antarctic environment, whereas skuas are migratory seabirds that breed in Antarctica during the austral summer. PBDEs in south polar skua eggs were much higher in concentration than in penguin eggs. In addition, the pattern of PBDE congeners differed between south polar skua and penguin eggs. Such differences are likely associated with the migration patterns of these seabirds during the non-breeding season. South polar skuas migrate northward and can be found in boreal oceans during the austral winter (i.e., closer to PBDE sources). The mixture of PBDEs in penguin eggs is similar to the pattern found in the local vegetation although additional congeners were detected in lichens and mosses. This is reflective of the endemism of penguins to Antarctica. Conversely, PBDEs in south polar skua eggs were similar to patterns found in seabirds along the coasts of China and Japan. These findings suggest that south polar skuas obtain most of their contaminant burden north of the Antarctic

Convergence. The pattern of PBDEs suggests that south polar skuas breeding at King George Island may winter in the northwestern Pacific Ocean.

Although persistent in the environment, POPs are subject to slow transformation in the environment. A potential metabolism of PBDEs in penguin eggs during the 5-week incubation period appears to be both species- and compound-specific. No potential metabolism was detected in gentoo penguin eggs during incubation. In contrast, BDE-28/33 showed a significant positive correlation with lipid content in chinstrap penguin eggs. The short incubation period for penguin eggs might limit the metabolism of PBDEs, especially considering that the most intense metabolic activity takes place in the last two weeks of embryo development. In addition, the amount of energy contained in eggs is restricted and may be preferentially directed toward the synthesis and maintenance of embryonic tissues rather than metabolism of xenobiotics. In this context, the low levels of PBDEs in penguin eggs might not activate the P450 enzyme systems responsible for the breakdown of xenobiotics.

5.2. Future studies

The studies presented in this dissertation expanded our knowledge of the environmental distribution of PBDEs. On the other hand, these studies have also raised many questions that remain to be addressed by future studies. For instance, long-term monitoring of the same species of lichen (*U. antarctica* and *U. aurantiaco-atra*) and moss (*S. uncinata*) as well as the eggs of penguins (*P. antarctica* and *P. papua*) should

be conducted to determine trends in PBDEs distributions in Antarctica. The hypothesis suggesting the role of marine aerosols on the long-range atmospheric transport of PBDEs remains to be tested. Marine phytoplankton emissions (i.e., DMS) and their oxidation products (i.e., MSA) need to be studied in relation to the levels of PBDEs in atmospheric aerosols over the Southern Ocean. Concentration of PBDEs should be measured at the ocean-atmosphere microlayer boundary as well. This interface is a film that is rich in organic material that might serve as a pool of contaminants for the "hopping" effect – similar to the role of plants on continents.

Investigation of PBDEs in a greater diversity of plant species collected at the same site (i.e., similar environmental conditions) may elucidate the role of plant characteristics (e.g., morphology) in the deposition and retention of contaminants. Measurement of PBDEs in air, snow and rain can be used to quantify the efficiency of contaminant washout from the atmosphere. The influence of snow on the retention of anthropogenic chemicals by Antarctic plants also needs to be studied as snow covers vegetation during winter and melts during summer. Investigation of PBDEs in the atmosphere of King George Island along with movement of air masses would be useful to better understand the potential sources of contamination in the southern hemisphere. Conversely, possible local sources also need to be quantified. For example, PBDEs should be measured in dust, indoor air, wastewater sludge and effluent from scientific stations such as Ferraz (Brazil).

Future analyses of PBDEs need to target a greater variety of seabird species at King George Island and along the Antarctic Peninsula. For example, brown and south

polar skuas have distinct migration ranges that might correspond to different contamination levels. The geographical distribution of the former is limited to the southern hemisphere while the latter undertakes trans-equatorial migration. Latitudinal variations in PBDEs concentrations might be used to infer distance from source regions as well. Moreover, collection of eggs must be accompanied by measurement of parameters such as egg volume, weight, dimensions and thickness of eggshell to control for natural variability. Concentration of total PBDEs and the pattern of individual congeners should be studied in the female-egg pairings to determine potential differences in the generational transfer of contaminants. Additionally, measurement of PBDEs in male and female birds may reveal sex differences in the level of contaminants as observed in several mammal species.

Laboratory experiments might be designed to more thoroughly document the metabolism of PBDEs in eggs of avian species during incubation. The metabolic products of PBDEs should be measured to confirm any observed transformations. Laboratory experiments are essential for controlling various environmental variables. Eggs of birds fed a PBDE-enriched diet might be used as a first approach to decipher bird physiological controls on PBDE contaminant loads. These experiments would serve to model observations in nature.

5.3. Conclusion

PBDEs are emerging global pollutants of growing concern. Given the widespread usage of PBDEs as fire retardants, it is expected that global concentrations and biomagnification will continue to increase for the foreseeable future. While current levels are at ultra-trace concentrations, history has shown that halogenated anthropogenic compounds have the potential for unforeseen environmental consequences and remain in the environment for years if not decades once released. As levels of PBDEs inevitably rise in the environment, it can be expected that biological effects thresholds will be exceeded and concomitant ecological concerns will only increase in importance and urgency. The addition of PBDEs to the list of POPs will be important in elevating these concerns to an appropriate level of societal awareness.

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APPENDIX A

EXAMPLES OF CALCULATION USING EQUATIONS 1-6

Example A-1. Calculation of the temperature-adjusted log K_{OA} of BDE-28 on November 22, 2004 using equation 1.

Parameters:

- A = -3.54 (for BDE-28; from Harner and Shoeib, 2002)
- B = 3889 (for BDE-28; from Harner and Shoeib, 2002)
- T = 1.665 ºC = 274.815 K (average air temperature over 5 days)

Eq. 1: $\log K_{OA} = A + \frac{B}{T} \Rightarrow \log K_{OA} = -3.54 + \frac{3889}{274.815} \Rightarrow \boxed{\log K_{OA} = 10.61}$

Example A-2. Calculation of the temperature-adjusted log K_{OA} of BDE-15 on November 22, 2004 using equations 2, 3 and 4.

Parameters:

- T = 1.665 ºC = 274.815 K (average air temperature over 5 days)
- t_R = 0.424 (for BDE-15; from Sjödin et al., 1998)

Eq. 3: $a' = \frac{2187.9}{T} - 2.020 \Rightarrow a' = \frac{2187.9}{274.815} - 2.020 \Rightarrow \boxed{a' = 5.941}$

Eq. 4: $b' = \frac{4003.7}{T} - 5.2425 \Rightarrow b' = \frac{4003.7}{274.815} - 5.2425 \Rightarrow \boxed{b' = 9.326}$

Eq. 2: $\log K_{OA} = a' + b' t_R \Rightarrow \log K_{OA} = 5.941 + (9.326 \times 0.424) \Rightarrow \boxed{\log K_{OA} = 9.90}$

Example A-3. Calculation of the percent fraction (Φ) of BDE-15 bound to atmospheric particles using equations 5 and 6.

Parameters:

- $\log K_{OA} = 9.91$ (for BDE-15; average from Table 12)
- $f_{OM} = 1.54\% = 0.0154$ (from Minikin et al., 1998; Wagenbach et al., 1998)
- TSP = 2343 ng m^{-3} (from Minikin et al., 1998; Wagenbach et al., 1998)

Eq. 5: $\log K_P = \log K_{OA} + \log f_{OM} - 11.91 \Rightarrow \log K_P = 9.91 + [\log(0.0154)] - 11.91 \Rightarrow$

$$\log K_P = 9.91 - 1.81 - 11.91 \Rightarrow \log K_P = -3.81 \Rightarrow \boxed{K_P = 0.000154}$$

Eq. 6: $\Phi = \dfrac{100 \times TSP \times K_P}{(TSP \times K_P) + 1} \Rightarrow \Phi = \dfrac{100 \times 2343 \times 0.000154}{(2343 \times 0.000154) + 1} \Rightarrow \boxed{\Phi = 26.5\%}$

APPENDIX B

COMPLETE ANTARCTIC SAMPLES DATA SETS

Table B-1

Concentration of PBDEs in lichen (n = 11) samples collected during the austral summer 2004-2005.

Page:	T1613	T1619	T1619	T1613	T1619	T1619
ID:	GY0068	GY0071	GY0064	GY0070	GY0065	GY0062
Site:	A	B	C	D	E	F
Location:	Refuge 2	Plaza Point	Ferraz (Chemistry)	Ferraz (VLF)	Stenhouse Point	Ullman Point
Species:	*U. aurantiaco-atra*	*U. antarctica*	*U. aurantiaco-atra*	*U. aurantiaco-atra*	*U. antarctica*	*U. aurantiaco-atra*
Collection:	3-Jan-2005	13-Jan-2005	1-Dec-2004	11-Jan-2005	20-Dec-2004	23-Nov-2004
Dry Weight (%)	85.4	86.1	79.3	68.3	86.7	50.3
Lipid Weight (%)	1.47	2.61	0.88	0.83	1.75	0.52
Analyte	Concentration (pg g^{-1} dry weight)					
BDE-7	nd	nd	nd	nd	nd	nd
BDE-8	nd	nd	nd	nd	nd	nd
BDE-10	nd	nd	nd	nd	nd	nd
BDE-11	nd	nd	nd	nd	nd	nd
BDE-12	nd	nd	nd	nd	nd	nd
BDE-13	nd	nd	nd	nd	nd	nd
BDE-15	nd	2.7	nd	nd	2.1	5.4
BDE-17	< MDL	< MDL	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	2.4	3.3	3.6	2.0	2.2	3.3
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	90.3	103.6	110.9	72.2	60.2	100.0
BDE-49	2.6	2.8	4.7	2.1	1.4	3.5
BDE-66	2.7	nd	nd	nd	nd	2.9
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	4.8	4.8	5.6	5.3	5.6	< MDL
BDE-99	94.5	100.0	117.7	75.9	64.8	136.5
BDE-100	22.1	20.7	24.0	14.9	12.8	25.9
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd
BDE-153	10.0	11.1	14.0	8.5	7.6	16.4
BDE-154	8.7	8.9	11.3	5.7	5.5	11.9
BDE-155	< MDL	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	3.1	3.4	4.0	3.5	nd	8.2
BDE-190	nd	nd	nd	nd	nd	nd
di-BDEs	nd	2.7	nd	nd	2.1	5.4
tri-BDEs	2.4	3.3	3.6	2.0	2.2	3.3
tetra-BDEs	95.6	106.4	115.6	74.3	61.5	106.4
penta-BDEs	121.4	125.5	147.2	96.1	83.2	162.5
hexa-BDEs	18.7	20.0	25.3	14.2	13.1	28.3
hepta-BDEs	3.1	3.4	4.0	3.5	nd	8.2
Total PBDEs	**241.2**	**261.3**	**295.7**	**190.1**	**162.1**	**314.1**

Table B-1 (continued)

Page:	T1619	T1619	T1619	T1619	T1619
ID:	GY0063	GY0069	GY0066	GY0067	GY0061
Site:	G	H	I	J	K
Location:	Hennequin Point	Vauréal Cape	Demay Point	Ezcurra Inlet	Machu Picchu
Species:	*U. aurantiaco-atra*	*Usnea* sp.	*Usnea* sp.	*U. antarctica*	*U. antarctica*
Collection:	24-Nov-2004	7-Jan-2005	24-Dec-2004	2-Jan-2005	22-Nov-2004
Dry Weight (%)	64.5	86.4	87.7	85.9	53.2
Lipid Weight (%)	1.05	2.90	1.41	1.86	0.89
Analyte	Concentration (pg g^{-1} dry weight)				
BDE-7	nd	nd	nd	nd	< MDL
BDE-8	nd	nd	nd	nd	nd
BDE-10	nd	nd	nd	nd	nd
BDE-11	nd	nd	nd	nd	nd
BDE-12	nd	nd	nd	nd	nd
BDE-13	nd	nd	nd	nd	nd
BDE-15	3.1	2.9	2.6	nd	4.4
BDE-17	nd	nd	nd	nd	< MDL
BDE-25	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd
BDE-33/28	3.1	2.9	2.9	2.2	4.3
BDE-35	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd
BDE-47	95.5	124.0	103.0	57.6	103.8
BDE-49	3.4	3.3	1.9	1.5	3.1
BDE-66	2.8	3.2	2.2	1.6	3.7
BDE-71	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd
BDE-85	< MDL	nd	6.5	< MDL	< MDL
BDE-99	111.5	142.6	133.8	63.0	126.9
BDE-100	23.1	33.1	25.4	12.5	26.1
BDE-116	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd
BDE-153	13.7	20.1	13.8	6.1	18.1
BDE-154	10.1	16.6	10.9	5.4	11.9
BDE-155	nd	< MDL	< MDL	nd	< MDL
BDE-166	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd	5.5
BDE-190	nd	nd	nd	nd	nd
di-BDEs	3.1	2.9	2.6	nd	4.4
tri-BDEs	3.1	2.9	2.9	2.2	4.3
tetra-BDEs	101.7	130.5	107.1	60.6	110.5
penta-BDEs	134.7	175.7	165.7	75.4	153.0
hexa-BDEs	23.8	36.7	24.7	11.5	30.0
hepta-BDEs	nd	nd	nd	nd	5.5
Total PBDEs	**266.5**	**348.7**	**303.0**	**149.8**	**307.8**

Table B-2

Concentration of PBDEs in lichen (n = 11) samples collected during the austral summer 2005-2006.

Page:	T1619	T1619	T1619	T1619	T1619	T1619
ID:	GY0156	GY0157	GY0154	GY0153	GY0150	GY0149
Site:	A	B	C	D	E	F
Location:	Refuge 2	Plaza Point	Ferraz (Chemistry)	Ferraz (VLF)	Stenhouse Point	Ullman Point
Species:	*U. aurantiaco-atra*	*U. antarctica*	*U. aurantiaco-atra*	*U. aurantiaco-atra*	*U. antarctica*	*U. aurantiaco-atra*
Collection:	11-Jan-2006	11-Jan-2006	27-Dec-2005	27-Dec-2005	21-Dec-2005	21-Dec-2005
Dry Weight (%)	87.0	85.5	86.5	85.2	89.4	87.3
Lipid Weight (%)	1.18	2.87	1.20	1.10	2.01	1.15
Analyte	Concentration (pg g^{-1} dry weight)					
BDE-7	nd	nd	nd	nd	nd	nd
BDE-8	nd	nd	nd	nd	nd	nd
BDE-10	nd	nd	nd	nd	nd	nd
BDE-11	nd	nd	nd	nd	nd	nd
BDE-12	nd	nd	nd	nd	nd	nd
BDE-13	nd	nd	nd	nd	nd	nd
BDE-15	2.2	2.6	3.2	3.0	2.6	2.4
BDE-17	nd	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	nd	2.0	2.8	1.8	1.5	1.5
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	37.4	65.5	70.0	49.9	48.7	57.9
BDE-49	nd	1.7	5.1	1.6	1.3	nd
BDE-66	nd	1.4	nd	nd	nd	1.3
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	nd	nd	8.3	nd	nd	< MDL
BDE-99	42.2	74.9	63.7	41.4	42.9	67.2
BDE-100	8.1	14.9	12.7	8.6	8.2	13.2
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd
BDE-153	4.2	8.9	6.8	6.3	5.4	8.4
BDE-154	4.2	6.7	5.0	3.3	3.0	5.8
BDE-155	nd	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	nd	nd	4.9	nd	nd	2.3
BDE-190	nd	nd	nd	nd	nd	nd
di-BDEs	2.2	2.6	3.2	3.0	2.6	2.4
tri-BDEs	nd	2.0	2.8	1.8	1.5	1.5
tetra-BDEs	37.4	68.6	75.1	51.5	50.0	59.1
penta-BDEs	50.3	89.8	84.7	50.0	51.1	80.4
hexa-BDEs	8.4	15.5	11.8	9.6	8.4	14.2
hepta-BDEs	nd	nd	4.9	nd	nd	2.3
Total PBDEs	**98.3**	**178.6**	**182.5**	**115.9**	**113.6**	**159.9**

Table B-2 (continued)

Page:	T1619	T1619	T1619	T1619	T1619
ID:	GY0155	GY0151	GY0152	GY0147	GY0148
Site:	G	H	I	J	K
Location:	Hennequin Point	Vauréal Cape	Demay Point	Ezcurra Inlet	Machu Picchu
Species:	*U. antarctica*	*U. antarctica*	*U. antarctica*	*U. aurantiaco-atra*	*U. antarctica*
Collection:	6-Jan-2006	23-Dec-2005	23-Dec-2005	15-Dec-2005	17-Dec-2005
Dry Weight (%)	82.2	87.7	87.1	86.9	88.1
Lipid Weight (%)	2.02	1.94	1.80	1.61	1.44
Analyte	Concentration (pg g^{-1} dry weight)				
BDE-7	nd	nd	nd	nd	nd
BDE-8	nd	nd	nd	nd	nd
BDE-10	nd	nd	nd	nd	nd
BDE-11	nd	nd	nd	nd	nd
BDE-12	nd	nd	nd	nd	nd
BDE-13	nd	nd	nd	nd	nd
BDE-15	2.8	3.2	3.2	2.3	2.5
BDE-17	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd
BDE-33/28	1.8	3.0	2.2	1.7	1.9
BDE-35	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd
BDE-47	64.0	138.3	55.3	54.1	51.8
BDE-49	2.1	3.1	nd	nd	1.8
BDE-66	1.9	nd	nd	nd	1.4
BDE-71	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd
BDE-85	nd	7.2	nd	< MDL	< MDL
BDE-99	72.6	155.4	55.6	58.6	59.4
BDE-100	14.8	32.5	11.4	11.4	11.4
BDE-116	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd
BDE-153	8.6	15.5	6.9	6.7	7.3
BDE-154	7.0	13.6	5.0	4.9	5.2
BDE-155	nd	< MDL	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd
BDE-183	nd	5.7	17.6	nd	5.2
BDE-190	nd	nd	nd	nd	nd
di-BDEs	2.8	3.2	3.2	2.3	2.5
tri-BDEs	1.8	3.0	2.2	1.7	1.9
tetra-BDEs	68.1	141.4	55.3	54.1	54.9
penta-BDEs	87.5	195.1	66.9	70.1	70.8
hexa-BDEs	15.6	29.1	12.0	11.6	12.5
hepta-BDEs	nd	5.7	17.6	nd	5.2
Total PBDEs	**175.8**	**377.4**	**157.2**	**139.8**	**147.9**

Table B-3

Concentration of PBDEs in angiosperm (n = 1) and moss (n = 10) samples collected during the austral summer 2004-2005.

Page:	T1628	T1622	T1622	T1628	T1622	T1622
ID:	GY0079	GY0082	GY0075	GY0081	GY0076	GY0073
Site:	A	B	C	D	E	F
Location:	Refuge 2	Plaza Point	Ferraz (Chemistry)	Ferraz (VLF)	Stenhouse Point	Ullman Point
Species:	*S. uncinata*	*S. uncinata*	*S. uncinata*	*S. uncinata*	*C. quitensis*	*S. princeps*
Collection:	3-Jan-2005	13-Jan-2005	1-Dec-2004	11-Jan-2005	20-Dec-2004	3-Dec-2004
Dry Weight (%)	15.9	23.6	21.7	24.0	48.7	13.4
Lipid Weight (%)	0.06	0.15	0.18	0.09	0.38	0.15
Analyte	Concentration (pg g^{-1} dry weight)					
BDE-7	nd	nd	nd	nd	nd	nd
BDE-8	nd	nd	nd	nd	nd	nd
BDE-10	nd	nd	nd	nd	nd	nd
BDE-11	nd	nd	nd	nd	nd	nd
BDE-12	nd	nd	nd	nd	nd	nd
BDE-13	nd	nd	nd	nd	nd	nd
BDE-15	25.2	18.7	nd	14.6	4.8	12.8
BDE-17	nd	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	13.0	14.5	11.3	5.2	3.4	10.0
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	495.3	358.7	270.3	195.0	120.0	260.4
BDE-49	13.2	20.7	11.7	5.6	3.0	10.0
BDE-66	11.8	17.5	12.4	4.6	3.2	7.6
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd	nd	nd
BDE-99	680.9	385.4	330.2	275.0	157.9	337.4
BDE-100	148.3	86.8	84.0	61.1	35.8	72.2
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	11.1	12.2	11.5	5.3	nd	7.2
BDE-190	nd	nd	nd	nd	nd	nd
di-BDEs	25.2	18.7	nd	14.6	4.8	12.8
tri-BDEs	13.0	14.5	11.3	5.2	3.4	10.0
tetra-BDEs	520.3	396.9	294.4	205.3	126.2	278.0
penta-BDEs	829.2	472.2	414.2	336.1	193.7	409.6
hepta-BDEs	11.1	12.2	11.5	5.3	nd	7.2
Total PBDEs	**1398.7**	**914.4**	**731.3**	**566.4**	**328.1**	**717.5**

Table B-3 (continued)

Page:	T1628	T1622	T1628	T1622	T1622
ID:	GY0074	GY0080	GY0077	GY0078	GY0072
Site:	G	H	I	J	K
Location:	Hennequin Point	Vauréal Cape	Demay Point	Ezcurra Inlet	Machu Picchu
Species:	*S. uncinata*	*S. uncinata*	*S. uncinata*	*Brachythecium sp.*	*S. uncinata*
Collection:	4-Dec-2004	7-Jan-2005	24-Dec-2004	2-Jan-2005	5-Dec-2004
Dry Weight (%)	11.7	16.6	17.1	50.6	31.2
Lipid Weight (%)	0.11	0.08	0.12	0.57	0.16
Analyte	Concentration (pg g^{-1} dry weight)				
BDE-7	nd	nd	nd	nd	nd
BDE-8	nd	nd	nd	nd	nd
BDE-10	nd	nd	nd	nd	nd
BDE-11	nd	nd	nd	nd	nd
BDE-12	nd	nd	nd	nd	nd
BDE-13	nd	nd	nd	nd	nd
BDE-15	28.3	15.3	15.8	4.7	9.2
BDE-17	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd
BDE-33/28	10.5	8.6	nd	2.6	8.5
BDE-35	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd
BDE-47	487.6	429.8	445.3	100.4	256.8
BDE-49	15.9	11.0	nd	2.7	8.5
BDE-66	nd	13.1	nd	3.8	4.3
BDE-71	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd
BDE-85	nd	24.6	nd	nd	nd
BDE-99	682.4	599.4	691.3	129.6	274.2
BDE-100	147.3	114.3	148.1	30.0	70.7
BDE-116	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd
BDE-183	16.5	10.0	8.8	1.8	12.7
BDE-190	nd	nd	nd	nd	nd
di-BDEs	28.3	15.3	15.8	4.7	9.2
tri-BDEs	10.5	8.6	nd	2.6	8.5
tetra-BDEs	503.5	453.9	445.3	106.9	269.7
penta-BDEs	829.7	738.4	839.4	159.6	344.9
hepta-BDEs	16.5	10.0	8.8	1.8	12.7
Total PBDEs	**1388.4**	**1226.2**	**1309.2**	**275.6**	**645.0**

Table B-4

Concentration of PBDEs in moss (n = 11) samples collected during the austral summer 2005-2006.

Page:	T1622	T1622	T1628	T1622	T1622	T1622
ID:	GY0167	GY0168	GY0165	GY0164	GY0161	GY0160
Site:	A	B	C	D	E	F
Location:	Refuge 2	Plaza Point	Ferraz (Chemistry)	Ferraz (VLF)	Stenhouse Point	Ullman Point
Species:	*S. uncinata*	*S. uncinata*	*S. uncinata*	*S. uncinata*	*S. uncinata*	*S. uncinata*
Collection:	11-Jan-2006	11-Jan-2006	27-Dec-2005	27-Dec-2005	21-Dec-2005	21-Dec-2005
Dry Weight (%)	55.9	49.0	18.2	33.9	72.8	41.4
Lipid Weight (%)	0.28	0.49	0.13	0.11	1.41	0.33
Analyte	Concentration (pg g^{-1} dry weight)					
BDE-7	nd	nd	nd	nd	nd	nd
BDE-8	nd	nd	nd	nd	nd	nd
BDE-10	nd	nd	nd	nd	nd	nd
BDE-11	nd	nd	nd	nd	nd	nd
BDE-12	nd	nd	nd	nd	nd	nd
BDE-13	nd	nd	nd	nd	nd	nd
BDE-15	11.3	18.3	23.1	10.3	9.6	12.9
BDE-17	nd	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	13.1	10.3	nd	4.9	7.1	5.8
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	402.9	377.3	302.7	131.5	205.6	179.5
BDE-49	10.3	11.8	nd	4.0	8.6	6.7
BDE-66	11.3	9.7	nd	2.5	4.4	8.0
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	22.2	35.0	nd	nd	nd	nd
BDE-99	402.5	564.1	456.9	129.7	311.7	249.7
BDE-100	80.2	105.6	100.0	36.5	82.5	71.4
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	6.2	4.9	nd	nd	nd	4.4
BDE-190	nd	nd	nd	nd	nd	nd
di-BDEs	11.3	18.3	23.1	10.3	9.6	12.9
tri-BDEs	13.1	10.3	nd	4.9	7.1	5.8
tetra-BDEs	424.5	398.7	302.7	138.0	218.6	194.1
penta-BDEs	504.8	704.8	556.9	166.2	394.2	321.1
hepta-BDEs	6.2	4.9	nd	nd	nd	4.4
Total PBDEs	**959.9**	**1137.0**	**882.7**	**319.3**	**629.5**	**538.4**

Table B-4 (continued)

Page:	T1628	T1628	T1622	T1622	T1622
ID:	GY0166	GY0162	GY0163	GY0158	GY0159
Site:	G	H	I	J	K
Location:	Hennequin Point	Vauréal Cape	Demay Point	Ezcurra Inlet	Machu Picchu
Species:	*S. uncinata*	*S. uncinata*	*S. uncinata*	*S. uncinata*	*S. uncinata*
Collection:	6-Jan-2006	23-Dec-2005	23-Dec-2005	15-Dec-2005	17-Dec-2005
Dry Weight (%)	55.7	12.4	71.5	13.2	70.3
Lipid Weight (%)	0.38	0.12	1.37	0.11	0.80
Analyte	Concentration (pg g^{-1} dry weight)				
BDE-7	nd	nd	nd	nd	nd
BDE-8	nd	nd	nd	nd	nd
BDE-10	nd	nd	nd	nd	nd
BDE-11	nd	nd	nd	nd	nd
BDE-12	nd	nd	nd	nd	nd
BDE-13	nd	nd	nd	nd	nd
BDE-15	14.4	30.7	15.7	19.0	10.3
BDE-17	nd	nd	nd	nd	< MDL
BDE-25	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd
BDE-33/28	5.0	10.5	9.8	8.2	13.7
BDE-35	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd
BDE-47	193.1	404.4	375.1	315.3	343.1
BDE-49	6.7	11.4	12.0	10.4	17.4
BDE-66	6.7	11.7	12.3	4.8	14.7
BDE-71	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd	nd
BDE-99	283.4	579.2	513.2	382.9	430.5
BDE-100	69.9	123.0	81.8	93.2	81.8
BDE-116	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd
BDE-183	4.2	12.7	nd	nd	nd
BDE-190	nd	nd	nd	nd	nd
di-BDEs	14.4	30.7	15.7	19.0	10.3
tri-BDEs	5.0	10.5	9.8	8.2	13.7
tetra-BDEs	206.5	427.6	399.4	330.5	375.2
penta-BDEs	353.3	702.3	595.0	476.1	512.3
hepta-BDEs	4.2	12.7	nd	nd	nd
Total PBDEs	**583.5**	**1183.7**	**1019.9**	**833.8**	**911.5**

Table B-5

Concentration of PBDEs in south polar skua eggs (n = 13) collected during the austral summer 2004-2005.

Page:	T1594	T1594	T1594	T1594	T1594
ID:	GY0043	GY0044	GY0045	GY0046	GY0047
Location:	Refuge 2	Refuge 2	Refuge 2	Refuge 2	Refuge 2
Species:	*C. maccormicki*	*C. maccormicki*	*C. maccormicki*	*C. maccormicki*	*C. maccormicki*
Collection:	18-Dec-2004	18-Dec-2004	18-Dec-2004	18-Dec-2004	18-Dec-2004
Notes:		embryo	embryo	embryo	
Dry Weight (%)	25.5	28.1	25.9	20.4	22.4
Lipid Weight (%)	7.54	7.88	9.05	4.52	6.82
Analyte	Concentration (ng g^{-1} lipid weight)				
BDE-17	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd
BDE-33/28	1.00	0.69	0.79	1.06	1.39
BDE-35	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd
BDE-47	31.39	3.45	13.12	5.60	42.41
BDE-49	2.03	0.63	1.39	1.85	1.77
BDE-66	0.15	nd	0.33	nd	0.25
BDE-71	nd	0.66	nd	2.41	nd
BDE-75	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd	nd
BDE-99	8.00	2.22	5.52	3.91	10.12
BDE-100	17.52	1.75	5.53	5.34	21.63
BDE-116	nd	nd	nd	nd	nd
BDE-118	0.45	nd	nd	nd	nd
BDE-119	1.40	0.39	nd	0.40	1.59
BDE-126	0.43	nd	nd	nd	0.36
BDE-138	nd	nd	nd	nd	nd
BDE-153	16.69	4.74	2.94	10.50	25.08
BDE-154	17.65	2.35	3.30	4.20	21.69
BDE-155	8.29	0.81	0.70	1.03	9.17
BDE-166	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd
BDE-183	0.71	1.28	nd	nd	1.81
BDE-190	nd	nd	nd	nd	nd
tri-BDEs	1.00	0.69	0.79	1.06	1.39
tetra-BDEs	33.58	4.75	14.84	9.86	44.43
penta-BDEs	27.80	4.37	11.05	9.65	33.70
hexa-BDEs	42.63	7.90	6.94	15.73	55.93
hepta-BDEs	0.71	1.28	nd	nd	1.81
Total PBDEs	**105.71**	**18.98**	**33.62**	**36.29**	**137.27**

Table B-5 (continued)

Page:	T1594	T1594	T1594	T1594	T1594
ID:	GY0048	GY0049	GY0050	GY0051	GY0052
Location:	Refuge 2	Refuge 2	Plaza Point	Refuge 2	Refuge 2
Species:	*C. maccormicki*	*C. maccormicki*	*C. maccormicki*	*C. maccormicki*	*C. maccormicki*
Collection:	18-Dec-2004	18-Dec-2004	31-Dec-2004	3-Jan-2005	3-Jan-2005
Notes:					embryo
Dry Weight (%)	22.4	21.6	24.8	23.8	18.4
Lipid Weight (%)	6.13	8.08	6.87	6.37	2.95
Analyte	Concentration (ng g^{-1} lipid weight)				
BDE-17	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd
BDE-33/28	0.72	1.29	1.42	12.01	7.18
BDE-35	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd
BDE-47	5.81	33.01	50.44	202.46	53.03
BDE-49	1.33	1.78	1.94	8.34	25.78
BDE-66	nd	0.18	0.24	1.38	2.94
BDE-71	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd	nd
BDE-99	4.13	5.96	29.23	39.40	10.51
BDE-100	2.53	18.79	38.62	93.27	18.24
BDE-116	nd	nd	nd	nd	nd
BDE-118	nd	nd	0.70	nd	nd
BDE-119	0.52	1.06	1.95	nd	1.92
BDE-126	nd	0.47	0.49	nd	nd
BDE-138	nd	nd	1.10	nd	nd
BDE-153	4.69	8.93	36.21	20.46	22.80
BDE-154	3.88	18.41	39.17	24.18	22.21
BDE-155	1.36	10.67	13.25	4.23	9.12
BDE-166	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd
BDE-183	nd	nd	4.20	nd	nd
BDE-190	nd	nd	nd	nd	nd
tri-BDEs	0.72	1.29	1.42	12.01	7.18
tetra-BDEs	7.14	34.96	52.62	212.17	81.76
penta-BDEs	7.18	26.28	70.98	132.67	30.67
hexa-BDEs	9.93	38.02	89.73	48.86	54.13
hepta-BDEs	nd	nd	4.20	nd	nd
Total PBDEs	**24.97**	**100.54**	**218.95**	**405.71**	**173.74**

Table B-5 (continued)

Page:	T1601	T1601	T1601
ID:	GY0053	GY0059	GY0060
Location:	Refuge 2	Hennequin Point	Hennequin Point
Species:	*C. maccormicki*	*C. maccormicki*	*C. maccormicki*
Collection:	3-Jan-2005	5-Jan-2005	11-Jan-2005
Notes:			embryo
Dry Weight (%)	24.7	24.6	20.8
Lipid Weight (%)	6.94	4.62	5.43
Analyte	Concentration (ng g^{-1} lipid weight)		
BDE-17	< MDL	< MDL	nd
BDE-25	nd	nd	nd
BDE-30	nd	nd	nd
BDE-32	nd	nd	nd
BDE-33/28	4.43	0.40	0.36
BDE-35	nd	nd	nd
BDE-37	nd	nd	nd
BDE-47	219.74	21.27	8.65
BDE-49	2.02	0.91	0.71
BDE-66	0.48	0.21	nd
BDE-71	2.97	nd	nd
BDE-75	< MDL	nd	nd
BDE-77	< MDL	nd	nd
BDE-85	nd	nd	nd
BDE-99	45.06	10.98	6.60
BDE-100	145.07	10.40	3.07
BDE-116	nd	nd	nd
BDE-118	2.15	nd	nd
BDE-119	4.04	< MDL	nd
BDE-126	1.31	nd	nd
BDE-138	nd	nd	nd
BDE-153	49.37	7.59	5.47
BDE-154	58.44	2.97	1.75
BDE-155	21.58	0.39	0.26
BDE-166	nd	nd	nd
BDE-181	nd	nd	nd
BDE-183	1.44	nd	1.76
BDE-190	nd	nd	nd
tri-BDEs	4.43	0.40	0.36
tetra-BDEs	225.22	22.39	9.36
penta-BDEs	197.64	21.38	9.67
hexa-BDEs	129.40	10.94	7.49
hepta-BDEs	1.44	nd	1.76
Total PBDEs	**558.13**	**55.11**	**28.63**

Table B-6

Concentration of PBDEs in chinstrap penguin eggs (n = 35) collected during the austral summer 2004-2005.

Page:	T1507	T1507	T1507	T1507	T1507	T1507
ID:	GY0013	GY0014	GY0015	GY0016	GY0017	GY0018
Location:	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock
Species:	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*
Collection:	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005
Notes:						
Dry Weight (%)	24.3	23.8	26.9	21.8	24.0	21.6
Lipid Weight (%)	6.69	6.55	8.00	5.72	6.59	5.85
Analyte	Concentration (ng g^{-1} lipid weight)					
BDE-17	nd	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	0.06	nd	0.05	0.15	0.16	nd
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	1.73	1.91	2.42	3.40	2.10	2.47
BDE-49	0.10	0.11	0.11	nd	0.17	nd
BDE-66	nd	nd	nd	nd	nd	nd
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd	< MDL	< MDL
BDE-99	1.84	2.58	2.75	2.93	2.06	2.76
BDE-100	0.40	0.50	0.62	0.55	0.54	0.71
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd
BDE-153	0.26	0.37	0.34	nd	0.29	0.34
BDE-154	0.30	0.36	0.42	0.65	0.35	0.32
BDE-155	nd	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd	nd	nd
BDE-190	nd	nd	nd	nd	nd	nd
tri-BDEs	0.06	nd	0.05	0.15	0.16	nd
tetra-BDEs	1.82	2.02	2.53	3.40	2.27	2.47
penta-BDEs	2.24	3.08	3.37	3.47	2.60	3.47
hexa-BDEs	0.56	0.74	0.76	0.65	0.63	0.66
hepta-BDEs	nd	nd	nd	nd	nd	nd
Total PBDEs	**4.68**	**5.83**	**6.71**	**7.66**	**5.66**	**6.60**

Table B-6 (continued)

Page:	T1507	T1601	T1507	T1507	T1601	T1601
ID:	GY0019	GY0020	GY0021	GY0022	GY0023	GY0024
Location:	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock
Species:	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*
Collection:	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005
Notes:						
Dry Weight (%)	26.9	20.4	21.4	23.2	18.8	25.2
Lipid Weight (%)	7.54	3.71	5.38	5.15	4.30	7.11
Analyte	Concentration (ng g^{-1} lipid weight)					
BDE-17	nd	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	0.17	nd	0.13	0.16	nd	nd
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	1.43	2.07	2.01	3.39	2.23	1.21
BDE-49	0.09	nd	0.07	0.12	0.13	0.09
BDE-66	nd	nd	nd	nd	nd	nd
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	< MDL	nd	nd
BDE-99	1.08	2.04	1.99	3.14	2.29	1.06
BDE-100	0.35	0.54	0.62	0.69	0.68	0.35
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd
BDE-153	0.09	0.40	0.29	0.26	0.47	0.28
BDE-154	0.19	0.39	0.23	0.49	0.42	0.31
BDE-155	nd	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd	nd	nd
BDE-190	nd	nd	nd	nd	nd	nd
tri-BDEs	0.17	nd	0.13	0.16	nd	nd
tetra-BDEs	1.51	2.07	2.08	3.51	2.36	1.30
penta-BDEs	1.43	2.58	2.61	3.83	2.97	1.41
hexa-BDEs	0.28	0.79	0.52	0.75	0.89	0.59
hepta-BDEs	nd	nd	nd	nd	nd	nd
Total PBDEs	**3.39**	**5.45**	**5.35**	**8.25**	**6.22**	**3.29**

Table B-6 (continued)

Page:	T1601	T1507	T1507	T1507	T1601	T1601
ID:	GY0025	GY0026	GY0027	GY0028	GY0029	GY0030
Location:	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock
Species:	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*
Collection:	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005
Notes:		embryo			embryo	embryo
Dry Weight (%)	24.4	22.4	25.9	21.9	22.0	19.7
Lipid Weight (%)	5.74	6.16	8.81	6.37	7.54	4.70
Analyte	Concentration (ng g^{-1} lipid weight)					
BDE-17	nd	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	nd	< MDL	0.07	nd	nd	nd
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	1.28	1.82	3.05	1.62	1.20	2.32
BDE-49	nd	0.12	0.16	0.07	0.17	0.22
BDE-66	nd	nd	nd	nd	nd	nd
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	nd	nd	< MDL	< MDL	nd	nd
BDE-99	1.05	2.33	2.84	1.87	1.06	2.14
BDE-100	0.35	0.45	0.62	0.43	0.30	0.59
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd
BDE-153	0.17	0.26	0.22	0.24	0.36	0.46
BDE-154	0.30	0.44	0.54	0.32	0.25	0.37
BDE-155	nd	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	0.85	nd	nd
BDE-190	nd	nd	nd	nd	nd	nd
tri-BDEs	nd	< MDL	0.07	nd	nd	nd
tetra-BDEs	1.28	1.93	3.21	1.69	1.37	2.54
penta-BDEs	1.40	2.78	3.46	2.30	1.36	2.73
hexa-BDEs	0.47	0.69	0.76	0.56	0.61	0.83
hepta-BDEs	nd	nd	nd	0.85	nd	nd
Total PBDEs	**3.15**	**5.40**	**7.51**	**5.40**	**3.34**	**6.10**

Table B-6 (continued)

Page:	T1601	T1601	T1594	T1594	T1594	T1594
ID:	GY0031	GY0032	GY0033	GY0034	GY0035	GY0036
Location:	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock
Species:	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*
Collection:	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005
Notes:						embryo
Dry Weight (%)	22.8	24.8	23.5	22.9	26.5	17.0
Lipid Weight (%)	4.81	6.72	7.28	6.51	7.68	3.46
Analyte	Concentration (ng g^{-1} lipid weight)					
BDE-17	nd	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	0.06	nd	0.08	0.10	0.12	0.88
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	1.89	1.39	1.29	1.06	4.19	15.80
BDE-49	0.11	0.09	nd	0.11	0.15	nd
BDE-66	nd	nd	nd	nd	nd	nd
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd	nd	nd
BDE-99	1.82	1.43	1.28	1.51	3.83	10.83
BDE-100	0.46	0.36	0.30	0.33	0.83	3.20
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd
BDE-153	0.26	0.37	nd	0.23	0.47	1.04
BDE-154	0.29	0.31	0.17	0.30	0.50	1.27
BDE-155	nd	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd	nd	nd
BDE-190	nd	nd	nd	nd	nd	nd
tri-BDEs	0.06	nd	0.08	0.10	0.12	0.88
tetra-BDEs	1.99	1.48	1.29	1.17	4.34	15.80
penta-BDEs	2.28	1.79	1.58	1.84	4.66	14.03
hexa-BDEs	0.55	0.68	0.17	0.54	0.97	2.30
hepta-BDEs	nd	nd	nd	nd	nd	nd
Total PBDEs	**4.88**	**3.94**	**3.13**	**3.65**	**10.09**	**33.00**

Table B-6 (continued)

Page:	T1594	T1594	T1594	T1594	T1594	T1594
ID:	GY0037	GY0038	GY0039	GY0040	GY0041	GY0042
Location:	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock
Species:	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*
Collection:	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005	6-Jan-2005
Notes:	embryo	embryo			embryo	embryo
Dry Weight (%)	22.1	23.3	26.1	24.9	20.9	19.9
Lipid Weight (%)	4.91	6.38	6.50	7.19	5.06	3.91
Analyte	Concentration (ng g^{-1} lipid weight)					
BDE-17	nd	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	nd	nd	nd	nd	nd	nd
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	1.94	1.88	1.11	1.21	0.71	1.41
BDE-49	nd	nd	0.07	0.09	nd	nd
BDE-66	nd	nd	nd	nd	nd	nd
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd	nd	nd
BDE-99	2.63	2.31	1.42	1.35	0.37	1.85
BDE-100	0.51	0.50	0.34	0.26	3.13	nd
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd
BDE-153	0.31	0.15	0.28	0.10	nd	0.41
BDE-154	0.39	0.33	0.24	0.21	nd	0.55
BDE-155	nd	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd	nd	nd
BDE-190	nd	nd	nd	nd	nd	nd
tri-BDEs	nd	nd	nd	nd	nd	nd
tetra-BDEs	1.94	1.88	1.18	1.30	0.71	1.41
penta-BDEs	3.14	2.81	1.76	1.61	3.50	1.85
hexa-BDEs	0.70	0.48	0.51	0.31	nd	0.96
hepta-BDEs	nd	nd	nd	nd	nd	nd
Total PBDEs	**5.78**	**5.17**	**3.46**	**3.22**	**4.22**	**4.22**

Table B-6 (continued)

Page:	T1601	T1601	T1601	T1601	T1601
ID:	GY0054	GY0055	GY0056	GY0057	GY0058
Location:	Demay Point	Demay Point	Chabrier Rock	Chabrier Rock	Chabrier Rock
Species:	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*
Collection:	29-Dec-2004	29-Dec-2004	6-Jan-2005	6-Jan-2005	6-Jan-2005
Notes:					
Dry Weight (%)	23.9	26.1	24.3	24.7	21.7
Lipid Weight (%)	5.63	7.45	6.11	6.31	5.20
Analyte	Concentration (ng g^{-1} lipid weight)				
BDE-17	nd	nd	nd	< MDL	nd
BDE-25	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd
BDE-33/28	nd	nd	nd	0.29	0.07
BDE-35	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd
BDE-47	1.84	2.45	1.77	11.41	1.92
BDE-49	0.06	0.14	0.08	0.34	0.09
BDE-66	nd	nd	nd	0.31	nd
BDE-71	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	< MDL	nd
BDE-99	1.58	2.83	1.91	12.69	1.84
BDE-100	0.49	0.72	0.61	2.54	0.49
BDE-116	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd
BDE-153	0.36	0.47	0.45	1.30	0.41
BDE-154	0.33	0.49	0.32	1.28	0.40
BDE-155	nd	nd	nd	0.13	nd
BDE-166	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd	nd
BDE-190	nd	nd	nd	nd	nd
tri-BDEs	nd	nd	nd	0.29	0.07
tetra-BDEs	1.90	2.59	1.85	12.05	2.01
penta-BDEs	2.07	3.55	2.51	15.23	2.33
hexa-BDEs	0.70	0.97	0.77	2.72	0.81
hepta-BDEs	nd	nd	nd	nd	nd
Total PBDEs	**4.67**	**7.11**	**5.13**	**30.29**	**5.22**

Table B-7

Concentration of PBDEs in chinstrap penguin eggs (n = 28) collected during the austral summer 2005-2006.

Page:	T1601	T1601	T1601	T1601	T1603	T1603
ID:	GY0102	GY0103	GY0104	GY0105	GY0106	GY0107
Location:	Demay Point	Demay Point	Telefon Point	Telefon Point	Telefon Point	Telefon Point
Species:	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*
Collection:	29-Dec-2005	8-Jan-2006	8-Jan-2006	8-Jan-2006	8-Jan-2006	8-Jan-2006
Notes:			embryo			
Dry Weight (%)	23.6	23.1	19.9	24.7	28.9	26.3
Lipid Weight (%)	5.47	6.53	5.59	6.28	7.75	7.73
Analyte	Concentration (ng g^{-1} lipid weight)					
BDE-17	< MDL	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	0.08	0.09	nd	0.10	nd	nd
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	1.50	2.40	1.96	5.26	1.28	1.12
BDE-49	0.08	0.14	nd	0.21	nd	0.10
BDE-66	nd	nd	nd	nd	nd	nd
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd	nd	nd
BDE-99	1.33	2.15	1.92	5.39	1.15	1.72
BDE-100	0.36	0.56	0.46	1.21	0.39	0.39
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd
BDE-153	0.22	0.39	nd	0.64	0.33	0.32
BDE-154	0.21	0.31	0.30	0.61	0.23	0.42
BDE-155	nd	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd	nd	nd
BDE-190	nd	nd	nd	nd	nd	nd
tri-BDEs	0.08	0.09	nd	0.10	nd	nd
tetra-BDEs	1.58	2.54	1.96	5.47	1.28	1.22
penta-BDEs	1.68	2.71	2.37	6.60	1.53	2.10
hexa-BDEs	0.43	0.69	0.30	1.24	0.56	0.75
hepta-BDEs	nd	nd	nd	nd	nd	nd
Total PBDEs	**3.77**	**6.04**	**4.64**	**13.42**	**3.37**	**4.07**

Table B-7 (continued)

Page:	T1603	T1603	T1603	T1603	T1603	T1603
ID:	GY0108	GY0109	GY0110	GY0111	GY0112	GY0113
Location:	Telefon Point	Telefon Point	Shag Island	Shag Island	Shag Island	Shag Island
Species:	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*
Collection:	8-Jan-2006	8-Jan-2006	8-Jan-2006	8-Jan-2006	8-Jan-2006	8-Jan-2006
Notes:						
Dry Weight (%)	24.1	26.7	24.0	22.9	25.5	26.3
Lipid Weight (%)	6.72	6.65	6.57	5.58	6.36	7.69
Analyte	Concentration (ng g^{-1} lipid weight)					
BDE-17	nd	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	0.17	nd	0.11	nd	nd	nd
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	6.14	1.67	1.48	1.11	1.62	0.81
BDE-49	nd	0.12	0.09	0.10	0.14	0.09
BDE-66	nd	nd	nd	nd	nd	nd
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd	nd	nd
BDE-99	4.42	1.83	1.63	1.18	1.94	1.00
BDE-100	1.21	0.44	0.36	0.30	0.44	0.31
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd
BDE-153	0.58	0.25	0.46	0.23	0.47	0.30
BDE-154	0.58	0.35	0.29	0.23	0.36	0.29
BDE-155	nd	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd	nd	nd
BDE-190	nd	nd	nd	nd	nd	nd
tri-BDEs	0.17	nd	0.11	nd	nd	nd
tetra-BDEs	6.14	1.78	1.58	1.21	1.77	0.91
penta-BDEs	5.63	2.27	1.99	1.48	2.38	1.31
hexa-BDEs	1.16	0.60	0.75	0.46	0.83	0.59
hepta-BDEs	nd	nd	nd	nd	nd	nd
Total PBDEs	**13.10**	**4.65**	**4.42**	**3.16**	**4.98**	**2.80**

Table B-7 (continued)

Page:	T1603	T1603	T1603	T1603	T1603	T1603
ID:	GY0114	GY0115	GY0116	GY0117	GY0118	GY0119
Location:	Shag Island	Shag Island	Shag Island	Shag Island	Chabrier Rock	Chabrier Rock
Species:	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*
Collection:	8-Jan-2006	8-Jan-2006	8-Jan-2006	8-Jan-2006	23-Dec-2005	23-Dec-2005
Notes:					embryo	embryo
Dry Weight (%)	21.7	23.7	21.1	27.0	18.7	20.6
Lipid Weight (%)	5.01	4.96	5.18	7.48	2.70	4.12
Analyte	Concentration (ng g^{-1} lipid weight)					
BDE-17	nd	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	nd	< MDL	< MDL	nd	< MDL	0.05
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	1.75	1.15	1.22	0.81	2.36	1.59
BDE-49	0.10	0.08	0.11	0.06	0.22	0.22
BDE-66	nd	nd	nd	nd	nd	nd
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd	nd	nd
BDE-99	2.01	1.21	1.69	1.09	2.36	1.92
BDE-100	0.47	0.30	0.39	0.23	0.94	0.40
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd
BDE-153	0.38	0.26	0.35	0.27	0.57	0.34
BDE-154	0.39	0.24	0.36	0.19	0.46	0.36
BDE-155	nd	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd	nd	nd
BDE-190	nd	nd	nd	nd	nd	nd
tri-BDEs	nd	< MDL	< MDL	nd	< MDL	0.05
tetra-BDEs	1.85	1.23	1.33	0.87	2.58	1.81
penta-BDEs	2.48	1.51	2.08	1.32	3.30	2.32
hexa-BDEs	0.77	0.50	0.71	0.46	1.03	0.70
hepta-BDEs	nd	nd	nd	nd	nd	nd
Total PBDEs	**5.11**	**3.24**	**4.11**	**2.65**	**6.90**	**4.88**

Table B-7 (continued)

Page:	T1603	T1603	T1603	T1603	T1603	T1603
ID:	GY0120	GY0121	GY0122	GY0123	GY0124	GY0125
Location:	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock
Species:	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*
Collection:	23-Dec-2005	23-Dec-2005	8-Jan-2006	8-Jan-2006	8-Jan-2006	8-Jan-2006
Notes:		embryo				embryo
Dry Weight (%)	19.9	18.7	24.3	24.6	23.1	23.1
Lipid Weight (%)	3.61	3.77	6.00	7.27	5.88	6.09
Analyte	Concentration (ng g^{-1} lipid weight)					
BDE-17	nd	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	0.05	nd	0.05	nd	nd	nd
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	2.97	3.79	1.79	0.74	1.07	1.72
BDE-49	0.13	0.20	0.09	nd	nd	0.08
BDE-66	nd	nd	nd	nd	nd	nd
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	< MDL	< MDL	nd	nd	nd	nd
BDE-99	5.59	8.08	2.13	0.80	0.78	2.99
BDE-100	1.10	1.56	0.47	0.17	0.27	0.68
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd
BDE-153	0.87	1.11	0.38	0.16	0.14	0.48
BDE-154	0.81	1.32	0.40	0.15	0.13	0.47
BDE-155	< MDL	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd	nd	nd
BDE-190	nd	nd	nd	nd	nd	nd
tri-BDEs	0.05	nd	0.05	nd	nd	nd
tetra-BDEs	3.10	3.98	1.88	0.74	1.07	1.80
penta-BDEs	6.68	9.63	2.60	0.98	1.06	3.67
hexa-BDEs	1.68	2.42	0.78	0.30	0.27	0.95
hepta-BDEs	nd	nd	nd	nd	nd	nd
Total PBDEs	**11.51**	**16.04**	**5.30**	**2.03**	**2.39**	**6.42**

Table B-7 (continued)

Page:	T1612	T1612	T1612	T1612
ID:	GY0126	GY0127	GY0128	GY0129
Location:	Chabrier Rock	Chabrier Rock	Chabrier Rock	Chabrier Rock
Species:	*P. antarctica*	*P. antarctica*	*P. antarctica*	*P. antarctica*
Collection:	8-Jan-2006	8-Jan-2006	8-Jan-2006	8-Jan-2006
Notes:	embryo			
Dry Weight (%)	22.8	24.1	24.9	22.1
Lipid Weight (%)	4.63	7.29	5.49	5.24
Analyte	Concentration (ng g^{-1} lipid weight)			
BDE-17	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd
BDE-33/28	nd	nd	0.04	nd
BDE-35	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd
BDE-47	1.91	0.94	1.44	1.09
BDE-49	nd	nd	0.08	nd
BDE-66	nd	nd	nd	nd
BDE-71	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd
BDE-99	2.11	0.84	1.43	0.99
BDE-100	0.57	0.21	0.33	0.25
BDE-116	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd
BDE-153	0.42	0.10	0.20	nd
BDE-154	0.33	0.16	0.20	0.25
BDE-155	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd
BDE-190	nd	nd	nd	nd
tri-BDEs	nd	nd	0.04	nd
tetra-BDEs	1.91	0.94	1.52	1.09
penta-BDEs	2.68	1.05	1.76	1.24
hexa-BDEs	0.75	0.26	0.40	0.25
hepta-BDEs	nd	nd	nd	nd
Total PBDEs	**5.34**	**2.26**	**3.72**	**2.58**

Table B-8

Concentration of PBDEs in gentoo penguin eggs (n = 17) collected during the austral summer 2005-2006.

Page:	T1612	T1612	T1612	T1612	T1612	T1612
ID:	GY0130	GY0131	GY0132	GY0133	GY0134	GY0135
Location:	Copacabana	Copacabana	Copacabana	Copacabana	Copacabana	Copacabana
Species:	*P. papua*	*P. papua*	*P. papua*	*P. papua*	*P. papua*	*P. papua*
Collection:	14-Dec-2005	5-Dec-2005	10-Dec-2005	10-Dec-2005	10-Dec-2005	15-Dec-2005
Notes:		embryo				embryo
Dry Weight (%)	22.8	26.3	21.2	24.4	25.5	21.2
Lipid Weight (%)	4.69	4.19	4.62	6.84	6.15	3.88
Analyte	Concentration (ng g^{-1} lipid weight)					
BDE-17	nd	nd	nd	nd	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	0.21	nd	0.04	0.08	0.10	0.06
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	6.93	3.08	1.18	1.26	1.45	2.10
BDE-49	0.49	0.27	0.07	0.08	0.05	0.16
BDE-66	nd	nd	nd	nd	nd	nd
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd	nd	nd
BDE-99	10.30	3.58	1.34	1.13	1.36	2.36
BDE-100	2.43	0.85	0.32	0.24	0.27	0.63
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd
BDE-153	1.21	0.40	0.25	0.11	0.18	0.29
BDE-154	1.10	0.49	0.19	0.13	0.17	0.31
BDE-155	nd	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd	nd	nd
BDE-190	nd	nd	nd	nd	nd	nd
tri-BDEs	0.21	nd	0.04	0.08	0.10	0.06
tetra-BDEs	7.42	3.35	1.25	1.34	1.50	2.27
penta-BDEs	12.73	4.43	1.65	1.37	1.63	2.99
hexa-BDEs	2.30	0.89	0.44	0.24	0.35	0.60
hepta-BDEs	nd	nd	nd	nd	nd	nd
Total PBDEs	**22.66**	**8.67**	**3.39**	**3.03**	**3.59**	**5.91**

Table B-8 (continued)

Page:	T1612	T1612	T1612	T1612	T1612	T1612
ID:	GY0136	GY0137	GY0138	GY0139	GY0140	GY0141
Location:	Copacabana	Copacabana	Copacabana	Copacabana	Copacabana	Copacabana
Species:	*P. papua*	*P. papua*	*P. papua*	*P. papua*	*P. papua*	*P. papua*
Collection:	19-Dec-2005	19-Dec-2005	19-Dec-2005	19-Dec-2005	19-Dec-2005	19-Dec-2005
Notes:		embryo				
Dry Weight (%)	22.5	18.1	24.8	22.9	23.3	23.5
Lipid Weight (%)	4.84	3.62	5.34	4.93	5.15	5.67
Analyte	Concentration (ng g^{-1} lipid weight)					
BDE-17	nd	nd	nd	< MDL	nd	nd
BDE-25	nd	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd	nd
BDE-33/28	nd	< MDL	0.04	0.10	0.06	0.05
BDE-35	nd	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd	nd
BDE-47	1.65	3.07	2.59	6.44	3.28	1.99
BDE-49	nd	nd	0.11	0.15	0.13	0.10
BDE-66	nd	nd	nd	nd	nd	nd
BDE-71	nd	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd	nd	nd
BDE-99	1.98	3.44	3.20	8.10	3.62	1.67
BDE-100	0.55	0.84	0.84	1.62	0.86	0.42
BDE-116	nd	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd	nd
BDE-153	0.21	0.49	0.52	0.76	0.50	0.24
BDE-154	0.28	0.37	0.44	0.75	0.44	0.22
BDE-155	nd	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd	nd	nd
BDE-190	nd	nd	nd	nd	nd	nd
tri-BDEs	nd	< MDL	0.04	0.10	0.06	0.05
tetra-BDEs	1.65	3.07	2.69	6.59	3.41	2.09
penta-BDEs	2.53	4.28	4.04	9.71	4.48	2.09
hexa-BDEs	0.49	0.86	0.96	1.52	0.94	0.47
hepta-BDEs	nd	nd	nd	nd	nd	nd
Total PBDEs	**4.67**	**8.21**	**7.73**	**17.92**	**8.88**	**4.69**

Table B-8 (continued)

Page:	T1612	T1612	T1612	T1612	T1613
ID:	GY0142	GY0143	GY0144	GY0145	GY0146
Location:	Copacabana	Copacabana	Copacabana	Copacabana	Copacabana
Species:	*P. papua*	*P. papua*	*P. papua*	*P. papua*	*P. papua*
Collection:	19-Dec-2005	27-Dec-2005	27-Dec-2005	27-Dec-2005	29-Dec-2005
Notes:					
Dry Weight (%)	23.7	24.6	23.9	19.1	26.5
Lipid Weight (%)	5.37	4.96	4.87	4.62	7.58
Analyte	Concentration (ng g^{-1} lipid weight)				
BDE-17	nd	nd	< MDL	nd	nd
BDE-25	nd	nd	nd	nd	nd
BDE-30	nd	nd	nd	nd	nd
BDE-32	nd	nd	nd	nd	nd
BDE-33/28	nd	0.06	0.08	0.08	nd
BDE-35	nd	nd	nd	nd	nd
BDE-37	nd	nd	nd	nd	nd
BDE-47	3.54	2.22	4.37	2.79	1.42
BDE-49	0.13	0.13	0.15	0.11	0.09
BDE-66	nd	nd	nd	nd	nd
BDE-71	nd	nd	nd	nd	nd
BDE-75	nd	nd	nd	nd	nd
BDE-77	nd	nd	nd	nd	nd
BDE-85	nd	nd	nd	nd	nd
BDE-99	3.96	2.26	5.58	3.02	1.31
BDE-100	0.87	0.49	1.14	0.84	0.33
BDE-116	nd	nd	nd	nd	nd
BDE-118	nd	nd	nd	nd	nd
BDE-119	nd	nd	nd	nd	nd
BDE-126	nd	nd	nd	nd	nd
BDE-138	nd	nd	nd	nd	nd
BDE-153	0.54	0.29	0.55	0.34	0.16
BDE-154	0.44	0.26	0.54	0.36	0.20
BDE-155	nd	nd	nd	nd	nd
BDE-166	nd	nd	nd	nd	nd
BDE-181	nd	nd	nd	nd	nd
BDE-183	nd	nd	nd	nd	nd
BDE-190	nd	nd	nd	nd	nd
tri-BDEs	nd	0.06	0.08	0.08	nd
tetra-BDEs	3.67	2.35	4.52	2.90	1.51
penta-BDEs	4.83	2.75	6.72	3.86	1.64
hexa-BDEs	0.97	0.55	1.08	0.70	0.36
hepta-BDEs	nd	nd	nd	nd	nd
Total PBDEs	**9.47**	**5.71**	**12.40**	**7.54**	**3.51**

VITA

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