Emerging Contaminants in the Antarctic - A Review

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Abstract

Emerging contaminants (ECs) in the Antarctic environment and Antarctic biota have been investigated in a very limited number of studies. ECs have been extensively studied in the Arctic and have confirmed presence in Antarctica, despite this, the small amount of Antarctic EC research is a barrier to accurate predictions about how the Antarctic environment and biota will respond to contamination. EC contamination in the Antarctic is identified through literature investigation. This report covers the ECs; polybrominated compounds (PBDEs), perfluorinated compounds (PFCs), pharmaceuticals and personal care products (PPCPs), organophosphate Esters (OPEs), chlorinated paraffins (CPs) and siloxanes which have been detected in the Antarctic environment and in Antarctic biota and compares the concentrations observed in the Antarctic to the more thoroughly studied Arctic. Further research into EC contamination in the Antarctic is required to fully understand how these contaminants will behave in the future.

I. Introduction

An emerging contaminant (EC) is defined by the United States Geological Survey as a synthetic or naturally occurring chemical or microorganism that is not commonly monitored in the environment and has the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects (United States Geological Survey [USGS], 2014). Emerging contaminants are expected to be chemicals that show potential to pose risks to human health or the environment but are not yet subjected to regulatory criteria for the protection of human health or the environment (Sauve & Desrosiers, 2014). Emerging contaminants include polybrominated compounds (PBDEs), perfluorinated compounds (PFCs), pharmaceuticals and personal care products (PPCPs), organophosphate Esters (OPEs), chlorinated paraffins (CPs) and siloxanes.

A large number of adverse effects caused by emerging contaminants in the environment have been reported in the literature, a select few examples include: acute toxicity in fish from pharmaceuticals, exemplified in two beta blocker research studies (Huggett, Brooks, Peterson, Foran & Schlenk, 2002; Owen et al., 2007); endocrine disruption in fish from perfluorinated compounds, exemplified in the analysis of estrogenicity in male tilapia (Liu, Du & Zhou, 2007); behavioural effects caused by polybrominated compounds, exemplified in mice and killifish (Eriksson, Fischer & Fredriksson, 2006; Timme-Laragy, Levin & DiGiulio, 2006) and the development of antibiotic resistance in pathogenic bacteria, where residual antibiotics are released into the environment and can exert selection pressure on microorganisms (Pruden, Pei, Storteboom & Carlson, 2006). Sauve & Desrosiers (2014) re-describe emerging contaminants as contaminants of emerging concern (CEC) due to the fact that CECs can be classified in any of the following categories;

- Truely new emerging contaminants in the form of new compounds or molecules that were not previously known or are recent additions to scientific literature.
- Contaminants of emerging interest which are known to exist but the environmental contamination issues were not fully realised or apprehended until recently.

- Old contaminants where new information is re-evaluating our understanding of environmental and human health risks related to such legacy contaminants.

Contaminants of emerging concern should be classified as emerging whilst there is a scarcity of information in the scientific literature or if little is known about the associated problems they may cause (Sauve & Desrosiers, 2014).

Antarctica is considered relatively isolated from anthropogenic influence but a number of recent studies have investigated emerging contaminants found near research bases and in the wider geographical areas and considered the effects they may have on the local environment (Emnet, Gaw, Northcott Storey & Graham, 2014; Hale et al., 2008; Wild et al., 2014; Zhang, Dickhut, DeMaster, Pohl & Lohmann, 2013). Contaminants of emerging concern can enter the Antarctic environment through long range transport (LRT) or direct input. Remote sampling in the Canadian Arctic of ringed seals for the persistent semi-volatile organic compounds, PBDEs, provides evidence for LRT (Ikonomou, Rayne Addison, 2002). The chemical properties of certain persistent compounds; hydrophobic and semivolatile or water soluble and relatively volatile, and the "'grasshopper"' effect predicts accumulation in the Arctic region (Wania, 2003; Gouin, Mackay, Jones, Harner Meijer, 2004). This accumulation may also be apparent on the similar polar environment, Antarctica. Direct human input from transport such as an aeroplane, boat or terrestrial vehicle can carry emerging contaminants in their fuel, physical components and extrinsic features such as anti-fouling agents or anti-freeze solutions. Additional sources of direct contamination in the Antarctic are high temperature incineration, food waste and wastewater treatment plant sewage - all waste disposal methods, with sewage effluent often being a studied source of Antarctic emerging contaminants (Emnet et al., 2014; Snape et al., 2001; Wild et al., 2014). The majority of emerging contaminants are of anthropogenic origin and the emission of ECs can be an issue for waste water treatment plants. Ia Farre, Perez, Kantiani & Barcelo (2008) emphasis the need to study the fate of emerging contaminants in waste water treatment plants. Research stations themselves are also contaminant sources with a wide range of synthetic organic compounds present in the building material, fittings and external finishes (Hale et al., 2008; Wild et al., 2014).

The cold Antarctic climate affects how the environment responds to contaminants in a different manner to warmer, more temperate climates. Antarctic soils have low moisture content, organic matter and microbial activity which reduces contaminant degradation rates. Ruberto, Vazquez & Mac Cormack (2008) review the effects of hydrocarbon pollution on bacteria in extremely cold Antarctic soils, emphasising reduced rates of contaminant degradation due to low temperature. Seasonal pulses of petroleum contamination consistent with summer melt phases have been recorded by Hale et al. (2008). Emerging contaminants are also likely to behave in this manner, administering a high dose of contaminants to the ecosystem web in one event.

This review provides information on contaminants of emerging concern; PBDEs, PFCs, PPCPs, organophosphate esters, chlorinated paraffins and siloxanes which have been detected in Antarctica, providing a summary of contaminant concentration levels from the literature. Comparisons are made with ECs from the Arctic.

II. Emerging contaminants in Antarctica

I. Polybrominated diphenyl ethers (PBDEs)

Polybrominated diphenyl ethers, commonly known as brominated flame retardants, are a group of chemical compounds that include 209 congeners, chemical substances related by origin, structure or function, in ten bromination levels from mono to deca. They are used

as flame retardants in textiles, building materials, polyurethane foam and in the plastic components of electronic equipment (Environmental Protection Agency[EPA], 2013a). The presence of PBDEs in Antarctica is the most documented emerging contaminant and has been summarised for the Antarctic environment, in table 1, and in Antarctic biota, in table 2. The most abundant PBDE congeners found in both Antarctic biota and environmental samples are BDE-47, BDE-99 and BDE-209.

Environment

Polybrominated diphenyl ether concentrations in and around research bases has been investigated in a small number of studies (Hale et al., 2008; Liu et al, 2012; Wang et al, 2012; Wild et al., 2014). Polybrominated diphenyl ethers were investigated and detected in soil, indoor dust and marine sediment in and around Casey Station by Wild et al. (2014). For indoor dust samples, the BDE congeners -47, -99, -183 and -209 were the main constituents of total PBDE levels for four areas of Casey Station. All indoor dust samples were heavily concentrated with BDE-209. Polybrominated diphenyl ether concentrations detected in samples collected at distances up to 800m from Casey Station included 8.5 ng/g dry weight (dw) in the soil sample at the fuel tank location and 0.43 ng/g (dw) at the distanced wharf location. Marine sediments were highest with PBDE concentrations at the wastewater outfall and the concentration dropped off with distance, locations remote from the wastewater outfall yielded negligible PBDE concentrations.

Hale et al. (2008) tested indoor dust, wastewater sludge, marine biota and sediment for PBDEs around Scott Base and McMurdo station. Polybrominated diphenyl ether concentrations for indoor dust were recorded as 9560 and 2240 ng/g (dw) for McMurdo and Scott Base respectively. Wastewater sludge total PBDE concentration was detected at 4690 and 637 ng/g (dw) for McMurdo and Scott Base respectively.

Polybrominated diphenyl ethers were not detected in biota or sediments at distances of 100 km from McMurdo. The highest PBDE biota concentration was recorded in rockcod at the wastewater outfall site, elevated concentrations were observed within 0.5 km of the outfall, and in the range 0.5 km - 25km from the outfall there were still detectable PBDE levels.

Wang et al. (2012) sampled eight soil locations and one sediment location for PBDE contamination in the vicinity of Great Wall Station, Fildes Peninsula. Total PBDE concentrations were detected in the range of 0.0028 - 0.0512 ng/g (dw).

Air concentration levels of total PBDE for five sites near Great Wall station on King George Island has been analysed by Liu et al. (2012) and found an average value of 1.52 pg m^{-3} with values ranging between 0.67 and 2.98 pg m^{-3}.

Table 1: *Total polybrominated diphenyl ether concentrations in the studied Antarctic environment*

	Antarctic Environment PBDEs			
	Sample	**Location**	**Concentration**	**Study**
BDE-47	Indoor Dust	Warehouse, Casey Station	ND	Wild et al. (2014)
	Indoor Dust	Living Quarters, Casey Station	7.7 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Comms Building, Casey Station	22.4 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Science Building, Casey Station	24.9 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Living Quarters, McMurdo	1100 (ng g^{-1} dw)	Hale et al. (2008)
	Indoor Dust	Living Quarters, Scott Base	111 (ng g^{-1} dw)	Hale et al. (2008)
	Soil Sample	Main fuel tanks, Casey Station	14.4 (ng g^{-1} of OC)	Wild et al. (2014)
	Wastewater Particulates	Casey Station	9.6 ng L^{-1}	Wild et al. (2014)
	Sediment Sample	Crane Cove (< 50m from Casey)	4.6 (ng g^{-1} of OC)	Wild et al. (2014)
	Sediment Sample	Brown Bay (0.75 km from Casey)	1.3 (ng g^{-1} of OC)	Wild et al. (2014)
	Sediment Sample	Crane Cove (2.04km from Casey)	1.5 (ng g^{-1} of OC)	Wild et al. (2014)
BDE-99	Indoor Dust	Warehouse, Casey Station	4.1 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Living Quarters, Casey Station	10.8 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Comms Building, Casey Station	20.6 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Science Building, Casey Station	49.7 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Living Quarters, McMurdo	1330 (ng g^{-1} dw)	Hale et al. (2008)
	Indoor Dust	Living Quarters, Scott Base	156 (ng g^{-1} dw)	Hale et al. (2008)
	Soil Sample	Main fuel tanks, Casey Station	41.3 (ng g^{-1} of OC)	Wild et al. (2014)
	Wastewater Particulates	Casey Station	9.1 ng L^{-1}	Wild et al. (2014)
	Sediment Sample	Crane Cove (< 50m from Casey)	2.9 (ng g^{-1} of OC)	Wild et al. (2014)
	Sediment Sample	Brown Bay (0.75 km from Casey)	0.3 (ng g^{-1} of OC)	Wild et al. (2014)
	Sediment Sample	Crane Cove (2.04km from Casey)	ND	Wild et al. (2014)
BDE-209	Indoor Dust	Warehouse, Casey Station	26.3 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Living Quarters, Casey Station	180.1 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Comms Building, Casey Station	246 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Science Building, Casey Station	822.2 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Living Quarters, McMurdo	4160 (ng g^{-1} dw)	Hale et al. (2008)
	Indoor Dust	Living Quarters, Scott Base	1650 (ng g^{-1} dw)	Hale et al. (2008)
	Soil Sample	Main fuel tanks, Casey Station	1593 (ng g^{-1} of OC)	Wild et al. (2014)
	Wastewater Particulates	Casey Station	181.6 ng L^{-1}	Wild et al. (2014)
	Sediment Sample	Crane Cove (< 50m from Casey)	531.2 (ng g^{-1} of OC)	Wild et al. (2014)
	Sediment Sample	Brown Bay (0.75 km from Casey)	ND	Wild et al. (2014)
	Sediment Sample	Crane Cove (2.04km from Casey)	ND	Wild et al. (2014)
	Soil Sample	Casey Wharf	205 (ng g^{-1} of OC)	Wild et al. (2014)
∑PBDEs	Indoor Dust	Warehouse, Casey Station	41.5 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Living Quarters, Casey Station	216.2 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Comms Building, Casey Station	281.8 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Science Building, Casey Station	903.3 (ng g^{-1} dw)	Wild et al. (2014)
	Indoor Dust	Living Quarters, McMurdo	9560 (ng g^{-1} dw)	Hale et al. (2008)
	Indoor Dust	Living Quarters, Scott Base	2240 (ng g^{-1} dw)	Hale et al. (2008)
	Wastewater Sludge	McMurdo treatment plant	4690 (ng g^{-1} dw)	Hale et al. (2008)
	Wastewater Sludge	Scott Base treatment plant	637 (ng g^{-1} dw)	Hale et al. (2008)
	Air Concentration	Great Wall Station, King George Island	1.52 (pg m^{-3}) average over five sites	Li et al. (2012)
	Soil Sample	Dengta, Ardley Island, Fildes Peninsula	0.0203 (ng g^{-1} dw)	Wang et al. (2012)
	Soil Sample	Badaling, Fildes Peninsula	0.0061 (ng g^{-1} dw)	Wang et al. (2012)
	Soil Sample	Main Fuel Tanks	1805 (ng g^{-1} of OC)	Wild et al. (2014)
	Soil Sample	Casey Wharf	205 (ng g^{-1} of OC)	Wild et al. (2014)
	Wastewater Particulates	Casey Station	213.8 ng L^{-1}	Wild et al. (2014)
	Sediment Sample	Crane Cove (< 50m from Casey)	566.9 (ng g^{-1} of OC)	Wild et al. (2014)
	ND denotes not detected			

Organisms

Antarctic lichen, phytoplankton, moss, amphipods and krill have been studied for PBDE contamination (Chiuchiolo et al., 2004; Cipro et al. 2011; Corsolini et al. 2006; Goutte et al., 2013; Nash et al. 2008; Wild et al., 2014; Yogui & Sericano 2008; Yogui, Sericano & Montone, 2011).

In general, as distances from wastewater outfalls or human residence areas increased the contamination levels of total PBDE contamination dropped, exemplified by Wild et al. (2014) where all levels of the four detectable PBDE congeners (BDE-47, -99, -206 and -209) showed decreasing concentration in the marine biota as distance from Casey Station, and the wastewater outfall at Crane Cove, increased. Nash et al. (2008) detected total PBDE concentration in krill, *Euphausia superba*, from the eastern Antarctic sector at 0.019 ng/g wet weight (ww), contamination levels were recorded at 0.2 $\pm$ 0.04 ng/g (ww) for *E.superba* in the Ross Sea by Corsolini et al. (2006).

Six Antarctic fish species have also been examined for PBDE contamination in the Ross Sea (Borghesi et al., 2008; Borghesi et al., 2009; Corsolini et al., 2006). Borghesi et al. (2009) detected total concentrations of all PBDEs tested in the range 0.089 $\pm$ 0.02 ng/g (ww) in *G. nicholsi* to 0.44 $\pm$ 0.10 ng/g (ww) in *C. gunnari. C. hamatus* and *T. eulepidotes* PBDE concentrations were assessed at 0.20 $\pm$ 0.04 ng/g (ww) and 0.14 $\pm$ 0.05 ng/g (ww) respectively. These findings are in agreement with Borghesi, Corsolini & Focardi (2008) who found total PBDE levels in the muscle of two Antarctic fish (*Chionodraco hamatus, Trematomus bernacchii*) as 0.16 $\pm$ 0.08 ng/g (ww) and 0.35 $\pm$ 0.115 ng/g (ww) respectively.

Antarctic seabirds (Petrels, Skuas and Adelie, Gentoo and Chinstrap penguins) have either been directly examined for PBDE contamination or through their eggs (Cipro et al., 2014; Colabuono et al., 2014; Corsolini et al., 2006; Corsolini et al., 2007; Goutte et al., 2013; Van den Brink et al., 2011; Yogui Sericano, 2009). Corsolini et al. (2006) examined penguins in the Ross Sea region. The Adelie penguin food web constituents; krill, rockcod and Adelie penguin eggs were examined in this study (Corsolini et al., 2006) which recorded the highest PBDE concentration in Adelie eggs at 0.29 $\pm$ 0.31 ng/g (ww). Antarctic petrels on Hop Island were assessed to have a total PBDE concentration of 4.1 ng/g lipid weight (lw) (Van den Brink et al., 2011). Colabuono et al. (2014) studied eggs of five bird species from the South Shetland Islands and found PBDE concentrations above 0.25 ng/g (ww) in four of the twenty-five samples, a maximum recorded at 0.88 ng/g (ww), detected in a Brown Skua, *Catharacta antarctica* egg.

Top level predators the Weddell seal, *Leptonychotes weddellii* and Antarctic Type C killer whales, *Orcinus orca* have also been briefly studied for PBDE contamination from blubber analysis (Krahn et al., 2008; Trumble et al., 2012. Polybrominated diphenyl ether 47 was detected in the blubber of 31 adult Weddell seals with average concentrations of 1.2 and 1.8 ng/g lipid for males and females respectively. Krahn et al. (2008) detected PBDEs in the blubber of Antarctic Type C killer whales with total concentrations being detected at 12 $\pm$ 28 and 4.1 $\pm$ 11 ng/g (lw) for males and females respectively.

Table 2: *Total Polybrominated diphenyl ether concentrations in studied Antarctic biota*

Antarctic Organisms ∑PBDEs				
Organism	**Species**	**Location**	**Concentration**	**Study**
Moss	*Brachitecyum sp.*	King George Island	0.276 (ng g^{-1} dw)	Cipro et al. (2011)
Moss	*S. uncinata*	King George Island	0.818 ± 0.270 (ng g^{-1} dw)	Yogui & Sericano (2008)
Moss	*S. uncinata*	King George Island	0.893 ± 0.280 (ng g^{-1} dw)	Cipro et al. (2011)
Moss	*S. uncinata*	Dengta, Ardley Island, Fildes Peninsula	0.019 (ng g^{-1} dw)	Wang et al. (2012)
Moss	*S. uncinata*	Badaling, Fildes Peninsula	0.0367 (ng g^{-1} dw)	Wang et al. (2012)
Moss	*S. princeps*	King George Island	0.718 (ng g^{-1} dw)	Cipro et al. (2011)
Lichen	*U. aurantiaco-atra*	Dengta, Ardley Island, Fildes Peninsula	0.0075 (ng g^{-1} dw)	Wang et al. (2012)
Lichen	*U. aurantiaco-atra*	Badaling, Fildes Peninsula	0.0188 (ng g^{-1} dw)	Wang et al. (2012)
Lichen	*U. antarctica*	King George Island	0.168 ± 0.075 (ng g^{-1} dw)	Yogui & Sericano (2008)
Lichen	*Usnea spp.*	King George Island	0.236 ± 0.05 (ng g^{-1} dw)	Cipro et al. (2011)
Angiosperm	*C. quitensis*	King George Island	0.328 (ng g^{-1} dw)	Cipro et al. (2011)
Sea Ice Algae	ND	Palmer LTER Region	13,920 ± 4116 (ng g^{-1} lipid)	Chiuchiolo et al. (2004)
Phytoplankton	*Thalassiosira*	Palmer LTER Region	49.7 ± 2.8 (ng g^{-1} lipid)	Chiuchiolo et al. (2004)
Krill	*E. superba*	Ross Sea	0.2 ± 0.04 (ng g^{-1} ww)	Corsolini et al. (2006)
Krill	*E. superba*	Eastern Antarctic Sector	0.019 (ng g^{-1} ww)	Nash et al. (2008)
Juvenile and Adult Krill	*E. superba*	Palmer LTER Region	1318 ± 203 (ng g^{-1} lipid)	Chiuchiolo et al. (2004)
Rockcod	*T. bernacchii*	Ross Sea	0.16 ± 0.01 (ng g^{-1} ww)	Corsolini et al. (2006)
Adelie Penguin Eggs	*P. adeliae*	Ross Sea	0.29 ± 0.31 (ng g^{-1} ww)	Corsolini et al. (2006)
Chinstrap Penguin Eggs	*P.antarctica*	King George Island	6.78 ± 6.42 (ng g^{-1} lipid)	Yogui & Sericano (2009)
Gentoo Penguin Eggs	*P. papua*	King George Island	8.12 ± 5.32 (ng g^{-1} lipid)	Yogui & Sericano (2009)
South Polar Skua Eggs	*S. maccormicki*	King George Island	146 ± 164 (ng g^{-1} lipid)	Yogui & Sericano (2009)
Adelie Penguin	*P. adeliae*	King George Island	0.291 ± 0.477 (ng g^{-1} ww) in blood	Corsolini et al. (2007)
Chinstrap Penguin	*P.antarctica*	King George Island	0.108 ± 0.105 (ng g^{-1} ww) in blood	Corsolini et al. (2007)
Gentoo Penguin	*P. papua*	King George Island	0.117 ± 0.108 (ng g^{-1} ww) in blood	Corsolini et al. (2007)
Antartic Petrels	*T. antarctica*	Hop Island, near Davis Station	4.1 (ng g^{-1} lipid)	Van den Brink et al. (2011)
Brown Skua	*C.antarctica*	South Shetland Islands	0.88 (ng g^{-1} ww)	Colabuono et al. (2014)
Antarctic Tern	*S. vittata*	South Shetland Islands	0.65 (ng g^{-1} ww)	Colabuono et al. (2014)
Antartic Fish	*C. hamatus*	Ross Sea	0.20 ± 0.04 (ng g^{-1} ww)	Borghesi et al. (2009)
Antartic Fish	*C. hamatus*	Ross Sea	0.16 ± 0.08 (ng g^{-1} ww)	Borghesi et al. (2008)
Antartic Fish	*C. gunnari*	Ross Sea	0.44 ± 0.10 (ng g^{-1} ww)	Borghesi et al. (2009)
Antartic Fish	*G. nicholsi*	Ross Sea	0.089 ± 0.015 (ng g^{-1} ww)	Borghesi et al. (2009)
Antartic Fish	*T. eulepidotes*	Ross Sea	0.14 ± 0.05 (ng g^{-1} ww)	Borghesi et al. (2009)
Antartic Fish	*T. bernacchii*	Ross Sea	0.350 ± 0.115 (ng g^{-1} ww)	Borghesi et al. (2008)
Weddell Seal	*L. weddellii*	Near McMurdo Sound	1.2 (male) 1.8 (female) (ng g^{-1} lipid) in blubber	Trumble et al. (2012)
Killer Whales	*O. orca*	McMurdo Sound Ice Edge	12 ± 28 (male) 4.1 ± 11 (female) (ng g^{-1} lipid)	Krahn et al. (2008)
ND denotes not detected				

II. Perfluorinated compounds (PFCs)

Perfluorinated compounds are synthetically derived compounds, fluorine atoms attach to carbon chains giving a chemical structure which has unique properties such as oil repellence, hydrophobia and thermal stability. Perfluorinated compounds are used in non-stick cookware, food packaging, waterproof clothing, lubricants and paints (Environmental Protection Agency[EPA], 2013b). The most commonly detected PFCs in both Antarctic biota and environmental samples are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).

Environment

Perfluorooctanoic acid and PFOS have been detected in the Southern Ocean (Zhao et al., 2012) with the average concentration recorded at 30 pg/L. Per- and polyfluoroalkyl substances (PFASs) were detected in snow, lake water, surface runoff and coastal seawater on and near to Fildes Peninsula, King George Island (Cai et al., 2012). Perfluorooctanoic acid was detected in all samples with the highest concentration, in a coastal seawater sample, recorded at 15,095 pg/L. Wei at al. (2007) detected perfluorosulfonates (PFSAs) and perfluorocarboxylates (PFCAs) at very low levels in the Southern Oean. Dreyer, Weinberg, Temme & Ebinghaus. (2009) also found low levels of PFSAs and PFCAs in the Southern Ocean with locations from Neumayer Station to 60°S. Wild et al. (2014) provides the first evidence of PFASs introduced to the Antarctic environment through research stations as a source. Fifteen perfluorinated carboxylates and sulfonates were tested for in indoor dust samples with all occurring at detectable levels at least once in the three sampling years (2011, 2012 and 2013) for areas of Casey Station. PFOS was regularly the most detected PFAS, often at concentrations 10 times any other PFAS. The highest concentration of PFOS was detected at 2370 ng/g (dw) in the 2011 warehouse indoor dust sample. Wild et al. (2014) also found PFAS contamination in the wastewater effluent of Casey Station, present in dissolved and particulate forms. The wastewater sampling was conducted twice, once in 2011 and once in 2012, with total PFAS concentration in 2011, the higher recorded concentration year, at 37.3 ng/L and 240.1 ng/L for particulate and dissolved fractions respectively.

Table 3: *Total perfluorinated compound concentrations in the studied Antarctic environment*

	Antarctic Environment PFCs			
	Sample	**Location**	**Concentration**	**Study**
PFOS	Surface Ocean Water Sample	Southern Ocean	25 - 45 pg L^{-1}	Zhao et al. (2012)
	Wastewater Particulates	Casey Station	4.87 ng L^{-1}	Wild et al. (2014)
	Wastewater Dissolved Phase	Casey Station	11.03 ng L^{-1}	Wild et al. (2014)
	Hallway New Wing	Casey Station	7.2 (ng g^{-1} dw)	Wild et al. (2014)
	Bedroom New Wing	Casey Station	6.9 (ng g^{-1} dw)	Wild et al. (2014)
	Hallway Old Wing	Casey Station	27.9 (ng g^{-1} dw)	Wild et al. (2014)
	Bedroom Old Wing	Casey Station	40 (ng g^{-1} dw)	Wild et al. (2014)
PFOA	Surface Ocean Water Sample	Southern Ocean	15 pg L^{-1}	Zhao et al. (2012)
	Wastewater Particulates	Casey Station	0.13 ng L^{-1}	Wild et al. (2014)
	Wastewater Dissolved Phase	Casey Station	9.37 ng L^{-1}	Wild et al. (2014)
	Hallway New Wing	Casey Station	81.7 (ng g^{-1} dw)	Wild et al. (2014)
	Bedroom New Wing	Casey Station	82.3 (ng g^{-1} dw)	Wild et al. (2014)
	Hallway Old Wing	Casey Station	86.1 (ng g^{-1} dw)	Wild et al. (2014)
	Bedroom Old Wing	Casey Station	13.1 (ng g^{-1} dw)	Wild et al. (2014)
∑PFASs	Snow Sample	Fildes Peninsula	1129 – 2491 pg L^{-1}	Cai et al. (2012)
	Coastal Seawater	Fildes Peninsula	532 – 15284 pg L^{-1}	Cai et al. (2012)
∑PFCs	Surface Ocean Water Sample	Southern Ocean	30 pg L^{-1}	Zhao et al. (2012)
	Wastewater Particulates	Casey Station	16.0 ng L^{-1}	Wild et al. (2014)
	Wastewater Dissolved Phase	Casey Station	35.1 ng L^{-1}	Wild et al. (2014)

Organisms

Perfluorinated compounds have been detected in Antarctic fur seal pups and in Gentoo and Adelie penguin eggs from Livingston Island, South Shetland, Antarctic Peninsula (Schiavone et al., 2009). The total PFC concentrations found in the muscle of fur seals, Gentoo eggs and Adelie eggs were 2.7 $\pm$ 1, 1.3 $\pm$ 1.2 and 7.35 $\pm$ 9 ng/g (ww) respectively. PFOS was the main PFC detected in the Antarctic fur seal pup, and the penguin egg profiles were dominated with perfluoroundecanoic acid (PFUnDA) and perfluoroheptanoic acid (PFHpA). This was the first profiling of PFCs in Antarctic penguin eggs and Antarctic fur seals (Schiavone et al., 2009). A small number of additional studies have documented the presence of perfluorooctane sulfonate (PFOS) only, in seals and birds from Antarctica and the Southern Ocean (Kannan et al., 2001; Giesy & Kannan, 2001; Tao et al., 2006), contamination levels of PFOS are considered as low in these studied Antarctic fauna. Wild et al. (2014) also found PFOS as the only PFAS detectable in two moss samples closest to Casey Station. Amphipods were also analysed for PFAS contamination by Wild et al. (2014) but no evidence of uptake or absorption was detected above the PFAS method level of detection. A more comprehensive study of Antarctic biota contaminated with PFCs was published in 2010 (Nash et al., 2010). Examination of; Antarctic Krill, Adelie Penguin, Antarctic Petrel, White-chinned Petrel, Antarctic Fur Seal, Weddell Seal and Humpback Whale was carried out and two of the fifty-seven tissue samples (an adult Antarctic fur seal sample and a White-chinned Petrel's pectoral muscle) produced detectable concentrations of PFC analytes.

III. Pharmaceuticals and personal care products (PPCPs)

A recent publication has described the first investigation of pharmaceutical and personal care products (PPCPs) as environmental pollutants in Antarctica, at two Antarctic research bases (Emnet et al., 2014). The comprehensive research component of the study focused on the presence of selected PPCPs in wastewater treatment effluents, sea ice, local biota and close vicinity coastal sea water over the 2012/2013 research season. Twelve analytes were detected in the sewage effluents of Scott Base with concentrations ranging from 3.1 ng/L for the steroid hormone estrone (E1) to 11,700 ng/L for the UV-filter 4-methylbenzylidene camphor (4-MBC). Antarctic seawater analysis detected eleven analytes with much smaller concentrations than the wastewater outfall with the highest concentration at 37.4 ng/L for mParaben and the lowest concentrations for most detected analytes at less than 1 ng/L. Seven analytes were detected in Antarctic sea ice with all values being less than 7 ng/L. In the Antarctic biota seven analytes were detected at least one of the samples of either an Antarctic clam, urchin composite or fish, Cstanol had the highest concentration in urchin composite at 1,260 ng/g (dw). Only the UV-filter 2-hydroxy-4 methoxybenzophenone (BP-3), the alkylphenol 4-t-octylphenol (OP) and the synthetic estrogenic steroid ethinylestradiol (EE2) were detected in all four sampling areas.

IV. Organophosphate Esters (OPEs)

Organophosphate esters (OPEs) are often used as flame retardants replacing the more common, but recently restricted PBDEs. Organophosphate esters have been detected for the first time on the East Antarctic ice sheet and inland Antarctica (Cheng et al., 2013a). Tris(2-carboxyethyl)phosphine (TCEP) was the most quantifiable and abundant OPE. Organophosphate ester concentrations have also been detected in the Southern ocean, Antarctic Peninsula and Terra Nova Bay, with the highest value of OPE concentration being recorded near relatively intense human activity, close to the Antarctic Peninsula which detected concentrations of TCEP and TDCP at 40.9 pg m^{-3} and 75.9 pg m^{-3} respectively (Cheng et al., 2013b; Ciccioli et al., 1994).

V. Chlorinated paraffins (CPs)

Chlorinated paraffins (CPs) are used as flame retardants and additives in sealants, paints, coating and metal working fluids. Chlorinated paraffins were detected in a January 16^{th} to February 8^{th} 2013 sampling period of air samples from King George Island, Fildes Peninsula with a total and averaged CP concentration found to be 19.4 ± 4.5 pg m^{-3} (Ma et al., 2014).

VI. Siloxanes

Siloxanes are synthetic chemicals with the characteristic feature of silicon atom pairs being separated by an oxygen atom. Volatile methyl siloxanes (VMS) in the cyclic and linear form (cVMS and lVMS, respectively) can be used in production of silicones, paints, cleaning products and in the formulation of personal care products. Cyclic volatile methyl siloxanes and lVMS have been detected for the first time in Antarctica (Sanchis et al., 2015). Cyclic volatile methyl siloxane compounds D3, D4 and D5 were the predominant chemicals in the study's samples, in each sample the predominant chemical was different and is described as follows. Cyclic volatile methyl siloxanes were found in samples of soil (D5 the highest mean concentration of 29.9 ng/g (dw)), vegetation (total cVMS median concentration 44.3 ng/g (dw), phytoplankton (D3 the highest median concentration of 3.0 ng/g (dw)) and krill (D4 the highest median concentration of 41.1 ng/g (dw)) while lVMS were detected in soil and phytoplankton only.The soil and vegetation samples were collected at Livingston and Deception Islands with krill and phytoplankton samples collected in the Drake Passage, Bransfield Strait, South Scotia Sea, Bellingshausen Sea and Weddell Sea (Sanchis et al., 2015).

III. Discussion and Comparisons

I. Polybrominated diphenyl ethers (PBDEs)

Environment

Overall the PBDE contamination detected in indoor dust samples, for the two Antarctic studies, are in the range quoted internationally for indoor areas (Harrad et al., 2008; Wilford, Shoeib, Harner, Zhu & Jones, 2005).

The soil and sediment analysis (Wang et al., 2012) of PBDE concentration was quality controlled utilising an isotope-dilution method. The US Environmental Protection Agency defined standards of 68A-LCS and PBDE-LCS (13C-BDE-47, 99, 153) were followed for specification and quantification. Soil samples from the Russian Arctic (Arctic Monitoring and Assessment Programme [AMAP], 2004) and Norway (Hassanin et al., 2004) yielded total PBDE concentrations of 0.16 - 0.23 ng/g (dw) and 0.71 ng/g (dw) respectively. The PBDE concentrations detected by Wang et al. (2012) were significantly below these values reported in the Arctic. Soil and sediment samples taken near research bases (Hale et al., 2008; Wild et al., 2014) show expectedly higher total PBDE concentrations than the remote Arctic measurements, in line with their hypotheses of Antarctic research bases being sources of PBDE contamination.

The PBDE contamination analysis in King George Island air samples (Li et al., 2012) was conducted according to the US Environmental Protection Agency method 1614 and the value of 1.52 (pg m^{-3}) averaged over five sites using passive air sampling is comparable to an Arctic country passive air sampling study (Jaward, Farrar, Harner, Sweetman & Jones, 2004), which included Iceland, Norway and Svalbard which produced total PBDE concentrations of 1.65, 1.62 and 3.89 ng/sample, where a sample size was 1 m^3.

Organisms

The Weddell seal and Type C killer whale studies have large uncertainties associated with their PBDE concentration and have only been examined in one study respectively (Krahn et al., 2008; Trumble et al., 2012). Both studies conducted in McMurdo Sound give little perspective about PBDE contamination in top end predators from other areas of Antarctica. Polybrominated diphenyl ether concentrations in killer whales (de Wit, Herzke & Vorkamp,

2010; Wolkers, Corkeron, Van Pariis, Simila & Van Bavel, 2007) and ringed seals (Letcher et al., 2009; Routti, Letcher, Chu, Van Bavel & Gabrielsen, 2009; Vorkamp, Riget, Glasius, Muir & Dietz, 2008; Wolkers et al., 2004) have been studied more extensively in the Arctic. For Arctic killer whales, total PBDE concentrations ranging from 76 - 790 ng/g (lw) were reported in northern Norwegian killer whale samples and the highest total PBDE concentration is reported in Alaskan offshore killer whales detected at 3,300 ng/g (lw). Ringed seal total PBDE concentrations in the Arctic range from 6 to 149 ng/g (lw). Comparing Weddell seals to ringed seals the total PBDE contamination seen in the Antarctic is relatively low, however, only one study has been conducted and warrants further examination.

Arctic fish show total PBDE concentrations ranging from 3 - 46 ng/g (lw) (Kelly, Ikonomou, Blair & Gobas, 2008; Tomy et al., 2008; Vorkamp et al., 2004; Wolkers et al., 2004) and are in the same concentration range as the studied Antarctic fish.

A selection of studied Arctic avian species; Arctic terns, glaucous gulls, ivory gulls and lesser black-backed gulls detected total PBDE concentrations of 41 ng/g (lw), 59 ng/g (ww), 44 ng/g (lw) and 2 ng/g (ww) respectively (Braune, Mallory, Gilchrist, Letcher & Drouillard, 2007; Bustnes, Erikstad, Lorentsen & Herzke, 2008; Haukas, Berger, Hop, Gulliksen & Gabrielsen, 2007; Jenssen et al., 2007) which overall represent higher PBDE concentrations than Antarctic penguins, terns and skuas.

Moss from London Island, Svalbard produced total PBDE concentrations of 0.119 ng/g (dw) (Zhu et al., 2015) and is in the range of moss PBDE concentrations detected in Antarctica (Cipro et al., 2011; Yogui et al., 2011), additionally, these concentrations are comparable to a Norwegian Arctic moss study (Mariussen et al., 2008).

II. Perfluorinated compounds (PFCs)

Environment

Perfluorinated compound measurements in the Arctic environment have been reviewed by Butt et al. (2010) and are considered limited, Antarctic abiotic PFC measurements comprising only a handful of studies (Cai et al., 2012; Dreyer et al., 2009; Wild et al., 2014), are therefore, nearly non-existent. The total PFAS concentration in snow samples analysed at Fildes Peninsula (Cai et al., 2012) were in the range of 1129 - 2491 pg/L which is higher than the values of the Greenland and remote Canadian Arctic areas, 22 - 80 pg/L and 271 - 1082 pg/L respectively (Theobald, Gerwinski, Caliebe & Haarich, 2007; Young et al., 2007), the higher Antarctic contamination levels may reflect the close proximity of sampling to the Great Wall and Frei research bases.

Coastal seawater sampling by Cai et al. (2012) measured total PFAS concentrations ranging from 532 - 15,284 pg/L, when compared to the Greenland Sea and Canadian Arctic concentrations (Rosenberg et al., 2008; Theobald et al., 2007) Antarctic measurements were consistently higher, possibly a result of the Fildes Peninsula samples being taken near human activites. More remote areas of Antarctica must be analysed for PFC contamination so accurate comparisons with the Arctic can be made.

Sewage sludge from Iceland and Faroe Island contained PFOA concentrations of 0.25 - 0.40 and 1.08 ng/g (ww) respectively (Kallenborn, Berger & Jarnberg, 2004). Wild et al. (2014) concludes that PFAS concentrations found in wastewater effluent of Casey Station are similar, though slightly higher than primary and secondary treated wastewater from the developed countries of Australia, Denmark and Germany. These results show that PFSA contamination in the Antarctic, near human activities, is similar to worldwide observations.

The levels of PFASs detected at Casey Station in indoor dust samples are comparable to levels detected in homes and offices worldwide (Bjorklund, Thresson & de Wit, 2009; Goosey & Harrad, 2011).

Organisms

Perfluorinated compound contamination in Arctic biota has been studied and reviewed far more extensively than Antarctic biota (Butt,

Berger, Bossi & Tomy, 2010; Letcher et al., 2010). An extensive review of PFSA and PFCA contamination conducted by Letcher et al. (2010) of Arctic wildlife and fish reported concentrations of total PFSA and PFCA ranges in ringed seals at 10 - 95 and 7 - 83 ng/g (ww) respectively. These results are comparable with the very limited seal data from the Antarctic but further investigation is required for accurate understanding of PFC contamination in Antarctic seals. Avian liver contamination in the Arctic for total PFSA and PFCA is has been found to be in the ranges 1 - 105 and 1 - 2 ng/g (ww) respectively (Letcher et al., 2010), little conclusions can be drawn in comparison to the Antarctic on account of different bird physiology and the Antarctic samples being primarily egg samples (Schiavone et al., 2009). The study conducted by Nash et al. (2010) found only two samples out of fifty-seven present with PFC contamination above detectable concentrations, initial evidence possibly showing that Antarctic biota PFC contamination levels are below that seen in the Arctic.

III. Pharmaceuticals and personal care products (PPCPs)

Emnet et al. (2014) reported that concentrations of PPCPs detected in the WWTP effluent of Scott Base are consistent with international values reported in the literature, the analytes 2,4-dihydroxybenzophenone (BP-1) and OP had upper concentrations exceeding those quoted in recent studies. The coastal seawater and sea ice had similar analyte concentration profiles and were in the lower range of concentrations reported internationally in coastal and ocean waters. Limited data on PPCP contamination in Antarctic and worldwide aquatic biota make it hard to draw international comparisons, however, from what has been studied Antarctic biota PPCP concentrations are in the lower range. Emnet et al. (2014) also provides the first evidence for bioaccumulation of paraben preservatives.

IV. Organophosphate Esters (OPEs)

Organophosphate esters have only recently been detected on the Antarctic ice sheet and inland Antarctica for the first time (Cheng et al., 2013a) and only limited quantification was conducted. Organophosphate esters were detected in the Arctic and Southern Oceans (Moller et al., 2012) with Tris(2-carboxyethyl)phosphine (TCEP) concentrations detected at 289 pg m^{-3} and 74 pg m^{-3} respectively. With further OPE analysis in the Antarctic region a more comprehensive comparison with the Arctic will be viable.

V. Chorinated paraffins (CPs)

Total short chain chlorinated paraffin (SCCP) concentrations for the Antarctic atmospheric air sampling (Ma et al., 2014) were slightly lower than the atmospheric Arctic sampled areas of Svalberg (Borgen, Schlabach & Gundersen, 2000) and Alert Station (Peters, Tomy, Stern & Jones, 1998). Limited CP research in the Antarctic region necessitates further investigation into chlorinated paraffin contamination for the southern most continent.

VI. Siloxanes

The siloxane concentrations detected by Sanchis et al. (2015) in Antarctica show increased concentrations in comparison to Arctic samples analysed by Warner et al. (2010). Siloxane presence in Antarctica has been studied for the first time by Sanchis et al. (2015) and requires further investigation before conclusive data can be drawn about VMS concentrations in the Antarctic region. The first report of a siloxane compound present in Arctic biota was presented by Knudsen et al. (2007), reinforcing siloxanes as a newly discovered contaminant in the polar regions, siloxanes in this contaminating context must be further examined in both polar regions.

VII. Priority emerging contaminants in the Antarctic

A recent study prioritising emerging contaminants in the freshwater environment based on concentration levels has reported that PPCPs should be considered very high priority pollutants and that PFOA and PFOS should be considered high priority pollutants (Murray, Thomas & Bodour, 2010). This classification is based upon the EC's acceptable daily intake, concentration in freshwater and the daily recommendation for human water intake. The concentrations of PPCPs and PFCs in the anthropogenic areas of Antarctic have shown similar levels to internationally quoted concentrations so it is reasonable to assume the same EC priority around Antarctic research stations. Water for human use at Antarctic research bases is often extracted from seawater using reverse osmosis plants (Goring & Pyne, 2003), the seawater is also where sewage outfalls deposit waste. Antarctic biota will have different EC tolerance levels to humans, however, the concerns to human health reported by Murray et al. (2010) may give an indication about PPCP and PFC concentrations being also of concern for all biota. The water solubility of PBDEs is relatively low so spread in the Antarctic environment is likely to be less than PFCs or PPCPs. A study on POPs and emerging contaminants reported PBDES as the lowest contributors to total toxicity in sediment and sludge samples (Eljarrat & Barcelo, 2003), however, PPCPs and PFCs were not analysed in this report. The priority order of ECs in the Antarctic should be PPCPs>PFCs>PBDEs based on their ability to spread and concentrations detected in the Antarctic environment.

IV. Conclusion

The studies conducted on ECs in biota of Antarctica generally show lower concentrations than seen in the Arctic. Presence of ECs near to and inside Antarctic research bases is reported at concentrations similar to those seen in urban living areas throughout the world. The presence of ECs in remote areas of Antarctic is unknown due to a lack of research. Further investigation of ECs in Antarctica is required and may lead to better understanding of EC's biotic effects, transport mechanisms and spread in the Antarctic environment.

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