2015

EMERGING PERSISTENT ORGANIC POLLUTANTS (POPS) IN THE WESTERN SOUTH ATLANTIC AND ANTARCTIC BIOTA

Erin Markham
University of Rhode Island, erinemarkham@gmail.com

EMERGING PERSISTENT ORGANIC POLLUTANTS (POPS)

IN THE

WESTERN SOUTH ATLANTIC AND ANTARCTIC BIOTA

BY

ERIN MARKHAM

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

OCEANOGRAPHY

UNIVERSITY OF RHODE ISLAND

2015

MASTER OF SCIENCE THESIS

OF

ERIN MARKHAM

APPROVED:

Thesis Committee:

Major Professor Rainer Lohmann

Brice Loose

Vinka Craver

Nasser H. Zawia

DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND

2015

ABSTRACT

Persistent organic pollutants (POPs) are largely synthetically produced chemicals that are known to persist in the environment, bioaccumulate, have the potential to be transported long distances, and cause adverse effects. There are legacy POPs that have been around for decades and have either been banned or strictly regulated, but are still found in the environment; and there are emerging POPs that are either not yet or are very newly regulated. This research focuses on contributions to the global dataset of emerging POPs by investigating hydrophilic perfluoroalkyl substances (PFAS) in surface waters and at depth of the Western South Atlantic; as well as hydrophobic polybrominated diphenyl ethers (PBDEs) in Antarctic biota (plankton, krill, fish, fur seal milk). PFAS were found in all surface waters (ΣPFAS 20.3 – 525.8 pg/L) and at depths of up to 5526 m. This confirms the infiltration of these compounds into our global oceans. PBDEs were detected at the highest concentrations in Antarctic plankton (plankton > krill > fur seal milk > fish). This is contrary to the biomagnification seen in many legacy compounds and indicates the potential for biodilution and species-specific metabolic processes occurring. These data contribute to the growing knowledge of emerging pollutants in the southern hemisphere, which is generally less prominently covered in terms of pollution studies.

ACKNOWLEDGEMENTS

I would like to sincerely thank everyone who helped me during this process over the past few years. To Dr. Rainer Lohmann: thank you for all of the unique opportunities I was able to take part in and thank you for all of the advice and feedback provided along the way. This work could not have been done without funding, which was largely provided by NSF. To everyone in the Lohmann lab, past and present: thank you for all of your peer-support; to Dr. Autumn Oczkowski and everyone at EPA for all of your help and guidance in getting me here; to everyone at the Research Centre for Toxic Compounds in the Environment (RECETOX): many thanks for all of your efforts and assistance in this work; and my deepest thanks to all family and friends for all of your encouragement and support.

PREFACE

This preface is included with the explicit intention to note that Manuscript Format has been used in the preparation of this thesis.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

PERFLUOROALKYL SUBSTANCES (PFAS) IN SURFACE WATERS AND AT DEPTH OF THE WESTERN SOUTH ATLANTIC

MANUSCRIPT IN PREPARATION FOR SUBMISSION TO *ENVIRONMENTAL SCIENCE AND TECHNOLOGY*

ERIN MARKHAM[1, 2], PAVLÍNA KARÁSKOVÁ[2], JITKA BEČANOVÁ[2], JANA KLÁNOVÁ[2], RAINER LOHMANN[1]

1 – UNIVERSITY OF RHODE ISLAND, GRADUATE SCHOOL OF OCEANOGRAPHY, 215 SOUTH FERRY RD, NARRAGANSETT, RI 02840

2 – RESEARCH COMPOUND FOR TOXIC COMPOUNDS IN THE ENVIRONMENT, MASARYK UNIVERSITY, KAMENICE 3/126, 625 00 BRNO, CZECH REPUBLIC

INTRODUCTION

Perfluoroalkyl substances (PFAS) are synthetically produced chemicals that have been in production since the 1950s and have only recently (within the last 15 years) become recognized as global contaminants of concern (Lindstrom et al. 2011). Poly- and per-fluorinated compounds are long chains of 4 or more carbons where either some (poly-) or all (per-) of the hydrogen atoms have been replaced with fluorine atoms. PFAS are categorized largely as either acids or sulfonates, differentiated by the functional group at the end of the carbon chain. The carbon-fluorine bond that is imparted during production is extremely strong, which makes these chemicals extremely useful in a wide range of consumer and industrial applications (e.g. non-stick cookware, stain-repellent fabrics, food packaging and water-resistant apparel). At the same time, it also makes them extremely stable and resistant to environmental degradation. Historical production focused largely on the eight-carbon (C8) chemistries with perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) being both the most heavily produced and utilized compounds. PFOA and PFOS are also the degradation end products of numerous other fluorinated (precursor) compounds, thus making their environmental concentrations the greatest. PFAS are now found ubiquitously in surface waters, wildlife, and humans (Giesy & Kannan 2001, Yamashita et al. 2005, Houde et al. 2006, 2011a, Lindstrom et al. 2011, Benskin et al. 2012). The Stockholm Convention added PFOS to Annex B in 2009, and there are currently 8 major companies signed on to a U.S. PFOA Stewardship Program aimed at completely phasing out use of the chemical by 2015. However, there are allowable exemptions to Annex B and while it may be easier to regulate production say, within the United States, there has been evidence that there is and may continue to be

"knock-on" production of C8 and other PFAS in some countries within Asia. In addition there is increasing production of shorter-chained (e.g. C4) PFAS as replacements of the eight-carbon compounds, along with the increased use of more volatile precursor compounds that have the capability of undergoing long-range transport through the atmosphere and ultimately degrading into compounds such as PFOA and PFOS (Paul et al. 2009, Lindstrom et al. 2011).

One of the unique physiochemical properties of PFAS is that unlike many of their legacy POP counterparts, they are largely hydrophilic, making their ultimate environmental fate our world's oceans (Yamashita et al. 2005). Atmospheric transport and deposition has been described for the neutral and volatile precursor compounds such as fluorotelomer alcohols (FTOHs) and perfluorinated sulfanomido alcohols (FOSEs). These can undergo oxidation to ionic PFAS, and quickly deposit thereafter. The other main transport mechanism that has been proposed is via the hydrodynamics of ocean circulation transporting these compounds away from source regions (Ahrens et al. 2010, Butt et al. 2010). Sources to riverine systems include nonpoint ones such as rainfall, runoff, and snowmelt, but wastewater treatment plants are also known point-source contributors of PFC loads to river systems (Furl et al. 2011).

While much of the world's surface waters have been surveyed for PFAS, little is known about PFAS at depth. If the oceans are indeed the final sink for these compounds, we need a more thorough understanding of how PFAS are moved to depth and affected by ocean circulation. Yamashita et al. (2008) proposed that perfluorinated acids may be used as novel tracers for global ocean circulation due to their high water solubility, persistence, measurability, and the fact that they (at least the acids) are less bioavailable

than many other POPs. Vertical profiles obtained from the Labrador Sea, the mid Atlantic Ocean, the South Pacific Ocean, and the Japan Sea provided some of the first available data to look at PFAS beneath the surface waters and it was estimated that approximately 1% of PFOA emissions since production began (around 60 years ago) has been transported to deep ocean waters.(Yamashita et al. 2008a) Later, Lohmann et al. (2013) proposed vertical eddy diffusion as a primary mechanism of PFOA removal from the surface, estimating that it accounts for 13% of the removal of PFOA from surface waters compared to 4% via deep water formation, with the surface waters (i.e. top 100m) storing at least 21% (Lohmann et al. 2013).

In this study, vertical seawater profiles were collected at 12 stations throughout the Western Atlantic Ocean in the spring of 2013 to better understand the presence of PFAS in the oceans. Particular care was taken to sample specific deep ocean water masses that might hold clues to the penetration efficiency and circulation of PFAS in the Atlantic Ocean. Our aims were to (i) investigate to what depth PFAS have penetrated the Atlantic Ocean off the coast of South America; (ii) assess whether the presence of PFAS in the deeper ocean can be linked to specific water masses; and (iii) confirm the influence of major rivers (Rio de la Plata and Amazon) on PFAS concentrations in the Atlantic Ocean; as well as in remote open ocean waters. Specific target water masses included Antarctic Bottom Water (AABW), Antarctic Intermediate Water (AAIW), and North Atlantic Deep Water (NADW).

METHODS

Sampling

PFAS were sampled using Fisherbrand™ HDPE bottles. All bottles were triple rinsed with Methanol and dried in a clean laboratory setting. Water samples were obtained onboard the *R/V Knorr* on cruise KN210-04 (25 Mar 2013 – 9 May 2013) via a Sea-Bird Electronics (SBE 911+) Deck Unit and CTD Rosette at a total of 12 stations between Uruguay and Barbados (37.11°S, 49.9°W – 9.7°N, 55.3°W, Figure 1.1). Bottles were triple rinsed with sampling water, filled to just over 1 L, and stored in an onboard freezer at -20°C until ready for shipment to the analysis facility. Samples were shipped in insulated containers to the Research Centre for Toxic Compounds in the Environment (RECETOX) located in Brno, Czech Republic where all extraction and analysis took place. Field Blanks were taken at intermittent intervals throughout the cruise and consisted of water from the ship's Milli-Q system, with which bottles were triple-rinsed and then stored in the same freezer as samples. Laboratory blanks were extracted at RECETOX and consisted of 4mL of cartridge-cleaned Milli-Q water extracted (Oasis® WAX SPE) in the same manner as all samples.

Extraction and Analysis

Samples were thawed, spiked with (50µL) of a (80 ng/mL) mass-labeled surrogate standard (MPFBA, MPFHxA, MPFOA, MPFNA, MPFDA, MPFUnDA, MPFDoDA, MPFHxS, MPFOS, dMeFOSA), shaken, and allowed to sit for 30 minutes. Extraction and elution was completed with Oasis® Wax 6cc, 150mg, 30µm cartridges, which were conditioned with 5mL methanol, 5mL basic methanol (1 L Methanol

amended with 4mL Ammonia Solution), and 5mL water (RECETOX Milli-Q water), followed by the passing of 1 L sample water through the cartridge at approximately 1-2 drips per second. Upon near completion of the sample passing through the cartridge, 4mL of a wash buffer solution (water, acetic acid, and ammonium acetate) was used to rinse the sides of reservoirs and cartridges used, then allowed to pass through the cartridge. Cartridges were centrifuged at 4000rpm for 2 minutes, followed by elution into two fractions; the first fraction being eluted with 6mL methanol and the second fraction with 8mL basic methanol. All eluent was captured in pre-cleaned (basic methanol and methanol-rinsed) polypropylene falcon tubes and blown down with N_2 gas on a heated evaporation plate. Samples were reconstituted to 1mL volume with 0.5mL MeOH and 0.5mL water. Prior to analysis, samples were vortexed and 100µL was transferred to an autosampler vial.

Separation and detection was achieved using HPLC/MS/MS (Agilent 1100 liquid chromatograph, Applied Biosystem QTRAP 5500 mass spectrometer). A Phenomenex column (50 mm x 2.1 mm) with 3 µm particles was used combined with a mobile phase (methanol + 5 mM ammonium acetate) gradient elution. 10µl of sample was injected onto the column, which had a temperature of 25°C; flow of the mobile phase was set at 200µl/min. Capillary voltage in the MS ion source was set at 4500V, temperature at 450°C, and the electrical voltage multiplier at 2000V. Evaluation and quantification of data was based on a standard calibration set (0.04 to 40 ng/ml). Two MRM transitions for each compound were used to identify analytes.

Quality Assurance and Control

Fraction 1 recoveries of mass-labeled compounds averaged <1.2% for all carboxylates and sulfonates, thus concentrations for PFAS presented are all from fraction 2. FOSA, which is targeted to elute in fraction 1, recovery only averaged 21.5 ± 2.21% (standard error) and is not discussed further. Other compounds with poor recoveries of mass-labeled compounds (mean ± standard error) are perfluorobutanoic acid (MPFBA, 7.38 ± 0.29%) and perfluorododecanoic acid (MPFDoDA, 29.03 ± 2.78%). MPFDoDA serves as the mass-labeled counterpart for perfluorotridecanoic acid (PFTrDA) and perfluorotetradecanoic acid (PFTeDA) and as such, none of these compounds will be discussed further. Compounds with acceptable average mass-labeled recoveries (i.e. > 50%; average ± standard error) were perfluorohexanoic acid (MPFHxA, 88.17 ± 1.85%), perfluoroocatanoic acid (MPFOA, 81.8 ± 3.07%), perfluorononanoic acid (MPFNA, 72.16 ± 3.81%), perfluorodecanoic acid (MPFDA, 63.81 ± 4.15%), perfluoroundecanoic acid (MPFUnDA, 51.42 ± 4.12%), perfluorohexane sulfonate (MPFHxS, 93.86 ± 2.17%), and perfluorooctane sulfonate (MPFOS, 81.26 ± 4.15%). Compounds without mass-labeled counterparts were quantified to the most structurally similar compound. That is, perfluoropentanoic acid (PFPA) to PFHxA, perfluoroheptanoic acid (PFHpA) to PFHxA, perfluorobutane sulfonate (PFBS) to PFHxS, and perfluoroheptane sulfonate (PFHpS) and perfluorodecane sulfonate (PFDS) to PFOS.

All samples were blank corrected for the average of 3 laboratory blanks (4mL WAX SPE cleaned water); compounds with detection > MQL were PFBA, PFPA, PRTrDA, and MeFOSA (SI Table 1.1.1 & 1.1.2). All samples with acceptable average recoveries (i.e. >50%) are reported and recoveries for individual samples can be accessed

in the supporting information (SI Table 1.2.1 & 1.2.2). Occasional lower recoveries were most likely due to matrix effects from the saltwater. Method quantification limits (MQL) were determined individually for each sample as 10 times the signal to noise ratio. In many cases the MQL had quite a large range and was within or occasionally, above, the normal range of what is expected to be found in ocean waters (i.e. 10s to 100s of pg/L). We recommend that in future work with saltwater, a freshwater flush of ultra-pure cartridge-cleaned water equivalent to 2% of the total sample volume (i.e. 20mL in the case of a 1L sample) be run through the cartridge prior to elution. All samples that were classified as < MQL were substituted for "0" in terms of means and sums. This is likely under representing PFC concentrations, but due to the variability in MQLs among samples, any other means of substitution would likely lead to an unacceptable overestimation of concentrations.

The eight-carbon PFOA and PFOS have been the most widely produced and utilized PFAS, and as such, they are typically the dominant compounds detected in the surface oceans (Yamashita et al. 2008b, Benskin et al. 2012). Initially, we did not find that this is the case for our samples. Instead, PFPA, PFNA, and PFDS appear to be the dominant compounds (average % composition ± standard error) in the western South Atlantic comprising of approximately 31% ± 0.02, 28% ± 0.01, and 17% ± 0.01 in all samples from all depths and 30% ± 0.1, 28% ± 0.06, and 11% ± 0.04 in all surface water samples (i.e. 5m). Conversely, PFOA, PFHxS, and PFOS make up the bulk of the rest of the sample composition averaging (± standard error) 7% ± 0.01, 9% ± 0.01, and 6% ± 0.01 for all samples for all depths and 9% ± 0.03, 8% ± 0.02, and 9% ± 0.03 for all surface water samples (i.e. 5m). However, when looking at concentrations of PFPA,

PFNA, and PFDS from the surface to depth, they appear to be nearly uniform at all depths, which is cause for concern of contamination and/or problems with these compounds, and so, for now, we will focus on the remaining compounds (SI Figure 1.1 & 1.2). "PFAS" from this point forward in the results and discussion refers to PFHxA, PFHpA, PFOA, PFDA, PFUnDA, PFBS, PFHxS, PFHpS, and PFOS.

RESULTS AND DISCUSSION

Surface

PFAS were detected in 100% of surface samples with variation among compounds and are reported as mean ± standard error. PFOA was detected in 83% of all surface samples ranging from no detect (< MQL) – 95.3 pg/L with a mean of 36.9 ± 8.66 and a median of 33.18 pg/L. PFHxS was detected in 75% of all surface samples ranging from no detect (< MQL) – 294 pg/L with a mean of 44.29 ± 23.44 and a median of 19.55 pg/L. PFOS was detected in 67% of all surface samples ranging from no detect (< MQL) – 115 pg/L with a mean of 43.03 ± 11.55 and a median of 40.1 pg/L. ΣPFAS ranged from 20.3 – 525.8 pg/L with a mean of 141.58 ± 41.9 pg/L and a median of 108.4 pg/L. Detection was < 50% for remaining the remaining compounds: PFHxA (42% detection, no detect (n.d., < MQL) – 32.5 pg/L); PFDA (17% detection, n.d. (< MQL) – 37 pg/L); and PFHpS (25% detection, n.d. (< MQL) – 40.9 pg/L). PFHpA, PFUnDA, and PFBS were not detected in any surface water samples (Figure 1.2).

Benskin et al (2012) report on Atlantic surface water concentrations compiled from their study and others (i.e. Ahrens et al. 2009, Ahrens et al. 2010, Yamashita et al. 2005, Theobald et al. 2007). PFOA concentrations in these prior Atlantic samples within

proximity to the same regions we sampled (i.e. Western Atlantic, Mid Atlantic, South Atlantic, and Mid to Southwest Atlantic) ranged from < 4 – 439 pg/L; our range falls within the lower end of that spectrum from n.d. – 95.3 pg/L. Prior PFHxS concentrations ranged from 1 –17 pg/L; and our range of PFHxS concentrations was much greater, from n.d. – 294 pg/L (at least 200 nautical miles offshore from any major coastal influences), however, excluding the one high value of 294 pg/L, our range only extends from n.d. – 61.2 pg/L. Prior PFOS data ranged from <10 – 78 pg/L, which is quite similar to our range of detects from n.d. – 115 pg/L. Additionally, although PFHxA was only detected in 42% of our surface water samples, our range of <MQL – 32.5 pg/L also falls within that of prior surface water PFHxA concentrations (< 5 – 75 pg/L) (Benskin et al., 2012, SI). We thus conclude that for the most common PFAS analyzed in our current work and previous studies, the range of concentrations is comparable, implying we achieved robust analytical results and contamination-free sampling.

Patterns of PFAS within the Atlantic Ocean

The samples collected in this study can be categorized into approximately 3 different groups in terms of regions sampled. The initial stations sampled closet to Uruguay were thought to possibly contain some influence of the Rio de la Plata, followed by a section of samples off the coast of Brazil that were considered remote open ocean waters, and finally ending with samples known to contain influence of the Amazon River plume. Many of the compounds investigated (PFHxA, PFOA, PFHxS, PFOS, and ΣPFAS) all show a spike in concentration at either Station 12, 13, or both, which were each located at approximately the same latitude (5.7°S) but different longitudes (26°W and 28.5°W, respectively). We propose that this pulse of PFAS may be coming from

Africa via the westward flowing South Equatorial Current in conjunction with influences from complex current dynamics in this region.

During April, surface flow in the tropical Atlantic is primarily westward everywhere averaging 20-40 cm s^{-1} (Philander 2001). Both the Congo and Orange Rivers are two major African rivers that flow into the South Atlantic. The Congo is Africa's second longest river at 4,700 km and discharges an average of 41,000 m^3 s^{-1}, second only to the Amazon in the equatorial region of the Atlantic Ocean (Sautter & Pourtier 2014). Little research has been done on perfluoroalkyl substances in Africa, but Booi (2013) did investigate PFAS in drinking water sources of the Western Cape, South Africa and detected seven compounds in both raw and treated water sources of the region (PFHpA, PFDoDA, PFNA, PFUA, PFDeDA, PFOA, and PFOS) ranging from approximately 2 – 44 ng/L (Booi 2013). Additionally, Mudumbi et al. (2014) reported on PFOA and PFOS in three major rivers from the same region finding detectable concentrations in all river water samples, as well as suspended solids (Mudumbi et al. 2014). . Kunacheva et al. (2012) investigated PFOS and PFOA in rivers from 41 cities across 15 different countries and while none of these rivers were located in Africa, both PFOS and PFOA were detected in all rivers sampled in both industrialized and non-industrialized cities with concentrations ranging as high as 1630 ng/L for PFOA (Kunacheva et al. 2012). Thus we suggest that PFAS in the Congo River, with one of the largest drainage basins in the world, and the Orange River, which flows through South Africa where PFAS have been reported in both drinking and riverine water, are likely delivering a significant PFAS contaminant load to the Atlantic ocean, which is then further carried to the western South Atlantic via the South Equatorial Current.

Gonzalez-Gaya et al. (2014) reported on surface concentrations of PFAS globally and observed a similar spike of elevated PFAS concentrations in the south Atlantic off the Brazilian coast, albeit one to two orders of magnitude higher than the levels we report on here (i.e. 3240 – 6560 pg/L). Potential explanations given for these elevated concentrations are both wet and dry deposition (Gonzalez-Gaya et al. 2014). Elevated FTOH concentrations have also been detected in this region and may be acting as a source of PFAS to the south Atlantic (Dreyer et al. 2009).

Detection of PFAS at depth

Unexpectedly, PFAS were detected at most depths at the majority of stations, with the deepest detection at 5526 m. Initially, we expected PFAS to spike off the coast of Uruguay, a reflection of the Rio de la Plata influence, as seen in Benskin et al (2012). However, the initial stations sampled closest to the river mouth reflected some of the lowest concentrations detected, and we believe that our sampling stations may have been too far offshore to in fact capture any riverine influence. Although, salinity at the time of sampling Station 1 was 34.9 PSU at the surface (5m), which was slightly less than that of Station 2 (salinity of 36.01 PSU at the surface). Guerrero et al. (1997) completed an assessment of the physical oceanography of the Rio de la Plata Estuary and found that in the months surrounding our sampling scheme (i.e. April – August), the flow out of the estuary drifts along the Uruguayan coast to the NNE direction (Guerrero et al. 1997). Additionally, the stations sampled by Benskin et al. (2012) were much closer to the river mouth than our further offshore stations (Benskin et al. 2012). The highest concentrations during this study, were in fact observed at the stations sampled off the easternmost point of Brazil (9.49°S, 25.99°W to 2.7°S, 28.51°W), with a peak in below

surface concentrations (i.e. 400, 760, 2500 m) at Station 12 (5.7°S, 26.0°W) and a peak in surface and subsurface water (i.e. 5, 150, 249 m) at Station 13 (5.7°S, 28.51°W). These were the only two stations sampled along the same latitude and there appears to be a transport of pollutants carried west in this region, which was also seen in surface waters. The efficient vertical mixing of PFAS seen at these stations could be due, in part, to the complex dynamics of currents that occurs near the edge of ocean basins (Knauss 1997). In total, PFAS were detected in 87% of 75 individual layers of water sampled (all depths), with PFHxS detected in 67% of those layers, PFOA in 56%, PFOS in 49%, and PFHxA, PFDA, and PFHpS making occasional detection (23%, 11%, and 7%, respectively). PFHpA, PFUnDA, and PFBS were never detected in surface waters or at depth (Figures 1.3.1 – 1.4.3).

PFAS in deep water masses

When possible, target water masses, such as Antarctic Intermediate Water (AAIW), North Atlantic Deep Water (NADW), and Antarctic Bottom Water (AABW) were sampled (Figure 1.5 & 1.6). AAIW was present between 700 and 1000 m depth throughout the entire cruise and sampled at the salinity minimum/oxygen maximum. PFAS were detected in 82% of AAIW samples as far north as 8.26°N, 42.99°W with ΣPFAS ranging from n.d. – 655.9 pg/L. PFHxS was the most prevalent compound in AAIW, present in 73% of all samples ranging from n.d. – 448 pg/L. PFOS ranked second at 55%, ranging from n.d. – 93.1 pg/L. PFOA was present in 45% of all samples ranging from n.d. – 84.4 pg/L. The only other two compounds detected were PFHxA (27%, n.d. – 32.1 pg/L) and PFHpS (9%, n.d. – 38.1 pg/L). NADW was also available throughout the entire cruise at every station sampled from approximately 2500 m depth

(excluding Station 1, which was only sampled to 100 m) and PFAS were detected in 82% of these stations as far south as 37.97°S (PFOA and PFHxS detected 55% of the time with ranges of n.d. – 96.6 pg/L and n.d. – 341 pg/L, respectively), PFHxA and PFDA, 18%, and PFOS, 27%). AABW was sampled at least 4 times as far north as 5.69°S, after which the NADW track was covering such a broad depth range, bottom water samples were just classified as "bottom." PFAS were detected in 75% of all AABW samples (3 out of 4 samples), though interestingly not from the furthest south point (37°S) and closest to the formation source of AABW. PFOA was present in 75% of AABW, at concentrations ranging from n.d. – 77.7 pg/L. PFHxS and PFOS were both present in 50% of AABW ranging from n.d. – 31.4 pg/L and n.d. – 37.9 pg/L, respectively. PFHxA and PFDA were only detected in 25% of AABW (1/4 samples) at concentrations of 12.6 and 46.8 pg/L, respectively. Other layers of water commonly sampled were usually along the thermocline at depths of approximately 150 m (100% PFC detection), 250m (91% detection), and 400-500m (83% detection), which may be indicative of efficient subsurface mixing caused by vertical eddy diffusion (Lohmann et al. 2013).

Very little research has been done regarding PFAS at depth. Yamashita et al (2005) first reported on detection of PFAS at depth in both the Sulu Sea of the western North Pacific, and the Central and Eastern Pacific. In the Sulu Sea at depths of 1000 – 3000 m, PFOS was detected at concentrations of <17 – 24 pg/L and PFOA 76 – 117 pg/L; and even in the remote Pacific, PFOS was detected at 3.2 – 3.4 pg/L and PFOA 45 – 56 pg/L (Yamashita et al. 2005). Later research, also by Yamashita et al (2008), further investigated PFAS at depth, this time investigating multiple regions (North Atlantic Ocean, Mid Atlantic Ocean, South Pacific Ocean, and Japan Sea) and attributing PFAS at

depth to the global ocean circulation theory. In the Labrador Sea, a region of deep water formation, profiles demonstrated relatively uniform, but still somewhat "noisy" profiles of PFOS and PFOA throughout the whole water column sampled, including notably increasing concentrations of PFOA below 2000m depth. Their profiles of the Japan Sea and the Mid-Atlantic Ocean show a more or less "gradual" decrease in concentrations below the surface layer, yet there are still detectable concentrations of (PFOA) up to at least 3000 m in one of the profiles (AO4) and a 'blip' of detection around 5000 and 5500 m depth (Yamashita et al. 2008b). Finally, Ahrens et al (2009) took 2 deep water samples in the middle of the North Atlantic at 200 and 3800 m depth, but [PFAS] were below the MDL (Ahrens et al. 2009).

Various estimates are available for the transport time of NADW to reach the Southern Hemisphere. Bengtson Nash et al (2010) review a model (Speich et al. 2007) to estimate a range of approximately 25 – 300 years for NADW to travel from 47°N to 30°S, with a most likely transit time of around 150 years (Speich et al. 2007, Bengtson Nash et al. 2010). While this range is fairly large, the lower end of the estimate is well within the time period during which PFAS have been widely produced (ca. 60 years). World Ocean Circulation Experiment (WOCE) data from line A17, which has a very similar cruise track to ours, running along the South American coast (10°N to 51°S; 60°W to 30°W), show the infiltration of chlorofluorocarbon-11 (CFC-11) in AABW as far north as the equator and in NADW at 24°S, 20°S, and 10°S in samples taken from 1994 (Schlosser et al. 2001). Given that our samples were taken nearly 20 years later, it is not unreasonable to see PFAS present in waters today that contained CFCs then. Schlosser et al. (2001) present compiled CFC data reported by Warner and Weiss (1992)

focused on AAIW, and note its renewal is on a decadal timescale. In 1992, CFC-11 was found in the majority of AAIW in the South Atlantic, with the water mass age averaging around 35 – 37 years when located off the easternmost tip of Brazil at approximately 10°S, and 1 – 3 years old when located south of 50°S and closest to its formation source region (Schlosser et al. 2001).

It is important to note, however, that in order for these deep and intermediate water masses to acquire PFAS at the surface, their surface formation waters would need to have substantial concentrations present. While this may be the case for the North Atlantic where NADW is formed, concentrations reported in Antarctic waters until now have been detected, but at fairly low concentrations. Ahrens et al. (2010) detected only PFOS in the Southern Ocean (range of <11 – 51 pg/L) and Wei et al. (2007) detected PFOS in the Antarctic region in a similar range (5.1 – 22.6 pg/L), along with PFBS and PFDoDA occasionally at very low levels (Wei et al. 2007, Ahrens et al. 2010). Additionally, volatile precursor compounds are known to undergo long range atmospheric transport and have been detected in the Antarctic atmosphere (Dreyer et al. 2009, Del Vento et al. 2012). However, the concentrations of PFAS reported so far are not enough to account for the concentrations we detect in our subsurface and deep water masses, so there must be some other mechanism contributing to the transport of these compounds to depth.

The most notable trait of our profiles is the exceptionally high PFC content found along latitude 5.7°S. Perhaps, in a region where there is divergence of the South Equatorial Current to the North Brazil Current along with the presence of Equatorial countercurrents, there is turbulence and mixing of subsurface waters, causing efficient

mixing of hydrophilic substances, such as PFAS, to depth. Alternatively, the biological pump may be an important transport mechanism that has not yet been investigated (Gonzalez-Gaya, presentation 2014). As our water samples were raw unfiltered seawater, it is plausible that PFAS are being transported to depth sorbed to particles and colloids. Regardless these data confirm the detection of PFAS at depths as great as 5526m and at concentrations greater than those detected in the early 2000s (Table 1.1).

Implications

Our data implies that PFAS have penetrated the global oceans to much greater depth than previously believed. The few previous profiles published have implied little presence of PFAS at depth outside of deep water formation regions. Yet our results suggest that ΣPFAS are widespread below the surface, being regularly detected at 100s pg/L in the South Atlantic down to bottom waters. Surprisingly, lower concentrations and less penetration of PFAS to depth was observed in samples collected in the North Atlantic. The South Equatorial Current emerged as a major source of PFAS to the tropical Atlantic Ocean, most likely delivering them from Africa westward. These results imply that the Atlantic Ocean is a much greater sink of PFAS than currently thought. For example, Wang et al. (2014) compared emission estimates with a global budget based on PFAS being confined to the top 100 – 200 m of the global oceans (Wang et al. 2014). Our results suggest that in most sites, PFAS show basically flat vertical profiles down to at least 1000 m depth, often even deeper than that.

We expect over time that the concentrations of shorter chain and precursors compounds may increase with the reduced usage of eight-carbon chemistries. Continued

monitoring of PFAS at depth and in target water masses, along with further comparisons to existing ocean tracers, such as CFCs and Tritium, will further confirm the utility of PFAS as water mass tracers. Additional field data could potentially pair agreeably with modeling efforts to predict ocean mixing and circulation below the surface.

Figures and Tables

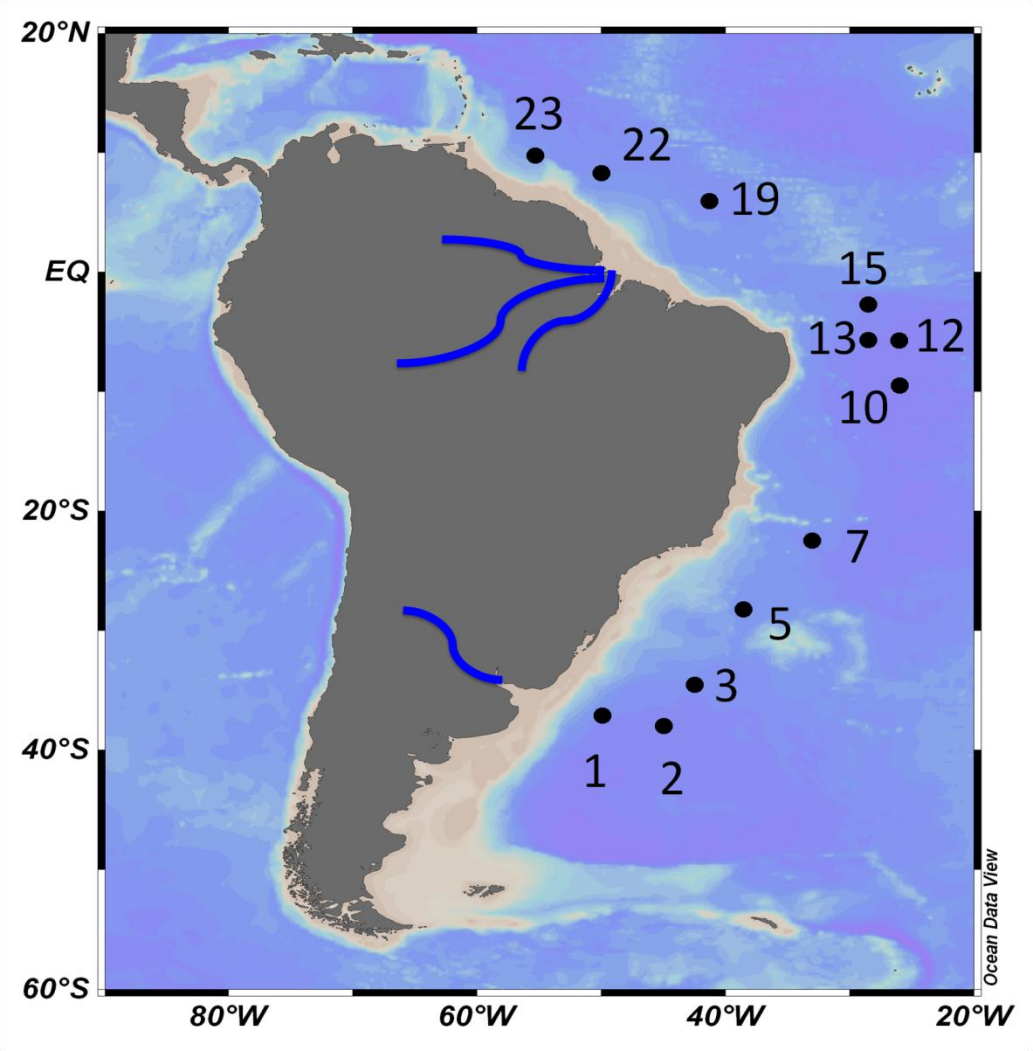


Figure 1.1 – Map of PFC sampling locations. The cruise left from the port of Montevideo, Uruguay and sampling was conducted from South to North along the coast of South America towards Barbados.

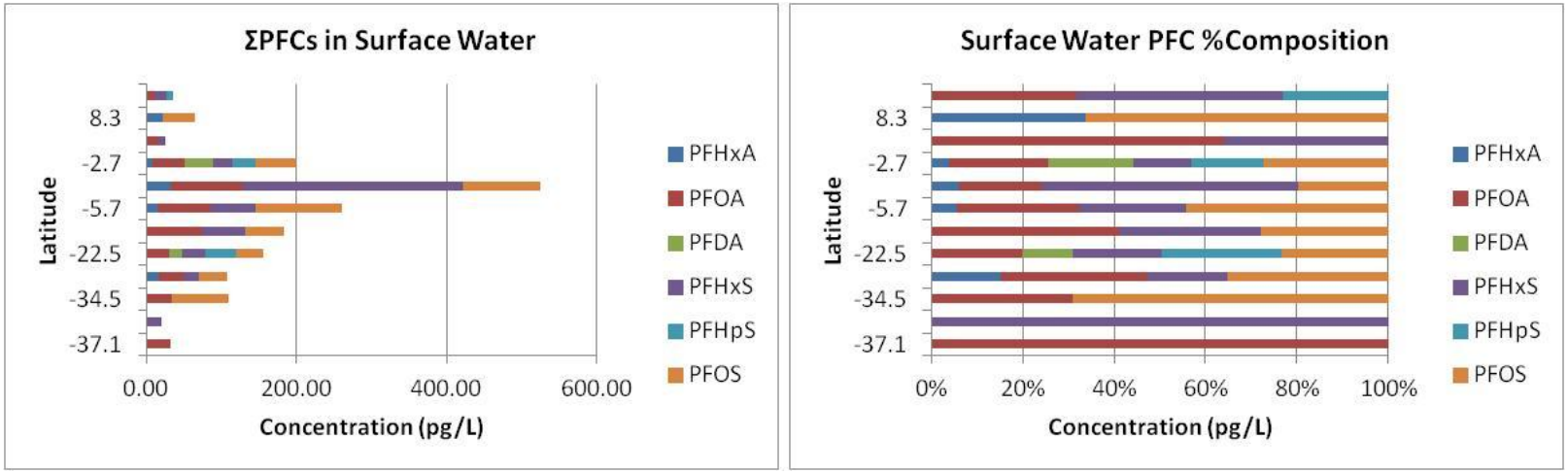


Figure 1.2 – A. ΣPFAS in Surface water samples. Y-axis is latitude from South to North in increasing station order (i.e. -37.1 = Station 1). Surface water indicates a sample taken from 5 - 10m depth, with the exception of station 1, which is an average of 5 and 51 m depth. B. Percent composition of PFAS in surface water samples. Y-axis and surface water are the same as in figure 2a.

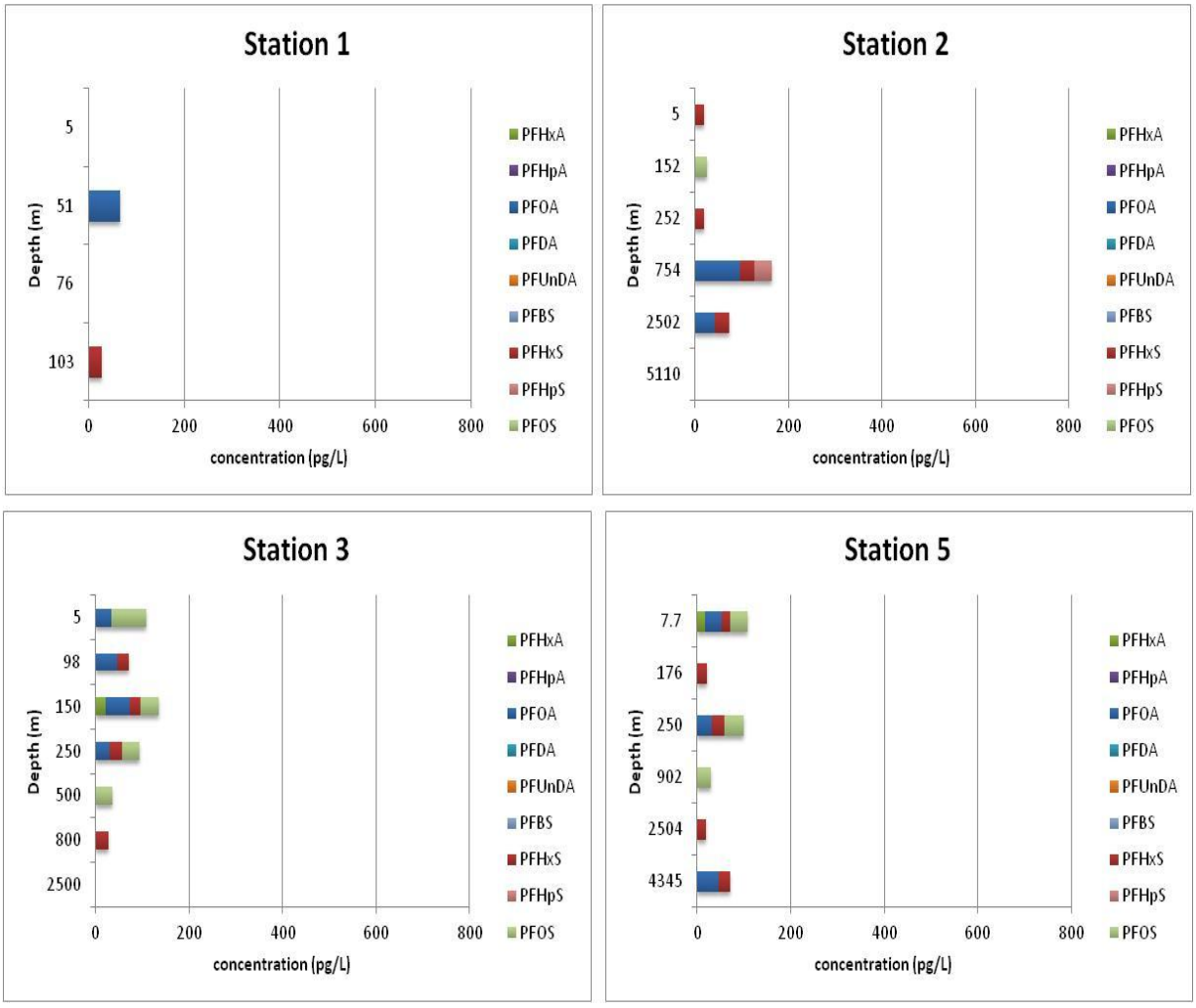


Figure 1.3.1 - (From left to right, top to bottom: a., b., c., d.) – PFAS profiles from Stations 1, 2, 3, and 5. Note different depth intervals.

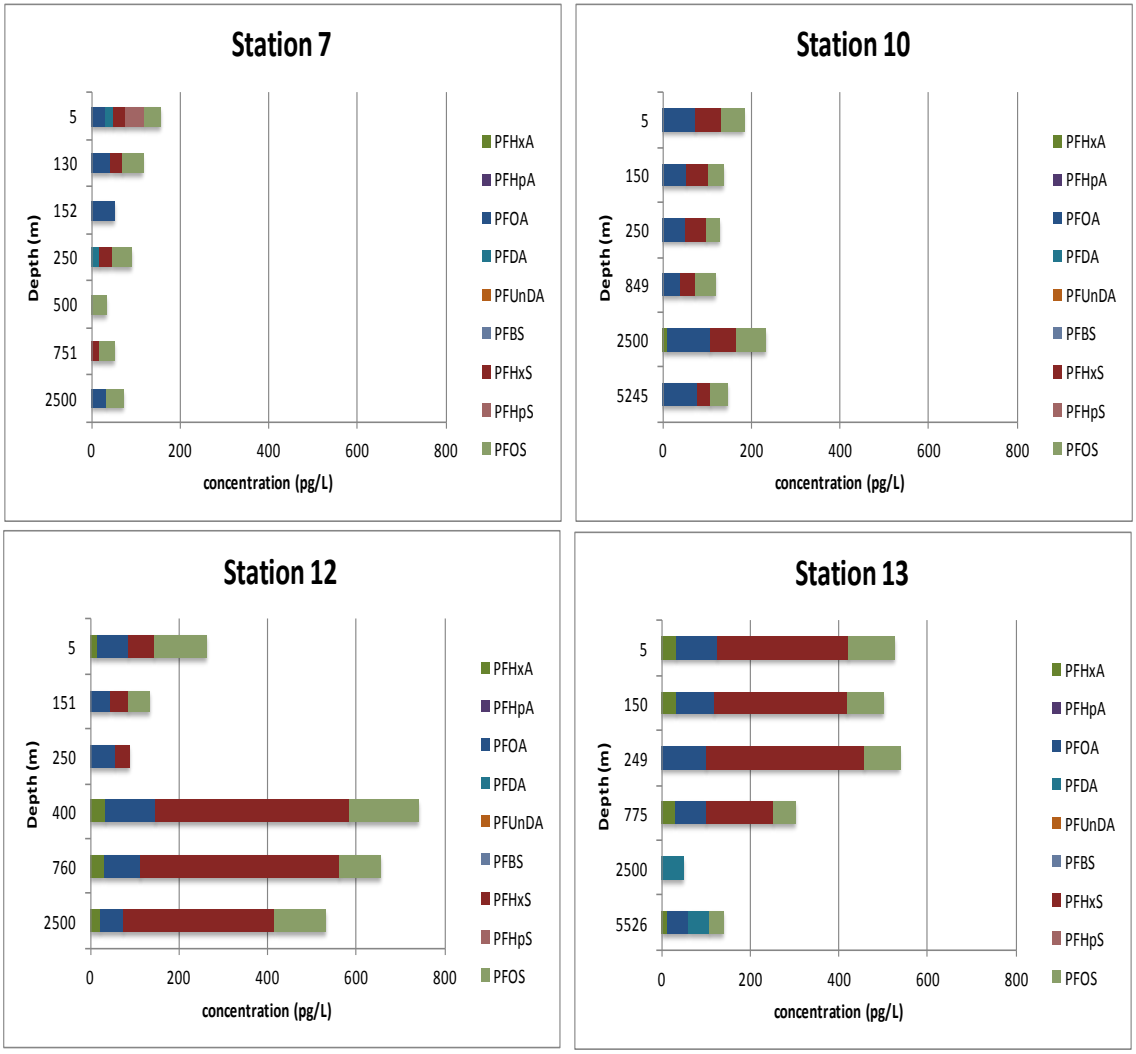


Figure 1.3.2 - (From left to right, top to bottom: e., f., g., h.) – PFAS profiles from Stations 7, 10, 12, 13. Note different depth intervals.

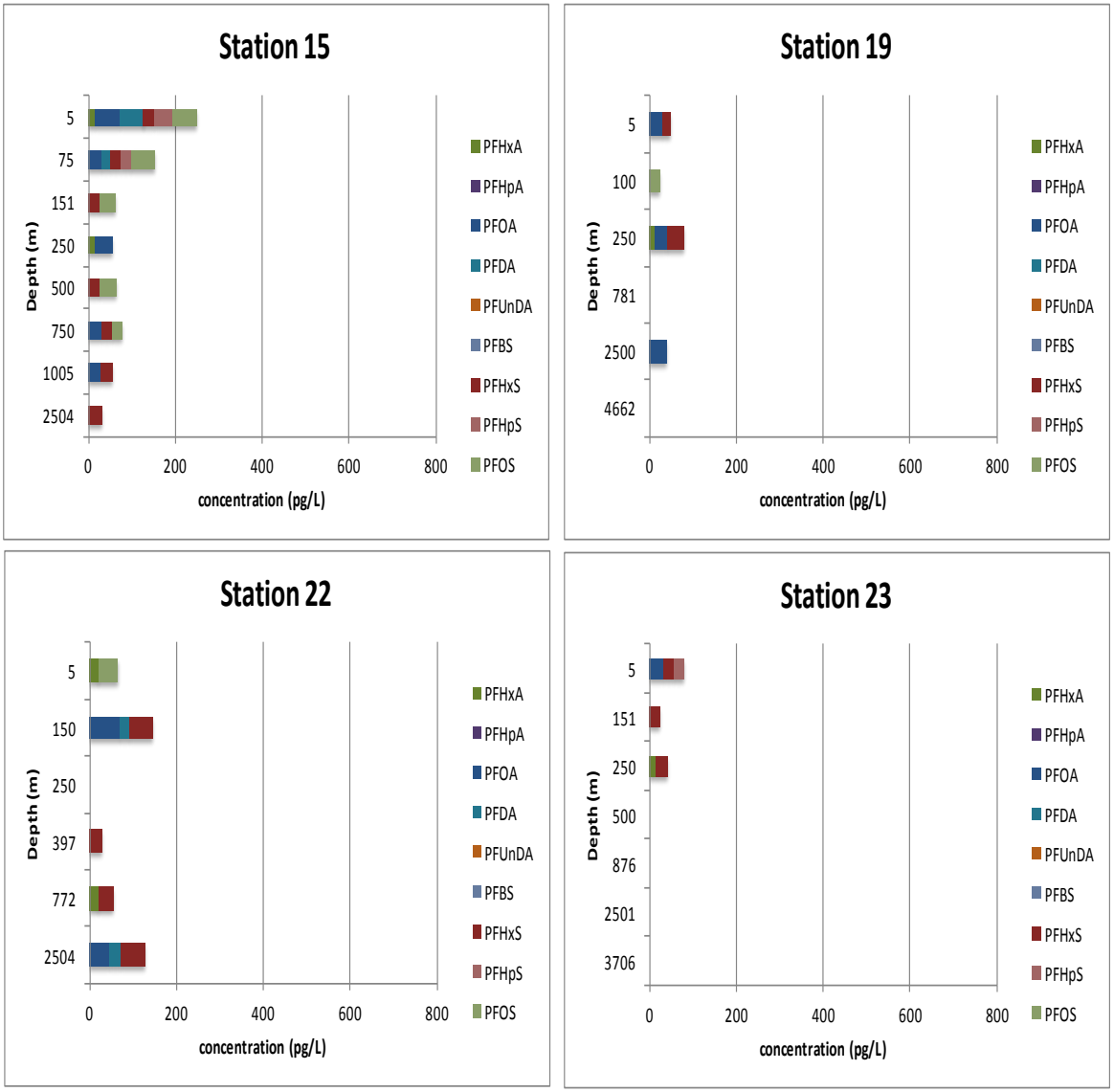


Figure 1.3.3 - (From left to right, top to bottom: i., j., k., l.) – PFAS profiles from Stations 15, 19, 22, and 23. Note different depth intervals.

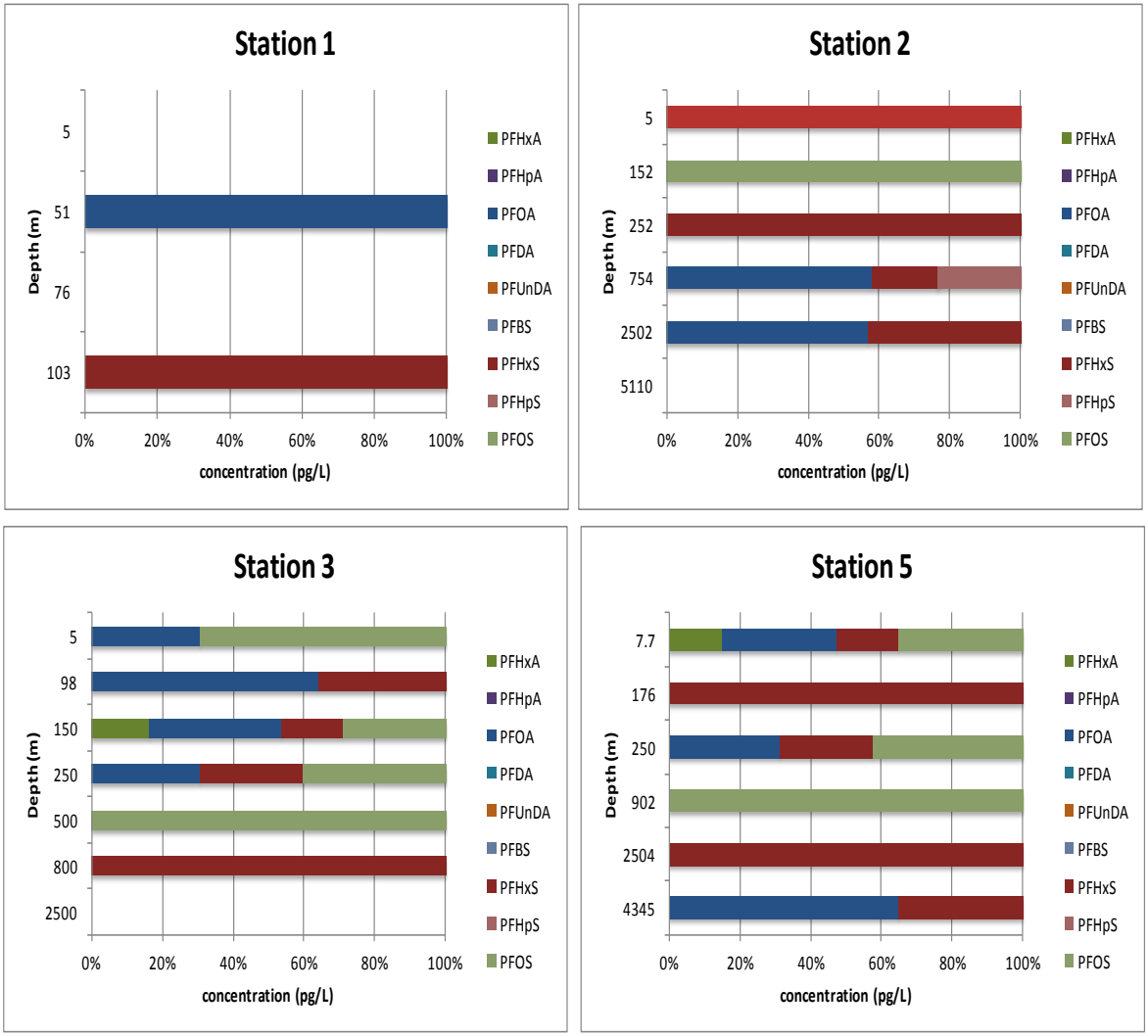


Figure 1.4.1 - (From left to right, top to bottom: a., b., c., d.) – Percent composition of PFAS profiles from Stations 1, 2, 3, and 5. Note different depth intervals.

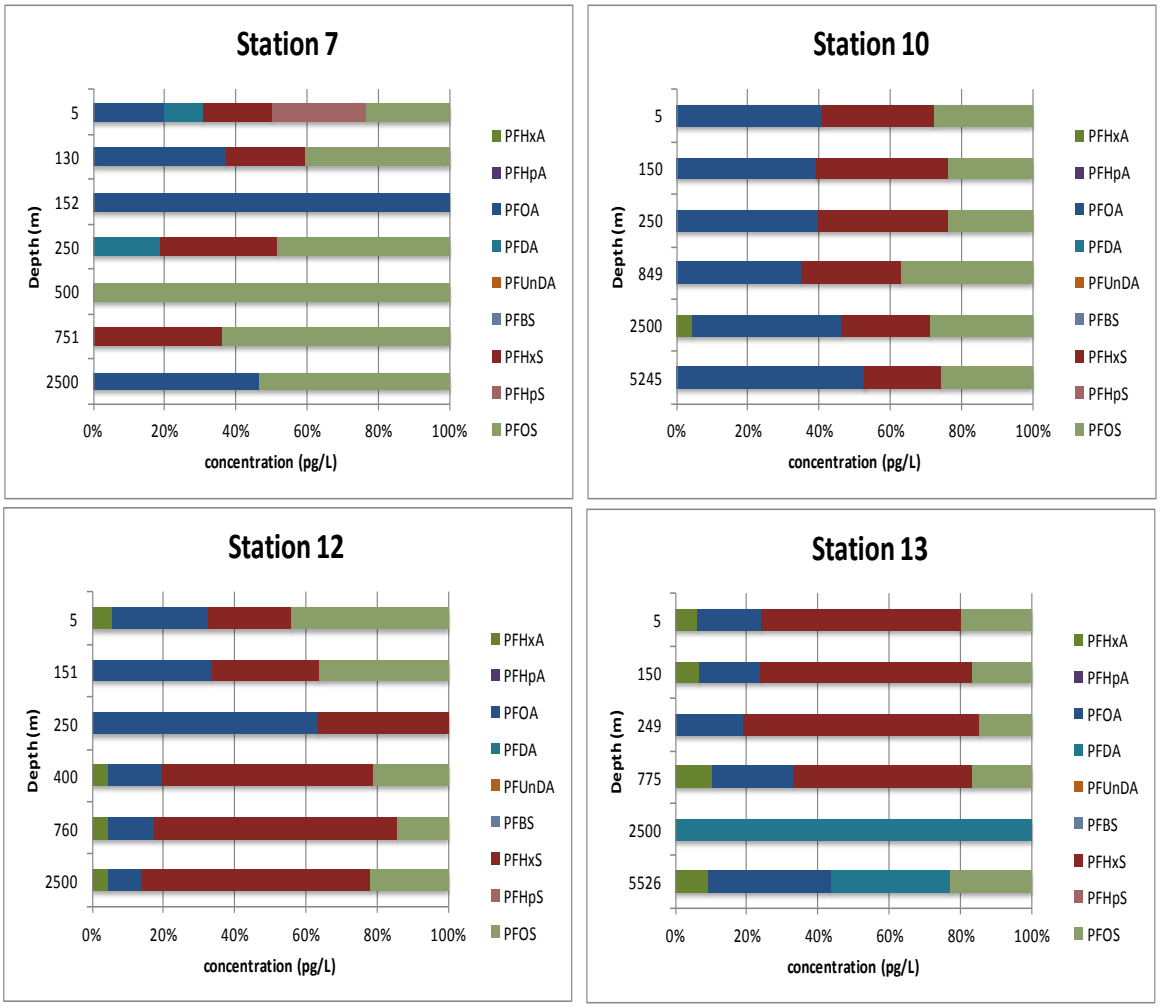


Figure 1.4.2 - (From left to right, top to bottom: e., f., g., h.) – Percent composition of PFAS profiles from Stations 7, 10, 12, and 13. Note different depth intervals.

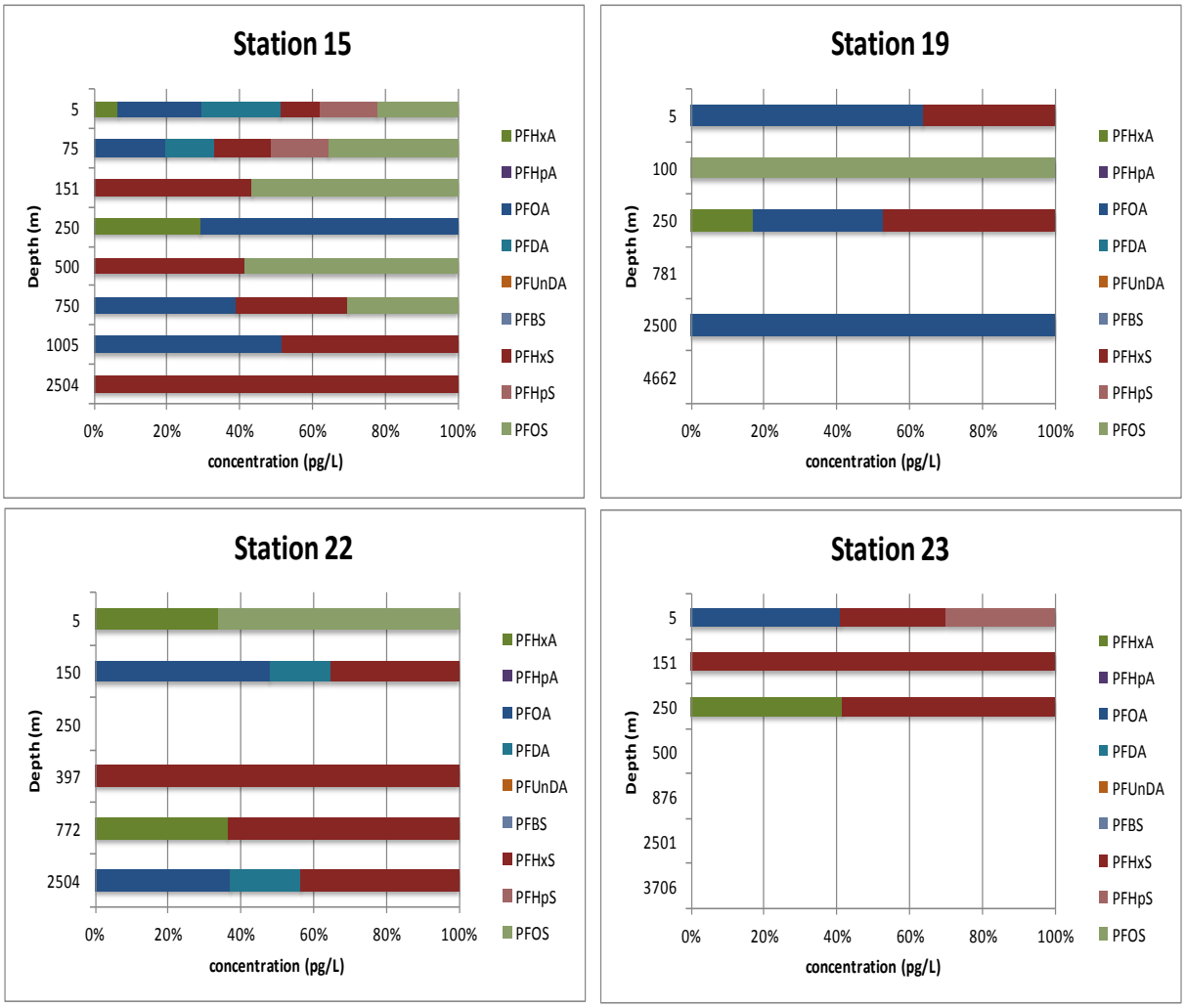


Figure 1.4.3 - (From left to right, top to bottom: i., j., k., l.) – Percent composition of PFAS profiles from Stations 15, 19, 22, and 23. Note different depth intervals.

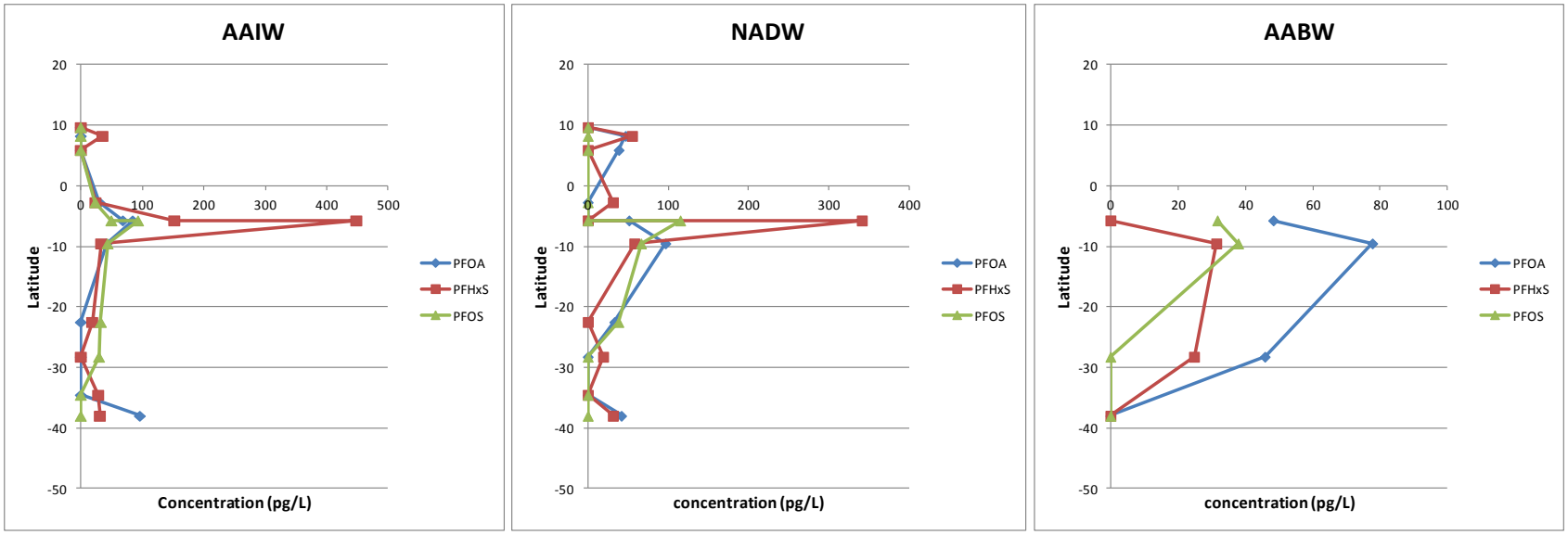


Figure 1.5 (a., b., c.) – Deep water masses sampled: a. AAIW (Antarctic Intermediate Water); b. NADW (North Atlantic Deep Water); c. and AABW (Antarctic Bottom Water). Compounds shown are the three most commonly detected, PFOA, PFHxS, and PFOS (pg/L).

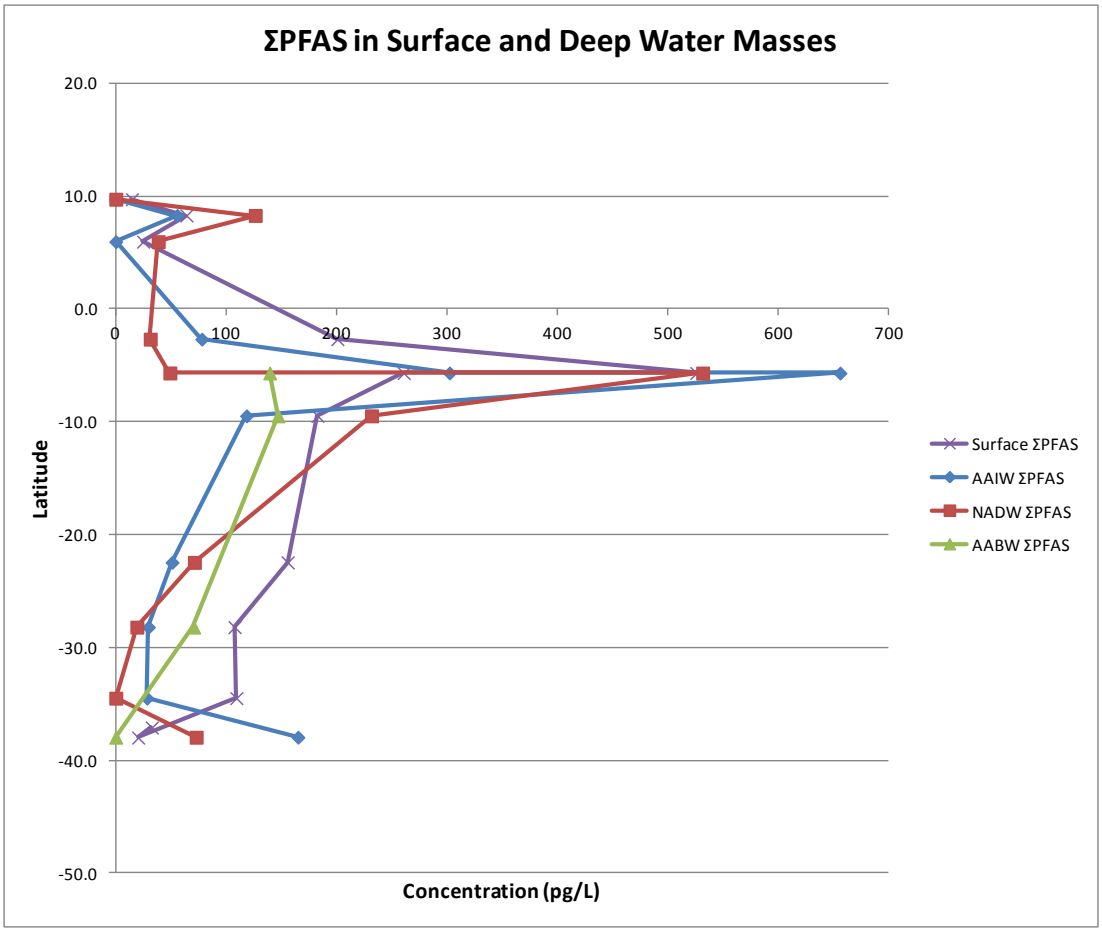


Figure 1. 6 – ΣPFAS (pg/L) in surface and deep-water masses.

Table 1.1 – Comparison of previous literature of PFAS at depth to this study.

		pg/L					
Location	**Depth (m)**	**PFOS**	**PFHxS**	**PFOA**	**Deepest Depth of Detection**	**Source**	
Sulu Sea (n = 2)	1000-3000	< 17 - 24	< 0.2	76 - 117		Yamashita et al. 2005	
Central to Eastern Pacific Ocean (n= 2)	4000 - 4400	3.2 - 3.4	0.4 - 0.6	45 - 56		Yamashita et al. 2005	
North Atlantic Ocean (n = 2)	45 - 3500	5 - 45'	N/A	7 - 75'	3500	Yamashita et al. 2008	Note these values were interpreted from figures.
Mid Atlantic Ocean (n = 3)	100 - 5500	< 0.4 - 30	N/A	< 7 - 150	5500	Yamashita et al. 2008	
South Pacific Ocean (n = 2)	0 - 5400	~ 2 (LOQ)	N/A	~ 6 (LOQ)	3000	Yamashita et al. 2008	
Japan Sea (n = 2)	10 - 3440'	~ 1 - 15	N/A	~ 6 - 50	2000	Yamashita et al. 2008	
Mid North Atlantic	200	< MQL	< MQL	< MQL	N/A	Ahrens et al. 2009	
Mid North Atlantic	3800	< MQL	< MQL	< MQL	N/A	Ahrens et al. 2009	
Western South Atlantic (37.1°S to 22.5°S)	0 - 5110	< MQL - 75.5	< MQL - 31.2	< MQL - 96	4345	This Study	
Mid to Equatorial South Atlantic (9.5°S - 2.7°S)	0 - 5526	< MQL - 156	< MQL - 448	< MQL - 114	5526	This Study	
Southwestern North Atlantic (5.9°N - 9.7°N)	0 - 4662	< MQL - 42.4	< MQL - 55.1	< MQL - 69.7	2504	This Study	

CHAPTER 2

TIME TRENDS OF POLYBROMINATED DIPHENYL ETHERS (PBDES) IN ANTARCTIC FUR SEAL MILK, AND THEIR TROPHIC TRANSFER

MANUSCRIPT IN PREPARATION FOR SUBMISSION TO *ENVIRONMENTAL SCIENCE AND TECHNOLOGY*

ERIN MARKHAM[1], EMILY BRAULT[2, 3+], MOHAMMED KHAIRY[1, 5-], MIKE GOEBEL[4], REBECCA DICKHUT[3†], RAINER LOHMANN[1*]

1 – UNIVERSITY OF RHODE ISLAND, GRADUATE SCHOOL OF OCEANOGRAPHY, 215 SOUTH FERRY RD, NARRAGANSETT, RI 02840

2 – UNIVERSITY OF CALIFORNIA SANTA CRUZ, 1156 HIGH STREET, SANTA CRUZ, CA 95064

3 – VIRGINIA INSTITUTE OF MARINE SCIENCE (+ FORMER, † AUTHOR IS DECEASED), 1208 GREAT RD, GLOUCESTER POINT, VA 23062

4 – NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION (NOAA)/NATIONAL MARINE FISHERIES SERVICE (NMFS), ANTARCTIC ECOSYSTEM RESEARCH DIVISION, SOUTHWEST FISHERIES SCIENCE CENTER

5 - DEPARTMENT OF ENVIRONMENTAL SCIENCES (- CURRENT), FACULTY OF SCIENCE, ALEXANDRIA UNIVERSITY, 21511 MOHARAM BEK, ALEXANDRIA, EGYPT

† DECEASED

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are emerging contaminants that were used as flame-retardants for decades in a wide range of consumer and industrial applications, and are found today ubiquitously in the environment. PBDEs share certain characteristics with legacy contaminants, such as polychlorinated biphenyls (PCBs), for example, they are hydrophobic and lipophilic and are likely to be found bound to sediments and biota tissues. In a large number of applications, PBDEs are applied as additives, allowing them to freely leach from their products into both humans and the environment. PBDEs were produced predominantly in 3 different commercial mixtures (penta-, octa-, and deca-BDE), and in 2009, tetra- and pentaPBDE mixtures were listed by the Stockholm Convention (UNEP 2009). While various mixtures have been banned throughout the EU and US (two of the largest production areas), there is still production of others occurring (i.e. decaBDE) and a massive reserve of products exists around the globe that will have these chemicals leaching out of them for years to come (Hites 2004, Chiuchiolo et al. 2004, Sacks & Lohmann 2012).

The continent of Antarctica is arguably home to some of the most untouched land on the planet. However, even in this remote region, the effects of humans are not unseen. Scientific and military exploration has now been going on for decades and the summer season can witness over 100 active facilities operated by 30 different nations (COMNAP 2014). Research that takes place in Antarctica spans an enormously broad range of fields, from astrophysics and deep-sea oceanography to the more controversial-as-of-late topic of climate change. While pollution in Antarctica is typically orders of magnitude

lower than concentrations found elsewhere around the globe, the fact remains that organic contaminants, particularly volatile ones, do reach the region via long range environmental transport through processes such as global fractionation and cold condensation (Wania & Mackay 1996). Legacy contaminants such as PCBs and organochlorine pesticides (OCPs) have been reported along with emerging contaminants such as PBDEs and perfluoroalkyl substances (PFAS) in numerous environmental matrices from the region (Chiuchiolo et al. 2004, Corsolini et al. 2006, Borghesi et al. 2008, Brault et al. 2013).

Various research groups have conducted previous studies of PBDEs in the Antarctic environment. Corsolini et al. (2005) reported on OCPs and PBDEs in an Adélie penguin food web consisting of Antarctic krill, emerald rockcod, and Adélie penguin. PBDEs were detected in all organisms, but when looking at biomagnification and biomagnification prime factors (BMF') values (BMF_x/BMF_{PCB153} to estimate biomagnification potential in the case of a low number of samples), BDE-28, -47, and -99 all had values < 1, indicating the presence of some sort of metabolic or excretion processes (Corsolini et al. 2006). Chiuchiolo et al. (2004) measured PBDEs in the base of an Antarctic food web (sea ice algae, water column plankton, and juvenile and adult krill) in 2004 (Chiuchiolo et al. 2004, Corsolini et al. 2006). The distribution of PBDEs in the base of the Antarctic food web was complex, but biomagnification of PBDEs between phytoplankton and adult krill was not observed (Chiuchiolo et al. 2004). While PBDE congeners have been shown to bioaccumulate, it is apparent that PBDE metabolism may be species specific and variations in arctic food chains have been observed (Wolkers et al. 2004, Kelly et al. 2008). Kelly et al. (2008) presented evidence from a Canadian

Arctic marine food web in which many PBDEs appeared to exhibit negligible biomagnification, with the exception of BDE-47, which did demonstrate food web biomagnification, albeit at a much lower level than PCBs (Kelly et al. 2008).

Trophic magnification factors (TMFs) represent an average biomagnification factor within food webs and are becoming increasingly useful tools in food web studies by allowing inter-ecosystem comparison. The application of TMFs has previously been used in the Arctic region and elsewhere globally, but to our knowledge, this will be their first use in the Antarctic ecosystem (Hobson & Welch 1992, Hobson & Ambrose 1995, Fisk et al. 2001, Hop et al. 2002, Kelly et al. 2008, Houde et al. 2011b, Borgå et al. 2012).

The PBDE data presented in this study are from a sample set of plankton, krill, fish, and fur seal milk post-2000 and will contribute to the unique dataset that comes from the remote Antarctic. Specific goals in this research were to (i) determine which PBDEs are being detected in Antarctic biota; (ii) establish trophic magnification factors (TMFs) to see if any observable biomagnification or biodilution is occurring; and (iii) to potentially establish temporal trends of congeners over a time period where global regulations and restrictions on production were being implemented (i.e. 2000s).

METHODS

Sample Collection

Breast milk samples were collected from Antarctic fur seals (*Arctocephalus gazella*) approximately 100 km off the Antarctic Peninsula on Cape Shirreff, Livingston Island (aprx. 62°28'S, 60°46'W) over the austral summers of 2000/01, 2001/02, 2004/05,

2009/10, 2010/11, 2011/12, and 2012/13 (Figure 2.1). All seals were multiparous females in their perinatal stage (i.e. the seals had all bred prior to the year of sample collection and milk was collected during lactation post-birth and prior to offshore foraging trips), with the exception of a small portion of the sample sets from the last two years (2011/12 and 2012/13) which consisted of both perinatal and non-perinatal (i.e. first pup) milk samples. For the purpose of this analysis, seals were assumed to have had at least one pup during the breeding season in which they were sampled as all seals were age 4 or older, with the majority being over the age of 7 (personal communication, Mike Goebel). Seal capture was performed following methods described in Polito and Goebel and as reported in Brault et al. (2013). In brief, seals were captured with hoop nets, sedated with 5mg Midazolam, and anesthetized with isoflurane as milk was collected in pre-cleaned vials and stored at -20°C until analysis (Polito & Goebel 2010, Brault et al. 2013).

Plankton samples were collected along western Antarctica spanning the region from the West Antarctic Peninsula to the Ross Sea (64.78°S, 64.07°W to 78.64°S, 164.3°W, Figure 2.1) over the austral summers of 2007/08, 2009/10, and 2010/11 using ring net tows that were predominantly 0.5 m in diameter with an 80 µm mesh ring net, after which contents were further sieved through a 25 µm mesh sieve. Occasionally some variability in the ring nets used due to equipment restrictions (various mesh sizes ranging from 80 – 450 µm), but all samples were collected from the surface mixed layer (aprx. 30 m). Plankton samples were predominantly phytoplankton and consisted of largely diatoms and *Phaeocystis sp.* Further specifics on sample collection can be referenced in Brault et al. (Brault et al.).

All krill and fish samples were collected from within the Palmer Long Term Ecological Research (LTER) Grid Survey Region (aprx.66.99°S, 69.28°W to 61.94°S, 73.78°W, Figure 2.1) via 700 µm ring net tows (taken at oblique angles). Krill samples consisted predominantly of *Euphausia superba* and were collected during the austral summers of 2007/08 and 2010/11 and split into 3 size classes of juveniles, adults (including mature females), or gravid females. At some sites, numerous krill were collected and provided enough biomass for "replicates" to be performed. In this case the replicates consisted of different individual krill from the same sample collection and were averaged and presented as one sample (SI Table 2.2 and 2.12 where * indicates multiple samples). Fish samples consisted of silverfish and myctophids collected in the same manner as krill.

Sample extraction

Seal milk extraction was conducted in two batches. The first batch, which consists of samples from the 5 austral summers spanning from 2000/01 – 2010/11, was extracted at the Virginia Institute of Marine Science (VIMS) following previously established POP procedures as reported in Brault et al. (2013) (Risebrough et al. 1976, Chiuchiolo et al. 2004, Geisz et al. 2008, Brault et al. 2013). In short, seal milk was freeze-dried, homogenized, sub-sampled (1 g dry-weight), solvent extracted (65:35 DCM: Acetone), and analyzed for several POPs including DDT, PCBs, and chlordane. Bulk lipid analysis was also performed as reported elsewhere (Brault et al. 2013) in order for sample concentrations to be lipid-normalized. Following analysis at VIMS, sample extracts were shipped to the University of Rhode Island's Graduate School of

Oceanography (URI-GSO) to be analyzed for polybrominated diphenyl ethers (PBDEs) (Brault et al. 2013).

The second batch of seal milk samples (samples from 2011/12 and 2012/13) was extracted at URI-GSO as follows: a 2mL aliquot of each seal milk sample was transferred to 50mL centrifuge tubes where samples were spiked with a surrogate mixture, vortexed for 1 minute, and left overnight in the fridge. The following day, each sample was vortexed for 1 minute, followed by extraction three times in an ultrasonic bath with 20mL each of n-hexane/acetone (2:1) for 5 minutes. After each extraction, the organic layer was separated by centrifugation at 4000 rpm for 5 minutes. Combined extracts were evaporated, solvent exchanged to n-hexane, and brought to a final volume of 5mL. 200µL (from the 5mL) was taken for determination of percent lipid. Extracts were treated with sulfuric acid (concentrated) in an ice bath to remove lipids. Treated extracts were then partitioned on water (to remove excess acid), evaporated to 1mL, and cleaned on SPE cartridges (6 cc) filled with 2 g silica and topped with 1 g acidic silica (40%). PBDEs were eluted with 50mL n-hexane/DCM (60:40). To determine percent lipid, the 200 µL aliquot to pre-weighed aluminum boats and left to dry overnight. The boats were re-weighed, with the difference in weights representing % lipid in the 200 µL, which was then extrapolated to % lipid in the 5 mL sample.

Plankton samples were investigated under a microscope in order to attempt basic species identification (i.e. diatoms or *Phaeocystis sp.*) and remove any visible zooplankton. Samples were then manually homogenized, freeze-dried at -80°C for approximately 72 hours, and solvent-extracted. Following analysis at VIMS, sample

extracts were shipped to URI-GSO to be analyzed for polybrominated diphenyl ethers (PBDEs).

Each krill sample consisted of multiple individual krill that were homogenized prior to freeze-drying with a Virtis "45" tissue homogenizer (Virtis Co. Inc.), freeze-dried, and solvent extracted; if there were enough individuals, location replicates were measured (i.e. a different batch of homogenized krill from the same station collection). Following analysis at VIMS, sample extracts were shipped to URI-GSO to be analyzed for polybrominated diphenyl ethers (PBDEs). Fish samples consisted of whole fish and followed the same extraction procedure as the krill samples. Further details on sample preparation can be gathered from Brault et al. (Brault et al.).

PBDE Analysis

All samples were analyzed for mono- through hepta-brominated congeners (BDE-2, -8, -15, -30, -28, -49, -47, -100, -99, -154, -153, and -183) via gas chromatography tandem mass spectrometry on an Agilent 6890N GC coupled to a Waters® Quattro Micro MS/MS under electron ionization/MS/MS (filament emission current of 150µA) in multiple reaction monitoring mode (MRM) using a DB-5MS column (Agilent J&W GC Columns, 122-5532, length 30m, ID 0.250 mm, film 0.25µm) and splitless injection. Injection port, GC/MS/MS interface, and ion trap temperatures were set to 260°C, 280°C, and 220°C respectively. The temperature program began at 140°C, held for 2 min, ramped at 10°C min^{-1} to 180°C, 3°C min^{-1} to 220°C, 10°C min^{-1} to 310°C and held for 5 min. Quantification ions were adapted from a Waters® method produced by Worrall et al. (2004) (Sacks & Lohmann 2012). A calibration standard curve was created for each

congener with concentrations ranging from 0.005 ng/µL – 0.500 ng/µL (Sacks & Lohmann 2012). Peak areas were measured, response factors calculated, and concentrations determined via surrogate and injection standards using a MassLynx/QuanLynx software package. Hexane was run every 5 samples and instrument drift was monitored with QC check standards every 10 samples (0.005 ng/µL and 0.05 ng/µL).

Results presented below are only for compounds that were detected > 30% of the time. Only peak areas with a signal to noise (S/N) ratio > 3 were considered quantifiable and for all samples with S/N < 3 or negatively corrected blank values, a value of "0" was used, which is likely underestimating ∑PBDEs.

Quality Control

For quality assurance and control purposes, sample extracts were spiked with 10µL of a 5ng/µL $^{13}C_{12}$ -labeled PBDE surrogate ($^{13}C_{12}$ BDE -183, -153, -99, -47, -28, Cambridge Isotope Laboratories) for a total concentration of 50ng, and 5µL of a 5ng/µL injection standard (p-terphenyl-d_{14}, AccuStandard) for a total concentration of 25 ng. Since these samples were not originally intended to be analyzed for PBDEs, the surrogate spike in this case was done post-extraction. We recognize that this is not ideal, however, the $^{13}C_{12}$ spike addition still allows for QA/QC regarding matrix effects that may be taking place and for all samples that were extracted at VIMS and spiked with the PBDE surrogate post-injection, an additional correction was applied using the average recoveries of previously analyzed POPs (i.e. DDT, PCBs, and chlordane), which were usually within an acceptable range (i.e. 65 – 110%), leading us to assume there were no

major extraction issues regarding hydrophobic POPs. Specifically, recoveries from previous POP analysis (average ± standard error) for phytoplankton were 78.94 ± 3.66 %, for krill 69.1 ± 1.8 %, and for seal milk 77.86 ± 1.81 %. The only sample set differing from this procedure is the second batch of seal milk samples that were extracted at URI-GSO (2011/12 and 2012/13). These samples were spiked prior to extraction with 20µL of a 2ng/µL surrogate standard in nonane. Recoveries from both batches of seal milk samples fell within the same range, which further affirms the acceptability of results presented from seal milk spiked post-extraction.

Laboratory blanks of a hydro matrix material were initially extracted alongside real samples and any blanks included in the vial files for shipment from VIMS to URI-GSO were analyzed for PBDEs. All samples were blank corrected to an average of blanks across 4 vial files where the main detects were primarily for BDE-47 and -99 with concentrations averaging 0.18 ± 0.20 (standard deviation) and 0.18 ± 0.23 for each congener respectively. (SI Table 2.26)

$\delta^{13}C$ and $\delta^{15}N$ Analysis

Stable isotopes have now been used in biogeochemical applications for decades and are extremely useful tools in determining the trophic dynamics of a particular ecosystem. Carbon and nitrogen stable isotopes were measured in the majority of samples and are further presented in delta notation, δ, as parts per thousand different from a standard, or "per mil," ‰, using the following equation adopted from Peterson and Fry (1987):

$$\delta X = \left[\left(\frac{R_{sample}}{R_{standard}}\right) - 1\right] * 10^3$$

Where *X* denotes either ^{13}C or ^{15}N and *R* is the ratio of heavy to light isotopes in a sample (i.e. $^{13}C/^{12}C$ or $^{15}N/^{14}N$) or standard, using a standard reference material of Vienna PeeDee Belemnite (PBD) or atmospheric nitrogen (N_2, AIR) (Peterson & Fry 1987, Brault et al. 2013).

$\delta^{13}C$ and $\delta^{15}N$ stable Isotopes for the majority of samples were determined via an elemental analyzer-isotope ratio mass spectrometer (EA-IRMS) at VIMS as described elsewhere (Brault et al. 2013). Some phytoplankton samples were analyzed at the University of California at Santa Cruz (UCSC) on a on a Carlo Erba EA 1108 elemental analyzer coupled to a Finnegan Delta-Plus isotope ratio mass spectrometer (EA-IRMS). In this case, $\delta^{13}C$ and $\delta^{15}N$ values were averaged and standard deviation was ≤ 0.5, 77% of the time or greater.

Trophic levels were determined using the following equation modified from Hobson and Welch (1992):

$$TL_{consumer} = 1 + \frac{D_c - 1.7}{3.4}$$

Where $TL_{consumer}$ is the trophic level of the consumer in question, D_c is the $\delta^{15}N$ of the consumer, 1.7 represents the average $\delta^{15}N$ of phytoplankton (1.7 ± 0.27‰ standard error), which is assumed to be trophic level 1 and the baseline of the food web in this system, and 3.4 represents the average trophic enrichment factor as recommended in Borgå et al. (2012) (Hobson & Welch 1992, Hobson & Ambrose 1995, Borgå et al. 2012).

Trophic magnification factors (TMFs) were further determined following the procedure in Borgå et al. (2012) to add certainty to the argument of whether or not these chemicals are biomagnifying or not. TMFs were calculated by plotting a regression of trophic level (x) vs. log (concentration +1) (y) where TMF = 10^{slope}. On average, for a slope of 0 and TMF = 1, it can be assumed that the compound is not biomagnifying, for a TMF > 1, there is some level of biomagnification occurring, and for TMF <1, there is no biomagnification but instead, trophic dilution (Gobas et al. 2009, Borgå et al. 2012).

Statistical Analysis

Data was tested for normality using the Shapiro-Wilks test in RStudio and IBM SPSS Statistics 22 software package. Concentrations were natural log transformed to make data have a normal or near-normal distribution. All other statistical analysis was performed using MS Excel. In order to ensure there was no artificial bias when comparing seal milk datasets from two separate analyses, the seal milk concentrations from the first five austral summers that were extracted prior to the PBDE spike were all divided by 0.7786 to compensate for any potential loses that may have occurred during extraction (Average Recovery for PCBs was 77.86%). Linear regressions were performed for each congener with >30% detection to determine whether or not there were significant correlations occurring between concentrations and age, breeding season, $\delta^{13}C$, or $\delta^{15}N$. For years in which there were both perinatal and non-perinatal milk samples, a student's two-sample t-test assuming unequal variances was applied to see if there were any significant differences. Phytoplankton and krill samples with concentrations detected in multiple years were analyzed for inter-year differences. Lastly, it was determined whether or not there were significant differences occurring between trophic levels.

RESULTS AND DISCUSSION

PBDE-47 and -99 were the most dominant congeners determined in all samples, constituting >60% of the PBDE composition majority of the time. Plankton samples demonstrate the highest overall concentrations, followed by fur seal milk, krill, and lastly fish, in which no PBDEs were detected at all.

Fur Seal Milk

Lipids in fur seal milk were quite high and ranged from 48 – 83.05%. PBDEs were detected in all fur seal milk samples. Lower brominated congeners (BDE-2, -8, -15, and -30) were not detected until 2011/12 and higher brominated congeners (BDE-154, -153, -183) were not detected until 2004/05. While we made our best efforts to account for any potential losses due to differences in sample extraction and clean-up, we acknowledge that there is still the potential that this late detection of lighter compounds may be due to said differences. On the contrary, the higher brominated compounds were only not detected in the first two years of sampling and they gradually increase and make a greater contribution to the overall PBDE composition beginning in 2009/10, indicating that perhaps heavier compounds are becoming more prevalent in later years. The ΣPBDEs from all samples had a range of 0.14 – 16.95 ng/g lipid with an overall average of 2.54 ng/g lipid ± 0.19 and a median of 2.10 ng/g lipid. BDE-47 was the most dominant congener with a range of 0.14 – 12.19 ng/g lipid, overall mean of 1.37 ng/g lipid ± 0.13, and a median of 1.00 ng/g lipid. BDE-99 was the second most dominant congener, but showed less variability with a range of no detect – 2.75 ng/g lipid, overall mean of 0.37 ng/g lipid ± 0.03, and a median of 0.28 ng/g lipid. Stable isotope analysis

was only available for fur seal milk collected during the first five austral summers (2000/01 – 2010/11). Both $\delta^{13}C$ and $\delta^{15}N$ demonstrated variability (mean ± standard error): $\delta^{13}C$ ranged from -23.71 to -19.62‰ with a mean of -22.20 ± 0.11‰, and a median of -22.14‰; $\delta^{15}N$ ranged from 8.96 – 13.80‰, with a mean of 10.74 ± 0.11‰, and a median of 10.76‰.

Fur Seal Milk Trends

Few significant correlations were found from regressions of fur seal milk concentrations vs. age, and any that were present had relatively low r^2 values. The dominant congeners, BDE-47 and -99 showed no correlations with age (SI Table 2.24). No significant trends appeared from regressions of fur seal milk concentration vs. $\delta^{13}C$. Few significant trends were observed between concentration and $\delta^{15}N$ (SI Table 2.25 & 2.26); most notably in 2000/01, BDE-47 and ΣPBDEs vs. $\delta^{15}N$ both demonstrate significantly negative trends (i.e. decreasing concentration with increasing $\delta^{15}N$). This is counterintuitive to what one might expect when looking at hydrophobic contaminants vs. $\delta^{15}N$. Instead of an increase in concentration up the trophic food level, there is a decrease, negating the connotation of biomagnification.

There were few significant differences in PBDE concentrations between perinatal vs. non-perinatal milk. The exception was for the last sampling year (2012/13) where the mean concentration of BDE-99 (0.36 ± 0.09 ng/g lipid) in non-perinatal milk was significantly greater than perinatal milk (0.19 ± 0.03 ng/g lipid; $p = 0.05$) and conversely, the mean concentrations of BDE-183 in perinatal

milk (0.09 ± 0.02 ng/g lipid) was significantly greater than that of non-perinatal milk (0.03 ± 0.01 ng/mL lipid; $p = 0.005$).

The most numerous significant relationships were determined when looking at congener trends over breeding seasons. When looking at the sampling scheme from 2000/01 – 2012/13, there is a significant relationship for every congener with > 30% detection. BDE-28, -49, -47, -100, -154, -153, -183, and ΣPBDEs all demonstrate positive trends of a significant or nearly significant increase in concentration over the years ($p = 0.0002$, 0.069, 1.78E-11, 0.0356, 5.62E-7, 0.003, 0.0001, 7.68E-10, respectively). On the contrary BDE-99 demonstrates the opposite trend showing a slight negative trend of decreasing concentration over time ($p = 0.044$, $r^2 = 0.03$). This significant decline in BDE-99 over the course of all 7 sampling summers is interesting and indicates confirmation that BDE-99 is likely being transformed either by metabolism within the fur seals or by other mechanisms. It is also possible that this transformation is occurring prior to the arrival of BDE-99 in the Antarctic region.

However, when analyzing only the first five austral summers, only congeners BDE-47, -153, and ΣPBDEs remain to have a significantly positive trend of increasing concentration over time ($p = 0.017$, 0.0004, and 0.003, respectively). Note that the correlation for BDE-183 vs. time also remains significantly positive; however, detection of BDE-183 occurred < 30% and thus, is not reported. Interestingly, when performing the t-test of means on congeners between the last two sampling years of 2011/12 and 2012/13, BDE-47, -100, -99, -164, -153, -183, and ΣPBDEs all demonstrate a significant decline in the mean (p

= 0.02, 0.049, 0.029, 0.039, 0.0005, 0.002, and 0.006, respectively) suggesting a decrease in concentration between these two most recent sampling years. These are counteracting results, but can be interpreted that concentrations have definitely increased since 2000, and while they may be either leveling out or possibly beginning to decline, it is impossible to make any further conclusions without continued monitoring.

Plankton

Lipid values in plankton were very low ranging from 0.104% - 6.72%. Three samples with lipid values <0.5% were discarded due to concerns of salt or sediment contamination from the phytoplankton tow and only samples with lipid values >0.5% are presented here. Due to extremely low lipid contents, lipid-normalized PBDE concentrations appear exceptionally high in certain cases. Yet lipid-normalizing concentrations of hydrophobic compounds is standard practice, and best reflects on their partitioning into apolar phases in the environment

PBDEs were detected in 100% of all plankton samples. The lower brominated congeners BDE-2, -8, -15, and -30 were not detected in any samples. ∑PBDEs varied greatly ranging from 4.83 – 702.59 ng/g lipids, with an average (mean ± standard error) of 131.65 ng/g lipid ± 31.55, and a median of 48.56 ng/g lipid. Stable isotope analysis of $\delta^{15}N$ on plankton samples resulted in quite a wide range of values from -1.1 – 6.1‰. Although attempts were made to remove any visible zooplankton from samples, it is important to note that although the dominant composition of the plankton samples were identified as phytoplankton (i.e. diatoms or *Phaeocystis sp.*), they should be considered

"plankton" due to the potential presence of zooplankton as indicated by the higher $\delta^{15}N$ values(SI Table 2.11). $\delta^{13}C$ of plankton also had quite a large range, spanning from -33.0 – 18.5‰, with a mean of -29.4‰ ± 0.61 and a median of -30.6‰.

Plankton ∑PBDEs ranged from 4.83 – 702.59 ng/g lipid with an average of 148.1 ng/g lipid ± 34.4 and a median of 56.7 ng/g lipid. BDE-47 and -99 were the two most prevalent congeners, with detection 97% and 91% of the time, respectively. BDE-47 in plankton ranged from 0.00 – 256.49 ng/g lipid with an average of 53.3 ng/g lipid ± 12.5 and a median of 22.2 ng/g lipidBDE-99 in plankton ranged from 0.00 – 284.67 ng/g lipid with an average of 55.1 ng/g lipid ± 14.2 and a median of 18.4 ng/g lipid.

Plankton Trends

Linear regressions were run to determine if there were any trends between plankton concentration and $\delta^{13}C$, $\delta^{15}N$, and/or date. For both $\delta^{13}C$ and $\delta^{15}N$, regressions were run for the whole sample set and then within years. Although it sometimes appears that there is a slightly negative trend between plankton and $\delta^{13}C$ (decreasing concentration as $\delta^{13}C$ becomes more enriched/less negative), only BDE-153 vs. $\delta^{13}C$ for all years was significant ($p = 0.045$; $r^2 = 0.136$) (SI Table 2.13). This trend largely appears driven by two samples (PH 32 and PH 34), which are the only two plankton samples with $\delta^{13}C$ values > -20‰ ($\delta^{13}C$ mean = -29.4 ± 0.61‰), along with the highest $\delta^{15}N$ values of all plankton (4.3‰ and 6.1‰ vs. mean of 1.7 ± 0.27‰). Although plankton concentrations vs. $\delta^{13}C$ for 2009/10 often appear to be slightly positive (i.e. increasing concentration as $\delta^{13}C$ becomes more enriched/less negative), none of these trends are significant

and all regressions were based off of only 3 samples with existing isotope data (SI Table 2.13).

Few significant correlations were detected between plankton and $\delta^{15}N$ until looking at the breakdown of concentration vs. $\delta^{15}N$ in 2010/11 alone, where almost all congeners detected showed a negative trend of decreasing concentration with increasing $\delta^{15}N$. BDE-28 vs. $\delta^{15}N$ was only nearly significant ($p = 0.060$), but BDE-47, -100, -99, -154, -153, and ∑PBDEs vs. $\delta^{15}N$ all had significantly negative trends at the 95% confidence interval (p-values of 0.036, 0.054, 0.019, 0.047, 0.022, and 0.023, respectively) (SI Table 2.14).

For plankton concentration vs. 'time', no significant correlations were found until analyzing plankton concentration vs. date for the 2010/11 sampling season, in which all congeners with > 30% detection (BDE-28, -49, -47, -100, -99, -154, -153, ∑PBDEs) have significantly negative trends, where concentrations decrease as the date increases towards the end of austral summer (p-values of 0.001, 0.022, 0.0009, 0.001, 0.006, 0.0005, 0.005, 0.002, respectively). It is likely that the reason we see this significant over the austral summer of 2010/11 and not 2007/08 or 2009/10 is because the 2010/11 sampling for phytoplankton has the largest range of sampling dates spanning from December through March. The 2007/08 sampling of plankton took place primarily in December and the 2009/10 sampling primarily in January over the course of 15 days. One possibility is that these trends observed in the 2010/11 season are reflecting a spike in concentrations picked up from the snow-melt/ice-melt taking place early-on in the austral summer, with a fading signal or dilution occurring as the season

progresses. Organic contaminants (e.g. PCBs, DDT, PAHs) have been detected in snow-packs and glacial ice from both Arctic and Antarctic environments and it has been proposed that in colder regions where the timing of the melt may be more concentrated as compared to a temperate environment, there is a stronger pulse of organic contaminants released to the surrounding water column (Wania et al. 1998). Chiuchiolo et al. (2004) detected various OCPs and BDEs (-47, -99, and -100) in plankton and suggest the plankton incorporation of POPs is related to snow and ice melt. Furthermore, the connection is made between the removal of POPs from the water column via sedimentation and organic carbon particle export that takes place in a relatively short time following phytoplankton blooms in this region (i.e. December and January) (Chiuchiolo et al. 2004). Additionally, Geisz et al. (2008) present further evidence of glacial meltwater acting as a source of, at least, ∑DDT to the Antarctic marine food web (Geisz et al. 2008).

A one-tailed two-sample t-test assuming unequal variances was performed to determine if there were any differences between the predominant plankton species of diatoms and *Phaeocystis*, and in all almost all cases (BDE-28, -47, -100, -153, and ΣPBDEs) *Phaeocystis sp.* have higher means than diatoms ($p = 0.009, 0.029, 0.033, 0.004, 0.010$, respectively) (Table 2.16). The same t-test was performed to determine if there were any differences between plankton with δ15N values < 2‰ and > 2‰ (referred to as "phyto" and "mixed" plankton based on this definition). In all cases, the mean of phytoplankton was greater than the mean of mixed plankton, however it was only significantly greater at the 95%

confidence interval for BDE-153 ($p = 0.036$) and very nearly significantly greater for ΣPBDEs ($p = 0.059$).

Krill

Lipid values in krill were much larger than plankton and average lipid % ranged from 13.7 – 32.6%. PBDEs were detected in 100% of all krill samples. The lower brominated congeners, BDE-2, -8, -15, and -30, were not detected in any samples with the exception of BDE-2 detected at 0.06 ng/g lipid in one juvenile krill sample. ∑PBDEs had much less variation than plankton and the average sum ranged from 0.09 – 4.99 ng/g lipid with an average (mean ± standard error) of 0.86 ng/g lipid ± 0.15, and a median of 0.74 ng/g lipid. BDE-47 was the dominant congener present in all size classes and species of krill, averaging around 70% of the total composition (SI Table 2.12), followed by BDE-28 and -99. Juvenile krill had the highest concentrations in *Euphausia superba* with a mean ΣPBDEs of 1.01 ng/g lipid ± 0.12, mean BDE-47 of 0.7 ng/g lipid ± 0.10, mean BDE-28 of 0.11 ng/g lipid ± 0.05, and mean BDE-99 of 0.07 ng/g lipid ± 0.03. Adult krill had the second highest concentrations in *Euphausia superba* with a mean ΣPBDEs of 0.88 ng/g lipid ± 0.28, mean BDE-47 of 0.42 ng/g lipid ± 0.08, mean BDE-28 of 0.05 ng/g lipid ± 0.02, and mean BDE-99 of 0.18 ng/g lipid ± 0.15. Gravid krill had the lowest concentrations in *Euphausia superba* with a mean ΣPBDEs of 0.50 ng/g lipid ± 0.11, mean BDE-47 of 0.26 ng/g lipid ± 0.07, mean BDE-28 of 0.09 ng/g lipid ± 0.03, and mean BDE-99 of 0.06 ng/g lipid ± 0.03. *Thysanoessa sp.* had the highest overall concentrations of the krill samples with a mean ΣPBDEs of 1.37 ng/g lipid ± 0.42, mean BDE-47 of 0.89 ng/g lipid ± 0.08, mean BDE-28 of 0.31 ng/g lipid ± 0.31, and mean BDE-99 of 0.18 ng/g lipid ± 0.03.

Stable isotope analysis was performed on a subset of each size class of krill, with the exception of *Thysanoessa sp.*, which were, unfortunately, not analyzed for stable isotopes. While the range of $\delta^{15}N$ was from 2.54 – 6.50‰, the mean of each size class did not differ greatly. Average $\delta^{15}N$ (mean ± standard error) was 4.01‰ ± 0.58 for juvenile krill, 4.17‰ ± 0.19 for adult krill, and 4.08‰ ± 0.43 for gravid krill. There was slightly more variability for $\delta^{13}C$, with a total range of -27.60 to -18.28‰. Average $\delta^{13}C$ was -24.42‰ ± 1.41 for juvenile krill, -25.20‰ ± 0.47 for adult krill, and -23.13‰ ± 0.68 for gravid krill.

Trends of Krill

No significant relationships were found between krill concentration and $\delta^{13}C$ or $\delta^{15}N$. Of all krill samples, there was one potential outlier (sample "Kr24," ΣPBDEs = 4.99 ng/g lipid vs. krill mean of 0.86 ng/g lipid), and as such, regressions and t-tests were run with and without the inclusion of this sample. No significant differences were found between krill concentrations means from the two sampling years of 2007/08 and 2010/11 with the exception of ΣPBDEs having a nearly significantly higher mean in 2010/11 vs. 2007/08 with the removal of "Kr24" ($p = 0.06$). When comparing different size classes of krill (i.e. juveniles vs. adults, adults vs. gravid, gravid vs. *Thysanoessa sp.*), BDE-47 and ΣPBDEs were both found to be significantly higher in juveniles than adults ($p = 0.009$ all samples, $p = 0.005$ without 'Kr24'; $p = 0.083$ all samples, $p = 0.009$ without 'Kr24', respectively). No significant differences were determined between adult and gravid krill and BDE-47 was determined to be significantly higher in *Thysanoessa sp.* than adult krill ($p = 0.001$, mean = 0.63 vs. 0.32 ng/g

lipid, respectively), but note that the *Thysanoessa sp.* sample set only consisted of two combined samples.

Fish

Lipid values in fish ranged from 21.65 – 51.94%. PBDEs were not detected in any of the 5 fish samples. Low concentration values for BDE-47 and -99 (aprx. 0.2 ng/sample) were initially determined from chromatogram interpretation, however, after blank corrections, all fish samples become classified as 'no-detects.' One potential explanation for this could be that high amounts of fish oil were not sufficiently removed during the extraction process, which may have interfered with the chromatogram interpretation. Another possible explanation is the fish samples consisted of whole homogenized fish, which may have diluted a signal. Perhaps if muscle tissue or specific organs (i.e. liver) were targeted, there would have been less 'noise' and PBDE detection potential would have increased. Previous studies have detected PBDEs in Antarctic fish samples, so we believe that a larger samples size combined with future improvements on sample collection and analysis will yield better results (Corsolini et al. 2006, Hale et al. 2008, Borghesi et al. 2008).

The total range of $\delta^{15}N$ for fish samples was 9.19 – 10.97‰ and for $\delta^{13}C$, -23.96 to -21.42‰. Average myctophid $\delta^{15}N$ was 9.58‰ ± 0.20 and $\delta^{13}C$, -23.62‰ ± 0.20. Average Antarctic silverfish $\delta^{15}N$ was 10.86‰ ± 0.11 and $\delta^{13}C$ was -21.44‰ ± 0.02. No statistical analyses could be performed on fish due to lack of detection in samples.

Trophic Levels

All plankton samples were assumed to be trophic level 1 and all other trophic levels were calculated from this baseline. No significant differences were found between the different trophic levels of each krill size class, and as such they were averaged together for a mean trophic level of 1.72 ± 0.05. Myctophid trophic level averaged 3.33 ± 0.06. Antarctic silverfish trophic level averaged 3.70 ± 0.03. Occasional slightly significant differences were found between some sampling years for fur seals trophic levels, likely due to the variability of isotopes, which reflect the variation in diet migratory species are subject to from year to year; thus, trophic levels for fur seals are presented per year. In ascending order of time, trophic levels of fur seals from 2000/01, 2001/02, 2004/05, 2009/10, and 2010/11 averaged 3.65 ± 0.04, 3.78 ± 0.06, 3.65 ± 0., 3.52 ± 0.07, and 3.76 ± 0.12, respectively.

Trophic Magnification Factors

TMFs were calculated for this food web using all samples with available isotope data from the one year of sampling (2010/11) in which samples were collected from all four groups. TMFs were calculated for a food web consisting of plankton, krill, fish, and fur seal milk, and separately for a scenario excluding fish in case there are discrepancies with the no detects. In both cases, all TMFs were found to be < 1 (range 0.33 – 0.87) indicating that there is some level of biodilution or metabolic excretion processes happening within this Antarctic food web (Table 2.1 & 2.2).

Kelly et al. (2008) investigated PBDEs and PCBs in an Arctic marine food web and found TMFs for all BDE congeners to be < 1 with the exception of BDE-47 and -49, which had TMFs of 1.6 and 1.2, respectively, and all congeners showed an overall TMF

range of 0.7 – 1.6. Comparatively, their TMF values for PCBs ranged from 2.9 – 11, demonstrating a much greater potential for food web biomagnification (Kelly et al. 2008). Our TMF range (all samples) is slightly less and on a whole, lower than what was observed in the Arctic. These data provide further evidence that PBDE transport through food webs is species specific and illustrate the usefulness of TMFs inter-ecosystem comparison, in this case between the Arctic and Antarctic.

Implications

It is clear that there is, if not an increase, than at least not a decrease of PBDEs in the Antarctic region over the last decade. Other parts of the world, primarily regions in close proximity to industrialized areas where there have been efforts to reduce PBDE production and utilization (i.e. Northwest Europe), have started to see a reduction in PBDE concentrations as a reflection of this action, which is clearly not yet the case in Antarctica. The extremely high concentrations of PBDEs in plankton compared to the upper trophic level Antarctic Fur Seal were unexpected, but not unprecedented, and illustrate the complexity of the Antarctic food web. Snow and ice melt have the potential to act as pulse of pollutant release at points in the austral summer; and the migratory nature and diverse diet of Antarctic fur seals confounds an additional layer of the puzzle. In a time of increasing climate change studies and increased efforts to regulate organic contaminant production and use, it is critical to continue monitoring efforts of pollutants in regions such as Antarctica that are removed from production of synthetic contaminants, but not unaffected.

Figures and Tables

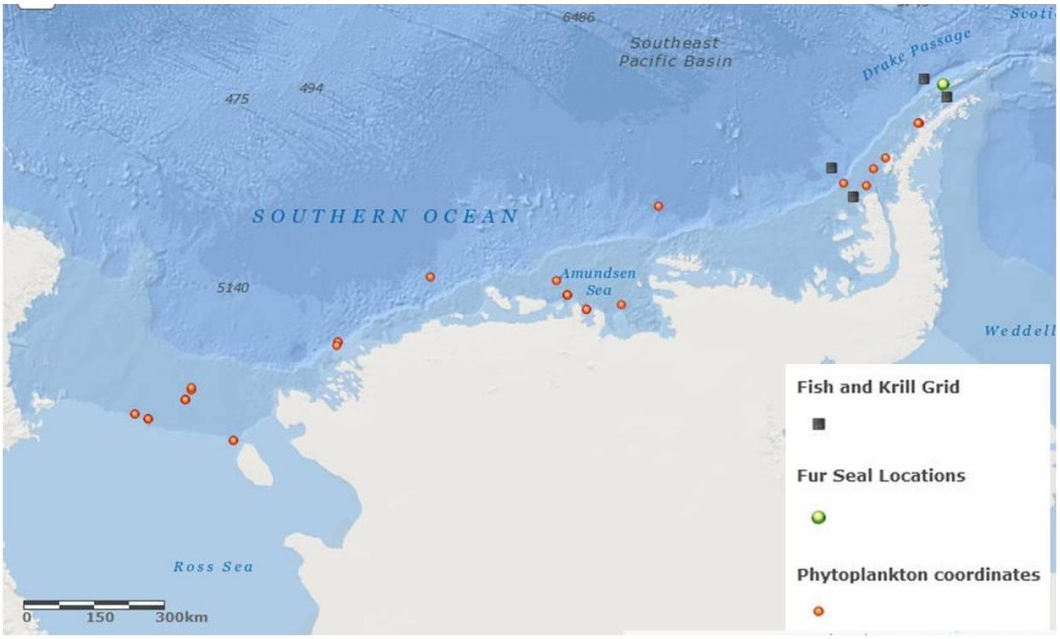


Figure 2.1 – Map of sampling location range. Created with ArcGIS Explorer.

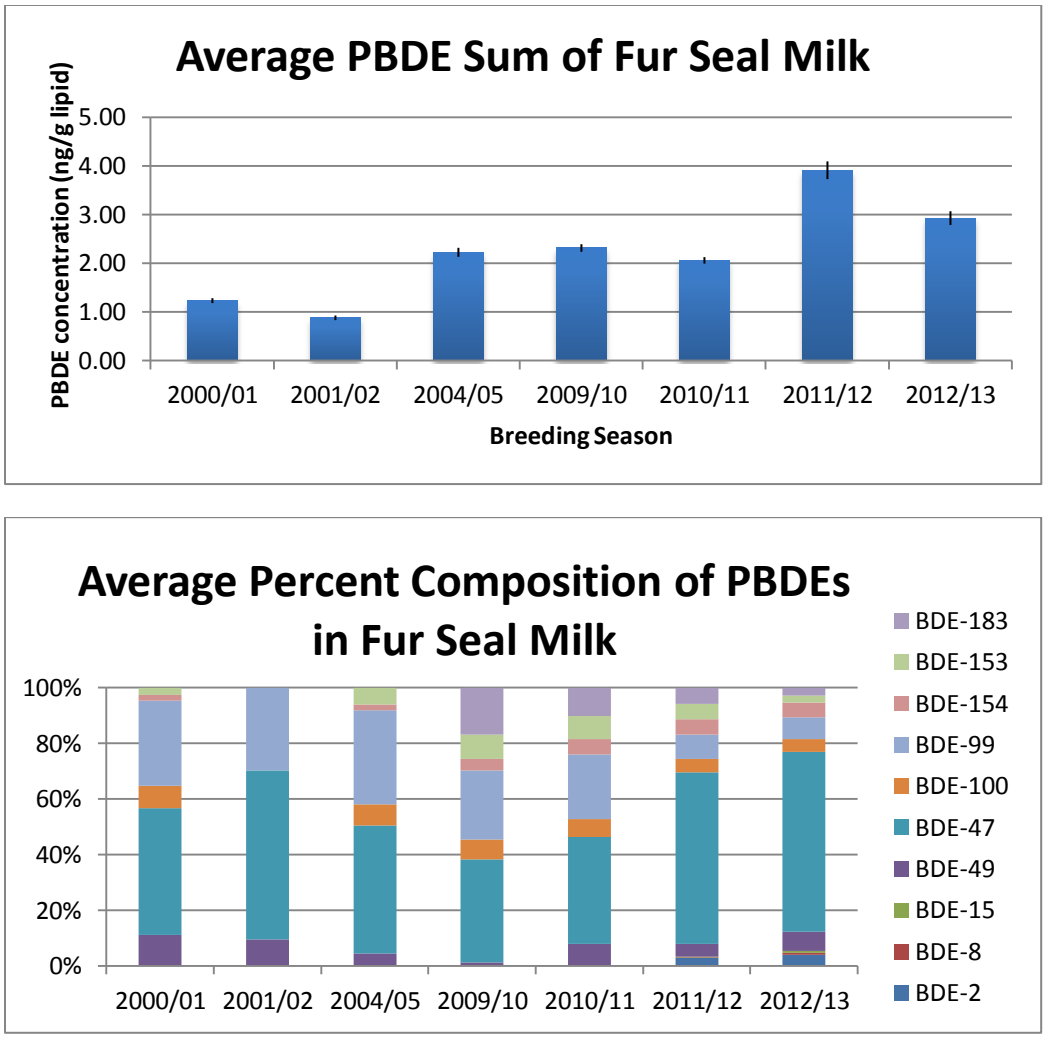
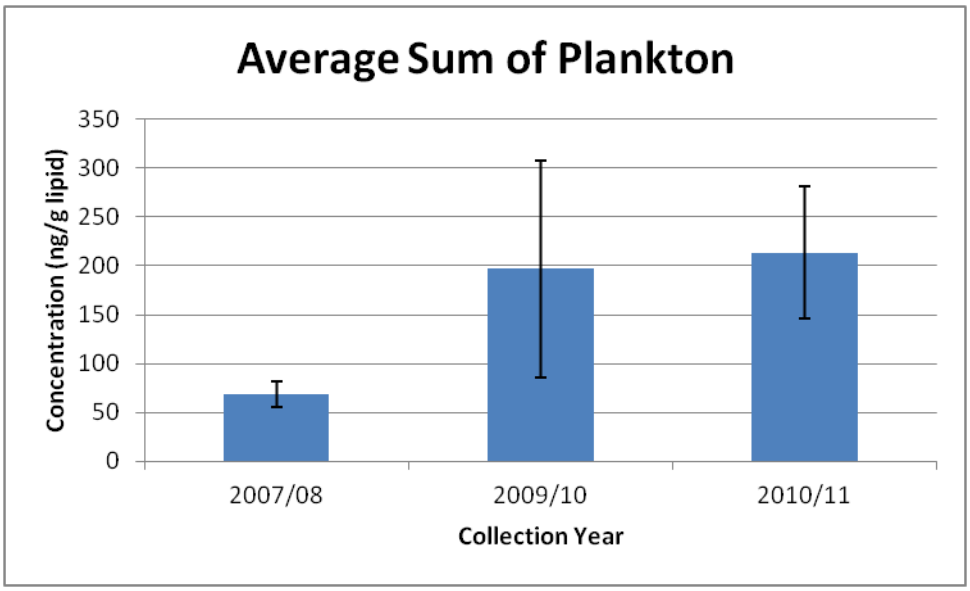


Figure 2.2 (a. and b.) – a. Average Sum of PBDEs per breeding season for the 7 austral summers sampled. Bars represent standard error and the first five austral summers (2000/01 – 2010/11) have had a recovery correction of 77.86% applied. Note the uneven intervals between years. b. Average percent composition of PBDEs in Fur Seal Milk from 2000/01 – 2012/13.



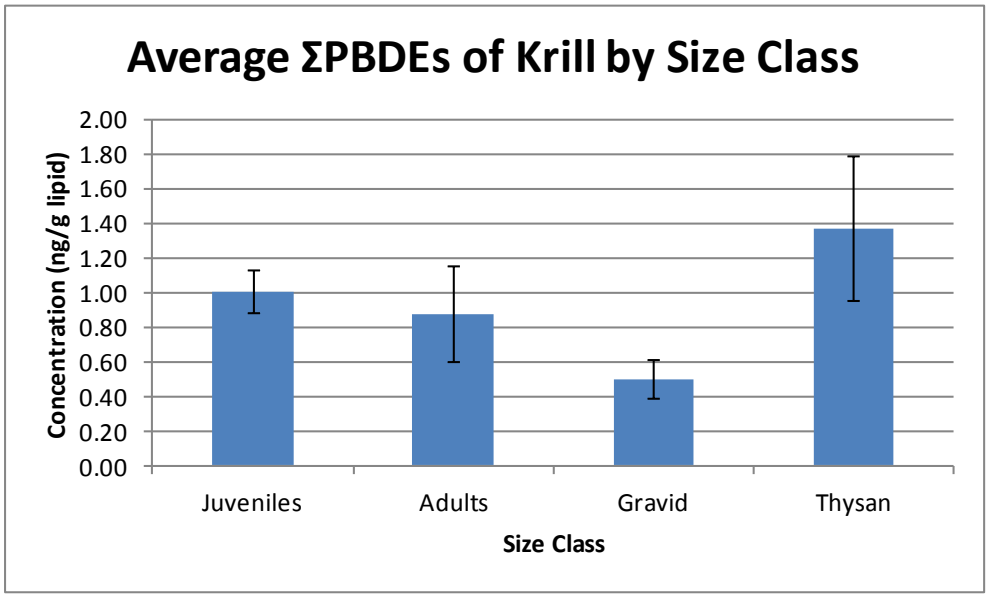


Figure 2.3 (a. and b.)– a. Average ΣPBDEs of plankton per sampling season. Note the uneven interval between years. Bars represent standard error. b. Average ΣPBDEs of Krill by Size Class in ng/g lipid. Error bars represent standard error.

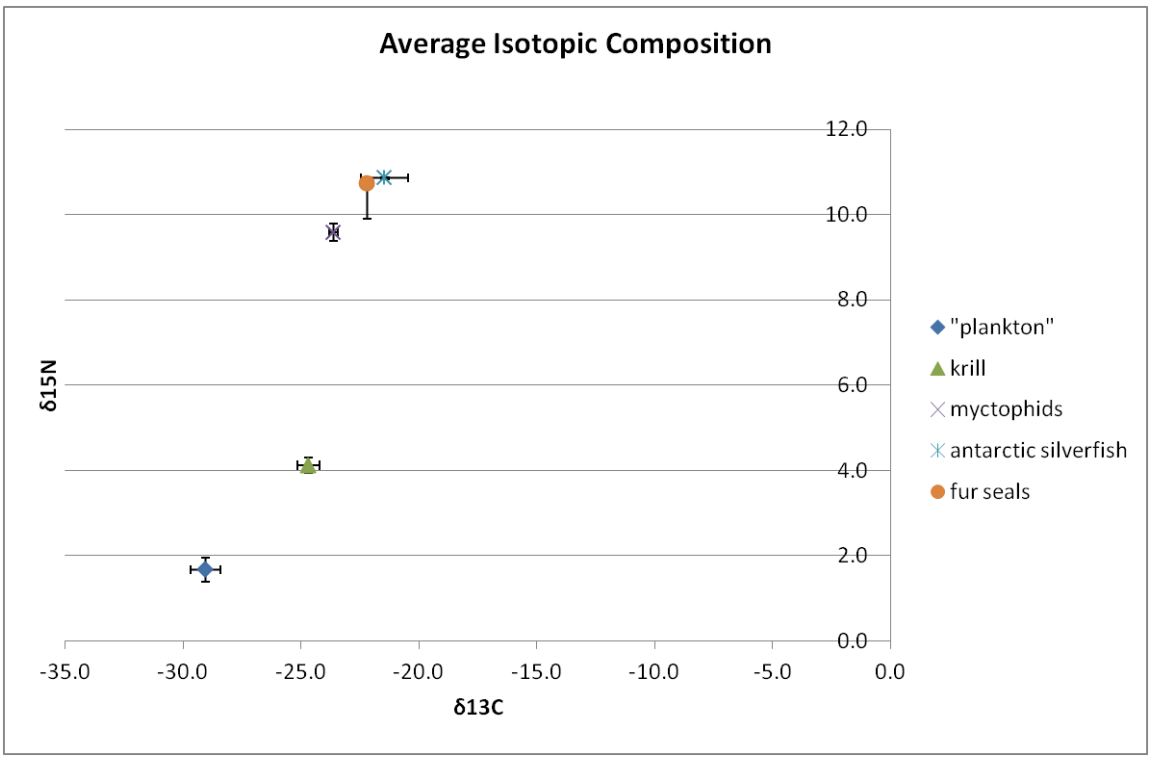


Figure 2.4 – Average isotopic composition of all biota sampled. Error bars represent standard error.

Table 2.1 – Average trophic levels (mean ± standard error) from 2010/11 sample set for all organisms with available isotope and concentration data.

	Trophic Level	
	mean	± S.E.
Plankton	1	n/a
Krill	1.79	0.12
Fish	3.75	0.1
Fur Seals	3.76	0.12

Table 2.2 – Average trophic magnification factors (TMFs) for the 2010/11 food web determined with and without the inclusion of fish samples. A TMF < 1 negates biomagnification and indicates some sort of biodilution is occurring in this food web.

		BDE-28	BDE-49	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	Sum
With Fish	**Slope**	-0.11	-0.09	-0.42	-0.26	-0.41	-0.17	-0.21	-0.06	-0.48
	TMF	0.77	0.82	0.38	0.55	0.39	0.68	0.61	0.87	0.33
Without Fish	**Slope**	-0.11	-0.08	-0.41	-0.26	-0.41	-0.17	-0.21	-0.05	-0.45
	TMF	0.77	0.82	0.39	0.55	0.39	0.68	0.61	0.89	0.36

SUPPORTING INFORMATION

Table 1.1.1 – Laboratory blank information of perfluorocarboxylic acids (PFCAs). Blanks consisted of 4mL cartridge-cleaned water and were extracted at the Research Centre for Toxic Compounds in the Environment (RECETOX).

	4mL Blanks	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
1st fraction	Rep1	<4	<4	<10	<13	<28	<27	<14	<103	<25	17.5	<41
	Rep2	<4	<4	<10	<13	<28	<27	<14	<103	<25	25	<41
	Rep3	<4	<4	<10	<13	<28	<27	<14	<103	<25	17.8	<41
2nd fraction	Rep1	9.7	19.8	<10	<13	<28	<27	<14	<103	<25	15.7	<41
	Rep2	<4	16.3	<10	<13	<28	<27	<14	<103	<25	<15	<41
	rep3	5.4	16.5	<10	<13	<28	<27	<14	<103	<25	<15	<41

Table 1.1.2 - Laboratory blank information of perfluorosulfonates (PFSAs) and perfluorooctane sulfonamide and sulfanomido ethanols (FOSA and FOSE). Blanks consisted of 4mL cartridge-cleaned water and were extracted at the Research Centre for Toxic Compounds in the Environment (RECETOX).

	4mL Blanks	PFBS	PFHxS	PFHpS	PFOS	PFDS	FOSA	MeFOSA	EtFOSA	MeFOSE	EtFOSE
1st fraction	rep1	<40	<17	<4	<10	<7	<4	4.3	<4	7.6	**<5.9**
	rep2	<40	<17	<4	<10	<7	<4	4.1	<4	10.2	**<7.8**
	rep3	<40	<17	<4	<10	<7	<4	<4	<4	6.7	4.7
2nd fraction	rep1	<40	<17	<4	<10	<7	<4	4.7	<4	<4	***<10.1***
	rep2	<40	<17	<4	<10	<7	<4	<4	<4	5.7	***<11.9***
	rep3	<40	<17	<4	<10	<7	<4	<4	<4	6.7	4.7

Table 1.2.1 Recovery information for the fraction 2 portion of seawater samples from stations 1 – 13.

2nd fraction	recovery [%] mass-labelled compounds									
Sample Name	MPFBA	MPFHxA	MPFOA	MPFNA	MPFDA	MPFUnDA	MPFDoDA	MPFHxS	MPFOS	dMeFOSA
Sta. 1 5m F2	3.4	39.8	42.3	36.3	25.8	29.3	21.7	45.8	37.3	0
Sta. 1 51m F2	2.7	33.8	100.5	101.8	90.8	70	49.3	17.6	102.3	0
Sta. 1 76m F2	0.6	3.7	2.7	3.1	3.9	3.9	2.9	4.6	3.2	0
Sta. 1 103m F2	5.5	87.3	85.8	90.8	81.8	98.3	81.3	96.3	95.8	0
Sta. 2 5m F2	5.7	89.5	81.3	78	41	11.2	4.3	108.5	85	0
Sta. 2 152m F2	5.4	82.3	88.5	90.3	80	98.3	60.8	90.5	89.5	0
Sta. 2 252m F2	6.2	90	87.3	97.5	89.8	85.8	74.5	105	112	0
Sta. 2 754m F2	9	103.8	90	98.5	96	80	80	95.8	102.5	0
Sta. 2 2502m F2	7.1	89.8	9.9	3.0	2.7	2.4	1.8	85	4.1	0
Sta. 2 5110m F2	6.6	74.5	8	1.4	1	1.1	0.9	69	4	0
Sta. 3 5m F2	5.5	84.8	89	87.3	97.8	88.3	61.3	105.3	97.5	0
Sta. 3 98m F2	6.7	92	103	100.8	101.3	83	31.3	112.5	114	0
Sta. 3 150m F2	5.2	72.8	84.5	9.8	1.8	0.7	0.9	64.8	6.8	0
Sta. 3 250m F2	7.8	91	100.3	84	36.5	11	3.4	91.8	92.8	0
Sta. 3 500m F2	6.5	93.8	96.8	103.8	83	83.8	36.3	102	101.8	0
Sta. 3 800m F2	7.3	91.3	69	48.3	15.2	9.5	6.6	77.5	64.5	0
Sta. 3 2500m F2	7.5	99	42	10	4.5	3.8	2.6	106.5	22.7	0
Sta. 5 7.7m F2	4.2	43.3	58.5	56.8	52.5	49.5	28	49.8	54.5	0
Sta. 5 176m F2	6.3	86.5	96	61.8	70.3	40.8	47.5	94.8	82.8	0
Sta. 5 250m F2	8.5	99.5	93.3	97.8	102.8	76	47.5	104.8	109.5	0
Sta. 5 902m F2	8.2	93.8	102	100.3	99.5	94.5	75.5	93.3	98.5	0
Sta. 5 2504m F2	9.1	97.5	104.3	72.8	65.8	32.3	17.8	108	96	0
Sta. 5 4345m F2	7.8	88.3	96.3	101	95	97.5	83.5	107.5	102	0
Sta. 7 5m F2	7.4	69.8	104.5	93	92.3	80	31.5	94.8	103.3	0
Sta. 7 130m F2	3.9	90.5	107.3	87	59.5	17.1	6	104.5	103.5	0
Sta. 7 152m F2	4.8	67.8	85.8	95	54.3	15.7	6.5	81.5	88.8	3.4
Sta. 7 250m F2	7.5	92.5	96.8	105.5	91	81	26	101.3	114.8	0
Sta. 7 500m F2	7.9	96.8	91	87.3	105.5	92.3	81.3	105.8	118	0
Sta. 7 751m F2	10.4	99	86	90.5	86.3	74.8	40.8	99.5	99	0
Sta. 7 2500m F2	10.6	72	67.8	63.8	33.8	17.7	8.5	90.5	74.5	0
Sta. 10 5m F2	7.4	95.5	101.3	99.3	103.5	77.8	45.8	101.5	99	1.7
Sta. 10 150m F2	7.2	101.5	90.5	89.5	103	99	65	99	107	3.1
Sta. 10 250m F2	8.1	101.8	79.5	44.3	26.8	17.9	13	92	47	0
Sta. 10 849m F2	8.3	97.3	99.3	93	101.5	64.5	19.5	106.3	122.8	0
Sta. 10 2500m F2	12.4	101.3	94	96.8	100.5	82	54	103.3	100.5	0
Sta. 10 5245m F2	8.1	103.3	82.8	86.5	89.5	78.3	39.3	103	109.5	0
Sta. 12 5m F2	14.1	95.8	109	101	90	50.8	23.4	104	109.3	0
Sta. 12 151m F2	7.6	91.5	106.5	97.5	75.5	51.3	15.2	110.3	105.8	0
Sta. 12 250m F2	13.4	110.8	126.8	110.3	97	116.5	43	118.8	112.5	0
Sta. 12 400m F2	11.7	73.8	96.8	93.5	88.3	101.5	57.8	92.8	101.8	0.9
Sta. 12 760m F2	11.6	100.8	105.8	98.3	96	90.3	45.3	122	131	0.3
Sta. 12 2500m F2	12.4	92.5	104	104	100.8	86.5	32.8	95.5	116.3	0.1
Sta. 13 5m F2	7	112.8	106.3	90.3	99.8	79.8	48.8	102.5	118	0.1
Sta. 13 150m F2	8.6	102.5	96	85.3	81.5	36	9.8	106.3	95.3	0
Sta. 13 249 m F2	11.4	105.3	92.3	80.8	85	53.8	21.7	114.8	105	0
Sta. 13 775m F2	11.4	94.5	93.5	92.8	102.8	100.8	74	91	105.3	1.1
Sta. 13 2500m F2	10.4	84.5	99	98.8	111	88.8	43.8	93.3	113.8	0
Sta. 13 5526m F2	7.4	99.8	86	85.8	98	82.3	42	94.3	124	2

Table 1.2.2 – Continuation of recovery information for the fraction 2 portion of seawater samples from stations 15 – 23. The mean, median, standard deviation, and standard error information included at the bottom of this table are for all seawater samples.

2nd fraction	recovery [%] mass-labelled compounds									
Sample Name	MPFBA	MPFHxA	MPFOA	MPFNA	MPFDA	MPFUnDA	MPFDoDA	MPFHxS	MPFOS	dMeFOSA
Sta. 15 5m F2	6	94.5	112.8	107	68	20.2	8.9	102.8	60	0
Sta 15 75m F2	8.5	101.5	95.3	96.3	103.5	83.8	50.3	92.5	109.3	0
Sta. 15 151m F2	8.5	93.8	93.3	100.8	100.8	79.3	36.5	98.3	105.5	0
Sta. 15 250m F2	5.5	92.8	72	40.3	13.5	9.4	5.5	93.8	37	0
Sta. 15 500m F2	15.2	103.8	97	104.5	87	110.3	87.5	102.3	111.3	0
Sta. 15 750m F2	9.1	82.8	83.3	45.5	31	18.6	13.6	117	74.3	0
Sta. 15 1005m F2	11.9	101	62.3	27.3	15.3	10.2	5.5	93.3	20.2	0
Sta. 15 2504m F2	7.5	104.3	67.3	15.8	7.5	5	3	113.5	25.8	0
Sta. 19 5m F2	4.7	99.8	90	90.8	89.5	87.3	53	98.8	98.8	0
Sta. 19 5m Dup. F2	4.3	92.5	87.3	82.5	44.5	7.7	1.7	99	97	0
Sta. 19 100m F2	3.8	82	99.5	76.8	73.5	43	16.6	94.5	89	0
Sta. 19 100m Dup. F2	4.3	78.3	85	90.3	99	74	33.5	96.8	99.8	0
Sta. 19 250m F2	7.1	79.8	95.5	84.3	64.5	28	8	98.8	98.8	0
Sta. 19 250m Dup. F2	6.1	88.8	94	91.5	86.3	75.3	30.8	109.8	89.3	0
Sta. 19 781m F2	6.1	87	36.5	6.7	1.9	1.6	1.5	97.3	15.6	0
Sta. 19 781m Dup. F2	5.7	91	90.3	82.3	85.5	41	17.5	86.3	87	0
Sta. 19 2500m F2	6.4	89.3	101.8	98.5	90.8	93.8	39	109.8	111.3	0
Sta. 19 2500m Dup. F2	6.1	96	81.3	53	12.7	7	3.2	100.8	78.5	0
Sta. 19 4662m F2	7.3	83	11.5	3.4	2.7	1.8	1.3	69.5	4.7	0
Sta. 19 4662m Dup. F2	7.9	94.3	64.3	9.4	1.4	0.6	0.9	100.3	18.5	0
Sta. 22 5m F2	4.6	60	34.3	6.5	6.3	5.8	3.4	77	11.9	0
Sta. 22 150m F2	6.6	98.3	101.3	100.5	87.8	69.3	20.1	108	105	0
Sta. 22 250m F2	7.8	100.3	9	3.1	4.4	4.2	3	83	8.4	0
Sta. 22 397m F2	7.5	91.5	96.8	99	93.5	87.3	34.3	102	114.8	0
Sta. 22 772m F2	8.4	90	95.8	91	90	83.8	34.8	103.3	92.3	0
Sta. 22 2504m F2	7.7	104	98.5	96.8	102.3	92.5	69.3	105.3	124.5	0
Sta. 23 5m Rep. 1 F2	4.4	85.3	24.5	1.8	1.2	0.6	1	77.8	2.3	0
Sta. 23 5m Rep. 2 F2	4.7	73	3	0.7	0.9	0.6	0.9	43.3	1.6	0
Sta. 23 5m Rep. 3 F2	4.3	89.3	93	47.8	8.5	2.4	0.9	88	64.8	0
Sta. 23 151m F2	4.8	75.3	37	17.1	6.9	3.4	1.5	66	19.8	0
Sta. 23 250m F2	7.6	90.3	96	97	92.3	83.3	37	97.8	98.5	0
Sta. 23 500m F2	7.1	88	90.5	79	60.8	30.5	15.5	104.3	100.5	0
Sta. 23 876m F2	7.8	82.3	73.8	44.5	18.1	6.9	2.9	94.3	55.8	0
Sta. 23 2501m F2	5.8	80.5	85	93.8	80.8	94	48.5	93.8	99.8	0
Sta. 23 3760m F2	7.5	92.3	97	98.3	51.5	18.1	4.5	106.3	108	0
Mean	**7.38**	**88.17**	**81.88**	**72.16**	**63.81**	**51.42**	**29.03**	**93.86**	**81.26**	**0.15**
Median	**7.40**	**91.50**	**91.00**	**89.50**	**81.80**	**53.80**	**23.40**	**98.80**	**98.50**	**0.00**
Standard Deviation	**2.62**	**16.85**	**27.93**	**34.70**	**37.77**	**37.55**	**25.37**	**19.77**	**37.84**	**0.59**
Standard Error	**0.29**	**1.85**	**3.07**	**3.81**	**4.15**	**4.12**	**2.78**	**2.17**	**4.15**	**0.06**

Table 1.3.1 – Station and supplementary information for stations 1 – 10.

Station	Date	GMT	Latitude	Longidtude	Depth	Water Mass	Temperature (°C)	Fluorescence	Salinity (PSU)	oxygen (ml/L)
1	26-Mar-13	16:25	-37.11	-49.90	5	surface	19.60	0.07	34.92	4.90
1	26-Mar-13	16:25	-37.11	-49.90	51		19.55	0.17	34.99	4.89
1	26-Mar-13	16:25	-37.11	-49.90	76	DCM	17.35	0.49	34.92	5.05
1	26-Mar-13	16:25	-37.11	-49.90	103		13.37	0.12	34.64	4.96
2	29-Mar-13	19:04	-38.00	-45.00	5	surface	20.10	0.08	36.01	4.69
2	29-Mar-13	12:56	-37.99	-44.99	152		16.54	0.03	35.80	4.38
2	29-Mar-13	12:56	-37.99	-44.99	252		14.61	0.03	35.51	4.43
2	28-Mar-13	0:55	-37.97	-44.98	754	AAIW	5.20	0.03	34.27	5.04
2	27-Mar-13	19:56	-37.97	-44.98	2502	NADW	2.89	0.05	34.86	4.71
2	27-Mar-13	19:56	-37.97	-44.98	5110	AABW	0.29	0.05	34.67	4.53
3	31-Mar-13	8:30	-34.51	-42.50	5	surface	21.24	0.06	35.83	4.63
3	31-Mar-13	8:30	-34.51	-42.50	98	DCM	17.33	0.37	35.87	4.56
3	31-Mar-13	8:30	-34.51	-42.50	150		16.20	0.05	35.78	4.41
3	31-Mar-13	8:30	-34.51	-42.50	250		14.78	0.02	35.56	4.47
3	31-Mar-13	8:30	-34.51	-42.50	500		10.51	0.00	34.87	4.30
3	31-Mar-13	8:30	-34.51	-42.50	800		4.81	0.03	34.22	5.23
3	31-Mar-13	8:30	-34.51	-42.50	2500		3.20	0.05	34.92	4.98
5	2-Apr-13	21:17	-28.21	-32.54	7.7		24.89	0.03	36.66	4.38
5	2-Apr-13	21:17	-28.21	-32.54	176		18.18	0.05	36.00	4.32
5	2-Apr-13	21:17	-28.21	-32.54	250		16.08	0.02	35.66	4.34
5	2-Apr-13	21:17	-28.21	-32.54	902	AAIW	4.57	0.03	34.30	4.60
5	2-Apr-13	21:17	-28.21	-32.54	2504	NADW	3.11	0.05	34.94	5.14
5	2-Apr-13	21:17	-28.21	-32.54	4335	AABW	0.34	0.05	34.68	4.51
7	5-Apr-13	0:00	-22.48	-33.02	5	surface	27.40	0.04	37.23	4.21
7	5-Apr-13	0:00	-22.48	-33.02	130	DCM	22.07	0.24	36.80	4.47
7	5-Apr-13	0:00	-22.48	-33.02	152		21.50	0.13	36.69	4.40
7	5-Apr-13	0:00	-22.48	-33.02	274		15.54	0.01	35.56	4.42
7	5-Apr-13	0:00	-22.48	-33.02	500		10.38	0.01	34.85	4.24
7	5-Apr-13	0:00	-22.48	-33.02	751	AAIW	5.03	0.03	34.36	4.24
7	5-Apr-13	0:00	-22.48	-33.02	2500	NADW	3.01	0.06	34.93	5.10
10	12-Apr-13	0:40	-9.49	-25.99	5	surface	28.37	0.02	36.63	4.15
10	12-Apr-13	0:40	-9.49	-25.99	150		18.66	0.16	36.10	3.60
10	12-Apr-13	0:40	-9.49	-25.99	250		11.04	0.02	35.03	2.16
10	12-Apr-13	0:40	-9.49	-25.99	849	AAIW	4.46	0.04	34.47	3.32
10	12-Apr-13	0:40	-9.49	-25.99	2500	NADW	2.94	0.05	34.93	5.06
10	12-Apr-13	0:40	-9.49	-25.99	5245	AABW?	0.77	0.05	34.71	4.49

Table 1.3.2 - Station and supplementary information for stations 12 – 23.

Station	Date	GMT	Latitude	Longidtude	Depth	Water Mass	Temperature (°C)	Fluorescence	Salinity (PSU)	oxygen (ml/L)
12	15-Apr-13	21:50	-5.70	-26.00	5	surface	28.65	0.03	36.09	4.16
12	15-Apr-13	21:50	-5.70	-26.00	151		14.97	0.11	35.55	2.19
12	15-Apr-13	21:50	-5.70	-26.00	250		10.61	0.01	34.99	1.98
12	15-Apr-13	21:50	-5.70	-26.00	400	OMZ	8.31	0.04	34.74	1.70
12	15-Apr-13	21:50	-5.70	-26.00	760	AAIW	4.60	0.03	34.46	3.37
12	15-Apr-13	21:50	-5.70	-26.00	2500	NADW	2.93	0.05	34.93	4.95
13	16-Apr-13	21:50	-5.69	-28.51	5	surface	28.66	0.04	36.09	4.14
13	16-Apr-13	21:50	-5.69	-28.51	150		15.29	0.11	35.59	2.64
13	16-Apr-13	21:50	-5.69	-28.51	249		9.95	0.02	34.90	2.34
13	16-Apr-13	21:50	-5.69	-28.51	775	AAIW	4.97	0.03	34.48	3.05
13	16-Apr-13	21:50	-5.69	-28.51	2500	NADW	2.96	0.06	34.93	5.00
13	16-Apr-13	21:50	-5.69	-28.51	5526	AABW	0.72	0.05	34.70	4.48
15	17-Apr-13	2:40	-2.70	-28.51	5	surface	28.80	0.07	35.88	4.26
15	17-Apr-13	2:40	-2.70	-28.51	75		16.22	0.30	35.62	2.57
15	17-Apr-13	2:40	-2.70	-28.51	151		13.05	0.03	35.29	2.44
15	17-Apr-13	2:40	-2.70	-28.51	250		11.84	0.02	35.13	1.85
15	17-Apr-13	2:40	-2.70	-28.51	500		7.60	0.05	34.66	2.07
15	18-Apr-13	21:15	-2.70	-28.50	750	AAIW*	4.82	0.02	34.48	3.30
15	17-Apr-13	2:40	-2.70	-28.51	1005	AAIW?	4.37	0.05	34.62	3.32
15	17-Apr-13	2:40	-2.70	-28.51	2500	NADW	2.92	0.05	34.93	4.96
19	27-Apr-13	11:35	5.94	-41.31	5	surface	27.86	0.05	35.70	4.16
19	27-Apr-13	11:35	5.94	-41.31	100		24.94	0.41	36.27	3.60
19	27-Apr-13	11:35	5.94	-41.31	250		9.71	0.02	34.91	2.70
19	27-Apr-13	11:35	5.94	-41.31	781	AAIW	5.59	0.03	34.58	2.80
19	27-Apr-13	11:35	5.94	-41.31	2500	NADW	3.03	0.04	34.95	5.18
19	27-Apr-13	11:35	5.94	-41.31	4662	Bottom	1.51	0.05	34.80	4.79
22	1-May-13	14:00	8.26	-49.99	5	surface	27.94	0.06	35.90	4.12
22	1-May-13	14:00	8.26	-49.99	150		17.64	0.05	36.26	2.65
22	1-May-13	14:00	8.26	-49.99	250		10.65	0.03	35.06	2.18
22	1-May-13	14:00	8.26	-49.99	397		9.07	0.02	34.89	2.21
22	1-May-13	14:00	8.26	-49.99	772	AAIW	5.62	0.05	34.62	2.75
22	1-May-13	14:00	8.26	-49.99	2504	NADW	3.06	0.05	34.95	5.24
23	4-May-13	7:00	9.70	-55.30	5	rep 1	28.17	0.10	33.50	4.17
23	4-May-13	7:00	9.70	-55.30	5	rep 2	28.17	0.10	33.50	4.17
23	4-May-13	7:00	9.70	-55.30	5	rep 3	28.17	0.10	33.50	4.17
23	4-May-13	7:00	9.70	-55.30	150		20.57	0.04	36.41	3.33
23	4-May-13	7:00	9.70	-55.30	250		12.36	0.00	35.23	3.32
23	4-May-13	7:00	9.70	-55.30	500	meso-pel	8.75	0.00	34.78	3.05
23	4-May-13	7:00	9.70	-55.30	876		5.53	0.03	34.61	2.78
23	4-May-13	7:00	9.70	-55.30	2501	NADW	2.97	0.03	34.94	5.31
23	4-May-13	7:00	9.70	-55.30	3760	Bottom	2.26	0.04	34.90	5.33

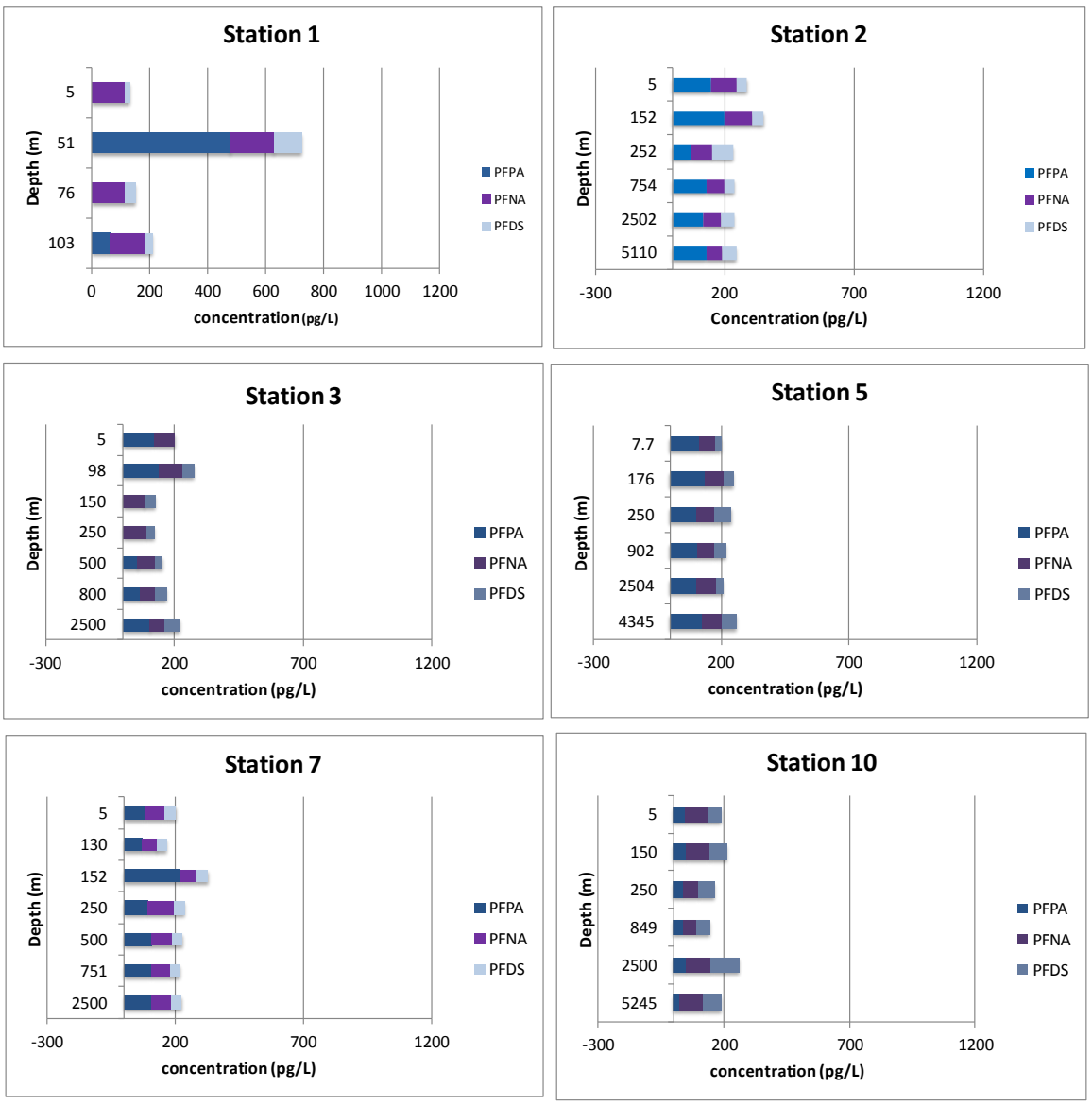


Figure 1.1 – PFPA, PFNA, and PFDS profiles from stations 1 – 10.

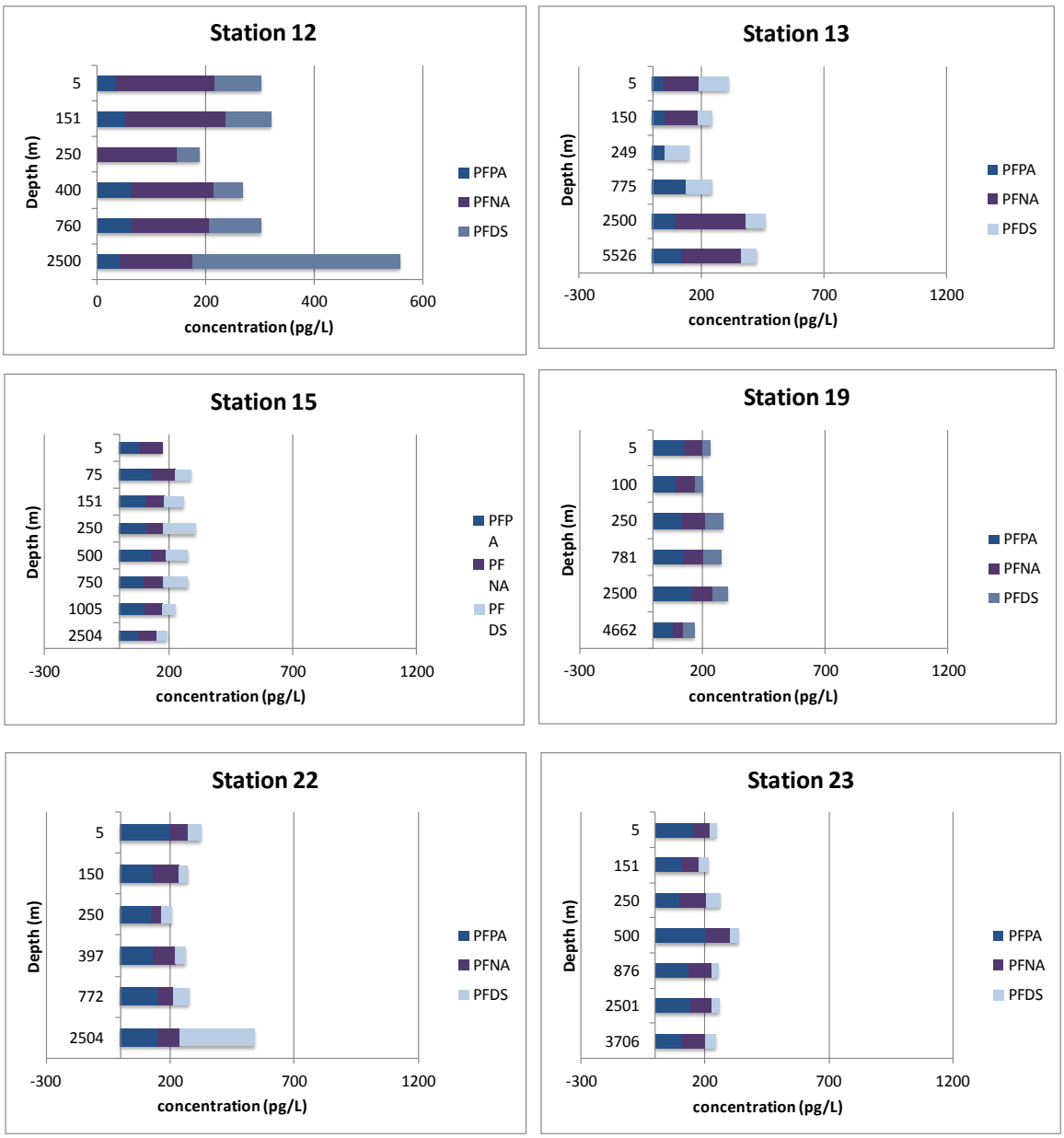


Figure 1.2 – PFPA, PFNA, and PFDS profile from stations 12 – 23.

Table 2.1 – Sample information for plankton.

Sample ID	Dominant Phytoplankton Species	Latitude	Longitude	Year	Date	Percent Lipid	$\delta^{13}C$ Avg	± StDev	$\delta^{15}N$ Avg	± StDev	General Area
PH 1	Likely phaeocystis	-77.98	-176.80	2007	Dec. 30	0.73	-28.9	0.14	-1.1	0.18	Ross Sea
PH 2	Likely phaeocystis	-74.18	-112.70	2007	Dec. 16	0.71	-30.4	0.13	0.2	0.24	Amundsen Sea
PH 3	Likely phaeocystis	-74.18	-112.70	2007	Dec. 16	1.05	-29.8	0.19	1.5	0.06	Amundsen Sea
PH 4	Likely phaeocystis	-73.57	-115.50	2007	Dec. 19	0.6	-31.7	0.11	1.0	0.56	Amundsen Sea
PH 5*	Likely phaeocystis	-77.08	-170.50	2008	Jan. 1	2.5	-24.6	0.23	3.3	0.61	Ross Sea
PH 6*	Likely phaeocystis	-77.98	-176.80	2007	Dec. 30	2.68	-24.6	0.38	3.2	0.80	Ross Sea
PH 7	Likely phaeocystis	-77.38	-171.30	2007	Dec. 31	1.19	-31.1	0.46	0.1	0.24	Ross Sea
PH 8	Likely phaeocystis	-77.38	-171.30	2007	Dec. 31	0.53	-32.7	0.18	-0.1	1.40	Ross Sea
PH 9	Likely phaeocystis	-77.98	-176.80	2007	Dec. 30	0.73	-28.9	0.30	-0.1	0.38	Ross Sea
PH 10	Likely phaeocystis	-73.97	-107.50	2007	Dec. 14	1.28	-32.0	0.03	0.9	0.31	Amundsen Sea Polynya
PH 11	Likely phaeocystis	-77.38	-171.30	2007	Dec. 31	1.27					Ross Sea
PH 13	Likely phaeocystis	-77.85	-178.70	2007	Dec. 30	0.982	-31.0	0.70	0.2	1.25	Ross Sea
PH 15	Likely phaeocystis	-73.57	-115.50	2007	Dec. 19	0.721	-31.8	0.07	-0.5	0.02	Amundsen Sea
PH 16	Diatoms	-69.53	-75.52	2010	Jan. 28	1.699	-27.1	0.39	1.8	0.17	Antarctic Peninsula
PH 17*	Diatoms	-66.89	-68.92	2010	Jan. 13	1.852	-33.0	0.37	2.7	0.34	Antarctic Peninsula
PH 19	Likely phaeocystis	-77.02	-170.50	2008	Jan. 2	0.459	-30.6	1.48	0.4	0.53	Ross Sea
PH 20	Diatoms	-68.97	-73.56	2010	Jan. 21	4.652	-30.5	0.41	1.1	0.44	Antarctic Peninsula
PH 21	Diatoms	-68.97	-73.56	2010	Jan. 21	4.652					Antarctic Peninsula
PH 23*	Phaeocystis	-69.46	-102.10	2010	Dec. 23	2.45	-27.5	0.18	2.1	0.12	Southern Bellingshausen Sea
PH 27	Phaeocystis	-72.96	-117.00	2010	Dec. 26	1.56	-27.8	1.38	1.6	0.25	Amundsen Sea
PH 24	Phaeocystis	-75.42	-149.00	2011	Jan. 5	1.24	-29.8	0.21	2.0	0.33	Southern Amundsen Sea
PH 26	Diatoms	-64.82	-64.04	2011	Mar. 5	2.01	-30.4	0.25	1.9	0.34	Antarctic Peninsula
PH 26b	Diatoms	-64.82	-64.04	2011	Mar. 5	2.53					Antarctic Peninsula
PH 28	Phaeocystis	-75.40	-149.00	2011	Jan. 5	0.93	-31.7	0.31	1.6	0.35	Southern Amundsen Sea
PH 29	Phaeocystis	-78.64	-164.30	2011	Jan. 8	0.66	-30.0	1.46	0.9	0.71	Ross Sea
PH 31*	Diatoms	-64.78	-64.07	2011	Mar. 7	3.04	-27.0	0.15	2.8	0.34	Antarctic Peninsula
PH 32*	Diatoms	-68.28	-75.12	2011	Feb. 1	1.89	-19.5	0.25	4.3	0.14	Antarctic Peninsula
PH 33*	Phaeocystis	-78.64	-164.30	2011	Jan. 1	6.72	-28.7	0.20	3.2	0.50	Ross Sea
PH 34*	Diatoms	-67.84	-69.78	2011	Jan. 18	2.85	-18.5	0.26	6.1	0.10	Antarctic Peninsula
PH 35*	Diatoms	-64.79	-64.07	2011	Mar. 1	3.7	-32.0	0.31	2.5	0.28	Antarctic Peninsula
PH 35b*	Diatoms	-64.79	-64.07	2011	Mar. 1	3.7	-32.0	0.31	2.5	0.28	Antarctic Peninsula
PH 36*	Diatoms	-64.79	-64.07	2011	Mar. 7	3.61	-28.3	0.19	2.2	0.28	Antarctic Peninsula

Table 2.2 – Sample information for krill.

Sample ID	Species	Size Class	Latitude	Longitude	Year	Date	Avg % Lipid	δ15N	δ13C	Avg Number of Krill per Sample
Kr1*	E. superba	Gravid	-66.991	-69.280	2007/08	Jan	28.4			22
Kr2	E. superba	Mature Females	-66.991	-69.280	2007/08	Jan	24.54			27
Kr3*	E. superba	Gravid	-66.991	-69.280	2007/08	Jan	30.2			18
KR4	E. superba	Mature Females	-66.991	-69.280	2007/08	Jan	23.46			24
Kr5*	E. superba	Gravid	-66.991	-69.280	2007/08	Jan	29.9			22
Kr6	E. superba	Mature Females	-66.991	-69.280	2007/08	Jan	26.17			19
Kr7	E. superba	Juveniles	-66.991	-69.280	2007/08	Jan	17.62			120
Kr9*	E. superba	Gravid	-66.991	-69.280	2007/08	Jan	26.2	5.04	-22.57	21
Kr10	E. superba	Mature females	-66.991	-69.280	2007/08	Jan	22.31	5.34	-22.64	26
Kr11*	E. superba	Gravid	-66.991	-69.280	2007/08	Jan	27.6	4.55	-22.10	41
Kr12	E. superba	Mature females	-66.991	-69.280	2007/08	Jan	19.85	4.75	-22.90	38
Kr13	E. superba	Juveniles	-64.895	-64.181	2007/08	Jan. 13	20.97			182
Kr14*	E. superba	Adult	-66.991	-69.280	2007/08	Jan	25.4	4.83	-24.80	40
Kr15*	E. superba	Adult	-64.895	-64.181	2007/08	Jan	25.7	3.48	-26.91	107
Kr16*	Thysan	Thysan	-64.895	-64.181	2007/08	Jan	13.7			
Kr17*	E. superba	Adult	-64.929	-64.251	2007/08	Jan	25.2	3.81	-27.60	86
Kr18*	E. superba	Juveniles	-68.030	-69.285	2007/08	Jan. 2008	19.5			272
Kr19*	E. superba	Adult	-64.929	-64.251	2007/08	Jan	24.6	3.41	-27.21	177
Kr20	Thysan	Thysan	-64.929	-64.251	2007/08	Jan	15.45			
Kr21	E. superba	Juveniles	-64.929	-64.251	2007/08	Jan	18.01	3.54	-27.55	216
Kr22*	E. superba	Adult	-68.030	-69.285	2007/08	Jan	24.8	4.06	-25.96	77
Kr23	E. superba	Juveniles	-66.991	-69.280	2007/08	Jan	16.79	4.03	-25.22	252
Kr24*	E. superba	Adults	-66.991	-69.280	2007/08	Jan	24.3	5.06	-24.32	59
Kr25*	E. superba	Adult	-64.929	-64.251	2007/08	Jan. 13	18.0	3.51	-27.14	89
Kr26*	E. superba	Adult	-67.379	-70.907	2007/08	Jan	25.8	3.16	-26.54	62
Kr27*	E. superba	Adults	-66.991	-69.280	2007/08	Jan	26.6	5.26	-23.41	59
Kr28*	E. superba	Adults	-64.929	-64.251	2007/08	Jan. 13	19.8	3.27	-27.20	118
Kr29*	E. superba	Juveniles	-67.379	-70.907	2007/08	Jan	20.0	2.92	-26.46	316
Kr30*	E. superba	Juveniles	-67.379	-70.907	2007/08	Jan	18.1	2.54	-26.47	308
Kr31a_Gravid	E. superba	Gravid	-69.102	-76.447	2011	Jan. 27	25.72	3.32	-22.73	11
Kr31c_Adults	E. superba	Adults	-69.102	-76.447	2011	Jan. 27	25.79	4.17	-22.84	41
Kr32*	E. superba	Juveniles	-69.527	-75.516	2011	Jan. 30	32.6	6.50	-18.28	107
Kr33a_Juvis*	E. superba	Juveniles	-64.933	-64.400	2011	Jan. 10	25.1	4.54	-22.53	205
Kr33c_Adults	E. superba	Adults	-64.933	-64.400	2011	Jan. 10	25.92	4.16	-23.55	26
Kr34a_Adults*	E. superba	Adults	-61.936	-73.783	2011	Jan. 9	21.0	4.27	-24.93	38
Kr34b_Gravid	E. superba	Gravid	-61.936	-73.783	2011	Jan. 9	26.84	3.39	-25.14	16

Table 2.3 – Sample Information for fish.

Sample ID	Species	Latitude	Longitude	Date	Percent Lipid	Individuals per sample (n)	$\delta^{13}C$	$\delta^{15}N$
FI 1	Myctophid	-67.62451408	-70.0512331	2010/11	48.09	3	-23.627	9.786
FI 2	Myctophid	-64.93325666	-64.3999942	2010/11	49.64	2	-23.96	9.188
FI 3	Myctophid	-67.51020125	-70.5895846	2010/11	51.94	3	-23.271	9.78
FI 4	Antarctic silverfish	-67.82179931	-69.0923135	2010/11	21.65	2	-21.462	10.968
FI 5	Antarctic silverfish	-67.82179931	-69.0923135	2010/11	31.43	2	-21.419	10.743

Table 2.4 - Fur Seal sample information for the breeding season 2000/01. "ND" indicates no data. For all of the attached fur seal ample info tables, the sampling location is the same at Cape Shirreff, Livingston Island (aprx. 62°28'S, 60°46'W).

Seal ID	Breeding Season	Date	% Lipid	$\delta^{13}C$	$\delta^{15}N$	Breed	Age
203	2000/01	8-Dec-00	75.0	-21.9	11.1	Perinatal	8
208	2000/01	10-Dec-00	69.0	-23.5	9.8	Perinatal	8
199	2000/01	7-Dec-00	73.4	-21.9	11.0	Perinatal	14
190	2000/01	5-Dec-00	60.2	-22.5	10.6	Perinatal	12
201	2000/01	8-Dec-00	82.4	-21.6	10.6	Perinatal	15
207	2000/01	10-Dec-00	61.3	-21.2	11.9	Perinatal	7
196	2000/01	7-Dec-00	64.8	-22.1	10.8	Perinatal	9
211	2000/01	11-Dec-00	66.4	-21.5	11.1	Perinatal	16
205	2000/01	8-Dec-00	56.4	-23.1	9.6	Perinatal	10
206	2000/01	10-Dec-00	66.9	-22.1	10.1	Perinatal	14
197	2000/01	7-Dec-00	66.9	-22.6	10.7	Perinatal	11
216	2000/01	12-Dec-00	63.1	-22.0	10.6	Perinatal	11
214	2000/01	12-Dec-00	58.7	-22.9	10.1	Perinatal	7
195	2000/01	7-Dec-00	65.4	-22.3	10.1	Perinatal	13
215	2000/01	12-Dec-00	62.0	-22.0	10.5	Perinatal	13
192	2000/01	6-Dec-00	60.9	-21.2	12.0	Perinatal	7
204	2000/01	8-Dec-00	67.2	-22.6	10.0	Perinatal	9
188	2000/01	5-Dec-00	73.1	-21.6	10.9	Perinatal	9
202	2000/01	8-Dec-00	69.6	-22.3	11.4	Perinatal	16
200	2000/01	8-Dec-00	74.3	-22.4	10.7	Perinatal	ND
213	2000/01	12-Dec-00	74.6	-21.5	10.9	Perinatal	9

Table 2.5 - Fur Seal sample information for the breeding season 2001/02.

Seal ID	Breeding Season	Date	% Lipid	$\delta^{13}C$	$\delta^{15}N$	Breed	Age
253	2001/02	11-Dec-01	64.51	-21.5	11.8	Perinatal	10
239	2001/02	6-Dec-01	67.08	-23.0	11.0	Perinatal	11
233	2001/02	5-Dec-01	74.96	-22.1	11.3	Perinatal	10
257	2001/02	15-Dec-01	57.90	-22.0	10.3	Perinatal	13
236	2001/02	6-Dec-01	69.73	-22.1	11.6	Perinatal	9
245	2001/02	7-Dec-01	70.23	-23.1	10.8	Perinatal	15
250	2001/02	9-Dec-01	75.27	-21.3	11.2	Perinatal	8

Table 2.6 - Fur Seal sample information for the breeding season 2004/05. "ND" indicates no data.

Seal ID	Breeding Season	Date	% Lipid	$\delta^{13}C$	$\delta^{15}N$	Breed	Age
353	2004/05	5-Dec-04	72.07	-22.8	10.3	Perinatal	14
364	2004/05	11-Dec-04	70.75	-20.6	10.9	Perinatal	8
367	2004/05	11-Dec-04	65.65	-23.1	11.2	Perinatal	9
373	2004/05	12-Dec-04	66.57			Perinatal	17
369	2004/05	12-Dec-04	69.20	-23.7	8.9	Perinatal	11
362	2004/05	7-Dec-04	70.45	-22.7	11.3	Perinatal	ND
361	2004/05	7-Dec-04	73.33	-22.1	10.5	Perinatal	13
358	2004/05	7-Dec-04	70.31	-22.5	10.7	Perinatal	ND
355	2004/05	5-Dec-04	71.09	-22.6	10.9	Perinatal	13
350	2004/05	4-Dec-04	82.42	-22.2	11.3	Perinatal	12
372	2004/05	12-Dec-04	69.85	-22.2	10.7	Perinatal	18
373	2004/05	16-Dec-04	58.79			Perinatal	17

Table 2.7 - Fur Seal sample information for the breeding season 2009/10. "ND" indicates no data.

Seal ID	Breeding Season	Date	% Lipid	$\delta^{13}C$	$\delta^{15}N$	Breed	Age
342	2009/10	2-Dec-09	59.20	-23.7	9.0	Perinatal	14
184	2009/10	5-Dec-09	65.81	-21.4	9.8	Perinatal	17
255	2009/10	4-Dec-09	58.99	-21.6	11.0	Perinatal	13
435	2009/10	13-Dec-09	65.27	-22.4	10.3	Perinatal	13
447	2009/10	7-Dec-09	74.37	-21.4	10.1	Perinatal	13
416	2009/10	14-Dec-09	64.68	-22.0	11.2	Perinatal	9
455	2009/10	14-Dec-09	66.69	-21.5	10.0	Perinatal	14
428	2009/10	4-Dec-09	71.81	-20.8	11.1	Perinatal	12
392	2009/10	4-Dec-09	60.65	-21.5	9.7	Perinatal	13

Table 2.8 – Fur Seal sample information for the breeding season 2010/11.

Seal ID	Breeding Season	Date	% Lipid	$\delta^{13}C$	$\delta^{15}N$	Breed	Age
184	2010/11	4-Dec-10	54.38	-21.2	10.4	Perinatal	17
341	2010/11	10-Dec-10	83.05	-21.8	11.8	Perinatal	16
367	2010/11	1-Dec-10	72.68	-22.8	10.8	Perinatal	14
479	2010/11	4-Dec-10	73.33	-22.0	11.4	Perinatal	13
491	2010/11	14-Dec-10	79.77	-19.6	13.8	Perinatal	ND
482	2010/11	7-Dec-10	70.50	-22.9	11.9	Perinatal	19
461	2010/11	29-Nov-10	78.38	-23.5	9.9	Perinatal	15
389	2010/11	7-Dec-10	68.21	-22.9	11.5	Perinatal	9
473	2010/11	3-Dec-10	74.62	-23.6	9.9	Perinatal	ND
460	2010/11	27-Nov-10	66.51	-23.6	9.2	Perinatal	10

Table 2.9 - Fur Seal sample information for the breeding season 2011/12. "ND" indicates no data.

Seal ID	Breeding Season	Date	% Lipid	$\delta^{13}C$	$\delta^{15}N$	Breed	Age
461	2011/12	28-Nov-11	63.4	-	-	perinatal	16
460	2011/12	29-Nov-11	64.6	-	-	perinatal	11
468	2011/12	2-Dec-11	53.8	-	-	perinatal	10
441	2011/12	3-Dec-11	65.9	-	-	perinatal	14
408	2011/12	4-Dec-11	64.6	-	-	perinatal	14
477	2011/12	5-Dec-11	61.5	-	-	perinatal	14
479	2011/12	4-Dec-11	67.4	-	-	perinatal	9
470	2011/12	5-Dec-11	68.2	-	-	perinatal	13
476	2011/12	5-Dec-11	65.9	-	-	perinatal	12
AO5	2011/12	6-Dec-11	63	-	-	perinatal	11
496	2011/12	7-Dec-11	58.9	-	-	perinatal	10
267	2011/12	8-Dec-11	66.5	-	-	perinatal	10
453	2011/12	8-Dec-11	68.1	-	-	perinatal	14
435	2011/12	10-Dec-11	55	-	-	perinatal	14
AO9	2011/12	13-Dec-11	62.3	-	-	perinatal	5
472	2011/12	3-Jan-12	70.3	-	-	non-perinatal	ND
495	2011/12	3-Jan-12	60.4	-	-	non-perinatal	14
479	2011/12	11-Jan-12	60.6	-	-	non-perinatal	14
461	2011/12	14-Jan-12	59.8	-	-	non-perinatal	16
AO5	2011/12	15-Jan-12	62.2	-	-	non-perinatal	11
460	2011/12	16-Jan-12	62.2	-	-	non-perinatal	11
476	2011/12	20-Jan-12	64.4	-	-	non-perinatal	12
496	2011/12	21-Jan-12	66.5	-	-	non-perinatal	10
AO9	2011/12	23-Jan-12	64.7	-	-	non-perinatal	5
477	2011/12	24-Jan-12	59	-	-	non-perinatal	14
470	2011/12	26-Jan-12	61.5	-	-	non-perinatal	13

Table 2.10 - Fur Seal sample information for the breeding season 2012/13. "ND" indicates no data.

Seal ID	Breeding Season	Date	% Lipid	$\delta^{13}C$	$\delta^{15}N$	Breed	Age
227	2012/13	28-Nov-12	55.8	-	-	Perinatal	15
A03	2012/13	29-Nov-12	50	-	-	Perinatal	11
460	2012/13	29-Nov-12	65.3	-	-	Perinatal	12
486	2012/13	1-Dec-12	67	-	-	Perinatal	11
A05	2012/13	1-Dec-12	51.7	-	-	Perinatal	12
479	2012/13	2-Dec-12	57.1	-	-	Perinatal	15
2975	2012/13	3-Dec-12	60.7	-	-	Perinatal	11
470	2012/13	3-Dec-12	52	-	-	Perinatal	14
477	2012/13	3-Dec-12	58	-	-	Perinatal	15
381	2012/13	4-Dec-12	64.4	-	-	Perinatal	19
359	2012/13	4-Dec-12	62.4	-	-	Perinatal	14
474	2012/13	14-Dec-12	60.7	-	-	Perinatal	15
423	2012/13	4-Dec-12	57.9	-	-	Perinatal	17
423	2012/13	4-Dec-12	53	-	-	Perinatal	17
267	2012/13	6-Dec-12	61.3	-	-	Perinatal	15
452	2012/13	6-Dec-12	57.6	-	-	Perinatal	20
A01	2012/13	6-Dec-12	60.5	-	-	Perinatal	12
408	2012/13	8-Dec-12	59.7	-	-	Perinatal	10
386	2012/13	8-Dec-12	63.9	-	-	Perinatal	13
475	2012/13	8-Dec-12	60.5	-	-	Perinatal	7
416	2012/13	10-Dec-12	63.7	-	-	Perinatal	11
416	2012/13	10-Dec-12		-	-	Perinatal	11
455	2012/13	10-Dec-12	68.2	-	-	Perinatal	16
488	2012/13	10-Dec-12	61.4	-	-	Perinatal	13
A09	2012/13	11-Dec-12	58.9	-	-	Perinatal	6
482	2012/13	11-Dec-12	59.7	-	-	Perinatal	21
400	2012/13	16-Dec-12	61.4	-	-	Perinatal	19
A06	2012/13	17-Dec-12	50.9	-	-	Perinatal	14
492	2012/13	26-Dec-12	48	-	-	Non-Perinatal	19
478	2012/13	29-Dec-12	52	-	-	Non-Perinatal	9
495	2012/13	30-Dec-12	52.5	-	-	Non-Perinatal	15
6093	2012/13	30-Dec-12	67	-	-	Non-Perinatal	4
472	2012/13	2-Jan-13	68.9	-	-	Non-Perinatal	ND
435	2012/13	5-Jan-13	59	-	-	Non-Perinatal	15

Table 2.11 - Plankton sample concentration information. BDEs-2, -8, -15, and -30 were not detected and are thus not presented. Concentrations are in ng/g lipid and the values below have a recovery correction factor of 78.94% (average Recovery for PCBs) applied to account for any potential losses. Sample IDs that are accompanied by an *asterisk** indicate a $\delta^{15}N$ value > 2.0‰.

Sample ID	Date	BDE-28	BDE-49	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	Sum (ng/g lipid)
PH 1	30-Dec-07	6.6	0.0	15.1	4.0	19.5	0.0	5.5	22.3	**73.0**
PH 2	16-Dec-07	3.5	5.1	49.7	12.0	48.3	7.7	8.6	13.1	**147.9**
PH 3	16-Dec-07	5.4	0.0	41.2	8.8	32.9	3.9	10.7	14.2	**117.2**
PH 4	19-Dec-07	0.0	0.0	0.0	0.0	0.0	0.0	6.6	0.0	**6.6**
PH 5*	1-Jan-08	2.7	0.0	10.9	2.6	5.8	1.9	2.4	0.0	**26.4**
PH 6*	30-Dec-07	2.4	0.0	12.8	2.5	7.2	0.0	3.0	4.7	**32.7**
PH 7	31-Dec-07	0.0	0.0	23.8	3.5	14.3	0.0	4.7	0.0	**46.3**
PH 8	31-Dec-07	8.5	0.0	51.1	9.6	34.8	7.7	14.0	46.1	**171.8**
PH 9	30-Dec-07	0.0	4.9	5.6	0.0	9.7	0.0	8.2	0.0	**28.4**
PH 10	14-Dec-07	0.0	0.0	32.4	9.3	24.9	2.8	7.4	16.0	**92.7**
PH 11	31-Dec-07	9.4	0.0	17.1	5.9	13.2	0.0	6.3	0.0	**51.8**
PH 13	30-Dec-07	0.0	0.0	29.2	5.6	18.3	0.0	8.5	0.0	**61.6**
PH 15	19-Dec-07	0.0	0.0	42.8	10.7	18.4	0.0	0.0	0.0	**71.9**
PH 16	28-Jan-10	4.2	5.5	134.0	34.6	140.3	15.6	19.8	0.0	**354.0**
PH 17*	13-Jan-10	7.7	0.0	131.0	42.9	173.2	17.6	30.8	19.0	**422.3**
PH 19	2-Jan-08	10.8	0.0	7.1	0.0	0.0	0.0	15.3	0.0	**33.2**
PH 20	21-Jan-10	1.4	0.0	1.0	0.7	1.4	0.0	1.7	0.0	**6.2**
PH 21	21-Jan-10	1.0	0.0	1.7	0.7	1.4	0.0	1.8	0.0	**6.6**
PH 23*	23-Dec-10	6.6	15.2	188.0	49.9	227.3	23.6	38.0	0.0	**548.6**
PH 24	5-Jan-11	6.7	0.0	161.8	40.5	187.8	22.3	30.5	0.0	**449.5**
PH 26	5-Mar-11	0.0	2.0	23.8	5.8	29.0	3.3	6.8	0.0	**70.7**
PH 26b	5-Mar-11	0.0	0.0	20.7	10.1	20.1	0.0	0.0	0.0	**50.8**
PH 27	26-Dec-10	7.3	19.1	138.8	33.7	142.2	12.6	20.0	20.9	**394.7**
PH 28	5-Jan-11	6.7	13.2	256.5	60.3	284.7	26.8	34.5	19.9	**702.6**
PH 29	8-Jan-11	8.1	0.0	219.1	52.2	218.3	24.0	24.0	0.0	**545.7**
PH 31*	7-Mar-11	2.0	0.0	10.3	0.0	4.9	0.0	0.0	0.0	**17.2**
PH 32*	1-Feb-11	0.0	0.0	4.8	0.0	0.0	0.0	0.0	0.0	**4.8**
PH 33*	1-Jan-11	1.4	2.0	45.2	13.9	58.0	5.9	7.1	4.1	**137.4**
PH 34*	18-Jan-11	0.0	0.0	10.6	1.9	6.6	0.0	0.0	0.0	**19.0**
PH 35*	1-Mar-11	0.0	0.0	7.1	1.7	9.8	0.0	2.4	0.0	**21.0**
PH 35b*	1-Mar-11	0.0	0.0	6.6	0.0	3.7	0.0	0.0	0.0	**10.3**
PH 36*	7-Mar-11	0.0	0.0	7.2	0.0	6.4	0.0	3.1	0.0	**16.7**
avg		**3.2**	**2.1**	**53.3**	**13.2**	**55.1**	**5.5**	**10.1**	**5.6**	**148.1**
median		**1.7**	**0.0**	**22.2**	**5.7**	**18.4**	**0.0**	**6.7**	**0.0**	**56.7**
stdev		**3.5**	**4.8**	**70.5**	**18.0**	**80.4**	**8.6**	**11.0**	**10.6**	**194.8**
sterr		**0.6**	**0.9**	**12.5**	**3.2**	**14.2**	**1.5**	**1.9**	**1.9**	**34.4**
%detect		59%	25%	97%	78%	91%	44%	81%	31%	100%

Table 2.12 – Krill sample concentration information. Concentrations are in ng/g lipid and the values below have a recovery correction factor of 69.1% (based on α-HCH-d_6 in a surrogate standard) applied to account for any potential losses. Sample IDs that are accompanied by an *asterisk** indicate a combined sample of replicates.

Sample ID	Year	Date	BDE-2	BDE-8	BDE-15	BDE-30	BDE-28	BDE-49	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	Sum
Kr1*	2007/08	Jan	0.00	0.00	0.00	0.00	0.09	0.30	0.14	0.00	0.00	0.00	0.00	0.00	0.54
Kr2	2007/08	Jan	0.00	0.00	0.00	0.00	0.00	0.00	0.34	0.00	0.02	0.00	0.20	0.41	0.97
Kr3*	2007/08	Jan	0.00	0.00	0.00	0.00	0.06	0.00	0.19	0.00	0.00	0.00	0.05	0.00	0.30
KR4	2007/08	Jan	0.00	0.00	0.00	0.00	0.17	0.00	0.54	0.00	0.02	0.00	0.00	0.00	0.73
Kr5*	2007/08	Jan	0.00	0.00	0.00	0.00	0.04	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.17
Kr6	2007/08	Jan	0.00	0.00	0.00	0.00	0.00	0.00	0.82	0.00	0.27	0.00	0.00	0.00	1.09
Kr7	2007/08	Jan	0.00	0.00	0.00	0.00	0.30	0.00	1.02	0.00	0.25	0.00	0.00	0.00	1.56
Kr9*	2007/08	Jan	0.00	0.00	0.00	0.00	0.15	0.00	0.56	0.00	0.06	0.00	0.15	0.00	0.92
Kr10	2007/08	Jan	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.10
Kr11*	2007/08	Jan	0.00	0.00	0.00	0.00	0.07	0.00	0.08	0.00	0.11	0.00	0.00	0.00	0.26
Kr12	2007/08	Jan	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.12
Kr13	2007/08	Jan. 13	0.00	0.00	0.00	0.00	0.00	0.00	0.37	0.28	0.10	0.00	0.00	0.00	0.75
Kr14*	2007/08	Jan	0.00	0.00	0.00	0.00	0.12	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.37
Kr15*	2007/08	Jan. 13	0.00	0.00	0.00	0.00	0.05	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.18
Kr16*	2007/08	Jan. 13	0.00	0.00	0.00	0.00	0.61	0.00	0.97	0.00	0.21	0.00	0.00	0.00	1.79
Kr17*	2007/08	Jan. 13	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.09
Kr18*	2007/08	Jan	0.00	0.00	0.00	0.00	0.06	0.00	0.42	0.00	0.03	0.00	0.00	0.00	0.51
Kr19*	2007/08	Jan. 13	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.03	0.00	0.00	0.00	0.12
Kr20	2007/08	Jan. 13	0.00	0.00	0.00	0.00	0.00	0.00	0.81	0.00	0.14	0.00	0.00	0.00	0.95
Kr21	2007/08	Jan. 13	0.00	0.00	0.00	0.00	0.00	0.00	1.11	0.00	0.13	0.00	0.00	0.00	1.24
Kr22*	2007/08	Jan	0.00	0.00	0.00	0.00	0.11	0.00	0.61	0.00	0.02	0.00	0.00	0.00	0.74
Kr23	2007/08	Jan	0.00	0.00	0.00	0.00	0.44	0.00	1.03	0.00	0.00	0.00	0.00	0.00	1.47
Kr24*	2007/08	Jan	0.00	0.00	0.00	0.00	0.00	0.00	0.89	0.69	2.69	0.30	0.43	0.00	4.99
Kr25*	2007/08	Jan. 13	0.00	0.00	0.00	0.00	0.19	0.00	0.50	0.00	0.04	0.00	0.04	0.00	0.77
Kr26*	2007/08	Jan	0.00	0.00	0.00	0.00	0.00	0.00	0.41	0.00	0.08	0.00	0.00	0.00	0.49
Kr27*	2007/08	Jan	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.00	0.05	0.00	0.00	0.00	0.24
Kr28*	2007/08	Jan. 13	0.00	0.00	0.00	0.00	0.00	0.00	0.17	0.00	0.02	0.00	0.00	0.00	0.20
Kr29*	2007/08	Jan	0.00	0.00	0.00	0.00	0.00	0.00	0.60	0.00	0.03	0.00	0.00	0.00	0.63
Kr30*	2007/08	Jan	0.00	0.00	0.00	0.00	0.09	0.00	0.72	0.00	0.04	0.00	0.00	0.00	0.84
Kr31a_Gravid	2011	Jan. 27	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.16	0.24	0.00	0.00	0.00	0.79
Kr31c_Adults	2011	Jan. 27	0.00	0.00	0.00	0.00	0.20	0.00	0.16	0.00	0.00	0.00	0.00	0.00	0.36
Kr32*	2011	Jan. 30	0.00	0.00	0.00	0.00	0.04	0.00	0.58	0.00	0.02	0.00	0.00	0.39	1.04
Kr33a_Juvis*	2011	Jan. 10	0.06	0.00	0.00	0.00	0.02	0.00	0.41	0.11	0.04	0.00	0.00	0.45	1.01
Kr33c_Adults	2011	Jan. 10	0.00	0.00	0.00	0.00	0.00	0.00	1.30	0.00	0.00	0.00	0.00	0.00	1.30
Kr34a_Adults*	2011	Jan. 9	0.00	0.00	0.00	0.00	0.07	0.00	0.50	0.00	0.02	0.00	0.36	1.57	2.52
Kr34b_Gravid	2011	Jan. 9	0.00	0.00	0.00	0.00	0.20	0.00	0.34	0.00	0.00	0.00	0.00	0.00	0.54

Table 2.13 - Summary of linear regressions of plankton concentration (ng/g lipid) vs. $\delta^{13}C$. Results are only shown for compounds that had > 30% detection and p-values are only highlighted when they are significant (<0.05) or nearly significant. In cases of a significant p-value, the + or – indicates a positive or negative trend, respectively. In this case, a positive trend would indicate increasing concentration as $\delta^{13}C$ values become more enriched (less negative) and negative trend indicates decreasing concentration as $\delta^{13}C$ values become more enriched (less negative).

Plankton Regressions of Concentration (ng/g lipid) v δ13C					
		All Years	2007/08	2009/10	2010/11
	Sample Size	30	13	3	14
BDE-2	**%Detection**	-	-	-	-
	p-value	-	-	-	-
BDE-8	**%Detection**	-	-	-	-
	p-value	-	-	-	-
BDE-15	**%Detection**	-	-	-	-
	p-value	-	-	-	-
BDE-30	**%Detection**	-	-	-	-
	p-value	-	-	-	-
BDE-28	**%Detection**	59%	54%	100%	50%
	p-value	0.57	0.503	0.805	0.428
BDE-49	**%Detection**	-	-	-	36%
	p-value	-	-	-	0.593
BDE-47	**%Detection**	97%	92%	100%	100%
	p-value	0.368	0.547	0.935	0.257
BDE-100	**%Detection**	78%	77%	100%	71%
	p-value	0.208	0.439	0.975	0.242
BDE-99	**%Detection**	91%	85%	100%	100%
	p-value	0.17	0.648	0.965	0.092, -
BDE-154	**%Detection**	44%	38%	67%	50%
	p-value	0.338	0.587	0.959	0.28
BDE-153	**%Detection**	81%	92%	100%	64%
	p-value	0.045, -	0.371	0.96	0.161
BDE-183	**%Detection**	31%	46%	-	-
	p-value	0.187	0.671	-	-
ΣPBDEs	**%Detection**	100%	100%	100%	100%
	p-value	0.118	0.315	0.962	0.159

Table 2.14 - Summary of linear regressions of plankton concentration (ng/g lipid) vs. $\delta^{15}N$. Results are only shown for compounds that had > 30% detection and p-values are only highlighted when they are significant (<0.05) or nearly significant. In cases of a significant p-value, the + or – indicates a positive or negative trend, respectively. In this case, a positive trend would indicate increasing concentration as $\delta^{15}N$ values become more enriched and negative trend indicates decreasing concentration as $\delta^{15}N$ values become more enriched.

Plankton Regressions Concentration (ng/g lipid) v δ15N					
		All Years	2007/08	2009/10	2010/11
	Sample Size	30	13	3	14
BDE-2	**%Detection**	-	-	-	-
	p-value	-	-	-	-
BDE-8	**%Detection**	-	-	-	-
	p-value	-	-	-	-
BDE-15	**%Detection**	-	-	-	-
	p-value	-	-	-	-
BDE-30	**%Detection**	-	-	-	-
	p-value	-	-	-	-
BDE-28	**%Detection**	59%	54%	100%	50%
	p-value	0.336	0.817	0.093, +	0.06, -
BDE-49	**%Detection**	-	-	-	36%
	p-value	-	-	-	0.24
BDE-47	**%Detection**	97%	92%	100%	100%
	p-value	0.619	0.512	0.354	0.036, -
BDE-100	**%Detection**	78%	77%	100%	71%
	p-value	0.542	0.668	0.314	0.054, -
BDE-99	**%Detection**	91%	85%	100%	100%
	p-value	0.514	0.41	0.323	0.019, -
BDE-154	**%Detection**	44%	38%	67%	50%
	p-value	0.962	0.743	0.329	0.047, -
BDE-153	**%Detection**	81%	92%	100%	64%
	p-value	0.069, -	0.627	0.248	0.022, -
BDE-183	**%Detection**	31%	46%	-	-
	p-value	0.204	0.691	-	-
ΣPBDEs	**%Detection**	100%	100%	100%	100%
	p-value	0.233	0.25	0.326	0.023, -

Table 2.15 - Summary of linear regressions of plankton concentration (ng/g lipid) vs. date. For the regressions performed for "All Years," all plankton concentrations were used for each sampling year to determine interannual variability. For regressions performed for individual years (i.e. 2007/08, etc…), plankton concentrations were plotted versus individual sampling date. Results are only shown for compounds that had > 30% detection and p-values are only highlighted when they are significant (<0.05) or nearly significant. In cases of a significant p-value, the + or – indicates a positive or negative trend, respectively. In this case, a positive trend would indicate increasing concentration over time (i.e. towards the end of the summer) and negative trend indicates decreasing concentration over time.

Regressions of plankton concentration (ng/g lipid) v date					
		All Years	2007/08	2009/10	2010/11
	Sample Size	32	14	4	14
BDE-2	**%Detection**	-	-	-	-
	p-value	-	-	-	-
BDE-8	**%Detection**	-	-	-	-
	p-value	-	-	-	-
BDE-15	**%Detection**	-	-	-	-
	p-value	-	-	-	-
BDE-30	**%Detection**	-	-	-	-
	p-value	-	-	-	-
BDE-28	**%Detection**	41%	100%	100%	50%
	p-value	0.681	0.276	0.656	0.001, -
BDE-49	**%Detection**	-	-	-	36%
	p-value	-	-	-	0.022, -
BDE-47	**%Detection**	97%	93%	100%	100%
	p-value	0.263	0.56	0.957	0.0009, -
BDE-100	**%Detection**	71%	79%	100%	71%
	p-value	0.332	0.153	0.906	0.001, -
BDE-99	**%Detection**	91%	85%	100%	93%
	p-value	0.173	0.336	0.918	0.006, -
BDE-154	**%Detection**	44%	36%	50%	50%
	p-value	0.107	0.122	0.926	0.0005, -
BDE-153	**%Detection**	81%	93%	100%	64%
	p-value	0.639	0.719	0.82	0.005, -
BDE-183	**%Detection**	31%	43%	-	-
	p-value	0.199	0.249	-	-
ΣPBDEs	**%Detection**	100%	100%	100%	100%
	p-value	0.562	0.422	0.922	0.002, -

Table 2.16 - Results for the two-sample t-test assuming unequal variances for diatom concentration vs. *Phaeocystis sp.* concentration. P-values presented are from the one-tailed test and a + icon indicates that the mean of *Phaeocystis sp.* was significantly greater than the mean of diatoms. The t-test was only run in the cases where both diatoms and *Phaeocystis sp.* had > 30% detection of the congener in question.

T-test		% Detection	p-value
BDE-28	**Diatoms**	42%	0.009, +
	Phaeocystis	70%	
BDE-47	**Diatoms**	100%	0.029, +
	Phaeocystis	95%	
BDE-100	**Diatoms**	67%	0.033, +
	Phaeocystis	90%	
BDE-99	**Diatoms**	92%	0.057, +
	Phaeocystis	90%	
BDE-153	**Diatoms**	58%	0.004, +
	Phaeocystis	95%	
ΣPBDEs	**Diatoms**	100%	0.01, +
	Phaeocystis	100%	

Table 2.17 - Results for the two-sample t-test assuming unequal variances for phytoplankton concentration vs. 'mixed' plankton concentration based on the definition that mixed plankton is any plankton sample with a $\delta^{15}N$ value >2.0‰. P-values presented are from the one-tailed test and a + icon indicates that the mean of phytoplankton was significantly greater than the mean of mixed plankton. The t-test was only run in the cases where both phyto and mixed plankton had > 30% detection of the congener in question.

T-test		% Detection	p-value
BDE-28	**Phyto**	58%	0.187
	Mixed	55%	
BDE-47	**Phyto**	95%	0.149
	Mixed	100%	
BDE-100	**Phyto**	84%	0.082
	Mixed	64%	
BDE-99	**Phyto**	95%	0.147
	Mixed	91%	
BDE-154	**Phyto**	53%	0.198
	Mixed	36%	
BDE-153	**Phyto**	89%	0.036, +
	Mixed	64%	
ΣPBDEs	**Phyto**	100%	0.059, +
	Mixed	100%	

Table 2.18 - Summary of krill regressions for concentration (ng/g lipid) v $\delta^{13}C$. Values presented here are only for those congeners that had detection > 30% of the time. All years* is indicative of the same regression run, excluding sample "Kr24."

Krill Regressions of Concentration (ng/g lipid) v δ13C			
		All Years	All Years*
	Sample Size	25	24
BDE-28	**%Detection**	52%	54%
	p-value	0.972	0.99
BDE-47	**%Detection**	100%	100%
	p-value	0.862	0.827
BDE-99	**%Detection**	64%	63%
	p-value	0.812	0.661
ΣPBDEs	**%Detection**	100%	100%
	p-value	0.596	0.577

Table 2.19 - Summary of krill regressions for concentration (ng/g lipid) v $\delta^{15}N$. Values presented here are only for those congeners that had detection > 30% of the time. All years* is indicative of the same regression run, excluding sample "Kr24."

Krill Regressions of Concentration (ng/g lipid) v δ15N			
		All Years	All Years*
	Sample Size	25	24
BDE-28	**%Detection**	52%	54%
	p-value	0.853	0.973
BDE-47	**%Detection**	100%	100%
	p-value	0.742	0.53
BDE-99	**%Detection**	64%	63%
	p-value	0.4	0.365
ΣPBDEs	**%Detection**	100%	100%
	p-value	0.475	0.966

Table 2.20 - Results for the two-sample t-test assuming unequal variances for krill concentrations in 2007/08 vs. 2010/11 (ng/g lipid). P-values presented are from the one-tailed test and a + icon indicates that the mean from 2010/11 is greater than that from 2007/08. The t-test was only run in the cases where there was > 30% detection of the congener in question and the right-hand side is the test excluding sample "Kr24."

		All Samples		Without 'Kr24'	
T-test		**% Detection**	**p-value**	**% Detection**	**p-value**
BDE-28	**2007/08**	52%	0.423	54%	0.401
	2010/11	71%		71%	
BDE-47	**2007/08**	100%	0.329	100%	0.293
	2010/11	100%		100%	
BDE-99	**2007/08**	72%	0.149	63%	0.34
	2010/11	57%		57%	
ΣPBDEs	**2007/08**	100%	0.11	100%	0.06, +
	2010/11	100%		100%	

Table 2.21 - Results for the two-sample t-test assuming unequal variances for juvenile vs. adult krill. P-values presented are from the one-tailed test and a + icon indicates that the mean of juveniles is greater than that of adults. The t-test was only run in the cases where there was > 30% detection of the congener in question and the right-hand side is the test excluding sample "Kr24."

				All Samples	Without 'Kr24'
T-test		**Sample Size (n)**	**% Detection**	**p-value**	**p-value**
BDE-28	**Juveniles**	**9**	52%	0.18	0.196
	Adults	**18**	71%		
BDE-47	**Juveniles**	**9**	100%	0.009, +	0.005, +
	Adults	**18**	100%		
BDE-99	**Juveniles**	**9**	72%	0.308	0.129
	Adults	**18**	57%		
ΣPBDEs	**Juveniles**	**9**	100%	0.083, +	0.009, +
	Adults	**18**	100%		

Table 2.22 - Results for the two-sample t-test assuming unequal variances for adult vs. gravid krill. P-values presented are from the one-tailed test and a + icon indicates that the mean of adults is greater than that of gravid krill. The t-test was only run in the cases where there was > 30% detection of the congener in question and the right-hand side is the test excluding sample "Kr24."

				All Samples	Without 'Kr24'
T-test		**Sample Size (n)**	**% Detection**	**p-value**	**p-value**
BDE-28	**Adults**	**18**	39%	0.117	0.138
	Gravid	**7**	86%		
BDE-47	**Adults**	**18**	100%	0.093, +	0.139
	Gravid	**7**	100%		
BDE-99	**Adults**	**18**	61%	0.261	0.286
	Gravid	**7**	57%		
ΣPBDEs	**Adults**	**18**	100%	0.183	0.349
	Gravid	**7**	100%		

Table 2.23 - Results for the two-sample t-test assuming unequal variances for adult vs. *Thysanoessa sp*. P-values presented are from the one-tailed test and a - icon indicates that the mean of *Thysanoessa sp.* is greater than that of adult krill. The t-test was only run in the cases where there was > 30% detection of the congener in question.

				All Samples
T-test		**Sample Size (n)**	**% Detection**	**p-value**
BDE-28	**Adults**	**18**	39%	0.285
	Thysan	**2**	50%	
BDE-47	**Adults**	**18**	100%	0.001, -
	Thysan	**2**	100%	
BDE-99	**Adults**	**18**	61%	0.235
	Thysan	**2**	100%	
ΣPBDEs	**Adults**	**18**	100%	0.121
	Thysan	**2**	100%	

Table 2.24 - Summary of fur seal milk regressions for concentration (ng/g lipid) vs. Age. Values presented here are only for those congeners that had detection > 30% of the time. A positive, +, indicates increasing concentration with increasing age and a negative, -, indicates decreasing concentration with increasing age.

		Regressions of Seal Milk Concentration vs. Age								
		All years 2000/01 - 2012/13	2000/01	2001/02	2004/05	2009/10	2010/11	2011/12	2012/13	2000/01 - 2010/11
	Sample Size	106.00	20.00	7.00	8.00	9.00	8.00	25.00	33.00	48.00
BDE-2	%Detection	-	-	-	-	-	-	-	67%	-
	p-value	-	-	-	-	-	-	-	0.10, +	-
BDE-8	%Detection	-	-	-	-	-	-	-	-	-
	p-value	-	-	-	-	-	-	-	-	-
BDE-15	%Detection	-	-	-	-	-	-	-	-	-
	p-value	-	-	-	-	-	-	-	-	-
BDE-30	%Detection	-	-	-	-	-	-	40%	55%	-
	p-value	-	-	-	-	-	-	0.37	0.96	-
BDE-28	%Detection	61%	-	-	38%	-	38%	100%	97%	-
	p-value	0.19	-	-	0.10, +	-	0.29	0.15	0.52	-
BDE-49	%Detection	70%	50%	-	38%	-	63%	100%	100%	33%
	p-value	0.18	0.52	-	0.053, +	-	0.40	0.34	0.02, +	0.84
BDE-47	%Detection	100%	100%	100%	100%	100%	100%	100%	100%	100%
	p-value	0.30	0.78	0.18, +	0.40	0.34	0.44	0.96	0.69	0.52
BDE-100	%Detection	72%	45%	-	75%	44%	50%	100%	97%	40%
	p-value	0.99	0.80	-	0.36	0.61	0.01, -	0.88	0.08, +	0.63
BDE-99	%Detection	93%	85%	71%	100%	100%	75%	100%	100%	85%
	p-value	0.28	0.72	0.78	0.27	0.79	0.32	0.94	0.97	0.68
BDE-154	%Detection	61%	-	-	-	-	50%	100%	97%	-
	p-value	0.84	-	-	-	-	0.09, -	0.66	0.72	-
BDE-153	%Detection	68%	-	-	50%	44%	63%	100%	79%	-
	p-value	0.64	-	-	0.10, -	0.37	0.30	0.81	0.89	-
BDE-183	%Detection	50%	-	-	-	44%	50%	88%	79%	-
	p-value	0.77	-	-	-	0.61	0.91	0.48	0.86	-
ΣPBDEs	%Detection	100%	100%	100%	100%	100%	100%	100%	100%	100%
	p-value	0.27	0.83	0.27	0.45	0.65	0.34	0.68	0.35	0.72

Table 2.25 - Summary of fur seal milk regressions for concentration (ng/g lipid) vs. $\delta^{13}C$. Values presented here are only for those congeners that had detection > 30% of the time. A positive, +, indicates increasing concentration with increasing $\delta^{13}C$ (more enriched, less negative) and a negative, -, indicates decreasing concentration with increasing $\delta^{13}C$ (more enriched, less negative).

Regressions of Seal Milk Concentration (ln) v $\delta^{13}C$							
		All years	**2000/01**	**2001/02**	**2004/05**	**2009/10**	**2010/11**
	Sample Size	57	21	7	10	9	10
BDE-2	**%Detection**	No detection in these years - N/A					
	p-value						
BDE-8	**%Detection**						
	p-value						
BDE-15	**%Detection**						
	p-value						
BDE-30	**%Detection**						
	p-value						
BDE-28	**%Detection**	-	-	-	40%	-	40%
	p-value	-	-	-	0.56	-	0.64
BDE-49	**%Detection**	37%	48%	-	40%	-	50%
	p-value	0.34	0.97	-	0.78	-	0.51
BDE-47	**%Detection**	100%	100%	100%	100%	100%	100%
	p-value	0.10, -	0.62	0.38	0.34	0.25	0.80
BDE-100	**%Detection**	47%	43%	-	80%	44%	60%
	p-value	0.09, -	0.53	-	0.67	0.09, -	0.27
BDE-99	**%Detection**	88%	86%	71%	100%	100%	80%
	p-value	0.14	0.21	0.92	0.57	0.57	0.70
BDE-154	**%Detection**	-	-	-	-	-	50%
	p-value	-	-	-	-	-	0.74
BDE-153	**%Detection**	32%	-	-	50%	44%	70%
	p-value	0.90	-	-	0.41	0.53	0.38
BDE-183	**%Detection**	-	-	-	-	44%	50%
	p-value	-	-	-	-	0.63	0.89
ΣPBDEs	**%Detection**	100%	100%	100%	100%	100%	100%
	p-value	0.25	0.44	0.66	0.60	0.63	0.72

Table 2.26 - Summary of fur seal milk regressions for concentration (ng/g lipid) vs. $\delta^{15}N$. Values presented here are only for those congeners that had detection > 30% of the time. A positive, +, indicates increasing concentration with increasing $\delta^{15}N$ and a negative, -, indicates decreasing concentration with increasing $\delta^{15}N$. For BDE-47 in 2009/10, the * indicates the regression was re-run without a potential outlier (FS10), and the re-run made the relationship nearly significantly negative at p = 0.12.

Regressions of Seal Milk (ln) Concentration v $\delta^{15}N$							
		All years	**2000/01**	**2001/02**	**2004/05**	**2009/10**	**2010/11**
	Sample Size	57	21	7	10	9	10
BDE-2	**%Detection**	No detection in these years - N/A					
	p-value						
BDE-8	**%Detection**						
	p-value						
BDE-15	**%Detection**						
	p-value						
BDE-30	**%Detection**						
	p-value						
BDE-28	**%Detection**	-	-	-	40%	-	40%
	p-value	-	-	-	0.31	-	0.28
BDE-49	**%Detection**	37%	48%	-	40%	-	50%
	p-value	0.84	0.72	-	0.80	-	0.91
BDE-47	**%Detection**	100%	100%	100%	100%	100%	100%
	p-value	0.11	0.75	0.04, -	0.80*	0.08, -	0.56
BDE-100	**%Detection**	47%	43%	-	80%	44%	60%
	p-value	0.39	0.72	-	0.16	0.86	0.33
BDE-99	**%Detection**	88%	86%	71%	100%	100%	80%
	p-value	0.073, -	0.46	0.16	0.53	0.21	0.35
BDE-154	**%Detection**	-	-	-	-	-	50%
	p-value	-	-	-	-	-	0.88
BDE-153	**%Detection**	32%	-	-	50%	44%	70%
	p-value	0.82	-	-	0.39	0.99	0.68
BDE-183	**%Detection**	-	-	-	-	44%	50%
	p-value	-	-	-	-	0.14	0.32
ΣPBDEs	**%Detection**	100%	100%	100%	100%	100%	100%
	p-value	0.27	0.79	0.008, -	0.63	0.94	0.80

Table 2.27 - Summary of analysis of seal milk concentration vs. breeding season. The first two columns (all years and 2000/01 – 2010/11) are linear regressions and a positive, +, indicates a significantly or nearly significantly increasing concentration with time (i.e. breeding season) and a negative, -, indicates a significantly decreasing concentration with time. The third column (2011/12 – 2012/13) is results from a two-sample t-test of means assuming unequal variances (one-tailed). In all cases, %detection was >30% and the negative, -, here represents a significant *decline* in the means between the two years. The asterisk, *, is indicative of the regression being run without a potential outlier to see if any differences were observed. In all cases, the trends remained the same, with some significance actually increasing.

Regressions and T-tests of Seal Milk Concentration vs. Breeding Season				
		All years	**2000/01 - 2010/11**	**2011/12- 2012/13**
	Sample Size	119	59	60
BDE-2	**%Detection**	-	-	>30
	p-value	-	-	0.26
BDE-8	**%Detection**	-	-	>30
	p-value	-	-	0.12
BDE-15	**%Detection**	-	-	>30
	p-value	-	-	0.16
BDE-30	**%Detection**	-	-	>30
	p-value	-	-	0.44
BDE-28	**%Detection**	61%	-	>30
	p-value	0.00017, +	-	0.28
BDE-49	**%Detection**	68%	36%	>30
	p-value	0.0685, +	0.57	0.46
BDE-47	**%Detection**	100%	100%	>30
	p-value	1.78E-11, +	*0.0165, +	0.0232, -
BDE-100	**%Detection**	72%	46%	>30
	p-value	0.0356, +	0.17	0.0494, -
BDE-99	**%Detection**	94%	88%	>30
	p-value	0.0438, -	0.22	0.0296, -
BDE-154	**%Detection**	56%	-	>30
	p-value	5.62E-07, -	*, +	0.039, -
BDE-153	**%Detection**	61%	31%	>30
	p-value	0.00263, +	*0.0004, +	0.00046, -
BDE-183	**%Detection**	48%	-	
	p-value	0.000127, +	*, +	0.0023, -
ΣPBDEs	**%Detection**	100%	100%	100%
	p-value	7.68E-10, +	*0.0025, +	0.0062, -

Table 2.28 - Results for the two-sample t-test assuming unequal variances for perinatal vs. non-perinatal milk. P-values are presented and a + icon indicates the mean of non-perinatal milk is greater than the mean of perinatal milk; a – icon indicated the mean of perinatal milk is greater than non-perinatal. The t-test was only run in the cases where there was > 30% detection of the congener in question. Sample size of perinatal milk in 2011/12 = 15 and in 2012/13 = 28. Sample size of non-perinatal milk in 2011/12 = 11 and in 2012/13 = 6.

	BDE-30	BDE-28	BDE-49	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	ΣPBDEs
2011/12	0.359	0.150	0.118	0.288	0.403	0.329	0.438	0.106	0.301	0.293
2012/13	0.408	0.222	0.098	0.085, +	0.200	0.050, +	0.134	0.143	0.005, -	0.010, +

Table 2.29 - Blank concentrations for all PBDE samples. All blanks consisted of a hydro matrix material and the average of all blanks was subtracted from all samples.

Concentration (ng/sample)	BDE-2	BDE-8	BDE-15	BDE-30	BDE-28	BDE-49	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183
Kr8_BLANK	0.0	0.0	0.0	0.0	0.0	0.0	0.14	0.00	0.19	0.0	0.0	0.0
Kr B6	0.0	0.0	0.0	0.0	0.0	0.0	0.35	0.16	0.60	0.0	0.0	0.0
Kr 20 Blank	0.0	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.0	0.0	0.0
Kr Blank 1	0.0	0.0	0.0	0.0	0.0	0.0	0.33	0.00	0.17	0.0	0.0	0.0
Blank 2	0.0	0.0	0.0	0.0	0.0	0.0	0.14	0.00	0.00	0.0	0.0	0.0
Kr Blank 3	0.0	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.0	0.0	0.0
Blank 7	0.0	0.0	0.0	0.0	0.0	0.0	0.42	0.00	0.33	0.0	0.0	0.0
Blank 8	0.0	0.0	0.0	0.0	0.0	0.0	0.70	0.22	0.65	0.16	0.14	0.0
Blank 11	0.0	0.0	0.0	0.0	0.0	0.0	0.31	0.00	0.41	0.0	0.0	0.0
B9	0.0	0.0	0.0	0.0	0.0	0.0	0.35	0.00	0.50	0.16	0.0	0.0
B10	0.0	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.0	0.0	0.0
B12	0.0	0.0	0.0	0.0	0.0	0.0	0.14	0.00	0.00	0.0	0.0	0.0
Mix9501	0.0	0.0	0.0	0.0	0.0	0.0	0.25	0.00	0.20	0.0	0.0	0.0
002-95-01	0.0	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.0	0.0	0.0
Blank 13	0.0	0.0	0.0	0.0	0.0	0.0	0.17	0.00	0.22	0.0	0.0	0.0
002-70-03RRF	0.0	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.0	0.0	0.0
Blank 4	0.0	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.0	0.0	0.0
PH B5	0.0	0.0	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.0	0.0	0.0
Blank Avg	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.18**	**0.02**	**0.18**	**0.02**	**0.01**	**0.00**
StDev	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.20**	**0.06**	**0.23**	**0.05**	**0.03**	**0.00**

Table 2.30 – Comparison of previous Antarctic PBDE research to this study. All concentrations are in ng/g lipid.

	ΣPBDEs	BDE-28	BDE-47	BDE-99	BDE-100
Plankton	131.65 ± 31.55 *		22.9 ± 3.5 '	22.3 ± 3.4 '	4.5 ± 0.7 '
Phytoplankton	165.86 ± 43.62 *		60.59 ± 60.58 *	59.97 ± 18.02 *	
Mixed Plankton	114.22 ± 57.05 *		39.48 ± 18.6 *	45.72 ± 23.81 *	
Juvenile Krill	1.01 ± 0.12 *		568 ± 209 '	622 ± 253 '	128 ± 50.5 '
		0.11 ± 0.05 *	0.7 ± 0.1 *	0.07 ± 0.03 *	
Adult Krill	0.88 ± 0.28 *		2.0 ± 0.5 '	2.5 ± 0.6 '	0.5 ± 0.1 '
		0.05 ± 0.02 *	0.42 ± 0.08 *	0.18 ± 0.15 *	
Gravid Krill	0.5 ± 0.11 *	0.09 ± 0.03 *	0.26 ± 0.07 *	0.06 ± 0.03 *	
"Krill"	5.6 ± 1.12 ^				
Rockcod muscle	5.81 ± 2.32 ^				
Rockcod Homogenate	4.57 ± 0.17 ^				
Antarctic Silverfish					
Myctophids					
Penguin eggs	3.06 ± 3.27 ^		1.37 ± 0.13 *	0.37 ± 0.03 *	
Fur Seal Milk	2.54 ± 0.19 *				

^ Corsolini et al. 2006, Ross Sea, aprx. 74°04'S, 179°06'E; ' Chiuchiolo et al. 2004, 64.7°S, 64.0°W; * This Study, Ross Sea to Antarctic Peninsula. Note that ΣPBDEs has variation in congeners included between studies

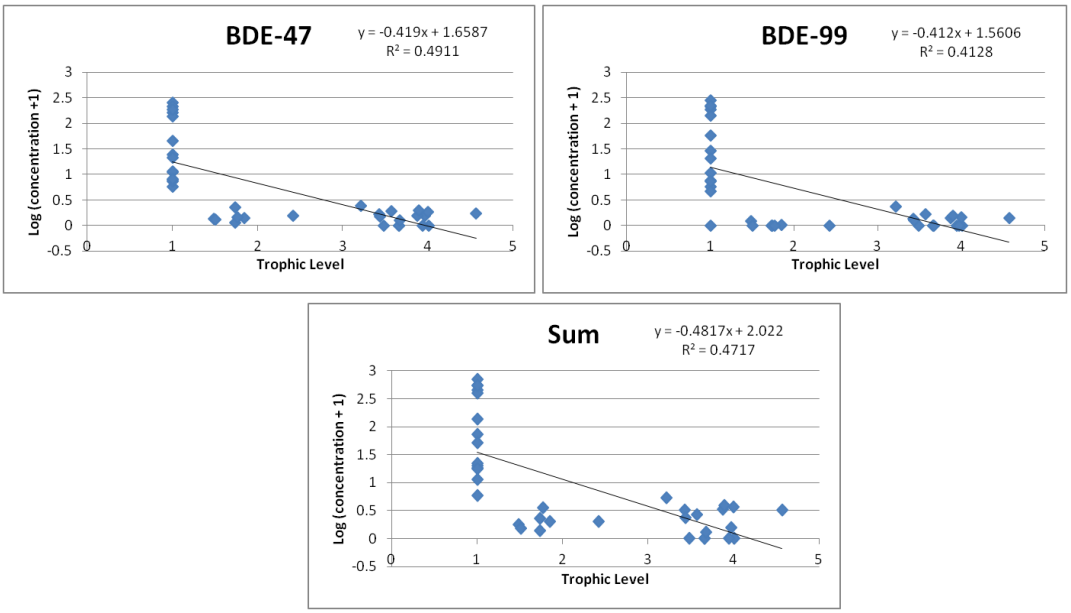


Figure 2.1 – Trophic level vs. log(concentration + 1) for BDE-47, -99, and ΣPBDEs. These slopes were used to determine TMFs for the food web.

Bibliography

Ahrens L, Barber JL, Xie Z, Ebinghaus R (2009) Longitudinal and latitudinal distribution of perfluoroalkyl compounds in the surface water of the Atlantic Ocean. Environ Sci Technol 43:3122–7

Ahrens L, Xie Z, Ebinghaus R (2010) Distribution of perfluoroalkyl compounds in seawater from northern Europe, Atlantic Ocean, and Southern Ocean. Chemosphere 78:1011–6

Bengtson Nash S, Rintoul SR, Kawaguchi S, Staniland I, Hoff J van den, Tierney M, Bossi R (2010) Perfluorinated compounds in the Antarctic region: ocean circulation provides prolonged protection from distant sources. Environ Pollut 158:2985–91

Benskin JP, Muir DCG, Scott BF, Spencer C, Silva AO De, Kylin H, Martin JW, Morris A, Lohmann R, Tomy G, Rosenberg B, Taniyasu S, Yamashita N (2012) Perfluoroalkyl acids in the Atlantic and Canadian Arctic Oceans. Environ Sci Technol 46:5815–23

Booi X (2013) Perfluorinated Compounds and Trihalomethanes in Drinking Water Sources of the Western Cape, South Africa. Cape Peninsula University of Technology

Borgå K, Kidd K a, Muir DCG, Berglund O, Conder JM, Gobas F a PC, Kucklick J, Malm O, Powell DE (2012) Trophic magnification factors: considerations of ecology, ecosystems, and study design. Integr Environ Assess Manag 8:64–84

Borghesi N, Corsolini S, Focardi S (2008) Levels of polybrominated diphenyl ethers (PBDEs) and organochlorine pollutants in two species of Antarctic fish (Chionodraco hamatus and Trematomus bernacchii). Chemosphere 73:155–60

Brault EK, Goebel ME, Geisz HN, Canuel EA, Dickhut RM Persistent Organic Pollutant (POP) and Total Mercury Concentrations in Lower Trophic Level Organisms of the West Antarctic Peninsula Food Web.

Brault EK, Goebel ME, Geisz HN, Canuel E a, Dickhut RM (2013) Inter-annual variation of persistent organic pollutants (POPS) in an Antarctic top predator Arctocephalus gazella. Environ Sci Technol 47:12744–52

Butt CM, Berger U, Bossi R, Tomy GT (2010) Levels and trends of poly- and perfluorinated compounds in the arctic environment. Sci Total Environ 408:2936–65

Chiuchiolo AL, Dickhut RM, Cochran M a, Ducklow HW (2004) Persistent organic pollutants at the base of the Antarctic marine food web. Environ Sci Technol 38:3551–7

COMNAP (2014) Antarctic Facilities List.

Corsolini S, Covaci A, Ademollo N, Focardi S, Schepens P (2006) Occurrence of organochlorine pesticides (OCPs) and their enantiomeric signatures, and concentrations of polybrominated diphenyl ethers (PBDEs) in the Adélie penguin food web, Antarctica. Environ Pollut 140:371–82

Dreyer A, Weinberg I, Temme C, Ebinghaus R (2009) Polyfluorinated compounds in the atmosphere of the Atlantic and Southern Oceans: evidence for a global distribution. Environ Sci Technol 43:6507–14

Fisk a T, Hobson K a, Norstrom RJ (2001) Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the northwater polynya marine food web. Environ Sci Technol 35:732–8

Furl C V, Meredith C a, Strynar MJ, Nakayama SF (2011) Relative importance of wastewater treatment plants and non-point sources of perfluorinated compounds to Washington State rivers. Sci Total Environ 409:2902–7

Geisz HN, Dickhut RM, Cochran M a, Fraser WR, Ducklow HW (2008) Melting glaciers: a probable source of DDT to the Antarctic marine ecosystem. Environ Sci Technol 42:3958–62

Giesy JP, Kannan K (2001) Global distribution of perfluorooctane sulfonate in wildlife. Environ Sci Technol 35:1339–42

Gobas F a PC, Wolf W de, Burkhard LP, Verbruggen E, Plotzke K (2009) Revisiting bioaccumulation criteria for POPs and PBT assessments. Integr Environ Assess Manag 5:624–37

Gonzalez-Gaya B Perfluoroalkylated Substances fate in the Global Ocean: The importance of the Biological Pump. :61

Gonzalez-Gaya B, Dachs J, Roscales JL, Caballero G (2014) Perfluoroalkylated Substances in the Global Tropical and Subtropical Surface Oceans. Environ Sci Technol ASAP

Guerrero RA, Acha EM, Framinan MB, Lasta CA (1997) Physical oceanography of the Rio de la Plata Estuary , Argentina 1. Cont Shelf Res 17:727–742

Hale RC, Kim SL, Harvey E, Guardia MJ La, Mainor TM, Bush EO, Jacobs EM (2008) Antarctic research bases: local sources of polybrominated diphenyl ether (PBDE) flame retardants. Environ Sci Technol 42:1452–7

Hites RA (2004) Critical Review Polybrominated Diphenyl Ethers in the Environment and in People : A Meta-Analysis of Concentrations. Environ Sci Technol 38:945–956

Hobson KA, Ambrose WG (1995) Sources of primary production , benthic-pelagic coupling , and trophic relationships within the Northeast Water Polynya : insights from 613c and 5 1 5 analysis. Mar Ecol Prog Ser 128:1–10

Hobson KA, Welch HE (1992) Determination of trophic relationships within a high Arctic marine food web using d13C and d15N analysis. Mar Ecol Prog Ser 84:9–18

Hop H, Borgå K, Gabrielsen GW, Kleivane L, Skaare JU (2002) Food Web Magnification of Persistent Organic Pollutants in Poikilotherms and Homeotherms from the Barents Sea. Environ Sci Technol 36:2589–2597

Houde M, Martin JW, Letcher RJ, Solomon KR, Muir DCG (2006) Critical Review Biological Monitoring of Polyfluoroalkyl Substances : A Review. Environ Sci Technol 40:3463–3473

Houde M, Silva AO De, Muir DCG, Letcher RJ, Canada E, Saint-laurent C, Street M (2011a) Monitoring of Perfluorinated Compounds in Aquatic Biota : An. Environ Sci Technol 45:7962–7973

Houde M, Silva AO De, Muir DCG, Letcher RJ, Canada E, Saint-laurent C, Street M (2011b) Monitoring of Perfluorinated Compounds in Aquatic Biota : An. Environ Sci Technol 45:7962–7973

Kelly BC, Ikonomou MG, Blair JD, Gobas F a PC (2008) Bioaccumulation behaviour of polybrominated diphenyl ethers (PBDEs) in a Canadian Arctic marine food web. Sci Total Environ 401:60–72

Knauss JA (1997) Major Ocean Currents. In: Introduction to Physical Oceanography, Second. Waveland Press, Inc., Long Grove, Illinois, p 147–149

Kunacheva C, Fujii S, Tanaka S (2012) Worldwide surveys of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in water environment in recent years. Water Sci Technol 66:2764–2772

Lindstrom AB, Strynar MJ, Libelo EL (2011) Polyfluorinated compounds: past, present, and future. Environ Sci Technol 45:7954–61

Lohmann R, Jurado E, Dijkstra H a, Dachs J (2013) Vertical eddy diffusion as a key mechanism for removing perfluorooctanoic acid (PFOA) from the global surface oceans. Environ Pollut 179:88–94

Mudumbi JBN, Ntwampe SKO, Muganza FM, Okonkwo JO (2014) Perfluorooctanoate and perfluorooctane sulfonate in South African river water. Water Sci Technol 69:185–94

Paul AG, Jones KC, Sweetman AJ (2009) A first global production, emission, and environmental inventory for perfluorooctane sulfonate. Environ Sci Technol 43:386–92

Peterson BJ, Fry B (1987) STABLE ISOTOPES IN ECOSYSTEM STUDIES. Annu Rev Ecol Syst 18:293–320

Philander SG (2001) Atlantic Ocean Equatorial Currents. Encycl Ocean Scicences:188–191

Polito MJ, Goebel ME (2010) Investigating the use of stable isotope analysis of milk to infer seasonal trends in the diets and foraging habitats of female Antarctic fur seals. J Exp Mar Bio Ecol 395:1–9

Risebrough R., Walker II W, Schmidt TT, Lappe BW De, Connors CW (1976) Transfer of chlorinated biphenyls to Antarctica. Nature 264:738–739

Sacks VP, Lohmann R (2012) Freely dissolved PBDEs in water and porewater of an urban estuary. Environ Pollut 162:287–93

Sautter GF, Pourtier R (2014) Congo River. Encycl Br:1–4

Schlosser JL, Fine R, Jenkins WJ, Key R, Lupton J, Roether W, Smethie, Jr WM (2001) Transformation and Age of Water Masses. In: Siedler G, Church J, Gould J (eds) Ocean Circulation & Climate: Observing and Modelling the Global Ocean. Academic Press, p 436–441

Speich S, Blanke B, Cai W (2007) Atlantic meridional overturning circulation and the Southern Hemisphere supergyre. Geophys Res Lett 34:n/a–n/a

UNEP (2009) The New POPs.

Vento S Del, Halsall C, Gioia R, Jones K, Dachs J (2012) Volatile per- and polyfluoroalkyl compounds in the remote atmosphere of the western Antarctic Peninsula: an indirect source of perfluoroalkyl acids to Antarctic waters? Atmos Pollut Res 3:450–455

Wang Z, Cousins IT, Scheringer M, Buck RC, Hungerbühler K (2014) Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. Environ Int 70:62–75

Wania F, Ho JT, Jia CQ, Mackay D (1998) The effects of snow and ice on the environmental behaviour of hydrophobic organic chemicals. Environ Pollut 102:25–41

Wania F, Mackay D (1996) Tracking the Distribution of Persistent Organic Pollutants. Environ Sci Technol 30:390–396

Wei S, Chen LQ, Taniyasu S, So MK, Murphy MB, Yamashita N, Yeung LWY, Lam PKS (2007) Distribution of perfluorinated compounds in surface seawaters between Asia and Antarctica. Mar Pollut Bull 54:1813–8

Wolkers H, Bavel B van, Derocher AE, Wiig O, Kovacs KM, Lydersen C, Lindström G (2004) Congener-specific accumulation and food chain transfer of polybrominated diphenyl ethers in two arctic food chains. Environ Sci Technol 38:1667–74

Yamashita N, Kannan K, Taniyasu S, Horii Y, Petrick G, Gamo T (2005) A global survey of perfluorinated acids in oceans. Mar Pollut Bull 51:658–68

Yamashita N, Taniyasu S, Petrick G, Wei S, Gamo T, Lam PKS, Kannan K (2008a) Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. Chemosphere 70:1247–55

Yamashita N, Taniyasu S, Petrick G, Wei S, Gamo T, Lam PKS, Kannan K (2008b) Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. Chemosphere 70:1247–55