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Polybrominated diphenyl ethers (PBDEs) in fish tissue may be an indicator of plastic contamination in marine habitats

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HIGHLIGHTS

- Plastic debris was found at all stations with large variability among stations.
- There was a relationship between plastic and bioaccumulation of PBDEs in fish.
- BDE#s 183–209 may be an indicator of plastic contamination in marine habitats.

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ABSTRACT

The accumulation of plastic debris in pelagic habitats of the subtropical gyres is a global phenomenon of growing concern, particularly with regard to wildlife. When animals ingest plastic debris that is associated with chemical contaminants, they are at risk of bioaccumulating hazardous pollutants. We examined the relationship between the bioaccumulation of hazardous chemicals in myctophid fish associated with plastic debris and plastic contamination in remote and previously unmonitored pelagic habitats in the South Atlantic Ocean. Using a published model, we defined three sampling zones where accumulated densities of plastic debris were predicted to differ. Contrary to model predictions, we found variable levels of plastic debris density across all stations within the sampling zones. Mesopelagic lanternfishes, sampled from each station and analyzed for bisphenol A (BPA), alkylphenols, alkylphenol ethoxylates, polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), exhibited variability in contaminant levels, but this variability was not related to plastic debris density for most of the targeted compounds with the exception of PBDEs. We found that myctophid sampled at stations with greater plastic densities did have significantly larger concentrations of BDE#s 183 –209 in their tissues suggesting that higher brominated congeners of PBDEs, added to plastics as flame-retardants, are indicative of plastic contamination in the marine environment. Our results provide data on a previously unsampled pelagic gyre and highlight the challenges associated with characterizing plastic debris accumulation and associated risks to wildlife.

1. Introduction

Reports of accumulations of floating plastic debris in rotating ocean currents, or gyres (Moore et al., 2001; Law et al., 2010; Goldstein et al., 2013; Eriksen et al., 2013), have led to a growing awareness of the hazards from plastic pollution. Although remote gyre accumulations tend to attract the most media attention, plastic pollution is not unique to pelagic open ocean habitats and is found in most marine and terrestrial habitats, including bays (Endo et al., 2005; Ashton et al., 2010), estuaries (Browne et al., 2010), coral reefs (Donohue et al., 2001), the deep-sea (Goldberg, 1997), beaches (Van et al., 2011), freshwater lakes (Zbyszewski and Corcoran, 2011) and terrestrial deserts (Zylstra, 2013). Plastic in subtropical oceanic gyres has now been reported in the North Pacific (Moore et al., 2001; Goldstein et al., 2013), North Atlantic (Carpenter and Smith, 1972; Law et al., 2010) and South Pacific (Eriksen et al., 2013).

Hazards from plastic debris are both physical e.g., entanglement, smothering (Gregory, 2009); and chemical e.g., bioaccumulation of the chemical ingredients of plastic or chemicals sorbed to plastic from seawater (Teuten et al., 2009). The chemical impacts to wildlife are

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poorly understood, but the complex mixture of chemicals associated with plastic debris is unequivocal (Teuten et al., 2009; Lithner et al., 2011). Plastics are associated with at least 78% of the priority pollutants and 61% of priority substances listed as toxic by the United States Environmental Protection Agency and European Union (Rochman et al., 2013a). These include chemical ingredients of plastic products (e.g., alkylphenols and polybrominated diphenyl ethers (PBDEs); Teuten et al., 2009; Lithner et al., 2011) and chemicals that sorb to plastic from the environment (e.g. toxic metals and persistent organic pollutants (Teuten et al., 2009; Holmes et al., 2012; Rochman et al., 2013b)).

The majority of the plastic debris found in the environment is generally less than 5 mm in diameter (Eriksen et al., 2013; Browne et al., 2010; Thompson et al., 2004) and thus available for ingestion by a wide range of animals, introducing plastic as a vector for hazardous pollutants into aquatic foodwebs. The introduction of plastics into marine foodwebs is well documented (Ryan, 2008; Davison and Asch, 2011; Murray and Cowie, 2011), and thus the extent that plastics transfer hazardous chemicals to wildlife upon ingestion is of concern (Teuten et al., 2009). Laboratory studies have shown the transfer of PBDEs from plastics to the tissues of freshwater fish, lugworms and crickets as a consequence of ingestion (Gaylor et al., 2012; Browne et al., 2013; Rochman et al., 2013c). In nature, the mass of ingested plastic debris has been found to correlate with the concentration of lower chlorinated polychlorinated biphenyls (PCBs) in pelagic seabirds from the North Pacific (PCBs; Yamashita et al., 2011). Furthermore, PBDE congeners BDE-183 and BDE-209 found on ingested plastics, but not in prey items, were found in seabird tissue (Tanaka et al., 2013). Both PCBs and PBDEs are associated with endocrine disrupting effects, teratogenicity and/or liver and kidney toxicity (Brouwer et al., 1999; Ulbrich and Stahlmann, 2004; Muirhead et al., 2006; Yogui and Sericano, 2009). Combined, this evidence suggests that the ingestion of plastic debris may be an important mechanism for the bioaccumulation of hazardous chemicals in wildlife.

Although pelagic habitats of subtropical gyres have historically been considered biological deserts (Polovina et al., 2008), several species of seabirds (Ryan, 2008; Young et al., 2009) and fish (Boerger et al., 2010; Davison and Asch, 2011) have been reported to ingest plastic debris within these regions. Moreover, several chemical contaminants have been identified on plastic debris recovered from subtropical gyres (Rios et al., 2010; Hirai et al., 2012) and from beaches on nearby islands (Rios et al., 2010; Hirai et al., 2012; Heskett et al., 2012), including polycyclic aromatic hydrocarbons (PAHs), PCBs, dichlorodiphenyltrichloroethanes (DDTs), PBDEs, alkylphenols and bisphenol A (BPA). Although the concentrations of chemicals on plastics collected near urban centers are generally greater than those in remote areas (Hirai et al., 2012), large concentrations of sorbed chemical pollutants and plastic ingredients (PCBs, alkylphenols, BPA and PBDEs) are found on plastic debris sampled from subtropical gyres, generally farther from the influence of large urban centers (Hirai et al., 2012). This suggests that pelagic marine animals in remote regions also may be at risk of bioaccumulating plastic-derived chemical pollutants.

The mesopelagic lanternfishes, from the family Myctophidae, have a widespread distribution and comprise at least 20% of marine fish species (McGinnis, 1982; Catul et al., 2011). Ecologically, they represent a critical link between primary consumers and higher trophic levels (Catul et al., 2011; Van Noord, 2013), and are commercially important as prey for commercial fish (e.g., mackerel and tuna; Madhupratap et al., 2001) and as fish meal (McGinnis, 1982). Globally, species within the family Myctophidae have similar trophic positions (Choy et al., 2012), making extensive vertical migrations during the night to feed on zooplankton from the epipelagic zone (Catul et al., 2011; Van Noord, 2013) where large concentrations of floating plastic debris are found (Moore et al., 2001; Law et al., 2010; Goldstein et al., 2013; Eriksen et al., 2013). As a consequence of their vertical migration, these fish ingest plastic debris (Boerger et al., 2010; Davison and Asch, 2011; Van Noord, 2013). The presence of plastic in the epipelagic zone may pose a hazard to myctophids, which may ultimately impact many other organisms, including the top predators and commercially important fish, in open ocean foodwebs (Catul et al., 2011).

Given the existing literature on the prevalence of plastic debris in open ocean gyres (Moore et al., 2001; Law et al., 2010; Goldstein et al., 2013; Eriksen et al., 2013), the associated presence of chemical contaminants (Rios et al., 2010; Hirai et al., 2012; Heskett et al., 2012), the ingestion of plastic in mesopelagic fish (Boerger et al., 2010; Davison and Asch, 2011; Van Noord, 2013) and evidence for bioaccumulation of plastic-derived contaminants (Yamashita et al., 2011; Gaylor et al., 2012; Browne et al., 2013; Rochman et al., 2013c; Tanaka et al., 2013), we consider the potential effects of plastic debris and associated organic chemicals in mesopelagic fish in the South Atlantic subtropical gyre, an unexplored ocean area for plastic debris and contamination. Using a plastic accumulation model (Maximenko et al., 2012) to identify zones where large accumulations of plastic are predicted, we sampled across a 2094 km-long transect of the South Atlantic (Fig. 1) where we expected mesopelagic fish residing in regions with relatively large densities of plastic to have greater concentrations of plastic-associated chemicals (including BPA, alkylphenols, alkylphenol ethoxylates, total PCBs and total PBDEs) in their tissues. In addition, concentrations of each chemical group were measured in water and from plastic debris sampled along our cruise track. Because literature suggests that lower chlorinated PCB (Teuten et al., 2009; Yamashita et al., 2011) and higher brominated PBDE (Tanaka et al., 2013; Gassel et al., 2013) congeners are indicative of plastic ingestion, we also examined this pattern. Here, we contribute novel information on plastic debris abundance and associated chemicals in an important prey fish in an understudied subtropical gyre in the South Atlantic.

2. Methods

2.1. Sample collection

To explore the presence and distribution of plastic pollution in the South Atlantic, the 5Gyres Institute carried out an expedition aboard the sailing vessel *Sea Dragon* from Rio de Janeiro, Brazil on November 8th to Cape Town, South Africa on December 8th 2010. Sampling locations were identified using a debris accumulation model from Maximenko et al. (2012). This model has been shown to accurately describe the observed distribution of plastic accumulations in the North Pacific and North Atlantic subtropical gyres (Law et al., 2010). Based on model predictions, we identified three sampling zones in the subtropical South Atlantic Gyre: inside the zone where plastic accumulation was predicted to be greatest (Location 2) and two areas outside this zone (one due west and the other due east, Locations 1 and 3 respectively) where plastic accumulation was predicted to be less dense (Fig. 1). Choosing two contiguous reference locations ensures that any interpretation regarding differences among locations is not confounded by intrinsic differences between any two locations (Underwood, 2000). Location 1 extended from 34°02′S, 18°11′W to 33°04′S, 11°54′E, Location 2 from 32°19′S, 9°10′W to 33°12′S, 1°17′W and Location 3 from 33°37′S, 1°04′E to 34°08′S, 4°48′E, with 325 km between Locations 1 and 2 and 226 km between Locations 2 and 3.

Fish from the family Myctophidae were sampled from November 25th through December 4th, 2010 from all three locations. At each location, we collected fish during 4–5 trawl deployments that were between 15 and 400 km apart. We refer to each trawl deployment where fish were collected as a station. Fish were collected opportunistically when caught in the manta trawl, towed for 1 h at 0.5 m/s collecting plastic to quantify plastic density, or when caught in the high-speed trawl, towed for as long as 12 h at speeds up to 3.6 m/s collecting plastic to quantify chemical contamination. Myctophids ($n = 1–7$ per trawl deployment) were collected using two types of surface trawls: 1) a manta trawl with a rectangular opening of 16 cm in height by 61 cm

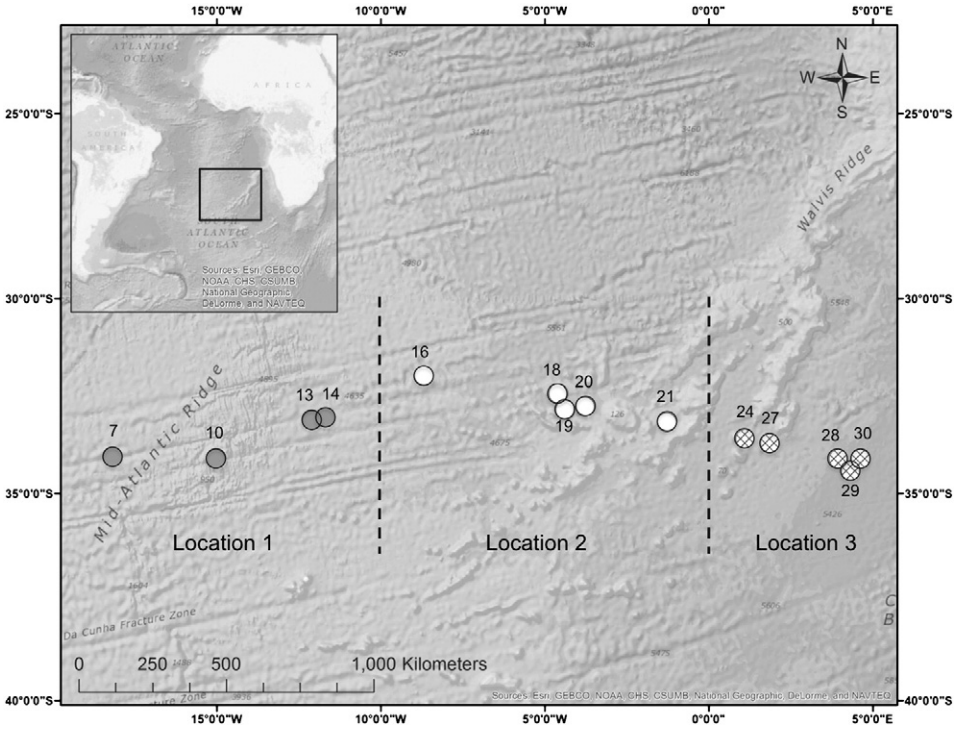

Fig. 1. Map of sampling locations and stations in the South Atlantic. Locations of the stations where fish were sampled during the expedition of S/V Sea Dragon in the South Atlantic in November–December 2010 are shown for each of the three locations (Location 1—gray, Location 2—white, Location 3—hatched). Stations numbers are ordered from west to east across the South Atlantic Ocean beginning with Station #7 and ending with Station #30. Figure generated in ArcGIS version 10.1.

in width with a 3 m long 333 μm mesh net with a 30 cm long × 10 cm diameter collecting bag and 2) a high-speed trawl with a rectangular opening of 45 cm in height by 15 cm in width with a 5 m long 500 μm mesh net with a 46 cm long × 13 cm diameter collecting bag. Before the cod-end of each net, a 5 mm nylon mesh was placed to separate the fish from the plastic to prevent confounding results from net feeding (Davison and Asch, 2011). Nets were towed along the surface on the starboard side using a spinnaker pole to position the towline outside the wake of the vessel. Fish caught were removed from the collection bag, wrapped in clean foil and stored in a −20 °C freezer until future analysis by AXYS Analytical Services Ltd.

Plastic debris was sampled for quantification from eleven manta trawls, deployed within the geographic range of our stations. Using the Beaufort Scale (Beer, 1996), the sea state was calculated using wave height observed by three crewmembers and decided by consensus. Plastic sampled for quantification was fixed in 5% formalin. Plastic densities were quantified from manta trawls using published methods (Eriksen et al., 2013). Briefly, plastic was floated using concentrated saltwater and removed from natural material using a dissecting microscope. Eight plastic samples were taken from high speed trawls, deployed along the cruise track, for chemical analysis. Plastic sampled for chemical analysis was immediately transferred to clean foil and stored at −20 °C until future analysis by AXYS Analytical Services Ltd.

Seven water samples were collected from within the geographic range of our stations. Water was sampled for chemical analysis using the C.L.A.M. (Continuous Low-level Aquatic Monitoring; C.I.Agent Stormwater Solutions; Huntington Beach, CA, USA) with HLB extraction disks, capable of extracting chemicals from up to 100 L of water in situ. Briefly, the C.L.A.M. was calibrated in a 18.9 L stainless steel vessel in freshwater, deployed off the side of the boat for a 6-hour time period, and immediately recalibrated upon retrieval. Calibration involves measuring the amount of water flowing through the disk for 3 consecutive 30-second intervals. The average flow rate among both calibrations is recorded and used to determine the amount of water extracted through the disk during each deployment. To account for background contamination from the disk or during calibration, three blank disks were employed as field blanks and were calibrated and stored in the same way as disks used for water samples. Immediately after each deployment, extraction disks were wrapped in clean foil and stored at 4 °C until future analysis by AXYS Analytical Services Ltd.

2.2. Chemical standards and solvent materials

All solvents and reagents for sample dissection were purchased from Fisher Scientific (Fisher Scientific, Fair Lawn, NJ, USA) and for analytical chemistry by AXYS Analytical Services Ltd. All solvents and reagents were equal or above pesticide grade. Surrogate standards used for analytical methods included bisphenol A-propane-d6 for analysis of BPA, $^{13}C_6$-4-nonylphenol for analysis of alkylphenols, $^{13}C_6$-NP1EO for analysis of alkylphenol ethoxylates, ^{13}C-labeled PCBs (CB#s 1, 3, 4, 15, 37, 54, 77, 81, 104, 105, 114, 118, 123, 126, 155, 156, 157, 167, 169, 170, 180, 188, 189, 202, 205, 206, 208 and 209) for analysis of PCBs and $^{13}C_{12}$-labeled PBDEs (BDE#s 15, 28, 47, 77, 99, 100, 126, 153, 154, 183, 197 and 209) for analysis of PBDEs. ^{13}C-labeled PCB#s 28, 111 and 178 and ^{13}C-labeled PBDE# 139 were used as clean-up standards during extraction of PCBs and PBDEs respectively. Recovery standards used for analytical methods included $^{13}C_{12}$-BPA for the analysis of BPA, d6-BPA for the analysis of alkylphenol ethoxylates, $^{13}C_3$-Atrazine for the analysis of alkylphenols, $^{13}C_{12}$-PCBs (CB#s 9, 52, 101, 138 and 194) for the analysis of PCBs and $^{13}C_{12}$-PBDEs (BDE#s 79, 180 and 206) for the analysis of PBDEs.

2.3. Sample preparation

Fish were removed from the freezer and thawed. The weight, length and sex for each fish were recorded and photos taken for taxonomic identification by P. Davison at the Scripps Institution of Oceanography. The digestive tract and gut were surgically removed from each fish and stored for future analysis. After dissection each fish was re-weighed and kept at −20 °C until chemical analysis. To account for procedural contamination during processing, three samples of clean sediment mixed with clean canola oil were treated as procedural blanks

and sent through the same procedure as each fish and stored for the analysis of the same suite of chemicals. Extractions and analyses of fish tissue, plastic and water samples were performed at AXYS Analytical Services Ltd.

For fish tissue, individual fish were homogenized and subsampled for individual analyses of BPA, alkylphenolics (4-nonylphenol, 4n-octylphenol, 4-nonylphenol monoethoxylate and 4-nonylphenol diethoxylate), PCBs (CB#s 1–209) and PBDEs (BDE#s 7, 8, 10–13, 15, 17, 25, 28, 30, 32, 33, 35, 37, 47, 49, 51, 66, 71, 75, 77, 79, 85, 99, 100, 105, 116, 119, 120, 126, 128, 138, 140, 153, 154, 155, 166, 181, 183, 190, 196, 197, 203, 204, 206–209). Extraction and analysis procedures were in accordance with AXYS Method MLA-084 for BPA, AXYS Method MLA-080 Rev 2 for alkylphenols and alkylphenol ethoxylates, AXYS Methods MLA-013 and MLA-010 (EPA Method 1668) for PCBs and AXYS Method MLA-013 and MLA-033 (EPA Method 1614) for PBDEs.

For the analysis of BPA, up to 1 g (wet-weight) of homogenized tissue were subsampled from each individual fish. Subsamples were spiked with deuterium-labeled BPA and solvent extracted twice with acetonitrile and pH2 phosphate buffer using ultrasonic extraction. The solvent was then evaporated and the resulting aqueous extract was diluted with reagent water and cleaned using solid phase extraction (SPE) on a Waters Oasis HLB cartridge (Waters, Milford, MA, USA). BPA was eluted with methanol and the final extracts were spiked with recovery standard in preparation for analysis by LC/MS/MS.

For the analysis of alkylphenolics, 2 g (wet-weight) of homogenized tissue were subsampled from each fish. Subsamples were acidified, spiked with labeled surrogate standards and extracted by steam distillation with concurrent liquid–liquid extraction into isooctane. The resulting extract was reduced to dryness and reconstituted in hexane prior to a cleanup step using SPE on an aminopropyl cartridge and eluted with 10 mL of 25% acetone in hexane. Sample extracts were reduced to dryness, reconstituted in 1 mL methanol and spiked with labeled recovery standard prior to analysis by LC/MS/MS.

The remaining homogenized tissue samples (approximately 5 g wet-weight) were prepared for the analysis of PCBs and PBDEs. Samples were spiked with ^{13}C-labeled surrogate standards for PCBs and PBDEs and Soxhlet extracted using dichloromethane. Duplicate gravimetric lipid determinations were made using aliquots of this extract (1/15th each). The remaining extract was spiked with ^{13}C-labeled cleanup standards and cleaned up by column chromatography on gel permeation, acid/base silica, florisil and alumina columns. Extracts were spiked with labeled recovery standards and concentrated to 20 μL in preparation for PCB analysis by gas chromatography with high-resolution mass spectrometric detection (GC/HRMS) for PCBs. The extracts were later diluted to 50 μL and analyzed by GC/HRMS for PBDEs.

Samples of plastic were analyzed for the same suite of chemicals as fish. Extraction procedures were in accordance with AXYS SOP SLA-126. Each sample (composed of multiple small pieces of plastic) was weighed and spiked with labeled quantification surrogate standards appropriate for all 4 classes of analytes and extracted twice by immersion in dichloromethane. Two sequential extractions were combined for analysis. The extracts were split gravimetrically into 2 equal portions, one for alkylphenolics by AXYS Method MLA-082 and for BPA by AXYS Method MLA-080 and the other for PCB by AXYS Methods MLA-010 (EPA Method 1668) and for PBDEs by AXYS Method MLA-033 (EPA Method 1614). The portion of the extract with BPA and alkylphenolics was exchanged into methanol, concentrated to a final volume of 1 mL and spiked with recovery standards in preparation for LC/MS/MS. The portion of the extract with PCBs and PBDEs was spiked with ^{13}C labeled PCB and PBDE cleanup standards and cleaned up by column chromatography on acid/base silica, florisil and alumina columns. Extracts were spiked with labeled recovery standards and concentrated to 20 μL in preparation for PCB analysis by GC/HRMS, then later diluted to 50 μL in preparation for PBDE analysis by GC/HRMS.

Disk extraction procedures for water samples, extracted by HLB disks in the field, were in accordance with AXYS SOP SLA-129. Each disk was spiked with labeled surrogate standards and eluted with methanol followed by dichloromethane. Each combined methanol/dichloromethane extract was split gravimetrically into 2 equal portions, a portion for BPA analysis by AXYS Method MLA-080 and for alkylphenolics by AXYS Method MLA-082 and the other for PCB analysis by AXYS Methods MLA-010 (EPA Method 1668) and for PBDEs by AXYS Method MLA-033 (EPA Method 1614). The portion of the extract used for BPA and alkylphenolics was exchanged into methanol, concentrated to a final volume of 1 mL and spiked with recovery standards in preparation for LC/MS/MS. The portion of the extract used for PCBs and PBDEs was spiked with ^{13}C labeled PCB and PBDE cleanup standards and cleaned up by column chromatography on acid/base silica, florisil and alumina columns. Extracts were spiked with labeled recovery standards and concentrated to 20 μL for PCB analysis by GC/HRMS and later diluted to 50 μL and analyzed for PBDEs by GC/HRMS.

2.4. Instrumental analyses

Sample extracts for BPA and alkylphenolics were analyzed using a Waters 2690 (Milford, MA, USA) high performance liquid chromatograph coupled to a triple quadrupole mass spectrometer with a Waters (Milford, MA, USA) Xterra C_{18}MS column. The mass spectrometer was run at unit mass resolution in the Multiple Reaction Monitoring (MRM) mode. Sample extracts for BPA were analyzed using a solvent gradient of aqueous NH_4OH (pH 10) and 1:1 acetonitrile:methanol and the MS/MS was run in ESI negative mode. Sample extracts for alkylphenolics were analyzed using a solvent gradient of ammonium acetate in methanol and ammonium acetate in water on the LC. Each sample extract was analyzed in two separate LC-MS/MS runs, one in the ESI negative mode (for alkylphenols) and the other in the ESI positive mode (for alkylphenol ethoxylates). PCBS and PBDEs were analyzed using a Micromass Ultima high resolution mass spectrometer coupled to an Agilent 6890 + gas chromatograph operated in the selected ion monitoring (SIM) mode with a mass resolution of 10,000 for PCB analysis and 5000 for PBDE analysis using a 30 m SPB-Octyl column for PCBs and a 30 m DB-5HT capillary column for PBDEs. Sample extracts for PCBs were analyzed using GC/HRMS and quantified using procedures described in EPA Method 1668A and sample extracts for PBDEs were analyzed using GC/HRMS and quantified using procedures described in EPA Method 1614. Concentrations of BPA and alkylphenolics are reported as ng/g wet weight and concentrations of PCBs and PBDEs as pg/g wet weight. The concentrations of some of the PCB and PBDE congeners are reported as the sum of two or more congeners due to the potential coelution of several congeners.

2.5. Quality assurance and quality control

Foil used to collect samples were cleaned and muffled at 450 °C for 6 h. All surgical tools were solvent rinsed in acetone and hexane between dissections of each individual fish. All extraction tools were rinsed in acetone, toluene, dichloromethane and methanol. Analysis glassware was cleaned with water and detergent, baked at 350 °C for 10 h and solvent rinsed (3× each methanol, toluene, hexane) before use. Each analysis batch (up to 20 field samples of a single sample matrix) included at least two quality control samples: a procedural blank and a known or control sample of a similar matrix as the field samples. Laboratory procedural blanks for dissection (sand with canola oil) and field blanks for water sampling (blank HLB extraction disk), laboratory procedural blanks for extraction and spiked matrix blank (canola oil for fish analyses, dichloromethane for plastics and both solvent and HLB for C.L.A.M. disks) were extracted and run with the analytical batch. Blank levels of BPA, alkylphenols, alkylphenol ethoxylates, PCBs and PBDEs measured in laboratory procedural dissection, field and extraction blanks were subtracted from the reported concentrations that were extracted from samples.

The following quality control criteria were used to guarantee correct identification of BPA: BPA must have an LC retention time within 0.1 min of the ^{13}C-labeled BPA, it must have a parent ion with a specific mass to charge ratio, and that parent ion must produce 2 daughter ions of specific mass to charge ratio, a signal-to-noise ratio was greater than 3 for the parent to daughter ion transitions and the retention time must be within ±0.4 min of the predicted retention time from the mean determination from the Initial Calibration. The following quality control criteria were used to guarantee correct identification of alkylphenols and alkylphenol ethoxylates: each target analyte must have a parent ion with a specific mass to charge ratio, and that parent ion must produce daughter ions of specific mass to charge ratio, LC retention times must be within ±0.4 min of the predicted retention time from the mean determination from the daily bracketing calibration standard, and signal-to-noise ratio was greater than 3 for the parent to daughter ion transitions. The quality control criteria identified in Section 16.0 of EPA Method 1668 and Section 16.0 of EPA Method 1614 were used to guarantee correct identification of PCBs and PBDEs respectively: the signals for the specified mass to charge ratio for the quantification and confirmation ions must be present and must maximize within the same 2 MS scans, the ratio of their intensities must be within 15% of the specified ratio, their relative retention time (with respect to the labeled surrogate) must be within method specifications and signal-to-noise ratio was greater than 2.5.

Quantification of all analytes was carried out by isotope dilution internal standard where exact labeled analog standards are available or by internal standard quantification using the labeled analog of a related compound when the exact labeled analogs are not available. This quantification protocol produces analytical results that are corrected for any losses during sample workup and any fluctuations of instrumental response due to the presence of sample matrix in the extracts. The reported concentrations of bisphenol A, alkylphenols, alkylphenol ethoxylates, PCBs and PBDEs are recovery corrected based upon the recovery efficiencies of surrogate standards.

For fish tissue, the limit of quantification ranged from 0.5–1.2 ng/sample for BPA, 0.5–9 ng/sample for alkylphenols, 0.5–5 ng/sample for alkylphenol ethoxylates, 0.1–3.4 pg/sample for PCBs to 0.2–50 pg/sample for PBDEs. Note that larger limits for PBDEs are mainly attributed to BDE209. The mean (range%) recoveries of the surrogate standards ranged from 47% (23–69) for BPA, 91% (22–128) for alkylphenols, 54% (40–78) for alkylphenol ethoxylates, 73% (17–158) for PCBs to 77% (35–152) for PBDEs. The recovery of spiked matrix blank samples ranged from 81–99% for BPA, 80–142% for alkylphenols, 75–139% for alkylphenol ethoxylates, 83–103% for PCBs to 89–146% for PBDEs.

For plastic samples, the limit of quantification ranged from 1–4 ng/sample for BPA, 2–20 ng/sample for alkylphenols, 0.6–24 ng/sample for alkylphenol ethoxylates, 1–11 pg/sample for PCBs to 1–674 pg/sample for PBDEs. Note that larger limits for PBDEs are mainly attributed to BDE209. The mean (range%) recoveries of the surrogate standards were 111% (94–136) for BPA, 55% (35–127) for alkylphenols, 79% (66–103) for alkylphenol ethoxylates, 76% (32–106) for PCBs and 65% (35–92) for PBDEs. The recovery of spiked matrix blank samples was 90% for BPA, from 84 to 93% for alkylphenols, from 124 to 128% for alkylphenol ethoxylates, from 97 to 116% for PCBs and from 91 to 104% for PBDEs.

For water samples, the limit of quantification ranged from 2–3 ng/sample for BPA, 1–16 ng/sample for alkylphenols, 1–18 ng/sample for alkylphenol ethoxylates, 1–7 pg/sample for PCBs to 2–482 pg/sample for PBDEs. Note that larger limits for PBDEs are mainly attributed to BDE209. The mean (range%) recoveries of the surrogate standards were 108% (86–123) for BPA, 57% (31–97) for alkylphenols, 119% (72–152) for alkylphenol ethoxylates, 64% (17–107) for PCBs to 61%(18–121) for PBDEs in water samples. The recovery of spiked matrix blank samples was 96% for BPA, from 97 to 99% for alkylphenols, from 97 to 103% for alkylphenol ethoxylates, from 96 to 119% for PCBs and from 46 to 106% for PBDEs.

2.6. Statistical analyses

We analyzed differences in plastic densities and chemical concentrations in fish among the three sampling locations and considered the relationship between plastic density and chemical concentrations measured in fish across all sampling stations. Plastic densities were compared among sampling locations using a 1-factor ANOVA ($\alpha = 0.05$; GMAV; EICC, University of Sydney). Homogeneity of variance was verified by Cochran's (1951) *C*-test.

To measure differences among chemical body burdens in fish among sampling locations, all concentrations were $[x]^{1/6}$ transformed to achieve normality. First, we tested that there was no effect from the trawl, to ensure that contaminants in individual fish could be treated as independent replicates, by analyzing differences among chemical concentrations in fish among trawls within a single sampling location. For each trawl where ≥2 fish were sampled, 2 fish were randomly selected and their chemical concentrations used to analyze differences among trawls using a 1-factor ANOVA (SYSTAT 12; SYSTAT Software, Chicago, IL). We found no significant difference ($P > 0.05$) among concentrations of all contaminant groups among trawls within each location with the exception of alkylphenols within Location 2 ($P < 0.05$). Because variation among stations within each location was generally not significantly different, individual fish from each station were treated as independent replicates. Next, we used individual 1-factor ANOVAs ($\alpha = 0.05$; GMAV; EICC, University of Sydney) to analyze the differences among the concentrations of each contaminant group in individual fish among locations. To assure equal sample sizes among locations, 7 fish were randomly selected from each location. Homogeneity of variance was verified by Cochran's (1951) *C*-test. Post-hoc Student–Newman–Keuls (SNK) tests were used to distinguish significantly different treatment means. To consider the relationship between plastic density and concentrations of contaminants in fish tissue among sampling stations, we used simple linear regression with untransformed data (SYSTAT 12; SYSTAT Software, Chicago, IL).

3. Results

3.1. Plastic density among locations

Plastic debris was present in trawls from all stations. Contrary to what was predicted by the Maximenko et al. (2012) accumulation model (Fig. 2a), we found no significant difference in plastic densities among the three sampling zones ($F_{2,18} = 1.25$, $n = 7$, $P > 0.05$). While the station with the greatest density of plastic was in Location 2 (station 16), plastic densities both within and among locations were highly variable: densities were greatest at stations 16, 14, 10 and 27 (>100,000 pieces/km^2), intermediate at stations 7, 13, 18, 19 and 21 and smallest at stations 20, 24, 28, 29 and 30 (<20,000 pieces/km^2; Fig. 3, Supplementary Table 1).

To determine if the observed deviation from the model predictions might have reflected sampling conditions or ambient environmental variables, we considered how plastic densities varied with changes in sea state. The density of plastic quantified in each trawl appears to be negatively correlated with sea state, consistent with a finding reported in the North Atlantic (Kulkulka et al., 2012; Fig. 3). If the plastic densities observed here are underestimations due to an elevated sea state, we would expect greater plastic densities in one trawl from Location 2 (station 21) and in three trawls from Location 3 (stations 28, 29 and 30). Thus, correcting our plastic densities to account for sea state would further confirm our conclusion that densities of plastic did not vary among locations.

3.2. Chemical concentrations on plastic debris

To consider how targeted chemicals in myctophid were associated with plastic debris, we analyzed plastic debris sampled along our cruise

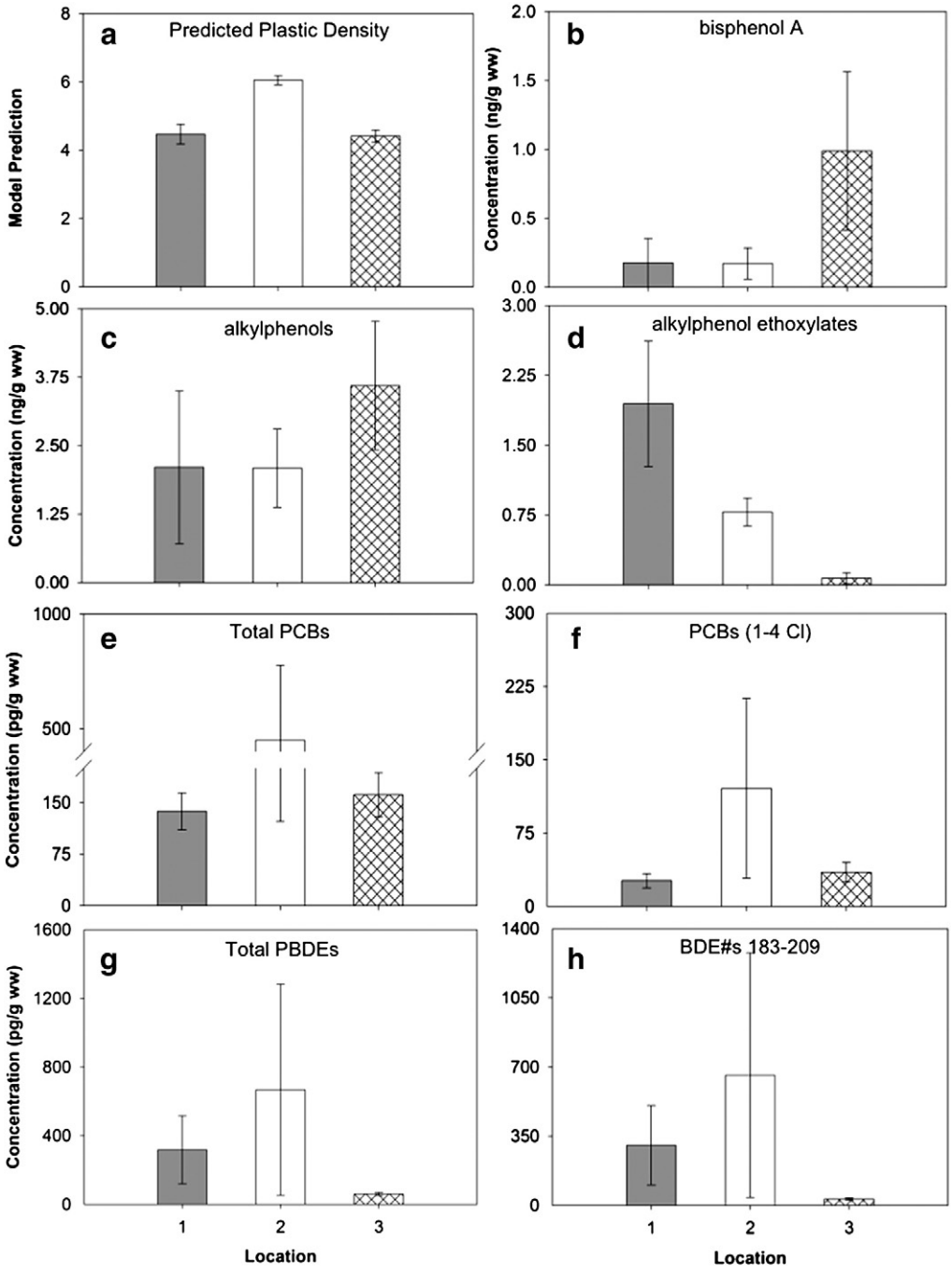

Fig. 2. Differences among locations for predicted plastic densities and observed chemicals in fish. Predicted plastic density (a) and concentrations of chemical groups (b—BPA, c—alkylphenols, d—alkylphenol ethoxylates, e—total PCBs, f—lower Cl PCBs, g—total PBDEs, h-BDE#s 183–209) measured in fish tissue are shown for each of the three locations (Location 1—gray, Location 2—white, Location 3—hatched) shown in Fig. 1 and ordered from west to east across the South Atlantic Ocean. Each bar represents the mean ± standard error. Note that scales along the y-axis differ among graphs.

track for the same suite of chemicals as in fish. As expected, all chemical groups were detected on plastic debris, some at concentrations up to 6 orders of magnitude above those found in the water column (see Tables S1 and S2 for concentrations in water and plastic samples). BPA was detected on 63% of plastic samples at concentrations ranging from 1.4 to 4.9 ng/g (Table S2). Alkylphenols and their ethoxylates were detected on all plastic samples ranging from 22.3 to 341.5 ng/g and 0.8 to 97.6 ng/g respectively (Table S2). PCBs were detected on all plastic samples ranging from 15.6 to 589.7 ng/g, 83–99% of which were lower chlorinated congeners (Table S2). Similarly, PBDEs were detected on all plastic samples ranging from 0.1 to 4.6 ng/g. On 38% of samples, whose concentrations were relatively large, 58–90% of total PBDEs were composed of higher brominated congeners (Table S2).

3.3. Chemical concentrations in water samples

PCBs and PBDEs were detected in several water samples, but BPA, alkylphenols and alkylphenol ethoxylates were not (Table S2). PCBs were detected in 86% of water samples ranging from 0.1 to 5.9 pg/L, the majority of which are lower chlorinated congeners (46% in one sample and 100% in the remaining; Table S2). PBDEs were detected in 43% of water samples ranging from 0.3 to 3.0 pg/L, the majority of which are

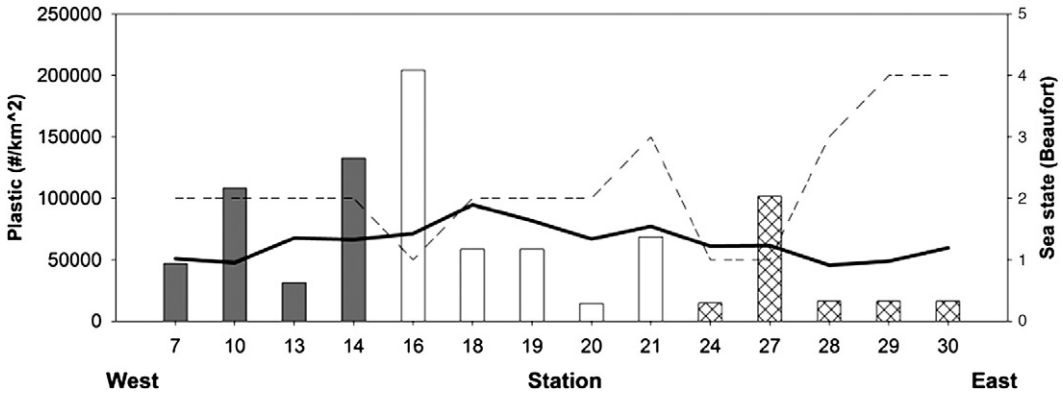

Fig. 3. Density of plastic at each station within each location. Densities of plastic (# pieces/km^2) are shown for each station where a trawl was deployed within each of the three locations (Location 1—gray, Location 2—white, Location 3—hatched) shown in Fig. 1 and ordered from west to east across the South Atlantic Ocean. The solid line represents the density of plastic (# pieces/km^2) predicted by the model and the dashed line represents the sea state using the Beaufort Scale. The density of plastic is along the y-axis on the left and the sea state is along the y-axis on the right.

lower brominated congeners (77% in one sample and 100% in the remaining; Table S2).

3.4. Chemical body burdens among sampling locations and stations

Overall, we found some evidence that chemical body burdens in myctophid were greatest in regions where plastic densities were relatively large. Yet, as expected, because plastic densities were not different among locations, this trend was not evident when comparing chemical body burdens in fish among Locations 1, 2 and 3. We observed a significant difference among the concentrations of BPA in fish tissue among locations ($F_{2,18} = 7.66$, n = 7, $P < 0.01$), but these were not linked to plastic densities as an SNK test showed that fish living in Location 3, where plastic densities were smallest, had significantly greater concentrations ($P < 0.05$) of BPA in their tissues than in Locations 1 and 2 (Fig. 2b). We also observed significant differences among concentrations of alkylphenol ethoxylates in fish tissue among locations ($F_{2,18} = 18.19$, n = 7, $P < 0.001$). This pattern may be moderately linked to plastic densities as an SNK test showed that fish living in Locations 1 and 2 had significantly greater concentrations ($P < 0.05$) of alkylphenol ethoxylates in their tissues than in Location 3 (Fig. 2d) where average plastic densities were smallest. We did not observe significant differences among the concentrations of alkylphenols, total PCBs, lower Cl PCBs, total PBDEs or higher brominated PBDEs in fish tissue among locations (alkylphenols: $F_{2,18} = 1.00$, n = 7, $P > 0.05$, Fig. 2c; total PCBs: $F_{2,18} = 1.53$, n = 7, $P > 0.05$, Fig. 2e; lower chlorinated PCBs: $F_{2,18} = 3.18$, n = 7, $P > 0.05$, Fig. 2f; total PBDEs: $F_{2,18} = 0.22$, n = 7, $P > 0.05$, Fig. 2g; BDE#s 183–209: $F_{2,18} = 0.74$, n = 7, $P > 0.05$, Fig. 2h).

We then examined the relationship between plastic density and the concentrations of chemicals in fish tissue at each station across all locations (Fig. 4). We observed a significant relationship between plastic density and the concentration of total PBDEs and BDE#s 183–209 in fish tissue among stations (total PBDEs: $F_{1,34} = 10.339$, n = 36, $P < 0.01$, $R^2 = 0.23$, Fig. 4f; BDE#s 183–209: $F_{1,34} = 10.394$, n = 36, $P < 0.01$, $R^2 = 0.23$, Fig. 4g), such that concentrations increase with increasing plastic density. Lower brominated BDEs (≤6 Br; Fig. 5) follow a contrasting pattern, suggesting that BDE#s 183–209 are driving the pattern we see for PBDEs in fish tissue among stations. We did not observe significant relationships ($P > 0.05$) among plastic density and concentrations of BPA, alkylphenols, alkylphenol ethoxylates, total PCBs or lower Cl PCBs in fish tissue among stations (Fig. 4a–e).

4. Discussion

Plastic debris is now a recognized threat to marine ecosystems globally by several governing bodies including the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection, United Nations Environmental Program, United States Environmental Protection Agency and National Oceanic and Atmospheric Administration. Physical effects of plastic debris have been described in the literature for decades (Gregory, 2009), but how the large mixture and concentrations of chemicals on plastic debris affects the health of aquatic life is poorly understood (Teuten et al., 2009). Of concern is the extent that plastics transfer hazardous chemicals to wildlife upon ingestion (Teuten et al., 2009). Testing whether such contaminants can bioaccumulate in nature is challenging due to the ubiquity of several contaminants across environmental media (Ross and Birnbaum, 2010). To tackle this question, researchers have attempted to determine if there are plastic-associated contaminants that can be used as indicators of bioaccumulation from plastic debris (Yamashita et al., 2011; Tanaka et al., 2013; Fossi et al., 2012). Here, we measured several contaminants, associated with plastic debris either as a chemical ingredient or via sorption from ambient water, in fish tissue and measured how concentrations changed in response to plastic contamination.

4.1. Plastic densities

We expected to observe differences in plastic densities and associated chemical concentrations in fish among the three locations, selected based upon predictions of the accumulation model (Maximenko et al., 2012). This model has been shown to predict zones of plastic accumulation in other ocean regions (Law et al., 2010; Eriksen et al., 2013). In contrast to these studies, data from our sampling locations did not conform to model predictions. We found that along our cruise track, neither of the putative reference sites served as a true reference, and plastic was observed in every station. Moreover, densities of plastic among locations were similar and we observed large variability among stations within each location (Fig. 3).

Predicting where plastic will accumulate is not trivial. Dynamics of the upper ocean and its mixed layer, where floating plastic debris resides, is complex (Maximenko et al., 2012). The location of debris is determined by local wind (Kulkulka et al., 2012), ocean currents (Maximenko et al., 2012) and coastal inputs from densely populated watersheds (Lebreton et al., 2012), all varying over different time scales. Thus, the assumption of statistical stationary in the model can be questioned (Maximenko et al., 2012), and the distribution of plastic debris assumed to be patchy. It is possible that designating reference locations farther from the contaminated location may support this approach, however, in this case, sites farther from the predicted accumulation zone should be closer to the coasts where offshore floating plastic debris is less dense (Law et al., 2010; Doyle et al., 2011).

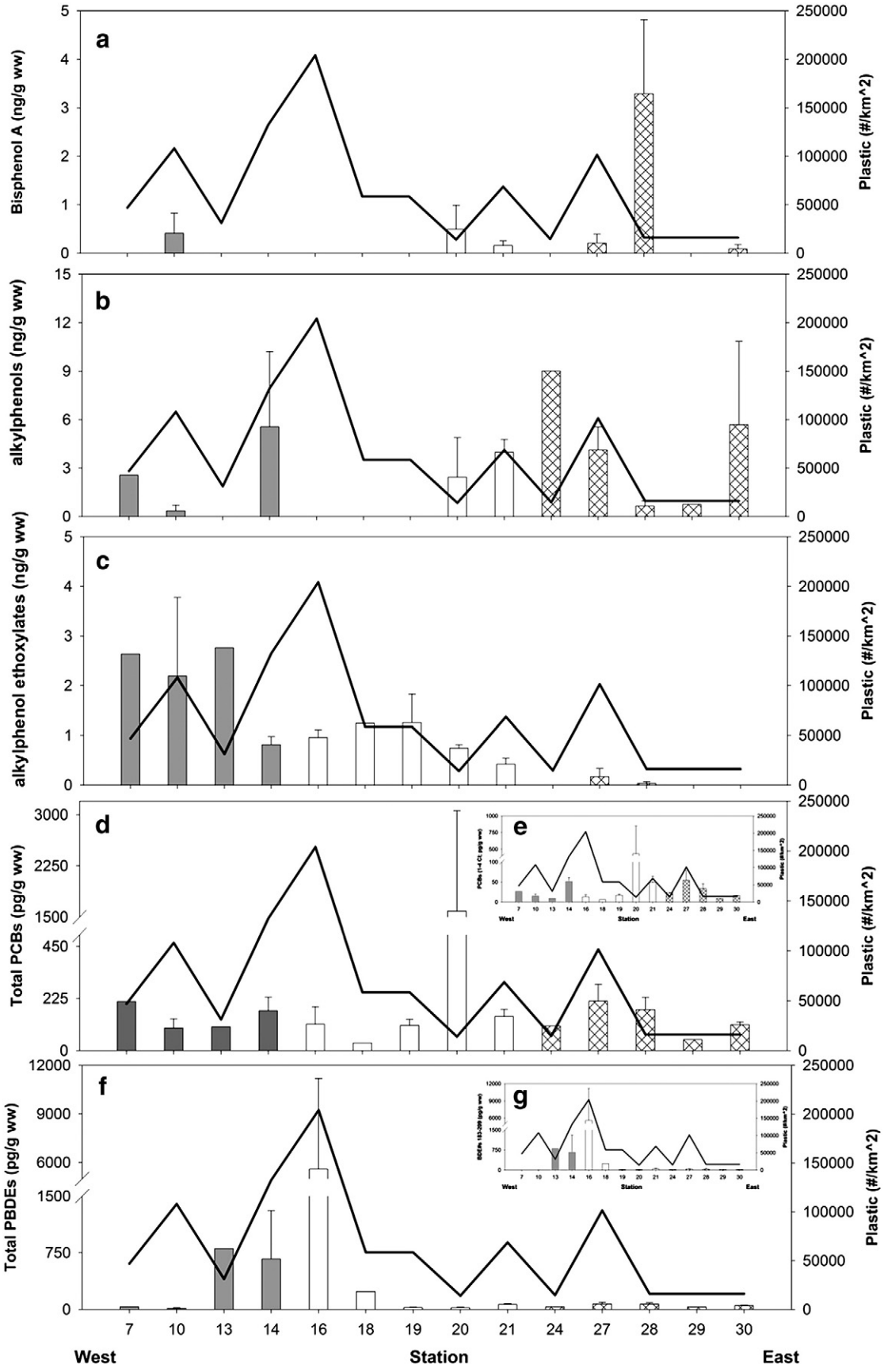

Fig. 4. Chemical body burdens and plastic density at each station. Concentrations of a) BPA (ng/g ww), b) alkylphenols (ng/g ww), c) alkylphenol ethoxylates (ng/g ww), d) total PCBs (pg/g ww), e) lower Cl PCBs (pg/g ww), f) total PBDEs (pg/g ww) and g) BDE#s 183–209 (pg/g ww) in fish tissue are shown for each station where a trawl was deployed within each of the three locations (Location 1—gray, Location 2—white, Location 3—hatched) shown in Fig. 1 and ordered from west to east across the South Atlantic. Each bar represents the mean concentrations in fish from each station + standard error. Where there is no bar, the chemical was non-detectable in all fish from that station. The solid line represents the observed density of plastic (# pieces/km^2). Concentrations of chemicals are along the y-axis on the left and density of plastic along the y-axis on the right. Note that y-axis scales (left) differ among graphs.

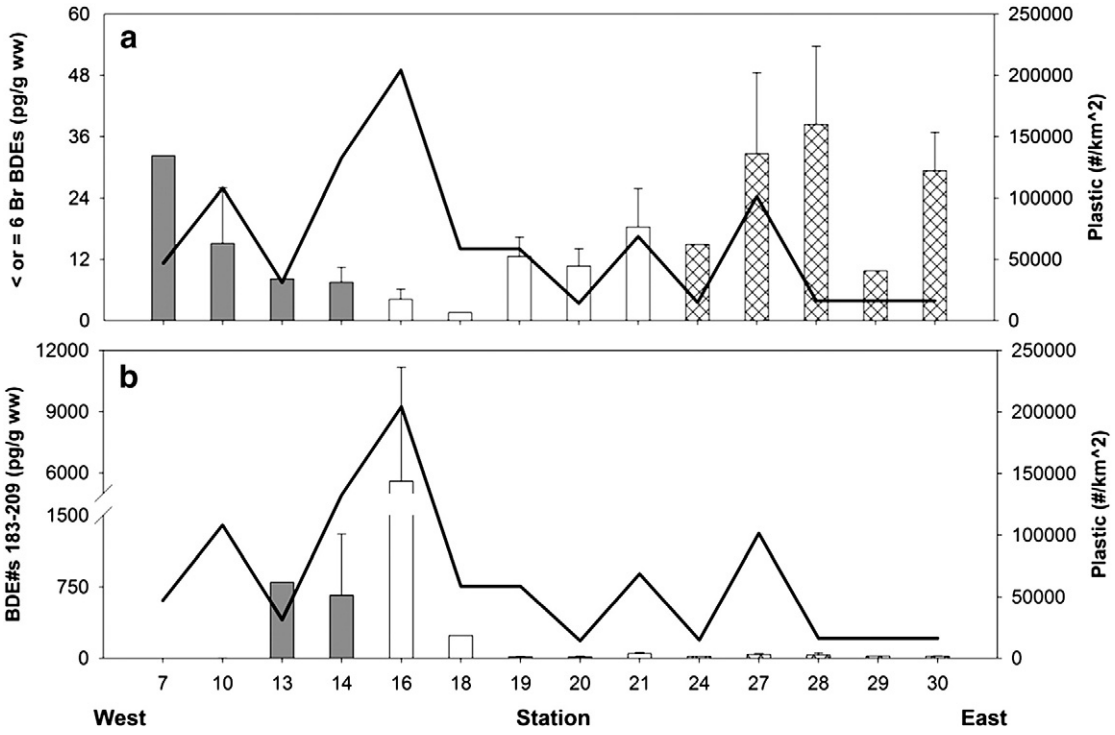

Fig. 5. Concentration of lower and higher brominated PBDEs at each station. Each bar represents the mean concentrations in fish from each station + standard error. The solid line represents the density of plastic (# pieces/km^2). Concentrations of a) lower Br BDEs (pg/g ww) and b) BDE#s 183–209 (pg/g ww) in fish tissue are shown for each station where a trawl was deployed within each of the three locations (Location 1—gray, Location 2—white, Location 3—hatched) shown in Fig. 1 and ordered from west to east across the South Atlantic. Note that y-axis scales (left) differ among graphs.

4.2. Chemical contamination on plastic debris and in water samples

Our chemical analyses of plastic debris from the South Atlantic confirms that the suite of targeted chemicals in myctophid were relevant to plastic debris. All targeted chemicals were detected on all plastic samples with the exception of BPA, which was detected on 63% of samples (Table S2). Our paired analyses of plastic debris and water samples provide some insights into the likely source of the chemicals detected (see Table 1). Because BPA was not detected in any water samples and is less likely to sorb to plastic from the environment due to its low hydrophobicity and persistence (Staples et al., 1998), concentrations observed here are likely a result of being a constituent of some plastic types. Similarly alkylphenols were not detected in water samples. It has been suggested that a greater ratio of 4-nonylphenol to 4n-octylphenol indicates being derived from plastic additives (Hirai et al., 2012). Here, the sum of alkylphenols was 100% 4-nonylphenol in all plastic samples, suggesting that alkylphenols on plastic samples here are constituents of plastic. Alkylphenol ethoxylates were also not detected in water samples, and thus are also likely detected on plastic as a result of being a plastic additive. The presence of PCBs on plastic debris, detected in most water samples, is likely due to sorption from ambient seawater. Greater than 82% of PCBs detected on plastic were composed of the sum of the lower chlorinated congeners, consistent with PCBs measured on water samples and plastic debris recovered from the open ocean in other studies (Hirai et al., 2012). PBDEs are likely present on plastic debris as plastic additives and from environmental sorption. For 62% of plastic samples, the lower brominated congeners, detected more often in seawater samples collected here and in other studies (Mizukawa et al., 2009), dominated and thus were likely due to environmental sorption. For the remaining 38% of plastic samples, the higher brominated congeners, used in commercial products (Hirai et al., 2012), dominated and thus were likely constituent ingredients of the plastic material. As expected, based on other studies showing greater concentrations of contaminants in coastal areas (Hirai et al., 2012), concentrations were 1–2 orders of magnitude smaller than those collected from coastal areas (Ogata et al., 2009) and generally similar to concentrations found on water and plastic debris sampled from other open oceans globally (Table 2).

4.3. Relationship between plastic density and chemical body burdens

Because we could not detect a difference in plastic densities among locations, statistical differences found for concentrations of BPA and alkylphenol ethoxylates in fish tissue among locations cannot be linked

Table 1
Potential sources of chemical contaminants found on plastic, water and fish tissue.

Chemical	Potential Sources
BPA	Chemical constituent and additives to plastics (Hirai et al., 2012; Peng et al., 2007)
	Wastewater treatment plant effluent and landfill leachate (Kang et al., 2007)
Alkylphenols	Degradation product of alkylphenol ethoxylates (Hirai et al., 2012)
	Wastewater treatment plant effluent and landfill leachate (Ying and Kookana, 2003; Kawahata et al., 2004)
Alkylphenol ethoxylates	Chemical additive to plastics (Hirai et al., 2012)
	Wastewater treatment plant effluent and landfill leachate (Ferguson et al., 2001)
PCBs	Sorption from ambient seawater (Ogata et al., 2009; Rochman et al., 2013b)
PBDEs	Chemical additive to plastics (Hirai et al., 2012)
	Sorption from ambient seawater (Mizukawa et al., 2009)

Table 2
Comparison of the concentration ranges of BPA, alkylphenols, alkylphenol ethoxylates, PCBs and PBDEs in plastic (ng/g pellet), water (pg/L) and myctophid (ng/g) samples collected in this study with other open ocean samples collected globally (nd=non-detectable).

Sample matrix	Sampling location	Study	BPA	Alkylphenols	Alkylphenol ethoxylates	PCBs	PBDEs	BDE209
Plastic	N. Atlantic	Hirai et al. (2012)	1–3	58–159		1–29[a]	9–16[a]	0.3–0.7
Water		Gioia et al. (2008)				1.5–6.4[b]		
		Iwata et al. (1993)				21–29[c]		
Plastic	S. Atlantic	This study	nd-5	22–342	0.8-98	16–589	0.1–5	nd-3
		Heskett et al. (2012)				3–11[d]		
Water		This study	nd	nd	nd	nd-5.9	nd-42.7	nd-11.8
		Gioia et al. (2008)				1–3.5[b]		
		Xie et al. (2011)					0.03–2.3[e]	
Myctophid		This study	nd-6.2 (ww)	nd-10.8 (ww)	nd-5.4 (ww)	18.1–5996.2 (ww)	2.2–11182 (ww)	nd-9078 (ww)
Plastic	N. Pacific	Hirai et al. (2012)	nd-283	nd-997		1–78[a]	0.3-9909[a]	nd-9907
		International Pellet Watch				0.7–10[d]		
		Rios et al. (2010)				nd-2856[f]		
Water		Iwata et al. (1993)				7.4–24[c]		
		Tanabe et al. (1984)				40–590[g]		
Myctophid		Takahashi et al. (2000)				20–370 (lipid)[h]		
		Takahashi et al. (2010)				34 (lipid)[i]	1.3 (lipid)[i]	
		Tanabe et al. (1984)				48 (ww)[g]		
		Tanaka et al. (2013)					0.1–1.7 (lipid)[j]	nd
Plastic	Indian	International Pellet Watch				7[a]		
Water		Iwata et al. (1993)				10–42[c]		

[a] PCBs—8, 18, 28, 52, 49, 44, 74, 66, 101, 99, 87, 110, 118, 105, 151, 149, 146, 153, 138, 158, 128, 167, 156, 157, 178, 187, 183, 177, 172, 180, 170, 189, 199, 206, 195, 194, 206, 209; BDEs—3, 7, 15, 28, 49, 66, 77, 100, 119, 99, 85, 126, 154, 153, 138, 183, 209.
[b] PCBs—28, 52, 90/101, 118, 153, 138, 180.
[c] PCBs—8, 18, 15, 17, 16/32, 34, 28/31, 20, 53, 33, 51, 49/69, 44, 37, 42, 41/64, 58/74, 70, 66, 91/95, 60, 101, 87/117, 118, 144/149, 128, 138.
[d] PCBs—66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170, 206.
[e] BDEs—47, 100, 99, 85,154, 183.
[f] PCBs—1, 5, 8, 11, 18, 28, 29, 44, 47, 50, 52, 66, 77, 87, 101, 104, 105, 118, 121, 126, 128, 136, 138, 153, 154, 170, 180, 185, 187, 188, 194, 195, 200, 206, 208.
[g] PCBs—1–209.
[h] Total PCB concentrations determined as Kanechlor equivalent (mixture of Kanechlor 300, 400, 500, and 600 used as a standard.
[i] PCBs—sum of 60 congeners, BDEs—47, 99, 100, 153,154, 183, 196, 197, 206, 207, 209.
[j] BDEs—1, 2, 3, 10, 7, 11, 8, 12/13, 15, 30, 32, 17/25, 33/28, 35, 37, 75, 49, 71, 47, 66, 77, 100, 119, 99, 116, 118, 85, 126, 155, 154, 153, 138, 166, 183, 181, 190, 188, 179, 202, 197, 203, 196, 208, 207, 206, 209.

to plastic debris. To examine the relationship between plastic density and body burden in fish, we measured the relationship between concentrations of chemicals in fish and amount of plastic at each station. Our results do not show a significant relationship between plastic densities and concentrations of BPA, alkylphenols, alkylphenol ethoxylates and PCBs in myctophids living in the South Atlantic Ocean; however, our results do show a significant relationship between plastic densities and PBDEs.

Although BPA is an ingredient of plastic (Table 1), we observed greater concentrations in fish where plastic densities were relatively low. Distance to the coast may explain the observed difference among locations. The primary route of BPA in the environment is thought to be from wastewater treatment plant effluent and landfill leachate (Kang et al., 2007) associated with urban areas (Kawahata et al., 2004) and may be the reason we observed greater concentrations of BPA in fish from regions closer to South Africa.

Alkylphenols are believed to enter the environment via similar sources as BPA (Ying and Kookana, 2003; Kawahata et al., 2004; Table 1). Thus, our results showing greater concentrations of alkylphenols in fish closer to the coast of South Africa may be expected. Because alkylphenols are degradation products of alkylphenol ethoxylates, we expected alkylphenol ethoxylates to follow the same pattern as alkylphenols. Yet, we observed an opposite pattern. Larger concentrations of these compounds in regions farther from the coasts may not be expected, but in the North Sea some of the largest concentrations of alkylphenol ethoxylates in seawater were also observed relatively far offshore (Jonkers et al., 2005). There, it was assumed that alkylphenol ethoxylates had been recently discharged into the area from heavy shipping activity (Jonkers et al., 2005). We observed minimal shipping activity along our cruise track and did not interact with other vessels until we approached South Africa. Alkylphenol ethoxylates are additives to plastics (Loyo-Rosales et al., 2004), were found in all plastic debris sampled here, and although not significant were found in greater concentrations in fish from stations with greater plastic densities (Fig. 4c). Thus, alkylphenol ethoxylates present in fish tissue here could be related to plastic debris. This hypothesis warrants further testing, particularly in a laboratory setting to determine if alkylphenol ethoxylates from plastic bioaccumulate in fish.

We did not observe a pattern between plastic densities and the concentration of PCBs in fish tissue. PCBs are ubiquitous in the marine environment, have a greater bioaccumulation property than other chemicals measured here and are the predominant organic contaminant in several marine organisms (Takahashi et al., 2010) making it difficult to determine the source of bioaccumulation. Thus, although previous research has reported a relationship between PCBs in seabird tissue and plastic debris (Yamashita et al., 2011) and that PCBs from plastic transfer to organisms in a laboratory setting (Besseling et al., 2013), it may be difficult to tease apart PCBs that have bioaccumulated in wild-caught myctophid from plastic debris versus their zooplankton diet. PCB congeners found in seawater are likely to be similar to those found in the zooplankton, as zooplankton sorb contaminants from ambient water in the same way that floating plastics do (Jaward et al., 2004; Tanabe et al., 1984).

We did observe a relationship between the concentration of PBDEs in myctophid and plastic densities. In this study, our results suggest that BDE#s 183–209 were present in myctophids as a consequence of living in regions with larger plastic densities. This further confirms previous research suggesting that the bioaccumulation of higher brominated PBDEs is indicative of plastic ingestion (Gassel et al., 2013; Tanaka et al., 2013). PBDE presence in fish is common, but the presence of higher brominated BDEs is not (Table 2). In a previous study, BDE#s 183–209 were only present in a few deep-sea fishes, including myctophid, sampled in the North Pacific (Takahashi et al., 2010; Tanaka et al., 2013; Table 2), suggesting the low bioaccumulation potential of these congeners (Takahashi et al., 2010). Moreover, in water samples taken in this study and from the South Atlantic Ocean in previous

studies (Xie et al., 2011), lower brominated BDEs dominated all samples, but BDE#s 183–209 were detected on all plastics sampled here, and were the most common congeners found in plastic samples from the North Pacific (Hirai et al., 2012; Tanaka et al., 2013). This suggests that higher brominated PBDEs may be associated with plastic debris as an additive ingredient and not sorbed from ambient seawater, further supporting our conclusion that BDE#s 183–209 contaminants in myctophid sampled here may be indicative, and consequential, of plastic pollution in their habitat.

5. Conclusion

This research was performed on a vessel of opportunity, across a remote region of the ocean, and is to the best of our knowledge the first study to examine concentrations of chemical burdens in myctophid from the South Atlantic Gyre (see Table 2 for comparisons with studies from other open oceans). Our results show a positive relationship between the density of plastic debris and the chemical body burden of BDE#s 183–209 in fish, a pattern that is consistent with previous research examining PBDEs in seabirds from the North Pacific Gyre (Tanaka et al., 2013). Moreover, experimental evidence demonstrates that PBDEs can transfer from plastic to organisms, including fish, upon ingestion (Gaylor et al., 2012; Browne et al., 2013; Rochman et al., 2013c). Combined, these lines of evidence suggest that higher brominated PBDEs, a chemical ingredient of plastic, may be an indicator for the exposure of plastic debris to marine animals. Future risk assessments are necessary to determine the risk-based threshold levels for PBDEs and other priority pollutants (e.g. PCBs) on plastic media for use in conducting site-specific risk assessments for contaminated plastic and for lower trophic-level fish, as laboratory studies demonstrate that PBDEs can cause endocrine disruption, including changes in gene expression (Han et al., 2011), reduced sperm count in male and failed egg production in female fish (Muirhead et al., 2006). Still, teasing apart whether the bioaccumulation of chemicals, already present in the environment, is a direct result of the addition of plastic debris to a habitat is not trivial. Thus, additional efforts are needed to compare the plastic in the gut content of each individual fish with the body burden of chemicals in their tissues.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.01.058.

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