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Baseline

Accumulation of plastic-derived chemicals in tissues of seabirds ingesting marine plastics

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ABSTRACT

We analyzed polybrominated diphenyl ethers (PBDEs) in abdominal adipose of oceanic seabirds (short-tailed shearwaters, *Puffinus tenuirostris*) collected in northern North Pacific Ocean. In 3 of 12 birds, we detected higher-brominated congeners (viz., BDE209 and BDE183), which are not present in the natural prey (pelagic fish) of the birds. The same compounds were present in plastic found in the stomachs of the 3 birds. These data suggested the transfer of plastic-derived chemicals from ingested plastics to the tissues of marine-based organisms.

Increasing amounts of plastics are entering the oceans on account of increases in production and poor waste management. Plastic resin pellets and plastic fragments are frequently observed in marine environments (Derraik, 2002; Arthur et al., 2009; Ogata et al., 2009), and even in the open ocean (Moore et al., 2001; Yamashita and Tanimura, 2007; Moret-Ferguson et al., 2010). Many species of marine-based organisms, such as seabirds, ingest these plastics, mistaking them for prey (Derraik, 2002; Ryan et al., 2009; van Franeker et al., 2011). The plastics cause injury and inhibit the digestion of food. Further concerns arise from the toxic chemicals both contained in the plastics as additives and adsorbed from ambient seawater (Teuten et al., 2009; Hirai et al., 2011). Such marine plastics can transport toxic chemicals in marine organisms (Mato et al., 2001).

Assessing the ecological effects associated with chemicals in marine plastics depends on whether the chemicals are transferred from the ingested plastics into the organisms' tissues, but there is no clear answer (GESAMP, 2010). Several studies have examined the transfer of polychlorinated biphenyls (PCBs) from ingested plastics to seabirds (Ryan et al., 1988; Teuten et al., 2009; Yamashita et al., 2011). However, the evidence was weak, because seabirds take in PCBs not only from plastics, but also from their prey which biomagnify them through the food web.

In the present study, we focused on polybrominated diphenyl ethers (PBDEs), which are applied to plastics and to textiles as flame retardants. Because of their bioaccumulation, persistence, and toxicity, some PBDE congeners are categorized as persistent organic pollutants (POPs) and are regulated by the Stockholm Convention (UNEP, 2001). PBDEs were detected in marine plastics (Hirai et al., 2011). PBDEs are biomagnified less than PCBs (Burreau et al., 2006; Mizukawa et al., 2009) and their exposure from prey could be smaller than PCBs. Therefore, contribution from plastic ingestion could be more clearly seen for PBDEs. Thus, we measured PBDEs in the fatty tissues of short-tailed shearwater and in plastics found in their stomachs, because these species of seabirds frequently ingest plastics (Yamashita et al., 2011). Our objective was to get more concrete evidence of the transfer of plastic-derived chemicals to the tissues of seabirds by comparing PBDE profiles between the tissues and the plastics in the seabirds.

Twelve short-tailed shearwaters (*Puffinus tenuirostris*) were caught as bycatch in experimental driftnets by the research vessel Wakatake-maru (Hokkaido Prefectural Government) in the northern North Pacific Ocean (40°00′–47°30′N, 180°00′; 55°30′–58°30′N, 178°00′E–178°00′W) during June to July 2005 (Yamashita et al., 2011). The carcasses were stored at −30 °C until analysis. In the laboratory, the carcasses were thawed and blotted dry with tissue paper, and then dissected with a solvent-rinsed stainless steel knife. The abdominal adipose tissue was removed, put in solvent-rinsed glass vials, and stored in the freezer at −30 °C until analysis. The stomachs were removed to examine the contents.

All the examined seabirds held plastics in their stomachs, at 0.04–0.59 g per bird (Fig. 1, Table S1). Plastic pieces found in the stomach contents were removed, washed in distilled water, dried at room temperature, and weighed on an electronic balance. The plastics were identified and sorted by polymer type by near-infrared spectrometry (PlaScan-W, OPT Research Inc., Tokyo, Japan). Specimens of lanternfish (Myctophidae) and squid (Gonatidae),

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Fig. 1. Photos of plastics in the short-tailed shearwater. Birds are identified by the last 2 digits of each code number. Grid: 5 mm × 5 mm.

prey species of short-tailed shearwaters, were collected in mid-water trawl nets from the training ship Oshoro-maru (Hokkaido University) in the northern North Pacific Ocean (NNPO) as follows. Three individuals of lanternfish and one squid were collected in the eastern part of NNPO (39°30′–43°15′N, 155°00′E) in May 2012. Another three individuals of lanternfish were collected in the western part of NNPO (45°33′N, 159°21′W) in July 2012. The fishes and squid were analyzed whole.

PBDEs were measured in the abdominal adipose of the 12 birds and in the ingested plastics, and in the whole tissues of 6 lanternfishes and one squid. All solvents for the chemical analyses were distilled in glass. All glass and stainless steel equipment was rinsed with the distilled solvents. Approximately 1 g (wet weight) of abdominal adipose tissue and 10 g (wet weight) of lanternfish were extracted in a Polytron PT2000 homogenizer with dichloromethane (DCM) and anhydrous sodium sulfate. Ingested plastic samples were extracted by Soxhlet extraction with DCM according to Hirai et al. (2011). The sample extracts were spiked with surrogate standards (^{13}C-labeled BDE3, BDE15, BDE28, BDE47, BDE99, BDE153, BDE154, and BDE183, and 4′-fluoro-2,2′,3,3′,4,5,5′,6,6′-nonabromo-diphenylether) and thoroughly purified by centrifugation (737 × g for 30 min), two-step silica gel column chromatography, and gel permeation chromatography. Details of the chromatography are described in Mizukawa et al. (2009) and Yamashita et al. (2011). Purified fractions were analyzed by gas chromatography–ion trap-mass spectrometry (GC–IT-MS) for lower-brominated congeners and by GC with electron capture detector for higher-brominated congeners. The detailed instrumental conditions are presented in Hirai et al. (2011). Forty-nine BDE congeners (mono- to deca-brominated; BDE 1, 2, 3, 7, 8, 10, 11, 12/13, 15, 17/25, 30, 32, 22/28, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 153, 154, 155, 166, 179, 181, 183, 184, 188, 190, 196, 197, 203, 206, 207, 208, 209) were quantified. PBDE concentrations are expressed on lipid weight base. PBDE concentrations in the samples were corrected against the recovery of the surrogates. Reproducibility and recovery were confirmed in advance through 4 replicate analyses of adipose tissue extracts with and without spiking of native PBDE standards. The relative standard deviations of concentrations of individual congeners were <10% and the recoveries were >87%. A procedural blank was run with every batch (4 samples). The limit of quantification (LOQ) was set at 3 times the amount detected in the procedural blank: 0.0006 ng/g-lipid weight for BDE47, 0.002 ng/g for BDE183, and 0.03 ng/g for BDE209. All reported values are over the LOQ.

PBDEs were detected in all birds, at 0.3–186 ng/g-lipid weight (Fig. 2A, Table S2), with median concentrations of 1.5 ng/g-lipid. These concentrations were similar to those found in pelagic seabirds (Fängström et al., 2005; Karlsson et al., 2006). In 9 of the 12 birds, lower-brominated congeners (i.e., tetra- to hexa-brominated congeners such as BDE47, BDE99, and BDE154) were dominant (Fig. 2B). These profiles, with a dominance of lower-brominated congeners, are similar to those found in pelagic fishes (Fig. 2C, Table S3), the prey of shearwaters. These data indicate that these lower-brominated congeners are accumulated in the body of the seabird through the food web.

In 2 birds (IDs #18 and #22), however, BDE209 was dominant over lower-brominated congeners, and in another bird (#27), BDE183 was dominant (Fig. 2B). These three birds had higher concentrations of PBDEs than the other seabirds whose PBDEs were dominated by lower brominated congeners. This indicates that there is some exposure source of PBDEs rich in these higher brominated congeners. BDE209 and BDE183 are major components of deca-BDE and octa-BDE technical products, respectively. BDE209 and BDE183 were not detected in the lanternfish (Fig. 2C) and squid (Table S3), which are the prey of the short-tailed shearwater and which were collected from the same area as the seabirds. BDE209 and BDE183 were not detected in the other species of pelagic fishes from the northern or southern hemisphere, whereas lower BDEs such as BDE47, BDE99, and BDE154 were abundant (Ueno et al., 2004). Thus, exposure of the short-tailed shearwaters to higher-brominated congeners through the food web is unlikely. However, shearwaters are very long-lived birds that may have a varied diet within and across years (Hunt et al., 2002), and our prey samples were limited in terms of species, area, and year (e.g., seabirds were collected in 2005 while the prey organisms were collected in 2012). More species of prey organisms collected in wider range of areas should be analyzed to examine the possibility of picking up the higher brominated congeners from other diet sources.

On the other hand, BDE209 and BDE183 were detected in marine plastics (Hirai et al., 2011), where their occurrence was

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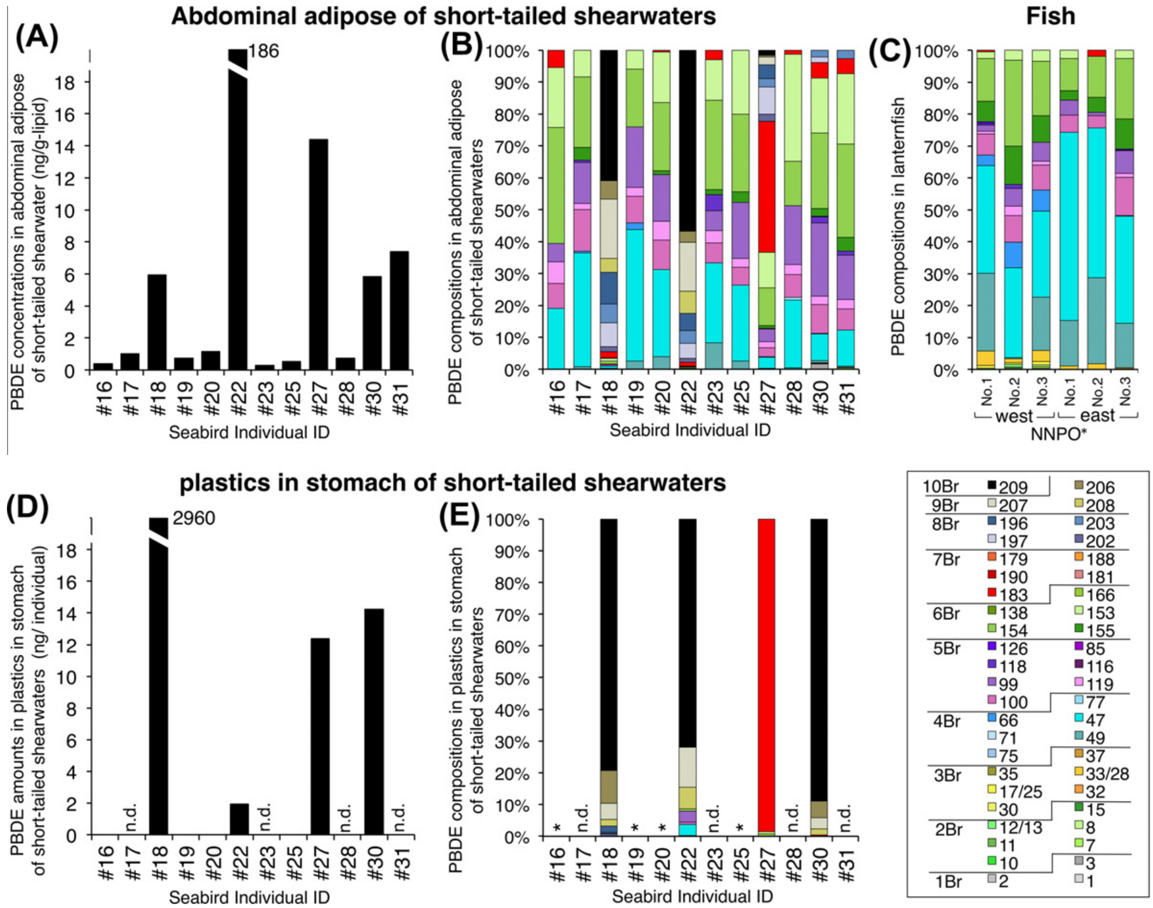

Fig. 2. PBDE concentrations and compositions in (A and B) abdominal adipose of short-tailed shearwaters, (D and E) the plastics in their stomachs, and (C) their prey. n.d., not detected. *Profile is not shown because only trace concentrations of one congener (BDE47 or BDE71) were detected; **NNPO: Northern North Pacific Ocean.

sporadic, because flame retardants are compounded in specific commercial products. This background is consistent with our sporadic detection of BDE209 and BDE183 among the shearwaters. Thus, plastic-mediated exposure of these congeners is likely. In fact, we detected BDE209 and BDE183 in the plastics found in the stomachs of the 3 birds (#18, #22, and #27) that contained mainly BDE209 or BDE183 in the adipose, and their congener profiles (Fig. 2E, Table S4) strongly resemble those in the adipose of the birds (Fig. 2B), suggesting the transfer of PBDEs from the ingested plastic to the adipose. BDE209 was not detected in the adipose of bird #30, although it was present in the ingested plastic. The plastic might not have been in the stomach long enough for the congener to be absorbed. The release of chemicals from plastics into the digestive fluids and their absorption into tissues need to be studied.

So far BDE209 has been detected in some species of seabirds, e.g., northern fulmars (*Fulmarus glacialis*: Fängström et al., 2005; Knudsen et al., 2007) and black-tailed gull (*Larus crassirostris*: Kunisue et al., 2008). Fängström et al. (2005) measured PBDEs in muscle tissue of 14 fulmars collected from the Faroe Islands. Although most birds had low concentrations of BDE209 (0.39–3.4 ng/g-lipid), one had a much higher concentration (62 ng/g-lipid). Among 9 fulmar egg samples from the same islands, BDE209 was detected in 1 sample, at 7.18 ng/g-lipid (Karlsson et al., 2006). It was also detected in 1 of 18 northern fulmars from Bjørnøya, in the Norwegian Arctic (Knudsen et al., 2007). Such sporadic detection is consistent with our observations. These studies did not investigate the plastics in the digestive tracts or correlate the detection of BDE209 with plastic ingestion. However, van Franeker et al. (2011) found frequent ingestion of plastics by fulmars. Our results suggest that their detection of BDE209 can be explained by the ingestion of plastics. Thus, the transfer of plastic-derived chemicals to biological tissues may occur in many species of birds over a wide range. More observations of the relationship between plastic ingestion and tissue PBDEs are needed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.marpolbul.2012.12.010.

References

Arthur, C., Baker, J., Bamford, H., 2009. Proceedings of the International Research Workshop on the occurrence, effects and fate of microplastic marine debris, in NOAA Technical, Memorandum.

Burreau, S., Zebuhr, Y., Broman, D., Ishaq, R., 2006. Biomagnification of PBDEs and PCBs in food webs from the Baltic Sea and the northern Atlantic Ocean. Sci. Total Environ. 366, 659–672.

Derraik, J.G.B., 2002. The pollution of the marine environment by plastic debris: a review. Mar. Pollut. Bull. 44, 842–852.

Fängström, B., Athanasiadou, M., Athanassiadis, I., Bignert, A., Grandjean, P., Weihe, P.L., Bergman, Ö., 2005. Polybrominated diphenyl ethers and traditional organochlorine pollutants in fulmars (*Fulmarus glacialis*) from the Faroe Islands. Chemosphere 60, 836–843.

van Franeker, J.A., Blaize, C., Danielsen, J., Fairclough, K., Gollan, J., Guse, N., Hansen, P.-L., Heubeck, M., Jensen, J.-K., Le Guillou, G., Olsen, B., Olsen, K.R.-O., Pedersen, J., Stienen, E.W.M., Turner, D.M., 2011. Monitoring plastic ingestion by the northern fulmar *Fulmarus glacialis* in the North Sea. Environ. Pollut. 159, 2609–2615.

GESAMP, 2010. in: Proceedings of the GESAMP international workshop on plastic particles as a vector in transporting persistent, bio-accumulating and toxic substances in the oceans. Bowmer, T., Kershaw, P.J., (Eds.) 2010 GESAMP Rep. Stud. No. 82, p. 68.

Hirai, H., Takada, H., Ogata, Y., Yamashita, R., Mizukawa, K., Saha, M., Kwan, C., Moore, C., Gray, H., Laursen, D., Zettler, E.R., Farrington, J.W., Reddy, C.M., Peacock, E.E., Ward, M.W., 2011. Organic micropollutants in marine plastics debris from the open ocean and remote and urban beaches. Mar. Pollut. Bull. 62, 1683–1692.

Hunt Jr, G.L., Baduini, C., Jahncke, J., 2002. Diets of short-tailed shearwaters in the southeastern Bering Sea. Deep Sea Res. Part II: Top Stud Oceanogr 49, 6147–6156.

Karlsson, M., Ericson, I., van Bavel, B., Jensen, J.K., Dam, M., 2006. Levels of brominated flame retardants in Northern Fulmar (*Fulmarus glacialis*) eggs from the Faroe Islands. Sci. Total Environ. 367, 840–846.

Knudsen, L.B., Borgå, K., Jørgensen, E.H., van Bavel, B., Schlabach, M., Verreault, J., Gabrielsen, G.W., 2007. Halogenated organic contaminants and mercury in northern fulmars (*Fulmarus glacialis*): levels, relationships to dietary descriptors and blood to liver comparison. Environ. Pollut. 146, 25–33.

Kunisue, T., Higaki, Y., Isobe, T., Takahashi, S., Subramanian, A., Tanabe, S., 2008. Spatial trends of polybrominated diphenyl ethers in avian species: utilization of stored samples in the environmental specimen bank of Ehime University (es-Bank). Environ. Pollut. 154, 272–282.

Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., Kaminuma, T., 2001. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. Environ. Sci. Technol. 35, 318–324.

Mizukawa, K., Takada, H., Takeuchi, I., Ikemoto, T., Omori, K., Tsuchiya, K., 2009. Bioconcentration and biomagnification of polybrominated diphenyl ethers (PBDEs) through lower-trophic-level coastal marine food web. Mar. Pollut. Bull. 58, 1217–1224.

Moore, C.J., Moore, S.L., Leecaster, M.K., Weisberg, S.B., 2001. A comparison of plastic and Plankton in the North Pacific Central Gyre. Mar. Pollut. Bull. 42, 1297–1300.

Moret-Ferguson, S., Law, K.L., Proskurowski, G., Murphy, E.K., Peacock, E.E., Reddy, C.M., 2010. The size, mass, and composition of plastic debris in the Western North Atlantic Ocean. Mar. Pollut. Bull. 60, 1873–1878.

Ogata, Y., Takada, H., Mizukawa, K., Hirai, H., Iwasa, S., Endo, S., Mato, Y., Saha, M., Okuda, K., Nakashima, A., Murakami, M., Zurcher, N., Boonyatumanond, R., Zakaria, M.P., Dung, L.Q., Gordon, M., Miguez, C., Suzuki, S., Moore, C., Karapanagiotis, H.K., Weerts, S., McClurg, T., Burres, E., Smith, W., Van Velkenburg, M., Lang, J.S., Lang, R.C., Laursen, D., Danner, B., Stewardson, N., Thompson, R.C., 2009. International pellet watch: global monitoring of persistent organic pollutants (POPs) in coastal waters. 1. Initial phase data on PCBs, DDTs, and HCHs. Mar. Pollut. Bull. 58, 1437–1446.

Ryan, P.G., Connel, A.D., Gardner, B.D., 1988. Plastic ingestion and PCBs in seabirds: is there a relationship? Mar. Pollut. Bull. 19, 174–176.

Ryan, P.G., Moore, C.J., van Franeker, J.A., Moloney, C.L., 2009. Monitoring the abundance of plastic debris in the marine environment. Philos Trans Royal Soc B – Biol Sci 364, 1999–2012.

Teuten, E.L., Saquing, J.M., Knappe, D.R.U., Barlaz, M.A., Jonsson, S., Bjorn, A., Rowland, S.J., Thompson, R.C., Galloway, T.S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Pham, H.V., Tana, T.S., Prudente, M., Boonyatumanond, R., Zakaria, M.P., Akkhavong, K., Ogata, Y., Hirai, H., Iwasa, S., Mizukawa, K., Hagino, Y., Imamura, A., Saha, M., Takada, H., 2009. Transport and release of chemicals from plastics to the environment and to wildlife. Philos Trans Royal Soc B – Biol Sci 364, 2027–2045.

Ueno, D., Kajiwara, N., Tanaka, H., Subramanian, A., Fillmann, G., Lam, P.K.S., Zheng, G.J., Muchitar, M., Razak, H., Prudente, M., Chung, K.-H., Tanabe, S., 2004. Global pollution monitoring of polybrominated diphenyl ethers using Skipjack Tuna as a Bioindicator. Environ. Sci. Technol. 38, 2312–2316.

UNEP (United Nations Environment Programme), Stockholm convention on persistent organic pollutants, stockholm, 22 May 2001 Adoption of Amendments to Annexes A, B and C Reference: C.N.524, 2009; TREATIES-4, <http://www.chm.pops.int>.

Yamashita, R., Tanimura, A., 2007. Floating plastic in the Kuroshio current area, Western North Pacific Ocean. Mar. Pollut. Bull. 54, 485–488.

Yamashita, R., Takada, H., Fukuwaka, M.-A., Watanuki, Y., 2011. Physical and chemical effects of ingested plastic debris on short-tailed shearwaters, *Puffinus tenuirostris*, in the North Pacific Ocean. Mar. Pollut. Bull. 62, 2845–2849.

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