PBDE METABOLITES ARE HIGHER THAN PARENT PBDES IN PELAGIC NORTH PACIFIC ALBATROSS: NATURAL OCCURRANCE?

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Introduction

Polybrominated diphenyl ethers (PBDEs), extensively used as flame retardants, follow the footsteps of many legacy POPs (long-range transport, biotransformation, and harmful effects to wildlife and humans due to their endocrine disruptive properties), and thus become an increasing concern. More alarming is that these compounds are biotransformed to even more toxic chemicals in the body. Particularly, hydroxylated BDEs (OH-BDEs) found in tissues of humans/wildlife are of more concern since they are known to be more potent than their parent compounds and/or other biotransformation products (e.g. methoxylated PBDEs), particularly affecting homeostasis[1]. Our recent results[2] showed that North Pacific albatrosses, which are at the top of the marine food chain, are still highly exposed to polychlorinated biphenyls (PCBs) and organchlorine pesticides (OCPs). In contrast to PCBs, our results indicate their PBDE exposures are much lower. However, in addition to enzymatic transformations[3, 4], OH- and MeO-PBDEs are known to occur both in natural marine environments (e.g., marine sponges and algae) and from industrial activities[5], complicating the ability to trace their sources, fate, and transformation mechanisms. This makes it increasingly difficult to predict metabolite levels relative to their parent PBDEs in biota. Scientific interest in these chemicals is still growing, but data is limited, particularly in remote ocean environments. This study aims to identify the hydroxylated metabolites of both PBDEs and PCBs in North Pacific albatrosses and to elucidate the sources, levels, and distributions of these metabolites with regards to species, foraging range, geographical location, and feeding patterns.

Materials and Methods

We collected blood samples from 56 adult albatrosses breeding on Guadalupe Island (29°3'9" N, 118°16'34" W), located off the coast of Baja California, Mexico and Tern Island (23°52'14" N, 166°16'52" W; French Frigate Shoals, NW Hawaiian Islands), USA in the North Pacific gyre during the 2005 breeding season. The species and location for the 33 samples analyzed are: (1) Tern Island: Black-footed (*Phoebastria nigripes*) (n=14) and Laysan Albatross (*Phoebastria immutabilis*) (n=10); and (2) Guadalupe Island: Laysan Albatross (n=9). MeO-BDE standards were purchased from Wellington Laboratory or donated by Dr. Robert Letcher; 6'-MeO-BDE17, 4'-MeO-BDE17, 2'-MeO-BDE28, 6'-MeO-BDE49, 2'-MeO-BDE68, ^{13}C-6-MeO-BDE47 (IS), 6-MeO-BDE47, 3-MeO-BDE47, 5-MeO-BDE47, 4'-MeO-BDE49, 6-MeO-BDE99, 5'-MeO-BDE100, 6-MeO-BDE90, 5'-MeO-BDE99, 4'-MeO-BDE101, 2-MeO-BDE123, 6-MeO-BDE85, 4'-MeO-BDE103, 6-MeO-BDE137. OH-PCB standards were purchased from Wellington Laboratory or donated by Dr. Åke Bergman; 4-OH-CB107, 3-OH-CB153, 4-OH-CB146, 3'-OH-CB138, 4'-OH-CB130, 4-OH-CB187, 4'-OH-CB159 (IS), 3'-OH-CB180, 4'-OH-CB172, 4-OH-CB193.

Samples were prepared using standard extraction, phase-separation, and column clean up techniques modified from our earlier studies [6, 7]. The neutral fractions were analyzed for twenty-eight PCBs and three major PBDEs (BDE-47, -99, and -153) using an Agilent 7890 GC-ECD equipped with DB-XLB (J & W Scientific, Folsom, CA; 60 m x 0.25 mm I.D., 0.25 µm film thickness) and RTX-5MS columns (Restek; 60 m x 0.25 mm I.D. x 0.25 µm film thickness). The phenolic fractions were analyzed for OH-PBDEs and OH-PCBs simultaneously by using high resolution GC/MS coupled with DB-5MS column (J & W Scientific, Folsom, CA; 60 m x 0.25 mm I.D., 0.25 µm film thickness). The mass spectrometer was operated in electron impact ionization mode using multiple ion detection, and the source temperature was set to 260°C. The ionization energy was set to 42 V. Recoveries from surrogate spikes were within reasonable analytical error ranges; 4'-OH-CB159 (76±14%) and ^{13}C 6-OH-BDE47 (78±25%). All chemical analyses were performed in the ultra clean laboratory at the Department of Toxic Substances Control, Berkeley, California. Concentrations of both neutral and polar compounds are presented as ng/mL wet weight for comparison purposes.

Results and Discussion

North Pacific albatross plasma samples showed different levels and distributions of OH-BDE and OH-PCB metabolites with regards to species and geographic location (Figure 1). Tern Island black-footed albatrosses (BFALs) showed the highest levels of hydroxylated metabolites, followed by Guadalupe Island Laysan albatrosses (LAALs). The levels of ∑OH-BDEs in these birds were higher than Norwegian Arctic glaucous gull and polar bear[8] and U.S. east coast bottle nose dolphin[9]. Strikingly, the levels of ∑OH-BDEs were higher than their possible parent PBDEs in these pelagic birds, in contrast to∑OH -PCB levels which were lower than their parent compounds (Figure 1). Similar higher OH-BDE levels compared to PBDEs were also reported from albatross liver samples collected from Indian and Atlantic Ocean[10] and Greenland polar bear blood[11]. However, the correlation between ∑OH-BDEs and PBDEs was poor in our study (Figure 2a), indicating multiple sources from both enzymatic oxidative metabolism in the body and/or marine organisms (e.g., algae and sponge). In contrast, OH-PCBs significantly correlated (R^2=0.69, p=0.001) with their parent PCBs (Figure 2b), indicating that OH-PCBs are formed mainly from metabolic activity.

Two tetra OH-BDEs (6-OH-BDE47 and 2'-OH-BDE68) were predominantly detected in all albatross plasma samples which had 6-OH-BDE47 as the major congener. In addition, 3-OH-BDE47, 5-OH-BDE47, and 4'-OH-BDE49 were also frequently detected, but in lower levels. However, penta and hexa OH-BDEs were rarely detected. 6-MeO-BDE47 and 2'-MeO-BDE68 were reported to be natural products[5] and possible sources for 6-OH-BDE47 and 2'-OH-BDE68 in marine organisms [10]. All nine OH-PCBs measured in this study were detectable in our albatross plasma samples where 4-OH-CB187 was the major congener, followed by 4-OH-PCB146. In addition, several unidentified penta- and hexa-OH-PCBs were detected.

The predominance of 6-OH-BDE47 and 4-OH-CB187 found in these pelagic birds is of great concern since these two congeners show the strong binding affinity to TTR and are more competitive than T3 and T4 in the gull[1]. These results warrant further investigation on the sources of metabolites, particularly OH-BDEs. Consequently, we are measuring the methoxy form (MeO-BDEs) of BDE metabolites in albatross plasma to find the relationship between these two PBDE metabolites. In addition, we plan to investigate if plastic debris in North Pacific gyre could be a substrate vector for transport of these naturally occurring PBDE metabolites to these Albatross.

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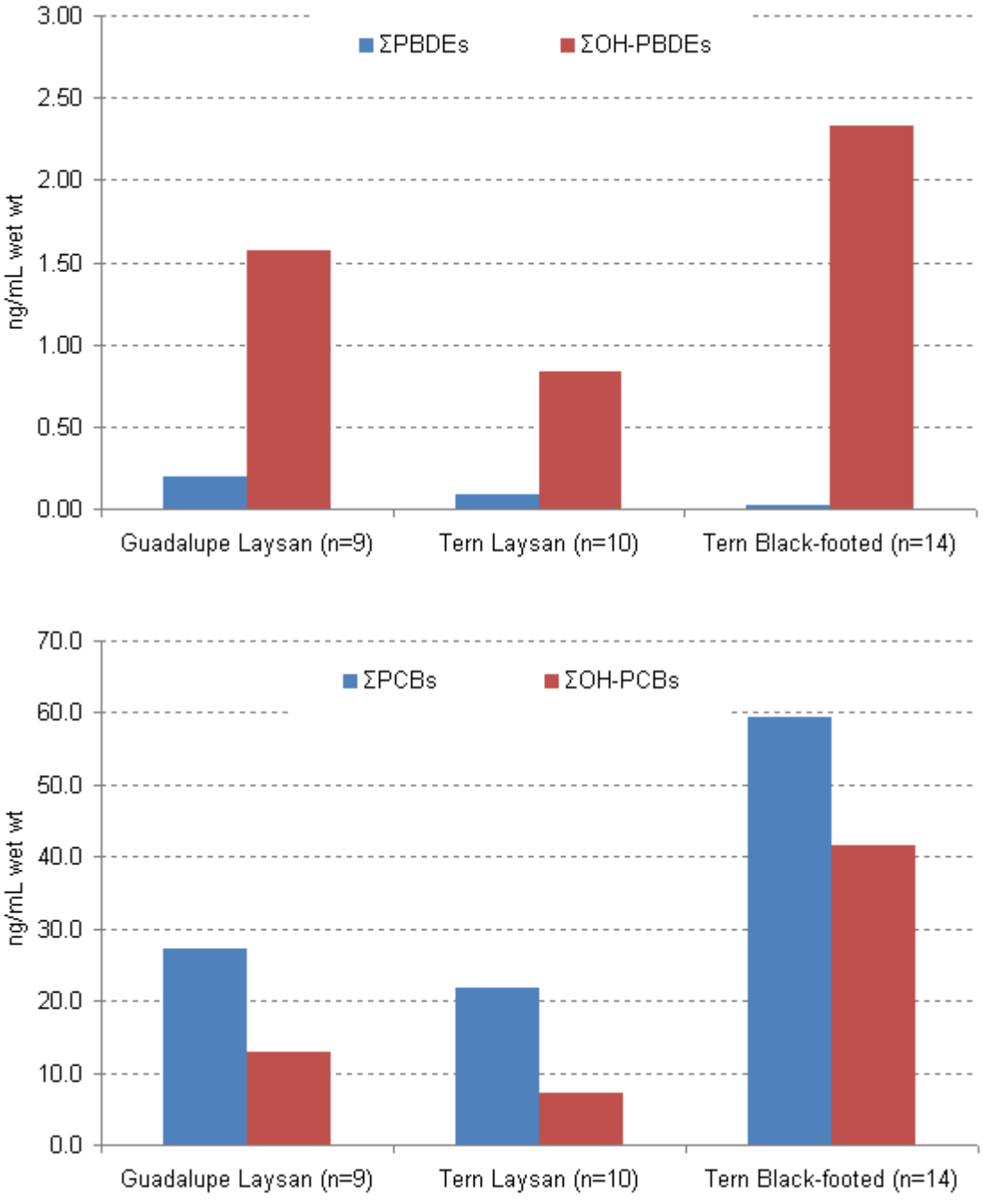

Figure 1. Levels of PBDEs and PCBs and their metabolites in North Pacific Albatross plasma. From Tern Island, Black-footed (n=14) and Laysan Albatross (n=10) and from Guadalupe Island, Laysan Albatross (n=9) and no Black-footed albatross samples.

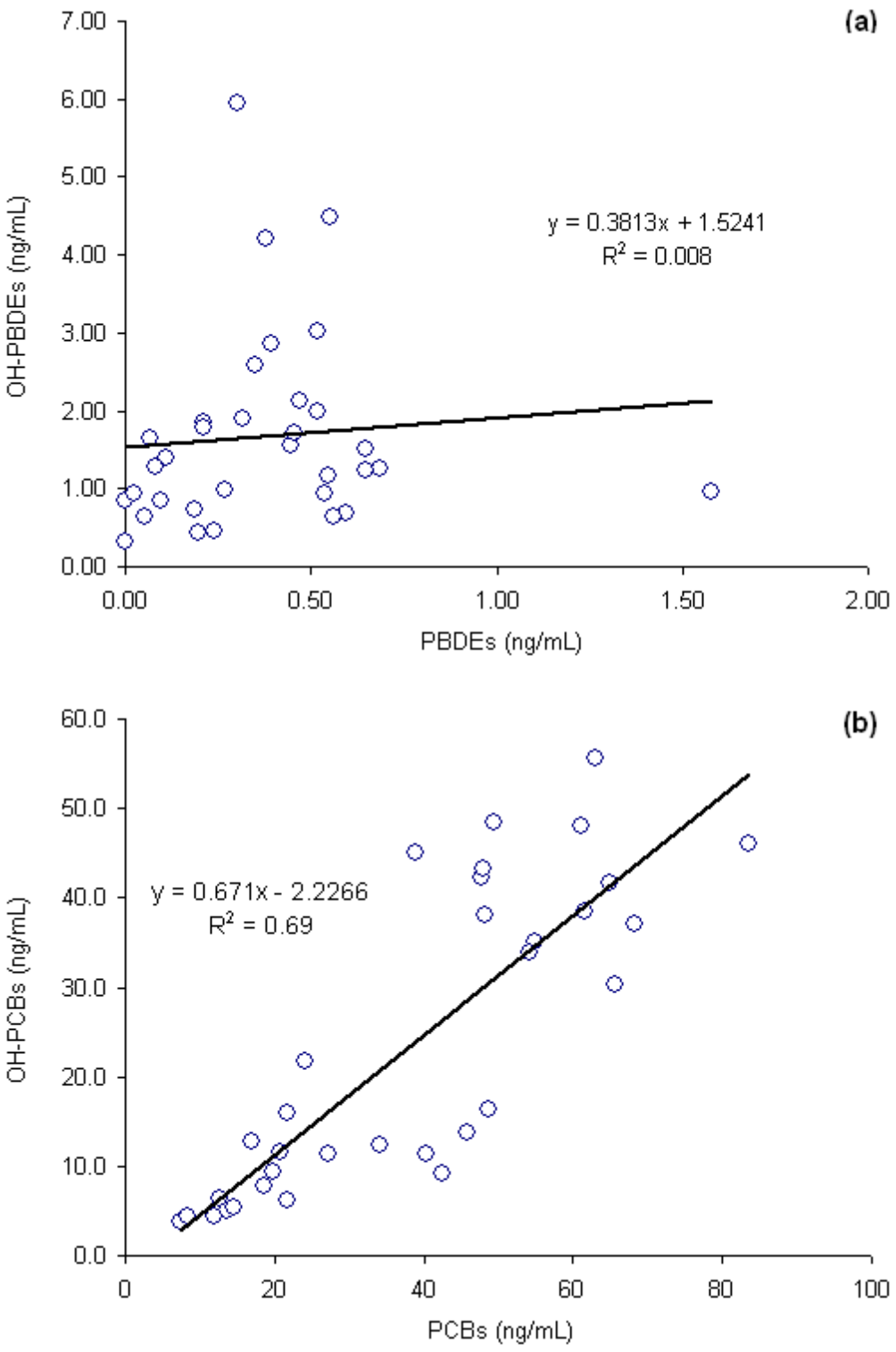

Figure 2. No correlations between PBDEs and OH-BDEs, contrasting to the pair of PCBs vs. OH-PCBs.