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Contamination Status and Accumulation Features of Organohalogen Compounds in Raccoon Dog and Masked Palm Civet

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Abstract—The present study investigated the contamination status and accumulation features of organohalogen compounds, such as CHLs (chlordane and related compounds), PCBs (polychlorinated biphenyls), DDTs (dichlorodiphenyltrichloroethane and metabolites), HCHs (hexachlorocyclohexanes), HCB (hexachlorobenzene), PBDEs (polybrominated diphenyl ethers) and HBCDs (hexabromocyclododecanes) in raccoon dogs (*Nyctereutes procyonoides*) and masked palm civet (*Paguma larvata*) collected from Kochi and Tochigi prefectures in Japan. Organohalogen compounds were detected in all the samples analyzed in this study, indicating ubiquitous contamination of Japanese terrestrial ecosystems. Significant differences in the concentrations of organochlorine pesticides (CHLs, DDTs, HCHs, HCB) in raccoon dogs were observed in the specimens of the above two prefectures; but no such difference was observed for PBDEs and HBCDs. This could be due to the region-specific usage of organochlorine pesticides in the past. Among the target chemicals, CHLs were the dominant followed by PCBs > PBDEs > DDTs in raccoon dogs, whereas DDTs were the dominant compounds, followed by PCBs > CHLs > PBDEs in masked palm civets. Masked palm civets had higher hepatic concentrations of PCBs than racoon dogs. This may reflect the difference in the metabolic capacity or feeding habits. These results suggest species-specific accumulation of organohalogen compounds in the liver of the tested animals.

Keywords: organochlorines, brominated flame retardants, PCBs, terrestrial mammals, raccoon dog, masked palm civet

INTRODUCTION

Contamination by organochlorines (OCs) in marine mammals and predatory

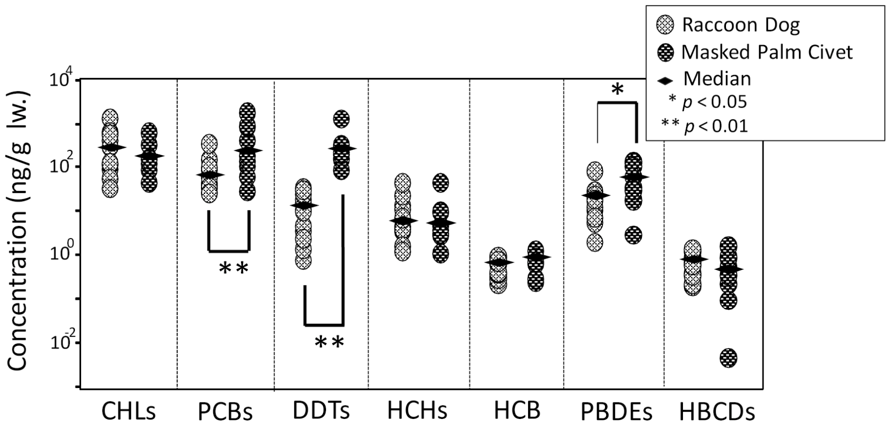

Fig. 1. Concentrations of organohalogen compounds in the liver samples of raccoon dogs and masked palm civets collected from Kochi prefecture.

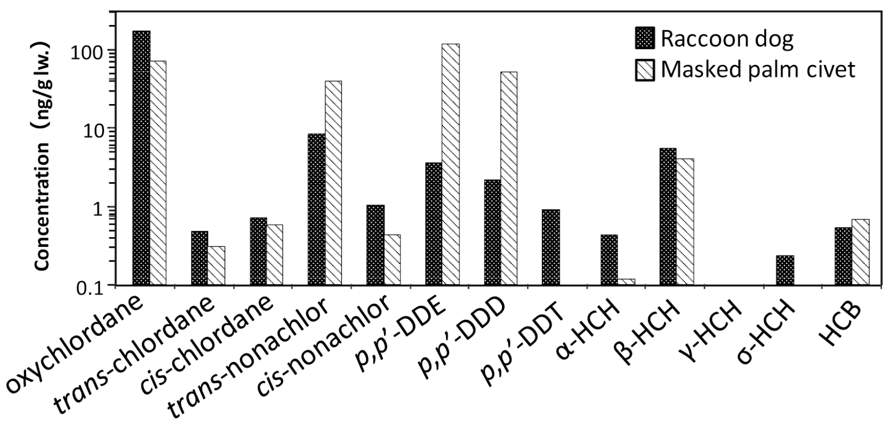

Fig. 2. Mean concentrations of OCs in the liver samples of raccoon dogs and masked palm civets collected from Kochi prefecture.

birds is still prominent and hence their toxic impacts on high trophic wildlife are of great concern. In recent years, environmental pollution by brominated flame retardants (BFRs) such as PBDEs and HBCDs has been drawing public attention due to their persistence, bioaccumulative nature, and possible adverse effects on human and wildlife. These chemicals are used as additive flame retardants in a wide variety of commercial products such as plastics, textiles, and electronic appliances. The usage of OCs was already terminated in most of the countries.

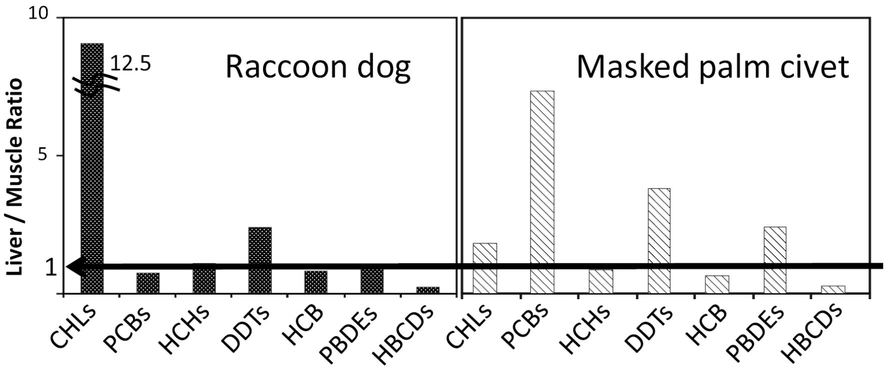

Fig. 3. Liver/muscle concentration ratios of organohalogen compounds in raccoon dogs and masked palm civets collected from Kochi prefecture.

Several reports on the environmental behavior and fate of OCs have been published (Christensen *et al.*, 2005; Voorspoels *et al.*, 2008). Our group previously investigated the contamination status of OCs in raccoon dog from Japan (Kunisue *et al.*, 2008). However, the regional trends and species specific contamination are still not very clear. Furthermore, almost no information is available on BFRs in Japanese terrestrial mammals. In this study, we attempted to elucidate the contamination status and accumulation features of organohalogen compounds in raccoon dogs and masked palm civet collected from Kochi and Tochigi prefectures in Japan.

MATERIALS AND METHODS

Samples

Liver samples of raccoon dogs from Kochi (n = 12) and Tochigi (n = 12) prefectures, and masked palm civets from Kochi (liver: n = 8; muscle: n = 8) were collected between 2005–2010. All samples were stored in the Environmental Specimen Bank (*es*-BANK) of Ehime University at –20°C until analysis. For regional comparison, published data in our previous study on raccoon dogs (Ehime, Osaka and Kanagawa prefectures) were used (Kunisue *et al.*, 2008).

Chemical analysis

Analysis of BFRs (PBDEs and HBCDs), PCBs and OCs (DDTs, CHLs, HCB and HCHs) were carried out following the methods described in previous reports (Minh *et al.*, 2001; Tanabe, 2002; Ueno *et al.*, 2004; Kajiwara *et al.*, 2006; Isobe *et al.*, 2007). Identification and quantification of OCs, PCBs and PBDEs, and HBCDs were performed using GC-ECD, GC-MS and LC-MS/MS, respectively.

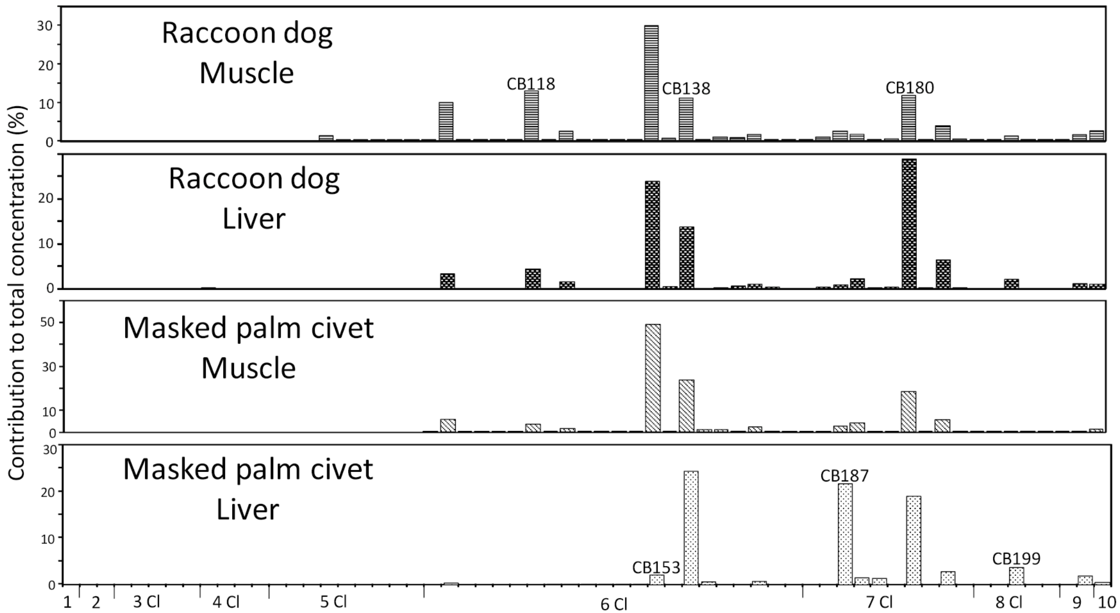

Fig. 4-1. Isomer and congener profiles of PCBs in liver and muscle of racoon dogs and masked palm civets.

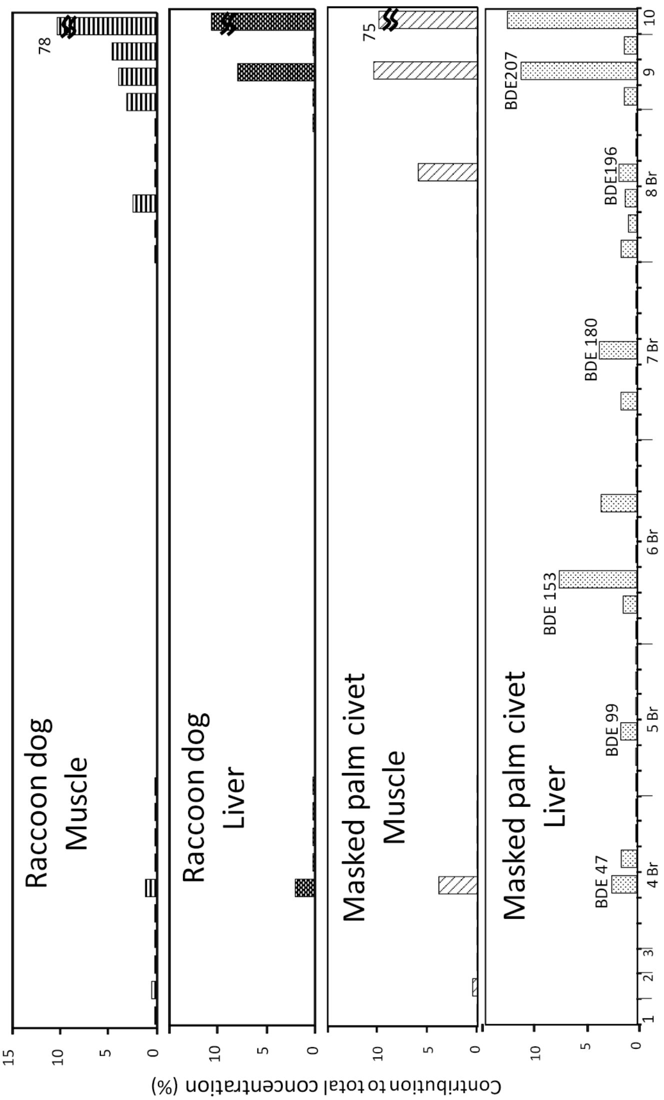

Fig. 4-2. Isomer and congener profiles of PBDEs in liver and muscle of racoon dogs and masked palm civets.

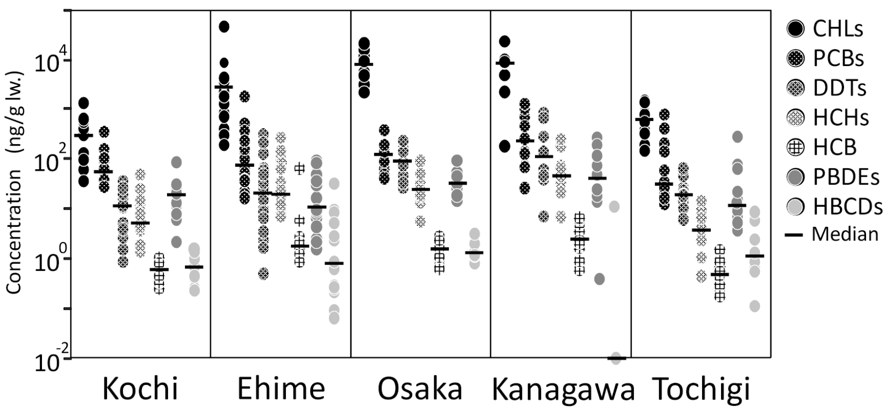

Fig. 5. Concentrations of organohalogen compounds in liver of raccoon dogs from Kochi, Ehime, Osaka, Kanagawa and Tochigi prefecture in Japan.

RESULTS AND DISCUSSION

Accumulation features

Organohalogen compounds were detected in all the samples analyzed in this study. To characterize the species specific accumulation of organohalogens in raccoon dogs and masked palm civets, concentrations in liver on lipid weight basis were shown for specimens from Kochi prefecture (Fig. 1). In raccoon dogs, CHLs (33–1200 ng/g lipid weight (lw.)) were dominant followed by PCBs (26–330 ng/g lw.) > PBDEs (2.0–87 ng/g lw.) > DDTs (0.8–33 ng/g lw.) > HCHs (1.2–45 ng/g lw.) > HBCDs (0.2–1.4 ng/g lw.) > HCB (0.2–1.0 ng/g lw.), whereas the chemicals in masked palm civets were in the order of DDTs (84–1200 ng/g lw.) > PCBs (29–1700 ng/g lw.) > CHLs (47–590 ng/g lw.) > PBDEs (3.0–130 ng/g lw.) > HCHs (1.1–44 ng/g lw.) > HCB (0.3–1.3 ng/g lw.) > HBCDs (0.1–1.7 ng/g lw.). These patterns are different from those in livers of Japanese human and avian species, where the levels of DDTs and PCBs were reported as 1–2 orders of magnitude higher than those of CHLs, HCHs and HCB (Minh *et al.*, 2001; Kunisue *et al.*, 2003). In the present study, PCBs, DDTs and PBDEs levels in raccoon dogs were significantly higher than those in masked palm civets ($p < 0.05$). These differences in accumulation pattern of organohalogens in two species may reflect the difference in the metabolic capacity or feeding habits. For example, raccoon dogs could be continuously exposed to relatively higher levels of CHLs and may have the specific metabolic capacity for DDTs. As shown in Fig. 2, concentrations of oxychlordane in raccoon dogs were slightly higher than those in masked palm civets. Oxychlordane is a metabolite from chlordane and nonachlor, components of technical CHLs mixture. Therefore, high ratio of oxychlordane may indicate the high metabolic capacity of the animal for chlordane compounds (Kawano *et al.*, 1988). This indicates that raccoon dogs had high

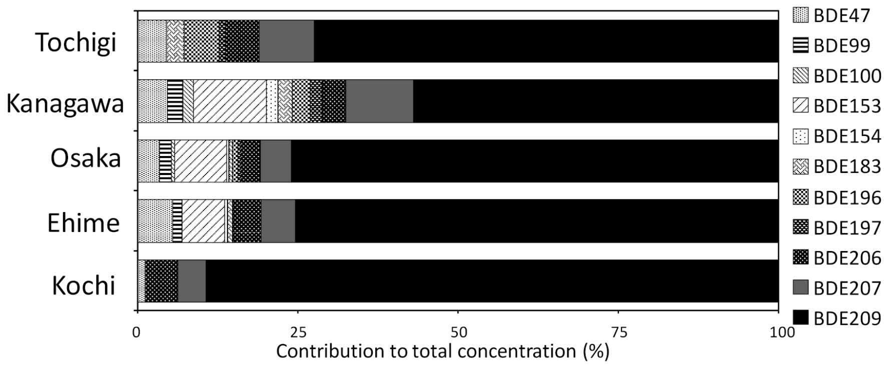

Fig. 6. Congener profiles of PBDEs in raccoon dogs from Kochi, Ehime, Osaka, Kanagawa and Tochigi prefecture in Japan.

metabolic capacity of CHLs compared to masked palm civets. Levels of DDT metabolites (*p*,*p*′-DDE and *p*,*p*′-DDD) in masked palm civets were higher than those in raccoon dogs. A previous study showed that the Canidae family could specifically metabolize and eliminate DDTs (Hoekstra *et al*., 2003; Kunisue *et al*., 2008). Raccoon dog also belongs to the Canidae family and the lower levels of DDT in their livers suggest higher metabolic capacity of this species to DDTs than those of masked palm civets.

Concentration ratios of organohlogen compounds in liver to muscle tissues were calculated (Fig. 3). In our previous study, liver/muscle ratios of CHLs and DDTs were greater than 1.0 in raccoon dogs (Kunisue *et al*., 2008) and, the ratios of HCHs, HCB, PBDEs and HBCDs were lower than 1.0 in all the specimens. The present study showed similar trends as the previous study, suggesting that the tissue distribution of HCHs, HCB, PBDEs and HBCDs are principally lipid-dependent whereas CHLs and DDTs showed liver-specific accumulation in raccoon dogs. On the other hand, masked palm civets showed a different trend. The liver/muscle ratios of PCBs and PBDEs were greater than 1.0. This indicates that the tissue distribution of these compounds differ between species and reflects the difference in metabolic capacity.

Congener profiles of PCBs and PBDEs expressed as contribution to total concentration (%) are shown in Figs. 4-1 and 4-2. Congener profiles of PCBs and PBDEs in muscle showed no obvious difference between raccoon dogs and masked palm civets. PCB congeners in raccoon dogs were dominated by CB180 followed by CB153, CB138, CB118 and CB99 and BDE209 was dominant among PBDE congeners (>80%) both in liver and muscle. In the case of bird and cat, CB153 was the main congener followed by CB180 (Kunisue *et al*., 2003, 2005; Voorspoels *et al*., 2006). The previous study reported that CB153 were immediately metabolized by CYP2B activity and thus, CB180 was the dominant congener in the Canidae family (Kunisue *et al*., 2005). The present study showed similar trends in congener patterns. On the other hand, CB138 and CB187 were predominant and CB180, CB153, CB118 and CB99 were at low levels in masked palm civets (Fig. 4-1). Lower brominated PBDE congeners were detected in liver of masked palm civet at higher levels than those of raccoon dogs (Fig. 4-2). This suggests that masked palm civet could debrominate BDE209 and accumulates lower brominated compounds as the debrominated products in the liver. These differences in accumulation patterns could be attributed to species specific metabolic capacities of raccoon dogs and masked palm civets.

Regional contamination status

Among the organohalogen compounds analyzed, CHLs were predominant in raccoon dog from all the locations (Fig. 5). CHLs levels were the highest in Osaka (2000–20000 ng/g lw.) followed by Kanagawa (170–22000 ng/g lw.), Ehime (180–43000 ng/g lw.), Tochigi (137–1410 ng/g lw.) and Kochi (33–1238 ng/g lw.) prefectures. This may be due to the past usage of CHLs mainly under the floor of timber houses as a termiticide that could still remain in CHLs-treated houses. Contamination by CHLs could be associated with extent of population in the study area. In fact, higher concentrations of CHLs in populous Osaka and Kanagawa prefectures were observed, which could be due to its past extensive use as a termiticide in houses. Concentrations of PCBs were in the order of Kanagawa (24–1200 ng/g lw.), Osaka (36–350 ng/g lw.), Ehime (15–1700 ng/g lw.), Kochi (26–330 ng/g lw.), Tochigi (12–720 ng/g lw.) prefectures and correlated with PCBs shipping volume into each prefecture (Japan POPs Network, 2011). This suggests that the levels in terrestrial ecosystems reflect past PCBs usage over long term. On the other hand, concentrations of PBDEs and HBCDs showed no difference among prefectures. This indicates that contamination by BFRs is ubiquitous in Japan and these chemicals are still present in various consumer products and consequently released into the terrestrial environment. HBCDs were dominated by α-HBCD, followed by γ-HBCD and β-HBCD in all the regions. Relative congener profiles of PBDEs varied among prefectures (Fig. 6). In all prefectures, BDE-209 was the dominant among 42 PBDE congeners. Residue levels of hepta-, octa- and nona-BDEs in raccoon dogs from Kanagawa prefectures were higher than those of the other regions, indicating that raccoon dogs from Kanagawa prefectures are exposed more to BDE congeners originating from technical octa-BDE mixtures. This may be attributed to the difference in usage pattern of PBDE technical mixtures in different regions.

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