Science of the Total Environment 514 (2015) 77–82

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Accumulation of Dechlorane Plus flame retardant in terrestrial passerines from a nature reserve in South China: The influences of biological and chemical variables

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HIGHLIGHTS

- We investigated the occurrence of DP in seven species of terrestrial passerines.
- Insectivorous birds accumulated higher ∑DP concentrations than omnivorous birds.
- Inter-species differences in the f_{anti} values were observed.
- The f_{anti} values were significantly correlated to DP concentrations.

ARTICLE INFO

Article history:
Received 20 November 2014
Received in revised form 5 January 2015
Accepted 27 January 2015
Available online xxxx

Editor: Adrian Covaci

Keywords:
Dechlorane Plus
Halogenated flame retardants
Bird
Terrestrial
Nature reserve

ABSTRACT

Although a number of studies have addressed the bioaccumulation of Dechlorane Plus (DP) flame retardant in wildlife, few data are available on terrestrial organisms. This study examined the presence of DP isomers in the muscle tissue of seven terrestrial resident passerine species, i.e., the great tit (*Parus major*), the oriental magpie-robin (*Copsychus saularis*), the red-whiskered bulbul (*Pycnonotus jocosus*), the light-vented bulbul (*Pycnonotus sinensis*), the streak-breasted scimitar babbler (*Pomatorhinus ruficollis*), the long-tailed shrike (*Lanius schach*), and the orange-headed thrush (*Zoothera citrina*), from a national nature reserve located in South China. The ∑DP (sum of *syn*-DP and *anti*-DP) concentrations ranged from 1.2 to 104 ng/g lipid weight, with significantly higher levels in insectivorous birds than in omnivorous birds. The overall exposure to DP isomers of the current passerines may be attributed to the intensive release of this pollutant from electronic waste recycling sites and industrial zones in the vicinity of the nature reserve. Species-specific DP isomeric profiles were also found, with significantly greater f_{anti} values (the isomer fractions of *anti*-DP) in the red-whiskered bulbul and the oriental magpie-robin. Additionally, the f_{anti} values were significantly negatively correlated to ∑DP concentrations for the individual bird samples, suggesting the influence of DP concentrations on the isomeric profiles.

1. Introduction

Dechlorane Plus (DP), a currently used flame retardant, was developed as a substitute for mirex which was banned in the 1970s (IPCS, 1984). The technical-grade product contains two isomers, the *syn*-DP and *anti*-DP, in a ratio of approximately 1:3 (Garcia and McLaughlin, 1991; Hoh et al., 2006). It is added to hard plastic used in electrical equipment such as computer monitors and televisions, electrical wire and cable coatings, and other polymeric systems for fire prevention (OxyChem, 2007). In addition, DP has been identified as a possible replacement for the Deca-BDE commercial mixture which was recently banned due to its environmental persistence, bioaccumulation in the

Abbreviations: DP, Dechlorane Plus; e-waste, electronic waste; GT, the great tit (*Parus major*); OMR, the oriental magpie-robin (*Copsychus saularis*); LVB, the light-vented bulbul (*Pycnonotus sinensis*); RWB, the red-whiskered bulbul (*Pycnonotus jocosus*); SBSB, the streak-breasted scimitar babbler (*Pomatorhinus ruficollis*); LTS, the long-tailed shrike (*Lanius schach*); OHT, the orange-headed thrush (*Zoothera citrina*); ww, wet weight; lw, lipid weight; PRD, the Pearl River Delta region; SNNR, Shimentai National Nature Reserve; GPC, gel permeation chromatography; CYPs, cytochrome P450s; SOD, superoxide dismutase; CAT, catalase

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http://dx.doi.org/10.1016/j.scitotenv.2015.01.095
0048-9697/

food chain, and toxic effects to humans and wildlife (Pakalin et al., 2007; US EPA, 2014). DP is not covalently bound to the polymers of the products and can be released to the environment during the use and disposal of the DP-containing consumer products. Recent studies have led to the prospect that DP exhibits long-range atmospheric transport (Möller et al., 2010), bioaccumulation in humans and wildlife (Guerra et al., 2011; Ren et al., 2009; Zhang et al., 2011), biomagnification in food webs (Tomy et al., 2007; Wu et al., 2010), and toxic effects (Li et al., 2013; Liang et al., 2014; Wu et al., 2012).

Since Hoh et al. (2006) first reported the environmental occurrence of DP isomers, numerous studies have demonstrated that DP is a worldwide contaminant (Sverko et al., 2011; Xian et al., 2011; Feo et al., 2012). The great majority of these studies were performed in areas near to DP manufacturing facilities or electronic-waste (e-waste) recycling sites and in urban/industrial regions, which are three of the most polluted types of area in the world (Sverko et al., 2011; Xian et al., 2011; Feo et al., 2012). Very few studies have examined the occurrence of DP isomers in the zones of ecological concern including nature reserves (Barón et al., 2014; Muñ oz-Arnanz et al., 2011). The occurrence of DP in wildlife from these zones is of concern given that DP has shown subchronic toxicities to organisms (Li et al., 2013; Liang et al., 2014; Wu et al., 2010). Moreover, investigations of the bioaccumulation of DP isomers in wildlife were almost exclusively carried out in aquatic ecosystems; studies of these chemicals in terrestrial wildlife are scarce (Feo et al., 2012). Previous studies indicated that bioaccumulation of persistent halogenated compounds (PHCs) with an octanol–water partition coefficient (K_{OW}) greater than 10^5 and octanol–air partition coefficient (K_{OA}) greater than 10^6 may be different between aquatic and terrestrial animals, resulting from the differing ability of water-respiring and air-breathing organisms to absorb, digest and eliminate these chemicals (Chen et al., 2010; Kelly et al., 2007). This is the case for DP, which has a log K_{OW} of 9.3 and a log K_{OA} of 12.26 (OxyChem, 2007). Therefore, research focusing on the accumulation characteristics of DP in terrestrial wildlife is essential to better understand the bioaccumulation behavior and impacts of this flame retardant.

Birds are ecologically versatile, and have proven to be very useful biological indicators for human-caused changes including chemical contamination (Furness, 1993). Some resident passerines have several characteristics which make them ideal monitors for environmental pollution. They spend their entire adult life in relatively small home ranges, territories and foraging areas. Additionally, they are widespread, sensitive to environmental changes, and easily sampled. For these reasons they have successfully been used as a biological model for studying local contamination of persistent pollutants (Van den Steen et al., 2009).

The Shimentai National Nature Reserve (SNNR) is situated on the north end of the Pearl River Delta (PRD), Guangdong Province, a region in South China that is undergoing rapid economic development (Fig. 1). The SNNR is the largest nature reserve in Guangdong Province, conserving the subtropical evergreen broad-leaved forest and the rare and endangered animals that live there. It is well documented that the PRD has been heavily contaminated by halogenated flame retardants (HFRs) including DP, due to the intensive activities of electronics manufacturing and assembly and e-waste recycling in this region (He et al., 2014; Wu et al., 2010; Zhang et al., 2011). Most of these chemicals are semi-volatile organic compounds, and could have been transported to the SNNR where they could accumulate in wildlife. In the present study, we examined residue levels and isomeric compositions of DP in the muscles of seven terrestrial passerines that reside in the SNNR. The influence of DP residues on the isomeric compositions in these birds was also examined.

2. Materials and methods

2.1. Chemicals

Standard solutions of *syn*- and *anti*-DP, and polybrominated diphenyl ether (PBDE) congeners (BDEs 77, 118, 128 and 181) were purchased from Wellington Laboratories (Guelph, ON, Canada). All organic solvents used were of analytical-reagent or guaranteed-reagent grade and were redistilled before use.

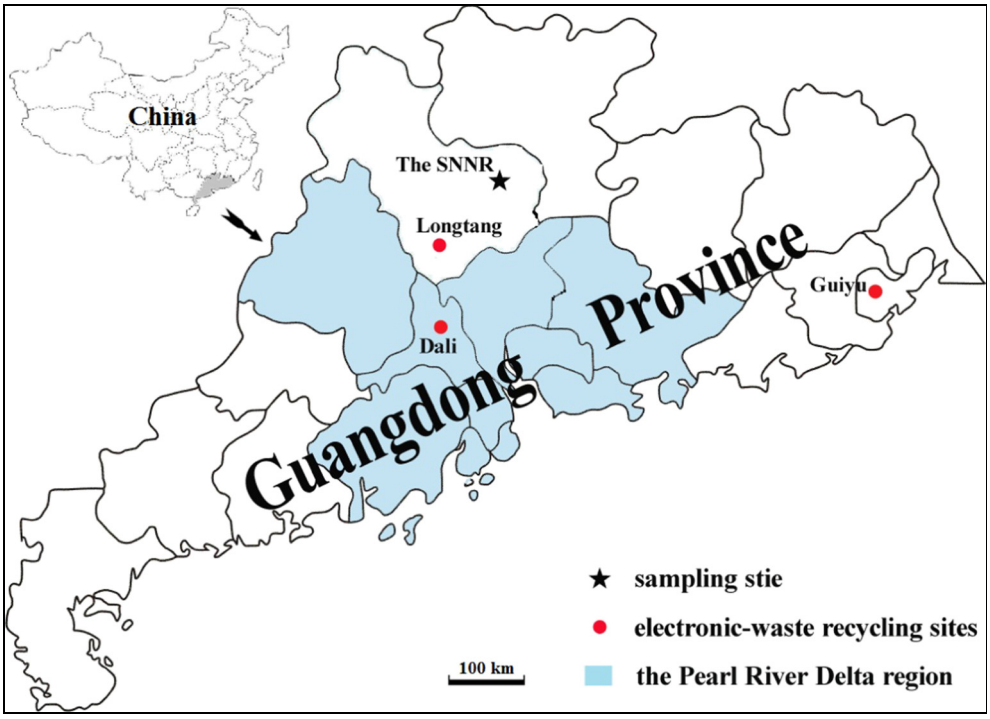

Fig. 1. Map of sampling site. SNNR = Shimentai National Nature Reserve.