Review article

Sources and environmental behaviors of Dechlorane Plus and related compounds — A review

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A B S T R A C T

Although Dechlorane Plus (DP) has been used as a polychlorinated flame retardant for almost half a century, its detection in the environment was not reported until 2006. The subsequent intensive research has confirmed its global ubiquity. A few reviews have presented the properties, analytical methods and environmental occurrence of DP and related compounds in the past several years. The present review emphasizes on the environmental behavior of DP isomers which is assessed by the variation of the isomer ratio of DP in various matrices. Other aspects including the analytical methods, emission sources, general environmental occurrence and bioaccumulation of DP are also summarized.

In this review, three typical emission sources in the environment are categorized after introducing the measurement method of DP. The temporal-spatial distribution is then evaluated at the global scale, which provides an integrated representation of the environmental occurrence of DP and potential impact on the human health and ecosystems. The variations of DP isomer ratio in various matrices reinforce its source related distribution and their stereoselective bioaccumulation. Thereafter, DP related compounds and dechlorinated analogs are briefly summarized in regards to their occurrence in various matrices, suggesting their ubiquity in the environment and bioavailability. Further studies are required to better assess the exposures and toxicological effects of DP and its analogs. A special concern is the serious contamination in e-waste recycling areas in developing countries, where long-term monitoring data on the association of DP exposure and adverse effects to human health and ecosystems is urgently needed.

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Contents

1. Introduction .............................................................. 207
2. Measurement methods for DP ...................................................... 208
  2.1. Sample collection ......................................................... 208
  2.2. Sample extraction and clean-up .............................................. 208
  2.3. Instrumental analysis and quantification ........................................ 208
3. Emission sources ............................................................ 209
  3.1. DP production .......................................................... 209
  3.2. E-waste dismantling activity .............................................. 209
  3.3. Urban/industrial activity ..................................................... 210
4. General environmental occurrence .................................................... 210
  4.1. Global distribution ......................................................... 210
  4.2. Temporal trends ........................................................ 210
5. Bioaccumulation and biomagnification potential ................................ 212
6. Isomer ratios of DP in various matrices .............................................. 212

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1. Introduction

Dechlorane Plus (DechPlus or Dechlorane 605, Abbreviation: DP, CAS# 13560-89-9) is a polychlorinated flame retardant with the chemical formula of C_{18}H_{12}Cl_{12} and a molecular weight of 653.70. It was developed as a substitute for Dechlorane (also called Mirex) which was commercialized as pesticide and additive flame retardant but banned in the 1970s due to its biological toxicity (Hoh et al., 2006). DP was produced by a Diels–Alder condensation of two equivalents of hexachlorocyclopentadiene with one equivalent of 1,5-cyclooctadiene as shown in Fig. 1. The commercially available formulation of DP contains two stereoisomers, syn-DP (CAS# 135821-03-3) and anti-DP (CAS# 135821-74-8), in the approximate ratio of 1:3 (Luo et al., 2013; Sverko et al., 2011a) (Fig. 1). The physicochemical properties of DP are listed in Table 1.

DP was first manufactured by OxyChem (Niagara Falls, NY, USA) and was mainly used as an additive flame retardant in electrical wire and cable coatings, plastic roofing materials, computer connectors and other polymeric systems since the 1960s. It has also been manufactured by Jiangsu Anpon Electrochemical Company located in East China (Huai’an, China) since 2003. Three commercial products of DP are available, DP-25, DP-35 and DP-515, all of which contain the same compound but with different particle sizes. DP is classified as a low production volume chemical in the EU, while it is categorized as a high production volume chemical in the USA. The annual productions were estimated to be 450–4500 tonnes in USA since 1986 (Qi et al., 2007) and 300–1000 tonnes by Anpon in China since 2003 (Wang et al., 2010a). The global annual production amount approximates 5000 tonnes (Ren et al., 2008).

Although DP has been produced and used for almost half a century, its first environmental detection was only reported in 2006 in the Great Lakes Basin in North America (Hoh et al., 2006). Since then, many studies gradually outlined the environmental occurrence and behavior of DP, as well as its toxic effects. DP was considered to be chemically stable in various environmental compartments, and the half-life was estimated to be over 24 years in water, with minimal or no anaerobic

![Fig. 1. The two stereoisomers of DP produced from the Diels–Alder condensation of hexachlorocyclopentadiene and 1,5-cyclooctadiene.](image-url)
degradation (OxyChem, 2007; Sverko et al., 2011a). It was also found to be persistent in suspended sediment (half-life: approximately 17 years, Sverko et al., 2008) and fish (half-life: 14 years, Ismail et al., 2009). It has been observed in the Arctic regions and marine environment, indicating its long-range atmospheric transport (LRAT) potential (Möller et al., 2010, 2011, 2012a). DP was also found to bioaccumulate and biomagnify in biota (Peng et al., 2014; Tomy et al., 2007, 2008; Wang et al., 2015; Wu et al., 2010). Recently, Toxicological research indicated that oral exposure to DP can induce hepatic oxidative damage and perturbations of metabolism and signal transduction of male mice (Wu et al., 2012). DP was also observed to alert mRNA expression levels of certain enzymes and their activities in liver of Sprague–Dawley rats, although there was no observable effect in histopathology and death (Li et al., 2013). Based on the protein responses induced by DP, Liang et al. (2014) suggested that DP may induce apoptosis in the liver of juvenile Chinese sturgeon. These studies provide further concerns on the potential threat of DP to human health and ecosystems.

A few reviews (Feo et al., 2012; Luo et al., 2013; Sverko et al., 2011a; Vorkamp and Rigét, 2014; Xian et al., 2011) have presented the properties, analytical methods and environmental levels of DP and related compounds in the past several years. This review is aimed at summarizing our current understanding of DP in the environment, including analytical methods, emission sources, and the environmental behaviors. DP isomer ratios in various matrices and tissues were specifically summarized to discuss plausible environmental processes and biotransformation of DP in biota and humans. The environmental occurrence of related compounds and dechlorination (or degradation) products of DP were also briefly reviewed. Most of the literatures on DP in the environment and in biota, published up until July 2015, was acquired and classified based on the Web of Science database. The available data on DP concentrations and isomer ratios were given in Tables S1–S7.

2. Measurement methods for DP

2.1. Sample collection

The environmental sampling strategy and devices used for DP were usually similar to those of persistent organic pollutants (POPs), e.g., polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), etc. For instance, water was collected in precleaned polyethylene, polystyrene or polycarbonate sampling containers and glass containers (preferably brown), and then stored at 4 °C until extraction. In some cases, C18, XAD-2 and XAD-4 resins were employed for adsorption of the organic matter in water, while glass fiber filter (GFF) was used to collect the particle phase (Möller et al., 2010, 2011, 2012b; Na et al., 2015; Salamova and Hites, 2011) or a multilayer column packed with acidic and basic silica gel (Jia et al., 2011; Kang et al., 2010; Liu et al., 2014; Wu et al., 2010; Zhang et al., 2013) except for sediment. It was also reported that alumina and Florisil columns, as well as commercial SPE columns (i.e., Oasis® HLB) were effective (Cequier et al., 2015; Zhang et al., 2011b; Zheng et al., 2015a). Florisil column was also used to separate Dechloranes from hexabromocyclododecane (HBCD) (Muller et al., 2009), while a column containing 3.5% (w/w) water deactivated silica gel could separate DP and brominated flame retardants (BFRs) from organophosphate esters (OPes) (Salamova et al., 2014). Hexane and hexane/dichloromethane were mainly used for elution of the analytes. For sediment samples, copper powder was commonly added into the sample during or after extraction to remove elemental sulfur (De la Torre et al., 2011; Feo et al., 2012). In addition, gel-permeation chromatography (GPC, Bio-Beads SX-3) was also employed to remove large molecules such as lipid and humus, as well as elemental sulfur in sediment (Davis et al., 2012; Feo et al., 2012). GPC was also widely used to remove lipid and protein in biota samples (Jia et al., 2011; Zhang et al., 2013). In some cases, sulfuric acid or acidic silica gel was alternatively added to the extract to remove lipid in biota prior to column cleanup (Ismail et al., 2009; Qiu and Hites, 2008; Ren et al., 2008). However, if DP mono adduct (DPMA), arising from the Diels–Alder reactions of impurities present in feedstock (1,3- or 1,5-cyclooctadiene) (Sverko et al., 2010b), would be analyzed along with DP, nondestructive methods such as GPC were strongly suggested for sample cleanup because acid treatment will degrade DPMA by attacking at its nonhalogenated double bond (Feo et al., 2012; Sverko et al., 2010b).

2.2. Sample extraction and clean-up

Soxhlet extraction (SE), liquid–liquid extraction (LLE), solid-phase extraction (SPE) and pressurized liquid extraction (PLE) including accelerated solvent extraction (ASE) could generally be utilized for DP extraction in various samples. SE and PLE (including ASE) were applied to solid samples, while LLE and SPE (e.g., C18) were used for liquid sample extraction (Na et al., 2015). Mixed organic solvents, such as n-hexane/acetone (v/v: 1/1) (Hoh et al., 2006; Ismail et al., 2009; Pevery et al., 2015; Ren et al., 2008; Salamova et al., 2014; Zhang et al., 2011a, b), n-hexane/dichloromethane (v/v: 1/1) (De la Torre et al., 2011; Möller et al., 2010, 2011; Zhang et al., 2013), and the same mixtures with different proportions (Kang et al., 2010; Tomy et al., 2008; Wu et al., 2010; Xian et al., 2011), were commonly used for extraction.

Cleanup or purification of the environmental sample extracts could be done by a silica gel column (Hoh et al., 2006; Ismail et al., 2009; Ren et al., 2008; Salamova et al., 2014) or a multilayer column packed with acidic and basic silica gel (Jia et al., 2011; Kang et al., 2010; Liu et al., 2014; Wu et al., 2010; Zhang et al., 2013) except for sediment. It was also reported that alumina and Florisil columns, as well as commercial SPE column (i.e., Oasis® HLB) were effective (Cequier et al., 2015; Zhang et al., 2011b; Zheng et al., 2015a). Florisil column was also used to separate Dechloranes from hexabromocyclododecane (HBCD) (Muller et al., 2009), while a column containing 3.5% (w/w) water deactivated silica gel could separate DP and brominated flame retardants (BFRs) from organophosphate esters (OPes) (Salamova et al., 2014). Hexane and hexane/dichloromethane were mainly used for elution of the analytes. For sediment samples, copper powder was commonly added into the sample during or after extraction to remove elemental sulfur (De la Torre et al., 2011; Feo et al., 2012). In addition, gel-permeation chromatography (GPC, Bio-Beads SX-3) was also employed to remove large molecules such as lipid and humus, as well as elemental sulfur in sediment (Davis et al., 2012; Feo et al., 2012). GPC was also widely used to remove lipid and protein in biota samples (Jia et al., 2011; Zhang et al., 2013). In some cases, sulfuric acid or acidic silica gel was alternatively added to the extract to remove lipid in biota prior to column cleanup (Ismail et al., 2009; Qiu and Hites, 2008; Ren et al., 2008). However, if DP mono adduct (DPMA), arising from the Diels–Alder reactions of impurities present in feedstock (1,3- or 1,5-cyclooctadiene) (Sverko et al., 2010b), would be analyzed along with DP, nondestructive methods such as GPC were strongly suggested for sample cleanup because acid treatment will degrade DPMA by attacking at its nonhalogenated double bond (Feo et al., 2012; Sverko et al., 2010b).

2.3. Instrumental analysis and quantification

Chromatographic separation was usually achieved using capillary gas chromatography (GC) columns with a non-polar stationary phase, such as DB-5MS (De la Torre et al., 2011; Hoh et al., 2006; Jia et al., 2011; Ren et al., 2008; Zeng et al., 2014; Zhang et al., 2013; Zheng et al., 2015a), DB-5HT (Muñoz-Arnanz et al., 2011), DB-XLB (Chen et al., 2013a, 2013b; Mo et al., 2013; Yan et al., 2012; Zhang et al., 2015).
respectively. Even lower MDL values were obtained in (Ma et al., 2015; Newton et al., 2015). The 15 m and 30 m columns were generally selected. GC run time depends on column length, while both syn-DP and anti-DP could be completely separated in a total run time of 35 min. Splitless injection was used on a high temperature, such as 280 °C and 285 °C, for flash vaporization of the sample but below the thermal degradation temperature of DP (approximately 285 °C) (Xian et al., 2011). The GC to mass spectrometry (MS) transfer line was generally held at the similar temperature as the injection port. Different GC–MS approaches, including electron capture negative ion (ECNI)–MS, negative chemical ionization (NCI)–MS, NCI-MS/MS and electron impact-high resolution mass spectrometry (EI-HRMS), were generally applied for DP analysis and quantification (Barón et al., 2012, 2014a, 2014b; De la Torre et al., 2010a; Hoh et al., 2006; Kang et al., 2010; Möller et al., 2010; Muñoz-Arnanz et al., 2011; Qiu and Hites, 2008; Xiao et al., 2012; Zeng et al., 2014). Molecular ion fragments at m/z 651.8/653.8 were generally selected for DP monitoring in ECNI-MS and NCI-MS, while the selected ion and transition at 654 > 35/ 654 > 37 were monitored in NCI-MS/MS (Barón et al., 2012). In order to obtain relatively high intensity of ion response, lower temperatures such as 150 °C (De la Torre et al., 2010a; Hoh et al., 2006; Möller et al., 2010; Zeng et al., 2014) and 200 °C (Qiu and Hites, 2008) were recommended in ECNI (or NCI) mode. In EI mode, fragmentation process was much more extensive and therefore the two most abundant ions of a fragment cluster (m/z: 271.8102/273.8072) were selected for DP monitoring when using HRMS (Feo et al., 2012; Shen et al., 2011a,b). EI mode was not recommended since an intense ion at m/z 270 (Cl<sub>5</sub>) will be formed in retro-Diels–Alder fragmentation, which may make the intensity of molecular ion low or even absent (Feo et al., 2012; Sverko et al., 2010b). Even so, there were many successful measurements conducted by monitoring the 271.8102/273.8072 ions using EI in HRMS (Brasseur et al., 2014; Shen et al., 2010, 2011a,b).

Liquid chromatography–tandem mass spectrometer system (LC–MS/MS) with an atmosphere pressure chemical ionization (APCI) interface was also reported to successfully measure halogenated flame retardants including DP in marine mammals (Zhu et al., 2013, 2014). Chromatographic separation was performed on a Zorbax SB-C18 column, and the mobile phase consisted of methanol/water (85:15) and methanol. The selected ion and transition were 632.6 > 560.8/634.6 > 560.8 for anti-DP and 632.7 > 560.8/634.7 > 560.8 for syn-DP, respectively.

Regarding DP quantification, 13C-labeled internal standards used for PBDEs were employed when isotopically labeled Dekaldehyde ethers were not available, such as 13C-3,3′-4,4′-tetrabromodiphenyl ether (13C-BDE-77) and 13C-2,2′,4,4′-tetrabromodiphenyl ether (13C-BDE-153) (Ren et al., 2009). Some BDE congeners, e.g., BDE-71, -77, -109, -110, -153, -183, and -196 which could not be detected in the environment, were also served as internal standards in some works (Peverly et al., 2015; Ismail et al., 2009). Besides these, 13C-PCB-180 and -209 were selected due to their similar chromatographic behaviors to DP (Peng et al., 2012, 2014; Zhang et al., 2013). In recent years, isotopically labeled DP were commercially produced (13C-syn-DP and 13C-anti-DP), making isotopic dilution feasible and practical for DP determination (Barón et al., 2012; Brasseur et al., 2014; Fang et al., 2014; Huber et al., 2015; Ma et al., 2015; Newton et al., 2015).

The method detection limits (MDLs) for DP were reported at the level of pg m<sup>-3</sup> in air (Ma et al., 2011; Möller et al., 2012a,b; Xiao et al., 2012), pg L<sup>-1</sup> in water (Ma et al., 2011; Na et al., 2015; Qi et al., 2010; Venier et al., 2014), pg g<sup>-1</sup> dry weight (dw) in soil and sediment (Barón et al., 2012, 2014a; Ma et al., 2011; Qi et al., 2010; Shen et al., 2011a,b; Wang et al., 2010a,b), and ng g<sup>-1</sup> lipid weight (lw) in biota samples (Guerra et al., 2011; Peng et al., 2015; Salamova and Hites, 2013; Yan et al., 2012; Zhang et al., 2011a, 2015; Zhu et al., 2014), respectively. Even lower MDL values were obtained in fish (pg g<sup>-1</sup> lw) when using GC-NCI-MS/MS and GC-EI-HRMS (Barón et al., 2012; Shen et al., 2010, 2011a), which guaranteed the detection of DP with lower levels in the background areas.

### 3. Emission sources

In general, the flame retardants include additive fire retardants and reactive fire retardants. DP was initially manufactured to replace Mirex and used as an additive flame retardant in industrial and household products. Therefore, DP production and application, as well as their recycling process could lead to DP emission into the environment.

#### 3.1 DP production

Considerable numbers of DP monitoring have been carried out in the vicinity of the North American Great Lakes and Hua’ian City, China, where the only two DP manufacturers in the world are located. Evidently high levels of DP (sum of the anti- and syn-isomers, the same below) have been generally reported in various matrices from these two areas, indicating an influence by DP production (Tables S1–S7). Air samples collected from the Integrated Atmospheric Deposition Network (IADN) stations located near the Great Lake shores demonstrated that the single highest DP concentration (490 pg m<sup>-3</sup>) occurred at the site nearby Niagara Falls, where OxyChem is situated (Hoh et al., 2006).

High average concentration of DP was observed in ambient air from the same sampling point (20 ± 6 pg m<sup>-3</sup>) in the following years (Venier and Hites, 2008). High levels of DP were also observed in sediments from Niagara River and Lake Ontario (Hoh et al., 2006; Sverko et al., 2008; Yang et al., 2011). In egg pools (pooled per year per site) of a Great Lakes biomonitoring species (herring gull, Lorus argentatus) spanning 1982–2006, a significant negative relationship was observed between DP concentrations and the distance from the DP production facility (p < 0.001) (Gauthier and Letcher, 2009). Qiu and Hites (2008) also found that the highest DP concentrations in tree barks were >100 ng g<sup>-1</sup> in the city of Niagara Falls, and dropped rapidly with distance from the production site, suggesting that OxyChem in Niagara Falls was the main DP contributor to the surrounding areas. In China, DP concentrations showed the highest levels in various matrices around the DP facility (Anpon) and soil concentrations surrounding the facility decreased by an order of magnitude within 7.5 km (Wang et al., 2010a; Zheng et al., 2015b). Zhang et al. (2013) assessed the occupational exposure to DP and found that DP concentrations were the highest in the blood and hair of workers in the plant, suggesting an evident occupational exposure of manufacturing workers to DP. All these studies provide solid evidences for elevating DP level in the surrounding environment due to DP production, which could add to increased risk for adverse effects in humans and ecosystems in the vicinity of the production site.

#### 3.2 E-waste dismantling activity

Discarded electrical and electronic equipment, often called e-waste, has raised great concern to the environment and human health, particularly in developing countries. Recycling of e-wastes could release particles loaded with heavy metals and flame retardants into the atmosphere and adjacent environmental compartments. In typical e-waste dismantling areas, e.g., Guiyu and Qingyuan in South China, where informal e-waste recycling activity was prevalent several years ago, DP concentration was 3327 ng g<sup>-1</sup> dw in soil from the e-waste recycling site (Yu et al., 2010). The levels fell dramatically with increasing distance away from the site, suggesting an evident influence of e-waste dismantling activities to the surrounding environment (Yu et al., 2010). In a reservoir in the vicinity of e-waste recycling workshops in South China, DP was detected in all the aquatic species (e.g., water snake, mud carp, crucian carp, northern snakehead, prawn and Chinese mystus snail) with concentrations of 19.1–9630 ng g<sup>-1</sup> lw, which were much higher than those in the reference mud carp (syn-DP: 1.35 ± 209

P. Wang et al. / Environment International 88 (2016) 206–220
1.35 ng g\(^{-1}\) lw; anti-DP: 7.41 ± 7.32 ng g\(^{-1}\) lw) (Wu et al., 2010). In common kingfishers (Alcedo atthis) collected from an e-waste dismantling site in the Pearl River Delta, DP levels (29–150 ng g\(^{-1}\) lw with a median of 58 ng g\(^{-1}\) lw) were one order of magnitude greater than those from the reference site (median: 3.9 ng g\(^{-1}\) lw) (Mo et al., 2013). A similar observation was obtained in the prey fishes (six species) with even larger differences between the levels in the e-waste area and the reference site (60–420 ng g\(^{-1}\) lw versus 0.96–8.8 ng g\(^{-1}\) lw) (Mo et al., 2013). Regarding the human body, the median concentration of DP in serum was three times higher in people from e-waste area (Guiyu Town, 42.6 ng g\(^{-1}\) lw) than those from nearby region (Haojiang, 13.7 ng g\(^{-1}\) lw). Yan et al. (2012) found that DP levels in serum were significantly higher (p < 0.05) in the occupationally exposed workers from the e-waste dismantling region (22–2200 ng g\(^{-1}\) lw) than in the urban residents (2.7–91 ng g\(^{-1}\) lw) in South China. Distinctly high DP levels were also obtained in human hair and indoor dust collected from e-waste dismantling area relative to the control areas (rural and urban) in South China (Zheng et al., 2010). This distribution pattern was consistent with the expected increase in exposure due to dismantling of e-waste (Ren et al., 2009).

### 3.3. Urban/industrial activity

As an additive flame retardant, DP has been widely used in industrial and household products. Therefore, DP may leach from these products and contaminate the surroundings. De la Torre et al. (2011) reported higher levels of DP in sewage sludge from 31 urban Spanish wastewater treatment plants (WWTP), and a significant positive correlation (r = 0.619, p < 0.05) was found between DP concentrations with the contribution of industrial input to waste streams. Zeng et al. (2014) also found relatively higher levels of DP in sewage sludge from the eastern China, especially in coastal areas where the urbanization and industrialization level is higher. In the residential indoor dust in the city of Ottawa, DP levels ranged from 2.3 to 5683 ng g\(^{-1}\), which were comparable to the levels in dust from Stockholm (<0.19–4800 ng g\(^{-1}\)) (Newton et al., 2015), but were several times higher than those in the sediment of the Great Lakes (Zhu et al., 2007). In the indoor dust from different microenvironments (i.e., home, workplace and car) in the Greater Cairo region, Egypt, both the syn- and anti-isomers were detected in 100% of the car dust samples reaching 4.94 and 5.65 ng g\(^{-1}\), respectively (Hassan and Shoeib, 2015). In the indoor dust in Beijing, China, the highest DP levels were found in kindergarten dust (231 ng g\(^{-1}\)), which was even higher than in house dust from Guanzhou, China (mean 18.9 ng g\(^{-1}\)) (Cao et al., 2014). A regular distribution pattern of DP in dust with particle size was also observed with stronger enrichment on fine particles than coarse particles, implying a potential human exposure to this chemical (Cao et al., 2014). In air, Ren et al. (2008) investigated DP across 97 Chinese urban and rural sites by using PUF disk passive air samplers, and found that DP concentration in urban centers (mean value 15.6 ± 15.1 pg m\(^{-3}\)) was approximately 5 times greater than those measured in rural areas (3.5 ± 5.6 pg m\(^{-3}\)). Areas where DP was not detected were primarily limited to rural regions. In the same study, a good correlation was obtained between air DP concentrations and population in urban centers with populations greater than 1 million, which was likely attributable to local sources rather than transboundary influences (Ren et al., 2008). Similar urban–rural distribution of DP in air and plant was also reported in an e-waste area in South China, where DP levels at the e-waste recycling site were at least one order of magnitude higher than those in the reference site (Chen et al., 2011). Salamova and Hites (2013) observed a similar result with significant correlation between DP concentrations in tree bark and human population (p = 0.028) when they measured brominated and chlorinated flame retardants including DP in the samples from 12 locations around the globe. Qi et al. (2010) determined DP in surface water and sediment samples from Songhua River in northeastern China. The mean concentration in urban waters of Harbin (0.55 ± 0.81 ng L\(^{-1}\)) was 3 times greater than those measured in the section of Songhua river within the city of Harbin (0.17 ± 0.38 ng L\(^{-1}\)) and more than 15 times greater than in rural area of Songhua River (0.03 ± 0.07 ng L\(^{-1}\)). Similar results were also obtained between the sediments from a section of the river within the city of Harbin (0.11 ± 0.05 ng g\(^{-1}\) dw) and rural area of Songhua River (0.04 ± 0.05 ng g\(^{-1}\) dw), which suggested the influence of urban activity on environmental DP concentration. In South Korea, Kang et al. (2010) measured DP in fish from 22 river sites around the country, the mean concentrations in the 15 urban sites (36.1 ± 35.3 ng g\(^{-1}\) lw) were approximately 25 times greater than those measured in the rural sites (1.4 ± 1.0 ng g\(^{-1}\) lw). Significantly different DP levels between rural and urban areas (p < 0.015) further suggested that urbanization and industrial activities could be the major emission source of DP rather than LRAT from distant sources (Kang et al., 2010).

### 4. General environmental occurrence

#### 4.1. Global distribution

Many studies have revealed occurrence of DP in different matrices since its first detection in the environment in 2006, such as air, water, sediment, wildlife as well as human blood and hair (Fig. 2, Tables S1–S7). These global observations indicated that high levels of DP generally occurred in the source areas, such as the North American Great Lakes and Hualian City in China, e-waste dismantling areas in South China and urban areas in the world as discussed in the previous section. The highest concentrations of DP could be up to several ng m\(^{-3}\) in ambient air and μg g\(^{-1}\) dw in soil close to the DP manufacturing facility in Hualian City (Wang et al., 2010a) and μg g\(^{-1}\) dw in sediment from an e-waste recycling site in South China (Zhang et al., 2011b). On the other hand, more evidence from all over the world has led to the vision that DP is a worldwide contaminant (Feo et al., 2012; Möller et al., 2010, 2011, 2012a; Sverko et al., 2011a, Vorkamp and Rigét, 2014; Wolschke et al., 2015). As reported by Möller et al. (2010), DP was detected in the marine air boundary layer (sampling at 15 m above sea level) with concentration ranges from 0.05 to 4.2 pg m\(^{-3}\) in atmosphere and <MDL to 1.3 pg L\(^{-1}\) in seawater from the East Greenland Sea to Antarctica. During the polar expedition cruise from East China Sea to the Arctic, DP was detected at 0.006–0.4 pg L\(^{-1}\) in seawater and 0.01–1.4 pg m\(^{-3}\) in marine boundary layer air samples (Möller et al., 2011). During another sampling cruise from the East Indian toward the Indian Ocean and further to the Southern Ocean, DP concentrations were observed in the range of 0.26–11 pg m\(^{-3}\) in the air samples (Möller et al., 2012a). These observations revealed a global background level of DP in ocean. The observation in the air samples from Global Atmospheric Passive Sampling (GAPS) indicated that DP could also be detected in some remote areas, especially in the background site at Cape Grim, Tasmania, extremely high level (348 pg m\(^{-3}\)) was obtained (Sverko et al., 2010a). Relatively higher levels of DP were also detected in the sites in Asia and North America (Sverko et al., 2010a). In tree barks collected around the globe, DP was measured in the range of 0.89–48 ng g\(^{-1}\) lw with a relatively high level at a remote site at Bukit Kototabang in Indonesia (46 ± 4 ng g\(^{-1}\) lw) (Salamova and Hites, 2013). In contrast to the observation by the GAPS project (Sverko et al., 2010a), DP concentrations in tree bark were the lowest at Cape Grim in Tasmania (0.89 ± 0.21 ng g\(^{-1}\) lw) (Salamova and Hites, 2013). Although the discrepancy between these two studies cannot be properly explained, the environmental occurrence in background sites suggested a widespread distribution of DP at the global scale.

#### 4.2. Temporal trends

To date, results from studies on the temporal distribution of DP were limited to the North American Great Lakes where the first DP manufacturing plant is located. The available data about annual
production amounts varied widely at an estimated range of 450–4500 tonnes since 1986 (Qiu et al., 2007). However, DP in ambient air tended to be at a constant level in the Great Lakes region. Results from the Integrated Atmospheric Deposition Network (IADN) sites located in the Great Lakes basin showed that mean concentrations of DP were in the range of 0.23–21.4 pg m\(^{-3}\) over the period of 2003–2007 (Salamova and Hites, 2010), 0.8–20 pg m\(^{-3}\) over the time of 2005–2006 (Venier and Hites, 2008) and 0.39–23.5 pg m\(^{-3}\) (sum of the concentrations in vapor phase and particle phase) over the years of 2005–2009 (Salamova and Hites, 2011). Even though there was a wide range for the means, the DP levels in each site showed a small variation over these sampling periods (Fig. 3). This lack of clear temporal trend suggested that the inputs of DP into the surrounding environment have not distinctly changed during the 2000s (Salamova and Hites, 2011). However, at a longer time scale, DP levels generally declined in sediment and biota collected from the Niagara River and Lake Ontario since the 1980s (Hoh, et al., 2006; Shen et al., 2010, 2011a; Sverko et al., 2008, 2010b). Some studies indicated a period of increasing levels since the 1970s in sediment from central Lake Ontario, and the levels peaked during 1980–1990s (Qiu et al., 2007; Sverko et al., 2010b; Yang et al., 2011). Although there was a time lag between the peak DP levels among the different studies, DP input to sediment appeared to begin in the 1970s, in agreement with DP production history (Qiu et al., 2007). The peak levels were also observed in Lake Ontario lake trout (Ismail et al., 2009) in 1980s and the eggs of herring gulls (Larus argentatus) from the Laurentian Great Lakes of North America in the mid-1990s (Gauthier and Letcher, 2009). The recent decline tendency of DP levels in sediment and biota could be mainly attributed to the fact that the manufacturing facility in Niagara Falls decreased the production volume and/or improved the control of the discharge (Sverko et al., 2010b; Yang et al., 2011). Although evident impact of the DP plants was observed at the downstream of Niagara River and Lake Ontario, the temporal trend of DP showed some distinctions between the individual lakes of the Great Lakes. Yang et al. (2011) analyzed DP in the sediment cores from all the five lakes. Most sites in Lake Superior and Lake Michigan were still receiving increasing fluxes of DP in recent years, in contrast with the trend in Lake Ontario. Combining with the observation of stronger correlation between the core average syn-isomer abundance and the distance from the DP manufacturing plant, the authors suspected that LRAT of DP has contributed to the contamination of the Great Lakes. This different pathway from source emission might also be the explanation for the disparity of DP temporal trend among the lakes. The study on temporal trend of DP in other region is scarce. Zhu et al. (2014) found a significant positive temporal shifting trend of the ratio of DP to BDE-209 between 2003 and 2012 in Indo-Pacific humpback dolphins (Sousa chinensis) (\(r = 0.67, p = 0.0005\)) and finless porpoises (Neophocaena phocaenoides) (\(r = 0.82, p = 0.0001\)) from the South China Sea, indicating a use-shift from PBDEs to other alternatives such as DP in China. Whereas, the temporal trend of DP in these biotas was not mentioned (Zhu et al., 2014). A very recent work by Barón et al. (2015) indicated that DP levels in the unborn eggs of three species (black kite, white stork and greater flamingo) from
Spain did not change significantly between 1999 (2003 for greater flamingo) and 2011 (2013 for greater flamingo) (p > 0.05), which was the first study of DP time trends in birds from Europe.

5. Bioaccumulation and biomagnification potential

DP was first reported to be detected in archived fish (walleye) from Lake Erie in 2006, which suggested that DP was at least bioavailable (Hoh et al., 2006). Thereafter, different levels of DP were obtained in various biota samples including the human body (Barón et al., 2014a; Gauthier and Letcher, 2009; Guerra et al., 2011; Ren et al., 2009; Salamova and Hites, 2013; Sun et al., 2012; Wu et al., 2010), confirming bioavailability of DP in both the terrestrial and aquatic biotas. Chemicals were considered to be bioaccumulative if the bioaccumulation factor (BAF) was greater than 5000 (Kelly et al., 2007), corresponding to a logBAF of 3.70. In coastal environment of northern China, biota-sediment accumulation factors (BSAF) of DP were determined in the range of 1.0–7.9 with mean value of 4.6 in oyster samples (Jia et al., 2011). In the freshwater food web from a highly contaminated site, South China, the logBAF values in all the species were higher than 3.70 except Chinese mystaysnail and northern snakehead (Wu et al., 2010), indicating a distinct bioaccumulation of DP in a majority of aquatic species. Besides, a significant biomagnification of syn- and anti-DP was also observed in the present food web, with trophic magnification factors (TMFs) of 11.3 and 6.6, respectively (Wu et al., 2010). In laboratory-based bioaccumulation experiment by Tomy et al. (2008), the biomagnification factors (BMF) were 5.2 for syn-DP and 1.9 for anti-DP on average in Juvenile Rainbow Trout. By contrast, in archived food web samples from Lake Winnipeg and Lake Ontario, trophic level (TL) adjusted biomagnification factors (BMFTL) in the predator–prey relationship indicated interspecies differences in bioaccumulation and biotransformation. BMFTL values could reach up to 12 in trout/smelt feeding relationship in Lake Ontario, while in Lake Winnipeg they were calculated as 2.5 and 0.45 for anti- and syn-DP, respectively (Tomy et al., 2007). Lower TMF was also found for DP isomers (2.2 for syn-DP and 1.6 for anti-DP) in the marine food web of Liaodong Bay, North China, where no significant trend was observed for TMF against the trophic level (p > 0.05) (Peng et al., 2014). Similar situations were observed in the waterbirds from an e-waste recycling region in South China (Zhang et al., 2011a) and in the unborn eggs of different species from Spain (Barón et al., 2014a), where no significant correlations were obtained between DP levels and trophic levels (p > 0.05), suggesting that the biomagnification of DP was not clear in waterbird and bird egg. By contrast, PBDEs were observed to be evidently biomagnified in waterbirds (Zhang et al., 2011a), bird eggs (Barón et al., 2014a) and the marine food web (Peng et al., 2014). This could be due to the lower logKow values of PBDEs (6.0 for BDE-47 and 6.8 for PBDE-99) than those of DP (9.3), and therefore leading to high bioavailability of PBDEs in organisms (Peng et al., 2014).

6. Isomer ratios of DP in various matrices

The isomer ratio of DP was commonly used to assess the fate and distribution of DP in the environment and biota. It was represented in the form of either the fractional abundance of anti-DP (fanti) in the total DP (anti- + syn-DP), or the fraction of syn-DP (fsyn) in the total DP. For the purpose of discussion and comparison in this review, all reported fsyn data were converted to fanti.

6.1. Commercial products

Commercial DP products consist of about 65% anti- and 35% syn-DP resulting in an fanti value of 0.65. However, reported fanti in commercial products were not always consistent because of different production lots and manufacturers (Ren et al., 2008). The fanti values of commercial DP from both Anpon and OxyChem were reported in the range of 0.59–0.80 (fanti: 0.20–0.41) (Wang et al., 2010a).

6.2. Atmosphere

In ambient air, reported fanti values were generally consistent with those in commercial DP products in emission source areas, while they widely deviated from the commercial values after LRAT. Therefore, the effects of source emission or LRAT could be evidently identified according to DP isomer composition. Most comparable fanti values in the continental atmosphere could be obtained with those in the technical DP mixture (Fig. 4). For instance, Ren et al. (2008) revealed that the mean fanti value was 0.67 (fanti: 0.33 ± 0.10) in air across 97 Chinese urban and rural sites, consistent with the observations in the Great Lakes, North America (Hoh et al., 2006; Salamova and Hites, 2011), Spain (De la Torre et al., 2010b) and Lake Victoria region, East Africa (Araitaite et al., 2014). These results suggested an apparent influence by local emission sources. However, apparent decline of fanti values could be observed in the marine environment, especially in the locations far away from anthropogenic activities. This could reflect the impact of LRAT on DP isomer composition. Möller et al. (2010) reported that the fanti value was 0.63 in the English Channel atmosphere, close to the commercial mixture, suggesting Western Europe was a source region of DP in the adjacent coastal waters. The fanti values then decreased to the range of 0.03–0.72 with a mean value of 0.33 (fanti: 0.67 ± 0.22) in the East Greenland Sea. Additionally, the fanti values significantly decreased with decreasing northern latitude toward an almost constant value of 0.33 (fanti: 0.67 ± 0.03) southwards of the equator along the Atlantic transect (Möller et al., 2010). These results indicated a higher stability of the anti-isomer toward photodegradation, leading to either a stereoselective depletion of the anti-isomer or isomerization of the anti-isomer to the syn-isomer during atmospheric transport (Möller et al., 2010, 2011, 2012a; Salamova and Hites, 2011). However, no case was available to buttress isomerization of the anti-isomer to the syn-isomer in air to date. As estimated by Fang et al. (2014), syn-DP possibly had a lower logKow than that of anti-DP. The logKow difference can affect LRAT of DP, which might partly contribute to the decreased fanti during LRAT (Fang et al., 2014). The decline of fanti values in the atmosphere with increasing distance from emission source was also found in the terrestrial environment, e.g., the average values were shown as a function of distance from Niagara Falls for the gas, particle, and precipitation phases in the Great Lakes, and a significant negative relationship
was obtained in particle phase ($r^2 = 0.772, p = 0.049$) (Salamova and Hites, 2011). However, it was notable that relatively higher $f_{anti}$ values were observed in the atmospheric particles from a European Arctic site (Longyearbyen, $f_{anti}$: 0.43–0.90 with a mean value of 0.72) (Xiao et al., 2012) and sub-Arctic environment in the Yukon Territory (mean $f_{anti}$: 0.51–0.61) (Yu et al., 2015). The occurrence of DP in these remote areas was ascribed to the fact that DP was primarily associated with particles and has the LRAT potential (Salamova et al., 2014; Xiao et al., 2012). Whereas, the $f_{anti}$ values close to the composition of commercial DP mixtures may also suggest an effect of local emission source, although it was not discussed in the previous works (Xiao et al., 2012; Yu et al., 2015).

6.3. Water

Limited data indicated the same distribution of DP composition in freshwater and seawater relative to that in atmosphere (Fig. 5). For example, the $f_{anti}$ values ranged between 0.45–0.80 (mean value 0.66) in seawater along the coast of the northern Chinese sea (Jia et al., 2011), the mean values were 0.66 ($f_{syn}$: 0.34 ± 0.10) in Songhua River in northeastern China (Qi et al., 2010) and 0.66 ± 0.06 in a reservoir near e-waste recycling workshops in South China (Wu et al., 2010). However, the mean $f_{anti}$ values in seawater were 0.39 ($f_{syn}$: 0.61 ± 0.11) from East China Sea to the Arctic (Möller et al., 2011), 0.47 ($f_{syn}$: 0.53 ± 0.13) for East Greenland Sea (Möller et al., 2010) and 0.35 ($f_{syn}$: 0.65 ± 0.07) along the Atlantic transect (Möller et al., 2010). The sampling sites of these seawaters were far away from the emission source area. The $f_{anti}$ values were commonly lower than that in the commercial products, but well comparable to the atmospheric distribution. As Salamova and Hites (2011) demonstrated, the $f_{anti}$ values had a significant decline along the increasing distance from emission source in the particle phase, while this correlation was not significant in precipitation phase. It suggested that the occurrence of DP in the remote oceans was closely related to the atmospheric deposition after its LRAT (Möller et al., 2010).

6.4. Soil, sediment and sewage sludge

The $f_{anti}$ values in soil were generally comparable to those in commercial DP products (Fig. 6), especially in source areas. This reflected the direct influence of the emission source. However, relatively higher and lower proportions were also reported in some cases. For example, in Huaian City of China, the $f_{anti}$ values varied from 0.65 to 0.97 (mean value 0.79) in soils (Wang et al., 2010a). While in North China, the parameter varied greatly with a range of 0.49–0.89 (Ma et al., 2014). Much lower $f_{anti}$ values (0.22–0.70, mean 0.37) were found in Indus River Basin, Pakistan where a rapid industrialization and urbanization was underway (Ali et al., 2015). The reason behind the lower $f_{anti}$ ratios was not clear. However, in the sedimentary environment, the $f_{anti}$ ratios were generally higher than the commercial DP composition from source areas (Fig. 7). For example, the $f_{anti}$ values were 0.84 ± 0.01 in suspended sediments from e-waste recycling areas in South China (Wu et al., 2010), in agreement with the observations in the Great Lakes (Hoh et al., 2006; Sverko et al., 2008; Yang et al., 2011). On the
other hand, a regular change of $f_{\text{anti}}$ could be observed in the sediment core from Lake Ontario, where the surficial value of $f_{\text{anti}}$ was 0.76 (on average), and increased to $\approx 0.90$ at the deeper layers (Qiu et al., 2007). A similar trend was observed in one sediment core from Lake Ontario (Yang et al., 2011) and two sediment cores from urbanized coastal zone in South China (Liu et al., 2014). The relatively higher $f_{\text{anti}}$ values and the increased $f_{\text{anti}}$ with the passage of time in sediment were attributed to anti-DP being more persistent in the sedimentary environment (Qiu et al., 2007; Sun et al., 2013; Sverko et al., 2008; Zhao et al., 2011). On the other hand, in marine sediment, the highest $f_{\text{anti}}$ was observed in the fraction with the fine particle size ($< 5 \mu m$), and $f_{\text{anti}}$ was significantly positively correlated with organic carbon content (OC) in the fractionized sediment samples ($r^2 = 0.78$, $p < 0.01$) (Fang et al., 2014). The enrichment of anti-DP over syn-DP was also attributable to preferential biodegradation of syn-DP in sediment (Fang et al., 2014). This assumption was supported by the observation in sewage sludge from WWTPs in China (Zeng et al., 2014). However, it could not explain the observations in Spanish and North Carolina sewage sludges, where significant syn-DP enrichment was observed during the biological elimination of N and P in WWTPs ($p < 0.05$) (De la Torre et al., 2011) and in biosolids (Davis et al., 2012). The discrepancy was also found in Lake Erie sediment cores, where no significant change of $f_{\text{anti}}$ ratios in relation to depth was observed, suggesting no DP stereospecific decomposition related to anaerobic microbial activity (OxyChem, 2007; Sverko et al., 2008). It was plausible that the aqueous solubility of DP isomers may affect their fate in the sedimentary environment. DP is hydrophobic ($\log K_{\text{ow}} = 9.3$, $\log K_{\text{f}} = 6.65$) with solubility of 207 ng L$^{-1}$ and 572 ng L$^{-1}$, respectively, for the two isomers (OxyChem, 2007). It suggested syn- and anti-DP possess different physicochemical properties, although no specific information was supplied as to which isomer exhibited which solubility. As estimated through the retention time index in LC columns by Fang et al. (2014), syn-DP was probably more hydrophobic than anti-DP, i.e., higher $\log K_{\text{ow}}$, which could be supported by the simulated experiment with preferentially adsorption of syn-DP by activated char carbon (ACC). However, the adsorption might be attributable to the larger molecular diameter of anti-DP (1.42 nm) than that of syn-DP (1.24 nm), which reduced the accessibility of anti-DP to the micropores of ACC (Fang et al., 2014). Therefore, further studies are needed to confirm the hypothesis on the isomer specific biodegradation and adsorption of DP in sediment.

6.5. Aquatic biota

The isomer composition of DP in aquatic biota showed a wide variation within and between species (Fig. 8). From the studies in the Great Lakes area and Chinese offshore areas, lower mean $f_{\text{anti}}$ values were generally observed in plankton, invertebrate and fish compared to the commercial DP composition. For instance, $f_{\text{anti}}$ was 0.44–0.58 in Lake Ontario lake trout (Shen et al., 2011a), 0.51–0.58 in trout, smelt, alewife and sculpin from Lake Ontario (Tomy et al., 2007), 0.60 ± 0.05 in Lake Erie fish (Hoh et al., 2006), 0.34–0.80 (mean 0.55) in oyster, northeast China (Jia et al., 2011). An enrichment of the syn-isomer may be expected since anti-DP is more reactive and susceptible to biological transformation due to that the four CH$_2$-groups of the cyclooctane structure are less shielded by chlorine atoms than those in the syn-isomer (Hoh et al., 2006). The bioaccumulation experiments by Tomy et al. (2008) also indicated that syn-DP showed higher assimilation efficiency and lower depuration rate relative to anti-DP in juvenile rainbow trout (Oncorhynchus mykiss), accounting for the low $f_{\text{anti}}$ values in fish. However, it is not well-known whether this happened in other aquatic species. Fang et al. (2014) calculated the molecular descriptors of anti- and syn-DP using Gaussian 03, the result showed that syn-DP had a higher dipole moment, slightly larger Van der Waals volume, but smaller maximal diameter, which might explain its higher uptake rate in biota (Fang et al., 2014). On the other hand, studies on trophic magnification around the DP facility and e-waste recycling areas showed a wide inter-species variation of $f_{\text{anti}}$ values and a significant negative correlation between these ratios and trophic levels of the aquatic species (Wang et al., 2015; Wu et al., 2010; Zhang et al., 2011a). Similarly, a regression line with negative slope ($R^2 = 0.29$) could be obtained based on the data of the entire food web in Lake Ontario, the $f_{\text{anti}}$ values declined from 0.65 in plankton to 0.51 in trout (Tomy et al., 2007). These results were attributed to the fact that species occupying higher trophic levels have lower uptake efficiencies and higher metabolic capacities for the anti-isomer compared to the syn-isomer (Tomy et al., 2007). Some studies on higher aquatic animals, e.g., Chinese sturgeon (Peng et al., 2012), Franciscana dolphin (De la Torre et al., 2012) and ringed seal (Vorkamp et al., 2015), showed relatively higher $f_{\text{anti}}$ values in various tissues. However, this was observed at relatively low concentrations of DP isomers (< ng g$^{-1}$ lipid weight or wet weight), similar to the finding in kingfishers and their preys in a reference site in the Pearl River Delta.

![Fig. 8. The distribution of $f_{\text{anti}}$ values in aquatic biota.](image-url)
of China (Mo et al., 2013). The higher $f_{\text{anti}}$ values in the aquatic animals were generally associated with lower DP residue levels, whereas it was not clear exactly what causes this relationship.

6.6. Terrestrial organism

The $f_{\text{anti}}$ ratios in tree bark were commonly higher but still comparable to that of technical mixture (Fig. 9). While in animals, a disparity of $f_{\text{anti}}$ values could be observed between those from source areas and reference sites. In passerine bird species in South China, the mean $f_{\text{anti}}$ values were in the range of 0.71–0.84, and the values in birds from rural sites were significantly higher than those from urban sites ($p < 0.05$) (Sun et al., 2012). A similar observation on urban–rural difference was also obtained in white stork eggs from Spain ($f_{\text{anti}}$: 0.40–0.87), although no statistical significance was observed between $f_{\text{anti}}$ values from Doñana National Park (mean: 0.66 ± 0.12) and Madrid (mean: 0.64 ± 0.07) (Muñoz-Arnanz et al., 2011). Furthermore, $f_{\text{anti}}$ values were significantly higher in the peregrine falcon (Falco peregrinus) eggs from Spain (0.62–1.0) than those from Canada (0.41–0.69) ($p = 0.02$) (Guerra et al., 2011). Higher $f_{\text{anti}}$ values were also observed in eggs of two gull species from southwestern Mediterranean Sea ($f_{\text{anti}}$: 0.70–1.0) (Muñoz-Arnanz et al., 2012) compared with those in the herring gull egg pools from the Laurentian Great Lakes of North America (mean 0.69 ± 0.08) (Gauthier and Letcher, 2009). The higher $f_{\text{anti}}$ values in the terrestrial organisms in reference areas were attributed to the possible alteration of DP (or the already transformed DP) prior.
to uptake by the biota since stereoselective enrichment of DP isomers has been observed in environmental matrices (Guerra et al., 2011; Sun et al., 2012). A toxicological study suggested that there was no significant stereoselectivity of DP isomers in the Sprague–Dawley rat tissues in the low DP exposure groups (< 1 mg kg\(^{-1}\) d\(^{-1}\)) \((f_{anti}: 0.74–0.78)\) (Li et al., 2013). However, significant reduction of \(f_{anti}\) values \((0.26–0.30)\) was observed in the high DP exposure groups \((10–100 \text{ mg kg}^{-1} \text{ d}^{-1})\) and syn-DP was predominant in all tissues (Li et al., 2013). This suggested that species-specific and dose-dependent absorption, deposition, or different excision of DP isomers could also account for the observed discrepancy of \(f_{anti}\) ratios associated with variation of DP residue levels (Peng et al., 2015).

6.7. Human beings

Studies on stereospecificity of DP isomers in human beings showed a generally consistent trend with those in terrestrial organisms (Fig. 10). In the general population from two Canadian cities (Kingston and Sherbrooke) the average \(f_{anti}\) value in human milk was 0.67 ± 0.10 (Siddique et al., 2012). In the human serum from France, this value was slightly higher (0.75 ± 0.07, range: 0.65–0.86) (Brasseur et al., 2014), but still consistent with those in the commercial DP products. However, in the e-waste dismantling regions in South China, the \(f_{anti}\) values ranged from 0.48 to 0.76 (median 0.66) in serum of the e-waste recycling workers (Yan et al., 2012), most of the samples tested were slightly lower than the reported commercial \(f_{anti}\) values. Similar results were obtained in serum of the residents (\(f_{anti}: 0.54–0.73\) with mean 0.65, Chen et al., 2015; 0.40–0.77 with mean 0.58 ± 0.11, Ren et al., 2009) and in hair of e-waste dismantling workers (\(f_{anti}: 0.20–0.64\) with mean 0.47, Chen et al., 2015; 0.25–0.75 with mean 0.55 ± 0.11, Zheng et al., 2010). DP was speculated to be stereoselected in the environment before entering the body via inhalation, ingestion, or dermal contact (Ren et al., 2009). However, the observation by Chen et al. (2015) revealed that the \(f_{anti}\) values in the hair of e-waste workers \((0.45 ± 0.11)\) were significantly lower than those in dust \((0.54 ± 0.15)\) and matched serum \((0.64 ± 0.06)\). The study on occupational exposure to DP also indicated that both the \(f_{anti}\) values in worker’s blood \((0.35–0.76\) with mean 0.56 ± 0.10) and hair \((0.40–0.79\) with mean 0.54 ± 0.09) were lower than those in the DP products (Zhang et al., 2013) and the surrounding air \((0.57–0.79)\) (Zhang et al., 2015). Considering that these observations generally referred to the human samples from emission source areas, it suggested that syn-DP may be stereoselectively enriched or bioaccumulated relatively to anti-DP in the human body in the case of the higher residual level of DP (Zhang et al., 2013, 2015). Stereoselective enrichment of DP in the human body was also supported by the observations on gender difference and tissue distribution. In serum from e-waste recycling workers, the \(f_{anti}\) values \((0.48–0.76)\) were generally lower than those in the commercial products but had a significantly gender difference \((p < 0.05)\) (Yan et al., 2012). In human tissues, \(f_{anti}\) values were significantly higher in the placentas relative to the maternal sera or cord sera \((p < 0.05)\) (Ben et al., 2014), they were also significantly higher in the maternal sera compared to the cord sera \((p < 0.001)\). The significant difference of the \(f_{anti}\) values in three compartments confirmed the occurrence of stereoselective bioaccumulation of DP during the transplacental DP passage (Ben et al., 2014).

7. DP related compounds and dechlorinated analogs

7.1. DP related compounds

In order to replace Mirex (CAS# 2385–85-5), a series of highly chlorinated compounds were produced by OxyChem such as Dechlorane (Dec) 602 \((\text{C}_{14}\text{H}_{4}\text{Cl}_{12}\text{O}, \text{CAS}\#\ 31107-44-5)\), Dec 603 \((\text{C}_{17}\text{H}_{8}\text{Cl}_{12}, \text{CAS}\#\ 13560-92-4)\), Dec 604 \((\text{C}_{13}\text{H}_{4}\text{Br}_{4}\text{Cl}_{6}, \text{CAS}\#\ 34571-16-9)\), Chlordene Plus \((\text{CP, C}_{15}\text{H}_{6}\text{Cl}_{12}, \text{CAS}\#\ 13560-91-3)\), and DP (Fig. 11). Dec 602 and 604 are on the Nondomestic Substances List published by Environment Canada, indicating possible commercial use of Dec 602 and 604 in Canada currently. The production and actual use of these chemicals are not available. However, these compounds have been globally detected along with DP in various matrices (Tables S8–S12).

In the Great Lakes region, the concentrations of mirex, Dec 602, 603 and 604 were up to several ng g\(^{-1}\) dw in sediment (Shen et al., 2010, 2011a, 2011b, 2014; Yang et al., 2011). CP had the lowest overall concentrations, but it was detected in most samples at levels up to 0.27 ng g\(^{-1}\) dw (Shen et al., 2011b). In Great Lakes fish, the level of mirex could reach up to 4300 ng g\(^{-1}\) lw (Shen et al., 2011a), while Dec 602, 603, 604 and CP could be detected to some extent with relatively lower concentrations \((-\text{LOD (limit of detection)} -180 \text{ ng g}^{-1} \text{ lw})\) (Shen et al., 2010, 2011a, 2014). Nevertheless, Dec 602 showed greater bioavailable or bioaccumulative than DP in many cases (Bardon et al., 2014a, 2015; Guerra et al., 2011; Peng et al., 2014; Shen et al., 2010, 2011a), proposing new concern on its potential ecological risk. The reason might be due to its relatively low \(\text{log}K_{\text{OW}}\) values \((\text{estimated log}K_{\text{OW}}: 8.1)\) and subsequent high bioavailability compared with DP \((\text{estimated value: 11.3})\) (Shen et al., 2011a). The temporal and spatial distribution of Dechloranes were generally in agreement with those of DP in the Great Lakes, indicating that the OxyChem plant in Niagara Falls was the potential emission source (Shen et al., 2011a; Sverko et al., 2010b; Yang et al., 2011). In addition, analogs of Dec 604 were recently identified in Lake Ontario sediment and fish (Jobst et al., 2013; Shen et al., 2014). These analogs contained fewer bromines and mixed substitutions of bromine and chlorine, such as tribromo-Dec 604 \((\text{Br}_{3}\text{Dec 604})\) analog (known as Dechlorane 604...
Component B (Dec 604 CB), BrDec604 and Br2Dec 604 analogs, and mixed BrClDec 604, BrClCIDec 604, Br2ClDec 604, and BrCl2Dec 604 analogs. The concentration of Dec 604 CB was even higher than those of Dec 604 in lake trout and whitefish (Shen et al., 2014).

In China, mirex and Dec 602 could be detected in air, soil and sediment around DP plant in Huai’an City (Wang et al., 2010a). However, all the DP related compounds were evidently observed in the aquatic organisms from this area (Wang et al., 2015), the levels of mirex, Dec 602, 603, 604 and CP could reached up to 19,800 ng g \(^{-1}\) lw, 122 ng g \(^{-1}\) lw, 119 ng g \(^{-1}\) lw, 329 ng g \(^{-1}\) lw, and 128 ng g \(^{-1}\) lw, respectively, which were much higher than those previous reports in other regions (De la Torre et al., 2012; Guerra et al., 2011; Shen et al., 2010). Mirex and Dec 602 were also detected in soil from 78 of 102 sampling sites around China with a concentration range of <0.8–230 pg g \(^{-1}\) dw (Sverko et al., 2011b), while Dec 603 and 604 were not detected. DP analogs have not been manufactured in China except mirex which has been basically eliminated since 2009, and no records are currently available about their use. As indicated by Shen et al. (2011b), CP was found in technical chlordene (0.05 ± 0.01%) and chlordane (0.76 ± 0.02% in the US EPA technical chlordane and 0.65 ± 0.03% in those from Restek), Dec 603 was observed in technical aldrin (0.73 ± 0.03%) and dieldrin (0.31 ± 0.01%). In addition, Dec 604 was an impurity (2%) in a commercial product of mirex. Therefore, the possible source in China could be the impurities or by-product from the manufacturing process of DP or other products such as organic chlorinated pesticides (OCPs) (Shen et al., 2011b; Wang et al., 2015). Related studies in e-waste dismantling areas, which are considered a main emission source of DP, are very limited. Li et al. (2014) reported that the concentrations of mirex and Dec 602 were 0.65–179 and 0.26–12.4 ng g \(^{-1}\) lw, respectively, in wild frogs (Rana limnocharis) from an e-waste dismantling site in Southeast China, comparable to the DP levels. In other regions of China, Sun et al. (2013) reported that the concentrations of mirex, Dec 602 and 603 ranged from <LOD-0.68 ng g \(^{-1}\) dw, <LOD-0.048 ng g \(^{-1}\) dw and <LOD-0.026 ng g \(^{-1}\) dw, respectively in sediments from the Qiantang River in eastern China, while Dec 604 was not detected. Jia et al. (2011) observed low levels of Dec 602 and 603 in marine coastal sediments and oysters from Bohai and Huanghai in northern China. Peng et al. (2012; 2014) found a wide distribution of Dec 602, 603 and mirex in sediments and organisms in marine food web of Liaodong Bay and Chinese sturgeon, indicating emission of these compounds into the marine environment.

At the global scale, Möller et al. (2011) observed Dec 602, 603, and 604 in the atmosphere in concentrations of 0.01–0.2 pg m \(^{-3}\), 0.4 pg m \(^{-3}\) and 0.03–0.05 pg m \(^{-3}\), respectively along a polar expedition cruise from East China Sea to the Arctic. Dechloranes were also detected in a few seawater samples with concentrations of 0.2 pg L \(^{-1}\), 0.007–0.2 pg L \(^{-1}\), and 0.02–0.05 pg L \(^{-1}\), respectively. Recently, Wolschke et al. (2015) reported Dec 602 and 604 in the biota from the King George Island, Filides Peninsula, Antarctica, where much higher concentrations of Dec 602 were observed in skua (324–12,400 pg g \(^{-1}\) dw) than those in penguin (<LOD-238pg g \(^{-1}\) dw) and fish (<LOD-4.8 pg g \(^{-1}\) dw). Moreover, Guerra et al. (2011) reported that mirex, Dec 602, 603 and 604 were significantly higher in peregrine falcon eggs from Canada than from Spain (p ≤ 0.005), which largely reflected local exposure on the breeding territory, as well as their persistence and bioaccumulation in biota at the top of the food chain. In southeastern and southern coast of Brazil, mirex, Dec 602 and 603 were also detected in Francisca dolphin (De la Torre et al., 2012). In Spain, mirex and Dec 602 were detected in air in both remote and urban sampling sites and Dec 603 could be detected in some portions (De la Torre et al., 2010b). Furthermore, Dec 602 and 603 were determined in European eel (Anguilla anguilla) samples, where Dec 602 were the dominating FRs in elvers (juvenile eels) (Sühring et al., 2013). DP analogs were also detected in French human serum samples, where Dec 603 was the most abundant Dechloranes (mean value: 2.61 ± 2.63 ng g \(^{-1}\) lw) and followed by DP - mirex > Dec 602 > CP (Brasseur et al., 2014). All these studies suggested a worldwide occurrence of DP related compounds and bio-availability of Dechloranes.

Apart from the above norbornene flame retardants, DPMA (CAS# 153852-04-4), arising from the Diels-Alder reactions of impurities present in feedstock (1,3- or 1,5-cyclooctadiene), were first identified in Great Lakes lake trout (Sverko et al., 2010b). The concentrations (1,3-DPMA, approximately 30 ng g \(^{-1}\) lw) were approximately 2 orders of magnitude greater than those of DP, suggesting their bioaccumulation potential (Sverko et al., 2010b). This was likely due to its smaller size and lower molecular weight. A similar pattern was also observed in the biota from the King George Island, west Antarctica, where 1,3-DPMA was detected with concentrations of <LOD-136 pg g \(^{-1}\) dw in skua (Catharacta lomnerbergi) (Wolschke et al., 2015). Extremely high levels (1,5-DPMA) were observed in Spanish and Canadian peregrine eggs with concentrations from 1.7 to 469 ng g \(^{-1}\) lw and 1.2 to 1660 ng g \(^{-1}\) lw, respectively, which was much higher than DP levels (Guerra et al., 2011). Although these observations indicated greater bioavailability of DPMA than DP, DPMA was not found in air, sediment and biota samples in many cases (Barón et al., 2012; De la Torre et al., 2010b; Muñoz-Arnanz et al., 2011; 2012). A recent study in Huai’an, China (close to the DP facility) suggested high levels of DPMA (mean: 13.3–65.5 ng g \(^{-1}\) lw) in the fresh water food web, while the ratios of DPMA:DP were very low (0.02–0.44%) (Wang et al., 2015). The reason was attributed to differences in the source of DP contamination from Spain and Canada. Furthermore, calculated TMF of DPMA was greater than 1, but not statistically significant (p = 0.29), suggesting no evident biomagnification in this fresh water food web (Wang et al., 2015). After all, the detection of DPMA was much less than the other DP analogs in the environmental and biota samples. More research work is worth on the environmental risk assessment of these DP related compounds in the future.

### 7.2. DP dechlorinated analogs

DP degradation was first reported by Sverko et al. (2008) in sediments of the lower Great Lakes, where the apparent presence of several mono- and didechlorination products were confirmed. Thereafter, DP dechlorination products were observed in various matrices, including air, dust, sediment and biota (Tables S8-S12). Two dechlorinated breakdown products of DP were generally reported including undecachloropentacyclooctadecadiene (anti-C11-DP) and dodecachloropentacyclooctadecadiene (anti-C12-DP). The concentrations in air, dust and sediment were generally low or even undetectable in most cases, especially for anti-C10-DP (Chen et al., 2011; Peng et al., 2014; Zeng et al., 2014; Zhao et al., 2011; Zheng et al., 2010). The exception was that relatively higher levels of anti-C11-DP were observed in e-waste recycling areas in South China, such as in air (3.68–671 pg m \(^{-3}\), Chen et al., 2011), indoor dust (nd-20.2 ng g \(^{-1}\), Zheng et al., 2010) and sediment (6.32–25.0 ng g \(^{-1}\) dw, Zhang et al., 2011b). Interestingly, anti-C11-DP was observed in air samples at concentrations <0.1 pg m \(^{-3}\) from East Asia to the Arctic (Möller et al., 2011). anti-C11-DP and anti-C10-DP could also be detected from <0.001 to 0.07 pg L \(^{-1}\) in seawater from the Arctic and mainly in the particulate fraction (Möller et al., 2010). The authors suspected that these decomposition products were either formed during LRAT by photodegradation or by biodegradation once DP entered into the ocean (Möller et al., 2010). Although photodegradation of DP was observed in the simulation experiment by Sverko et al. (2008), Raff and Hites (2007) indicated that atmospheric particle bound semivolatile organic compounds (SOCs) might not be photodegraded due to the shielding effect of carboxenous aerosols on sorbed SOC molecules. However, thermal degradation of DP may occur during e-waste burning processes since the recommended operating temperature of DP is 285 °C, and decomposition may occur at 350 °C (OxyChem, 2007). Therefore, these two hypotheses are still needed to be confirmed.
DP dechlorination products were commonly reported in biota including human tissues, the levels were generally much lower than those of DP (Ben et al., 2013; Chen et al., 2011, 2013a; Guerra et al., 2011; Li et al., 2014; Mo et al., 2013; Muñoz-Arnanz, et al., 2011, 2012; Peng et al., 2012, 2014; Sun et al., 2012; Yan et al., 2012; Zhang et al., 2011b; Zheng et al., 2010, 2014). However, an extremely high level was observed in a fresh water food web around DP facility in Hua’ian, China, where the concentrations of anti-Cl₂-DP and anti-Cl₁-DP was 84.4 ng g⁻¹ hw and 1030 ng g⁻¹ lw, respectively (Wang et al., 2015). The dechlorinated products of DP in biota were mainly attributed to accumulation from the external habitat environment rather than internal metabolism, although the gender difference observed in some cases suggested that anti-Cl₁-DP in the human body may be partly formed from in vivo dechlorination of the anti-isomer (Yan et al., 2012). Tomy et al. (2008) investigated DP metabolites in juvenile rainbow trout and found that even when a high dose was employed in the uptake phase, none of the transformation products including dechlorinated, hydroxylated, methoxylated and methyl sulfone products were detected in the liver extracts. Zheng et al. (2010) found significant correlations and similar slopes of the regression line between anti-Cl₁₁-DP and anti-DP in both human hair (r = 0.865, p < 0.0001) and indoor dust samples (r = 0.845, p < 0.0001), suggesting that the dechlorinat ed products in the human body was likely not from in vivo metabolism but accumulated from environmental matrices through various external exposures. The concentration ratios of anti-Cl₁₁-DP to anti-DP in bionic tissues also provide further evidence. Zhang et al. (2011a,b) observed no significant difference in the ratios of anti-Cl₁₁-DP to anti-DP between liver and muscle tissues of mud carp, indicating a possible bioaccumulation of anti-Cl₁₁-DP in fish from the external environment. This was mainly based on the assumption that the hepatic metabolism in liver could induce a higher ratio of anti-Cl₁₁-DP to anti-DP. A similar result was obtained in wild frogs from an e-waste recycling area in Southeast China (Li et al., 2014). Studies on DP in mother–infant pairs from this area also showed a marginally insignificant difference of anti-Cl₁₁-DP/anti-DP ratios between the maternal sera and placentaes (Ben et al., 2014), suggesting that the maternal transfer was the primary source for anti-Cl₁₁-DP in the placental tissues.

8. Conclusions and recommendations

The detection of DP in the environment points to its global occurrence. The awareness of its spatial distribution benefits from the rapidly increasing research on the subject in the last decade, while data on its temporal trends are mainly limited to the North American Great Lakes region except for some studies from Spain and China (Barón et al., 2015; Zhu et al., 2014). There seems to be a consensus that DP shows most characteristics of POPs, such as environment persistency, bioaccumulation and LRAT potential. However, its toxicological effects were mainly observed at the transcriptome and metabolome levels (Li et al., 2013; Liang et al., 2014; Wu et al., 2012). More complementary research is warranted to assess its potential for adverse effects on organisms in the future.

The environmental behaviors and fate of the syn- and anti-isomers were well evaluated by the f∞ values. It demonstrated a discrepancy in terms of their environmental persistency, bioaccumulation and bio-transformation. The effect of source emission and LRAT could be identified according to DP isomer fraction (f∞) in the environmental matrices. The occurrence of DP in the remote oceans was closely related to the atmospheric deposition after its LRAT. It is most likely that syn-DP is vulnerable to microbial degradation in sediment relative to the anti-isomer, resulting in general higher f∞ values in sediment. However, the situation is more complex in biota. A higher f∞ ratio was commonly observed associating with lower DP residue levels in both aquatic and terrestrial organisms including the human body, suggesting occurrence of stereoselective processes in vivo apart from stereoselection in the environment prior to entering the body. Despite all that, more studies are still needed to clarify environmental behavior and stereoselective enrichment of DP isomers.

It is worth mentioning that the concentrations of DP and its related compounds have declined in the Great Lakes of North America since the 1990s. However, relatively high levels were reported in the e-waste recycling areas, especially in China. The temporal trend of these contaminants is still unclear. Differently from the DP production status, it is expected that more e-wastes will be generated in the future due to the fast turnover of electronics. Most of these e-wastes end up in the developing countries including China, leading to serious pollution and potential health concerns in the local area since many primitive and improvised recycling activities still exist. Therefore, more attention should be paid to the levels of DP and its analogs in these areas.

To the best of our knowledge, there is no published data available on the toxicological effects of DP analogs except Mirex. Although the levels of DP analogs were in general lower than DP in most cases, their widespread occurrence in the environment and biota necessitates more studies.

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Appendix A. Supplementary data

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