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Trophic magnification of chlorinated flame retardants and their dechlorinated analogs in a fresh water food web

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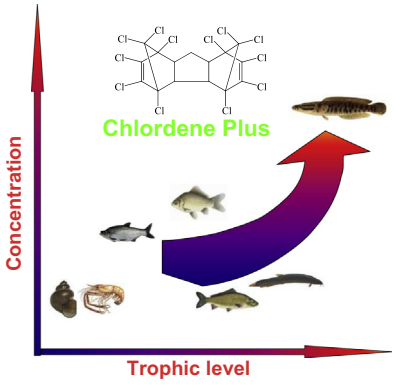
HIGHLIGHTS

- Chlordene plus was biomagnifying in this food web as well as mirex and dechlorine plus.
- Dechlorinated product has higher food web magnification potential than dechlorine plus.
- Environmental risk assessment is needed because of biomagnification.

GRAPHICAL ABSTRACT



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ABSTRACT

Chlorinated flame retardants, particularly dechlorane plus (DP), were widely used in commercial applications and are ubiquitous in the environment. A total of seven species of aquatic organisms were collected concurrently from the region of a chemical production facility in Huai'an, China. DP and structurally related compounds including mirex, dechloranes 602, 603, 604, chlordene plus (CP), DP monoadduct (DPMA), and two dechlorinated breakdown products of DP, decachloropentacyclooctadecadiene (*anti*-Cl_{10}-DP) and undecachloropentacyclooctadecadiene (*anti*-Cl_{11}-DP), were detected in these aquatic organisms. Nitrogen stable isotope ratios were also measured to determine the trophic levels of the organisms. Trophic magnification factors (TMFs) for these chemicals were calculated with values ranging from 1.0 to 3.1. TMFs for CP, mirex, *anti*-DP, and $\sum$DP were statistically greater than 1, showing evidence of biomagnification in the food web. Concentration ratios of *anti*-Cl_{11}-DP to *anti*-DP showed a significant relationship with trophic level, implying that *anti*-Cl_{11}-DP had a higher food-web magnification potential than its precursor. The biota-sediment accumulation factors and TMFs for DP demonstrated stereoselectivity, with *syn*-DP having a greater bioaccumulation potential than *anti*-DP in the aquatic environment.

1. Introduction

Chlorinated flame retardants (CFRs) such as dechlorane plus (DP) have been used in commercial polymer products like electrical wires and cables, plastic roofing materials, and connectors used

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in computers and televisions for more than 40 years (Sverko et al., 2011). DP and the dechlorinated breakdown products of DP, decachloropentacyclooctadecadiene (*anti*-Cl_{10}-DP) and undecachloropentacyclooctadecadiene (*anti*-Cl_{11}-DP), have been detected in human blood, bird eggs, dolphin, and sediments (Sverko et al., 2008; de la Torre et al., 2012; Yan et al., 2012; Ben et al., 2013). Structurally related CFRs, including mirex, dechlorane (Dec) 602, Dec 603, Dec 604, chlordene plus (CP), and DP monoadduct (DPMA), have been reported in biota and other environmental matrices (Sverko et al., 2010, 2011; Shen et al., 2012; Suebring et al., 2013). Occurrences of CFRs in biota samples have increased recently throughout the world (Sverko et al., 2011; Xian et al., 2011; Feo et al., 2012). The increasing trend may be explained by two main factors: production and use increased starting in 2007 because of a new manufacturing facility in China, where production is about 3000 tons per year (Wang et al., 2010); and (2) their physical–chemical properties and persistence in the environment tend to accumulation in the food web with increasing trophic level (TL) (Wu et al., 2010).

Bioaccumulation is an inherent property expressing a chemical's capacity to accumulate in organisms and is an important factor for risk assessment to the environment and human health. Bioaccumulation is referred to as a process in which the chemical concentration in an organism achieves a level that exceeds that in the respiratory medium, the diet, or both. Bioaccumulation of chemicals can be assessed by several parameters such as the bioconcentration factor (BCF), bioaccumulation factor (BAF), biomagnification factor (BMF), and Trophic magnification factors (TMFs). TMF is the "gold standard" for assessing biomagnification potential of Persistent Organic Pollutants (POPs) for those chemicals that have been in commerce long enough to detect them in environmental samples. TMFs represent the average prey to predator transfer of POPs through food webs, rather than the individual species biomagnification metrics that are highly variable from one predator–prey combination to another (Gobas et al., 2009).

The bioaccumulation and biomagnification potential of DP in freshwater food webs have been well documented in several recent studies (Tomy et al., 2007, 2008; Wu et al., 2010; Zhang et al., 2011). However, there is little information about the bioaccumulation potential of the dechlorinated analogs of DP and other related compounds. Recently, we reported very high concentrations of DP in air, soil, sediment and biota samples collected from a new DP manufacturing facility in China (Wang et al., 2010). Additionally, some related compounds including Mirex and Dec 602 were measured in these samples. These results spurred our efforts to examine a series of additional related DP compounds, including Dec 603, Dec 604, CP, DPMA, and two dechlorinated analogs of DP, *anti*-Cl_{10}-DP (aCl10DP) and *anti*-Cl_{11}-DP (Cl11DP), in biota from a canal in South of China to assess and compare their bioaccumulation processes in a fresh water food web. The major objectives of the present study were to (1) determine concentrations of CFRs in different biota samples collected from the region of the manufacturing facility, and (2) to evaluate the bioaccumulation and biomagnification potential of these compounds in the freshwater aquatic environment.

2. Materials and methods

2.1. Sample collection

A total of seven species of aquatic organisms were collected concurrently in Huai'an in Jiangsu province of China in May, 2010, from the Beijing-Hangzhou Grand Canal. Wild aquatic species included two invertebrates, river snail (*Viviparus*) and freshwater shrimp (*Macrobrachium nipponense*); five fish species, bleeker (*Pseudolaubuca sinensis*), loach (*Misgurnus anguillicaudatus*), crucian carp (*Carassius auratus*), common carp (*Cyprinus carpio*), and northern snakehead (*Channa argus*).To eliminate individual diversity, composite samples were used comprised of five individuals of the same species. Detailed information on the biota sample name, number, and lipid content are highlighted in Table 1. After collection, all samples were stored at −20 °C until chemical analysis.

2.2. Chemicals and reagents

All solvents used were of pesticide grade purity (J.T. Baker, USA). Silica gel (pore size 60 Å, 70–230 mesh) was purchased from Merck (Merck, Germany). Dec 602 (95%), Dec 603 (98%), and Dec 604 (98%) were purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada). CP, DP, DPMA, aCl10DP, and aCl11DP were obtained from Wellington Laboratories Inc. (Guelph, ON, Canada), and Mirex was obtained from Cambridge Isotope Laboratories Inc. (Andover, MA). The surrogate and internal standards used for all compounds were 2,2′,4,4′,6,6′-hexachlorobiphenyl (CB-155) and octachloronaphthalene (OCN) purchased from Accustandard Inc. (New Haven, CT).

2.3. Extraction and analyses

Fish muscle tissues were homogenized individually. Soft tissues of two freshwater shrimps and five river snails for each group were homogenized for CFR concentration analysis. Approximately 5 g of each sample was mixed with ashed anhydrous sodium sulfate, spiked with the surrogate standard CB-155, and Soxhlet-extracted in a mixture of hexane/acetone (1:1, v/v) for 24 h. An aliquot of each extract was removed for gravimetric lipid determination, while the remaining extract was added to a separatory funnel and treated three times with 98% H_2SO_4 for lipid removal. The lipid-free eluate was purified using fully activated neutral silica (7 g) capped with anhydrous sodium sulfate (2 g). The column was prewashed with 60 mL of dichloromethane (DCM):hexane (1:1, v/v). Then 2 mL of extract was loaded onto the column, and the target compounds were eluted using 70-mL of DCM:hexane (1:1, v/v). The eluant was rotary-evaporated to approximately 4 mL, solvent-exchanged into isooctane and reduced to <1 mL by evaporation with a steam of nitrogen. Then OCN (250 ng/sample) was added into the eluants and the final volume was adjusted to 1 mL prior to GC-HRMS analysis.

The sample extracts were analyzed using a HRMS Micromass AutoSpec Ultima MS (Micromass, Manchester, UK) connected to a Hewlett–Packard 6890 GC (Hewlett–Packard, Palo Alto, CA, USA) equipped with a 15 m DB-5HT column (0.25 mm i.d., 0.10 μm film thickness J&W Scientific, Folsom, CA). The initial oven temperature was set to 100 °C for 2 min., ramped at 25 °C min^{-1} to 250 °C, ramped at 1.5 °C min^{-1} to 260 °C, ramped at 25 °C min^{-1} to 325 °C, and held at 325 °C for 10 min. The HRMS system was operated in electron ionization (EI) mode and was tuned to 10000 resolving power (RP) at 10% valley definition. Concentrations of mirex, CP, DPMA, Dec 602, Dec 603, Dec 604, aCl10DP, Cl11DP, and DP were determined by monitoring the two most abundant ions of the fragment cluster. All compounds were identified with retention times ±0.10 min of the calibration standard, and verified using selected mass ions, corresponding mass ions ratios, and signal–noise ratio (>3). The names, structures, retention times, mass ions, and ion ratios are summarized in Appendix (Table S1).

2.4. Stable isotope analysis

For stable isotope analysis, muscle tissues of the aquatic organisms were freeze-dried and ground to homogeneous powders with a mortar and pestle. A 0.8–1.0 mg sample was weighed into a tin