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Enantioselectivity of polychlorinated biphenyl atropisomers in sediment and biota from the Turtle/Brunswick River estuary, Georgia, USA

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ABSTRACT

To investigate the potential for enantioselective transformation and accumulation, the enantiomer distributions of seven polychlorinated biphenyl (PCB) atropisomers were measured in the sediment and biota from a sub-tropical estuary heavily contaminated with Aroclor 1268, a technical mixture of highly chlorinated PCB congeners. Enantiomer fractions (EFs) of PCBs 91, 95, 136, 149, 174, 176, and 183 in marsh sediment, invertebrate, forage and predatory fish species, and bottlenose dolphins were determined. Non-racemic EFs greater than 0.75 were found in sediments for PCBs 136 and 174, likely the result of microbial dechlorination. Although enantiomer fractions in grass shrimp (*Palaemonetes* spp.) mirrored those of sediment, fish species had EFs that differed significantly from sediment or grass shrimp. Similarly, bottlenose dolphins were also found to contain non-racemic quantities of PCBs 91, 136, 174, 176, and 183. Non-racemic EFs in these biota were likely a result of both uptake of non-racemic proportions of PCBs from the diet and enantioselective biotransformation.

1. Introduction

Due to their persistence within the environment, polychlorinated biphenyls (PCBs) continue to pose risks to humans and biota more than 30 years after their use was discontinued. High concentrations of PCBs are still found in some environmental compartments. In aquatic environments, their hydrophobicity causes PCBs to partition into sediments, where they may be may be taken up by lower trophic level organisms and enter the food web.

Microbially-mediated reductive dehalogenation is one possible transformation process for highly chlorinated PCBs in anaerobic sediments. Sediment microbes remove chlorines from more highly chlorinated congeners, resulting in an enrichment of lower chlorinated congeners in the environment (Bedard, 2001). The presence of *in situ* dechlorination activity can be inferred by analyzing congener and homolog patterns in sediments and comparing those to congener and homolog patterns found in the original Aroclor mixtures (Bedard and May, 1996; Brown et al., 1987; Magar et al., 2005). While such techniques provide strong evidence for microbial activity, they do no necessarily prove that it exists, as changes in congener patterns may also result from vaporization or selective sorption. Furthermore, dechlorination rates may also be sufficiently slow to make it difficult to detect changes in the congener patterns over short durations of time.

The use of enantioselective analytical techniques and the detection of non-racemic proportions of chiral molecules can provide unequivocal evidence for biological activity. Nineteen of the 209 PCB congeners are chiral and exist in the environment as stable atropisomers (Kaiser, 1974). These congeners were released into the environment as racemic mixtures, and although individual enantiomers possess identical physical and chemical properties, non-racemic distributions of PCB enantiomers have been found in sediment and biota samples (Wong et al., 2001a,b). Biological processing may change the enantiomer distribution of a compound within the environment due to differential interaction between enantiomers with other chiral molecules, such as proteins. Previous studies have found that dechlorination of PCBs by sediment microbes and *in vivo* biotransformation by biota can occur in an enantioselective manner (Buckman et al., 2006; Pakdeesusuk et al., 2003; Singer et al., 2002; Warner and Wong, 2006; Wong et al., 2002b). Therefore, the use of stereoisomer analysis and the detection of non-racemic enantiomer distributions provides a sensitive means of detecting and tracing biologically-mediated

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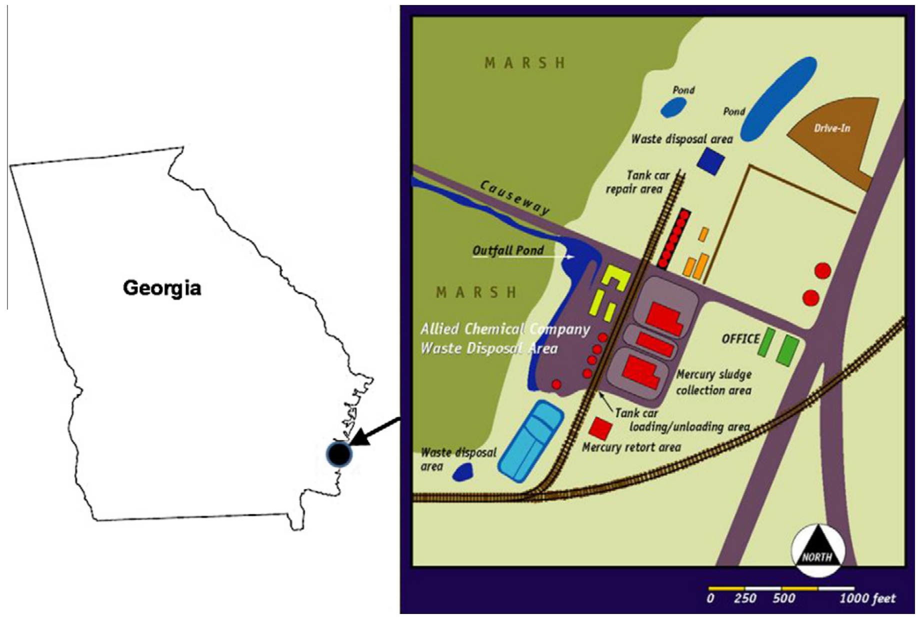

Fig. 1. Map of the study area.

processes, for instance the presence of microbial dehalogenation activity, that may otherwise be difficult to detect using achiral methods (Wong et al., 2004, 2007).

The LCP Chemicals Superfund site, a marshfront industrial site located on the margins of the Turtle/Brunswick estuary in southeastern Georgia, USA (Fig. 1), was home to an oil refinery, a power plant, and a paint manufacturing plant over the past 70 years. Most recently, a chlor-alkali plant operated on the site from 1955 to 1994. During this time, industrial wastes were discharged directly into the surrounding marsh areas known as Purvis Creek. This resulted in the sediment from the marsh and creek areas surrounding the LCP site being highly contaminated with mercury and Aroclor 1268, an uncommon PCB formulation comprised primarily of octa- to decachlorinated biphenyls (Table 1; Kannan et al., 1997). Previous studies on the site have found that the highly chlorinated PCBs are bioavailable to organisms, which has also resulted in widespread contamination of local biota (Kannan et al., 1998; Maruya and Lee, 1998a). However, due to the recalcitrance of these congeners, these studies were not designed to investigate whether biotransformation was occurring, either in sediments or biota.

In this study, we analyzed the enantiomer distribution of seven chiral PCB congeners in sediment cores from the contaminated estuary around the LCP Superfund site to determine whether or not microbial dechlorination was occurring at this site. Additionally, the high concentrations of heptachlorinated biphenyls found in biota at this site provide a unique opportunity to investigate the enantioselective behavior of highly chlorinated PCB homologs. Therefore, enantiomer distributions were determined in invertebrates, fish species, and resident dolphins to determine the extent of biotransformation occurring within these species. This study provides insight into the biological processing occurring at the LCP Superfund site, and allows for a further understanding of the environmental behavior of highly chlorinated PCBs.

Table 1
Polychlorinated biphenyl relative homolog distributions (%) in Aroclor 1268 and marsh sediments from the LCP Superfund site, Brunswick, GA.

Homolog	Aroclor 1268[a]	Marsh sediment[a,b]
Di-	0	0
Tri-	0.006	0.16
Tetra-	0.12	0.30
Penta-	0.19	1.57
Hexa-	4.38	7.2
Hepta-	10.1	14.6
Octa-	45	33.1
Nona-	35	37.9
Deca-	4.8	5.2

[a] Data from Kannan et al. (1997).
[b] Average of left and right south marsh transect.

2. Materials and methods

2.1. Sample collection

Three sediment core samples were collected using a polyvinylchloride push core (7.6 cm diameter × 61 cm length) from two areas of the intertidal marsh (Fig. 1). Intact cores were sealed with end caps lined with solvent-rinsed aluminum foil and were sectioned using solvent-rinsed stainless implements upon return to the lab. All sediment samples were stored frozen at −20 °C in pre-cleaned glass (I-Chem) jars prior to analysis. The south marsh area (cores NSM and LCP) is located adjacent to waste pits on the LCP Superfund site, and is characterized by high concentrations of PCBs and mercury (Kannan et al., 1997; Winger et al., 1993). A causeway bisects the marsh area, and sediments collected from the north side of the causeway (core 311A) contain significantly lower concentrations of PCBs.

Biota was collected from various locations around the LCP site in an effort to represent the basic trophic levels of the local estuarine food web. Grass shrimp (*Palaemonetes pugio*), an abundant crustacean macroinvertebrate in estuaries of this region, were collected from Purvis Creek by dip netting (Maruya and Lee, 1998a). Silver perch (*Bairdiella chrysoura*), spot (*Leiostomus xanthurus*), spotted seatrout (*Cynoscion nebulosus*), and striped mullet (*Mugil cephalus*) were collected from Purvis Creek by trawl, gill and cast netting (Pulster et al., 2005). These fish species were collected to represent likely prey items of the bottlenose dolphins (*Tursiops truncatus*), the predominant marine mammal species that frequent the region's estuaries (Pulster and Maruya, 2008). Blubber samples from free ranging bottlenose dolphins were collected from the Turtle/Brunswick estuary by means of a dart biopsy (Pulster and Maruya, 2008; Pulster et al., 2009).