CHIRALITY AS INDICATION FOR PCB ACCUMULATION IN FOREST SOILS ALONG AN URBAN-RURAL GRADIENT

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Introduction

Although PCBs were banned in the 1970s, concentrations in the environment remain elevated, particularly in urban areas. Urban-rural gradients of PCBs have been documented in air[1], organic film on impervious surfaces[2,3], and soil[4]. Soils are a primary sink for PCBs due to their high capacity for retaining hydrophobic chemicals and slow removal rate. Their accumulation in soils provides a long-term source to other media[5] and, as such, influences the overall environmental fate of these chemicals in the environment.

Chiral analysis is an emerging tool for investigating environmental fate and sources of atmospheric organic pollutants[6]. Nineteen of the 209 individual PCB congeners are atropisomers and are known to be racemic in the technical products. The detection of non-racemic PCB signatures indicates the presence of enantioselective degradation which is assumed to be microbially mediated. To date, the analysis of chiral PCBs has been reported for sediments[7], biological tissues[8], and soils[9].

Fulthorpe and Schofield[10] found that pristine forest soils had higher microbial degradation rates for some chlorinated aromatics but lower rates for others relative to agricultural and suburban soils. Gingrich et al.[3] reported "fresher" signatures of DDT and chlordane at urban than rural sites in window films, the reason for which was not known. Finally, Law et al.[11] found less enantioselective degradation of α-HCH in urban than remote surface waters, which they attributed to differences in carbon availability and the selectivity of microbial communities. These inconsistent and somewhat confusing results led us to investigate enantioselective degradation of chiral PCBs along an urban-rural transect where this degradation is indicative of microbial degradation processes.

Methods and Materials

Forest soils were sampled at six sites along an 80 km urban-rural transect in the Greater Toronto Area (GTA), Ontario, Canada. At each site, a composite sample of 40 cores was taken from 0-5 cm depth with a stainless steel auger over an area of ~200 m^2. All sites were characterized by predominantly mature forest stands of Sugar Maple, *Acer saccharum*. and soils were of loam-type with organic carbon contents ranging from 4 to 8% and pH from 5.1 to 7.5 (Soil and Nutrient Laboratory, University of Guelph).

Soil samples (10g) were extracted with DCM using Dionex ASE-200 Accelerated Solvent Extractor (ASETM). Details of the extraction and cleanup procedures are described by Wong et al.[12] A total of 51 PCBs were quantified and results are reported on a dry weight basis. Enantiomeric fractions (EFs) of CB-95, -136 and -149 were determined according to the method of Robson and Harrad[9].

Results and Discussion

PCB Levels in Forest Soils

Highest ΣPCB was observed at the two urban sites (High Park, 52 ng g^{-1} and Riverdale, 51 ng g^{-1}) which are located at downtown Toronto, followed by the two semi-urban sites (North York, 30 ng g^{-1} and Downsview 27 ng g^{-1}) which are ~ 25 km north of downtown Toronto, and then the semi-rural site (Richmond Hill, 23 ng g^{-1}) which is ~ 40 km north of Toronto. Lowest ΣPCB was observed at the rural site (Borden, 9 ng g^{-1}) which is located 80 km from downtown Toronto. PCB concentrations at the urban sites were 5 times greater than the rural site, similar to the findings of Krauss and Wilcke[4], but less than the 10-fold difference in ΣPAH concentrations measured in the same soils[12]. The PCB congener patterns at all sites were dominated by hexa- and penta-homologues. This is consistent with the PCB patterns found in organic films collected in downtown Toronto[3] and Baltimore[2]. The congener profiles do not indicate fractionation as seen in air whereby the lighter congeners dominate the rural profiles. Rather, the rural site is enriched in mid-molecular weight congeners, notably the recalcitrant congeners 149, 153 and 183, which has been noted by Lead et al.[5] More congeners are detected in urban sites which are closer to source areas.

Chiral PCBs

Results of the enantioselective analysis are expressed as EFs whereby an EF of 0.500 indicates that the compound is racemic and an EF that deviates from 0.500 suggests enantioselective degradation. The EFs of CB-95 showed great variability, ranging from 0.386 to 0.516, while EFs of CB-136 ranged from 0.428 to 0.566 (Table 1) and confirms their enantioselective degradation[9]. In contrast, EFs of CB-149 ranges from 0.466 to 0.517, which is close to racemic and does not indicate appreciable enantioselective degradation. It is interesting to compare these data with those obtained at a single urban grassland location in Birmingham, UK[9]. While the range of EFs obtained in Birmingham for CB-95 and -136 are consistent with those in this study, the range of EFs for CB-149 (0.440-0.474) in Birmingham, demonstrate greater enantioselective degradation of this congener than in the GTA.

EFs were also expressed as deviation from racemic EF value of 0.500 (DFR)[13] and then regressed against PAH and PCB concentrations in the soils. Figure 2 shows that DFR of CB-136 and CB-149 has an inverse relationship with PAH and PCB concentrations. This suggested that there is less microbial degradation in the more contaminated (urban) than the less contaminated (rural) soils. This inverse relationship was also reported for CB-149 in the lake sediments in UK[13]. EFs of CB-95 show a greater range of values that are not related to PCB nor PAH[12] concentrations.

It is unclear as to the factors controlling the enantioselective degradation of the PCBs studied here since the soils sampled were similar in terms of the vegetative community, organic matter content and grain size[12]. Clearly, the relationship between EFs and soil contamination levels and other edaphic properties including the size, variety and type of soil microbial populations is complex and further detailed study is required.

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Figure 1. PCB concentration in the forest soils of Greater Toronto Area

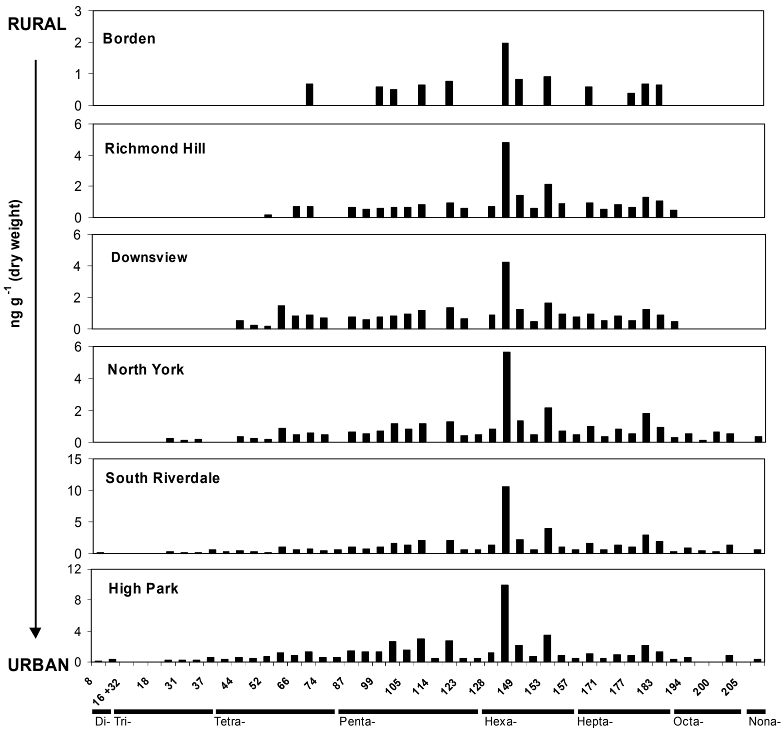
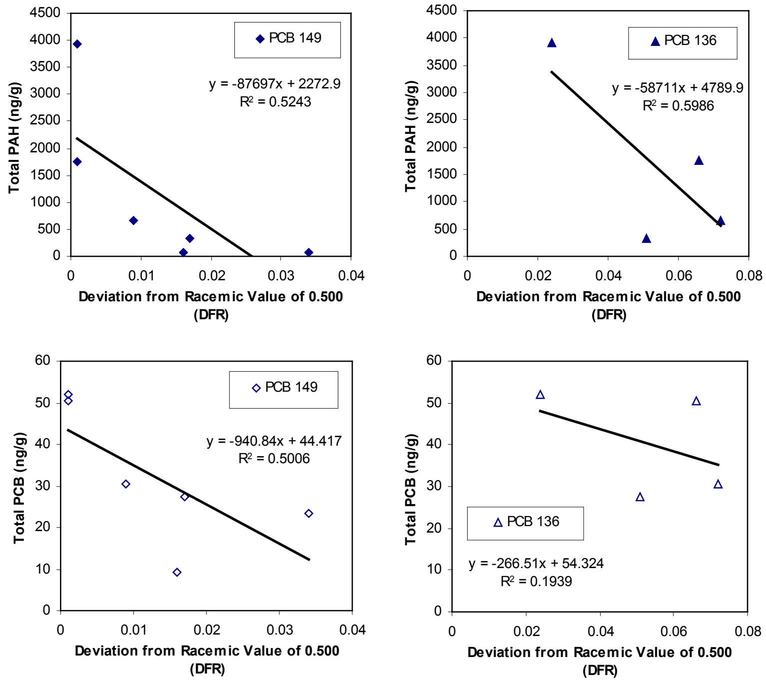


Table 1. Enantiomeric fractions (EFs) of PCB 95, 136 and 149 in the forest soils of Greater Toronto Area

Site	PCB 95	PCB 136	PCB 149
Borden	0.488	n.d.	0.484
Richmond Hill	0.386	n.d.	0.466
Downsview	0.516	0.449	0.517
North York	0.510	0.428	0.509
South Riverdale	0.452	0.566	0.501
High Park	0.425	0.476	0.499

n.d. not determined

Figure 2. Relationship between extent of enantiomeric degradation and contaminant burden in the forest soils of Greater Toronto Area



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