# PCB PATTERNS IN ORGANICALLY CHARACTERIZED MARINE SEDIMENT CORES FROM HUDSON BAY

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#### Introduction

Many of the key pathways and processes that determine the fate of organic contaminants such as polychlorinated biphenyls (PCBs) in marine systems are linked to the movement and transformations of organic particles, i.e., the organic carbon cycle<sup>1-3</sup>. Changes in the flow of terrestrial and/or marine organic carbon resulting from altered climate<sup>4</sup> may thus be accompanied by changes in contaminant pathways<sup>5-7</sup>. Sediment cores preserve records of organic carbon and contaminants together with physical and geochemical processes operating within a system and therefore provide an invaluable tool for understanding the linkages between these components, for constructing modern and past budgets and for inferring the potential impacts of climate change. Here, we examine PCB congener data for <sup>210</sup>Pb-dated and organically characterized (C, N,  $\delta^{13}$ C, lignin) marine sediment cores from Hudson Bay, Canada. While Hudson Bay shares many key attributes with other Arctic marine systems, models predict greater and perhaps faster climate-related changes, owing to its more southerly latitude and close contact with terrestrial systems<sup>4, 8-10</sup>. As a Mediterranean, shallow sea, Hudson Bay receives inordinate loadings from the surrounding basin, thus integrating both land-based and marine climate impacts. PCB levels in the system's biota are well known but as yet we know very little about the environmental pathways and processes in the PCB cycle, such as the role of terrestrial vs. marine inputs, circulation and scavenging processes, and loss mechanisms such as sediment burial.

#### Material and methods

Thirteen sediment cores (Figure 1) were collected from the Canadian Coast Guard Ship Amundsen in September-October 2005. Cores were retrieved using a box corer (maximum penetration 50 cm) and were sectioned aboard the ship, generally into 1 cm intervals for the top 10 cm, 2 cm intervals for the next 10 cm, and 5 cm intervals for the remainder of the core. Each section (sample) was homogenized in a thoroughly precleaned I-Chem glass jar, subsampled for elemental and isotopic analyses, and then frozen. Freeze-dried subsamples were used for <sup>137</sup>Cs analysis by gamma spectrometer, <sup>210</sup>Pb analysis via its <sup>210</sup>Po daughter<sup>11</sup>, and <sup>226</sup>Ra analysis (selected samples) by the radon de-emanation method<sup>12</sup>. Geochronologies were constructed for each core using profiles of excess <sup>210</sup>Pb and a model that incorporates a surface mixed layer<sup>13</sup>, and were verified against <sup>137</sup>Cs. Organic carbon content (%OC) was determined by difference from measurements of total C using a Carlo Erba NA-1500 Elemental Analyzer<sup>14</sup> and total inorganic C determined by CO<sub>2</sub> coulometer. Stable isotopes ( $\delta^{13}$ C) were determined on acidified samples using the element analyzer coupled to an isotope ratio mass spectrometer. Lignin yields were determined by alkaline CuO oxidation in a microwave digestion system<sup>15</sup>. PCB congeners were quantified from the frozen archives (all surface samples and subsurface samples from six cores) at AXYS Analytical Services Ltd., Sydney BC, using high-resolution gas chromatography with detection by low-resolution mass spectrometry. Rigorous quality assurance/quality control (QA/QC) was maintained and blank values (sum of all detected congeners ( $\Sigma$ PCBs)) were generally <0.05 pg g<sup>-1</sup>. PCB concentrations were salt-corrected using the salinity of the bottom water at the coring site.

#### **Results and discussion**

# ΣPCBs

Total PCB concentrations ( $\Sigma$ PCBs) in 37 analyzed samples varied from 5 to 181 pg g<sup>-1</sup>, with the major individual congeners having concentrations of 0.068 to 12 pg g<sup>-1</sup>. Earlier reported Arctic sediment  $\Sigma$ PCBs were generally higher (250 to >8000 pg g<sup>-1</sup>)<sup>16, 17</sup> however similar congener concentrations were reported recently for quality-assured sediment core data from northern Baffin Bay<sup>18</sup>.

Vertical profiles of  $\Sigma PCBs$  for six cores (Figure 2) show lowest concentrations in the deepest slices of the cores and highest concentrations generally just below the surface. <sup>210</sup>Pb-derived sedimentation rates for the cores varied from ca. 0.03 to 0.18 g cm<sup>-2</sup> yr<sup>-1</sup> and the geochronologies constructed from these data place peak  $\Sigma PCB$  concentrations between the years 1966 and 1986. This is consistent with the estimated timing of the PCB maximum in a core from the Canadian High Arctic (ca. 1984)<sup>18</sup>.

According to the <sup>210</sup>Pb-dating, the surface sections (0-1 cm) of the cores represent sedimentation over the last 5-22 years. However, because surface mixed layers (1-10 cm) were present in most cores and sedimentation rates were relatively low (ca. 0.03 to 0.25 g cm<sup>-2</sup> yr<sup>-1</sup>), the intrinsic time resolution of the cores is generally 30 years or more. This may explain in part why age was not a significant source of variation in the wide range of  $\Sigma PCBs$  (40 to 150 pg  $g^{-1}$ ) among the surface sections. The major sources of variation in surface  $\Sigma PCBs$  appear to be sediment porosity (R=0.73, p=0.004), which we interpret as a rough proxy for particle size (especially the presence of sand), and sedimentary organic carbon content (%OC: R=0.63, p=0.02, Figure 3), with which porosity was closely associated (R=0.88). None of the examined indicators of organic carbon form or origin (molar C/N ratios,  $\delta^{13}$ C, lignin) explained the residual variance in  $\Sigma$ PCBs. Nevertheless, OC-normalized PCB concentrations retained as much variability as the mass-based concentrations (range  $5.4-15.7 \text{ ng g OC}^{-1}$ ) and the normalized concentrations showed a significant correlation with  $\delta^{13}C$  (R= -0.62, p=0.024), with OC-normalized concentrations decreasing as  $\delta^{13}C$  values increased (Figure 3B).  $\delta^{13}C$  values are generally used as an indicator of organic matter origin in marine sediments<sup>19</sup> and indeed suspended sediment entering Hudson Bay via rivers bears a  $\delta^{13}C$  signature of about -28‰, whereas marine particulate organic matter (POM) has an average  $\delta^{13}C$ value of about -21‰ (Kuzyk et al., unpub.). Thus, the negative  $\delta^{13}$ C-PCB relationship could indicate that allochthonous POM from the surrounding land has higher loadings of PCBs (per g of organic carbon) than autochthonous marine organic matter. This would imply a relatively important role for PCBs deposited in the watershed and subsequently transported (e.g., by rivers) to Hudson Bay. Alternatively, the organic carbon origin may not be the controlling factor but rather the history of the POM within the marine system, as reflected distance from shore (R= -0.60, p=0.038). Sediment resuspension and lateral transport are recognized as very important sedimentation processes in Hudson Bay<sup>20, 21</sup> and the decrease in PCB loadings with distance and  $\delta^{13}C$ may reflect PCB losses during this kind of transport. This is consistent with recent findings that organic matter may evolve considerably as it travels from a terrestrial source to ultimate burial at sea $^{22,23}$ 

### PCB congener patterns

Variation in PCB congener composition was explored using principal components analysis (PCA) of the relative (%) abundance of 19 prominent congeners, spanning low- to high chlorination (4-7 Cl), and samples representing sedimentation during the last roughly 60 years (n=23). Two outliers with elevated proportions of highly chlorinated congeners (IUPAC 138, 153, 180) were removed. The first two components of the PCA explained, respectively, 52% and 15% of the total variance (Figure 4). Loadings on PC1 were closely related to the degree of chlorination of the PCB congeners (R=0.84), with less chlorinated congeners (18, 28, 52, 70) having lower (more negative) loadings than the medium- (101, 118) and highly chlorinated congeners (138, 149, 153, 180). This relationship suggests physico-chemical control over variation in PCB congener composition and indeed, sample scores on PC1 were correlated with the latitude of the core site (R=-0.69, p=0.001). The less chlorinated congeners contributed an increasingly larger fraction of total PCBs with distance northward, which is consistent with latitudinal trends observed in Canadian lake sediments<sup>24</sup> and over a 40°N-76°N latitudinal gradient in marine sediments<sup>18</sup>, and supports the global fractionation concept (i.e., lighter congeners favoured during long range atmospheric transport northward). The occurrence of this compositional gradient within Hudson Bay, over about 8 latitudinal degrees, suggests that direct air-sea exchange may be a significant component of the Bay's PCB budget, despite the tremendous annual river discharge into the system (equivalent to ca. 0.6 m distributed over the surface of the Bay)<sup>25</sup>. Sample scores and congener loadings on PC2, however, show that other factors also significantly shape the PCB composition of the sediments. A plot of PC2 scores vs.  $\delta^{13}$ C (Figure 4B) shows remarkably close correspondence between these parameters (R=0.85, p<0.0001) for all  $\delta^{13}$ C values greater than about -23‰ (all but cores 6, 7, and 9). The more isotopically enriched cores (e.g., cores 3, 10 and 15) contain relatively elevated proportions of less chlorinated and moderately chlorinated congeners (e.g., 118), while the isotopically depleted samples (e.g., cores 8 and 12) contain relatively more highly chlorinated congeners. Although the  $\delta^{13}$ C gradient may relate to the relative influence of terrestrial and marine

carbon sources, we propose the alternative explanation that they relate to different types of marine OM sources, for example, phytoplankton vs. ice algae, which typically differ by a few units in their  $\delta^{13}$ C values<sup>19</sup>. The  $\delta^{13}$ C values of both these marine sources lie above -23‰ (roughly at -22‰ and -18‰, respectively), which is the lower limit above which the  $\delta^{13}$ C-PCB composition relationship seems to occur (Figure 4B). Independent support for our hypothesis is that the sites of cores 3 and 15 are known to be major areas of ice import and  $melt^{26}$ . Futhermore, if the relationship were related to the balance between terrestrial and marine OM sources, we would expect a clearer distribution over the whole  $\delta^{13}$ C range. Accordingly, we propose that areas receiving a greater proportion of ice algal carbon inputs have a generally less-chlorinated PCB signature than areas where phytoplankton are dominant. Presently, we cannot explain the mechanism for this fractionation, but it may relate to differences between winter and summer sources or alternatively biogeochemical processes associated with ice<sup>27</sup>. The picture beginning to emerge from the contaminant and geochemical data sets for the sediment cores is one of both organic carbon content and origin or composition playing important roles in  $\Sigma PCB$  distribution and compositional variation in Hudson Bay. The PCB loadings associated with marine and terrestrial OM, alterations of loadings during lateral transport and the relative importance of ice algae compared to phytoplankton are key components of the system requiring further study to connect carbon and contaminant cycling and to predict how PCBs in the system may respond to climate change.

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Figure 1: Locations of sediment cores

Figure 2: **SPCB** profiles in 6 dated cores



Figure 3: Surface  $\Sigma$ PCBs (pg g<sup>-1</sup>) vs. %OC (A) and OC-normalized PCBs (ng g OC<sup>-1</sup>) vs  $\delta^{13}$ C (B)



Figure 4: PCA scores and congener loadings (A) and relationship between PC2 scores and  $\delta^{13}C$  (B)

