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Characterization and Interpolation of Sediment PCBs and PBDEs in Resident Killer Whale Habitat along the Coast of British Columbia, Canada

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INTRODUCTION

- The northeastern Pacific Resident Killer Whales (*Orcinus orca*) were listed under the Canadian Species at Risk Act (SARA) in 2003 as 'threatened' and 'endangered' for the Northern and Southern Resident populations, respectively.
- Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) have been identified as primary contaminants of concern for the NRKWs and SRKWs (Baird, 2001; Krahn et al., 2007; Ross et al., 2000; Ross, 2006).
- Sediment can act as both a sink and a source of persistent, bioaccumulative, and toxic (PBT) contaminants in the marine environment. And upon mobilization (Burd et al., 2014), PCBs and PBDEs can biomagnify at each trophic level, ultimately affecting killer whale health (Lachmuth et al., 2010).
- Recently, sediment quality guidelines (SQGs) deemed to be protective of SRKWs (PCBs: 3.7 pg/g dry weight (dw) and PBDEs: 1,000 pg/g dw) were derived (Alava et al., 2012, 2016) and adopted as 'working' guidelines by the BCMoE.

OBJECTIVE: In this study, we combined PCB and PBDE concentration data from Ocean Wise Conservation Association's *PollutionTracker* Program, Fisheries and Oceans Canada's *Whale Contaminants* Program, and Environment and Climate Change Canada's *Disposal at Sea* Program to assess resident killer whale habitat quality.

SPECIFIC OBJECTIVE: Geostatistical and multivariate analyses were used to identify distributions and patterns of PCBs and PBDEs in and around resident killer whale critical habitat and to compare levels in sediments to relevant Canadian SQGs.

METHODS

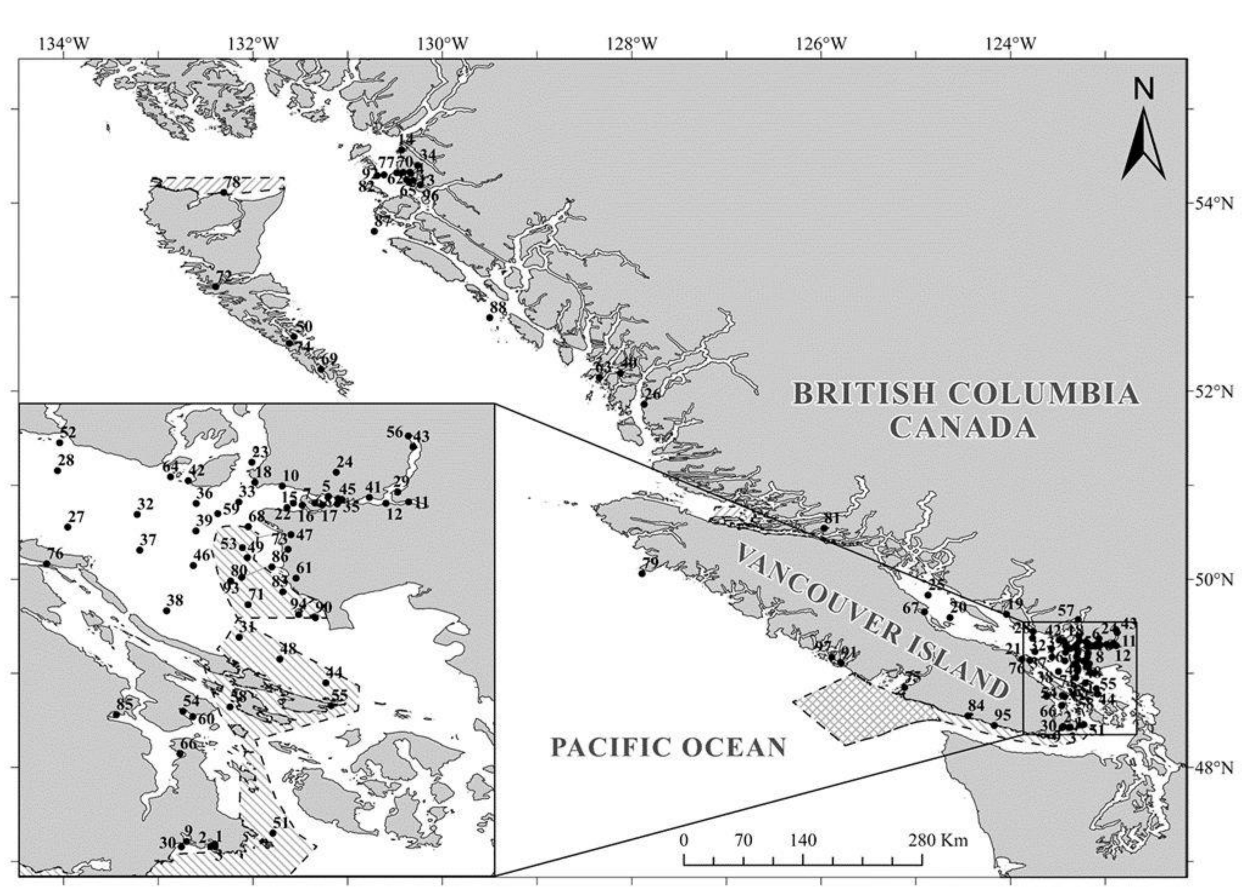

Figure 1. Subtidal surface sediments collected from 97 sites along the coast of British Columbia, Canada. Critical habitat of NRKWs (45˚) and SRKWs (135˚) are shown as hatched areas. The cross-hatched area represents shared critical habitat.

- Subtidal surface sediments for 97 sites along the BC coast, Canada, between 2018 and 2020 (Figure 1)
- Principal component analysis was performed to identify distributions and patterns of PCBs and PBDEs.
- Spatial interpolations of measured concentrations and probabilities of exceeding established sediment-derived thresholds for killer whale risk were conducted using Kernel interpolation with barrier (KB) in ArcGIS Pro geostatistical package.

RESULTS

Profiling of PCBs and PBDEs

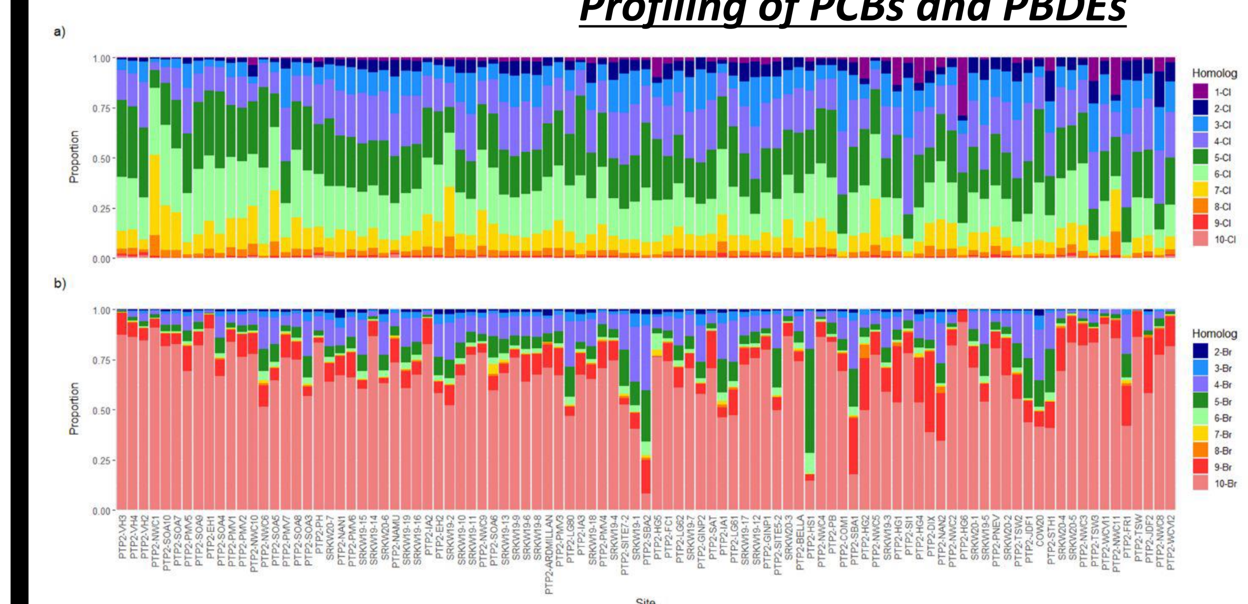

Figure 2. Proportions of a) PCBs and b) PBDEs in homolog groups for sediment samples collected at 97 sites.

→ Homologs with three (triCB), four (tetraCB), five (pentaCB), six (hexaCB), and seven (heptaCB) Cl atoms accounted for a total average of approximately 89 ± 1% (SE) for PCBs, whereas for PBDEs, decaBDE alone (ten Br atoms) accounted for an average of approximately 67 ± 2% (SE) of all sites.

Characterization of PCB and PBDE patterns

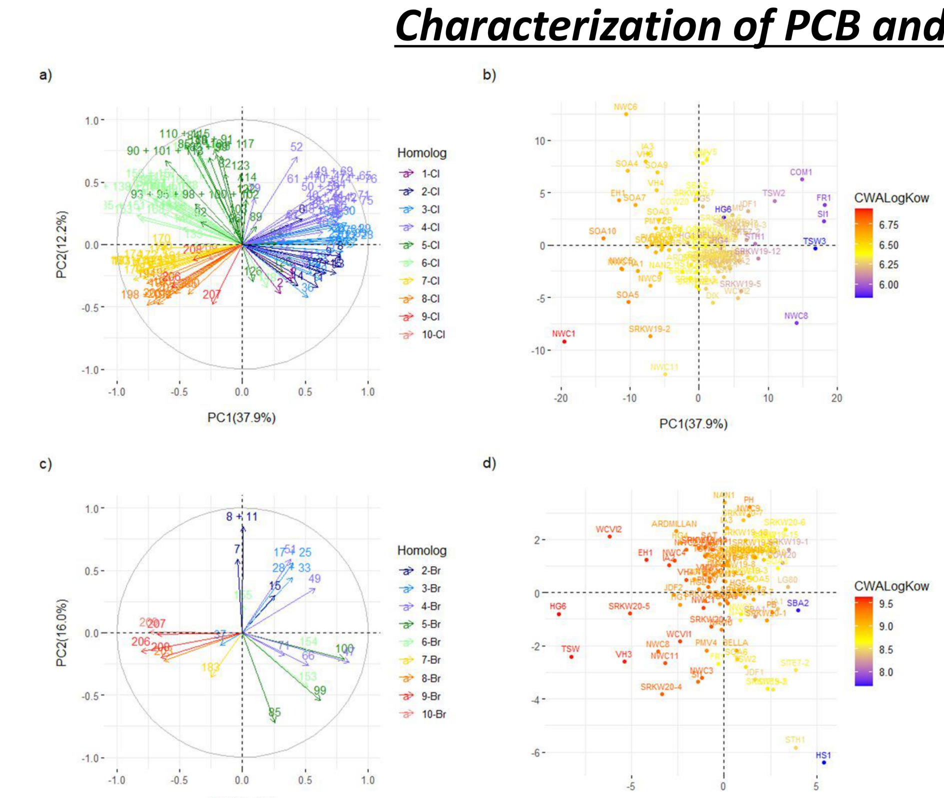

Figure 3. A principal component analysis (PCA) for PCB and PBDE mean-adjusted congener concentrations at 97 sites. Top two panels are for PCBs: a) loading and b) score plots; bottom two panels are for PBDEs: c) loading and d) score plots. All points are color coded based on homolog groups, a) and c) and concentration-weighted average octanol-water partition coefficient (CWALogKow), b) and d).

→ Sites in closer proximity to source mixtures of PCBs and PBDEs would generally be represented by heavier signatures, as lighter congeners tend to disperse more readily and may be relatively more abundant at locations distant from the sources.

Factors governing PCB and PBDE distribution

Table 1. Correlation coefficients to quantify the relationships among principal component analysis (PCA) projections (i.e., PCBs, PBDEs, and sediment particle sizes (SPSs)), total organic carbon (TOC), water depth, octanol-water partition coefficient ($LogK_{ow}$), and concentration-weighted average $LogK_{ow}$ ($CWALogK_{ow}$).

	SPS PC1 (69.5%)	TOC	DEPTH	$LogK_{ow}$	$CWALogK_{ow}$
PCB					
PC1	R = - 0.089; $p > 0.05$	R = - 0.41; $p < 0.001$	R = 0.15; $p > 0.05$	R = - 0.8; $p < 0.001$	R = - 0.93; $p < 0.001$
PC2	R = - 0.075; $p > 0.05$	R = 0.2; $p > 0.05$	R = - 0.18; $p > 0.05$	-	-
PBDE					
PC1	R = 0.45; $p < 0.001$	R = 0.0035; $p > 0.05$	R = 0.31; $p < 0.003$	R = - 0.66; $p < 0.003$	R = - 0.77; $p < 0.001$
PC2	R = 0.27; $p < 0.05$	R = 0.35; $p < 0.001$	R = 0.24; $p < 0.05$	-	-

→ Sites with a heavier PBDE signature were characterized by shallow sediments with larger SPS, while those with a lighter signature were deeper samples with smaller SPS.

→ PCBs are more evenly distributed vertically in the sediments than PBDEs likely reflecting their longer presence in the marine environment compared to PBDEs.

→ Transport processes for PCBs and PBDEs were influenced by the octanol-water partition coefficient ($LogK_{ow}$) and TOC along the coast of British Columbia.

Risk assessment of PCBs and PBDEs

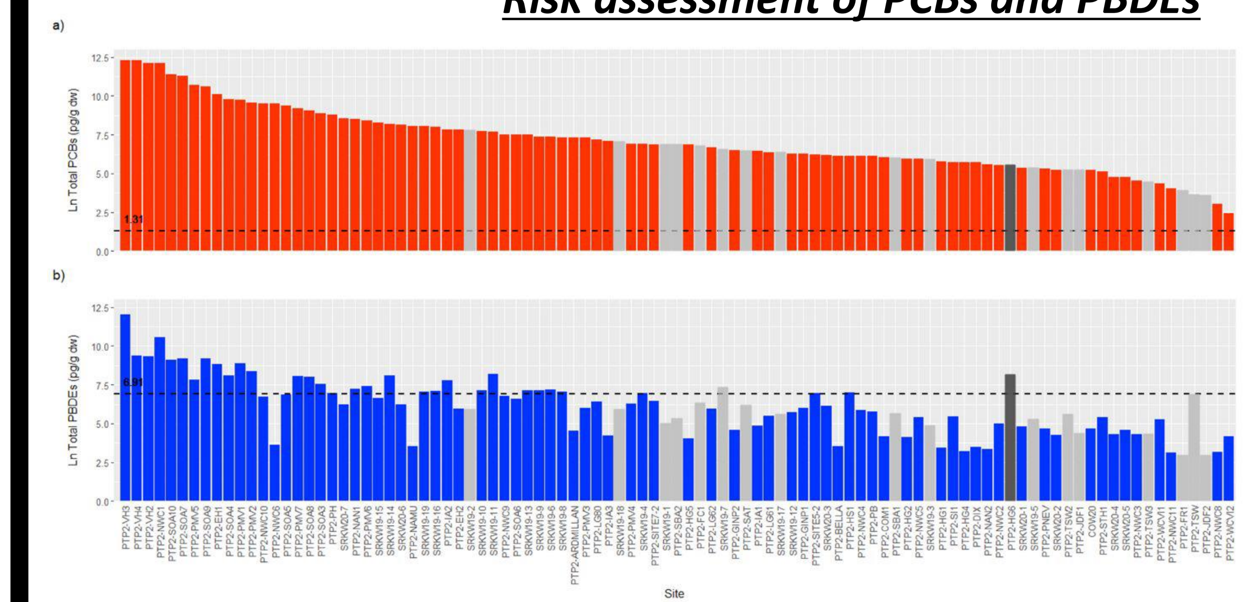

Figure 4. Ln transformed total a) PCB and b) PBDE concentrations are presented for 97 sediment samples, including 1 and 17 samples within NRKW and SRKW critical habitat (darker and lighter grey bars), respectively. Ln transformed BCMoE Working Sediment Quality Guidelines (WSQGs) are shown as dotted lines.

→ Total PCB and PBDE concentrations at 100% and 34% of the sites, respectively, exceeded the WSQGs, with 100% PCB exceedances (18/18 sites) and 10% PBDE exceedances (2/18 sites) located within killer whale critical habitat.

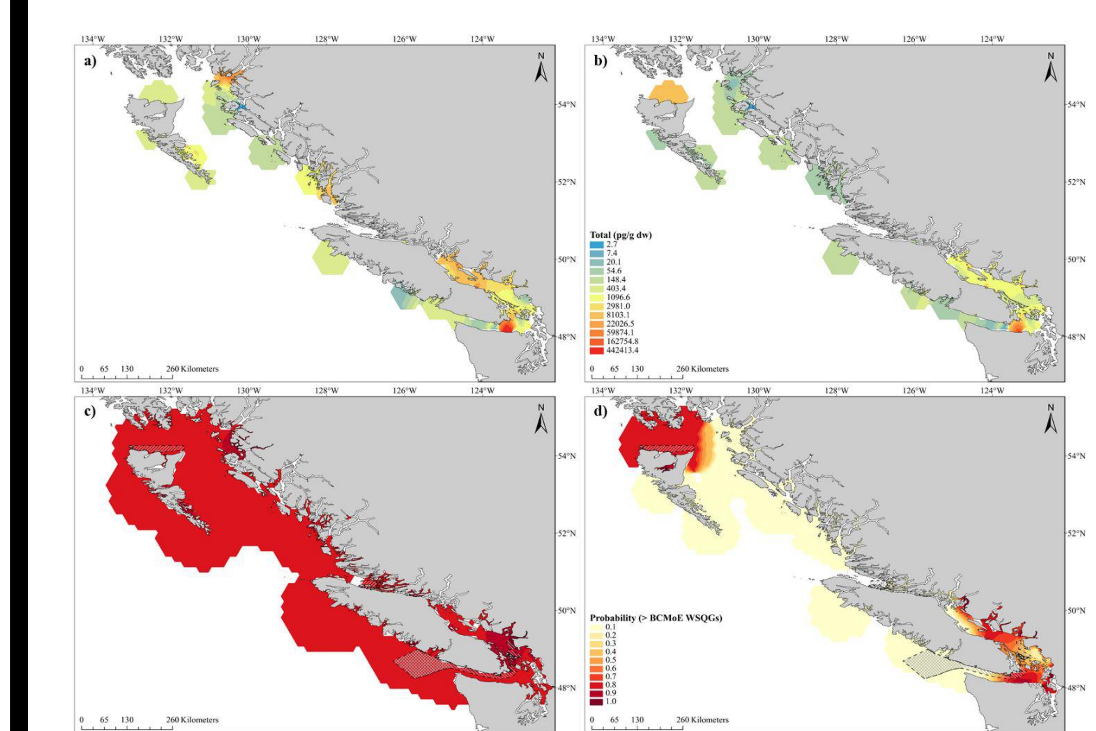

Figure 5. Contour maps of total concentration for a) PCBs and b) PBDEs. Contour maps for probability of exceeding established sediment-derived thresholds for killer whale risk are depicted for c) PCBs and d) PBDEs. Kernel interpolation with barrier (KB) was used to predict total concentrations of PCBs and PBDEs in sediment and probabilities of given points to exceed pre-defined thresholds (PCBs: 3.7 pg/g dw and PBDEs: 1,000 pg/g dw; Alava et al., 2012, 2016).

→ All of the interpolated areas for PCBs and parts of interpolated areas for PBDEs had > 0.5 probability of exceeding BCMoE WSQGs, including all and most of NRKW and SRKW critical habitat, respectively.

CONCLUSION

- Our findings strengthen the understanding of the dominant roles of $LogK_{ow}$ and TOC as two interconnected factors governing their divergent distributions and profiles in the environment.
- Water depth played an important role in the distribution of PBDEs, with a gradient of heavier to lighter PBDE congeners from shallow to deeper sediments.
- Current levels of sediment PCBs and PBDEs pose a threat to the health of both NRKW and SRKW populations and highlight the degraded nature of legally-protected critical habitat.

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