Chlorinated Diphenyl Ethers in Sediments, Biota, and the Water Column from Coastal British Columbia, Canada

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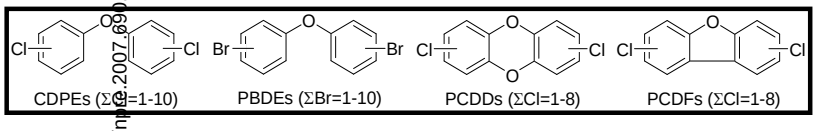
INTRODUCTION

OVERVIEW

- Chlorinated diphenyl ethers (CDPEs) are a halogenated diaryl ether contaminant class.
- 209 different mono- through deca-chlorinated CDPE congeners are possible.
- CDPEs are similar in structure to the polybrominated diphenyl ethers (PBDEs; well-known flame retardants) and polychlorinated dibenzo[1,4]dioxins and furans (PCDD/Fs; well-known highly toxic products of combustion and chlorination processes).



- CDPEs have received significantly less attention towards their environmental levels, patterns, and fate.

SOURCES TO ENVIRONMENTAL SYSTEMS

- Common impurities in technical chlorophenol mixtures (used as wood preservatives) at concentrations up to 100-1000 mg/L.
- Used as dielectric fluids in capacitors (e.g., Dow Chemical Dielectric Fluid C4) and have historically been used as flame retardants.
- Chlorination of effluents containing suitable precursors is a potential source of CDPEs in environmental systems.

STUDY OBJECTIVES

- To better understand the environmental levels and patterns of CDPEs in coastal BC, we analyzed
  - archived sediment and biota samples collected between 1988-1996
    - from marine regions in the Strait of Georgia near the major urban centers of Vancouver and Victoria, and
    - from more remote and pristine marine regions on the North Coast of BC near the islands of Haida Gwaii and on the western coast of Vancouver Island near the outlet of the Strait of Juan de Fuca.
  - and semi-permeable membrane devices (SPMDs) deployed in the Fraser River freshwater system during 1996.

MATERIALS AND METHODS: SAMPLE COLLECTION AND PROCESSING

SEDIMENT SAMPLING

- Sediment grabs collected with modified stainless steel Ponar Grab or stainless steel Smith-MacIntyre grab. Minimum of three grabs were collected at each station.
- Undisturbed sample of top 2 cm of sediment from each grab was collected using a stainless steel spoon after carefully decanting overlying water.

WATER SAMPLING

- Semi-permeable membrane devices (SPMDs; combination of 3 separate bags measuring 3.2 cm × 76.2 cm) were placed in the Fraser River between August 6th and September 30th at 2-3 cm depth during low tide.

BIOTA SAMPLING

- Fish were collected using a small otter trawl with a 3.8 cm mesh net and a 5.8 m throats towed at 1-1.5 knots.
- Crabs were collected by trawl and crab traps.
- Mussels were collected by hand off rocks, pilings, and docks at low tide.

SAMPLE PROCESSING

- Details on SPMD construction, deployment locations, and procedures used for extraction and cleanup have been discussed elsewhere (Rayne, S., and Ikonomou, M.G. (2002) *Environ. Toxicol. Chem.*, **21**, 2292-2300).
- Dissections were performed on Teflon boards using sterilized stainless steel scalpels, scissors, and forceps.
- Tissues collected for analysis included the following: tail muscle from shrimp and prawns, leg muscle and hepatopancreas from crabs, dorsal muscle (skin removed, liver and gill [without gill arch] from fish), and soft tissue from bivalves.
- Crab hepatopancreas removed shortly after the crab was taken from the water.
- ~30 to 50 g aliquots of homogenized tissue were placed in solvent-rinsed and heat treated 125 mL glass jars.
- Samples were kept frozen at -20°C until analysis.

MATERIALS AND METHODS: SAMPLE ANALYSES

PARTICLE SIZE DISTRIBUTIONS

- Particle size analyses conducted using pipette method and the following classifications:
  - silt and clay (<0.063 mm [>230 mesh])
  - very fine sand (0.063-0.125 mm [230 mesh])
  - fine sand (0.125-0.250 mm [120 mesh])
  - medium sand (0.250-0.500 mm [60 mesh])
  - coarse sand (0.500-1.000 mm [35 mesh])
  - very coarse sand (1.000-2.000 mm [18 mesh])
  - granules (>2.00 mm [10 mesh])

LIPID CONTENT DETERMINATIONS

- Gravimetric lipid analyses were performed on extracts using a wet tissue weight.
- Colourimetric lipid analyses were performed on a subset of tissue samples. Lipid extract prepared by homogenizing dry tissue sample with $CHCl_3$:CH_3OH (2:1 v/v), filtering the residue, and diluting the filtrate to a known volume. The lipid concentration was quantified colourimetrically using the sulphophosphovanillin method.

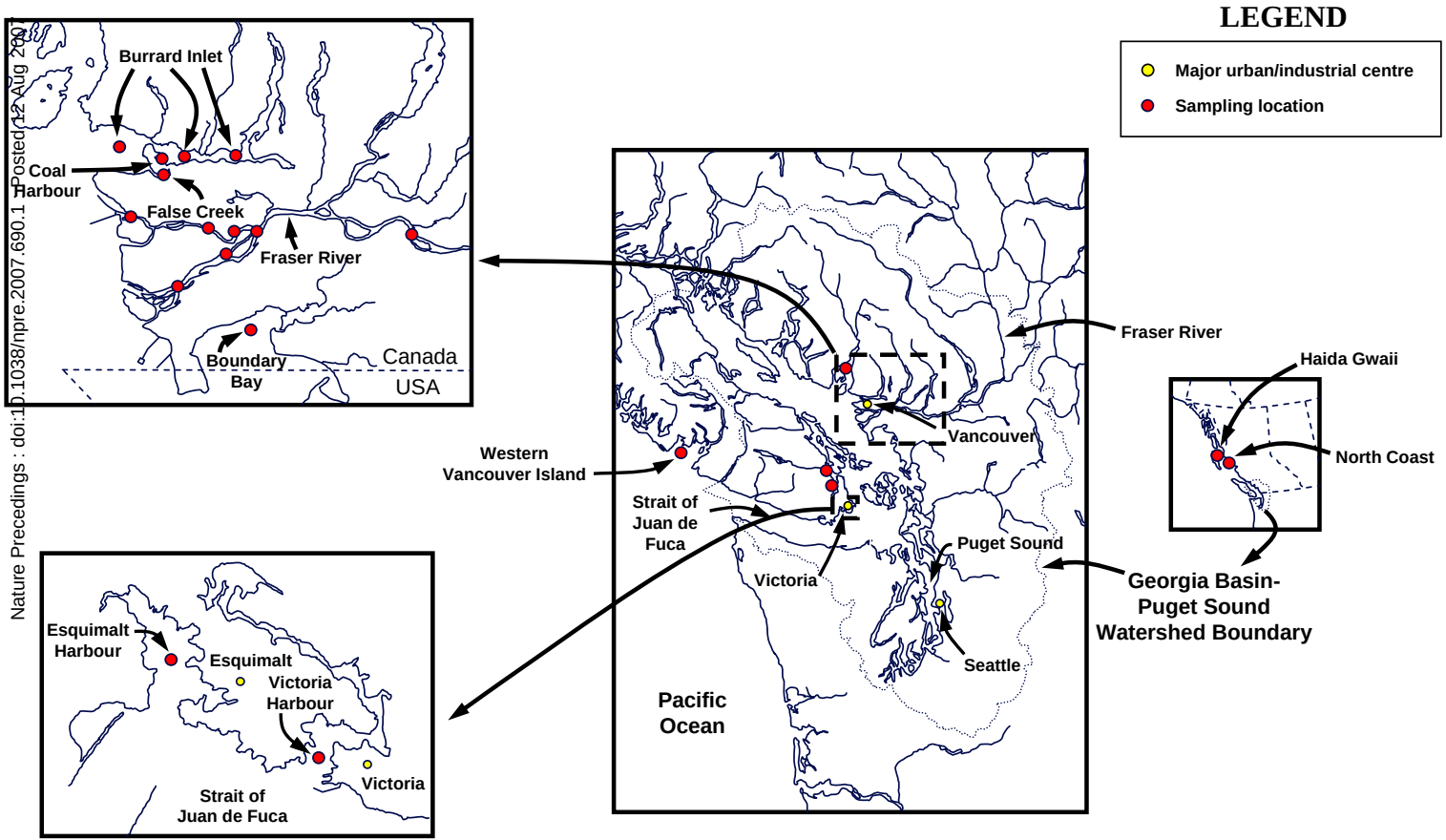
SFR/SVR ANALYSIS

- Samples were oven dried and then ignited at 550°C in a muffle furnace.
- Loss of weight on ignition is sediment volatile residue (SVR); remaining residue is sediment fixed residue (SFR).

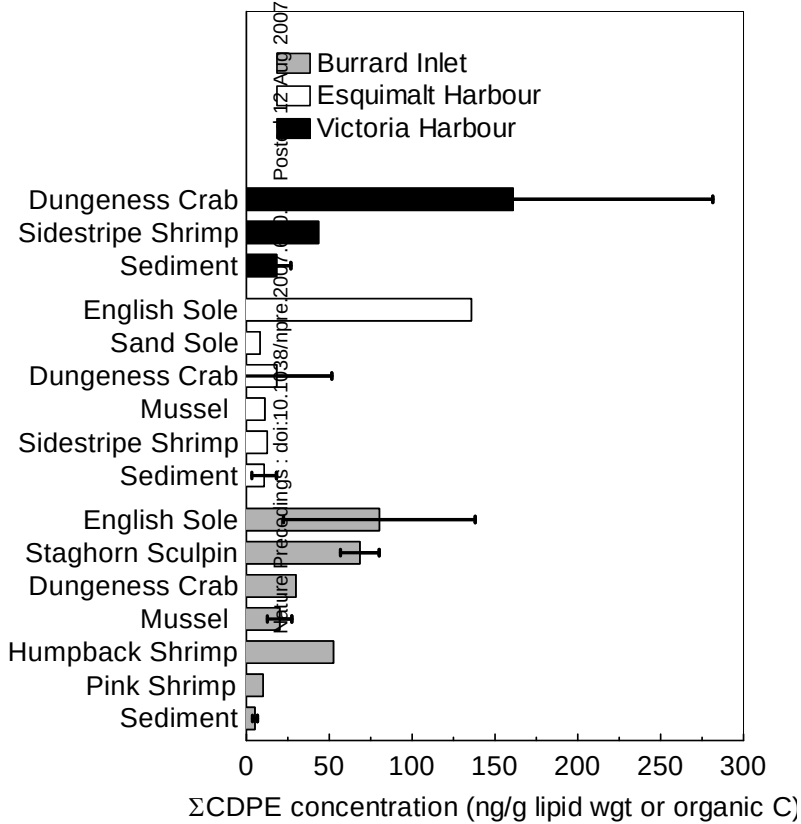
CHLORINATED DIPHENYL ETHER (CDPE) ANALYSES

- Samples were first spiked with ^{13}C-labeled surrogate standards.
- Sediment samples were solvent extracted on a shaker table.
- Tissue samples were ground with Na_2SO_4, eluted through a chromatographic column, and the extract applied to a Biobeads SX-3 column to remove lipids and other large molecular weight components.
- Extracts were cleaned up and fractionated on a Florisil column prior to instrumental analysis by high resolution gas chromatography with high resolution mass spectrometric detection (HRGC-HRMS).

SAMPLING LOCATIONS



INTER-MATRIX DIFFERENCES AT A SITE: FOOD CHAIN BIOACCUMULATION

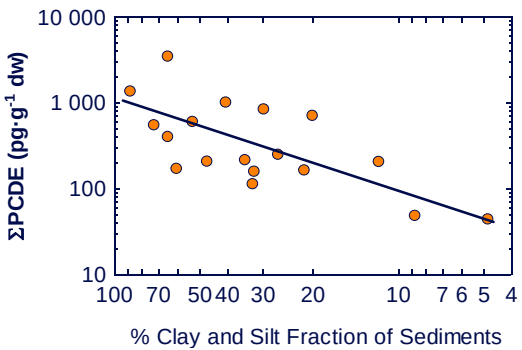


TRENDS WITHIN MAJOR HARBOURS:

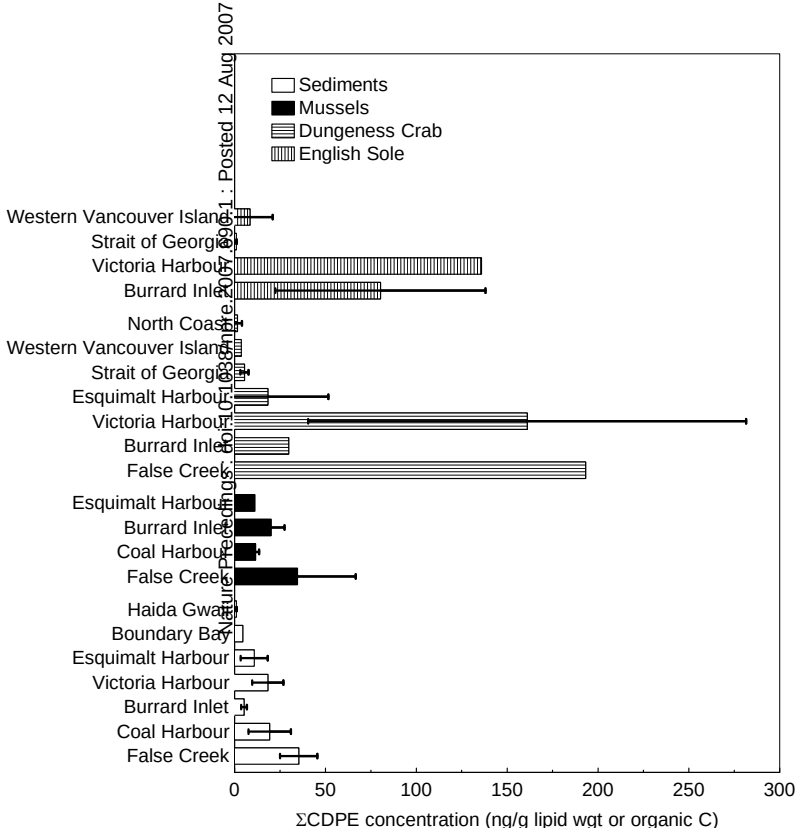
- ΣCDPE increases with higher trophic levels at all sites.
- Pelagic species (sole, sculpin) have higher CDPE burdens than benthic species (crab, shrimp, mussels).
  - Lowest concentrations found in sediments.
  - Bioaccumulation factors between shrimp/mussels and sediments: 1.0 to10.
  - Biomagnification factors betweeen.
    - Crab and mussels/shrimp: 0.6 to 3.7
    - Sculpin and shrimp: 1.3 to 6.8
    - Sole and shrimp: 1.5 to 11
- No significant difference in concentrations between sites within a particular matrix.

SEDIMENT PARTICLE SIZE AND CONTAMINANT LOAD

- Finer grained sediments in Burrard Inlet accumulate higher mass normalized CDPE concentrations than corresponding coarser sediments from the same locale.
- Typically >95% of CDPEs are associated with particulate organic matter (POM; i.e., sediments) vs. dissolved organic matter (DOM).
- Suggests limited potential for mobilization and transport in low DOM systems (e.g., marine environments).
- Supports observations of highly localized sediment contamination near Vancouver and Victoria.



INTRA-MATRIX GEOGRAPHIC VARIATIONS



TRENDS:

- Higher ΣCDPE localized in urbanized and industrial regions (Vancouver, Victoria).
  - High variation at a site means few significant differences between sites in the major regions.
- Limited CDPE transport away from populated areas.
  - Much lower levels even within 50 km of Vancouver at Boundary Bay and Strait of Georgia sites.

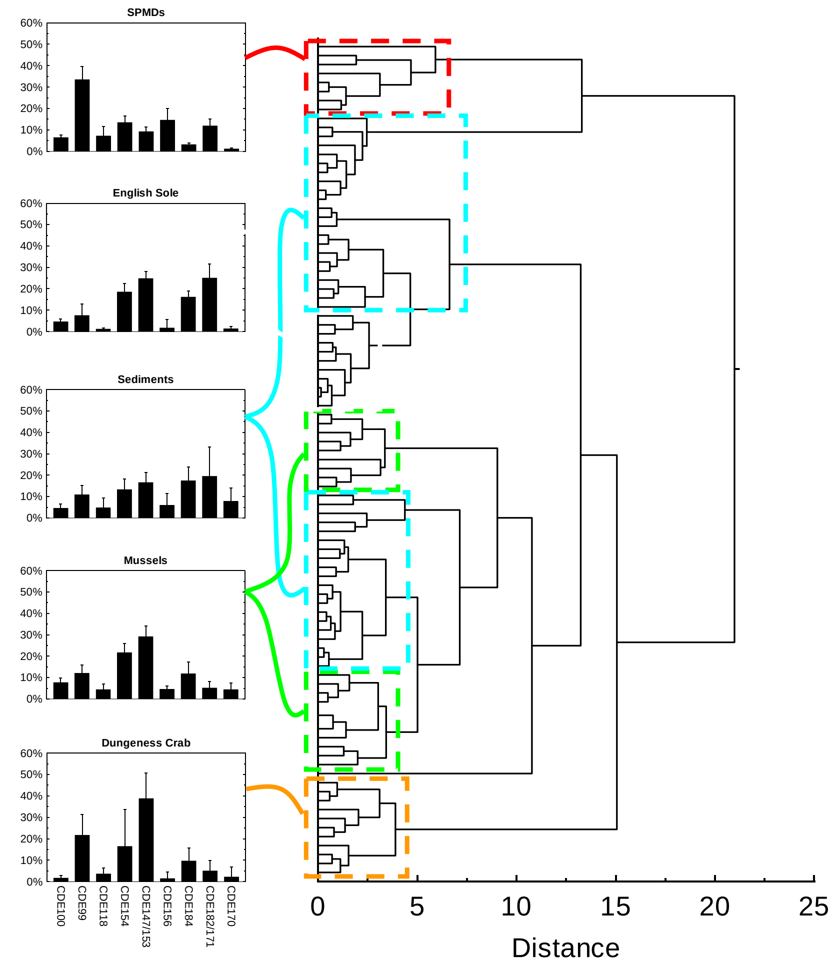
COMPARISON WITH WORLDWIDE DATA:

- **Sediments (ng/g dw):**
  - Finland: 0.1 to 110
  - Baltic Sea: <0.4
  - **Vancouver region: 0.2 to 9.1**
  - **Victoria region: 0.3 to 8.0**
  - **Northern BC: 0.2 to 0.3**
- **Mussels (ng/g ww):**
  - Spain: 0.05 to 0.11
  - **Vancouver region: 0.1 to 1.3**
  - **Esquimalt: 0.5**
- **Fish (ng/g lw):**
  - Pike (Finland): <3 to 160
  - Cod (Norway): 0.4 to 0.5
  - Salmon (Finland): 25 to 800
  - Trout (Great Lakes): 820
  - **Sole (Vancouver): 12 to 300**
  - **Sole (Victoria): 140**
  - **Sole (Strait of Georgia): 3 to 21**
  - **Sole (Pacific Ocean): 1**

MATRIX-SPECIFIC CONGENER PROFILES

CONGENER PATTERNS:

- Major congeners in all matrices are penta-, hexa-, and hepta-chlorinated
- All mono- through tetra- and octa- through deca-chlorinated congeners below method detection limits.
- Cluster analysis indicates matrix-specific congener profiles, regardless of individual sample levels and geographic locations.
  - Both mussels and sediments uncouple into two major sub-groupings, but not based on levels or location.
- SPMDs enriched in C_5DPEs > C_6DPEs > C_7DPEs.
  - CDE 99 dominates.
  - Consistent with increased mobility of smaller congeners in the water column, and greater uptake rates into SPMD.
- Sediments enriched in C_7DPEs > C_6DPEs > C_5DPEs.
  - CDEs 182/171/184 dominate.
  - Consistent with equilibrium partitioning into sediment organic carbon (i.e., based on log K_{oc}).
- Mussels enriched in C_6DPEs > C_5DPEs ≈ C_7DPEs.
  - CDEs 147/153 dominate.
- Crabs enriched in C_6DPEs > C_5DPEs > C_7DPEs.
  - CDEs 147/153 dominate.
- Sole enriched in C_6DPEs ≈ C_7DPEs > C_5DPEs.
  - CDEs 147/153 and 182/171 dominate.
- Patterns in benthic biota appear to be a ‘balance’ between higher chlorinated congeners in sediments, and lower chlorinated congeners in water column.
  - Pelagic biota reflect preferential biomagnification of hexa- and hepta-chlorinated homologues.



CONCLUSIONS

- Evidence for food-chain bioaccumulation/biomagnification at three major harbour sites: pelagic > benthic > sediments.
- Sediments near Vancouver and Victoria much less contaminated with CDPEs than regions in Scandinavia near chlorophenol manufacturing sites.
  - BC levels in range of other heavily populated marine areas (e.g., Baltic Sea).
- Mussels near major urban BC marine regions have the <u>highest levels reported worldwide.</u>
  - Samples from Vancouver and Esquimalt are 5- to 10-fold higher than upper range reported in Spain.
  - Notable absence of data from other populated areas makes these findings difficult to contextualize.
- Fish known to be major dietary intake of CDPEs in Spain:
  - No comparable work to date in Canada ...
  - English Sole in BC marine waters have similar ΣCDPE levels to other areas of N. America and Europe.
  - Clear gradient of decreasing concentrations moving from Vancouver/Victoria out into Strait of Georgia and the Pacific Ocean.
- CDPEs appear highly concentrated in sediments and biota near the major urban regions.
  - Consistent with physico-chemical properties that favor partitioning into particulate organic carbon on sediments, and lack of mobility in low organic matter marine waters.
- Congener patterns are matrix dependent, and independent of levels or geographic location within a matrix.
  - Lower chlorinated congeners dominate in the water column, higher chlorinated in the sediments.
  - Biotic patterns in benthic species (mussel/crab) reflect averaging of water and sediment patterns.
    - Patterns in pelagic species (sole) show evidence of preferential biomagnification of higher chlorinated congeners.

ACKNOWLEDGEMENTS

- Natural Sciences and Engineering Research Council (NSERC)
- Fisheries and Oceans Canada
- Environment Canada
- University of Victoria
- The University of British Columbia at Okanagan