Characterization and Source Apportionment of Polycyclic Aromatic Hydrocarbons in Small Craft Harbour Sediments in Nova Scotia, Canada

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BACKGROUND

- Small craft harbours (SCHs) (n=*178*) in the coastal province of Nova Scotia (NS), Canada, are an integral part of the Canadian fishing industry and are managed by Fisheries and Oceans Canada (DFO). NS SCHs are organized into 3 management regions (**Fig.1**).
- SCH sediments in Canada are evaluated for various contaminant concentrations on a routine site-specific basis by federal custodians (DFO), with a focus on bulk concentration and little emphasis on source apportionment of contaminants. Polycyclic aromatic hydrocarbons (PAHs) are notoriously present in NS SCH sediments (Walker et al., 2013).
- PAHs may pose a risk to biota and/or human health and are produced by various processes.
- To date, a spatio-temporal assessment of PAHs in SCH sediments in NS has yet to be completed. This study aimed to complete a comprehensive evaluation of PAHs across 31 SCHs in NS, over a 16-year period (2001-2017) (**Fig.2**).

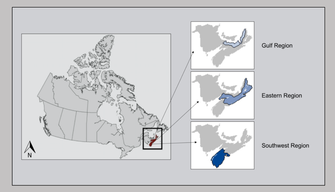


Fig 1. Location of DFO-SCH management regions in Nova Scotia. Regional figures are adapted from Fisheries and Oceans Canada (DFO, 2018). [Map produced by DMTI™]

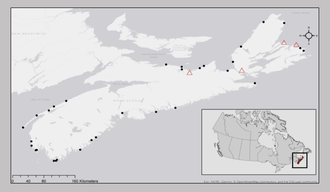
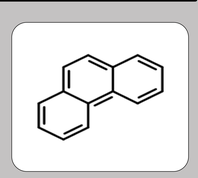


Fig 2. Spatial distribution of selected 31 small craft harbour sites across Nova Scotia, Canada. Triangles represent locations of four NS Power coal and/or pet coke power generation stations [Adapted from Davis et al. (2018)].

RESEARCH STRATEGY

Selection of 31 SCHs in NS

Evaluation of federal historical sediment data



Characterize PAHs and estimate source apportionment

METHODS

- To characterize PAHs, concentrations were compared to empirical sediment quality guidelines (SQGs), including National Oceanic and Atmospheric Administration (NOAA) effects range low (ERL) and effects range median (ERM) guideline values for total PAHs.
- Individual PAH compounds were assessed across the regions of the province by calculating relative abundance of individual US EPA priority PAHs (n=*16*).
- Source apportionment of PAHs in sediment was assessed by employing multiple lines of evidence:

- PAH diagnostic ratios were applied to distinguish between PAH sources by assessment of the molecular proportion of isomeric PAH pairs.

- US EPA Unmix Optimum (UnmixO) (a receptor model) was applied to aggregate data to estimate source apportionment by factor analysis. Unmix O determines how many sources best fit the data, the specific composition of the source(s), and source contributions to the data set (Henry, 2003; Lang and Yang, 2014).

RESULTS and DISCUSSION

- Twenty SCHs (64.5%) exhibit mean $\sum PAH_{16}$ values below NOAA ERL (4.022 mg/kg), while Canso and Fox Point SCHs deviate from the collective and exceed the NOAA ERM guideline (**Fig 3**).

- The distribution of individual PAHs is consistent across the province, with high molecular weight PAHs forming a greater proportion of the PAH profile (**Fig 4**). This trend is consistent with sediments of the world (McCready et al., 2000).

- UnmixO identified four sources which are contributing to NS SCH sediments (**Fig 5**). Source 1 and Source 2 contribute 32 and 47% to total PAHs, respectively, while Source 3 and 4 contribute 11 and 10%, respectively.
  - Source 1 is estimated to be a mixed source representative of coal combustion and vehicular emissions.
  - Source 2 is estimated to be a biomass/coal combustion source.
  - Source 3 is estimated to be a mixed petrogenic-dominated source.
  - Source 4 is estimated to be a mixed source of petrogenic and pyrogenic origins.

- PAH diagnostic ratios suggest pyrogenic (combustion) PAH sources are dominant (**Fig 6**).

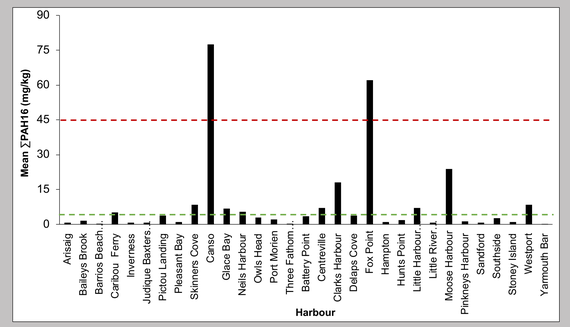


Fig 3. Mean $\sum PAH_{16}$ concentrations in sediments of NS SCHs. Lower dashed horizontal line represents NOAA ERL guideline for total PAHs (4.022 mg/kg), upper horizontal line represents NOAA ERM for total PAHs (44.792 mg/kg).

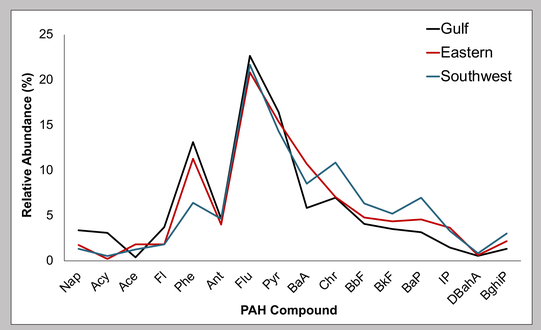


Fig 4. Distribution of individual PAHs (EPA 16) across Gulf, Eastern, and Southwest regions, reflected as relative abundance (%). Relative abundance values for each compound are a function of the total concentration of the compound relative to all samples within each respective region.

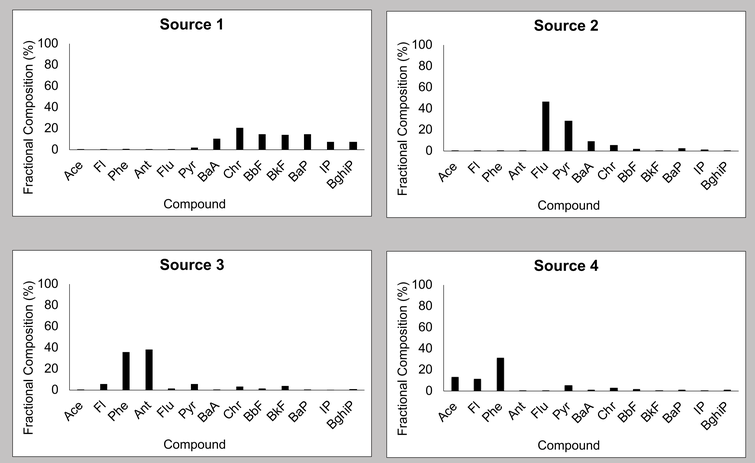


Fig 5. Fractional composition of 14 individual PAH species in a) UnmixO Source 1; b) UnmixO Source 2; c) UnmixO Source 3; d) UnmixO Source 4.

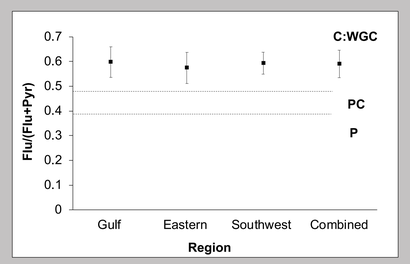


Fig 6. PAH diagnostic ratio plot of Flu/(Flu+ Pyr). Standard deviation is presented. *n*=116, 83, 162, and 361 for the Gulf, Eastern, Southwest and Combined regions, respectively. C: Combustion; WGC: Wood, grass, coal; PC: Petroleum Combustion; P: Petroleum. Transition values adopted from Yunker et al. (2002).

Pleasant Bay Harbour, NS.

KEY FINDINGS

- NS SCH sediments do not appear to be heavily contaminated by PAHs. Total PAH concentrations for NS SCH sediments are typically low and fall below SQGs.
- Canso and Fox Point deviate from collective and represent sites which require further assessment and contaminant delineation.
- Lines of evidence suggest a strong pyrogenic (combustion) origin for PAHs in selected SCH sediment.
- Coal combustion, biomass combustion, and vehicular emissions are estimated sources.

RECOMMENDATIONS and CONCLUSIONS

- Focus sediment sampling efforts and contaminant delineation on most impacted NS SCHs (e.g., Canso/Fox Point).
- Adoption of a total PAH sediment quality guideline (e.g., ERM for $\sum PAH_{16}$) as a coarse screening tool for prioritization may prove useful for SCHs.
- SCH sediment data (aggregate) lends itself to source apportionment estimations, which may aid in source control/characterization by federal custodians.
- This study highlights that selected NS SCH sediments are not heavily contaminated by PAHs. Results indicate that PAHs which are present are predominantly pyrogenic, which presents an environmental management challenge for federal custodians.

ACKNOWLEDGEMENTS

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