SECTION 4

Hydrocarbons

HYDROCARBONS

Capsule

Hydrocarbon concentrations of concern to fish health were detected at many surface water sites in the former Semá:th X̱ó:tsa (Sumas Lake) after the catastrophic British Columbia floods of late 2021. Levels of total polycyclic aromatic hydrocarbons (PAHs) were 6.5 times higher in Sumas waterways compared to our upstream reference site. The average PAH concentration increased by 1.7 times in the early weeks after the floods, suggesting that flooding resulted in the early release of hydrocarbons into fish habitat. We observed up to six exceedances of Environmental Quality Guidelines in a given surface water sample, indicating that hydrocarbons in these waterways are at levels harmful to fish. The profile of PAHs suggest that the combustion of solid fuel (wood and plant materials) and petroleum products dominated the sources of these toxic contaminants in this fish habitat.

Introduction

The catastrophic floods of late 2021 in British Columbia and Washington State overwhelmed urban, agricultural and industrial infrastructure in the *Semá:th X̱ó:tsa* (Sumas Lake) area, raising concerns about the impacts of contaminant discharges into fish habitat. The absence of pre-flood baseline data and ongoing monitoring of freshwater quality highlighted the urgent need for water sampling and analysis to assess the level of risk to fish and the environment.

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that contain two or more benzene rings and have both natural and anthropogenic sources (1). They are a diverse group of substances, and variations in their structures can influence their fate and effects in marine and freshwater ecosystems.

Anthropogenic sources of PAHs include incomplete combustion, petroleum and its derivatives . They can be found in sewage, storm water runoff, landfill leachate, wood preserving residues and at waste disposal sites (1). Crude oil seeps, coal and shale deposits, and forest fires are the main sources of natural releases of PAHs (2).

PAHs are persistent in the environment and can accumulate in tissues (3). There are several PAHs that are carcinogenic or otherwise toxic, with benzo(a) pyrene being the most toxic PAH (4). PAHs can be metabolized in fish (3), while invertebrates have a lower capacity to metabolize PAHs and are therefore able to bioaccumulate these compounds (5). The additive nature of PAHs can also allow combinations of different PAHs to become more toxic to organisms than the original compound (6). This can result in tumors and harmful effects on reproduction, development and the immune system of various organisms (3,7). PAHs cause malformations, swimming impairments, premature hatching, and mortality in fish (7).

Methods

We collected 26 surface water samples from 11 sites in the Sumas Lake area of the Fraser Valley (British Columbia; 9 on December 15 2021; 9 on December 23 2021; 6 on January 27 and 2 on February 2 2022) as well as 4 groundwater samples on February 2, 2022. Two of these latter samples from Abbotsford groundwater sources will be evaluated separately. Details for sampling sites are listed in the Executive Summary. Samples were stored in the field at 4°C in suitable containers supplied by partnering laboratories, and submitted to (CARO Analytical Services - Water, Soil, Air, Plant, Food Testing) in Richmond, BC for analysis of 21 analytes using their in-house EPA 3511/ EPA 8270D protocol. Samples were also submitted to SGS AXYS for analysis of 75 analytes using their internal method MLA-021 Rev 12 by LR GC/MS 8270D. Data are presented as nanograms per litre (ng/L).

To interpret the risk of PAH-related effects in fish and fish habitat at our sample locations, we compared our concentrations of these analytes to the most protective Environmental Quality Guidelines (EQGs) for fish and fish habitat available in a Canadian provincial or federal jurisdiction. Jurisdictions with EQGs in Canada include British Columbia, Alberta, Saskatchewan, Manitoba, Ontario, Quebec, Canada (federal) and the Canadian Council of Ministers of the Environment (CCME). Environmental Quality Guidelines are not available for all PAHs. Nonetheless, they provide an important benchmark to gauge the health of fish habitat.

We refer to the most protective EQG in Canada herein as the 'pan-Canadian Environmental Quality Guideline to protect fish and fish habitat' or the 'pan-Canadian EQG'.

We report here on total PAH concentrations in 26 surface and 2 ground water samples following the British Columbia floods of late 2021, and evaluate results against pan-Canadian Environmental Quality Guidelines to protect fish and fish habitat.

Results

Surface water

» PAH data are reported here only for the results from SGS-AXYS, as there were no detections using CARO labs.

» We detected PAHs at all 11 surface water sites in the Sumas Lake area.

» The concentration of total PAHs (all detected compounds summed by site) at surface water sites in former Sumas Lake averaged to 61.3 ± 11.3 ng/L, ranging from 10.2 to 160 ng/L.

» The average number of PAH compounds detected at 11 surface sites ranged from 17 to 62, with an average of 44 ± 4.

» The most frequently detected PAHs compounds (100% of surface water sites) were:

- phenanthrene/anthracenes,
- methylnaphthalenes,
- biphenyls,
- naphthalenes,
- dibenzothiophenes,
- fluoranthene/pyrenes, and
- chrysene/benz[a]anthracenes.

» Surface water sites with the highest PAH concentrations also had the highest average number of PAHs detected.

» The average total PAH concentration increased by 1.7 times between December 15 (2021) and December 23 (2021), and by 1.2 times between December 15, 2021 and January 27, 2022 in surface water samples collected across field sites after the flooding.

» We detected a 6.4 times increase in the average concentrations of the PAHs in the 10 Sumas lake surface water sites relative to our upstream reference site (Frost Creek).

Groundwater

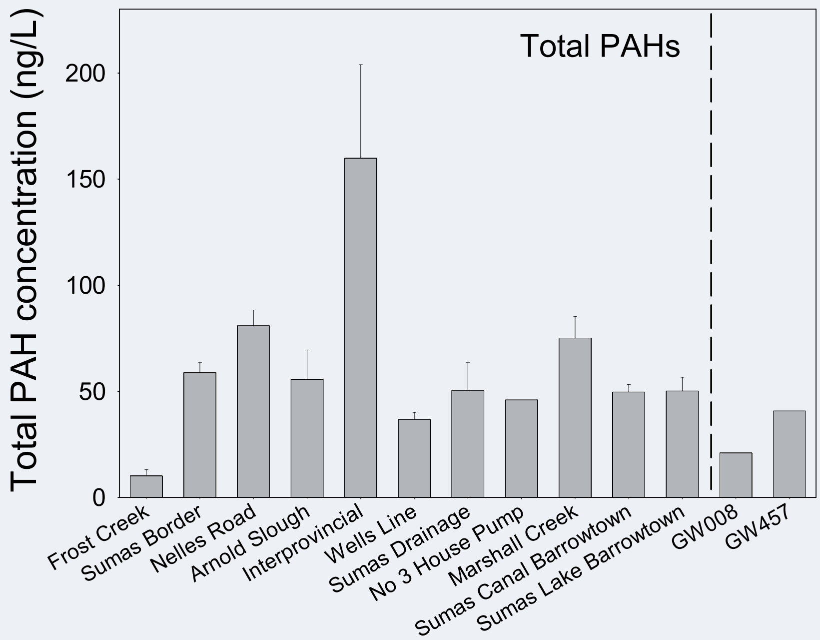
» The average number of PAHs detected at two groundwater sites averaged 31.5 ± 10.5, ranging from 21 to 42.

» The most frequently detected PAHs (detected at 100% of groundwater sites) were:

- 1,4,6,7 - tetramethylnaphthalene
- benz[a]anthracene
- indeno[1,2,3-cd]pyrene
- phenanthrene/anthracenes
- methylnaphathalenes
- biphenyls
- dimethylnaphthalenes
- trimethlynaphthalenes
- naphthalene
- fluoranthene/pyrenes

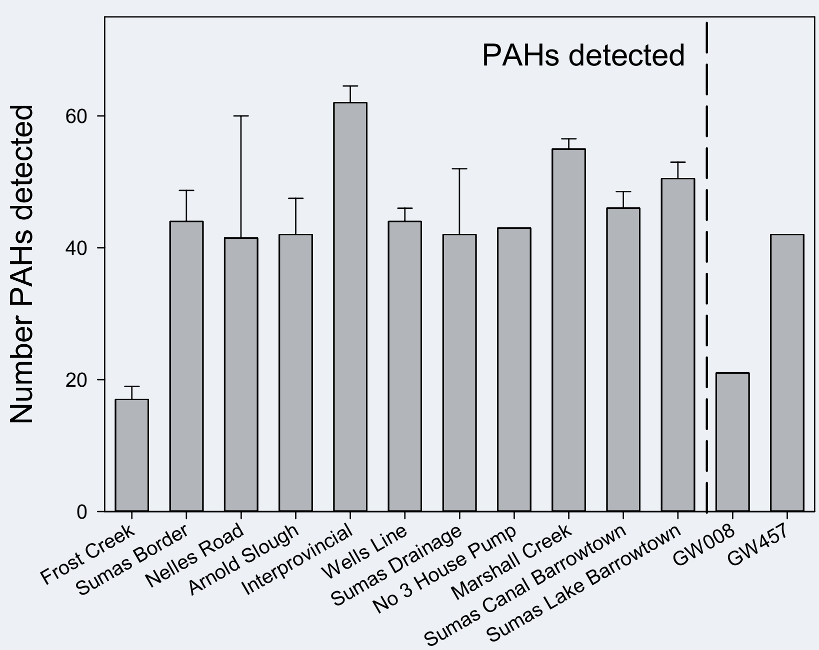
» No significant change in the average PAH concentrations was observed over the course of our study. The total concentration of PAHs at groundwater sites averaged 30.9 ± 9.9 ng/L, ranging from 21.0 to 40.9 ng/L.

Figure 4.1: Polycyclic aromatic hydrocarbons permeated surface waters



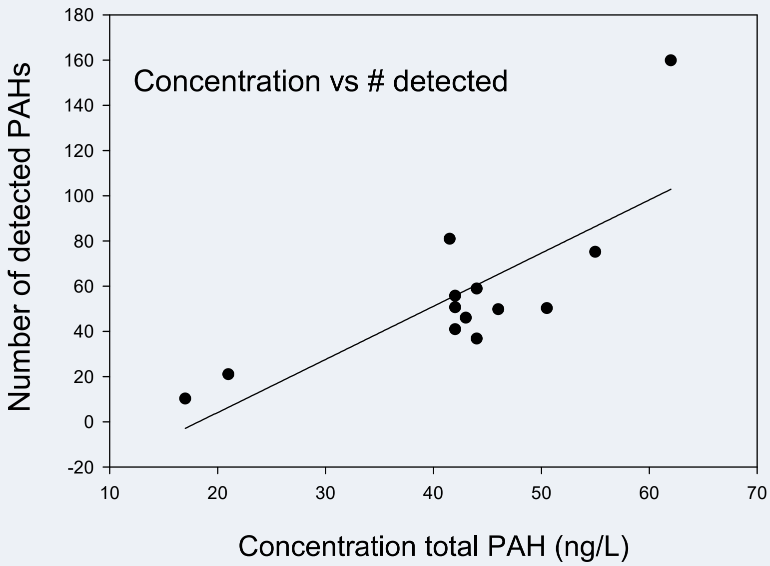
Total concentration of PAHs that were detected at each of the surface water sites sampled. Results display the average (+/- standard error) for the samples collected over time, from the reference site (Frost Creek) through the Sumas Lake area, and to the two Barrowtown pump stations prior to release into the Fraser River, and two groundwater samples.

Figure 4.2: Many hydrocarbons were detected in water samples



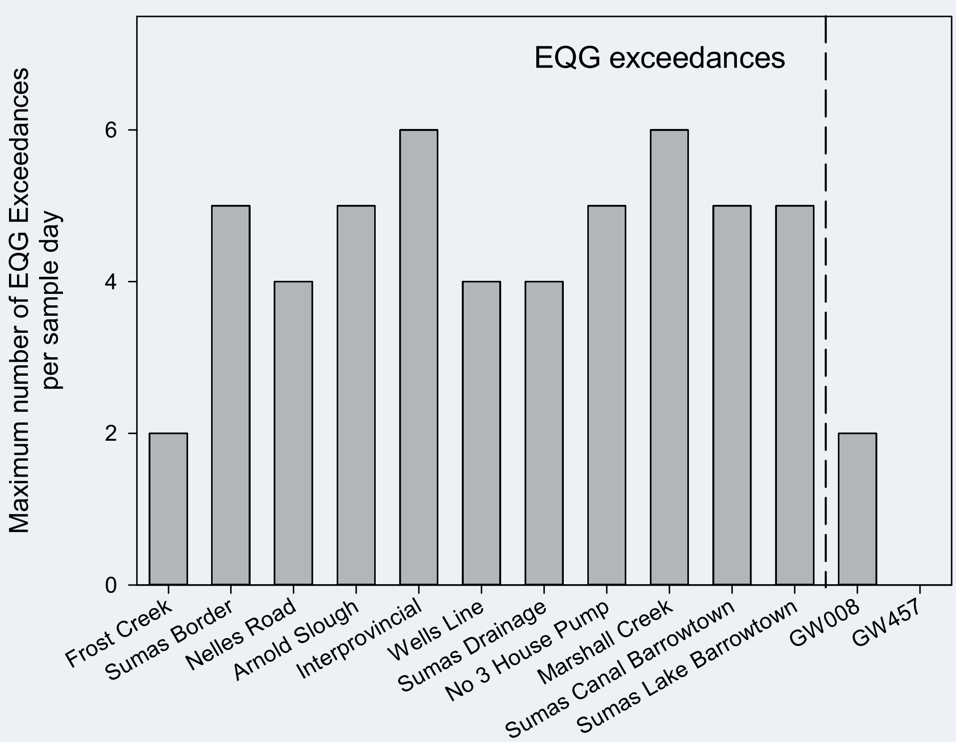
The number of PAHs detected was higher in surface water sites in former Sumas Lake and in groundwater compared to the upstream reference site at Frost Creek.

Figure 4.3: Increasing hydrocarbon levels meant more hydrocarbons



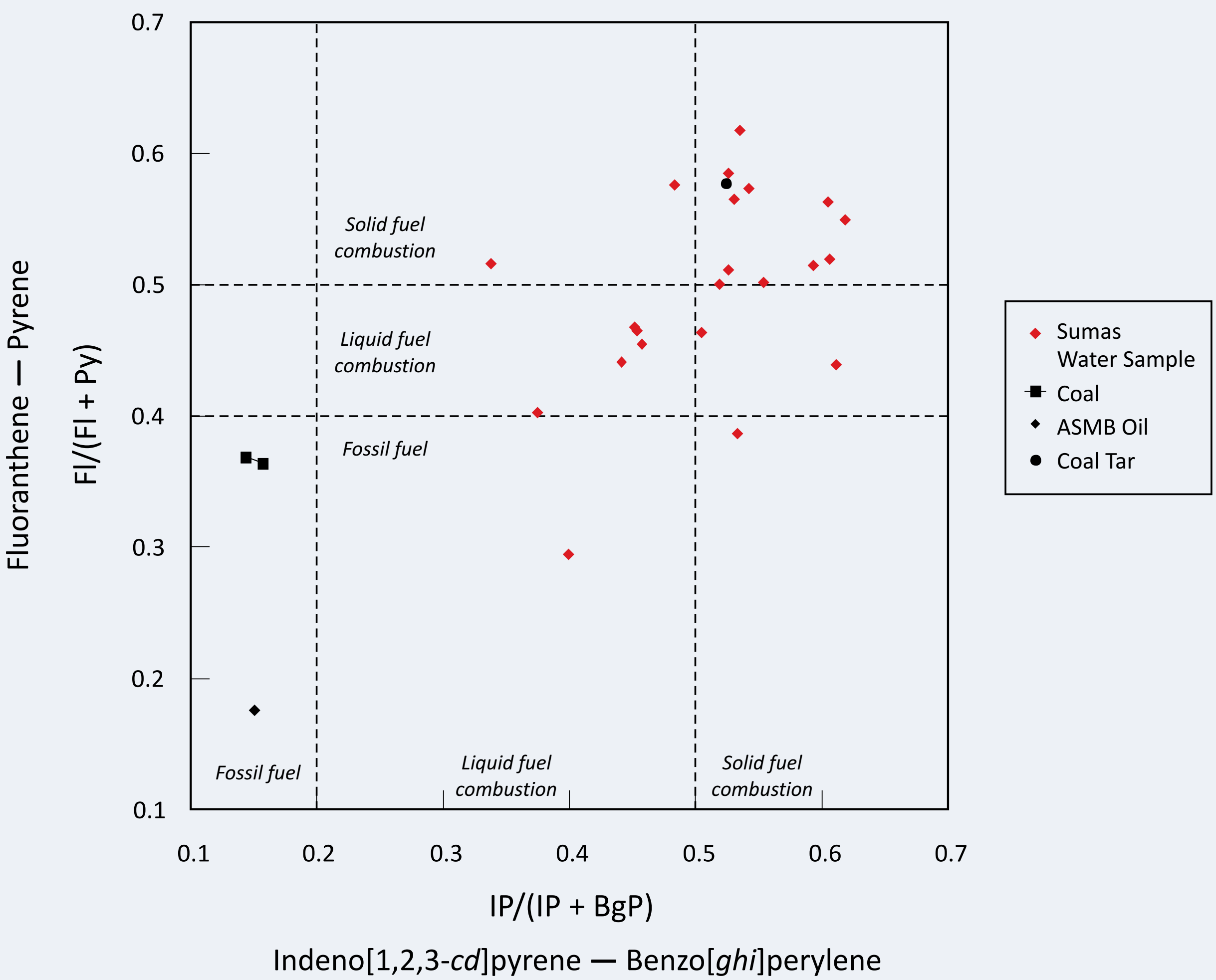
The number of PAHs detected increased with increasing total PAH concentration across all sites.

Figure 4.4: Hydrocarbon levels exceeded Guidelines in surface waters



The concentrations of several PAHs were higher than pan-Canadian EQG deemed to protect fish and fish habitat, with Sumas area surface waters consistently having more exceedances of Environmental Quality Guidelines than the upstream reference site or groundwater.

Figure 4.5: Hydrocarbon profiles from wood combustion and fuels



Characteristic PAH ratios in surface water sites in former Sumas Lake were consistent with a dominant contribution of solid fuel combustion (wood, plant materials), and a contribution of the combustion of liquid petroleum products.

Conclusions

There are pan-Canadian Environmental Quality Guidelines for the protection of aquatic life for 18 out of 75 individual PAHs detected. We found up to 6 exceedances of these guidelines in a given surface water sample and up to two exceedances in a given groundwater sample.

Exceedances for the following PAHs were observed:

- benz[a]anthracene (Ontario Provincial Water Quality Objectives (PWQO) of 0.4 ng/L)
- benzo[ghi]perylene (PWQO of 0.02 ng/L)
- benzo[jk]fluoranthene (PWQO 0f of 0.2 ng/L, specifically for benzo[k]fluoranthene)
- chrysene (PWQO of 0.1 ng/L)
- fluoranthene (PWQO of 0.8 ng/L)
- perylene (PWQO of 0.07 ng/L)

The average number of exceedances of EQGs was 4.2 times higher in the Sumas surface water sites compared to our upstream reference site at Frost Creek.

There is little information about these compounds in BC freshwater environments, but samples of marine water collected previously from Burrard Inlet had levels of chrysene and benzo[a]pyrene above the BC Water Quality Guidelines for marine water quality (8).

Characteristic ratios of parent PAHs demonstrate that solid fuel combustion (wood, plant materials) and liquid fuel combustion (gasoline, diesel) dominate PAH sources for the Sumas Lake waterways (9). The lowest sample on the figure (Marshall Creek from Jan. 22) likely has some contribution of petroleum, since it shows mixed sources with both a fossil fuel source (fluoranthene – pyrene) and a liquid fuel combustion source (indeno[1,2,3-*cd*]pyrene – benzo[*ghi*]perylene).

The presence of potentially harmful levels of several PAHs in Sumas Lake waterways indicates the degradation of this fish habitat, with risks of both carcinogenic and non-carcinogenic effects in fish, including effects on development, bone metabolism, liver metabolism and reproduction (10).

High concentrations of PAHs in Sumas surface water warrant further monitoring to better identify sources and trends over space and time, with road runoff, stormwater, wastewater, and seasonal weather patterns affecting the quality of fish habitat in the area.

References

1. Canadian Council Of Ministers Of The Environment. 1999. Canadian environmental quality guidelines. Winnipeg: Canadian Council Of Ministers Of The Environment.

2. Government of Canada. 2013. Toxic substances list: PAHs. Available at: https://www.canada.ca/en/environment-climate-change/services/management-toxic-substances/list-canadian-environmental-protection-act/polycyclic-aromatic-hydrocarbons.html

3. Abdel-Shafy, H. I., & Mansour, M. S. M. 2016. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum*, 25(1): 107–123. https://doi.org/10.1016/j.ejpe.2015.03.011

4. United States Environmental Protection Agency (US EPA). 2014. Priority pollutant list. Available at: https://www.epa.gov/sites/production/files/2015-09/documents/priority-pollutant-list-epa.pdf

5. Hylland, K. 2006. Polycyclic aromatic hydrocarbon (PAH) ecotoxicology in marine ecosystems. *Journal of Toxicology and Environmental Health*, Part A, 69(1-2): 109–123

6. Ball, A., & Truskewycz, A. 2013. Polyaromatic hydrocarbon exposure: an ecological impact ambiguity. *Environmental Science and Pollution Research*, 20(7): 4311–4326.

7. Harris, K. A., Yunker, M. B., Dangerfield, N., & Ross, P. S. 2011. Sediment-associated aliphatic and aromatic hydrocarbons in coastal British Columbia, Canada: Concentrations, composition, and associated risks to protected sea otters. *Environmental Pollution*, 159(10): 2665–2674.

8. Braig, S., Delisle, K, Noël, M., LeNoble, J., Thompson, H.C. and A.S. Rao. 2021. Water Quality Assessment and Proposed Objectives for Burrard Inlet: Polycyclic Aromatic Hydrocarbons (PAHs) Technical Report. Prepared for Tsleil-Waututh Nation and the Province of B.C.

9. Yunker, M.B., Macdonald, R.W., Ross, P.S., Johannessen, S.C., Dangerfield, N. 2015. Alkane and PAH provenance and potential bioavailability in coastal marine sediments subject to a gradient of anthropogenic sources in British Columbia, Canada. *Organic Geochemistry* 89-90, 80-116.

10. Honda, M., & Suzuki, N. 2020. Toxicities of polycyclic aromatic hydrocarbons for aquatic animals. *International Journal of Environmental Research and Public Health*, 17(4): 1363.