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Baseline

Occurrence, source and ecological assessment of baseline hydrocarbons in the intertidal marine sediments along the shoreline of Douglas Channel to Hecate Strait in British Columbia

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ABSTRACT

The occurrence, source and ecological assessment of baseline hydrocarbons in the intertidal zone along the northern British shoreline were evaluated based on analyzing total petroleum hydrocarbons (TPH), *n*-alkanes, petroleum related biomarkers such as terpanes and steranes, and polycyclic aromatic hydrocarbons (PAHs) including non-alkylated and alkylated homologues (APAHs). The TPH levels, *n*-alkanes, petroleum biomarkers and PAHs in all the sampling sites, except for Masset Harbor/York Point at Gil Island were low, without obvious unresolved complex mixture (UCM) and petroleum contamination input. Specifically, *n*-alkanes showed a major terrestrial plants input; PAHs with abundant non-alkylated PAHs but minor APAHs showed a major pyrogenic input. However, obvious petroleum-derived hydrocarbons have impacted Masset Harbor. A historical petroleum input was found in York Point at Gil Island, due to the presence of the low level of petroleum biomarkers. Ecological assessment of 13 non-alkylated PAHs in Masset Harbor indicated no potential toxicity to the benthic organisms.

Douglas Channel is one of the principal inlets of the Northern BC Coast connecting Western Canada's Pacific Inland Coast with deep-sea, its waterway spans from the head of Kitimat Arm to the open water of the Hecate Strait outside the coastal archipelago. Haida Gwaii is an archipelago on the North Coast of BC along the water of the Hecate Strait. The coast along Douglas Channel to Hecate Strait belongs to the First Nations traditional territories with multiple-use environments.

In history, the shipping artery along Douglas Channel has serviced for the methanol import terminal and the aluminum smelter at Kitimat sitting at the head of Kitimat Arm, Douglas Channel. Emissions generated by aluminum production at the smelter have been proved to be the major anthropogenic source of polycyclic aromatic hydrocarbons (PAHs), especially for those with high molecular weights, in the intertidal and subtidal sediment of Kitimat Arm since 1980s to 2004 (Cretney et al., 1983; Paine et al., 1996; Simpson et al., 1998; Johnson et al., 2015).

The areas of Hecate Strait have remained relatively pristine compared to the southern coast of BC. The main environmental impacts in this area are from the local shipping, fishing, logging and some mining near small remote communities (Yunker et al., 2014; Yunker et al., 2015). Given the possibility of further oil exploration in the Queen Charlotte, the proposal for pipeline terminals in Kitimat and oils tankers through Douglas Channel for transporting oil sands products or bitumen mobilized with condensate for shipment to reach the world market, an oil spill would have catastrophic impacts to the environment, economy, and society along the northern BC shoreline. It is urgent to understand the ecological and geological sensitivity, and collect the background information for future emergency response. The purpose of this study is to investigate the occurrence, source and ecological assessment of petroleum related hydrocarbons based on analyzing total petroleum hydrocarbons (TPH), *n*-alkanes from n-C_9 to n-C_{40}, petroleum related biomarkers like terpanes, hopanes, and steranes, PAHs and their alkylated homologues (APAHs).

A baseline shoreline survey along Douglas Channel to the open sea has been performed from July 2014 to July 2015. Intertidal shoreline sediment samples (from low to upper tidal zone) were collected (5 sites along the shoreline of Kitimat Arm, near Kitimat (between 53°51908′N/128°5006′W and 53°59875′N/128°39698′W), 9 sites along the shoreline of South Douglas Channel (between 50°49924′N/126°39356′W and 53°58468′N//129°44841′W), and 9 sites along the shoreline of Haida Gwaii (between 52°41899′N/131°35757′W and 54°15525′N/132°81511′W)) (Fig. 1 and Table S1).

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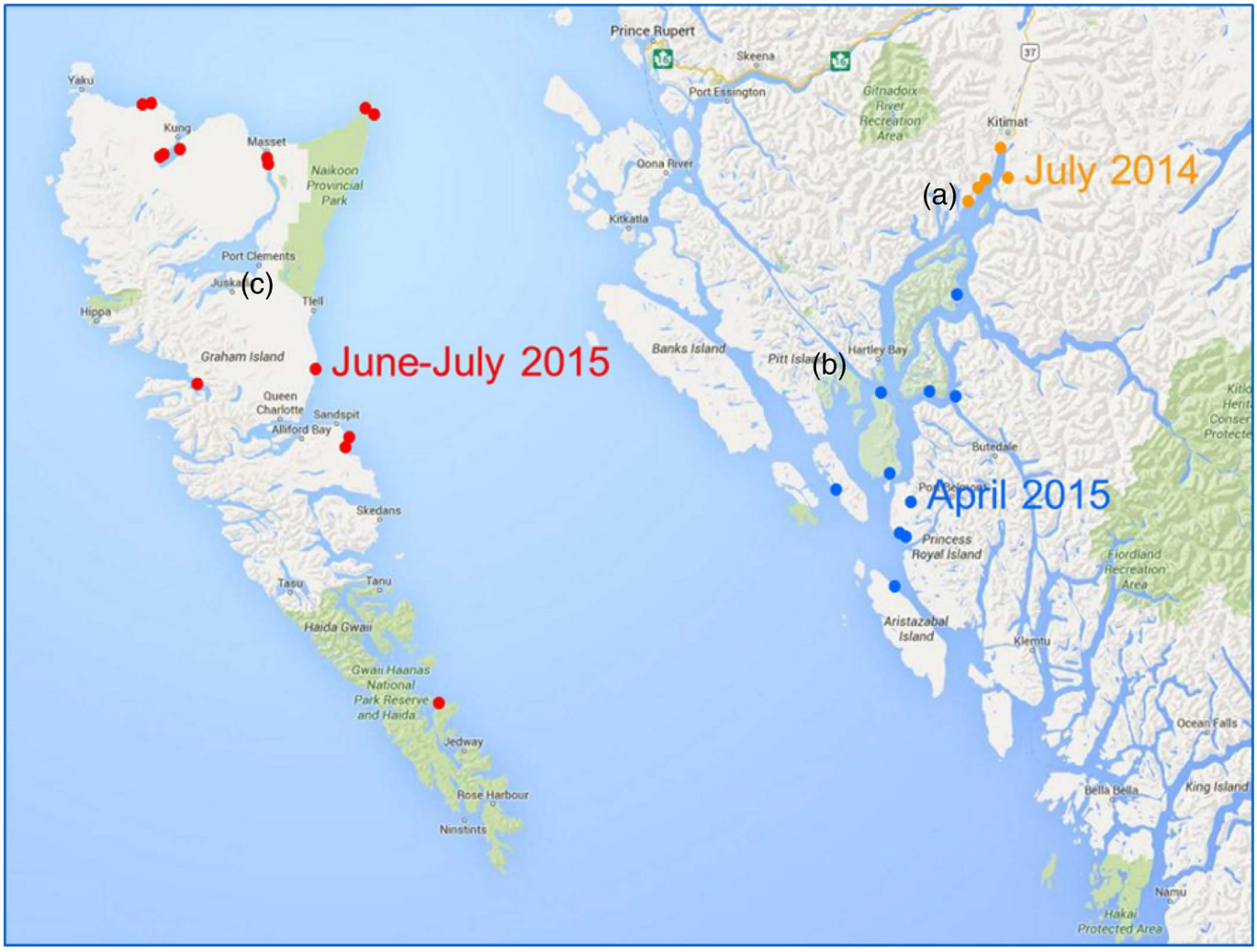

Fig. 1. Map illustrating sampling locations. (a), Kitimat Arm; (b), South Douglas Channel; (c), Haida Gwaii.

All collected samples, trip blanks and lab control samples spiked with appropriate surrogates were gone through Soxhlet extraction, column clean up and instrument analysis for specific targets (Wang et al., 2012; Lu et al., 2015). Specifically, around 10-g of sediment samples spiked with appropriate surrogates (*o*-terphenyl and deuterated PAH mixture, [$^2H_8$] naphthalene (d_8-N), [$^2H_{10}$] acenaphthene (d_{10}-Ace), [$^2H_{10}$] phenanthrene (d_{10}-P), [$^2H_{12}$] benz(*a*)anthracene (d_{12}-BaA), and [$^2H_{12}$] perylene (d_{12}-Pe) and [$^2H_{24}$] tetracosane ($C_{24}D_{50}$)) were Soxhlet extracted with dichloromethane. The extracts were concentrated and solvent exchanged to hexane, and then cleaned and fractionated by a 3-g silica gel column. 12 mL of hexane was used to elute the saturated fraction (F_{sat}) for *n*–alkanes (n-C_9 to n-C_{40}), and biomarkers of terpane and sterane analysis. 15 mL of 50% DCM in hexane was used to elute the aromatic hydrocarbons (F_{arom}) for analysis of alkylated homologous PAHs, other unsubstituted PAHs and aromatic biomarkers by GC–MS. The combined F_{sat} and F_{arom} was used for GC-FID analysis of total GC-detectable petroleum hydrocarbons and the unresolved complex mixture of hydrocarbons (UCM), which were calibrated by normal alkane standards from n-C_9 to n-C_{36}.

Unsubstituted PAHs identified include biphenyl (Bph), naphthalene (N), acenaphthylene (Acl), acenaphthene (Ace), fluorene (F), phenanthrene (P), anthracene (An), fluoranthene (Fl), pyrene (Py), benzo(*a*)anthracene (BaA), chrysene (C), benzo(*b*)fluoranthene (BbF), benzo(*k*)fluoranthene (BkF), benzo(*a*)pyrene (BaP), indeno(1, 2, 3-*cd*)pyrene (IP), dibenzo(*a*, *h*)anthrathene (DA), and, benzo(*e*)pyrene (BeP) and perlyene (Pe), benzo(*g*, *h*, *i*)perylene (BgP). The seven APAH families include naphthalenes (C_i-N), phenanthrenes (C_i-P), dibenzothiophenes (C_i-D), fluorenes (C_i-F), fluoranthenes (C_i-Fl), chrysenes (C_i-C), and benzonaphthothiophenes (C_i-B), where i = (0, 1, 2, 3, or 4) indicates the degree of alkylation.

Method quality control included trip blanks at every sampling site, a triplicate spiked blank (surrogates spiked into solvent), and 13.1% weathered Produle Bay crude oil as the reference oil. The average recoveries of surrogates for all the analyzed samples were determined to be 54.4 ± 12.0% for d_8-N, 70.0 ± 10.5% for d_{10}-Ace, 82.0 ± 11.5% for d_{10}-P, 87.0 ± 11.3% for d_{12}-B(*a*)A, 82.8 ± 9.7% for d_{12}-Pe, and 90.9% ± 9.4% for $C_{24}D_{50}$, respectively. Instrument stability was calibrated at every 10 injections of samples with standard solutions, and daily calibrations were < 20% for all of the target analyses. The report limits in the present study range from 0.08–1.3 ng/g, 0.02–0.2 ng/g, and 0.3–0.7 ng/g for *n*-alkanes, PAHs, and biomarkers of terpanes and steranes (defined as the ratio of signal to noise (S/N) > 10) by assuming 5-g dry sediment was used for analysis, respectively. All reported results in the present study were expressed on a dry weight basis.

The presence of a hump in a GC/FID chromatogram is the indicative of the presence of UCM. In this study, most of the sampling sites do not have obvious UCM. However, the sample from Masset Harbor has obvious UCM; similar small hump was found in the sample from Gil Island/York Point (Fig. S1), suggesting the possible petroleum presence. Except for Masset Harbor in Haida Gwaii region, the average quantified TPH in all the other sampling sites are < 15 μg/g (Fig. 2), indicating