Final
Long-Term Environmental Monitoring Program

2021 Summary Report

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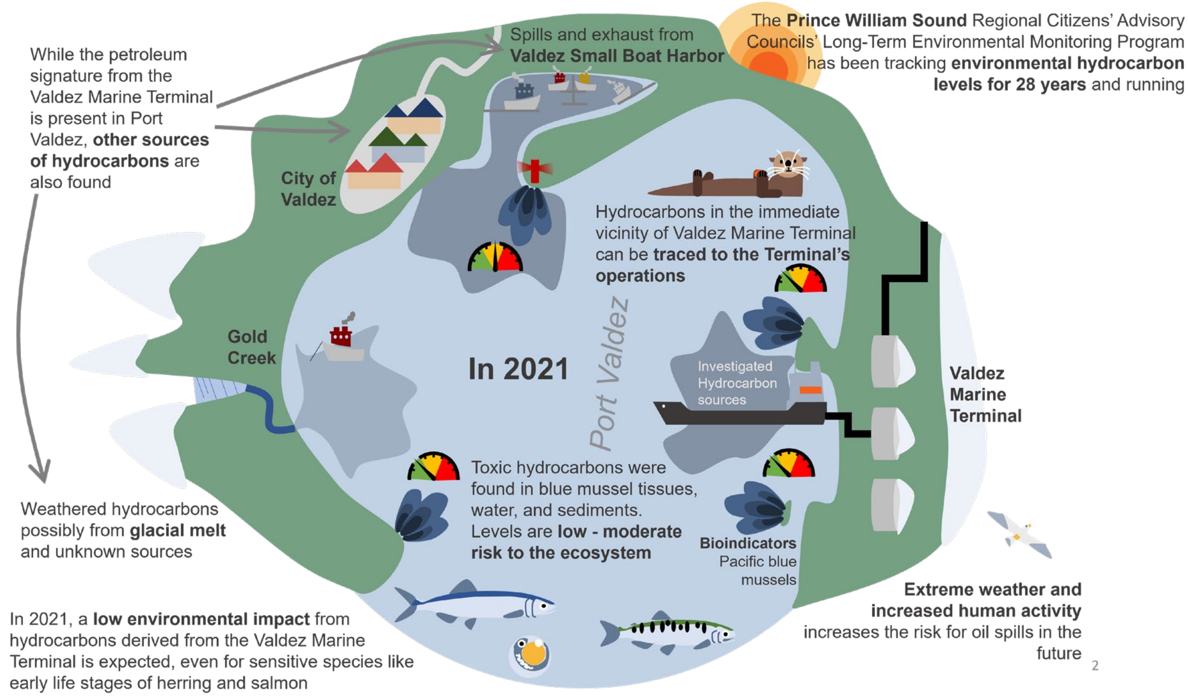
ABSTRACT



To understand the environmental impact, fate, and source of hydrocarbons related to the operations of Alyeska Pipeline Service Company's Valdez Marine Terminal, hydrocarbon concentrations were monitored in sediments, in intertidal Pacific blue mussels, and in the water via passive sampling devices. In the 2021 results, we see low levels of petroleum (petrogenic) hydrocarbons in sediments at the terminal which can be attributed to terminal operations. Passive water sampling devices and Pacific blue mussels sampled near the terminal had low levels of toxic hydrocarbons. Sediment and mussels sampled from sites away from the terminal in Port Valdez contained more combustion (pyrogenic) related compounds than detected at the terminal. Mussels from the Valdez Small Boat Harbor had the highest levels of hydrocarbons, likely due to frequent spills and heavy human activity.

In 2021, the hydrocarbons contributed by the terminal and tankers posed low potential environmental and toxicological risk. Since 1993, hydrocarbon concentrations are generally low with localized spikes corresponding with spill events like the April 2020 oil spill at the terminal. Following an all-time low in 2013, hydrocarbon concentrations in sediments and mussels have slowly increased across all sites but are still below any threshold for adverse effects on aquatic life. Fjord-wide trends in these hydrocarbon concentrations may be influenced by environmental factors such as increased freshwater input, glacial melt, and warming ocean temperatures.

We recommend that future monitoring efforts maintain the current three matrix design with a focus on higher resolution of the potential sources of hydrocarbons in Port Valdez. Furthermore, the inclusion of biological exposure and stress molecular indicators for Pacific blue mussels, especially following spill events, would illuminate the environmental impacts on this chronically exposed marine ecosystem.

1. INTRODUCTION

The Long-Term Environmental Monitoring Program (LTEMP), managed by the Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), is in its 28th year of monitoring hydrocarbons in the wake of the Exxon Valdez oil spill. Through LTEMP, we are able to determine the source of hydrocarbons and the potential adverse effects on the ecosystem from Alyeska Pipeline Service Company's Valdez Marine Terminal (terminal) and tanker activity. These data have been insightful in understanding the influence of terminal and non-terminal sources of hydrocarbons and environmental factors on hydrocarbon dynamics across Prince William Sound and the Gulf of Alaska.

Hydrocarbons are an extremely diverse group of compounds that make up the bulk of petroleum products like crude oil, fuel, and asphalt. However, hydrocarbons are also readily created by marine and terrestrial plants, locked up in organic sediments and rocks, and produced by combustion. Hydrocarbons in the environment undergo processes called weathering, which includes dissolution, evaporation, UV degradation, and microbial degradation. These change the physical and chemical properties of the released oil. Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrocarbons with varying numbers of benzene rings and have the greatest toxic potential to living organisms. This group of chemicals tends to adsorb rapidly on suspended materials, sediments, and biological tissues once released into the marine environment.

PAHs, as a group, are comprised of hundreds of compounds, each with its own degree of toxicity, and their mixtures can exhibit a wide range of toxicities. Specific hydrocarbons, patterns, and diagnostic compounds (i.e., chemical biomarkers) aid in the identification of specific hydrocarbon sources and are indicative of their weathering history (e.g., degree of weathering, degradation, dissolution). PAH profiles are used to identify petrogenic (of crude oil origin) or pyrogenic (of combustion origin), based on well-established pattern changes (e.g., on the ratio of parent and alkylated compounds). Chemical biomarkers, comprising the hopanes, steranes, terpenes, triaromatic and monoaromatic steroids, are much more resistant to degrading in the environment and thus used to confirm sources (e.g., crude oil vs diesel) even when the PAH patterns are heavily weathered. Saturated hydrocarbons (n-alkanes) are used to identify naturally occurring plant hydrocarbons and determine the degree of weathering and biodegradation.

While many aquatic organisms like fish can metabolize PAHs, marine invertebrates, such as Pacific blue mussels, are less able to efficiently metabolize these compounds, remain sedentary in a fixed location, filter particles from their immediate surroundings, and therefore serve as efficient natural samplers and indicators of overall environmental PAH exposure (Neff and Burns 1996). Toxic responses to PAHs in aquatic organisms include inhibiting reproduction, developmental effects, tissue damage, cellular stress, oxidative stress, damage to genetic material, and mortality. While the body of knowledge on the adverse effects of petroleum exposure is immense, specifics regarding PAH mixtures, exposure routes, duration and magnitude, species and life stages exposed, and other environmental factors that may act synergistically on organisms, challenge the predictive ability of any hydrocarbon study and necessitate the continued monitoring efforts of LTEMP.

The ubiquity of hydrocarbons in the environment complicates tracing sources, understanding toxic thresholds, and following dynamics over time and space. Environmental samples, like sediments, can accumulate multiple hydrocarbon sources over time, resulting in a mixed or unresolved profile. Organisms such as blue mussels can accumulate, eliminate, or alter hydrocarbon compounds, which complicates the task of identifying the sources. Passive sampling devices are specifically designed to complement the biological and toxicological interpretations by measuring just the dissolved compounds available to biota (the bioavailable fraction) and but are not well suited for hydrocarbon forensics. Sources investigated for the present study are those associated with terminal operation, including Alaska North Slope (ANS) crude oil (which is pumped through the trans-Alaska pipeline and is loaded into tankers at the terminal), effluent from the Ballast Water Treatment Facility (BWTF) at the terminal, and samples from recent spills at the terminal.

The following study presents the 2021 results from the LTEMP in Port Valdez and aims to determine:

- The extent, if any, that the terminal and associated tankers' hydrocarbon fingerprint is present in 2021 samples.
- The potential environmental and toxicological risk posed by the measured hydrocarbon contribution from the terminal and tankers.
- Other factors (e.g., environmental or anthropogenic) that may be influencing hydrocarbon presence and composition in 2021 samples and the toxicological relevance of these results.
- How the 2021 data compare to historical LTEMP trends and whether new analysis supports previous conclusions.
- Recommendations for future monitoring of petroleum hydrocarbons at the terminal and in Prince William Sound.

2. RESULTS AND DISCUSSION

Sediment, passive sampling device, and Pacific blue mussel tissue samples were collected in June and July of 2021 from traditional and new LTEMP monitoring stations in Port Valdez. The 2021 sampling program investigated three matrices: sediment, Pacific blue mussels, and water quality. Sediments were sampled at two sites –Alyeska's Valdez Marine Terminal and Gold Creek; Pacific blue mussel samples were taken from five sites around the Port of Valdez with a focus on the terminal – Saw Island, Jackson Point, Gold Creek, Valdez Small Boat Harbor entrance (RED - a known polluted site that is chemically different from the ANS terminal source signature and is being tested in 2021 as polluted, non-ANS reference site), and the April 2020 oil spill site (HOT). Water was sampled with passive sampling devices at three sites – Gold Creek, Jackson Point, and Saw Island (Figure 1). All mussels were collected under Alaska Department of Fish and Game Aquatic Resource Permit number CF-21-077.

Samples were analyzed for PAHs, saturated hydrocarbons, and petroleum biomarkers using advanced analytical techniques at the NewFields/Alpha Analytical Laboratory in Mansfield, Massachusetts (sediments and tissues) and the Oregon State University Food Safety and Environmental Stewardship lab in Corvallis, Oregon (passive sampler). These are the same laboratories that have participated in the LTEMP effort for the last six years. Briefly, the results continue to be of acceptable precision and accuracy and can be compared to previous years' data.

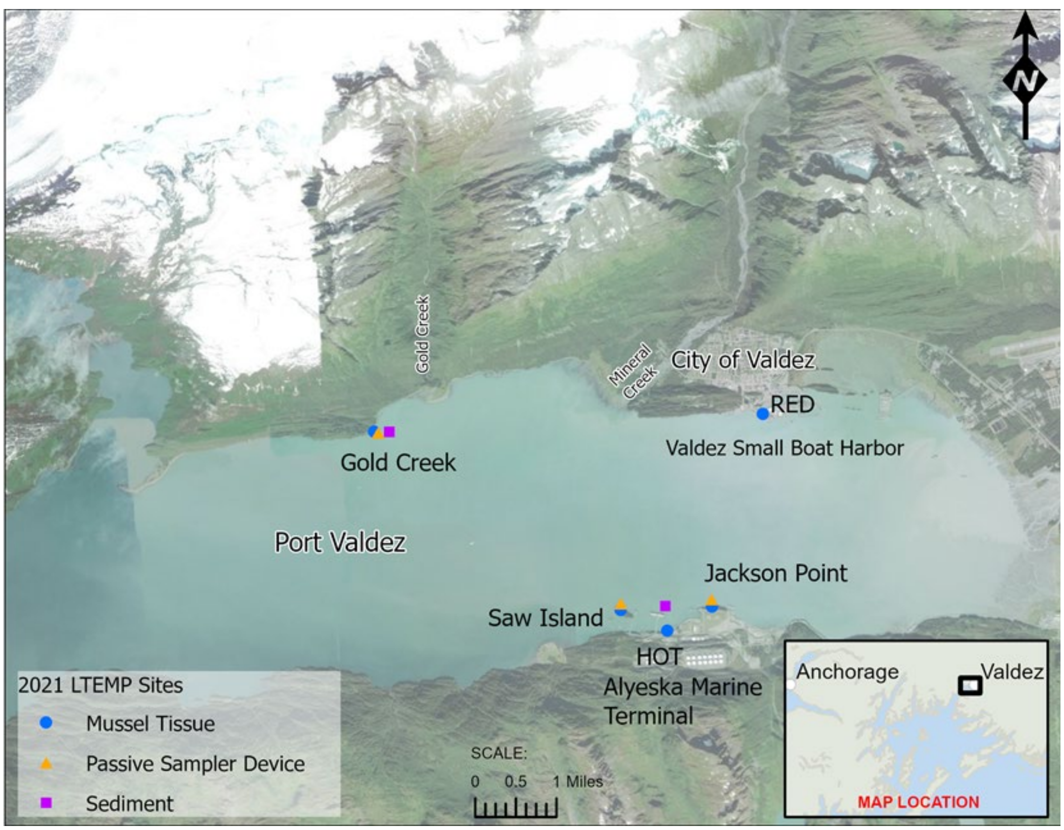


Figure 1. Map of 2021 LTEMP sites in Port Valdez, Alaska.

Many compounds, especially in the mussel tissues, were below or near the analytical methods detection limit or were not detected in the sample. Sediment and mussel tissue concentrations are plotted and discussed as a sum of multiple PAHs (sum PAH) either by dry weight or wet weight where appropriate. Passive sampling device concentrations have been converted by the analytical lab into the dissolved-phase water concentration, C-free concentration. By converting the concentration units, comparisons can be made across other studies, areas, and toxicological effect thresholds. Concentrations below the method level of detection threshold, plotted on PAH profile figures, were included in sum calculations; compounds that were not detected in a sample were not included in the sum calculations. Comparisons are also made between low and high molecular-weight PAHs which include the 2–3 ring naphthalenes through phenanthrenes and 4–6 ring fluoranthenes to benzo[g,h,i]perylene, respectively. Total saturated hydrocarbons and common petroleum biomarkers and diagnostic ratios are employed in the forensic analysis together with analyte profile pattern comparisons for likely petroleum sources (i.e., ANS Crude, a sample of the April 2020 oil spill at the terminal, and a Spring 2017 effluent sample from the BWTF). Analytical results and calculations for all samples and all analytes, pattern profiles, and laboratory blanks are presented in the Technical Summary Tables 2 through 4 and Figures 2 through 32 with diagnostic ratios (Table 5) (Owl Ridge 2022) to support the assertions made in this summary report.

2.1. Sediments

Hydrocarbons were detected in all sediments sampled at the terminal and Gold Creek sites in the low parts per billion range (ppb or ng/g). One (1) ng/g or 1 ppb can be visualized as the concentration of 50 drops in an Olympic-sized swimming pool. The highest sum (∑) PAH concentrations were found in the terminal sediment (72–91 ng/g dry weight) compared to the Gold Creek sediments (26–38 ng/g dry weight) (Figure 2). The most abundant PAHs at the terminal were C3-chrysenes, an alkylated 4-ringed compound, while the molecularly lighter PAHs, anthracene and fluoranthene, were most abundant at Gold Creek (Figure 3). For comparison, PAH concentrations across both Port Valdez sites are lower than those reported in Norwegian fjords, Novia Scotia small boat harbors, and the Baltic Sea (Oen et al. 2006; Davis et al. 2018; Pikkarainen 2010). Present Port Valdez concentrations were more similar to those reported from sediments of Cook Inlet and St. Paul Island, Alaska (Nesvacil et al. 2016). PAH concentrations in the present study are slightly lower but otherwise comparable to those sediment concentrations reported in the 2021 Alyeska Pipeline Service Company wastewater discharge permit compliance report for a similar area and analysis regime (Shaw and Blanchard 2021).

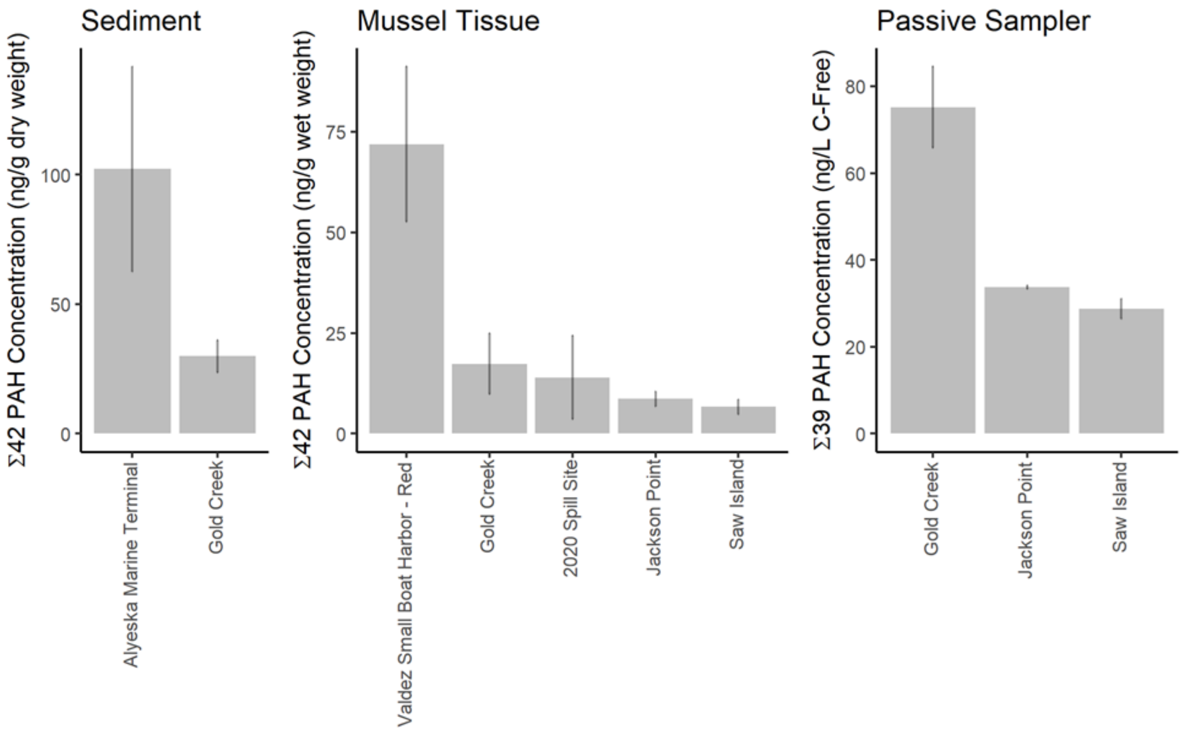


Figure 2. ∑ PAH concentrations for 2021 sediments, Pacific blue mussel tissues, and passive sampling devices by site plotted at the mean ± 1 standard deviation. Note that the passive sampling device results represent fewer PAHs than sediment and mussel tissues.

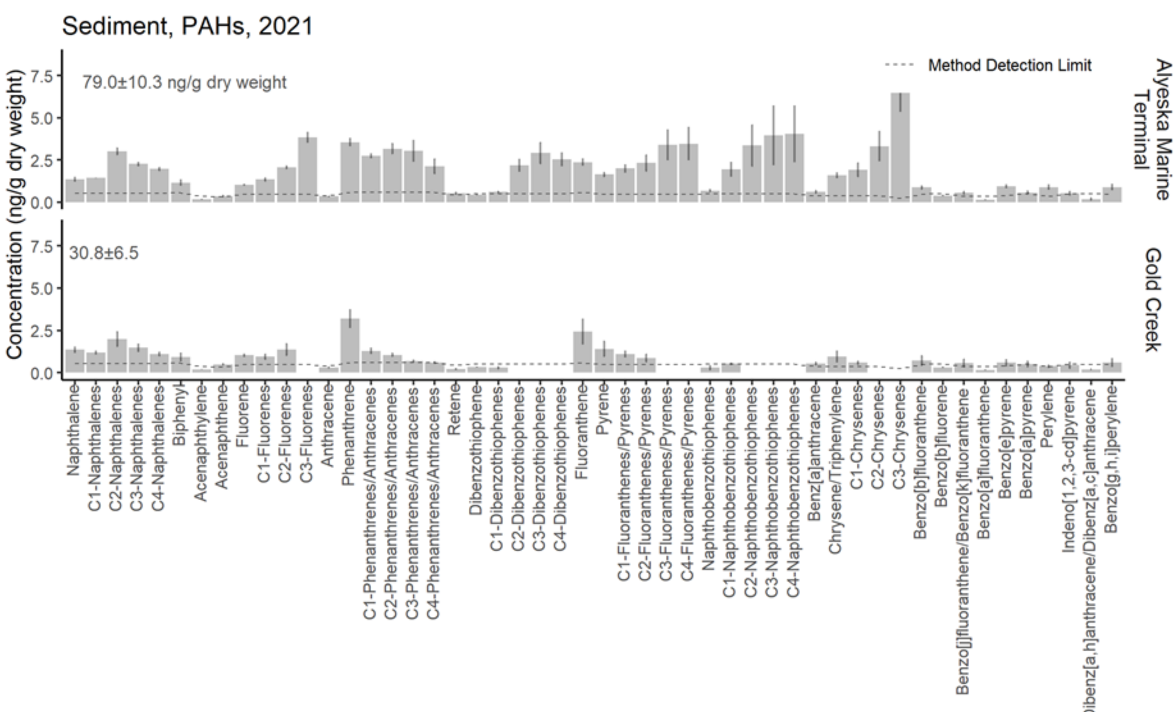


Figure 3. PAH profiles from sediments sampled at the terminal and Gold Creek site plotted at the mean ± 1 standard deviation with sum values in the upper left of each site profile.

2.1.1. Toxicological Interpretation

Individual and ∑ PAH concentrations in sediment at the terminal and Gold Creek sites pose little to no acute or chronic risk for marine organisms with concentrations of individual compounds and sums one percent or less than the U.S. Environmental Protection Agency (EPA) sediment quality PAH benchmarks for aquatic life (EPA 2016). While benthic communities adapted to the cold and sediment-rich waters of Port Valdez may not be adequately represented in these EPA benchmarks, past monitoring efforts around the terminal have indicated little to no change in the benthic community with varying PAH concentrations (Shaw and Blanchard 2021). The total organic carbon concentration in the sediment is low (0.4–0.6%), which indicates high bioavailability of PAHs to marine organisms. High molecular weight PAHs, which are of greater toxicological concern, represented 42–47 percent of the PAH load but concentrations of this group do not exceed any protective benchmarks. Known carcinogenic PAHs are present in low concentrations at both sites (≤ 5 ng/g dry weight).

2.1.2. Site-Specific Source Identification

Using PAH and biomarker profiles, the source of the hydrocarbons in the terminal sediments is determined to be mostly petrogenic and derived from ANS crude oil. Biomarker patterns closely match those of previous oil spills at the terminal in 2017 and April 2020 (HOT) (Payne and Driskell 2021) and particulate-phase oil in the effluent from the BWTF (Payne and Driskell 2018). The diagnostic biomarkers confirm ANS crude oil as the source. Accumulation of higher molecular weight alkylated PAHs, likely from local combustion sources, indicates residuals of prior PAH inputs inefficiently degraded over time. Saturated hydrocarbons in the terminal sediment reveal strong microbial degradation and weathering of the hydrocarbons leaving the higher molecular weight compounds (and in some cases, terrestrial plant wax compounds).

At Gold Creek, chemical biomarkers were sparse compared to those at the terminal, still petrogenic biomarker traces confirm the oil signal as a distant source. However, the PAH patterns are mostly pyrogenic. Gold Creek sediments are moderately weathered with a near complete loss of saturated hydrocarbons, except those contributed by terrestrial plants. In summary, relatively low hydrocarbon concentrations in the terminal sediments are linked to the terminal activities and incidents (BWTF effluent, spills, and combustion) with residues that have undergone environmental degradation and accumulated over time. Gold Creek sediments show mixed pyrogenic and lower petrogenic sources with a greater degree of weathering.

2.1.3. Historical Perspective

Hydrocarbon concentrations have varied widely throughout the LTEMP monitoring period from 1993 to the present (Figure 4). The highest sediment PAH concentrations were measured in the early 2000s at nearly 36 times present concentrations. Since 2005, hydrocarbon concentrations have remained low with an all-time low measured in 2013. Since 2013, a gradual increase in PAHs has been measured in sediments at the terminal and Gold Creek (Figure 4B) and may be indicative of larger environmental changes in Port Valdez such as increased glacial melt/freshwater runoff (Campbell 2018). Terminal sediments have generally contained higher PAH loads than Gold Creek.

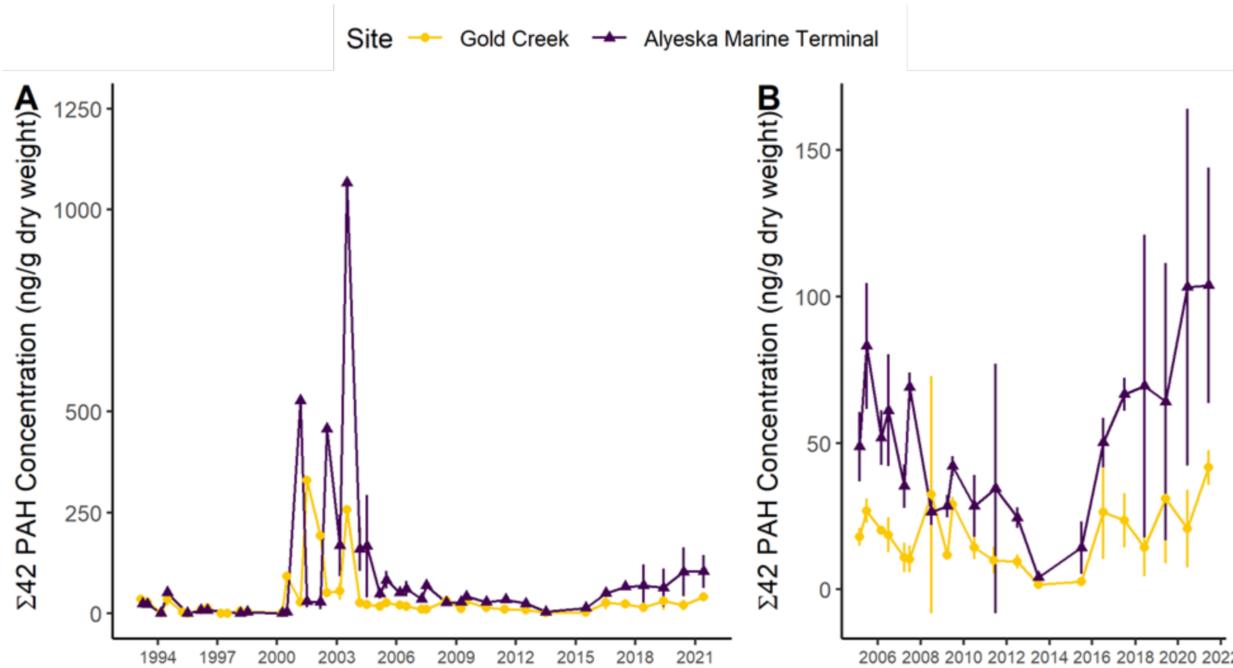


Figure 4. Sum 42 PAH concentrations in sediments (A) over the entire duration of the LTEMP and (B) since 2005 when concentrations have remained relatively low. Colors and shapes indicate sampling site, mean values ± 1 standard deviation are plotted for each sampling event.

2.2. Pacific Blue Mussels

PAHs were detected in Pacific blue mussels (*Mytilus trossulus*) at low to moderate concentrations at all sites (5.6–95 ng/g wet weight; 42–581 ng/g dry weight; Figure 2). In 2021, the highest PAH concentrations were found at the Valdez Small Boat Harbor entrance, a non-ANS positive control site at the red harbor navigation light, followed by mussels sampled at Gold Creek. PAH concentrations in 2021 were similar at the April 2020 oil spill site (HOT), Saw Island, and Jackson Point—all stations near the terminal. Naphthalene, a low molecular weight two-ring PAH, was the most abundant PAH at most sites, followed by phenanthrene, except at the Valdez Small Boat Harbor where fluoranthene, a 4-ringed compound, was at concentrations as high as 12.3 ng/g wet weight (Figure 5). Mussels from the Jackson Point and Saw Island sites had a higher proportion of low molecular weight PAHs (72%) than all other sites (~54%).

The 2021 mussel tissue PAH concentrations in Port Valdez are comparable to those found in pristine locations in national parks and forests around southcentral and southeast Alaska and well below the high concentrations (>1000 ng/g dry weight) found in the harbor at Skagway, Alaska (Rider 2020). Only mussels from the Valdez Small Boat Harbor exceeded National Oceanic and Atmospheric Administration's (NOAA) national long-term monitoring status "Low Concentration" range (0–173 ng/g dry weight). Like the Valdez Small Boat Harbor location, fluoranthene was also the most abundant PAH in mussels in a Norwegian fjord with moderate human activity where sum PAH concentrations were otherwise comparable to this study (Schøyen et al. 2017). Mussel tissue PAH concentrations were comparable to those measured in pelagic zooplankton in Valdez Arm (610–1310 ng/g dry weight) (Carls et al. 2006) and to mussels caged two kilometers or greater from an oil rig in the North Sea (Sundt et al. 2011).

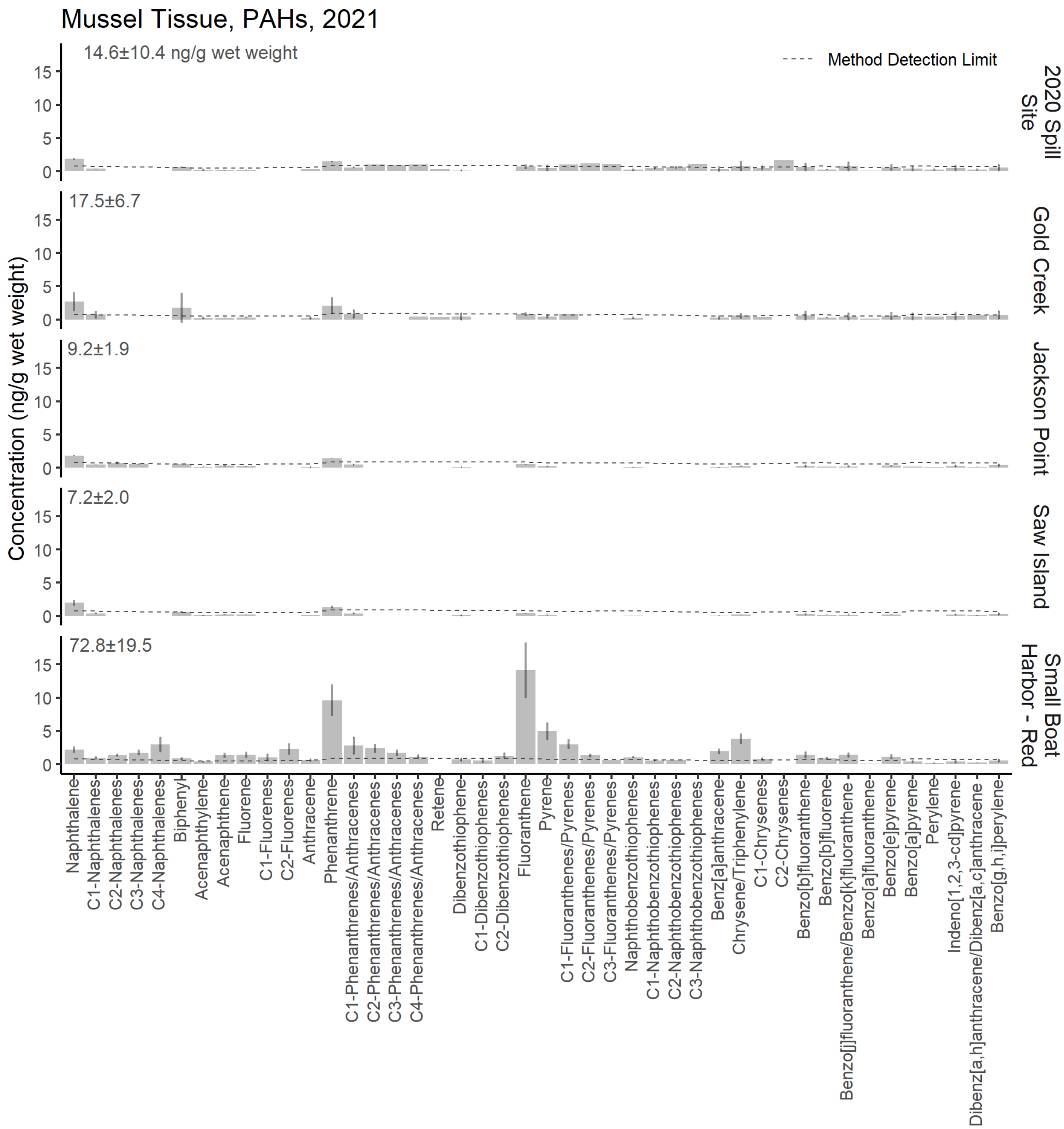


Figure 5. PAH profiles from Pacific blue mussels sampled at five sites in Port Valdez . Values represent mean ± 1 standard deviation and sum 43 PAH values are displayed in the upper left of each profile.

2.2.1. Toxicological Interpretations

At the 2021 tissue concentrations, no adverse biological effects are predicted. Considering the behavior of larger PAHs to adhere to lipids, mussel tissue concentrations are likely higher in the winter and early spring, before Pacific blue mussel spawning events (i.e., lipid-rich eggs will carry away significant amounts of PAHs). In this case, the post-spawning July sampling may represent the lowest PAH accumulation over the annual cycle.

Similar mussel tissue concentrations did not elicit early warning signs for genotoxicity or cellular toxicity in laboratory and field studies (Hylland et al. 2008; Sundt et al. 2011). At tissue PAH concentrations two orders of magnitude greater, laboratory studies observed reduced body size and greater cellular stress but no significant differences in gamete development in fuel-oil-exposed mussels (Ruiz et al. 2014).

Mussels accumulate more than just hydrocarbons. Across Prince William Sound and the North Gulf Coast, elevated concentrations of arsenic, cadmium, copper, lead, mercury, nickel, butyltins, chlordane, chlorobenzenes, DDT, dieldrins, HCHs, PBDEs, and PCPs are found locally in Pacific blue mussels (Rider 2020). While some of these concentrations are directly related to local past and present anthropogenic sources (e.g., mining, chemical storage, shipping, accidents and spills, and human activities), long-range transport of chemicals is likely also occurring. The potential for adverse effects on biota from the combined stressors either through contaminant mixtures and/or environmental stressors should be highlighted but any further assertion as to the degree of injury would be speculative.

2.2.2. Site-Specific Source Identification

As tissue hydrocarbon concentrations and chemical compositions are driven by the bioavailability of compounds, environmental conditions, and physiological, cellular, and molecular processes in the mussels, which govern exposure, uptake, metabolism, and elimination, source identification analysis should be performed with caution. In the 2021 mussel tissue data, Gold Creek, Jackson Point, and Saw Island mussels exhibited similar PAH profiles amongst their sparse pyrogenic PAHs. PAH profiles were dominated by parent compounds of naphthalene, phenanthrene, and fluoranthene with few biomarkers detected. In 2021, the April 2020 oil spill site (HOT) had a similar pattern as the terminal adjacent sites (Saw Island and Jackson Point) and Gold Creek for the 2–3 ring PAHs but had greater representation of alkylated 3–4 ring PAHs and biomarker indications of crude oil from the previous year's event although agreement between replicates was poor. The Valdez Small Boat Harbor site had a mix of pyrogenic and petrogenic signals together with a prominent T19-hopane spike and a water-washed naphthalene profile. All sites have 4–6 ring, higher molecular weight PAHs which accumulated in mussel tissue. Similar findings of high molecular weight pyrogenic PAH bioaccumulation in mussels despite no detectable concentration in seawater were made in past studies (Boehm et al. 2004). Analysis of the saturated hydrocarbons notably reveals a larger portion of unresolved, highly complex heavy oil compounds in some samples from Gold Creek and Jackson Point suggesting patchy hydrocarbon distribution from a moderately weathered source. Mussel tissues from all sites were also dominated by hydrocarbons (n-C15, n-C17, and pristane) of marine biogenic origin.

2.2.3. Historical Perspective

Historical trends in Pacific blue mussel tissue PAH concentrations are variable, reflecting known oil spill incidents in 2004 at Gold Creek, and 2017 and April 2020 spills at the terminal and Saw Island (Figure 6A). Within the larger trend, PAH variability and mean tissue concentrations have increased since 2013 regardless of site (Figure 6B). In the absence of a spill event, mussel tissue concentrations have remained below < 1000 ng/g wet weight, indicating the mussels are likely not under PAH exposure-induced stress. However, extremely high values have been recorded following spill incidents (e.g., 244, 000 ng/g wet weight after the April 2020 terminal spill), a value likely to induce adverse effects at the molecular to the individual level for organisms. Results show that under a spill incident, local mussel populations respond quickly with elevated tissue concentrations and eliminate compounds within a year to background concentrations as is seen following the April 2020 spill at the terminal in the 2021 results (Figure 6A). Although, petrogenic biomarkers are still present in some mussels from the April 2020 spill site in the 2021 results.

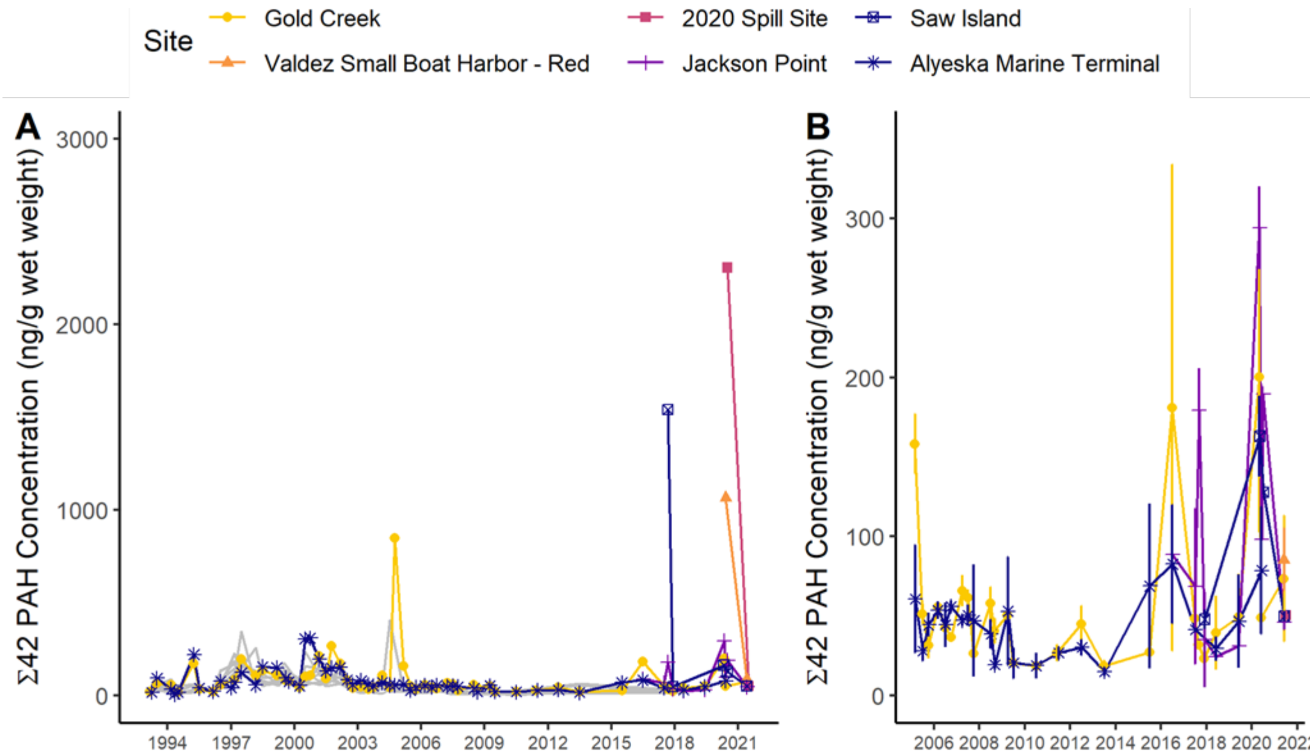


Figure 6. Total PAH concentrations in Pacific blue mussel tissue (A) over the entire duration of the LTEMP with grey lines indicating long term LTEMP stations from greater Prince William Sound and the Gulf of Alaska to add historical and environmental context; note concentrations > 3000 ng/g wet weight (i.e., known spill events) were removed for clarity (max post spill concentration >200 000 ng/g wet weight), and (B) over the last 16 years and excluding concentrations >350 ng/g wet weight for clarity. Colors and shapes indicate sampling site and mean values ± 1 standard deviation are plotted for each sampling event.

The range of the 2021 Port Valdez mussel tissues is within the historical range of locations with limited human use and not oiled during the Exxon Valdez oil spill (Boehm et al. 2004).

2.3. Passive Sampling Device

Hydrocarbons were found at low concentrations in passive sampling devices at all sites in Port Valdez in concentrations ranging from 26–86 ng/L sum PAHs (Figure 2). These concentrations represent the dissolved constituents (C-free) and are not traditional total water concentrations, but in this report the passive sampling device C-free concentrations are used as a proxy for water concentrations of PAHs. The highest passive sampling device-derived concentrations were measured at Gold Creek (75±9 ng/L) followed by Jackson Point (34±0.4 ng/L and Saw Island (28±3 ng/L). Dissolved and heavily water-washed naphthalenes made up 94–95 % of the sum concentrations across all samples and sites (Figure 7). Smaller, 2–3 ring PAHs made up 99 % of the sum concentrations, indicative of the more readily water-soluble fraction targeted by the passive sampling device. Other PAHs that were detected at lower concentrations at all sites were fluorenes, fluoranthene, dibenzothiophenes, phenanthrenes, and anthracenes. Sum PAH concentrations without naphthalene were 1–4 ng/L. Concentrations of alkylated compounds were greater than those of parent compounds indicating a water-washed oil source, evaporative transfer of dissolved compounds into the atmosphere, or weathering of a surface oil film before it was entrained into near-surface water and dissolved to an appreciable extent. While direct comparison of the passive sampling data to other environmental hydrocarbon studies is challenging due to methodological differences, present dissolved PAH concentrations from the passive sampling devices are comparable to water concentrations at unoiled sites and sites with medium human activity around Prince William Sound (Short et al. 2008; Lindeberg et al. 2017). The present passive sampling device-derived water concentrations in Port Valdez were all at least two to three orders of magnitude below published water quality standards and below those of polluted areas across the United States (EPA 2002).

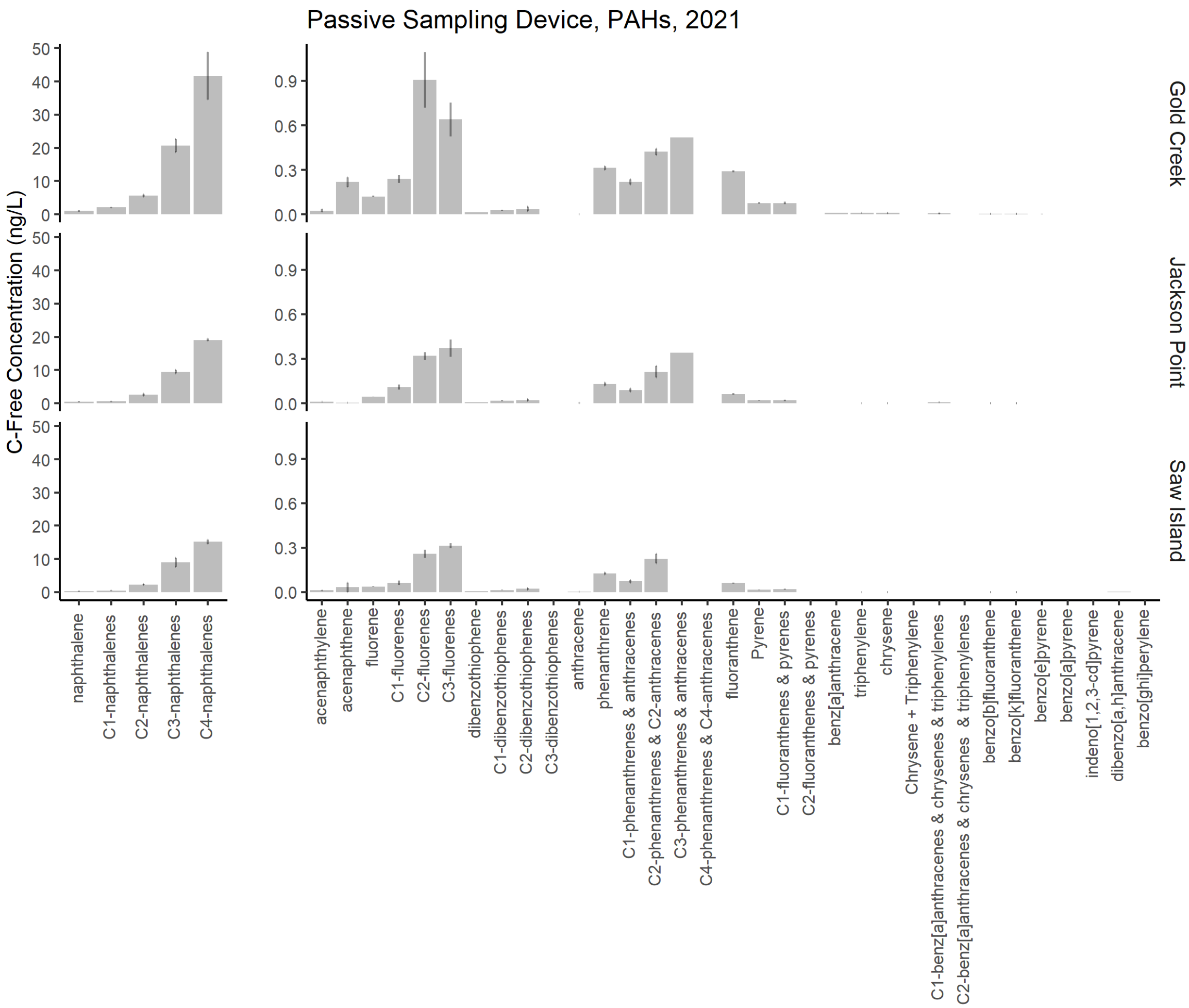


Figure 7. PAH Profiles in 2021 passive sampling devices placed at Gold Creek, Jackson Point, and Saw Island. Values represent mean ± standard deviation for the three replicates.

2.3.1. *Site-Specific Source Identification*

Though not the focus of the passive sampling device which measures the dissolved and bioavailable fraction (C-free concentrations) in the water, PAH profiles can be used conservatively for source identification and forensic analysis. One striking observation is the large naphthalene peak with ascending alkylation, indicative of a water-washed and weathered petrogenic source. Similar patterns are seen in the fluorenes at Saw Island and Jackson Point; however, the pattern is more petrogenic at Gold Creek. A petrogenic signal was confirmed for all sites using a passive sampler specific ratio (P0/A0 > 30) (Stogiannidis and Laane 2015).

2.3.2. *Toxicological Interpretations*

Concentrations reported in the Port Valdez passive sampling devices are below those reported to cause adverse effects even in the most sensitive of life stages for marine organisms. The 2021 PAH concentrations in the parts per trillion range (i.e., one drop in 20 Olympic-sized swimming pools) are an order of magnitude lower than those reported to cause developmental and delayed effects in herring and salmon early life stages (Incardona et al. 2015). Studies on Arctic cod embryos, a Bering Sea species not present in Prince William Sound, report malformations and reduced survival at concentrations similar to those measured by the passive samplers; however, the exposure PAH composition differs with the Arctic cod study using whole crude oil (Bender et al. 2021). Naphthalene, while present at greater concentrations than other PAHs, is of low toxicological concern at present concentrations and is not a carcinogen.

2.3.3. *Historical Perspective*

PAH concentrations in passive samplers have remained low over the last six years (Figure 8) with the all-time lowest concentrations measured around the terminal (e.g., Saw Island and Jackson Point) in 2021. While alkylated naphthalenes make up the bulk of the dissolved PAHs in the 2021 sample, these compounds were not quantified in past years (2016 and 2018) and therefore results are displayed as 16 EPA priority PAHs to allow for historical comparisons. A spike in PAHs at Jackson Point and Saw Island and wide variation between samples is likely a result of the April 2020 spill at the terminal. Passive sampler PAH profiles over time have also remained consistent with high naphthalene spikes dominating PAH profiles as noted in previous LTEMP reports (Payne and Driskell 2021).

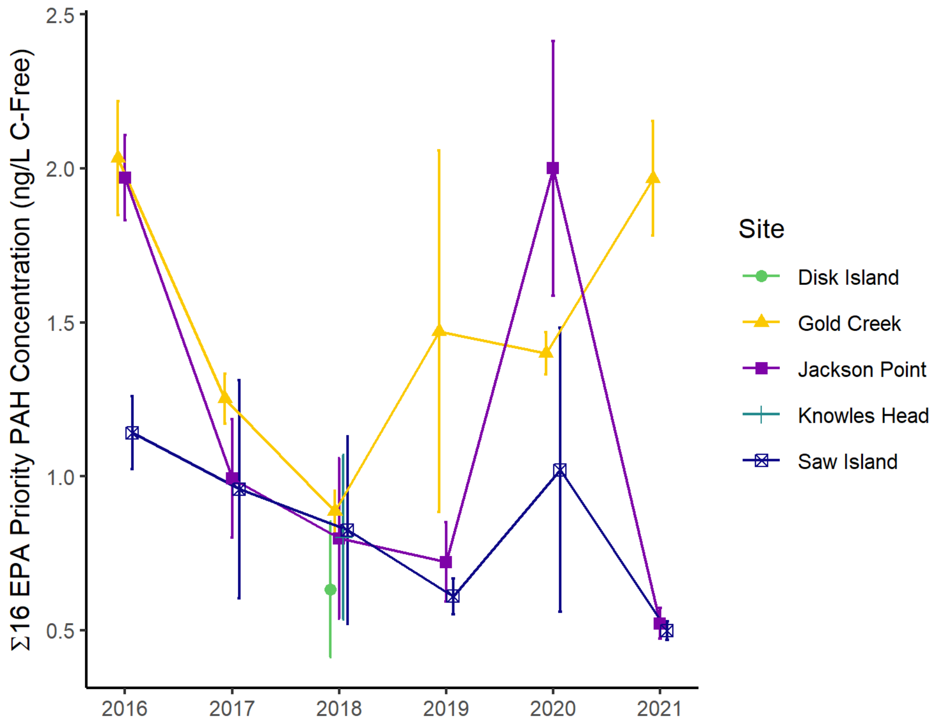


Figure 8. Sum 16 EPA PAH concentrations in passive sampling devices from 2016–2021 at five sites. Sites are distinguished by color and shape and plotted by mean ± 1 standard deviation.

2.4. Holistic Interpretation

Sediment and Pacific blue mussel hydrocarbon concentrations were at an all-time low in 2013 and since then a general increase in concentrations and in variability between samples from the same sites is observed through 2021. In 2013, hydrological condition shifted from cold to warm anomalies and northwest Prince William Sound experienced an increase in meltwater and greater freshening and cooling of surface waters (Campbell 2018). Note that 2013 was also the start of the latest warm anomaly (i.e., 'The Blob') in the Gulf of Alaska when winter surface waters warmed by as much as 3°C compared to 1981-2010 averages (Bond et al. 2015). Wind and freshwater input drive surface water circulation patterns and retention time within Port Valdez and Prince William Sound (Gay 2018) indicating the importance of these environmental factors to hydrocarbon transport. Within Port Valdez residence times could range from 7 hours for surface waters to prolonged or indefinite in waters >40 meters depending on season and conditions (Gay 2018). Large and regional scale changes in climate could affect the fate and transport of petroleum compounds through changes in freshwater and the oil-adsorptive, glacial flour inputs into Port Valdez.

The 2021 Port Valdez hydrocarbon and biomarker profiles vary with a decrease in the number of analytes detected across the sampling matrixes of sediments, mussel tissue, and passive sampling devices, respectively. All sampling matrixes indicate a petrogenic crude oil source at or near the terminal with varying degrees of weathering while Gold Creek sources are more weathered and pyrogenic with a larger proportion of higher molecular weight PAHs. The Valdez Small Boat Harbor is a clear outlier, as expected due to frequent spills and heavy human use, with a strong pyrogenic signal indicative of combustion sources like engine exhaust, creosote, fuel, and refined oils and starkly different from the ANS-related signals found near the terminal.

Naphthalene was ubiquitous across all sampling matrixes and especially prominent, although water-washed, in the passive sampling device results. The origin of the naphthalene compounds can be identified as petrogenic in the sediments, likely petrogenic in the mussel tissues although higher alkylates are absent, and heavy weathered/water-washed petrogenic in the passive sampling devices. Naphthalene is more water-soluble than larger hydrocarbons and yet found bound up in sediments, shales, and glacial silt/flour mostly transported from east of Prince William Sound (Boehm et al. 2001) or locked away for decades in glacial ice (Vehviläinen et al. 2002). Therefore, Naphthalene can be readily transported from its original source and remain intact in sediments and glaciers to become ubiquitous in the environment.

While overall concentrations measured in sediment, mussel tissue, and dissolved in water were low and pose low risk for toxic effects in the aquatic ecosystem, hydrocarbons can accumulate in organisms and in the food web through processes called bioaccumulation and biomagnification. Bioaccumulation and biomagnification of PAHs in invertebrate food webs (e.g., benthic) pose risks for increased tissue concentrations and greater risk for adverse effects (Meador et al. 1995). However, active biotransformation of PAHs in vertebrates (e.g., fish, birds, marine mammals, and humans) precludes the accumulation and magnification of PAHs in tissues for the most part. Even without elevated tissue concentrations, vertebrates are impacted by PAH exposure. Evidence of this sublethal exposure can be seen in multiple physiological systems including in effects on DNA, oxidative stress, growth, and reproduction. Invertebrates chronically exposed to moderate PAH contamination, like harbors, are less physiologically stressed than mussels from more pristine sites when exposed to elevated PAHs (Lacroix et al. 2015). It is unknown whether this adaptation is through phenotypic plasticity or genetic adaptation nor on what time scale these changes occur.

3. FUTURE PERSPECTIVE

Hydrocarbons at LTEMP sites have remained at or near background concentrations since 2005 making further significant reductions unlikely. In the period between the 2020 and 2021 LTEMP sampling, 82 petroleum spills in Prince William Sound have been reported to the Alaska Department of Environmental Conservation, with 73% of those occurring in Port Valdez: seven spills at the terminal and 43 spills related to the Valdez Small Boat Harbor and fuel dock (ADEC 2022). These spills, while small in volume, result in chronic input of hydrocarbons into Port Valdez and highlight the importance of continued environmental monitoring efforts. Even with lower throughput of crude oil at the terminal, increasing extreme weather events and increased human activity in Prince William Sound contribute to a greater risk of hydrocarbon spills by structural/mechanical failure, accident, or human factors. Maintaining the three matrix sampling regimes with a full suite of PAHs, saturated hydrocarbons, and chemical biomarkers ensures the power of LTEMP to detect change in environmental hydrocarbon levels.

Incorporating biological biomarkers into the LTEMP program would directly address the real health effects of the chronic and acute exposure to hydrocarbons in the ecosystem. The traditional chemical approach now employed in LTEMP limits the understanding of how combined effects of non-hydrocarbon pollutants, ongoing environmental change, or chronic exposure affects organisms. Recent investigations into gene expression in Pacific blue mussels following the April 2020 oil spill at the terminal show upregulation of genes related to detoxification, stress, and cell death several weeks after the oil spill was discovered and clean up was initiated (Bowen et al. 2021). Mussel tissue hydrocarbon concentrations were far quicker to return to baseline levels than stress and detoxification related gene expression levels indicating that the mussels have delayed and prolonged stress even after a minor spill (Bowen et al. 2021). Elucidating changes in gene expression provides an early warning sign for potential adverse sublethal effects on growth or reproduction from minor spills or chronic hydrocarbon exposure. The inclusion of a battery of biomarkers is recommended in hydrocarbon environmental monitoring programs and are readily becoming part of the health assessment and management of aquatic ecosystems worldwide (Lehtonen et al. 2019; Hylland et al. 2008). For successful implementation, significant effort should be made to define appropriate biomarkers, site- and season-specific baseline variability, manageable protocols, and standard procedures for analysis and interpretation of risk. Suitable petroleum biomarkers for LTEMP could include well-described mussel biomarkers like glutathione S-transferase (GST) enzyme activity, a measure of biotransformation of PAHs; Acetylcholinesterase (AChE) activity, a measure of stress; and lipid membrane peroxidation, a biochemical damage response, all linked to petroleum exposure in laboratory and field studies. The development of petroleum exposure specific biomarkers of effect is informed by molecular work such as the transcriptomics study done by Bowen et al. (2021) in the wake of the April 2020 spill at the terminal.

To address the original aims of the LTEMP set out in the Oil Pollution Act of 1990 Section 5002 [are] *to devise and manage a comprehensive program of monitoring the environmental impacts of the operations of terminal facilities and of crude oil tankers while operating in Prince William Sound. [Furthermore] the monitoring strategy will permit early detection of environmental* *impacts of terminal facility operations and crude oil tanker operations while in Prince William Sound*. We recommend the following expansions of LTEMP with a brief explanation:

- Continuation/addition of biological biomarkers (see previous paragraph).
- Incorporating contemporary and non-ANS sources of hydrocarbons into the LTEMP database to increase the diagnostic power of LTEMP to distinguish terminal and tanker related inputs (Payne et al. 2005)
    - Recent Ballast Water Treatment Facility effluent to account for changes in the treatment process
    - Local freshwater inputs from glacial melt and runoff (e.g., Gold Creek or the Lowe River)
    - Continuing / expanding sampling efforts at the Valdez Small Boat Harbor
- Quantifying oxygenated hydrocarbons, which are potentially highly toxic and make up a large component of the Ballast Water Treatment facility effluent (Payne and Driskell 2021).
- Incorporating relevant environmental/anthropogenic/terminal operation covariates into the interpretation of the hydrocarbon results (e.g., local precipitation/freshwater discharge, sea surface temperature, local human activity, volume of BWTF effluent) to better understand the factors that influence fate and transport of hydrocarbons from the terminal, tankers, and other sources. Even at low environmental hydrocarbon concentrations, historical and current trends can be compared and may be explained by changes in environmental factors. Investigating a few of the most likely covariates during the LTEMP reporting process could elucidate other factors driving hydrocarbon concentrations.

4. CONCLUSION

The hydrocarbon fingerprints in the 2021 samples vary by site with those at or near the Valdez Marine Terminal revealing ANS crude and its associated products (i.e., BWTF effluent) as the primary source for hydrocarbons. Gold Creek and the Valdez Small Boat Harbor cannot be linked directly to the terminal operations. Low potential environmental and toxicological risk is posed by hydrocarbons contributed by the terminal and tankers in 2021. Since 1993, hydrocarbon concentrations are generally low with localized spikes corresponding with spill events like the April 2020 oil spill at the terminal. Following an all-time low in 2013, hydrocarbon concentrations in sediments and mussels has slowly increased across all sites but are still below any threshold for adverse effects on aquatic life. Hydrocarbon presence in Port Valdez may be influenced by environmental factors which are driving fjord-wide trends such as increased freshwater input, glacial melt, and warming ocean temperatures. These environmental changes may act in concert with hydrocarbon exposure to stress the biota. Future monitoring efforts should maintain the current three-matrix design (sediment, Pacific blue mussel tissue, and passive sampling device) with a focus on sources of hydrocarbons in the Port Valdez including the Valdez Small Boat Harbor, freshwater input/glacial melt, and the BWTF effluent, which are currently poorly understood. The inclusion of biological biomarkers to assess exposure and potential effects, especially following spill events, would illuminate the environmental impact on this chronically exposed system.

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