fjord & fish sciences

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Final

2024 Summary Report

Long-Term Environmental Monitoring Program

PREPARED FOR

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PRINCE WILLIAM SOUND RCAC REGIONAL CITIZENS' ADVISORY COUNCIL

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Acronyms and Abbreviations

ADEC .... Alaska Department of Environmental Conservation
ANS .... Alaska North Slope
BWTF .... Ballast Water Treatment Facility
EPA .... U.S. Environmental Protection Agency
EVOS .... Exxon Valdez Oil Spill
LTEMP .... Long-Term Environmental Monitoring Program
NOAA .... National Oceanic and Atmospheric Administration
PAHs .... Polycyclic aromatic hydrocarbons
PPB (or ng/g) .... Parts Per Billion (or nanograms per gram)
PWSRCAC .... Prince William Sound Regional Citizens' Advisory Council
rSTD .... Relative Standard Deviation

1. Abstract

Following the 1989 Exxon Valdez oil spill, concerned citizens and congressional legislation established the Prince William Sound Regional Citizens' Advisory Council (Council). The Council's mission is, citizens promoting the environmentally safe operation of the Valdez Marine Terminal and associated oil tanker activities within the spill-affected area. Since 1993, annual monitoring of marine sediments and intertidal blue mussels (*Mytilus trossulus*) has been conducted, focusing on polycyclic aromatic hydrocarbons, saturated hydrocarbons, and petroleum geochemical biomarkers essential for oil spill forensics. Sampling sites include areas with current oil tanker activities (e.g., loading, anchoring, transport routes), previously oiled sites from the Exxon Valdez spill, and reference locations with varying hydrocarbon sources.

Over the past 31 years of the Council's Long-Term Environmental Monitoring Program (LTEMP), the data have shown fluctuating hydrocarbon levels in sediments and mussels, with some measurements indicating toxic concentrations. Monitoring in the last two decades has generally recorded low levels of hydrocarbons. However, localized spikes—such as from the 2020 spill at the Valdez Marine Terminal—indicate small-scale oil releases. Low levels of petroleum hydrocarbons, traceable to Alaska North Slope crude oil, have been detected in marine sediments near the Valdez Marine Terminal. However, pyrogenic compounds from combustion processes are also prevalent. Similarly, in recent years, passive water sampling in Port Valdez and mussel sampling across Prince William Sound and the North Gulf of Alaska indicate low toxic hydrocarbon levels. An accompanying pilot study on metal accumulation in sediment samples revealed four metals—aluminum, copper, iron, and vanadium—that exceeded protective sediment quality guidelines and are significantly elevated in the terminal sediments compared to the Gold Creek reference site.

This extensive dataset contains over 280,000 accredited chemical measurements from sediments, mussels, and water collected at numerous remote and rural sites on the traditional lands and waters of the Chugach, Eyak, and Alutiiq/Sugpiaq peoples. This program provides valuable information about temporal trends in petroleum hydrocarbon contamination in the region and baseline data critical for detecting and monitoring lingering contamination, impacts from current activities, and potential future releases. Despite its breadth and annual analytical review focusing on hydrocarbon forensics and concentrations of concern, the dataset remains underutilized. It holds significant potential for further exploration, offering insights into environmental change, hydrocarbon weathering, fate and transport processes, lingering oil, and the biological impacts of hydrocarbons. The utility of the LTEMP in maintaining a robust baseline hydrocarbon database continues to be critical in light of rapid environmental change and continued petroleum pollution risk.

2. Introduction

The Long-Term Environmental Monitoring Program (LTEMP), managed by the Prince William Sound Regional Citizens' Advisory Council (PWSRCAC), is in its 31st year of monitoring hydrocarbons after the Exxon Valdez oil spill (EVOS) in 1989. Through LTEMP, we aim 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 a highly diverse group of compounds that comprise the bulk of petroleum products like crude oil, fuel, and maritime products like hydraulic and motor oil. 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 weathering, including dissolution, evaporation, ultraviolet degradation, and microbial degradation. Weathering changes hydrocarbons' physical and chemical properties, altering their relative abundance, environmental fate, transport, and toxic potential. Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrocarbons in oil with varying numbers of benzene rings that are relatively resistant to degradation and toxic to living organisms. This group of chemicals tends to adsorb rapidly on suspended materials and sediments and accumulate in biological tissues once released into the marine environment.

As a group, PAHs comprise hundreds of compounds, each with its degree of toxicity, and their mixtures can exhibit a wide range of toxicities. Specific hydrocarbons, patterns, and diagnostic compounds (i.e., (petrogeo)chemical biomarkers) aid in identifying specific hydrocarbon sources and indicate 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., between different crude oils) 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 metabolize these compounds efficiently. Pacific blue mussels also remain sedentary in a fixed location and filter particles from their immediate surroundings, and therefore serve as efficient natural samplers and indicators of overall environmental PAH exposure (Neff & 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 and hydrocarbon sources necessitates using multiple matrices to understand the source, environmental fate, and potential ecotoxicological effects. Marine sediments, which accumulate hydrocarbons, petrogeochemical biomarkers, and saturated hydrocarbons, are appropriate for source analysis and risk assessment. Sources investigated for the present study are those associated with terminal operations, including Alaska North Slope (ANS) crude oil pumped through the trans-Alaska pipeline and loaded into tankers at the terminal. Sessile filter-feeding organisms like intertidal blue mussels reflect the chemicals that bioaccumulate in local, native biota and can be an ecotoxicological risk. Passive sampling devices measure the dissolved, bioavailable fraction of hydrocarbons, which may pose a risk to organisms and the ecosystem.

The following study presents the 2024 results from the LTEMP and aims to determine the following:

- The extent, if any, that the terminal and associated tankers' hydrocarbon fingerprint is present in 2024 samples with varying ranges from the terminal.
- The potential ecotoxicological risk posed by the measured hydrocarbon contribution from the terminal and tankers.
- The historical trends, ecotoxicological risk, and hydrocarbon fingerprint from mussels collected from extended sampling sites across greater Prince William Sound in 2024.
- The ecotoxicological relevance of these results, given other factors (e.g., environmental or anthropogenic) that may influence hydrocarbon presence and composition in 2024 samples.
- Recommendations for future monitoring of petroleum hydrocarbons at the terminal and in Prince William Sound.

3. Briefly, The Methods

Sediment, passive sampling device, and Pacific blue mussel tissue samples were collected in June of 2024 from annual monitoring stations in Port Valdez and those stations that were missed in the greater Prince William Sound and North Gulf of Alaska in 2023. The sampling program investigated three matrices: sediment, Pacific blue mussels, and seawater. Sediments were sampled at Alyeska's Valdez Marine Terminal and Gold Creek

(Figure 1). Pacific blue mussel samples were taken from four sites around the Port of Valdez with a focus on the terminal – Alyeska's Valdez Marine Terminal (also referred to as Saw Island), Jackson Point, Gold Creek, and Valdez Small Boat Harbor entrance (RED - a site that is chemically different from the ANS terminal source signature and currently acts as a high human use, non-ANS reference site). Three Gulf of Alaska stations (i.e., Aialik Bay, Windy Bay, and Shuyak Harbor) planned to be included in the five-year survey in 2023 were instead included in the 2024 campaign due to weather preventing sampling in 2023. These sites are EVOS-oiled sites. Water was sampled with passive sampling devices at three sites in 2024 — Gold Creek, Jackson Point, and the terminal/Saw Island. Sampling was replicated using triplicates collected from each site across each matrix with three sediment grabs, three composite blue mussel samples, and three composite passive sampling device samples.

Samples were analyzed for PAHs, saturated hydrocarbons, and geochemical petroleum biomarkers using advanced analytical techniques at 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, PAHs only). These are the same laboratories that have participated in the LTEMP effort for the last nine years. Briefly, the results continue to be of acceptable precision and accuracy and

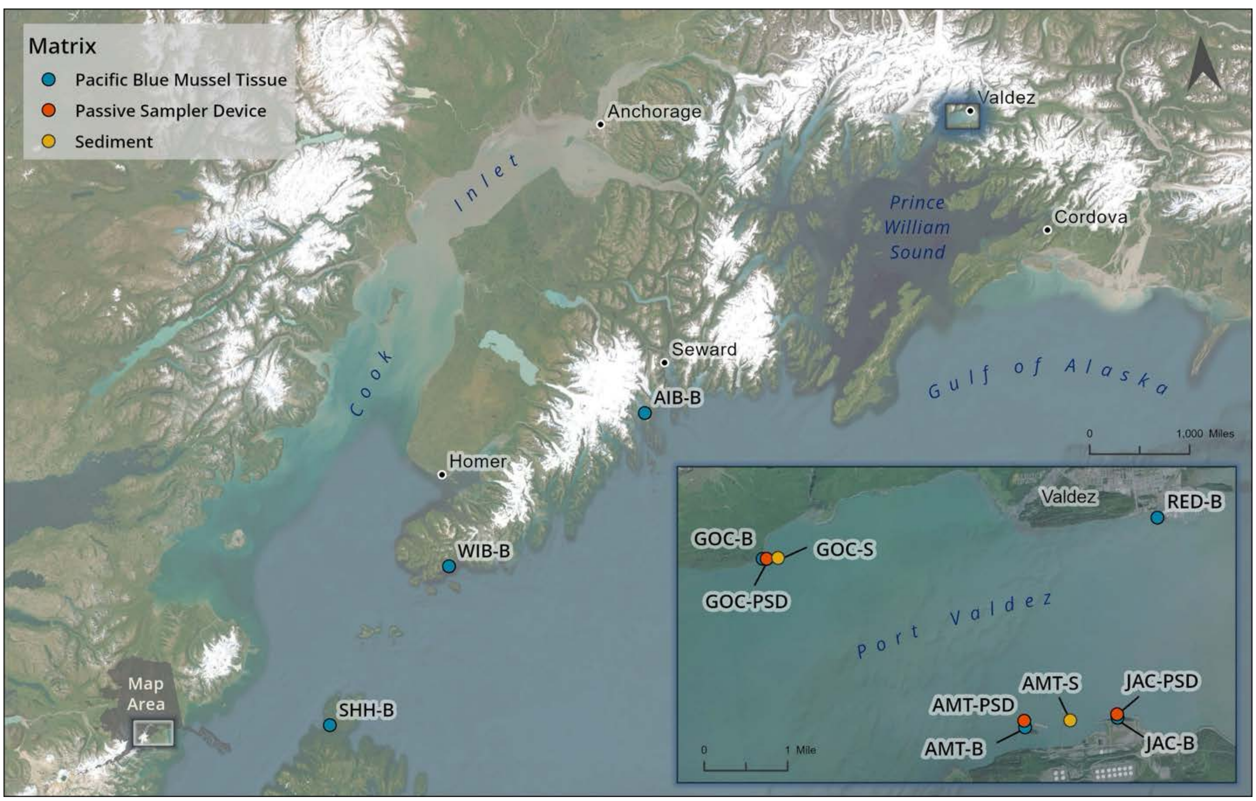

Figure 1. Long-Term Environmental Monitoring Program sites from the 2024 campaign in Port Valdez and the North Gulf of Alaska. The color of the points and labels represent differences in sampling matrices.

can be compared to previous years' data. The physical characteristics of sediments were also reported in laboratory results, though they are not presented herein.

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, and corrected by factors influencing bioavailability, like total organic carbon in sediments or lipid content in mussel tissues. 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 ecotoxicological effect thresholds. Concentrations below the method level of detection threshold were provided by the lab as an estimate. These estimated concentrations were plotted on PAH profile figures and included in sum calculations; compounds that were not detected in a sample or were biased by laboratory issues (i.e., matrix interference) were not included in the sum calculations. Forensic interpretation was done using analyte profile pattern comparisons for ANS crude for PAH, geochemical petroleum biomarkers, and saturated hydrocarbons in sediment samples. Blue mussels and passive sampling devices tentative forensic assertions were made by qualitative ratios of parent to alkylated compounds and low and high molecular weight PAH compounds. Analytical results and calculations for all samples and all analytes, pattern profiles, forensic ratios, and laboratory blanks are presented in the Technical Summary (Fjord & Fish, 2024) to support the assertions made in this summary report.

4. Results & Discussion

4.1. Subtidal Marine 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 one ppb can be visualized as the concentration of 50 drops in an Olympic-sized swimming pool. In 2024, the highest sum (∑) PAH concentrations were found at the terminal (159.6±11.7 ng/g dry weight) compared to Gold Creek sediment (26.4±4.8 ng/g dry weight; Figure 2). Parent and alkylated 3-ring phenanthrenes/anthracenes, 4-ring fluoranthenes/pyrenes, and heterocyclic dibenzothiophenes and napthobenzothiophenes made up the bulk of PAHs at the terminal in 2024 (Figure 3). At Gold Creek, similar compounds made up the bulk of detectable PAHs but with greater contribution from naphthalenes and less from benzothiophenes. Greater variability in PAH analytes from the terminal sediments indicates a heterogeneous distribution, likely reflecting the distance of grab samples from the outfall pipe. 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

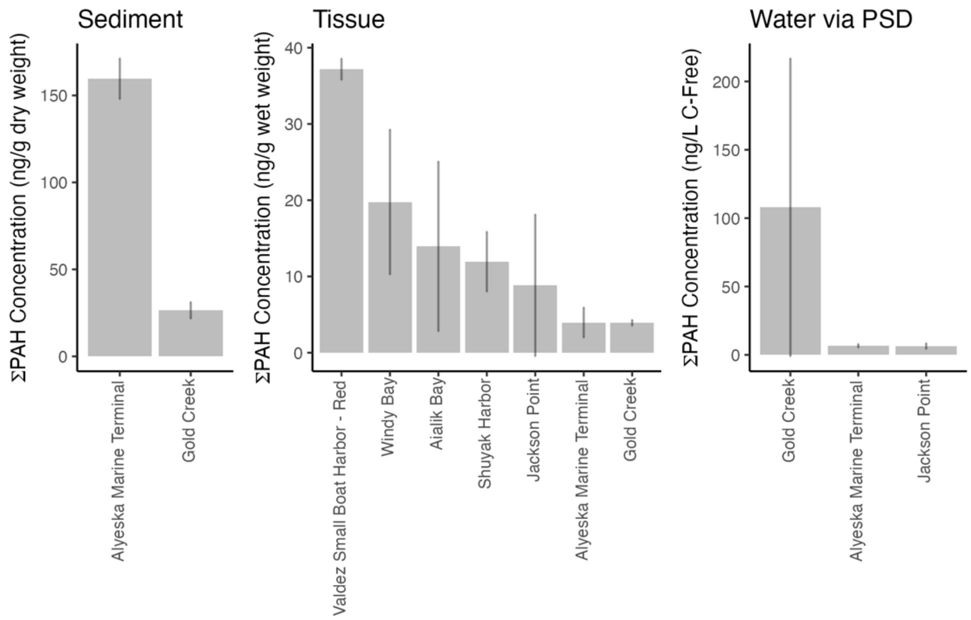

Figure 2. Sum PAH concentrations for 2024 sediments, Pacific blue mussel tissues, and water sampled via passive sampling devices by site plotted at the mean ± 1 standard deviation. Note the unit difference between matrices (i.e., parts per billion for sediments and mussel tissues, and parts per trillion for passive sampling devices).

more similar to those reported from sediments of Cook Inlet and St. Paul Island, Alaska (Nesvacil et al., 2016).

4.1.1. Sediments - Ecotoxicological Interpretation

In 2024, individual and sum 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 1% or less than the U.S. Environmental Protection Agency (EPA) sediment quality PAH benchmarks for aquatic life (EPA, 2016). Individual PAH Threshold Effect Levels set by the National Oceanic and Atmospheric Administration (NOAA) were not exceeded for any analyte in the 2024 campaign (Lourenço et al., 2023). While these EPA benchmarks may not adequately represent benthic communities adapted to Port Valdez's cold and sediment-rich waters, past monitoring efforts around the terminal have indicated little to no change in the benthic community with varying PAH concentrations (Shaw & Blanchard, 2021). The total organic carbon concentration in the sediment is low (0.4–0.5%), which indicates a higher bioavailability of PAHs to marine organisms.

For nine higher molecular weight PAHs, the American and Canadian guidelines set a Threshold Effect Level at 1684 ng/g (Lourenço et al., 2023). For comparison, Denmark has the lowest known threshold for potential injury to aquatic life at 20 ng/g dry weight for the same group of PAHs. In 2024, this highly conservative threshold is exceeded at the Valdez

Marine Terminal (42.6 ng/g) but not at Gold Creek (6.4 ng/g). High molecular weight PAHs are detected in sediments, especially at the terminal, but concentrations of this group do not exceed any protective benchmarks. Carcinogenic PAHs are present in low concentrations at both sites.

4.1.2. Sediments - Site-Specific Source Identification

The hydrocarbons in the 2024 terminal sediments are determined to be derived from ANS crude oil. Biomarker patterns closely match ANS crude oil; however, PAH profiles indicated ANS crude with other sources as high molecular weight PAHs with greater than four rings were overrepresented. The diagnostic biomarkers and their ratios confirm ANS crude oil as the source of hydrocarbons at the terminal. Additional hydrocarbons from non-ANS sources are present in the Ballast Water Treatment Facility (BWTF) effluent, contributing to the PAH profile and the elevated sum PAH concentration. The ratios of several PAHs differed between the terminal and Gold Creek, suggesting some pyrogenic sources at the terminal compared to more petrogenic sources at Gold Creek.

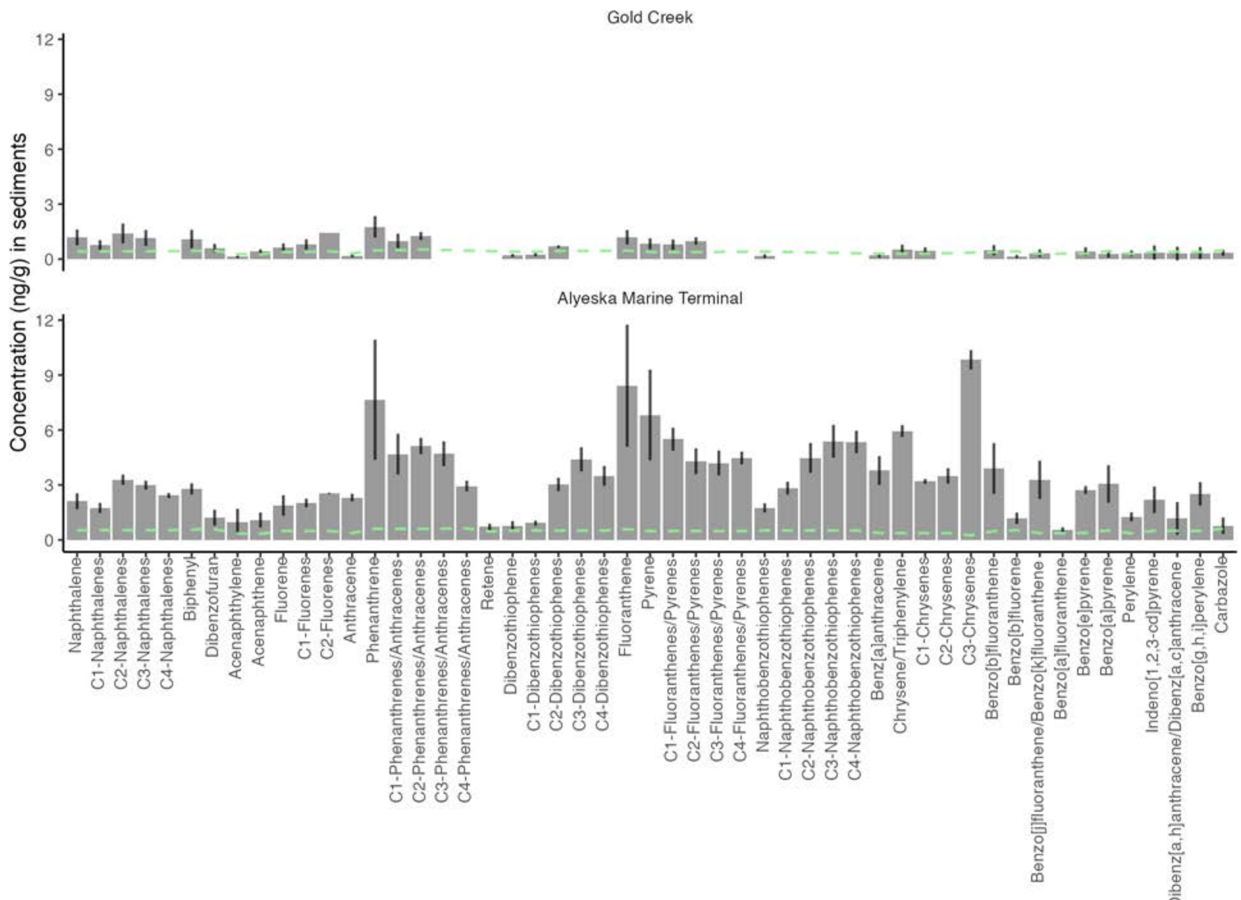

Figure 3. 2024 PAH profiles from sediments sampled at Gold Creek and the terminal site plotted as the mean ± 1 standard deviation for the three replicate samples. A dashed, green line indicated the analyte-specific method detection limit.

Accumulation of higher molecular weight alkylated PAHs, likely from local combustion sources, indicates residuals of prior PAH inputs inefficiently degraded over time. Diagnostic ratios point to wood and coal-type combustion and petrol emissions sources over diesel emissions at both sites. Saturated hydrocarbons at both sites reveal strong microbial degradation and weathering of the hydrocarbons, leaving the higher molecular weight saturated 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 mixed petrogenic and pyrogenic. Gold Creek sediments are moderately weathered with a near complete loss of saturated hydrocarbons, except those contributed by terrestrial plants. In summary, hydrocarbon concentrations in the terminal sediments are linked to the terminal activities and are similar to incidents and activities reported in previous LTEMP reports (e.g., BWTF effluent, spills, and combustion) with residues that have undergone environmental degradation and accumulated over time. Gold Creek sediments show lower hydrocarbon levels and fewer constituents, likely indicative of less recent sources.

4.1.3. Sediments - 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. Since 2005, hydrocarbon concentrations have remained low. While recent years have seen similar hydrocarbon concentrations between the two sites, the 2024 terminal concentrations were substantially higher than values those at Gold Creek or any site in the last 18 years. Terminal sediments have generally contained higher, more

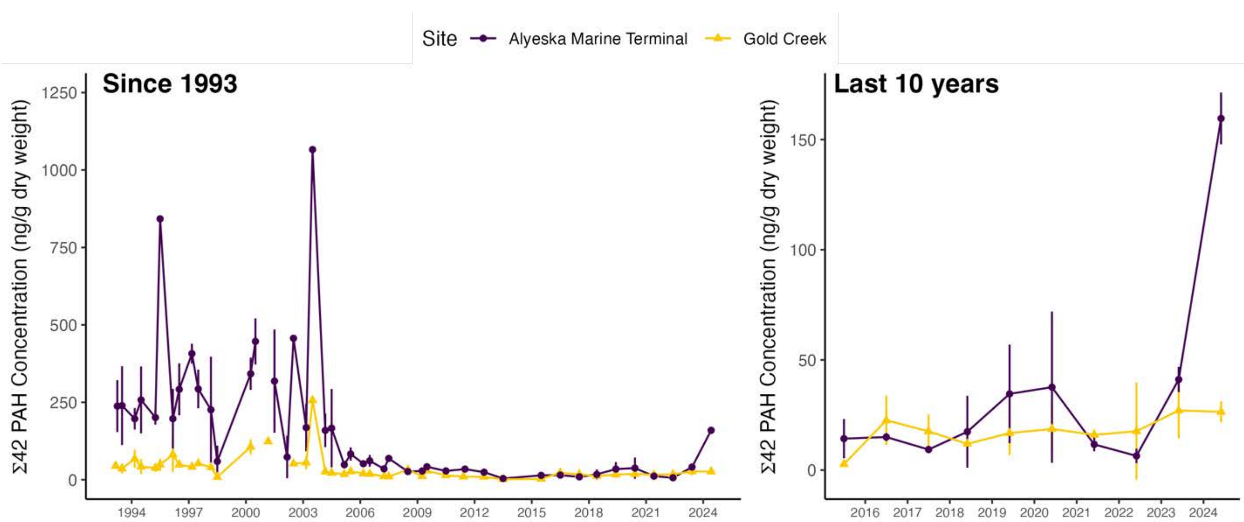

Figure 4. Sum PAH concentrations in sediments over the duration of LTEMP (left panel) and the most recent decade (right panel). Note the differences in scale. Colors and shapes indicate the sampling site; mean values ± 1 standard deviation are plotted for each sampling event.

variable PAH loads than Gold Creek, although considerable overlap in PAH concentration ranges between the two stations has persisted from 2008-2023. Comparing 2022 and 2023 terminal sediments, the increased hydrocarbon load seen in 2024 is from a broad swath of PAHs, including parent and alkylated 3, 4, and 5-ringed PAHs and higher molecular weight PAHs.

4.2. Pacific Blue Mussels

PAHs were detected in Pacific blue mussels at low to moderate concentrations at all sites in 2024 (Figure 2). As in previous years, 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 (39.1±1.6 ng/g wet weight). The remote stations of Windy Bay, Aialik Bay, and Shuyak Harbor had elevated PAH levels compared to sites in Port Valdez. Gold Creek had the lowest PAH levels of all 2024 sites sampled (4.3±0.3 ng/g wet weight). Variability between replicates was relatively high for mussels from remote sites and those from Jackson Point. At Windy Bay, a single group of compounds (C1-Phenathrene/Anthracenes) in a single replicate drives the relatively high PAH values and should be interpreted cautiously.

Phenanthrene was the most abundant PAH at sites except for the Valdez Small Boat Harbor, where larger PAHs, such as flouranthrene, were more prevalent (Figure 5). The 2024 mussel tissue PAH concentrations in Port Valdez are comparable to those found in relatively pristine locations in national parks and forests around southcentral and southeast Alaska, and well below the high concentrations (>1000 ng/g dry weight (138 ng/g wet weight when using mean conversion factor from LTEMP mussel data)) found in the harbor at Skagway, Alaska (Rider, 2020). Mussels from the Valdez Small Boat Harbor and Windy Bay exceeded NOAA's national long-term monitoring status "Low Concentration" range (0–173 ng/g dry weight (0–24 ng/g wet weight)). The mussel community from Windy Bay, sampled every five years in LTEMP, was small and likely suffered from intense sea star predation (Figure 6), which may affect the sample quality, bioavailability, or toxicodynamics of PAHs in this community. Combined natural and pollutant stressors can impose a higher risk to populations than toxicants alone (Gergs et al., 2013); however, no published scientific evidence was located specifically linking predation pressure with increased body burden.

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 comparable to this study (Schøyen et al., 2017). Mussel tissue PAH concentrations were comparable to those measured in pelagic zooplankton in Valdez Arm (Carls et al., 2006) and to mussels caged two kilometers or greater from an oil rig in the North Sea (Sundt et al., 2011). Zebra Mussels sampled from the Great Lakes had lower PAH body burdens (12.6-8.7 ng/g 16 PAHs; Metcralfe et al., 1997) than mussels sampled from the Valdez Small Boat Harbor.

4.2.1. Mussels - Ecotoxicological Interpretations

At the 2024 tissue concentrations, no adverse biological effects are predicted at the low exposure levels (Bowen et al., 2018). 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). Sampled mussels did not approach the calculated food safety threshold for bivalves in the European Union nor the U.S. Food and Drug Administration risk criteria levels for vulnerable populations developed after the BP Deepwater Horizon oil spill (Rotkin-Ellman et al., 2012; Shen et al., 2020).

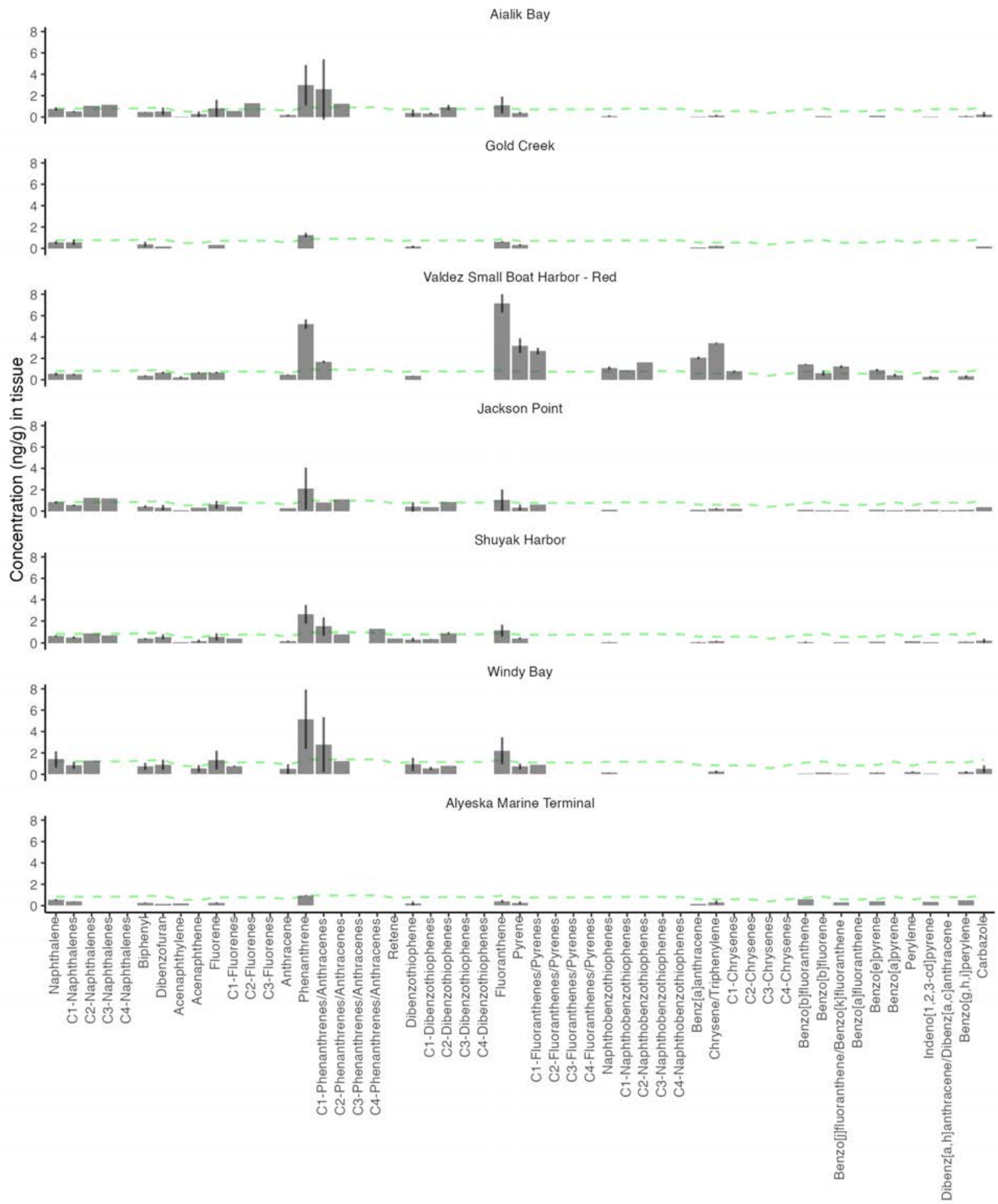

Figure 5. 2024 PAH profiles from Pacific blue mussels plotted as the mean ± 1 standard deviation for the three replicate samples. A dashed, green line indicates the analyte-specific method detection limit.

4.2.2. Mussels - 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 cautiously.

In 2024, Gold Creek, Jackson Point, and Valdez Marine Terminal (i.e., Saw Island) mussels exhibited similar PAH profiles with very few PAHs and petroleum biomarkers detected, indicating low available petroleum hydrocarbons. When PAHs were above detection limits (e.g., phenanthrene and fluoranthene), clear pyrogenic patterns were seen in Aialik Bay, Valdez Small Boat Harbor, Shuyak Harbor, and Windy Bay. Windy Bay, Aialik Bay, and Shuyak Harbor are historically oiled sites from the Exxon Valdez oil spill, and hydrocarbon ratios and biomarkers indicated heavily weathered petrogenic hydrocarbon sources mixed with pyrogenic sources of diesel combustion emissions and/or wood/coal combustion.

Diagnostic ratios of PAHs strongly support pyrogenic sources of hydrocarbons at the Valdez Small Boat Harbor; this site also had the least weathered hydrocarbon input as interpreted by higher saturated hydrocarbon levels compared to other sites.

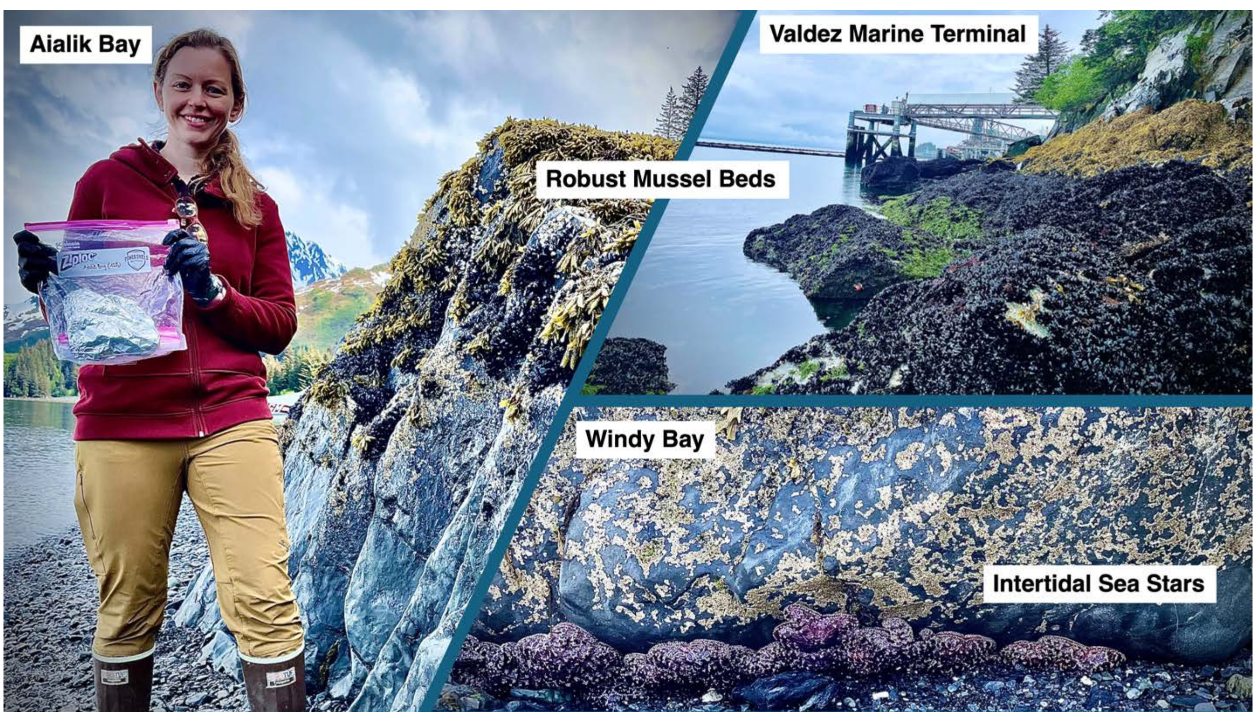

Figure 6. Examples of 2024 mussel sampling sites with Danielle Verna sampling a mussel-covered boulder in Aialik Bay (left), the mussel-covered rocks near the Valdez Marine Terminal at Saw Island (top right), and numerous purple sea stars (likely *Pisaster ochraceus*) in the absence of robust mussel beds in Windy Bay (bottom right).

4.2.3. Mussels - 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 mirroring high concentrations found in sediments pre-2005 (Figure 7). Within the larger trend, PAH variability and mean tissue concentrations have stabilized since ~2010 in the absence of known spills. In non-spill conditions, mussel tissue concentrations have remained below < 1,000 ng/g wet weight, indicating the mussels are likely not under PAH exposure-induced stress. However, high values have been recorded following spill incidents (e.g., 244,000 ng/g wet weight after the April 2020 terminal spill, not shown in Figure 7), a value likely to induce adverse effects at the molecular to the individual level for organisms. Expanded sampling stations (e.g., Aialik Bay, Windy Bay, and Shuyak Harbor) have shown less variability in recent years, likely due to less exposure to recent spill events and the bias of less frequent sampling. The 2024 PAH concentrations in Port Valdez mussel tissues are within the historical range of locations with limited human use and not oiled during the Exxon Valdez oil spill (Boehm et al., 2004).

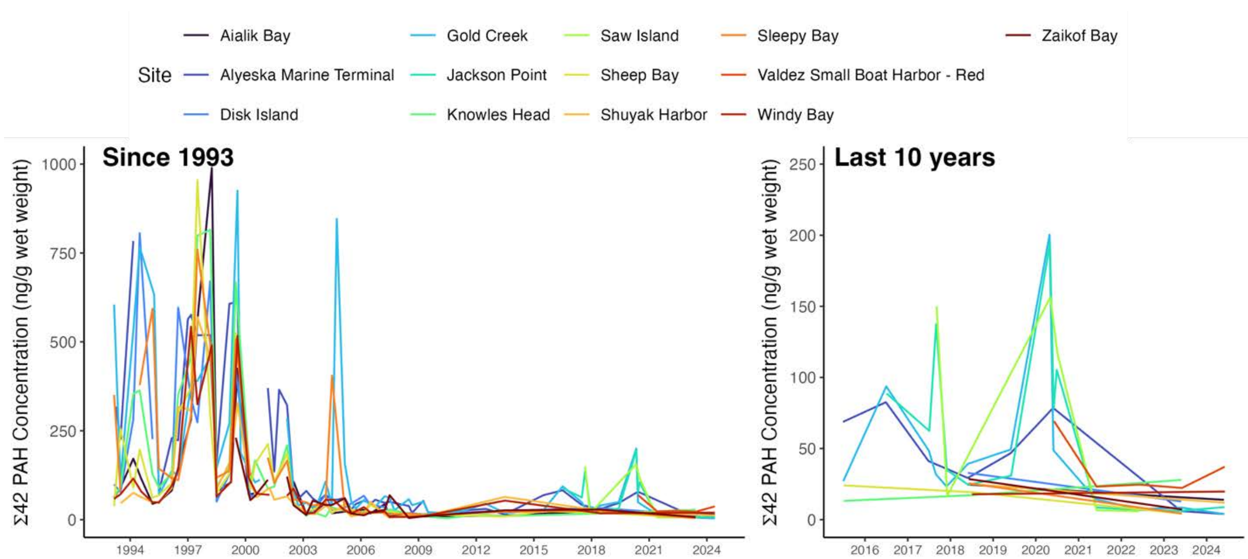

Figure 7. Sum PAH concentrations in Pacific blue mussel tissue (left) over the entire duration of the LTEMP; note concentrations > 1000 ng/g wet weight (i.e., known spill events) were removed for clarity - for reference, (e.g., max post-spill concentration >200 000 ng/g wet weight), and (right) the last decade with all current LTEMP mussel monitoring sites. Colors distinguish sampling sites, and mean values are plotted for each sampling event.

4.3. Seawater

In 2024, petroleum hydrocarbons were found at low seawater concentrations at all Port Valdez sites (Figure 2). These hydrocarbon concentrations represent the dissolved constituents (C-free). They 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. These dissolved concentrations represent the bioavailable fraction and can be directly associated with exposure levels for organisms in the water, such as sensitive early-life stage fish. In 2024, the highest relative passive sampling device-derived water concentrations were measured at Gold Creek (107.9±108.9 ng/L), followed by Valdez Marine Terminal / Saw Island (6.7±1.3 ng/L) and Jackson Point (6.4±2.2 ng/L).

The typical LTEMP dissolved hydrocarbon pattern of dominating and heavily water-washed naphthalenes was present at all sites and in most replicates (Figure 8). Smaller, 2–3 ring PAHs comprised 97-99% of the sum concentrations, indicating the more readily water-soluble fraction. Other PAHs detected at lower concentrations at all sites were fluorenes, fluoranthenes, dibenzothiophenes, phenanthrenes, and anthracenes. At Gold Creek, parent and alkylated naphthalenes, fluorenes, and phenanthrene contributed to the increase in overall load compared to the other Port Valdez stations.

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 those of polluted areas across the United States (EPA, 2002).

4.3.1. Seawater - Ecotoxicological Interpretations

Concentrations reported in the Port Valdez subsurface seawater derived by passive sampling devices are below those reported to cause adverse effects even in marine organisms' most sensitive life stages. The 2024 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). However, no analytical lower limit measured from water or tissues has been identified for developmental cardiac effects in herring (Incardona et al., 2023). Naphthalene, while present at greater concentrations than other PAHs, is of low toxicological concern at present concentrations and is not a carcinogen.

Water quality guidelines set by the U.S. and Canada to represent the lowest observed acute effect concentration are not exceeded by any individual PAH or the sum PAHs (set at 300 ug/L). In 2024, water concentrations did not exceed conservative, protective individual PAH threshold concentrations set for Brazil, British Columbia, Canada, or the United Kingdom (Lourenço et al., 2023).

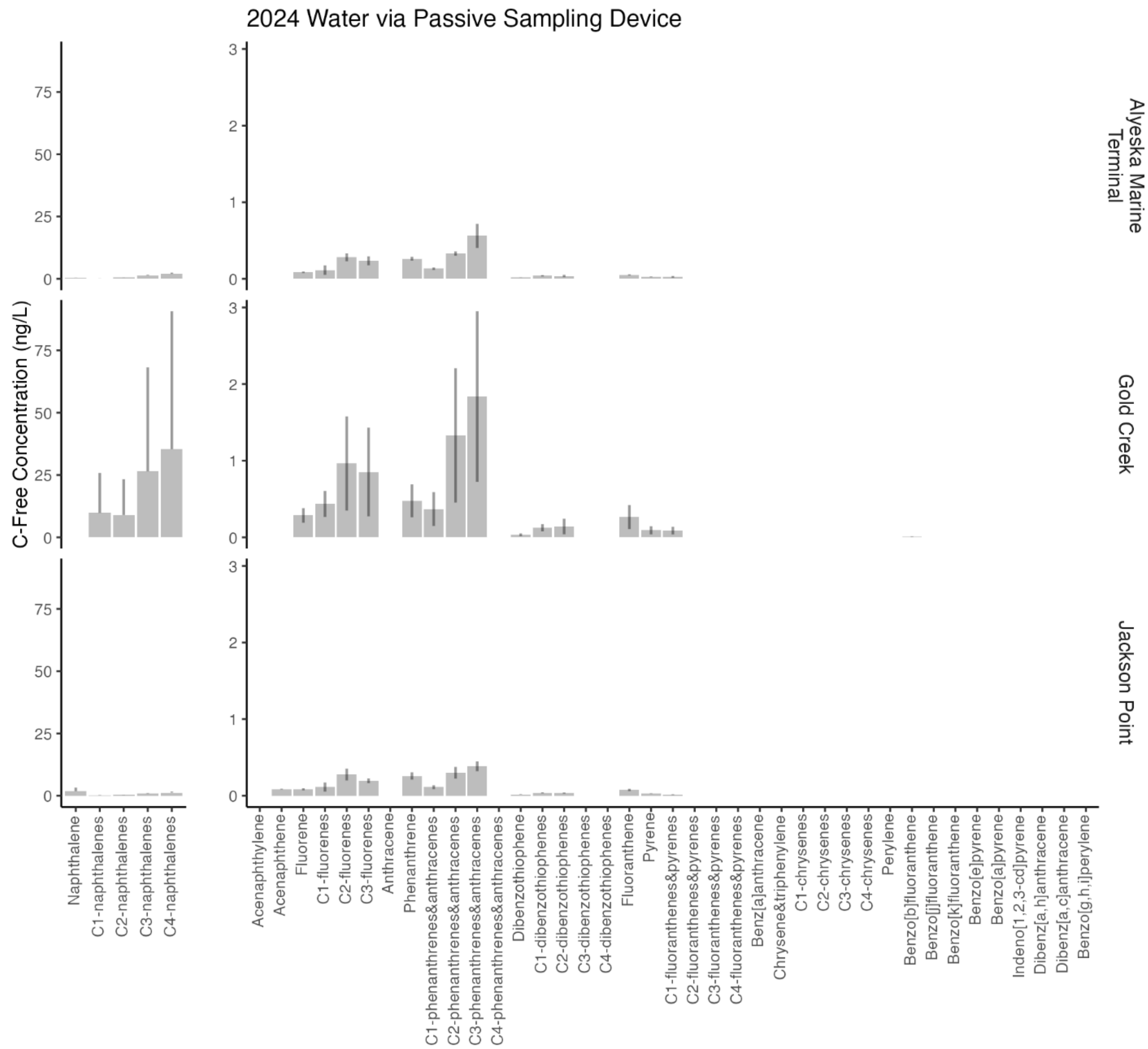

Figure 8. PAH profiles in water sampled via passive sampling devices placed at Valdez Marine Terminal, Gold Creek, and Jackson Point in 2024. Values represent mean ± standard deviation for the three replicates. Note the changes in scale between the Naphthalenes on the left and the other PAHs.

4.3.2. Seawater - Site-Specific Source Identification

Seawater primarily reflects petrogenic sources of hydrocarbons with few higher molecular weight PAHs. One striking observation is the prominent naphthalene peak with ascending alkylation, indicative of a water-washed and weathered petrogenic source in all samples. Several samples were also relatively high in the parent naphthalene compound, indicating a fresh hydrocarbon source. Weak pyrogenic signals are present, and ratios indicate diesel emissions sources across all sites.

4.3.3. Seawater - Historical Perspective

2024 marked one of the lowest years on record for seawater hydrocarbon concentrations around the Valdez Marine Terminal. Gold Creek had uncharacteristically high variability between replicates, leading to the highest average concentration in Gold Creek seawater since passive sampler monitoring began. Higher concentrations of the volatile parent naphthalene and alkylated naphthalenes were seen in some replicates of the Gold Creek sample. These levels could be explained by variability in the recovery efficiencies in the laboratory quantification process. PAH concentrations in passive samplers have remained low since the 2016 inclusion of passive sampling device-derived water concentrations into LTEMP (Figure 9). A peak in PAH levels is seen at the terminal adjacent site, Jackson Point, following the 2020 terminal spill. Passive sampler PAH profiles have also remained consistent, with high naphthalene spikes dominating PAH profiles, as noted in previous LTEMP reports (Payne & Driskell, 2021).

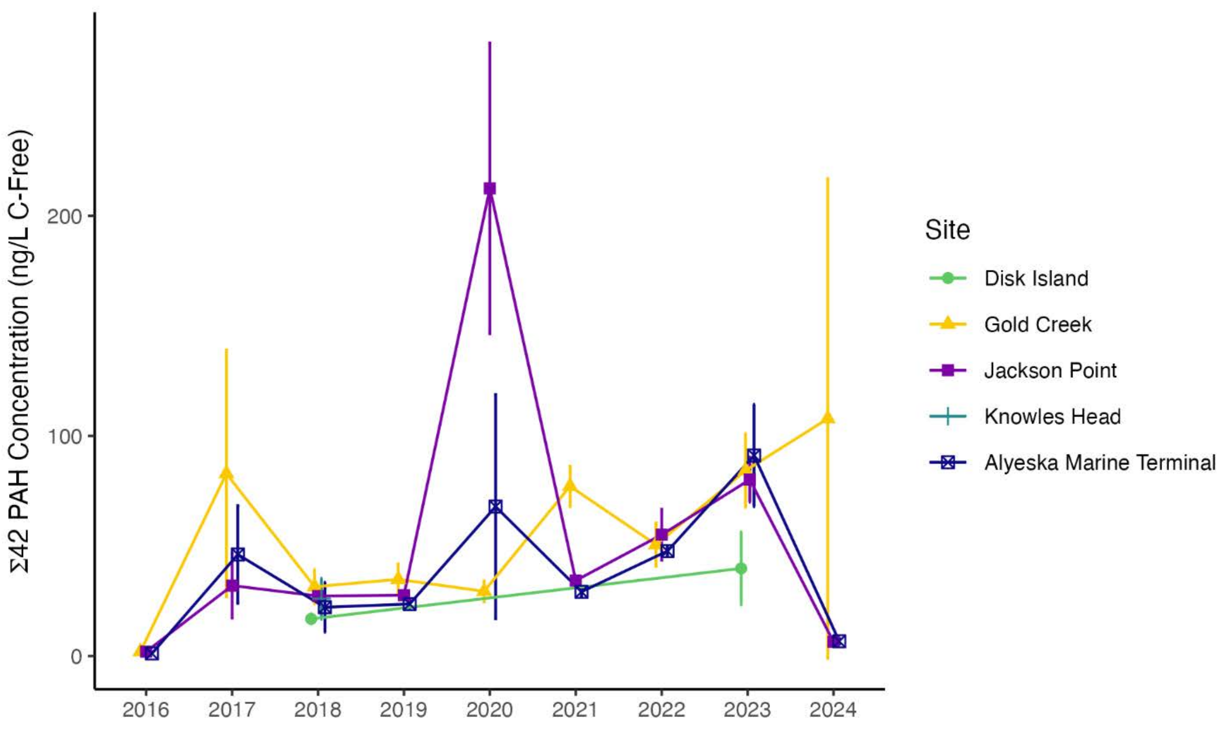

Figure 9. Sum PAH concentrations in seawater derived by passive sampling device at five sites for 2016–2024. Sites are distinguished by color and shape and plotted by mean ± 1 standard deviation. Note that 2016 values only include parent PAHs, no alkylated PAHs were quantified in 2016.

5. Holistic Interpretation

In 2024, we saw agreement on low-level PAHs at similar concentrations across the three standard LTEMP stations in Port Valdez (i.e., Gold Creek, Valdez Marine Terminal, and Jackson Point). While an increase in sum PAH concentrations in sediments was seen at the terminal, which was determined to be of ANS origin, levels are still predicted not to cause adverse effects to marine life. Sites were not ranked similarly by the three matrices (Table 1). Gold Creek has more heterogeneous hydrocarbon dispersion with the greatest variability across all matrices. While Gold Creek mussels exhibit baseline PAH levels, PAHs dissolved in seawater were elevated compared to other sites. The high variability in the passive sampling-derived seawater measurement could explain this difference. Mussel PAH levels found at the Valdez Small Boat Harbor were higher than those of other stations but could not be confirmed by sediment or passive sampler results as these samples were not taken. As each matrix measures a different section of the environmental hydrocarbon load, the differences between matrices are likely not in error but rather reflect differences in the accumulation, degradation, elimination, and dispersion of hydrocarbons across the sites.

As in the expanded site sampling in 2023, the expanded LTEMP sites at Aialik Bay, Windy Bay, and Shuyak Harbor had average PAH concentrations more similar to those of the Valdez Small Boat Harbor. Notably, these sites had high variability between samples, so interpreting these relatively elevated hydrocarbon levels was challenging. As mentioned, Windy Bay had a noticeably different intertidal community, with few mussels, than other LTEMP sampling locations. Understanding the background and current use of these sites, such as historic logging regions or high cruise boat traffic, provides context to these findings, highlighting the importance of maintaining LTEMP sampling over time and space.

Table 1. A tabular visualization of the calculated mean sum PAH concentrations and variability between replicates for all sites sampled in the 2024 LTEMP campaign across the three sediment, mussel tissue, and seawater matrices. Red colors indicate higher values, and blue colors indicate lower values relative to the measurements made in 2024 in that matrix. The relative standard deviation (rSTD) was calculated using the standard deviation divided by the mean sum PAH measurement, displayed as the scaled, yellow horizontal bar plots. Units for sum PAH measurements are ng/g dry weight, ng/g wet weight, and ng/L for the sediments, tissues, and seawater, respectively.

	Sediment		Tissue		Seawater	
2024 Sampled Site	**∑ PAH**	**rSTD**	**∑ PAH.**	**rSTD.**	**.∑ PAH**	**.rSTD**
Alyeska Marine Terminal	159.6	0.1	6.0	0.03	6.7	0.2
Gold Creek	26.4	0.2	4.3	0.08	107.9	1.0
Jackson Point			15.1	0.03	6.4	0.3
Valdez Small Boat Harbor			39.1	0.04		
Aialik Bay			17.8	0.04		
Windy Bay			24.2	0.04		
Shuyak Harbor			15.0	0.04		

The ubiquity of hydrocarbons in the environment complicates tracing sources, understanding ecotoxic 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, complicating identifying the sources. Passive sampling devices are designed to complement the biological and toxicological interpretations by measuring just the dissolved compounds available to aquatic organisms (the bioavailable fraction) but are not well suited for hydrocarbon forensics. The forensic agreement between the 2024 samples is a mixed source petrogenic signal closer to the terminal and the pyrogenic signal of stations further away. This is consistent with the forensic determinations made in the last 5 years. Again, strong pyrogenic and mixed sources contribute to blue mussel hydrocarbon profiles at the Valdez Small Boat Harbor. As blue mussel tissues did not provide robust forensic data (e.g., few biomarkers of detection), the interpretation of the expanded LTEMP sampling locations is limited. Further analysis using available data is possible.

The ecotoxicological risk to organisms from the hydrocarbon levels present in the sediments, mussel tissue, and dissolved in the water from 2024 was low. Previous work focusing on how low levels of hydrocarbon exposure can influence ecologically and commercially important fish species in Prince William Sound has found profound effects on heart development (Incardona et al., 2021). Recent herring research reveals that analytical chemistry with detection levels in the sub parts per billion level (ng/g) is not sensitive enough to distinguish between exposure and background concentrations in water or embryo tissue even when crude oil-induced effects on heart development and PAH-induced enzymatic response were detected (Incardona et al., 2023). Instead, enzymatic induction related to nominal crude oil exposure (e.g., CYP1A induction) is directly related to cardiac deformities in herring. It may provide a more sensitive assessment of injury at the low end of PAH exposure levels (Incardona et al., 2023).

A Note on Site Selection

A review of original LTEMP documentation (KLI 1993a, 1994) and more recent written reports (Payne & Driskell, 2020, 2018) has shed light on the original site selection criteria (Table 2).

Sites were chosen to fall into one of the following three categories:

1. EVOS oiled sites
2. Sites with active or potential oil pollution-causing activities related to terminal and tanker operations
3. Reference sites to act as background control sites

Additionally, sites must be accessible by boat and skiff for safe sampling, have a robust mussel community, and contain suitable soft bottom sediments at a subtidal depth for sediment sampling (a widespread sampling technique used previously at all sites).

Table 2. Overview of the full suite of LTEMP sampling locations, the original purpose of site selection, and significant notes or events found in the literature supporting that selection. Colors represent categories, with gray indicating the active terminal and tanker sites, pink for EVOS-oiled sites, and blue for non-EVOS-impacted reference sites.

Site	Code	Purpose	1st Year	Significant Events / Notes
Jackson Point	JAC-B | PSD	Active - Terminal, Distance	2016	"Evaluate a potential PAH gradient to either side of the BWTF outfall" – Payne & Driskell 2020
Terminal / Saw Island	AMT-B | SAW-B | PSD	Active - Terminal	1993	Closest mussel bed, multiple terminal spills
Terminal / BWTF Effluent Outfall	AMT-S	Active - Terminal	1993	Outfall of Ballast Water Treatment Facility, multiple terminal spills
Zaikof Bay (Hitchinbrook Entrance)	ZAB1-B | ZAB2-B	Active - Tanker Transport Hazard Area	1999 | 2023	Hinchinbrook Entrance site, moved to a less protected outer bay location in 2023
Knowles Head	KNH-B | PSD	Active -Tanker Anchorage Area	1993	"Clean site" – Payne & Driskell 2020; "Undisturbed Control Site" – Payne & Driskell 2018
Disk Island	DII-B | PSD	EVOS Oiled	1993	"known to have fresh-looking, residual EVOS oil" – Payne & Driskell 2018, confirmed by 2001 sampling - Lindeberg et al., 2018; visible sheen during early survey years
Shuyak Harbor	SHH-B	EVOS Oiled	1993	"Selected as an EVOS oiled site" (KLI 1993, Survey Report), no other reference to oiling found
Sleepy Bay	SLB-B	EVOS Oiled	1993	
Windy Bay	WIB-B	EVOS Oiled	1993	"Windy Bay (WIB) was selected as a heavily-oiled EVOS site on the Kenai Peninsula. Extensive logging in the area was taken into consideration during station selection within the bay; the site was positioned on the southeast end of the bay somewhat removed from the log transfer facility and the most heavily logged areas." (KLI 1994)
Sheep Bay	SHB-B	non-EVOS-impacted control in PWS	1993	
Gold Creek	GOC-S | B | PSD	non-EVOS-impacted control in Port Valdez	1993	"Reference site", several small diesel spills, FW input, upstream mining, 6 km from terminal, "less likely to be affected by AMT [Alyeska Marine Terminal] or tanker operations and because it had also been sampled as part of the AMT permit program in the past" (KIL, 1994)
Aialik Bay	AIB-B	non-EVOS-impacted control in Gulf of AK	1993	2024 observation-lots of large cruise boat and pleasure boat traffic, kayaking groups, camp sites

6. Future Perspective

The 2024 LTEMP sampling for hydrocarbons was complimented by sediment sampling for trace metals. This work will be framed in light of the hydrocarbon findings to assess potential metal accumulation in sediments. Heavy metal monitoring is routinely done in other petroleum and hydrocarbon monitoring efforts, including forensic studies in marine sediments and offshore petroleum industry monitoring efforts, although typically focusing on mercury, lead, cadmium, and barium (e.g., Norwegian Environmental Agency, 2020). The recent 2019 Alaska Department of Environmental Conservation (ADEC) report cites that the principal water quality concerns from the terminal BWTF effluent are zinc, total aromatic hydrocarbons, and whole effluent toxicity (ADEC 2019). The 2024 sediment sampling was accompanied by sediment sampling for 23 metals, and the results are presented in a separate report (Fjord & Fish, 2024b). These results show that four metal levels—aluminum, copper, iron, and vanadium—exceeded protective sediment quality guidelines and are significantly elevated in the terminal sediments compared to Gold Creek.

Frequent reanalysis of LTEMP's aims and methodology is necessary to maintain the utility of such a robust monitoring program even in its 31st year. While maintaining the program's integrity with the three matrix approaches, efforts must be taken to ensure that future monitoring and reporting are conducted to guarantee comparability to previous analyses and utility for future projects. A review of contemporary hydrocarbon biomonitoring study designs confirms the validity of using multiple matrices, including intertidal mussels (Kasiotis & Emmanouil, 2015), sediments, and passive sampling devices with a suite of hydrocarbon (e.g., beyond the 16 EPA parent PAHs), petro-geochemical markers for more definitive forensic determination. These matrices are suitable for trend- and problem-oriented monitoring, the two main objectives of LTEMP (Beyer et al., 2017).

The following represents a list of potential additions, subtractions, and alterations in methodology that could be considered for future LTEMP cycles.

Expand sampling efforts

1. **Add a seawater sample**
   Place a passive sampling device at the Valdez Small Boat Harbor (RED) to allow for direct comparability for mussels sampled from this site during the annual Port Valdez sampling. Considerations must be made to allow for safe vessel traffic.

2. **Increase biological sampling effort**
   From sediment sampling sites, include wild-caught resident fish species (e.g., sculpin) PAH analysis in muscle, liver, and bile.

3. **Gather additional recent sources**

Together with the triannual ANS chemical characterization, include potential sources that have hampered LTEMP's forensic strength, including a new BWTF effluent sample and freshwater running out of Gold Creek.

Increase project visibility

1. **Draft a scientific manuscript**
Pursue scientific publishing for greater visibility and utilization of LTEMP data; abstract already submitted for a poster presentation at the January 2025 Alaska Marine Science Symposium.

2. **Archive data**
Continue to work with data librarians at the National Center for Ecological Analysis & Synthesis (NCEAS) and the Alaska Ocean Observing System (AOOS) for external data management and archival.

3. **Improve program dissemination**
Address broader community concern for local pollution issues using alternative dissemination methods (e.g., short explainer video, updates to the PWSRCAC LTEMP website, popular science articles, participating at community events like the Prince William Sound Natural History Symposium, attending and presenting at relevant conferences, creating educational content). Community needs identified through these outreach projects could be integrated with LTEMP data interpretation and future sampling programs.

4. **Project coordination**
Project awareness and coordination with other EVOS monitoring programs, including lingering oil ADEC projects (GeoSyntec, 2023), Gulf Watch, and other Exxon Valdez Oil Spill Trustee Council (EVOSTC) related programs.

Evaluate specific aspects of LTEMP.

1. **Changes in intertidal community**
Evaluate the suitability of the Windy Bay site, where few blue mussels were found in 2024.

2. **Address high variability in sampling**
Recently, high variability has been observed at remote mussel sampling sites. To counteract the light sampling effort over time, it might be a good idea to increase the sample size at these sites.

7. Conclusion

In the 31st year of the LTEMP run by PWSRCAC, concentration, source, and potential ecotoxicological effects of hydrocarbons were assessed in marine subtidal sediments and Pacific blue mussels, and dissolved in the nearshore waters via passive sampling devices. The hydrocarbon fingerprints in the 2024 samples vary by site, with those at or near the Valdez Marine Terminal revealing ANS crude and its associated products as the primary hydrocarbon source. Hydrocarbons found in Pacific blue mussels from Gold Creek, Aialik Bay, Windy Bay, Shuyak Harbor, and the Valdez Small Boat Harbor cannot be linked directly to the terminal operations. However, these samples revealed various sources, including petroleum and combusted petroleum products. Low potential environmental and toxicological risk is posed by hydrocarbons contributed by the terminal and tankers in 2024. Surprisingly, concentrations of toxic hydrocarbons were similar at the remote site of Windy Bay and the Valdez Small Boat Harbor, a site of high human activity and potential chronic petroleum pollution. Passive sampling devices continue to report low levels of bioavailable hydrocarbons in the water column within Port Valdez.

Since 1993, hydrocarbon concentrations in Prince William Sound have been generally low, with localized spikes corresponding to events like the April 2020 oil spill at the terminal. Following an all-time low in the mid-2010s, hydrocarbon concentrations in sediments and mussels have slowly increased across all sites. However, they are still below any threshold for adverse effects on aquatic life. A 2024 accompanying pilot study on metals accumulated in sediment revealed several metals in terminal sediments that exceeded national protective sediment quality guidelines, thus warranting further investigation. The utility of the LTEMP in maintaining a robust baseline hydrocarbon database continues to be critical in light of rapid environmental change and continued petroleum pollution risk.

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