Briefing for PWSRCAC Board of Directors – January 2025

ACTION ITEM

Sponsor: Danielle Verna and the Scientific Advisory Committee

Project number and name or topic: 9510 - Long-Term Environmental Monitoring Program

1. **Description of agenda item:** The Board is being asked to accept the 2024 Summary Report and Technical Supplement for the Council's Long-Term Environmental Monitoring Program (LTEMP) by Dr. Morgan Bender of Fjord & Fish Sciences, both dated December 2024. The report and technical supplement provide data and results from the 2024 sampling excursions in Port Valdez and the northern Gulf of Alaska coast for LTEMP, now in its 31st year.

The Board is also being asked to accept the 2024 Sediment Metals Report, a pilot study of LTEMP, by Dr. Morgan Bender of Fjord & Fish Sciences, dated December 2024. The report provides a summary of 23 metals analyzed in sediments collected adjacent to the Valdez Marine Terminal and Gold Creek reference site.

2. **Why is this item important to PWSRCAC:** The Oil Pollution Act of 1990 directs PWSRCAC to "devise and manage a comprehensive program of monitoring the environmental impacts of the operations of terminal facilities and crude oil tankers while operating in Prince William Sound" – LTEMP is designed to address this directive. LTEMP results are used to assess the environmental impacts of the Valdez Marine Terminal and the crude oil tankers operating in Prince William Sound, including the long-term impacts of the Exxon Valdez oil spill.

3. **Previous actions taken by the Board on this item:** The Long-Term Environmental Monitoring Program has been conducted by PWSRCAC since 1993, and many actions have been taken by the Board on this item since that time. In the interest of providing recent pertinent information, only the last five years of actions related to LTEMP are presented below. All historic actions pertaining to this agenda item are available for review upon request (for more information contact Danielle Verna).

Meeting	Date	Action
Board	5/2/2019	Authorized contract negotiations with Payne Environmental Consultants for sampling and analytical report work on mussels and sediments to be performed under LTEMP for FY20, at an amount not to exceed $65,866; and authorized contract negotiations with Newfields Environmental Forensics Practice for analytical laboratory work and sample storage to be performed under LTEMP for FY20 at an amount not to exceed $28,506. Authorized contract negotiations with Oregon State University for passive sample device purchase and analytical laboratory work on passive sampling devices to be performed under LTEMP for FY20, at an amount not to exceed $20,590; and authorized contract work to commence prior to the start of FY20, as approximately $20,000 of these funds will need to be expended in May and June 2019 because of the supply prerequisites and sampling timing.

Board	9/19/2019	Accepted the report titled "Long Term Environmental Monitoring Program: 2018 Sampling Results and Interpretations" by Dr. James R. Payne and William B. Driskell, dated July 2019 as meeting the terms of the contract and for distribution to the public.
Board	5/7/2020	Accepted the report titled "Long-Term Environmental Program: 2019 Sampling Results and Interpretations," by Dr. James Payne and William B. Driskell, dated March 2020, as meeting the terms and conditions of contract number 951.20.04, and for distribution to the public.
Board	5/21/2020	Approved the following: Authorizing a contract negotiation with Payne Environmental Consultants Inc., for work to be performed under LTEMP, at an amount not to exceed $115,064. Authorizing a contract negotiation with Newfields Environmental Forensics Practice, for work to be performed under LTEMP, at an amount not to exceed $95,807. Authorizing a contract negotiation with the United States Geological Survey, for work to be performed under LTEMP, at an amount not to exceed $65,371. Authorizing a contract negotiation with Oregon State University, for work to be performed under LTEMP, at an amount not to exceed $22,030. Authorizing a contract work to commence prior to the start of FY2021, as approximately $33,000 of these funds will need to be expended in May and June 2020.
Board	5/6/2021	Accepted the reports titled "Long Term Environmental Monitoring Program: 2020 Sampling Results & Interpretations," by Dr. James R. Payne and William Driskell, dated March 2021 as meeting the terms and conditions of contract 951.21.04, and for distribution to the public.
Board	5/21/2021	Authorized individual contracts with NewFields Environmental Forensics Practice, Oregon State University, and the USGS with the aggregate total not to exceed the amount approved in the final FY2022 LTEMP budget (project #9510) for contract expenses, and delegated authority to the Executive Director to enter into individual contracts with the aforementioned consultants; and authorized that the contract work to commence prior to the start of FY2022 as approximately $30,000 of these funds will need to be expended in May and June 2021.
Board	1/27/2022	Authorized a budget modification, adding $53,880 to Project 9510-Long-Term Environmental Monitoring Program; and authorized a contract negotiation with Owl Ridge Natural Resource Consultants, to complete the LTEMP scope of work in RFP 951.21.06, and with Payne Environmental Consultants, to support Owl Ridge's work, at a total aggregate cost not to exceed $77,000.
Board	6/21/2022	Approved an FY2023 budget modification, adding $6,478 to project #9510 – Long-Term Environmental Monitoring Program, for contract expenses; and, approved a negotiation of a contract change order, for contract #951.22.06, with Owl Ridge Natural Resource Consultants, adding $6,478 for compensation to archive the 1993-2021 LTLEMP data in the Alaska Ocean Observing System.
Board	1/26/2023	Authorized an FY2023 budget modification from the contingency fund to project #9510 – Long Term Environmental Monitoring Program adding $836 for contract expenses and approval of negotiation of a contract change order, for contract #951.22.06, with Owl Ridge Natural Resource Consultants, adding $5,058 for compensation to archive the 1993-2021 LTEMP data in the Alaska Ocean Observing System and extending the term of the contract to March 31, 2023. [Note: This change order would increase the total contract amount to $68,007.]
Board	5/4/2023	Approved the following: a) authorization of individual contracts with Alpha Analytical and Owl Ridge Natural Resource Consultants, Inc. with the aggregate total not to exceed the amount approved in the final FY2024 LTEMP budget (Project #9510) for contract expenses, and b) authorization of contract work to commence prior to the start of the 2024 fiscal year to accommodate timing considerations and purchasing needs. It is estimated that up to $15,000 of the above contract work may be performed before June 30, 2023.

Board	9/19/2024	Authorized a budget modification in the amount of $6,006 from the contingency fund to Project 9510 in the FY2025 budget and authorization for the Executive Director to carry out a corresponding change order to increase Contract 9510.25.06 with Fjord & Fish Sciences in an amount not to exceed $61,731.

4. **Summary of policy, issues, support, or opposition:** None.

5. **Committee Recommendation:** The Scientific Advisory Committee has reviewed the summary report, technical supplement, and the metals report, and recommended the Board accept the material as final, via email poll in December 2024.

6. **Relationship to LRP and Budget:** Work associated with this project was included in the FY2025 budget under contract 9510.25.06 in an amount not to exceed $61,731.

7. **Action Requested of the Board of Directors:** Accept the reports titled “Long-Term Environmental Monitoring Program 2024 Summary Report,” “Long-Term Environmental Monitoring Program 2024 Technical Supplement,” and “Long-Term Environmental Monitoring Program 2024 Sediment Metals Report” by Morgan Bender of Fjord & Fish Sciences dated December 2024, as meeting the terms and conditions of contract number 9510.25.06, and for distribution to the public.

8. **Alternatives:** None.

9. **Attachments:**

A) Long-Term Environmental Monitoring Program 2024 Summary Report
B) Long-Term Environmental Monitoring Program 2024 Technical Supplement
C) Long-Term Environmental Monitoring Program 2024 Sediment Metals Report

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fjord & fish sciences

December 2024

Final

2024 Summary Report

Long-Term Environmental Monitoring Program

PREPARED FOR

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"The opinions expressed in this PWSRCAC commissioned report are not necessarily those of PWSRCAC. PWSRCAC Contract #9510.25.06."

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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

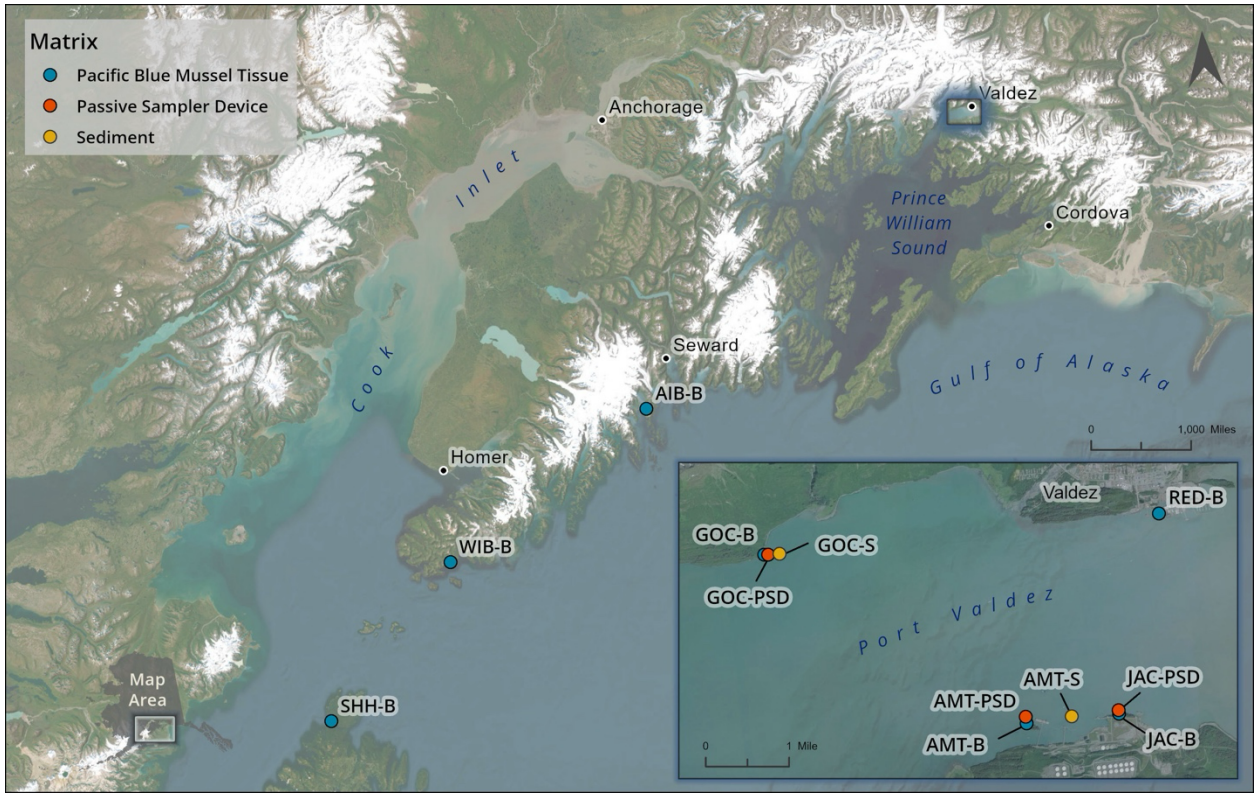

Figure 1. Long-Term Environmental Monitoring Program sites from the 2024 campaign in Port Valdez and the North Gulf of Alaska. The color of the points and labels represent differences in sampling matrices.

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

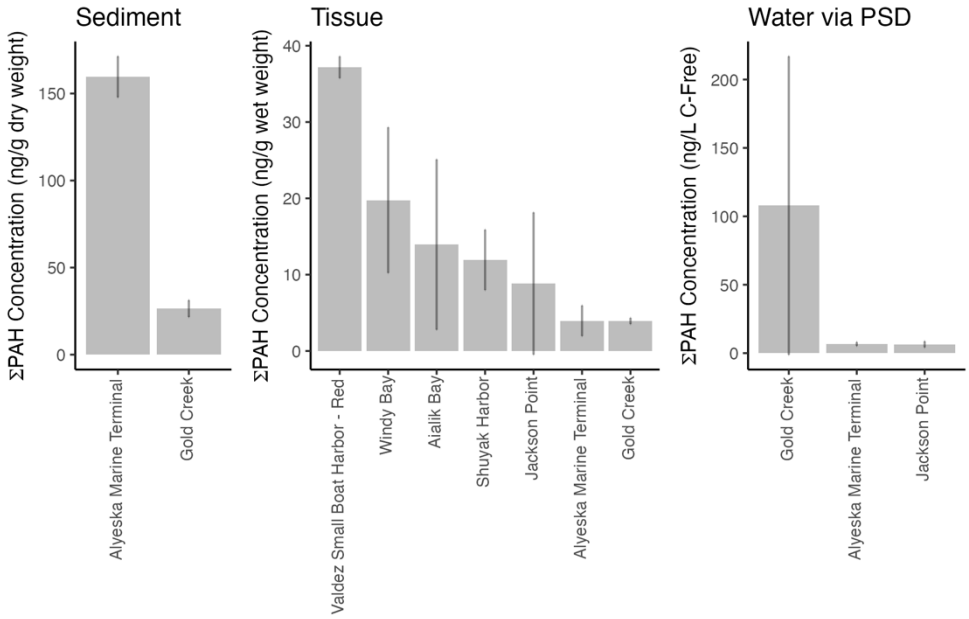

Figure 2. Sum PAH concentrations for 2024 sediments, Pacific blue mussel tissues, and water sampled via passive sampling devices by site plotted at the mean ± 1 standard deviation. Note the unit difference between matrices (i.e., parts per billion for sediments and mussel tissues, and parts per trillion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

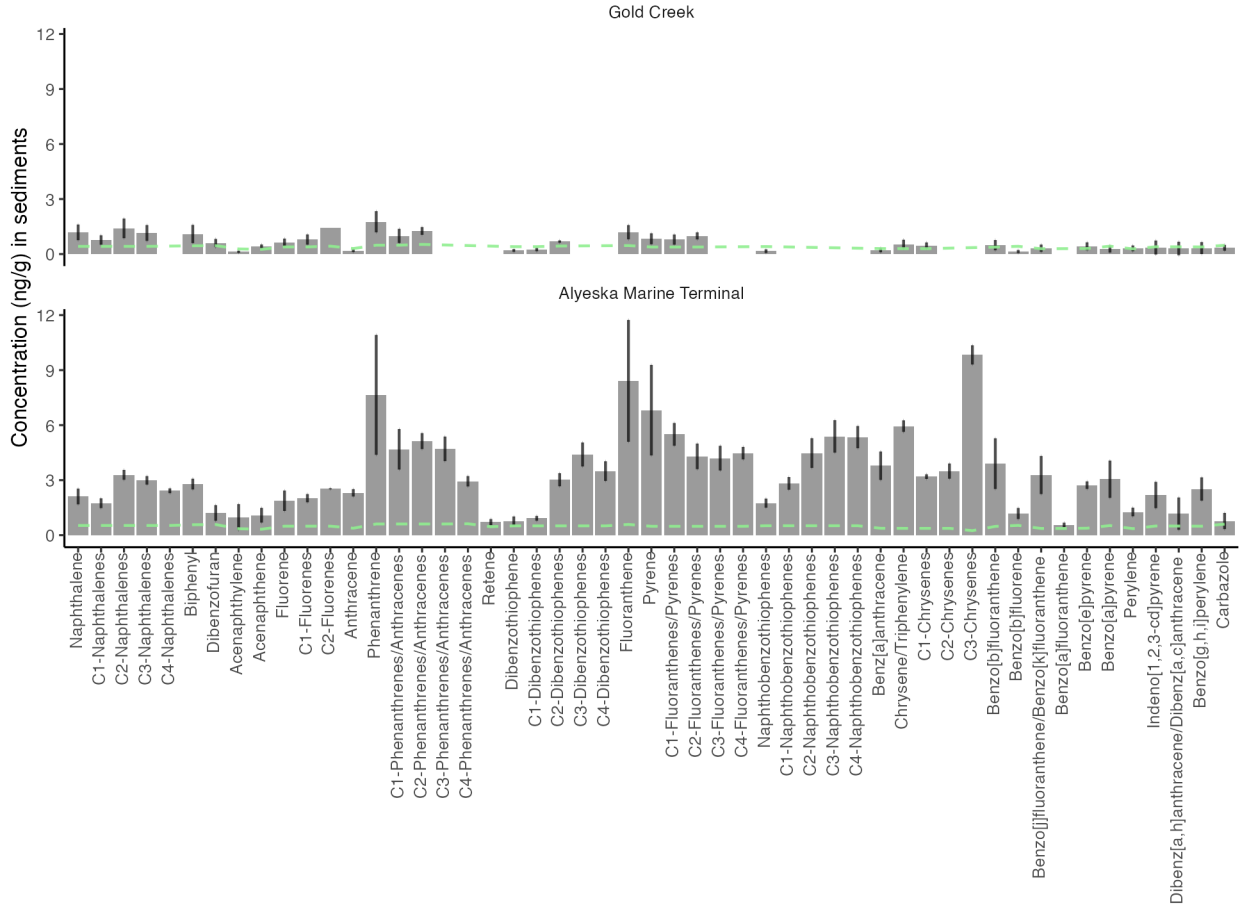

Figure 3. 2024 PAH profiles from sediments sampled at Gold Creek and the terminal site plotted as the mean ± 1 standard deviation for the three replicate samples. A dashed, green line indicated the analyte-specific method detection limit.

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

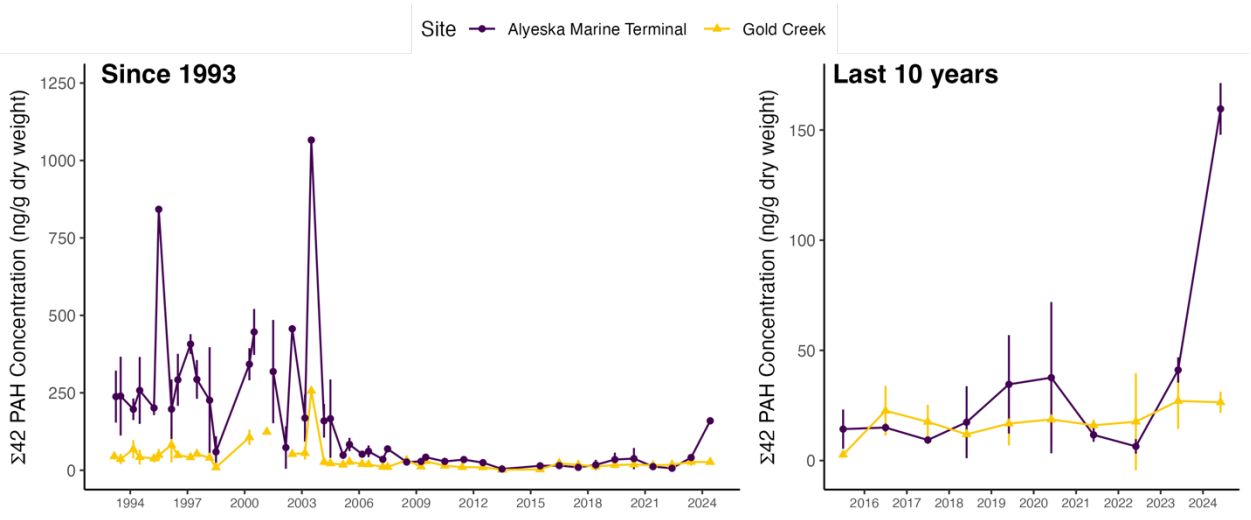

Figure 4. Sum PAH concentrations in sediments over the duration of LTEMP (left panel) and the most recent decade (right panel). Note the differences in scale. Colors and shapes indicate the sampling site; mean values ± 1 standard deviation are plotted for each sampling event.

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).

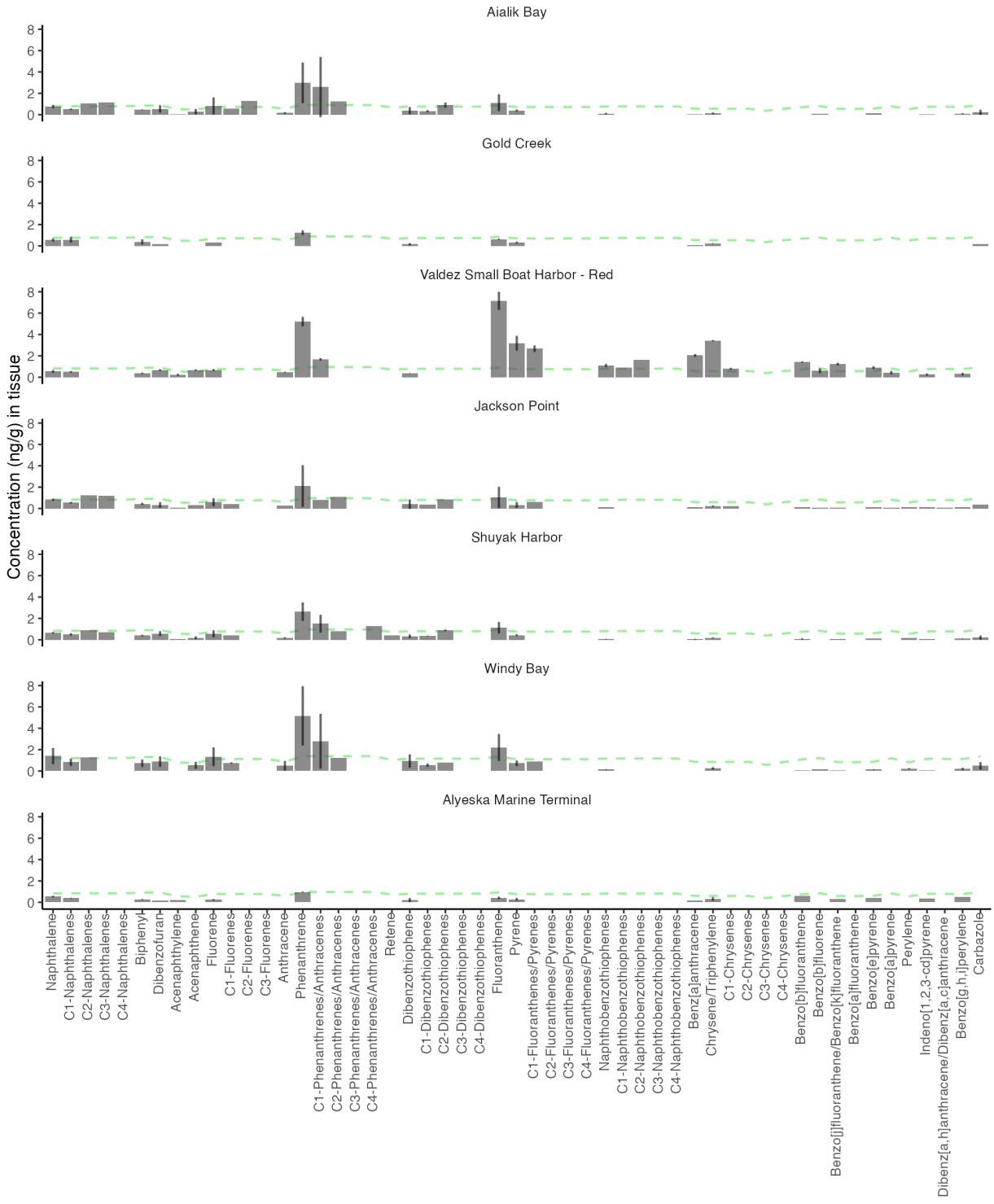

Figure 5. 2024 PAH profiles from Pacific blue mussels plotted as the mean ± 1 standard deviation for the three replicate samples. A dashed, green line indicates the analyte-specific method detection limit.

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.

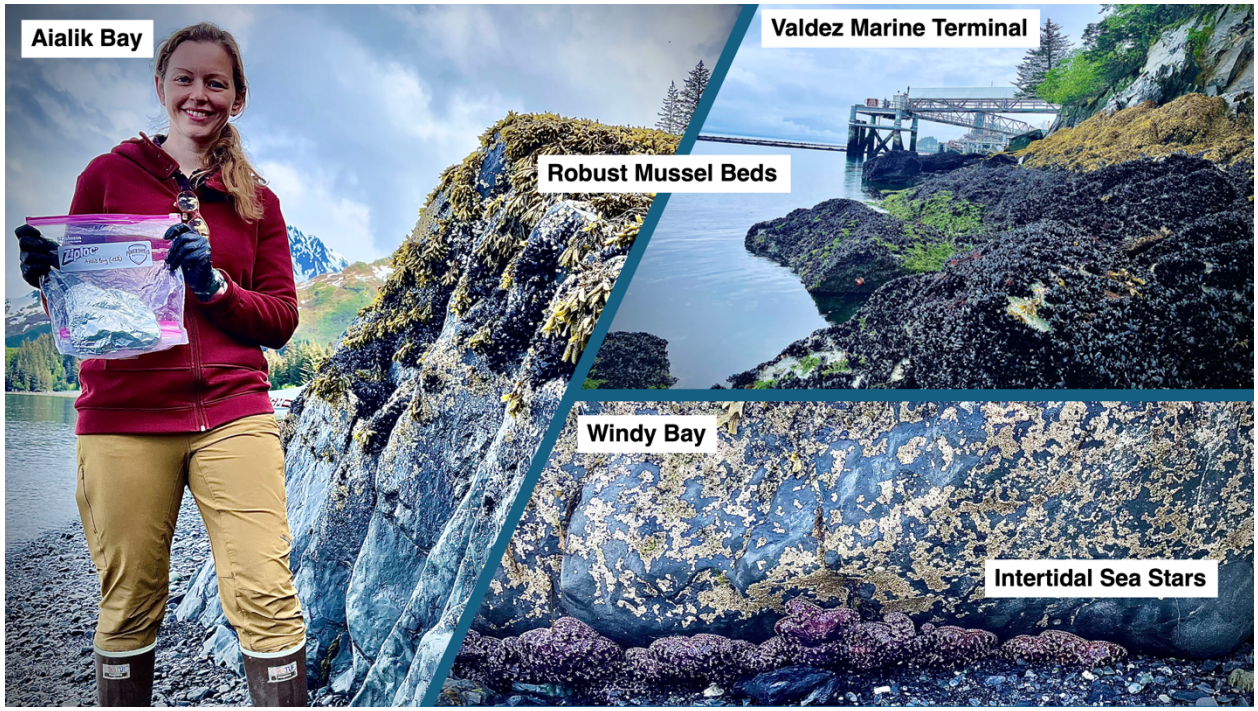

Figure 6. Examples of 2024 mussel sampling sites with Danielle Verna sampling a mussel-covered boulder in Aialik Bay (left), the mussel-covered rocks near the Valdez Marine Terminal at Saw Island (top right), and numerous purple sea stars (likely *Pisaster ochraceus*) in the absence of robust mussel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

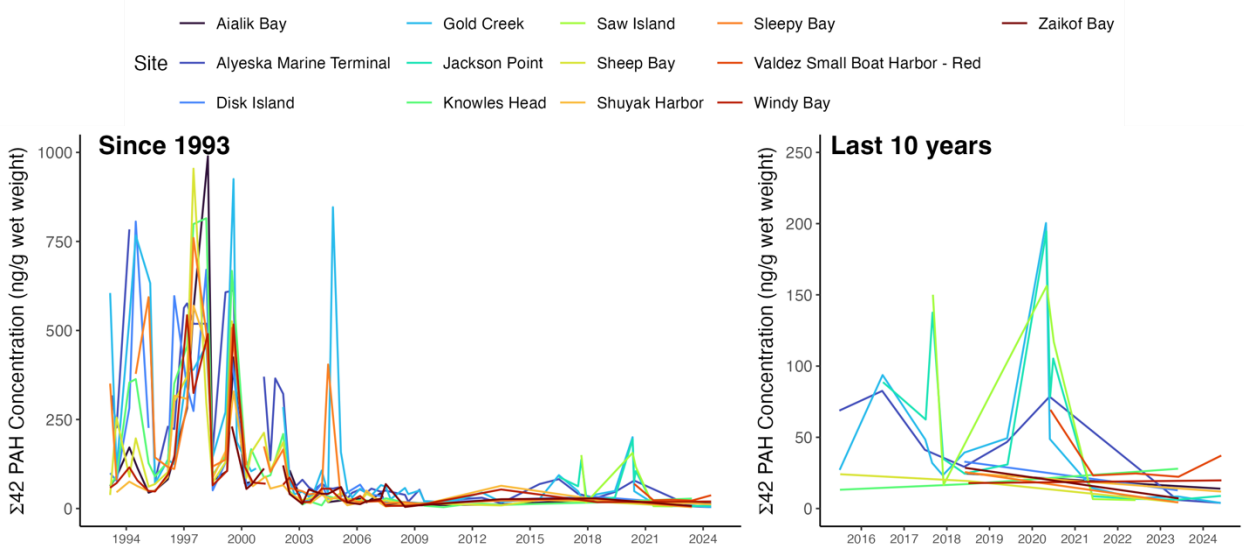

Figure 7. Sum PAH concentrations in Pacific blue mussel tissue (left) over the entire duration of the LTEMP; note concentrations > 1000 ng/g wet weight (i.e., known spill events) were removed for clarity - for reference, (e.g., max post-spill concentration >200 000 ng/g wet weight), and (right) the last 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).

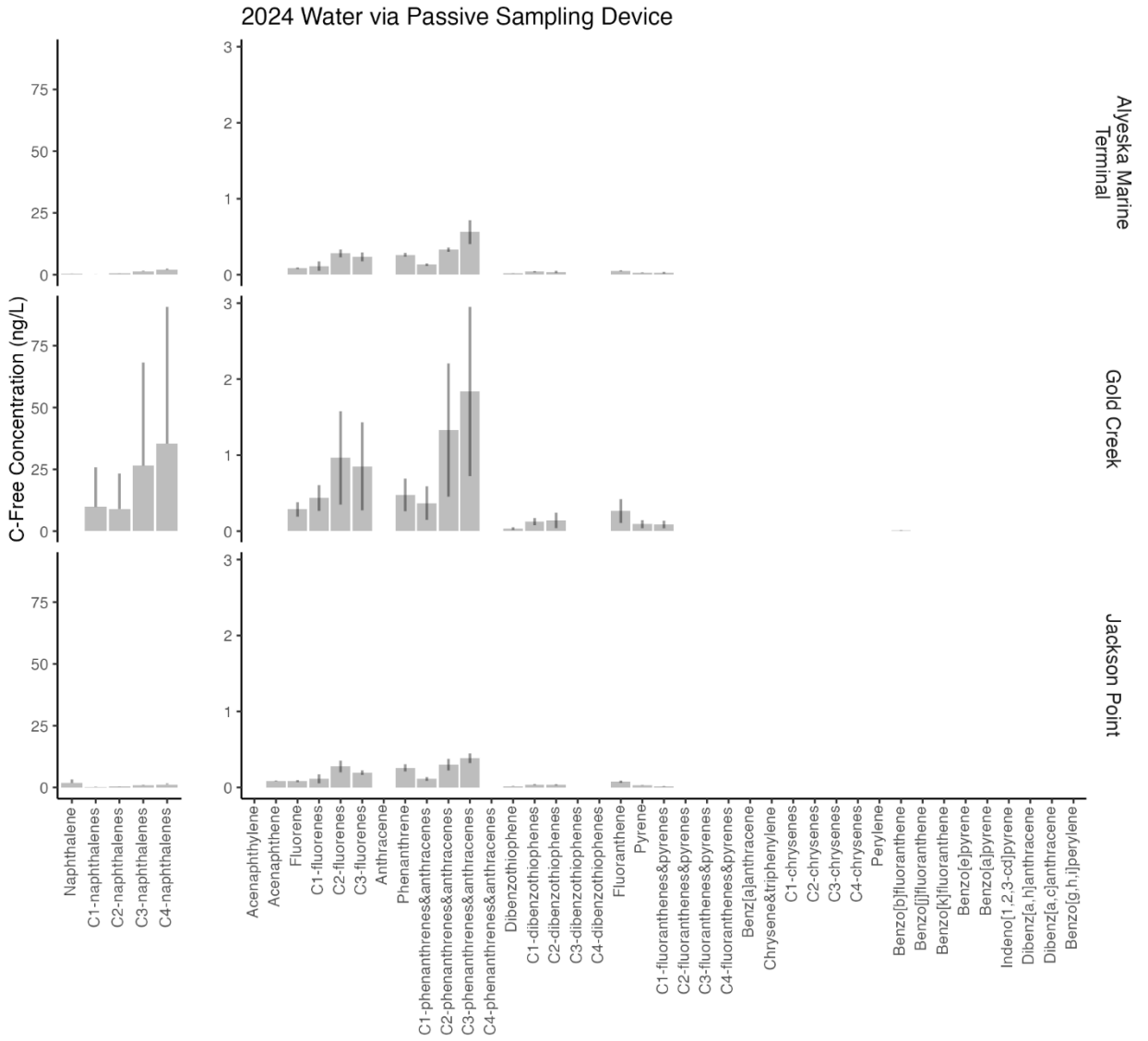

Figure 8. PAH profiles in water sampled via passive sampling devices placed at Valdez Marine Terminal, Gold Creek, and Jackson Point in 2024. Values represent mean ± standard deviation for the three replicates. Note the changes in scale between the Naphthalenes on the left and the other PAHs.

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).

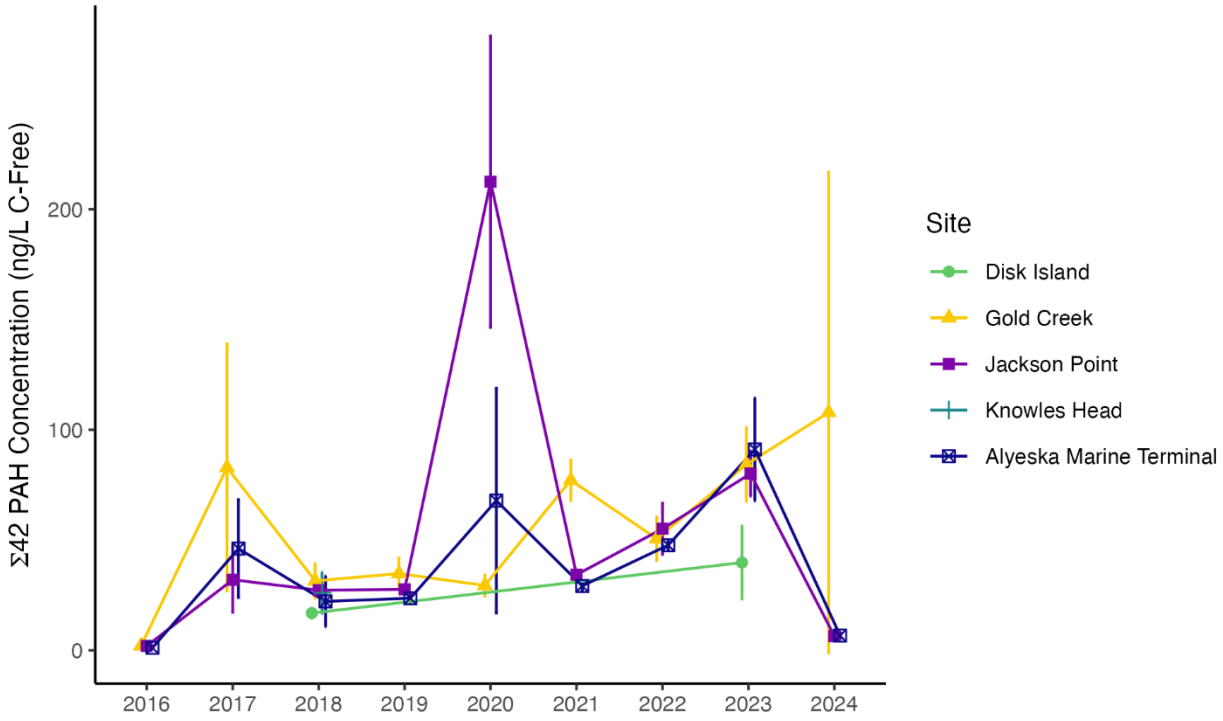

Figure 9. Sum PAH concentrations in seawater derived by passive sampling device at five sites for 2016–2024. Sites are distinguished by color and shape and plotted by mean ± 1 standard deviation. Note that 2016 values only include parent PAHs, no alkylated PAHs were quantified in 2016.

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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Long-Term Environmental Monitoring Program

PREPARED FOR

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"The opinions expressed in this PWSRCAC commissioned report are not necessarily those of PWSRCAC. PWSRCAC Contract #9510.25.06."

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ACRONYMS AND ABBREVIATIONS

°C	Degrees Celsius
AIB	Aialik Bay
AMT	Alyeska Marine Terminal [officially known as the Valdez Marine Terminal]
ANS	Alaska North Slope [Crude Oil]
BWTF	Ballast Water Treatment Facility
cm	Centimeter
CV	Calibration Verification
DII	Disk Island
DQO	Data Quality Objective
EPA	U.S. Environmental Protection Agency
FID	Flame Ionization Detector [FID chromatogram]
FSES	Food Safety and Environmental Stewardship [Oregon State University lab]
GC/MS	Gas Chromatography/Mass Spectrometry
GOC	Gold Creek
HOT	Site of the April 2020 oil spill at the Valdez Marine Terminal
HMW	High Molecular Weight [PAH]
JAC	Jackson Point
KNH	Knowles Head
LMW	Low Molecular Weight [PAH]
LTEMP	Long-Term Environmental Monitoring Program
mL	Milliliter
MDL	Method Detection Limit
ng/g	Nanogram per Gram
OSU	Oregon State University
PAH	Polycyclic Aromatic Hydrocarbons
pg/µL	Picogram per Microliter
PSD	Passive Sampling Device
PWSRCAC	Prince William Sound Regional Citizens' Advisory Council
QC	Quality Control
RED	Valdez Small Boat Harbor Entrance [red light]
SAW	Saw Island
SHB	Sheep Bay
SHH	Shuyak Harbor
SHC	Saturated Hydrocarbons
SIM	Specific Ion Monitoring
SLB	Sleepy Bay
SOP	Standard Operating Procedure
WIB	Windy Bay
ZAB	Zaikof Bay

Executive Summary

This technical supplement contains information on field sampling and analytical and data analysis methods used to monitor and assess environmental hydrocarbons and their potential environmental risk in Prince William Sound Regional Citizens' Advisory Council's (PWSRCAC) Long-Term Environmental Monitoring Program (LTEMP). Here, we have plotted and summarized all sediment, Pacific blue mussel tissue (*Mytilus trossulus*), and passive samples collected in the 2024 campaign in Port Valdez and selected extended sampling sites in the north Gulf of Alaska coast. This document should aid in the assertions made in the 2024 Long-Term Environmental Monitoring Program Summary Report (fjord & fish sciences, 2024).

1. Methods

1.1. Field Methods

1.1.1. Sediments and Mussel Tissue

In 2024, sediment sampling at Valdez Marine Terminal (Alyeska Marine Terminal (AMT)) and Gold Creek (GOC) took place on June 5 (Figure 1; Table 1). Samples were collected using a modified Van Veen grab and deployed to a depth of 65–67 meters (m) at AMT and 26–27 m at GOC from the salmon seining/fishing vessel, Equinox, contracted as a research vessel and fitted with an aluminum davit. For each replicate, a ~250 milliliters (mL) sample of the surface 1–5 centimeters (cm) was collected at each site, placed in a hydrocarbon-free jar, and frozen for hydrocarbons and total organic carbon analysis. Three replicates were taken at each site. Samples were frozen at the end of the sampling day and sent to the lab for analysis within a week of sampling.

The 2024 Port Valdez Pacific blue mussel (*Mytilus trossulus*) sampling was performed at Jackson Point (JAC) and Saw Island (AMT/SAW) on June 5, and at the Valdez Small Boat Harbor – RED (RED) and GOC on June 6. On June 11 and 12, blue mussel samples were collected from Shuyak Harbor (SHH), Aialik Bay (AIB), and Windy Bay (WIB) via float plane out of Homer. Three replicates of ~30 large mussels were collected by hand at each site. Sample replicates are usually taken from multiple locations spaced along 30 m of shoreline. Mussel samples were wrapped in aluminum foil and double bagged in plastic zip-locks, frozen, and shipped to the laboratory, where they remained frozen until analysis. The analytical lab performed dissections of a whole mussel, including all internal organs.

1.1.2. Passive Sampling Devices

In 2024, the Passive sampling devices (PSDs) were collected on June 5 at sites JAC and AMT/SAW, and on June 6 from GOC after a May 9 deployment. The PSDs are a low-density polyethylene membrane submerged in shallow water to absorb passing hydrocarbons. The PSD is intended to sample only a fraction of the total hydrocarbon analytes present, namely, freely dissolved compounds and labile complexes that diffuse into the membrane that, for biota, are the most bioavailable hydrocarbons. As a critical part of the method, various deuterated surrogate compounds are pre-infused into the membrane before deployment. This known starting concentration allows the time-integrated back calculation of dissolved chemical concentrations specific to the environmental conditions experienced by the PSDs. The PSDs were deployed in 4–7 m of water, attached to new polypropylene rope with hydrocarbon-free steel cables and shackles, anchored to a concrete cinder block at each location. At each site, three replicates of 5 PSDs were deployed such that they floated approximately 1 m above the seafloor. The PSDs were collected from stations, transferred to hydrocarbon-free Teflon bags, sealed, and stored at room temperature following LTEMP field protocols (2019 LTEMP PSD standard operating procedure (SOP)). A deployment field blank and a retrieval field blank were included in each annual analysis.

Samples were sent to the Oregon State University (OSU) Food Safety and Environmental Stewardship (FSES) lab in Corvallis, Oregon, for analysis and frozen at -20°C upon arrival.

1.2. Analytical Methods

1.2.1. Sediments and Mussel Tissue

Tissue and sediment samples were analyzed for semi-volatiles, biomarkers, and saturated hydrocarbon analytes at Pace Analytical Services (previously Alpha Analytical and NewFields) lab in Mansfield, Massachusetts. Extractions used the ALPHA OP-018 method for tissues and the ALPHA OP-013 method for sediments. Polycyclic aromatic hydrocarbons (PAH), sterane/triterpene petrogeochemical markers, and saturated hydrocarbons (SHC) are quantified as a concentration in the extracted sediments and mussel tissues. Parent PAHs, alkylated PAHs, and petrochemical markers are analyzed using selected ion monitoring gas chromatography/mass spectrometry (SIM GC/MS) via a modified U.S. Environmental Protection Agency (EPA) Method 8270 (aka 8270M). This analysis provides the concentration of 1) approximately 80 PAH, alkylated PAH homologs, individual PAH isomers, and sulfur-containing aromatics, and 2) approximately 50 tricyclic and pentacyclic triterpenes, regular and rearranged steranes, and triaromatic and monoaromatic steroids. Complete lists of PAH, SHC, and petrogeochemical markers are presented in Tables 2-4.

Using a modified EPA Method 8015B, SHC in sediments are quantified as total extractable materials (C9-C44) and as concentrations of n-alkanes (C9-C40) and selected (C15-C20) acyclic isoprenoids (e.g., pristane and phytane). A diluted Alaska North Slope (ANS) crude standard sample, collected in 2020, was run in parallel to sediment samples and used for forensic purposes.

Surrogates are novel or deuterated compounds added in known amounts to each raw sample to assess the efficiency of extraction and analysis by their final percent recovery. Surrogate recoveries are considered acceptable if they are between 50-130%. Surrogate percent recovery concentrations are acceptable across all analytes analyzed. One lab-performance quality control (QC) measure is the EPA-formulated, statistically derived, analyte-specific Method Detection Limit (MDL) that EPA defines as “the minimum measured concentration of a substance that can be reported with 99 percent confidence that the measured concentration is distinguishable from method blank results.” Alpha Analytics Laboratory’s method detection limits (MDLs) for hydrocarbons exceed the performance of most commercial labs and are within the lower detection limits needed for forensic purposes. Duplicate sediment and tissue samples were run for method QC and precision assessment.

1.2.2. Seawater Sampled by Passive Sampling Device

To remove any biofouling (e.g., periphyton or particulates), the PSD strips were cleaned in the laboratory by light scrubbing and sequential washing in 1 N HCl, 18 MΩ*cm water, and twice with isopropanol, then dried. PSDs were extracted twice at room temperature with 200 mL n-hexane before the volume was reduced. 82 PAHs were quantified on a modified

Agilent 7890 gas chromatograph (GC) and Agilent 7000 triple quadrupole mass spectrometer. The internal standard, Perylene-D12, was added to each sample or parallel aliquots of bioassay samples immediately before analyses. Calculating freely dissolved water concentration of organic compounds was done following the lab-specific SOP. Continuing calibration verification (CV) analysis was performed at the start and end of every analytical batch (maximum of 15 samples). CVs met FSES data quality objectives (DQOs) with an average of 98% of the target analytes within 30% of the known value. Instrument blanks were analyzed after each CV, and in all cases, FSES DQOs were met for all target analytes. An over-spike analysis was performed to demonstrate instrument accuracy where the sample was spiked with target compounds post-extraction. The average percent recovery was 92.2%, meeting FSES DQOs.

1.3. Data Analysis

Data analysis and management were done using the R statistical program (R Core Team 2021). Briefly, data were reformatted to allow for individual locations and analytes to be accessed, and analysis nomenclature was reconciled against the historical dataset. All data with concentrations reported as “non-detect” by Alpha Analytics were removed for summary purposes. However, detected values under the method detection concentration were retained if no other issues were reported with the value. Any sample with matrix interference (i.e., “G” lab flag) was removed from the analysis for matrix interference. For sediment analysis, samples with negative detection and matrix interference were plotted for forensic determination. A select group of commonly used analytes was plotted to ease interpretation at the author’s discretion and ordered using previously used LTEMP standards when possible. Method detection limits were plotted for sediment (Figures 2-7) and tissue samples (Figures 8-21). Corrections for dry weight, total organic carbon, and lipid content are reported in the tables and text when appropriate. Data from multiple labs were merged to compare historical data (Auke Bay Lab, NewFields/Alpha Analytical, and GERG).

Passive sampling device data were extracted and merged into a single dataset. Common lab flags were “B” for background correction applied broadly to Naphthalene and Fluorene and “J”, which is close to the detection level and therefore estimated. For summary purposes, all data with concentrations reported as “non-detect” by FSES were not included in summary calculations and figures, though the qualitative data was included in tables for transparency purposes. PAH profiles were plotted for individual replicates for all sites (Figures 22-24).

1.4. Toxicological Interpretations

Multiple avenues were used to investigate the possibility of toxicological effects as no single standard exists, and development in the field of ecotoxicology is rapid. The most commonly accepted method is summing a select group of PAHs. This includes 44, 42, 16, and other specific PAHs, referred to as summed (∑) PAHs due to the various methods used. This metric is similar to the Total PAH metric used before the BP Deepwater Horizon oil spill in 2010, but accounts for the complex mixture and multitude of calculations that can

be used. Calculations were made of the relative proportion on low (2–3 ring) and high (4–6 ring) molecular weight PAHs as well as sum totals of known carcinogenic PAHs (i.e., benzo(a)pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, and indeno(1,2,3-c,d)pyrene).

Furthermore, these values were adjusted for dry and lipid weights for mussel tissues to aid in cross-study comparisons. Sediment values were compared to acute and chronic EPA sediment-quality benchmarks (Table 5), and tissue concentrations were compared against the most recently available published literature and concentration-of-concern guidelines, as appropriate (Table 6). Seawater samples are treated similarly (Table 8). Concentrations were compared to other field measurements across similar environments (sub-arctic, temperate fjord systems), areas with moderate human activity converted for wet or dry weight in tissues as appropriate, other lab studies with analogous aims as LTEMP (e.g., monitoring of ongoing petroleum operations, sublethal effects, chronic exposure).

Saturated hydrocarbons and petrogeochemical biomarkers were not a focus of toxicological interpretations as they are not known to have specific modes of toxic action.

1.5. Source Identification, Petroleum Fingerprinting, and Biomarker Analysis

Source identification through petroleum fingerprinting and petrogeochemical markers analysis was performed using ANS whole crude oil collected in 2020, and was run as laboratory standard with 2024 samples. For accurate comparisons, the ANS chemical profile is displayed for each replicate sediment sample (Figure 2-7). Profiles were scaled to C2-naphthobenzothiophenes for PAHs, T19-hopane for petrogeochemical markers, and n-heptacosane (C27) for saturated hydrocarbons to aid in interpretation. Profiles were qualitatively evaluated for the best match between individual replicates and potential ANS source using practices outlined in previous LTEMP reports (Payne and Driskell 2021; Wang et al. 2014; Stout and Wang 2016). ANS crude oil profile line is shown for illustrative purposes and does not suggest continuity between measured points where an analyte specific result is not available. Biomarkers in tissues were displayed in tabular form as few analytes were detected (Table 8). Common hydrocarbon diagnostic ratios of low and high molecular weight PAHs and petrogeochemical biomarkers were calculated for sediments and tissue samples for quantitative source identification (Table 9).

2. TABLES

Table 1. Long-Term Monitoring Program sites sampled in 2024 for subtidal marine sediments, Pacific blue mussels and deployment/retrieval of the passive sampling devices. Coordinates are displayed in the WGS84 datum.

Site	Latitude	Longitude	Matrix
AMT-S	61.0906	-146.3928	Sediment
GOC-S	61.1242	-146.4906	Sediment
AMT-B	61.0903	-146.4092	Pacific Blue Mussel Tissue
JAC-B	61.0901	-146.3757	Pacific Blue Mussel Tissue
GOC-B	61.1244	-146.4961	Pacific Blue Mussel Tissue
RED-B	61.1237	-146.3532	Pacific Blue Mussel Tissue
AIB-B	59.8792	-149.6569	Pacific Blue Mussel Tissue
WIB-B	59.2189	-151.5186	Pacific Blue Mussel Tissue
SHH-B	58.5017	-152.6250	Pacific Blue Mussel Tissue
GOC-PSD	61.1243	-146.4947	Water via Passive Sampler Device
JAC-PSD	61.0907	-146.3757	Water via Passive Sampler Device
AMT-PSD	61.0914	-146.4092	Water via Passive Sampler Device

Table 2. Analytes quantified in marine subtidal sediments of the 2024 Long-Term Environmental Monitoring Program

Analysis	Analyte
8270E-SIM(M)	cis/trans-Decalin
8270E-SIM(M)	C1-Decalins
8270E-SIM(M)	C2-Decalins
8270E-SIM(M)	C3-Decalins
8270E-SIM(M)	C4-Decalins
8270E-SIM(M)	Naphthalene
8270E-SIM(M)	C1-Naphthalenes
8270E-SIM(M)	C2-Naphthalenes
8270E-SIM(M)	C3-Naphthalenes
8270E-SIM(M)	C4-Naphthalenes
8270E-SIM(M)	2-Methylnaphthalene
8270E-SIM(M)	1-Methylnaphthalene
8270E-SIM(M)	Benzothiophene
8270E-SIM(M)	C1-Benzo(b)thiophenes
8270E-SIM(M)	C2-Benzo(b)thiophenes
8270E-SIM(M)	C3-Benzo(b)thiophenes
8270E-SIM(M)	C4-Benzo(b)thiophenes
8270E-SIM(M)	Biphenyl
8270E-SIM(M)	C26 Tricyclic Terpane-22S (T6b)
8270E-SIM(M)	C26 Tricyclic Terpane-22R (T6c)
8270E-SIM(M)	C28 Tricyclic Terpane-22S (T7)
8270E-SIM(M)	C28 Tricyclic Terpane-22R (T8)
8270E-SIM(M)	C29 Tricyclic Terpane-22S (T9)
8270E-SIM(M)	C29 Tricyclic Terpane-22R (T10)
8270E-SIM(M)	18a-22,29,30-Trisnorneohopane-TS (T11)
8270E-SIM(M)	C30 Tricyclic Terpane-22S
8270E-SIM(M)	C30 Tricyclic Terpane-22R
8270E-SIM(M)	17a(H)-22,29,30-Trisnorhopane-TM
8270E-SIM(M)	17a/b,21b/a 28,30-Bisnorhopane (T14a)
8270E-SIM(M)	17a(H),21b(H)-25-Norhopane (T14b)
8270E-SIM(M)	30-Norhopane (T15)
8270E-SIM(M)	18a(H)-30-Norneohopane-C29Ts (T16)
8270E-SIM(M)	C26,20R+C27,20S TAS
8270E-SIM(M)	C28,20S TAS
8270E-SIM(M)	17a(H)-Diahopane (X)
8270E-SIM(M)	30-Normoretane (T17)
8270E-SIM(M)	18a(H)&18b(H)-Oleananes (T18)
8270E-SIM(M)	Moretane (T20)
8270E-SIM(M)	30-Homohopane-22S (T21)
8270E-SIM(M)	30-Homohopane-22R (T22)
8270E-SIM(M)	Gammacerane/C32-Diahopane
8270E-SIM(M)	30,31-Bishomohopane-22S (T26)
8270E-SIM(M)	30,31-Bishomohopane-22R (T27)
8270E-SIM(M)	30,31-Trishomohopane-22S (T30)
8270E-SIM(M)	30,31-Trishomohopane-22R (T31)
8270E-SIM(M)	Tetrakishomohopane-22S (T32)
8270E-SIM(M)	Tetrakishomohopane-22R (T33)
8270E-SIM(M)	Pentakishomohopane-22S (T34)
8270E-SIM(M)	Pentakishomohopane-22R (T35)
8270E-SIM(M)	13b(H),17a(H)-20S-Diacholestane (S4)
8270E-SIM(M)	13b(H),17a(H)-20R-Diacholestane (S5)
8270E-SIM(M)	13b,17a-20S-Methyldiacholestane (S8)
8270E-SIM(M)	17a(H)20SC27/C29dia
8270E-SIM(M)	17a(H)20rc27/C29dia
8270E-SIM(M)	Unknown Sterane (S18)
8270E-SIM(M)	13a,17b-20S-Ethyldiacholestane (S19)
8270E-SIM(M)	14a,17a-20S-Methylcholestane (S20)
8270E-SIM(M)	14a,17a-20R-Methylcholestane (S24)
8270E-SIM(M)	14a(H),17a(H)-20S-Ethylcholestane (S25)
8270E-SIM(M)	14a(H),17a(H)-20R-Ethylcholestane (S28)
8270E-SIM(M)	14b(H),17b(H)-20R-Cholestane (S14)
8270E-SIM(M)	14b(H),17b(H)-20S-Cholestane (S15)
8270E-SIM(M)	14b,17b-20R-Methylcholestane (S22)
8270E-SIM(M)	14b,17b-20S-Methylcholestane (S23)
8270E-SIM(M)	14b(H),17b(H)-20R-Ethylcholestane (S26)
8270E-SIM(M)	14b(H),17b(H)-20S-Ethylcholestane (S27)

Table 2. Analytes quantified in marine subtidal sediments of the 2024 Long-Term Environmental Monitoring Program

Analysis	Analyte	Analysis	Analyte
8270E-SIM(M)	C27,20R TAS	8270E-SIM(M)	2-Methylanthracene (2MA)
8270E-SIM(M)	C28,20R TAS	8270E-SIM(M)	9/4-Methylphenanthrene (9MP)
8270E-SIM(M)	3-Methylphenanthrene (3MP)	8270E-SIM(M)	1-Methylphenanthrene
8270E-SIM(M)	1-Methylphenanthrene (1MP)	8270E-SIM(M)	C1-Phenanthrenes/Anthracenes
8270E-SIM(M)	C24 Tetracyclic Terpane (T6A)	8270E-SIM(M)	C2-Phenanthrenes/Anthracenes
8270E-SIM(M)	C26 Tricyclic Terpane-22S (T6B)	8270E-SIM(M)	C3-Phenanthrenes/Anthracenes
8270E-SIM(M)	C26 Tricyclic Terpane-22R (T6C)	8270E-SIM(M)	C4-Phenanthrenes/Anthracenes
8270E-SIM(M)	18A-22,29,30-Trisnorneohopane-TS (T11)	8270E-SIM(M)	Retene
8270E-SIM(M)	17A(H)-22,29,30-Trisnorhopane-Tm (T12)	8270E-SIM(M)	Anthracene
8270E-SIM(M)	17A/B,21B/A 28,30-Bisnorhopane (T14A)	8270E-SIM(M)	Carbazole
8270E-SIM(M)	18A(H)-30-Norneohopane-C29TS (T16)	8270E-SIM(M)	Fluoranthene
8270E-SIM(M)	17A(H)-Diahopane (X)	8270E-SIM(M)	Benzo[b]fluorene
8270E-SIM(M)	Naphthalene-d8	8270E-SIM(M)	Pyrene
8270E-SIM(M)	Phenanthrene-d10	8270E-SIM(M)	C1-Fluoranthenes/Pyrenes
8270E-SIM(M)	2,6-Dimethylnaphthalene	8270E-SIM(M)	C2-Fluoranthenes/Pyrenes
8270E-SIM(M)	Dibenzofuran	8270E-SIM(M)	C3-Fluoranthenes/Pyrenes
8270E-SIM(M)	Acenaphthylene	8270E-SIM(M)	C4-Fluoranthenes/Pyrenes
8270E-SIM(M)	Acenaphthene	8270E-SIM(M)	Naphthobenzothiophenes
8270E-SIM(M)	2,3,5-Trimethylnaphthalene	8270E-SIM(M)	C1-Naphthobenzothiophenes
8270E-SIM(M)	Fluorene	8270E-SIM(M)	C2-Naphthobenzothiophenes
8270E-SIM(M)	C1-Fluorenes	8270E-SIM(M)	C3-Naphthobenzothiophenes
8270E-SIM(M)	C2-Fluorenes	8270E-SIM(M)	C4-Naphthobenzothiophenes
8270E-SIM(M)	C3-Fluorenes	8270E-SIM(M)	Benz[a]anthracene
8270E-SIM(M)	Dibenzothiophene	8270E-SIM(M)	Chrysene/Triphenylene
8270E-SIM(M)	4-Methyldibenzothiophene(4MDT)	8270E-SIM(M)	C1-Chrysenes
8270E-SIM(M)	2/3-Methyldibenzothiophene(2MDT)	8270E-SIM(M)	C2-Chrysenes
8270E-SIM(M)	1-Methyldibenzothiophene(1MDT)	8270E-SIM(M)	C3-Chrysenes
8270E-SIM(M)	C1-Dibenzothiophenes	8270E-SIM(M)	C4-Chrysenes
8270E-SIM(M)	C2-Dibenzothiophenes	8270E-SIM(M)	Benzo[b]fluoranthene
8270E-SIM(M)	C3-Dibenzothiophenes	8270E-SIM(M)	Benzo[j]fluoranthene/Benzo[k]fluoranthene
8270E-SIM(M)	C4-Dibenzothiophenes	8270E-SIM(M)	Benzo[a]fluoranthene
8270E-SIM(M)	Phenanthrene	8270E-SIM(M)	Benzo[e]pyrene
8270E-SIM(M)	3-Methylphenanthrene	8270E-SIM(M)	Benzo[a]pyrene
8270E-SIM(M)	2-Methylphenanthrene (2MP)	8270E-SIM(M)	Perylene

Table 2. Analytes quantified in marine subtidal sediments of the 2024 Long-Term Environmental Monitoring Program

Analysis	Analyte	Analysis	Analyte
8270E-SIM(M)	Indeno[1,2,3-cd]pyrene	EPA 8015D(M)	Norpristane (1650)
8270E-SIM(M)	Dibenz[a,h]anthracene/Dibenz[a,c]anthracene	EPA 8015D(M)	n-Heptadecane (C17)
8270E-SIM(M)	Benzo[g,h,i]perylene	EPA 8015D(M)	Pristane
8270E-SIM(M)	Hopane (T19)	EPA 8015D(M)	n-Octadecane (C18)
8270E-SIM(M)	C23 Tricyclic Terpane (T4)	EPA 8015D(M)	Phytane
8270E-SIM(M)	C24 Tricyclic Terpane (T5)	EPA 8015D(M)	n-Nonadecane (C19)
8270E-SIM(M)	C25 Tricyclic Terpane (T6)	EPA 8015D(M)	n-Eicosane (C20)
8270E-SIM(M)	C24 Tetracyclic Terpane (T6a)	EPA 8015D(M)	n-Heneicosane (C21)
8270E-SIM(M)	Benzo[a]pyrene-d12	EPA 8015D(M)	n-Docosane (C22)
8270E-SIM(M)	5B(H)Cholane	EPA 8015D(M)	n-Tricosane (C23)
9060A	Total Organic Carbon (Rep1)	EPA 8015D(M)	n-Tetracosane (C24)
9060A	Total Organic Carbon (Rep2)	EPA 8015D(M)	n-Pentacosane (C25)
9060A	Total Organic Carbon (Average)	EPA 8015D(M)	n-Hexacosane (C26)
D6913/D7928	Cobbles	EPA 8015D(M)	n-Heptacosane (C27)
D6913/D7928	% Coarse Gravel	EPA 8015D(M)	n-Octacosane (C28)
D6913/D7928	% Fine Gravel	EPA 8015D(M)	n-Nonacosane (C29)
D6913/D7928	Gravel	EPA 8015D(M)	n-Triacontane (C30)
D6913/D7928	% Coarse Sand	EPA 8015D(M)	n-Hentriacontane (C31)
D6913/D7928	% Medium Sand	EPA 8015D(M)	n-Dotriacontane (C32)
D6913/D7928	% Fine Sand	EPA 8015D(M)	n-Tritriacontane (C33)
D6913/D7928	Sand	EPA 8015D(M)	n-Tetratriacontane (C34)
D6913/D7928	% Silt Fine	EPA 8015D(M)	n-Pentatriacontane (C35)
D6913/D7928	% Clay Fine	EPA 8015D(M)	n-Hexatriacontane (C36)
D6913/D7928	Fines	EPA 8015D(M)	n-Heptatriacontane (C37)
EPA 8015D(M)	Nonane (C9)	EPA 8015D(M)	n-Octatriacontane (C38)
EPA 8015D(M)	Decane (C10)	EPA 8015D(M)	n-Nonatriacontane (C39)
EPA 8015D(M)	Undecane	EPA 8015D(M)	n-Tetracontane (C40)
EPA 8015D(M)	Dodecane (C12)	EPA 8015D(M)	n-Undecane
EPA 8015D(M)	Tridecane	EPA 8015D(M)	Tridecane (C13)
EPA 8015D(M)	2,6,10 Trimethyldodecane (1380)	EPA 8015D(M)	n-Hentatriacontane (C31)
EPA 8015D(M)	n-Tetradecane (C14)	EPA 8015D(M)	Total Petroleum Hydrocarbons (C9-C44)
EPA 8015D(M)	2,6,10-Trimethyltridecane (1470)	EPA 8015D(M)	Total Saturated Hydrocarbons
EPA 8015D(M)	n-Pentadecane (C15)	EPA 8015D(M)	o-terphenyl
EPA 8015D(M)	n-Hexadecane (C16)	EPA 8015D(M)	d50-Tetracosane

Table 3. Analytes quantified in intertidal mussels of the 2024 Long-Term Environmental Monitoring Program

ANALMETH	ANALYTE	ANALMETH	ANALYTE	ANALMETH	ANALYTE
EPA 8015D(M)	Nonane (C9)	EPA 8015D(I	n-Octatriacontane (C38)	8270E-SIM(I	4-Methyldibenzothiophene(4MDT)
EPA 8015D(M)	Decane (C10)	EPA 8015D(I	n-Nonatriacontane (C39)	8270E-SIM(I	2/3-Methyldibenzothiophene(2MDT)
EPA 8015D(M)	Undecane	EPA 8015D(I	n-Tetracontane (C40)	8270E-SIM(I	1-Methyldibenzothiophene(1MDT)
EPA 8015D(M)	Dodecane (C12)	EPA 8015D(I	Total Petroleum Hydrocarbons (C9-C44)	8270E-SIM(I	C1-Dibenzothiophenes
EPA 8015D(M)	Tridecane	EPA 8015D(I	Total Saturated Hydrocarbons	8270E-SIM(I	C2-Dibenzothiophenes
EPA 8015D(M)	2,6,10 Trimethyldodecane (1380)	EPA 8015D(I	d50-Tetracosane	8270E-SIM(I	C3-Dibenzothiophenes
EPA 8015D(M)	n-Tetradecane (C14)	8270E-SIM(	cis/trans-Decalin	8270E-SIM(I	C4-Dibenzothiophenes
EPA 8015D(M)	2,6,10-Trimethyltridecane (1470)	8270E-SIM(	C1-Decalins	8270E-SIM(I	Phenanthrene
EPA 8015D(M)	n-Pentadecane (C15)	8270E-SIM(	C2-Decalins	8270E-SIM(I	3-Methylphenanthrene
EPA 8015D(M)	n-Hexadecane (C16)	8270E-SIM(	C3-Decalins	8270E-SIM(I	2-Methylphenanthrene (2MP)
EPA 8015D(M)	Norpristane (1650)	8270E-SIM(	C4-Decalins	8270E-SIM(I	2-Methylanthracene (2MA)
EPA 8015D(M)	n-Heptadecane (C17)	8270E-SIM(	Naphthalene	8270E-SIM(I	9/4-Methylphenanthrene (9MP)
EPA 8015D(M)	Pristane	8270E-SIM(	C1-Naphthalenes	8270E-SIM(I	1-Methylphenanthrene
EPA 8015D(M)	n-Octadecane (C18)	8270E-SIM(	C2-Naphthalenes	8270E-SIM(I	C1-Phenanthrenes/Anthracenes
EPA 8015D(M)	Phytane	8270E-SIM(	C3-Naphthalenes	8270E-SIM(I	C2-Phenanthrenes/Anthracenes
EPA 8015D(M)	n-Nonadecane (C19)	8270E-SIM(	C4-Naphthalenes	8270E-SIM(I	C3-Phenanthrenes/Anthracenes
EPA 8015D(M)	n-Eicosane (C20)	8270E-SIM(	2-Methylnaphthalene	8270E-SIM(I	C4-Phenanthrenes/Anthracenes
EPA 8015D(M)	n-Heneicosane (C21)	8270E-SIM(	1-Methylnaphthalene	8270E-SIM(I	Retene
EPA 8015D(M)	n-Docosane (C22)	8270E-SIM(	Benzothiophene	8270E-SIM(I	Anthracene
EPA 8015D(M)	n-Tricosane (C23)	8270E-SIM(	C1-Benzo(b)thiophenes	8270E-SIM(I	Carbazole
EPA 8015D(M)	n-Tetracosane (C24)	8270E-SIM(	C2-Benzo(b)thiophenes	8270E-SIM(I	Fluoranthene
EPA 8015D(M)	n-Pentacosane (C25)	8270E-SIM(	C3-Benzo(b)thiophenes	8270E-SIM(I	Benzo[b]fluorene
EPA 8015D(M)	n-Hexacosane (C26)	8270E-SIM(	C4-Benzo(b)thiophenes	8270E-SIM(I	Pyrene
EPA 8015D(M)	n-Heptacosane (C27)	8270E-SIM(	Biphenyl	8270E-SIM(I	C1-Fluoranthenes/Pyrenes
EPA 8015D(M)	n-Octacosane (C28)	8270E-SIM(	2,6-Dimethylnaphthalene	8270E-SIM(I	C2-Fluoranthenes/Pyrenes
EPA 8015D(M)	n-Nonacosane (C29)	8270E-SIM(	Dibenzofuran	8270E-SIM(I	C3-Fluoranthenes/Pyrenes
EPA 8015D(M)	n-Triacontane (C30)	8270E-SIM(	Acenaphthylene	8270E-SIM(I	C4-Fluoranthenes/Pyrenes
EPA 8015D(M)	n-Hentriacontane (C31)	8270E-SIM(	Acenaphthene	8270E-SIM(I	Naphthobenzothiophenes
EPA 8015D(M)	n-Dotriacontane (C32)	8270E-SIM(	2,3,5-Trimethylnaphthalene	8270E-SIM(I	C1-Naphthobenzothiophenes
EPA 8015D(M)	n-Tritriacontane (C33)	8270E-SIM(	Fluorene	8270E-SIM(I	C2-Naphthobenzothiophenes
EPA 8015D(M)	n-Tetratriacontane (C34)	8270E-SIM(	C1-Fluorenes	8270E-SIM(I	C3-Naphthobenzothiophenes
EPA 8015D(M)	n-Pentatriacontane (C35)	8270E-SIM(	C2-Fluorenes	8270E-SIM(I	C4-Naphthobenzothiophenes
EPA 8015D(M)	n-Hexatriacontane (C36)	8270E-SIM(	C3-Fluorenes	8270E-SIM(I	Benz[a]anthracene
EPA 8015D(M)	n-Heptatriacontane (C37)	8270E-SIM(	Dibenzothiophene	8270E-SIM(I	Chrysene/Triphenylene

Table 3. Analytes quantified in intertidal mussels of the 2024 Long-Term Environmental Monitoring Program

ANALMETH	ANALYTE	ANALMETH	ANALYTE	ANALMETH	ANALYTE
8270E-SIM(M)	C1-Chrysenes	8270E-SIM(	18a(H)-30-Norneohopane-C29Ts (T16)	NOAA NOS (	Percent Lipids
8270E-SIM(M)	C2-Chrysenes	8270E-SIM(	17a(H)-Diahopane (X)	2540G	Moisture
8270E-SIM(M)	C3-Chrysenes	8270E-SIM(	30-Normoretane (T17)		
8270E-SIM(M)	C4-Chrysenes	8270E-SIM(	18a(H)&18b(H)-Oleananes (T18)		
8270E-SIM(M)	Benzo[b]fluoranthene	8270E-SIM(	Moretane (T20)		
8270E-SIM(M)	Benzo[j]fluoranthene/Benzo[k]fluoranth	8270E-SIM(	30-Homohopane-22S (T21)		
8270E-SIM(M)	Benzo[a]fluoranthene	8270E-SIM(	30-Homohopane-22R (T22)		
8270E-SIM(M)	Benzo[e]pyrene	8270E-SIM(	Gammacerane/C32-Diahopane		
8270E-SIM(M)	Benzo[a]pyrene	8270E-SIM(	30,31-Bishomohopane-22S (T26)		
8270E-SIM(M)	Perylene	8270E-SIM(	30,31-Bishomohopane-22R (T27)		
8270E-SIM(M)	Indeno[1,2,3-cd]pyrene	8270E-SIM(	30,31-Trishomohopane-22S (T30)		
8270E-SIM(M)	Dibenz[a,h]anthracene/Dibenz[a,c]anthı	8270E-SIM(	30,31-Trishomohopane-22R (T31)		
8270E-SIM(M)	Benzo[g,h,i]perylene	8270E-SIM(	Tetrakishomohopane-22S (T32)		
8270E-SIM(M)	Naphthalene-d8	8270E-SIM(	Tetrakishomohopane-22R (T33)		
8270E-SIM(M)	Phenanthrene-d10	8270E-SIM(	Pentakishomohopane-22S (T34)		
8270E-SIM(M)	Benzo[a]pyrene-d12	8270E-SIM(	Pentakishomohopane-22R (T35)		
8270E-SIM(M)	Hopane (T19)	8270E-SIM(	13b(H),17a(H)-20S-Diacholestane (S4)		
8270E-SIM(M)	C23 Tricyclic Terpane (T4)	8270E-SIM(	13b(H),17a(H)-20R-Diacholestane (S5)		
8270E-SIM(M)	C24 Tricyclic Terpane (T5)	8270E-SIM(	13b,17a-20S-Methyldiacholestane (S8)		
8270E-SIM(M)	C25 Tricyclic Terpane (T6)	8270E-SIM(	17a(H)20SC27/C29dia		
8270E-SIM(M)	C24 Tetracyclic Terpane (T6a)	8270E-SIM(	17a(H)20rc27/C29dia		
8270E-SIM(M)	C26 Tricyclic Terpane-22S (T6b)	8270E-SIM(	Unknown Sterane (S18)		
8270E-SIM(M)	C26 Tricyclic Terpane-22R (T6c)	8270E-SIM(	13a,17b-20S-Ethyldiacholestane (S19)		
8270E-SIM(M)	C28 Tricyclic Terpane-22S (T7)	8270E-SIM(	14a,17a-20S-Methylcholestane (S20)		
8270E-SIM(M)	C28 Tricyclic Terpane-22R (T8)	8270E-SIM(	14a,17a-20R-Methylcholestane (S24)		
8270E-SIM(M)	C29 Tricyclic Terpane-22S (T9)	8270E-SIM(	14a(H),17a(H)-20S-Ethylcholestane (S25)		
8270E-SIM(M)	C29 Tricyclic Terpane-22R (T10)	8270E-SIM(	14a(H),17a(H)-20R-Ethylcholestane (S28)		
8270E-SIM(M)	18a-22,29,30-Trisnorneohopane-TS (T1:	8270E-SIM(	14b(H),17b(H)-20R-Cholestane (S14)		
8270E-SIM(M)	C30 Tricyclic Terpane-22S	8270E-SIM(	14b(H),17b(H)-20S-Cholestane (S15)		
8270E-SIM(M)	C30 Tricyclic Terpane-22R	8270E-SIM(	14b,17b-20R-Methylcholestane (S22)		
8270E-SIM(M)	17a(H)-22,29,30-Trisnorhopane-TM	8270E-SIM(	14b,17b-20S-Methylcholestane (S23)		
8270E-SIM(M)	17a/b,21b/a 28,30-Bisnorhopane (T14a)	8270E-SIM(	14b(H),17b(H)-20R-Ethylcholestane (S26)		
8270E-SIM(M)	17a(H),21b(H)-25-Norhopane (T14b)	8270E-SIM(	14b(H),17b(H)-20S-Ethylcholestane (S27)		
8270E-SIM(M)	30-Norhopane (T15)	8270E-SIM(	5B(H)Cholane		

Table 4. Analytes quantified in seawater by passive sampling device of the 2024 Long-Term Environmental Monitoring Program

Analysis Method	Analytes
GC-MS/MS	1,2-dimethylnaphthalene
GC-MS/MS	1,4-dimethylnaphthalene
GC-MS/MS	1,5-dimethylnaphthalene
GC-MS/MS	1,6and1,3-Dimethylnaphthalene
GC-MS/MS	1,8-dimethylnaphthalene
GC-MS/MS	1-methylnaphthalene
GC-MS/MS	1-methylphenanthrene
GC-MS/MS	1-methylpyrene
GC-MS/MS	2,3-dimethylanthracene
GC-MS/MS	2,6-diethylnaphthalene
GC-MS/MS	2,6-dimethylnaphthalene
GC-MS/MS	2-ethylnaphthalene
GC-MS/MS	2-methylanthracene
GC-MS/MS	2-methylnaphthalene
GC-MS/MS	2-methylphenanthrene
GC-MS/MS	3,6-dimethylphenanthrene
GC-MS/MS	5-methylchrysene
GC-MS/MS	6-methylchrysene
GC-MS/MS	7,12-dimethylbenz[a]anthracene
GC-MS/MS	9,10-dimethylanthracene
GC-MS/MS	9-methylanthracene
GC-MS/MS	Acenaphthene
GC-MS/MS	Acenaphthylene
GC-MS/MS	Anthanthrene
GC-MS/MS	Anthracene
GC-MS/MS	Benz[a]anthracene
GC-MS/MS	Benz[j]and[e]aceanthrylene
GC-MS/MS	Benzo[a]chrysene
GC-MS/MS	Benzo[a]fluorene
GC-MS/MS	Benzo[a]pyrene
GC-MS/MS	Benzo[b]fluoranthene
GC-MS/MS	Benzo[b]fluorene
GC-MS/MS	Benzo[b]perylene
GC-MS/MS	Benzo[c]fluorene

Analysis Met	Analytes
GC-MS/MS	Benzo[e]pyrene
GC-MS/MS	Benzo[ghi]perylene
GC-MS/MS	Benzo[j]fluoranthene
GC-MS/MS	Benzo[k]fluoranthene
GC-MS/MS	Chrysene
GC-MS/MS	Coronene
GC-MS/MS	Cyclopenta[cd]pyrene
GC-MS/MS	Dibenzo[a,e]fluoranthene
GC-MS/MS	Dibenzo[a,e]pyrene
GC-MS/MS	Dibenzo[a,h]anthracene
GC-MS/MS	Dibenzo[a,h]pyrene
GC-MS/MS	Dibenzo[a,i]pyrene
GC-MS/MS	Dibenzo[a,l]pyrene
GC-MS/MS	Dibenzo[e,l]pyrene
GC-MS/MS	Dibenzothiophene
GC-MS/MS	Fluoranthene
GC-MS/MS	Fluorene
GC-MS/MS	Indeno[1,2,3-cd]pyrene
GC-MS/MS	Naphthalene
GC-MS/MS	Naphtho[1,2-b]fluoranthene
GC-MS/MS	Naphtho[2,3-a]pyrene
GC-MS/MS	Naphtho[2,3-b]fluoranthene
GC-MS/MS	Naphtho[2,3-e]pyrene
GC-MS/MS	Naphtho[2,3-j]andNaphtho[1,2-k]fluoranthene
GC-MS/MS	Naphtho[2,3-k]fluoranthene
GC-MS/MS	Perylene
GC-MS/MS	Phenanthrene
GC-MS/MS	Pyrene
GC-MS/MS	Retene
GC-MS/MS	Triphenylene
GC-QQQ	C1-benz[a]anthracenes&chrysenes&triphenylenes
GC-QQQ	C1-dibenzothiophenes
GC-QQQ	C1-fluoranthenes&pyrenes
GC-QQQ	C1-fluorenes

Analysis Met	Analytes
GC-QQQ	C1-naphthalenes
GC-QQQ	C1-naphthalenes
GC-QQQ	C1-phenanthrenes&anthracenes
GC-QQQ	C2-benz[a]anthracenes&chrysenes&triphenylenes
GC-QQQ	C2-dibenzothiophenes
GC-QQQ	C2-fluoranthenes&pyrenes
GC-QQQ	C2-fluorenes
GC-QQQ	C2-naphthalenes
GC-QQQ	C2-phenanthrenes&C2-anthracenes
GC-QQQ	C3-dibenzothiophenes
GC-QQQ	C3-fluorenes
GC-QQQ	C3-naphthalenes
GC-QQQ	C3-phenanthrenes&anthracenes
GC-QQQ	C4-naphthalenes
GC-QQQ	C4-phenanthrenes&C4-anthracenes

Table 5. Sediment PAH loads and toxicity comparisons from 2024 samples.

Analyte (ng/g dry weight)	AMT-S-24-1	AMT-S-24-2	AMT-S-24-3	GOC-S-24-1	GOC-S-24-2	GOC-S-24-3	GOC-S-24-2-DUP	Threshold Effect Level (CCME/NOAA)	Acute Potency Divisor (µg/kg Organic Carbon)[5]	Chronic Potency Divisor (µg/kg Organic Carbon)[5]
Naphthalene	2.560	2.060	1.710	1.380	0.937	1.680	0.737	34.6	1600000	385000
C1-Naphthalenes	1.970	1.450	1.810	0.929	0.641	1.030	0.471		1850000	444000
C2-Naphthalenes	3.000	3.340	3.530	1.410	1.100	2.150	0.942		2120000	510000
C3-Naphthalenes	2.740	3.030	3.200	1.370	0.768	1.650	0.815		2420000	581000
C4-Naphthalenes	2.320	2.370	2.570	-	-	-	-		2730000	657000
Acenaphthylene	1.640	1.080	0.226	0.147	0.120	0.187	0.048	5.87	1880000	452000
Acenaphthene	1.390	0.632	1.240	0.516	0.379	0.492	0.292	6.71	2040000	491000
Fluorene	2.120	1.240	2.270	0.720	0.558	0.876	0.407		2240000	538000
C1-Fluorenes	1.790	2.020	2.240	0.953	0.640	1.090	0.486		2540000	611000
C2-Fluorenes	2.540	2.550	2.500	-	-	1.440	-		2850000	686000
C3-Fluorenes	-	-	-	-	-	-	-		3200000	769000
Dibenzothiophene	0.580	0.688	1.050	0.267	0.146	0.252	0.119		-	-
C1-Dibenzothiophenes	0.802	0.891	1.060	0.347	0.178	0.298	0.163		-	-
C2-Dibenzothiophenes	2.880	2.760	3.430	0.636	-	0.726	-		-	-
C3-Dibenzothiophenes	4.090	3.960	5.150	-	-	-	-		-	-
C4-Dibenzothiophenes	3.010	3.400	4.070	-	-	-	-		-	-
Phenanthrene	5.400	6.150	11.400	2.060	1.480	2.400	1.110	86.7	2480000	596000
C1-Phenanthrenes/Anthracenes	3.420	5.460	5.170	1.180	0.698	1.440	0.638		2790000	670000
C2-Phenanthrenes/Anthracenes	4.630	5.340	5.420	1.410	-	1.110	-		3100000	746000
C3-Phenanthrenes/Anthracenes	4.430	4.220	5.470	-	-	-	-		3450000	829000
C4-Phenanthrenes/Anthracenes	2.740	-	3.140	-	-	-	-		3790000	912000
Anthracene	2.220	2.170	2.540	0.180	0.129	0.288	0.129	46.9	2470000	594000
Fluoranthene	4.700	11.100	9.440	1.210	1.070	1.710	0.782	113	2940000	707000
Pyrene	4.150	9.020	7.280	0.801	0.740	1.250	0.546	153	2900000	697000
C1-Fluoranthenes/Pyrenes	5.340	6.180	4.970	0.924	0.606	1.110	0.514		3200000	770000
C2-Fluoranthenes/Pyrenes	3.940	5.100	3.850	0.804	1.230	1.060	0.874		-	-
C3-Fluoranthenes/Pyrenes	3.960	3.680	4.960	-	-	-	-		-	-
C4-Fluoranthenes/Pyrenes	4.460	4.140	4.820	-	-	-	-		-	-
Benz[a]anthracene	4.680	3.310	3.370	0.219	0.160	0.369	0.101	74.8	3500000	841000
Chrysene/Triphenylene	5.630	6.260	5.950	0.515	0.458	0.878	0.302	108	3510000	844000
C1-Chrysenes	3.330	3.080	3.170	0.479	0.336	0.698	0.332		3870000	929000
C2-Chrysenes	3.280	3.230	3.970	-	-	-	-		4200000	1010000
C3-Chrysenes	-	9.460	10.200	-	-	-	-		4620000	1110000
C4-Chrysenes	-	-	-	-	-	-	-		5030000	1210000
Benzo[b]fluoranthene	5.460	3.410	2.830	0.483	0.374	0.870	0.216		4070000	979000
Benzo[j]fluoranthene/ Benzo[k]fluoranthene	4.420	3.030	2.390	0.297	0.200	0.607	0.173		4080000	981000
Benzo[e]pyrene	2.920	2.750	2.510	0.395	0.286	0.736	0.262		4020000	967000
Benzo[a]pyrene	4.210	2.320	2.620	0.182	0.150	0.501	-	88.8	4020000	965000
Indeno[1,2,3-cd]pyrene	3.010	1.680	1.880	0.218	0.147	0.924	0.130		4620000	1110000

Table 5. Sediment PAH loads and toxicity comparisons from 2024 samples.

Analyte (ng/g dry weight)	AMT-S-24-1	AMT-S-24-2	AMT-S-24-3	GOC-S-24-1	GOC-S-24-2	GOC-S-24-3	GOC-S-24-2-DUP	Threshold Effect Level (CCME/NOAA)	Acute Potency Divisor (µg/kg Organic Carbon)[5]	Chronic Potency Divisor (µg/kg Organic Carbon)[5]
Dibenz[a,h]anthracene/ Dibenz[a,c]anthracene	2.190	0.669	0.659	0.122	0.133	0.856	0.099	6.22	4660000	1120000
Benzo[g,h,i]perylene	3.220	1.990	2.340	0.205	0.185	0.811	0.102		4540000	1090000
Total Organic Carbon (Average)	0.485	0.557	0.518	0.472	0.494	0.533	-	-		
Sum 42 PAH (ng/g dry weight)	125.17	135.22	146.41	20.36	13.85	29.49	10.79			
Sum 42 PAH (ng/g DOC corrected)	258.09	242.76	282.64	43.13	28.03	55.33	-			
Sum 16 PAH[1] (ng/g dry weight)	57.00	56.12	58.15	9.26	7.22	14.70	5.17			
Sum low molecular weight PAH[2] (ng/g)	44.91	43.11	54.44	12.26	7.45	15.83	6.08			
Sum high molecular weight PAH[3] (ng/g)	65.98	77.66	74.70	6.46	5.79	11.64	4.17			
% low molecular weight PAH	40%	36%	42%	65%	56%	58%	59%			
% high molecular weight PAH	60%	64%	58%	35%	44%	42%	41%			
Sum of Carcinogenic PAH[4] (ng/g dry weight)	32.820	22.669	22.039	2.241	1.807	5.816	1.123			
Sum of 9 PAHs	37.220	44.000	46.820	5.590	4.519	9.131	3.202	1684		

1- 16 EPA Priority PAHs - naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene , benzo[a]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene, and dibenz[a,h]anthracene

2- Low molecular weight PAHs : napthalenes - phenanthrenes (2-3-ring PAH)

3- High molecular weight PAHs: fluoranthene - benzo (g,h,i)perylene (3-6 ring PAH)

4 - Carcinogenic PAHs: benzo[a]pyrene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene

Table 6. Mussel Tissue PAH loads from 2024 LTEMP samples.

	ANALYTE (ng/g)	RED-B-24-1	RED-B-24-2	RED-B-24-3	JAC-B-24-1	JAC-B-24-2	JAC-B-24-3	AMT-B-24-1	AMT-B-24-2	AMT-B-24-3	GOC-B-24-1	GOC-B-24-2	GOC-B-24-3	SHH-B-24-1
1	Naphthalene	0.526	0.435	0.666	0.909	0.843	0.734	0.603	0.481	0.541	0.655	0.408	0.617	0.606
2	C1-Naphthalenes	0.451	0.478	0.571	0.528	0.613	0.487	0.397	-	0.375	0.821	0.31	0.614	0.394
3	C2-Naphthalenes	-	-	-	1.26	-	-	-	-	-	-	-	-	0.88
4	C4-Naphthalenes	-	-	-	1.17	-	-	-	-	-	-	-	-	0.704
5	C3-Naphthalenes	-	-	-	-	-	-	-	-	-	-	-	-	-
6	Biphenyl	0.324	0.34	0.42	0.528	0.336	0.437	0.24	-	0.286	0.548	0.224	-	0.342
7	Dibenzofuran	0.613	0.651	0.759	0.504	0.158	-	0.14	-	-	-	0.198	-	0.519
8	Acenaphthylene	0.175	0.314	0.202	0.071	-	-	0.189	-	-	-	-	-	0.051
9	Acenaphthene	0.731	0.611	0.66	0.306	-	-	-	-	-	-	-	-	0.33
10	Fluorene	0.763	0.627	0.631	0.841	-	0.334	0.199	-	0.279	-	0.311	-	0.933
11	C1-Fluorenes	-	-	-	0.433	-	-	-	-	-	-	-	-	0.404
12	C2-Fluorenes	-	-	-	-	-	-	-	-	-	-	-	-	-
13	Dibenzothiophene	0.37	0.346	0.357	0.708	-	0.093	-	0.337	0.08	0.177	0.06	0.234	0.51
14	C1-Dibenzothiophenes	-	-	-	0.356	-	-	-	-	-	-	-	-	0.343
15	C2-Dibenzothiophenes	-	-	-	0.871	-	-	-	-	-	-	-	-	0.901
16	C3-Dibenzothiophenes	-	-	-	-	-	-	-	-	-	-	-	-	-
17	C4-Dibenzothiophenes	-	-	-	-	-	-	-	-	-	-	-	-	-
18	Phenanthrene	5.66	4.8	5.16	4.35	0.977	0.979	0.994	0.955	0.933	1.46	1.05	1.24	3.58
19	C1-Phenanthrenes/Anthracenes	1.76	1.57	1.72	0.812	-	-	-	-	-	-	-	-	2.45
20	C3-Phenanthrenes/Anthracenes	-	-	-	1.1	-	-	-	-	-	-	-	-	0.786
21	C2-Phenanthrenes/Anthracenes	-	-	-	-	-	-	-	-	-	-	-	-	-
22	C4-Phenanthrenes/Anthracenes	-	-	-	-	-	-	-	-	-	-	-	-	-
23	Anthracene	0.458	0.498	0.491	0.294	-	-	-	-	-	-	-	-	0.228
24	Fluoranthene	8.01	6.34	7.11	2.17	0.441	0.496	0.534	0.33	0.386	0.667	0.622	0.578	1.71
25	Benzo[b]fluorene	0.802	0.389	0.618	0.067	-	-	-	-	-	-	-	-	-
26	Pyrene	3.96	2.71	2.89	0.626	0.133	0.229	0.37	0.311	0.155	0.311	0.267	0.4	0.458
27	C1-Fluoranthenes/Pyrenes	3.01	2.44	2.57	0.587	-	-	-	-	-	-	-	-	-
28	C2-Fluoranthenes/Pyrenes	-	-	-	-	-	-	-	-	-	-	-	-	-
29	C3-Fluoranthenes/Pyrenes	-	-	-	-	-	-	-	-	-	-	-	-	-
30	Naphthobenzothiophenes	1.25	1.06	1	0.137	-	-	-	-	-	-	-	-	0.078
31	C1-Naphthobenzothiophenes	-	0.905	-	-	-	-	-	-	-	-	-	-	-
32	C2-Naphthobenzothiophenes	-	1.64	-	-	-	-	-	-	-	-	-	-	-
33	Benz[a]anthracene	2.05	1.93	2.16	0.126	-	-	0.171	-	-	-	0.06	-	0.046
34	Chrysene/Triphenylene	3.45	3.46	3.38	0.256	0.165	0.236	0.482	0.278	0.168	0.246	0.233	0.243	0.194
35	C1-Chrysenes	0.873	0.789	0.745	0.235	-	-	-	-	-	-	-	-	-
36	Benzo[b]fluoranthene	1.37	1.41	1.46	0.115	-	-	0.593	-	-	-	-	-	0.061
37	Benzo[j]fluoranthene/Benzo[k]fluoranthene	1.29	1.11	1.31	0.077	-	-	0.319	-	-	-	-	-	-
38	Benzo[e]pyrene	0.983	0.779	0.957	0.112	-	-	0.414	-	-	-	-	-	-
39	Benzo[g,h,i]perylene	0.232	0.248	0.415	0.148	-	-	0.505	-	-	-	-	-	0.114
40	Benzo[a]pyrene	-	0.338	0.528	0.076	-	-	-	-	-	-	-	-	-
41	Indeno[1,2,3-cd]pyrene	-	0.192	0.31	0.118	-	-	0.361	-	-	-	-	-	0.055
42	Carbazole	-	-	-	0.386	-	-	-	-	-	-	0.194	-	0.413
43	Perylene	-	-	-	0.147	-	-	-	-	-	-	-	-	0.168
44	Dibenz[a,h]anthracene/Dibenz[a,c]anthracene	-	-	-	0.087	-	-	-	-	-	-	-	-	-
45	Retene	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 6. Mussel Tissue PAH loads from 2024 LTEMP samples.

ANALYTE (ng/g)	RED-B-24-1	RED-B-24-2	RED-B-24-3	JAC-B-24-1	JAC-B-24-2	JAC-B-24-3	AMT-B-24-1	AMT-B-24-2	AMT-B-24-3	GOC-B-24-1	GOC-B-24-2	GOC-B-24-3	SHH-B-24-1
Percent Lipids (%)	1.64	2.11	2.25	1.54	1.69	1.74	2.04	1.84	1.78	1.92	1.5	2.01	1.81
Moisture (%)	85	85.9	85.5	83	86	85.4	85.3	84.9	85.1	85.8	83.4	84.8	84.5
Sum 42 PAH (ng/g wet weight)	36.55	31.47	34.55	17.02	3.17	3.50	6.13	2.36	2.84	4.16	3.26	3.69	14.15
Sum 42 PAH (ng/g dry weight)	5.48	4.44	5.01	2.89	0.44	0.51	0.90	0.36	0.42	0.59	0.54	0.56	2.19
Sum 42 PAH (ng/g lipid corrected)	2228.90	1491.37	1535.73	1105.26	187.69	200.86	300.54	127.99	159.38	216.67	217.40	183.68	781.88
Sum 16 PAH[1] (ng/g wet weight)	28.68	25.02	27.37	10.57	2.56	3.01	5.32	2.36	2.46	3.34	2.95	3.08	8.37
Sum 16 PAH[1] (ng/g dry weight)	4.30	3.53	3.97	1.80	0.36	0.44	0.78	0.36	0.37	0.47	0.49	0.47	1.30
Sum low molecular weight PAH[2] (ng/g wet weight)	10.52	9.33	10.10	12.07	2.43	2.53	2.38	1.44	2.13	2.94	2.08	2.47	11.35
Sum high molecular weight PAH[3] (ng/g wet weight)	26.03	22.14	24.45	4.95	0.74	0.96	3.75	0.92	0.71	1.22	1.18	1.22	2.81
% low molecular weight PAH	29%	30%	29%	71%	77%	73%	39%	61%	75%	71%	64%	67%	80%
% high molecular weight PAH	71%	70%	71%	29%	23%	27%	61%	39%	25%	29%	36%	33%	20%
Sum of Carcinogenic PAH[4] (ng/g wet weight)	8.16	8.44	9.148	0.855	0.165	0.236	1.926	0.278	0.168	0.246	0.293	0.243	0.356

1 16 EPA Priority PAHs - naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene , be

2 Low molecular weight PAHs : napthalenes - phenanthrenes (2-3-ring PAH)

3 High molecular weight PAHs: fluoranthene - benzo (g,h,i)perylene (3-6 ring PAH)

4 Carcinogenic PAHs: benzo[a]pyrene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene,

Table 6. Mussel Tissue PAH loads from 2024 LTEMP samples.

	ANALYTE (ng/g)	SHH-B-24-2	SHH-B-24-3	AIB-B-24-1	AIB-B-24-2	AIB-B-24-3	WIB-B-24-1	WIB-B-24-2	WIB-B-24-3
1	Naphthalene	0.635	0.716	0.915	0.622	0.739	0.827	1.13	2.25
2	C1-Naphthalenes	0.565	0.563	0.566	0.454	0.516	0.589	0.709	1.2
3	C2-Naphthalenes	-	-	1.04	-	-	-	1.3	-
4	C4-Naphthalenes	-	-	1.16	-	-	-	-	-
5	C3-Naphthalenes	-	-	-	-	-	-	-	-
6	Biphenyl	0.398	0.453	0.456	0.479	0.438	0.514	0.578	1.12
7	Dibenzofuran	0.822	0.396	0.927	0.32	0.377	0.343	1.23	1.09
8	Acenaphthylene	-	-	0.051	-	-	-	-	-
9	Acenaphthene	0.104	0.146	0.556	0.153	0.14	0.174	0.73	0.701
10	Fluorene	0.354	0.395	1.73	0.342	0.4	0.348	1.92	1.75
11	C1-Fluorenes	-	-	0.568	-	-	-	0.718	0.792
12	C2-Fluorenes	-	-	1.31	-	-	-	-	-
13	Dibenzothiophene	0.234	0.265	0.751	0.164	0.227	0.235	1.22	1.35
14	C1-Dibenzothiophenes	0.369	0.349	0.412	0.245	0.323	0.378	0.607	0.654
15	C2-Dibenzothiophenes	0.816	0.95	1.15	0.698	0.846	0.81	-	-
16	C3-Dibenzothiophenes	-	-	-	-	-	-	-	-
17	C4-Dibenzothiophenes	-	-	-	-	-	-	-	-
18	Phenanthrene	1.9	2.42	5.15	1.76	2.03	1.97	6.76	6.75
19	C1-Phenanthrenes/Anthracenes	1.14	0.938	5.83	0.954	0.97	0.981	13	4.59
20	C3-Phenanthrenes/Anthracenes	-	-	1.24	-	-	-	1.21	-
21	C2-Phenanthrenes/Anthracenes	-	-	-	-	-	-	-	-
22	C4-Phenanthrenes/Anthracenes	1.26	-	-	-	-	-	-	-
23	Anthracene	0.135	0.162	0.232	0.111	0.134	0.118	0.37	0.975
24	Fluoranthene	0.699	0.968	2.02	0.575	0.776	0.843	3.28	2.5
25	Benzo[b]fluorene	-	-	0.075	-	-	-	0.189	-
26	Pyrene	0.358	0.488	0.493	0.352	0.346	0.445	0.939	0.798
27	C1-Fluoranthenes/Pyrenes	-	-	-	-	-	-	0.89	-
28	C2-Fluoranthenes/Pyrenes	-	-	-	-	-	-	-	-
29	C3-Fluoranthenes/Pyrenes	-	-	-	-	-	-	-	-
30	Naphthobenzothiophenes	0.062	0.071	0.134	-	0.052	-	0.161	0.15
31	C1-Naphthobenzothiophenes	-	-	-	-	-	-	-	-
32	C2-Naphthobenzothiophenes	-	-	-	-	-	-	-	-
33	Benz[a]anthracene	0.079	0.047	-	0.046	-	0.041	-	-
34	Chrysene/Triphenylene	0.178	0.139	0.202	0.116	0.081	0.135	0.34	0.256
35	C1-Chrysenes	-	-	-	-	-	-	-	-
36	Benzo[b]fluoranthene	-	0.12	-	-	-	-	0.069	-
37	Benzo[j]fluoranthene/Benzo[k]fluoranthene	-	0.091	-	-	-	-	0.065	-
38	Benzo[e]pyrene	-	0.142	0.125	-	-	-	0.156	0.147
39	Benzo[g,h,i]perylene	0.108	0.122	0.127	0.076	0.077	0.306	0.124	0.164
40	Benzo[a]pyrene	-	-	-	-	-	-	-	-
41	Indeno[1,2,3-cd]pyrene	-	-	0.05	-	-	-	0.081	-
42	Carbazole	0.11	0.098	0.481	0.087	0.114	0.11	0.751	0.609
43	Perylene	-	-	-	-	-	0.252	0.194	-
44	Dibenz[a,h]anthracene/Dibenz[a,c]anthracene	-	-	-	-	-	-	-	-
45	Retene	0.418	-	-	-	-	-	-	-

Table 6. Mussel Tissue PAH loads from 2024 LTEMP samples.

ANALYTE (ng/g)	SHH-B-24-2	SHH-B-24-3	AIB-B-24-1	AIB-B-24-2	AIB-B-24-3	WIB-B-24-1	WIB-B-24-2	WIB-B-24-3
Percent Lipids (%)	1.5	1.53	2.19	2.46	1.56	2.29	2.69	1.68
Moisture (%)	84.3	84.3	83.2	83.1	82.4	83.4	80.7	78.9
Sum 42 PAH (ng/g wet weight)	7.52	7.46	23.44	5.56	6.21	7.03	34.17	22.87
Sum 42 PAH (ng/g dry weight)	1.18	1.17	3.94	0.94	1.09	1.17	6.60	4.83
Sum 42 PAH (ng/g lipid corrected)	501.00	487.39	1070.32	226.06	398.01	306.94	1270.41	1361.49
Sum 16 PAH[1] (ng/g wet weight)	4.55	5.81	11.53	4.15	4.72	5.21	15.81	16.14
Sum 16 PAH[1] (ng/g dry weight)	0.71	0.91	1.94	0.70	0.83	0.86	3.05	3.41
Sum low molecular weight PAH[2] (ng/g wet weight)	6.09	5.34	20.35	4.40	4.93	5.01	27.85	19.01
Sum high molecular weight PAH[3] (ng/g wet weight)	1.42	2.12	3.09	1.17	1.28	2.02	6.33	3.87
% low molecular weight PAH	81%	72%	87%	79%	79%	71%	81%	83%
% high molecular weight PAH	19%	28%	13%	21%	21%	29%	19%	17%
Sum of Carcinogenic PAH[4] (ng/g wet weight)	0.257	0.397	0.252	0.162	0.081	0.176	0.555	0.256

1 16 EPA Priority PAHs - naphthalene, acenaphthyleneenzo[a]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene, and dibenz[a,h]anthracene

2 Low molecular weight PAHs : napthalenes - phenantl

3 High molecular weight PAHs: fluoranthene - benzo (g

4 Carcinogenic PAHs: benzo[a]pyrene, benz[a]anthrac

Table 7. 2024 Water PAH concentrations quantified via passive sampling device

Analyte (ng/L C free)	GOC-PSD-24-1	GOC-PSD-24-2	GOC-PSD-24-3	JAC-PSD-24-1	JAC-PSD-24-2	JAC-PSD-24-3	AMT-PSD-24-1	AMT-PSD-24-2	AMT-PSD-24-3
Naphthalene	23.5	< 0.0387 U	36	0.998	3.44	1.07	0.317	0.457	0.415
C1-naphthalenes	0.333	28.3	0.652	0.103	0.322	9.19E-02	0.168	0.203	0.242
C2-naphthalenes	0.399	25.5	0.86	0.3	0.424	0.243	0.371	0.564	0.483
C3-naphthalenes	1.29	74.6	3.63	0.904	1.06	0.536	1	1.66	1.34
C4-naphthalenes	1.68	99.2	5.36	1.52	1.43	0.808	1.41	2.32	2.24
Acenaphthylene	< 0.0150 U	< 0.0148 U	< 0.0183 U	< 0.0177 U	< 0.0160 U	< 0.0158 U	< 0.0181 U	< 0.0217 U	< 0.0195 U
Acenaphthene	0.201	< 0.00718 U	0.305	8.79E-02	9.17E-02	8.03E-02	6.79E-02	< 0.0103 U	0.133
Fluorene	0.22	0.243	0.393	9.26E-02	9.20E-02	6.89E-02	7.97E-02	9.63E-02	8.12E-02
C1-fluorenes	0.239	0.542	0.524	8.56E-02	0.181	7.21E-02	0.146	0.154	4.38E-02
C2-fluorenes	0.567	0.651	1.67	0.358	0.266	0.205	0.224	0.32	0.298
C4-fluorenes	0.502	0.535	1.52	0.215	0.208	0.16	0.172	0.286	0.249
C3-fluorenes	-	-	-	-	-	-	-	-	-
Anthracene	< 0.00236 U	< 0.00227 U	< 0.00391 U	< 0.00371 U	< 0.00298 U	< 0.00290 U	< 0.00394 U	< 0.00528 U	< 0.00447 U
Phenanthrene	0.328	0.378	0.723	0.312	0.239	0.225	0.241	0.29	0.26
C1-phenanthrenes&anthracenes	0.242	0.239	0.623	0.139	0.104	9.18E-02	0.115	0.143	0.141
C2-phenanthrenes&anthracenes	0.763	0.889	2.34	0.387	0.265	0.246	0.3	0.356	0.333
C3-phenanthrenes&anthracenes	1.14	1.25	3.12	0.44	0.399	0.315	0.417	0.727	0.538
C4-phenanthrenes&anthracenes	< 0.127 U	< 0.118 U	< 0.269 U	< 0.251 U	< 0.186 U	< 0.178 U	< 0.274 U	< 0.394 U	< 0.320 U
Dibenzothiophene	2.25E-02	2.61E-02	5.37E-02	1.98E-02	1.71E-02	1.42E-02	1.59E-02	0.02	1.79E-02
C1-dibenzothiophenes	9.58E-02	0.101	0.178	4.37E-02	3.88E-02	3.17E-02	3.26E-02	4.75E-02	3.93E-02
C2-dibenzothiophenes	0.132	4.40E-02	0.246	4.23E-02	3.42E-02	2.68E-02	2.18E-02	4.62E-02	4.68E-02
C3-dibenzothiophenes	< 0.0251 U	< 0.0243 U	< 0.0403 U	< 0.0382 U	< 0.0311 U	< 0.0303 U	< 0.0404 U	< 0.0537 U	< 0.0455 U
C4-dibenzothiophenes	-	-	-	-	-	-	-	-	-

[1-4]: See Tables 5 6

Table 7. 2024 Water PAH concentrations quantified via passive sampling device

Analyte (ng/L C free)	GOC-PSD-24-1	GOC-PSD-24-2	GOC-PSD-24-3	JAC-PSD-24-1	JAC-PSD-24-2	JAC-PSD-24-3	AMT-PSD-24-1	AMT-PSD-24-2	AMT-PSD-24-3
Fluoranthene	0.177	0.171	0.445	9.27E-02	7.13E-02	6.48E-02	4.58E-02	6.04E-02	4.98E-02
Pyrene	6.06E-02	6.03E-02	0.152	3.26E-02	2.55E-02	2.63E-02	2.52E-02	3.27E-02	2.52E-02
fluoranthenes&pyren	6.10E-02	5.61E-02	0.145	1.89E-02	1.10E-02	1.26E-02	1.62E-02	3.81E-02	2.33E-02
fluoranthenes&pyren	< 0.00171 U	< 0.00161 U	< 0.00348 U	< 0.00326 U	< 0.00245 U	< 0.00235 U	< 0.00354 U	< 0.00503 U	< 0.00412 U
fluoranthenes&pyren	-	-	-	-	-	-	-	-	-
fluoranthenes&pyren	-	-	-	-	-	-	-	-	-
Benz[a]anthracene	< 0.000974 U	< 0.000910 U	< 0.00204 U	< 0.00191 U	< 0.00141 U	< 0.00136 U	< 0.00209 U	< 0.00298 U	< 0.00244 U
Perylene	< 0.00154 U	< 0.00143 U	< 0.00324 U	< 0.00304 U	< 0.00224 U	< 0.00215 U	< 0.00332 U	< 0.00474 U	< 0.00388 U
Benzo[b]fluoranthene	5.28E-03	4.14E-03	1.20E-02	< 0.000949 U	< 0.000700 U	< 0.000673 U	< 0.00104 U	< 0.00148 U	< 0.00121 U
Benzo[e]pyrene	< 0.00120 U	< 0.00112 U	< 0.00252 U	< 0.00236 U	< 0.00174 U	< 0.00167 U	< 0.00258 U	< 0.00369 U	< 0.00302 U
Benzo[a]pyrene	< 0.00172 U	< 0.00161 U	< 0.00363 U	< 0.00340 U	< 0.00251 U	< 0.00241 U	< 0.00372 U	< 0.00531 U	< 0.00435 U
Benzo[j]fluoranthene	< 0.000812 U	< 0.000758 U	< 0.00171 U	< 0.00160 U	< 0.00118 U	< 0.00113 U	< 0.00175 U	< 0.00250 U	< 0.00205 U
Benzo[k]fluoranthene	< 0.000768 U	< 0.000717 U	< 0.00162 U	< 0.00152 U	< 0.00112 U	< 0.00107 U	< 0.00166 U	< 0.00236 U	< 0.00194 U
Indeno[1,2,3-cd]pyrene	< 0.000506 U	< 0.000472 U	< 0.00107 U	< 0.00100 U	< 0.000737 U	< 0.000708 U	< 0.00109 U	< 0.00156 U	< 0.00128 U
Sum 42 PAHs	31.95818	232.78964	58.9517	6.1921	8.7196	4.3894	5.1861	7.8212	6.9993
Sum 42 PAH w/o Naphthalene	4.756	5.190	12.450	2.367	2.044	1.641	1.920	2.617	2.279
Sum 16 PAHs[1]	24.492	0.856	38.030	1.616	3.960	1.535	0.777	0.936	0.964
Sum low molecular weight PAH[2]	31.654	232.498	58.198	6.048	8.612	4.286	5.099	7.690	6.901
Sum high molecular weight PAH[3]	0.304	0.292	0.754	0.144	0.108	0.104	0.087	0.131	0.098
Percent low molecular weight PAH	0.990	0.999	0.987	0.977	0.988	0.976	0.983	0.983	0.986
Percent high molecular weight PAH	0.010	0.001	0.013	0.023	0.012	0.024	0.017	0.017	0.014
Sum of Carcinogenic PAHs[4]	0.005	0.004	0.012	0.000	0.000	0.000	0.000	0.000	0.000
Analyte Count	21	19	21	20	20	20	20	19	20
Percent Naphthalene	0.851	0.978	0.789	0.618	0.766	0.626	0.630	0.665	0.674

[1-4]: See Tables 5 6

Table 8. Mussel tissue biomarkers from 2024 LTEMP samples. All positive analyte detections are reported for every sample with positive detections (i.e., not all samples had positive detections).

	ANALYTE	RED-B-24-1	RED-B-24-2	RED-B-24-3	JAC-B-24-1	JAC-B-24-2	JAC-B-24-3	GOC-B-24-3	SHH-B-24-1	SHH-B-24-2	SHH-B-24-3	AIB-B-24-1	AIB-B-24-2	AIB-B-24-3	WIB-B-24-1	WIB-B-24-2	WIB-B-24-3
1	Hopane (T19)	1.82	1.6	1.55	0.649	0.483	0.624	-	0.73	0.5	-	-	-	-	-	-	-
2	C23 Tricyclic Terpane (T4)	0.397	0.456	0.462	-	-	-	-	-	-	-	-	-	-	-	-	-
3	C24 Tricyclic Terpane (T5)	0.208	0.193	0.203	-	-	-	-	-	-	-	-	-	-	-	-	-
4	C24 Tetracyclic Terpane (T6a)	0.348	0.263	0.281	-	-	-	-	-	-	-	-	-	-	-	-	-
5	18a-22,29,30-Trisnorneohopane-TS (T11)	0.513	0.389	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	30-Norhopane (T15)	1.09	1.49	0.958	0.523	-	0.373	-	-	-	-	-	-	-	-	-	-
7	30-Homohopane-22S (T21)	0.766	0.833	0.519	-	-	-	-	-	-	-	-	-	-	-	-	-
8	30,31-Bishomohopane-22S (T26)	3.14	3.71	3.9	2.93	3.52	2.1	-	4.96	3.86	5.13	4.72	5.49	4	5.11	5.42	4.7
9	13b(H),17a(H)-20S-Diacholestane (S4)	0.263	0.219	0.299	-	-	-	-	0.07	-	-	-	-	-	-	-	-
10	13b(H),17a(H)-20R-Diacholestane (S5)	0.202	0.168	0.119	-	-	-	-	-	-	-	-	-	-	-	-	-
11	17a(H)20SC27/C29dia	0.58	0.503	0.603	-	0.232	0.217	-	0.16	0.15	-	-	0.26	0.21	0.34	-	-
12	17a(H)20rc27/C29dia	0.688	0.652	0.747	0.159	0.186	0.224	0.218	0.18	0.16	0.15	-	0.26	0.18	-	-	-
13	14a,17a-20R-Methylcholestane (S24)	0.506	0.484	0.508	-	-	-	-	-	-	-	-	-	-	-	-	-
14	14a(H),17a(H)-20S-Ethylcholestane (S25)	0.202	0.29	0.209	-	-	-	-	-	-	-	-	-	-	-	-	-
15	14a(H),17a(H)-20R-Ethylcholestane (S28)	0.479	0.762	0.52	-	-	-	-	-	-	-	-	-	-	-	-	-
16	14b(H),17b(H)-20R-Cholestane (S14)	0.263	0.245	0.299	-	-	-	-	-	-	-	-	-	-	-	-	-
17	14b(H),17b(H)-20S-Cholestane (S15)	0.297	0.29	0.287	-	-	-	-	-	-	-	-	-	-	-	-	-
18	14b,17b-20R-Methylcholestane (S22)	0.337	0.297	0.251	-	-	-	-	-	-	-	-	-	-	-	-	-
19	14b,17b-20S-Methylcholestane (S23)	0.344	0.4	0.37	-	-	-	-	-	-	-	-	-	-	-	-	-
20	14b(H),17b(H)-20R-Ethylcholestane (S26)	0.425	0.406	0.478	-	-	-	-	-	-	-	-	-	-	-	-	-
21	14b(H),17b(H)-20S-Ethylcholestane (S27)	0.29	0.413	0.263	-	-	-	-	-	-	-	-	-	-	-	-	-
22	18a(H)-30-Norneohopane-C29Ts (T16)	-	0.436	-	-	-	-	-	-	-	-	-	-	-	-	-	-
23	13b,17a-20S-Methyldiacholestane (S8)	-	0.239	-	-	-	-	-	-	-	-	-	-	-	-	-	-
24	14a,17a-20S-Methylcholestane (S20)	-	0.258	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Count		21	24	20	4	4	5	1	5	4	2	1	3	3	2	1	1

Table 9. Diagonistic Ratios for petroleum fingerprinting in marine sediment, intertidal mussel tissue, and seawater sampled by PSD for all replicates of the 2024 LTEMP campaign.

	SAMPID	Matrix	Total Petroleum Hydrocarbons (C9-C44 ng/g)	Total Saturated Hydrocarbons (µg/g)	Ratio of T15/T19[1]	Ratio of Pristane/ Phytane[2]	Ratio of Pristane/ C17[3]	Ratio of Phytane/ C18[4]	ANT/(ANT+ PHE)[5]	ΣLMW/ΣHMW[6]	FL/(FL + PYR)[7]	FLA/(FLA + PY R)[8]
Whole ANS Crude Oil			563000	77351.80	0.557	1.729	0.863	0.578	0.000	-	0.848	0.213
Cutoff Value (s)									0.100	1.000	0.500	0.400
1	AMT-S-24-1	Sediment	25.10	1.270	0.569	1.400	0.412	0.455	0.291	0.681	0.338	0.531
2	AMT-S-24-2	Sediment	33.90	1.490	0.572	3.750	0.714	0.235	0.261	0.555	0.121	0.552
3	AMT-S-24-3	Sediment	37.10	1.390	0.543	2.400	0.545	0.250	0.182	0.729	0.238	0.565
4	GOC-S-24-1	Sediment	21.90	1.020	0.575	6.333	1.462	0.429	0.080	1.897	0.473	0.602
5	GOC-S-24-2	Sediment	8.45	0.942	0.755	1.667	0.714	0.375	0.080	1.287	0.430	0.591
6	GOC-S-24-3	Sediment	27.10	1.310	0.709	15.000	4.615	0.364	0.107	1.360	0.412	0.578
7	GOC-S-24-2-DUP	Sediment	8.20	0.769	0.771	1.333	0.667	0.500	0.104	1.456	0.427	0.589
8	RED-B-24-1	Tissue	7.30	0.615	0.599	4.167	0.962	0.667	0.586	0.404	0.162	0.669
9	RED-B-24-2	Tissue	8.65	1.220	0.931	5.167	0.795	0.600	0.569	0.422	0.188	0.701
10	RED-B-24-3	Tissue	5.84	1.120	0.618	5.500	1.031	0.600	0.579	0.413	0.179	0.711
11	JAC-B-24-1	Tissue	1.43	0.652	0.806	0.465	2.323	31.000	0.333	2.441	0.573	0.776
12	JAC-B-24-2	Tissue	7.39	1.320	3.188	1.208	5.636	15.400	0.311	3.292	-	0.768
13	JAC-B-24-3	Tissue	5.26	0.722	0.598	0.477	1.850	8.158	0.336	2.637	0.593	0.684
14	AMT-B-24-1	Tissue	6.14	0.811	-	1.007	4.667	17.000	0.349	0.635	0.350	0.591
15	AMT-B-24-2	Tissue	4.44	0.592	-	0.427	2.792	19.625	0.257	1.563	-	0.515
16	AMT-B-24-3	Tissue	6.60	0.808	-	0.955	5.172	19.625	0.293	3.001	0.643	0.713
17	GOC-B-24-1	Tissue	4.51	0.570	-	0.245	0.897	14.300	0.314	2.399	-	0.682
18	GOC-B-24-2	Tissue	4.18	0.533	-	0.160	0.793	20.571	0.372	1.759	0.538	0.700
19	GOC-B-24-3	Tissue	4.49	0.664	-	0.369	1.625	20.143	0.318	2.024	-	0.591
20	SHH-B-24-1	Tissue	11.30	1.030	2.138	0.503	1.857	22.143	0.323	4.043	0.671	0.789
21	SHH-B-24-2	Tissue	5.51	1.200	3.072	0.431	1.886	30.600	0.269	4.285	0.497	0.661
22	SHH-B-24-3	Tissue	3.86	0.613	-	0.525	2.594	26.333	0.286	2.522	0.447	0.665
23	AIB-B-24-1	Tissue	4.97	1.110	-	1.286	10.909	35.000	0.282	6.581	0.778	0.804
24	AIB-B-24-2	Tissue	4.64	1.220	-	2.577	7.529	7.450	0.246	3.773	0.493	0.620
25	AIB-B-24-3	Tissue	3.44	1.020	-	1.148	5.182	21.286	0.277	3.851	0.536	0.692
26	WIB-B-24-1	Tissue	5.21	1.800	-	25.200	3.150	0.714	0.300	2.476	0.439	0.655
27	WIB-B-24-2	Tissue	3.72	0.996	-	0.653	4.683	26.727	0.327	4.401	0.672	0.777
28	WIB-B-24-3	Tissue	5.14	1.860	-	0.371	3.676	33.364	0.270	4.918	0.687	0.758

Table 9. Diagonistic Ratios for petroleum fingerprinting in marine sediment, intertidal mussel tissue, and seawater sampled by PSD for all replicates of the 2024 LTEMP campaign.

	SAMPID	Matrix	Total Petroleum Hydrocarbons (C9-C44 ng/g)	Total Saturated Hydrocarbons (µg/g)	Ratio of T15/T19[1]	Ratio of Pristane/ Phytane[2]	Ratio of Pristane/ C17[3]	Ratio of Phytane/ C18[4]	ANT/(ANT+ PHE)[5]	ΣLMW/ΣHMW[6]	FL/(FL + PYR)[7]	FLA/(FLA + PYR)[8]
29	GOC-PSD-24-1	Water PSD	31.958	-	-	-	-	-	0.000	104.167	0.784	0.745
30	GOC-PSD-24-2	Water PSD	232.790	-	-	-	-	-	0.000	797.483	0.801	0.739
31	GOC-PSD-24-3	Water PSD	58.952	-	-	-	-	-	0.000	77.185	0.721	0.745
32	JAC-PSD-24-1	Water PSD	6.192	-	-	-	-	-	0.000	41.941	0.740	0.740
33	JAC-PSD-24-2	Water PSD	8.720	-	-	-	-	-	0.000	79.887	0.783	0.737
34	JAC-PSD-24-3	Water PSD	4.389	-	-	-	-	-	0.000	41.328	0.724	0.711
35	AMT-PSD-24-1	Water PSD	5.186	-	-	-	-	-	0.000	58.474	0.760	0.645
36	AMT-PSD-24-2	Water PSD	7.821	-	-	-	-	-	0.000	58.613	0.747	0.649
37	AMT-PSD-24-3	Water PSD	6.999	-	-	-	-	-	0.000	70.203	0.763	0.664

[1] T15-Norhopane to T19-Hopane is a diagnostic ratio that identifies crude oil presence

[2] Higher values are indicative of greater marine biogenic sources over oil

[3] Higher values are indicative of greater weathering for oil and biogenic mixtures

[4] Higher values are indicative of oil-derived material and microbial degradation of the straight-chain alkanes

[5] Ratio of Anthracene to Anthracene+ Phenanthrene is indicative of petrogenic sources with values <0.1 and pyrogenic with values > 0.1 (Pies et al 2008)

[6] ΣLMW/ΣHMW; A higher prevelance of low molecular weight PAHs compared to high molecular weight PAHs (e.g., values >1) indicates petrogenic sources (Zang et al 2008)

[7] FL/(FL + PYR); Flourene and pyrene ratios indicate types of emissions with values <0.5 suggesting petrol while values >0.5 diesel (Ravindra et al. 2008b)

[8] FLA/(FLA + PYR); Flouranthene and Pyrene ratios indicate types of combustion with values >0.4 indicating wood and coal combustion (De La Torre-Roche et al., 2009)

3. FIGURES

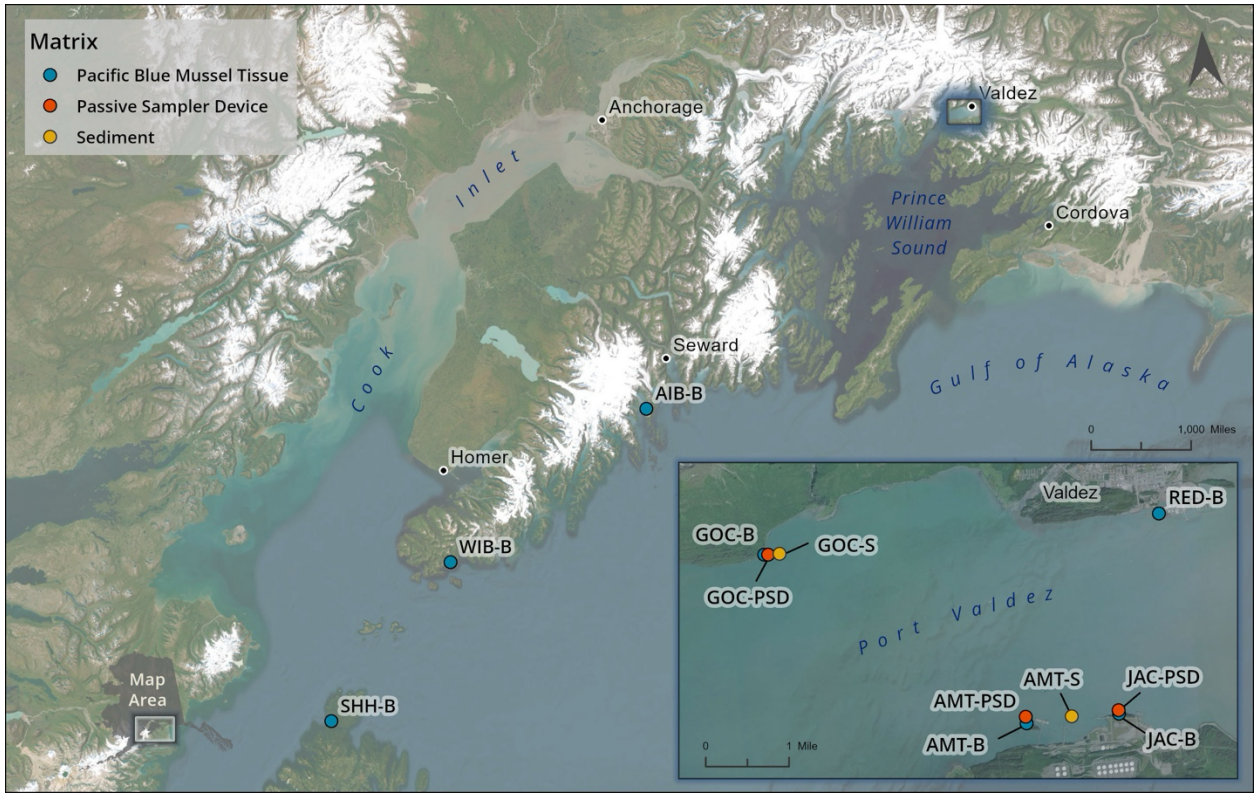

Figure 1. Long-Term Environmental Monitoring Program sites from the 2024 campaign.

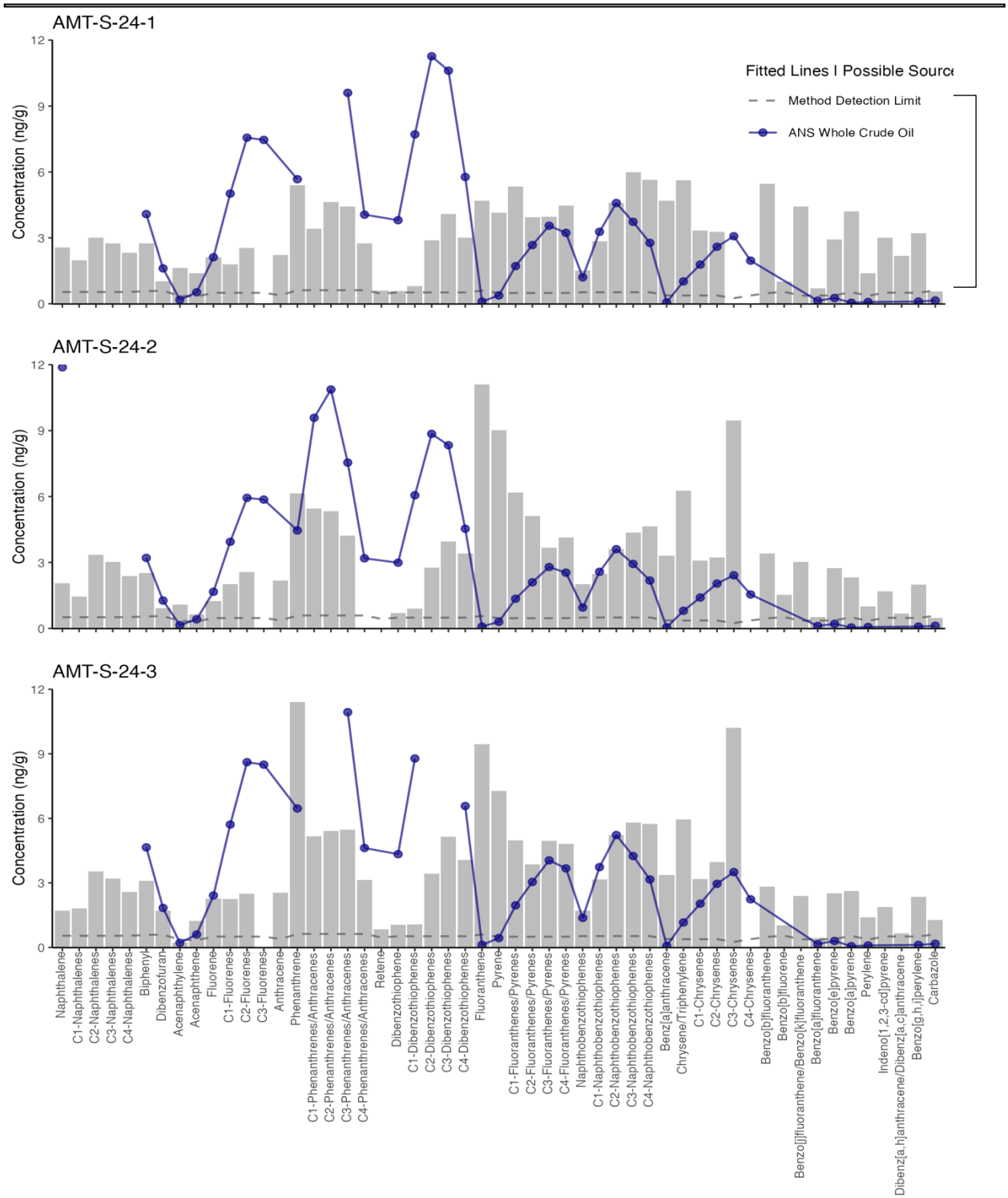

Figure 2. 2024 PAH profiles from individual sediment samples at the Valdez Marine Terminal (AMT) with the ANS potential source profile and the analyte-specific method detection limit superimposed as different lines. ANS profile lines are scaled to C2-Napthobenzothiophenes and represent data only where points are present.

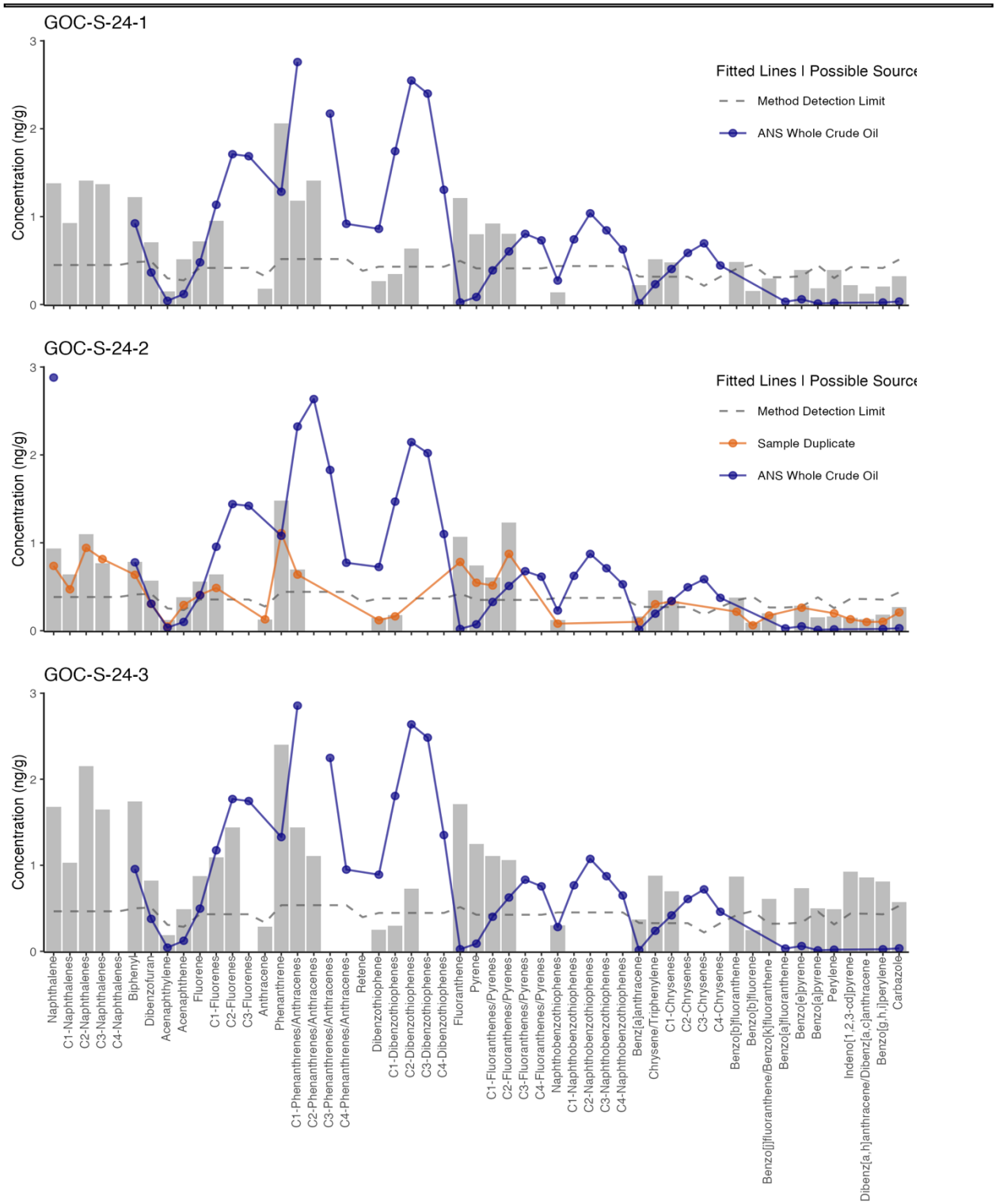

Figure 3. 2024 PAH profiles from individual sediment samples at the Gold Creek (GOC) reference site with the ANS potential source profile, sample duplicate, the analyte-specific method detection limit superimposed as different lines. ANS profile lines are scaled to Napthobenzothiophenes in the third replicate and represent data only where points are present.

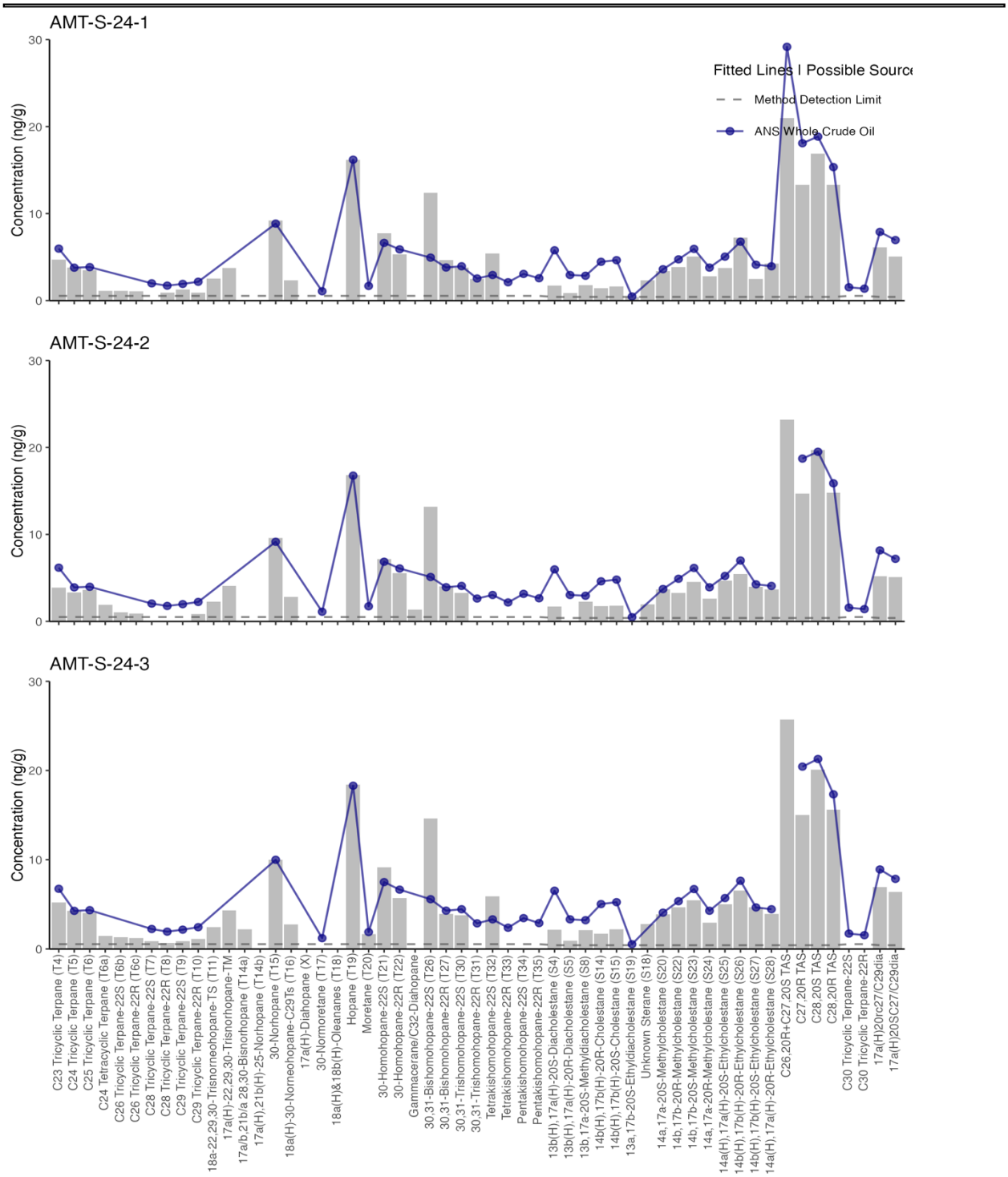

Figure 4. 2024 petro-geochemical profiles from individual sediment samples at the Valdez Marine Terminal (AMT) with the ANS potential source profile and the analyte-specific method detection limit superimposed as different lines. ANS profile lines are scaled to Hopane (T19) and represent data only where points are present.

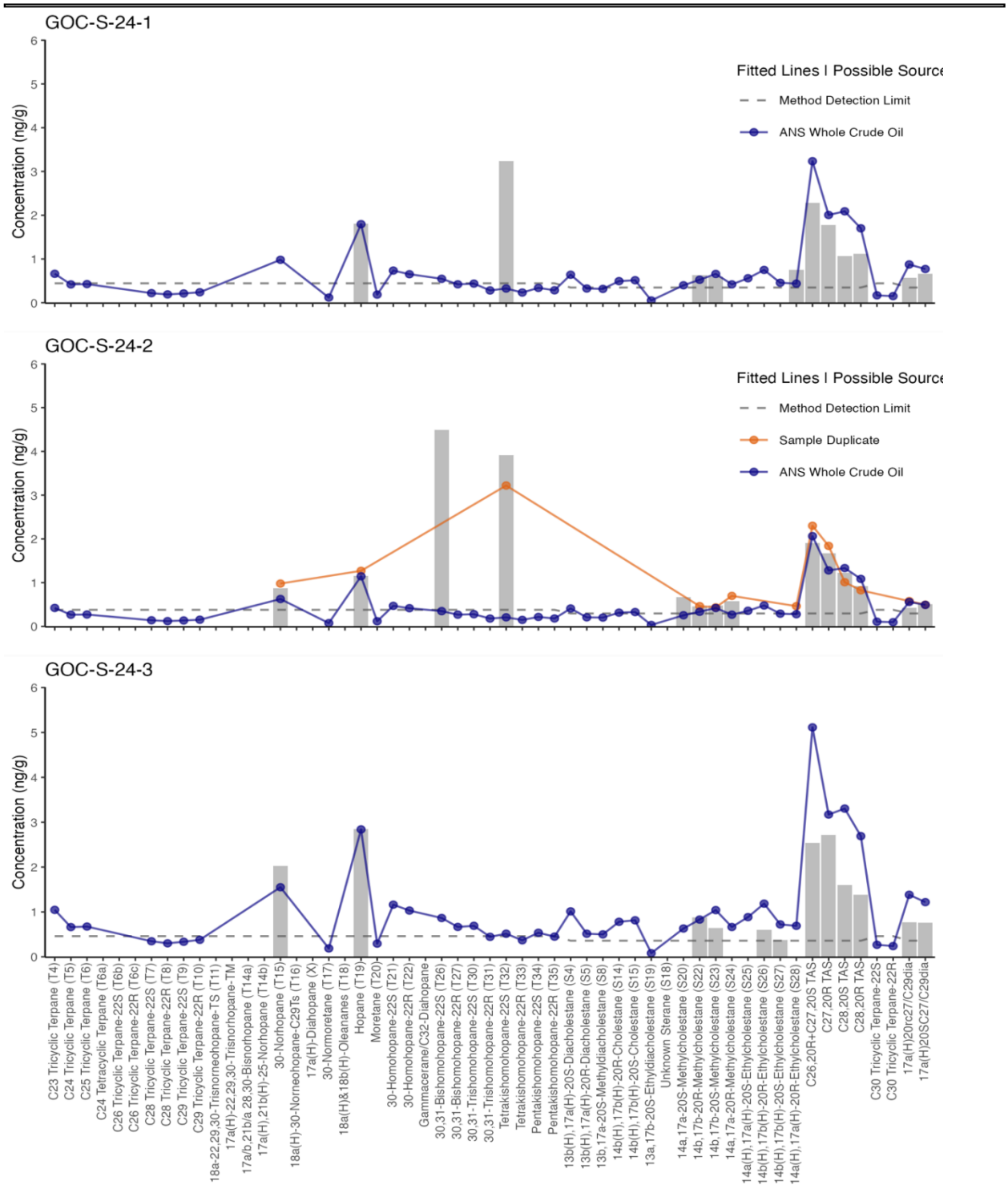

Figure 5. 2024 petro-geochemical biomarker profiles from individual sediment samples at the Gold Creek (GOC) reference site with the ANS potential source profile, sample duplicate, and the analyte-specific method detection limit superimposed as different lines. ANS profile lines are scaled to Hopane (T19) and represent data only where points are present.

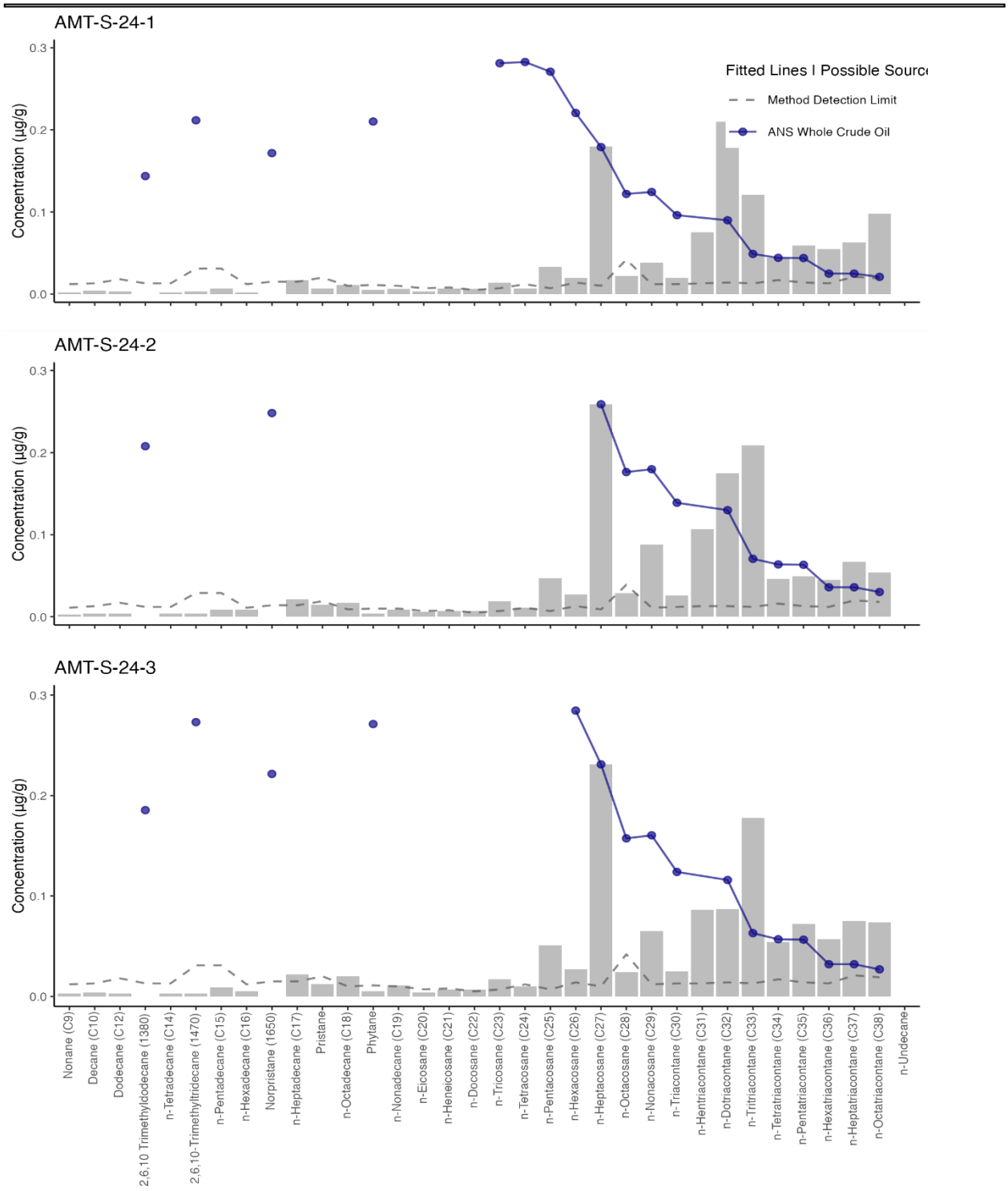

Figure 6. 2024 saturated hydrocarbon profiles from individual sediment samples at the Valdez Marine Terminal (AMT) with the ANS potential source profile and the analyte-specific method detection limit superimposed as different lines. ANS profile lines are scaled to n-Heptacosane (C27) and represent data only where points are present.

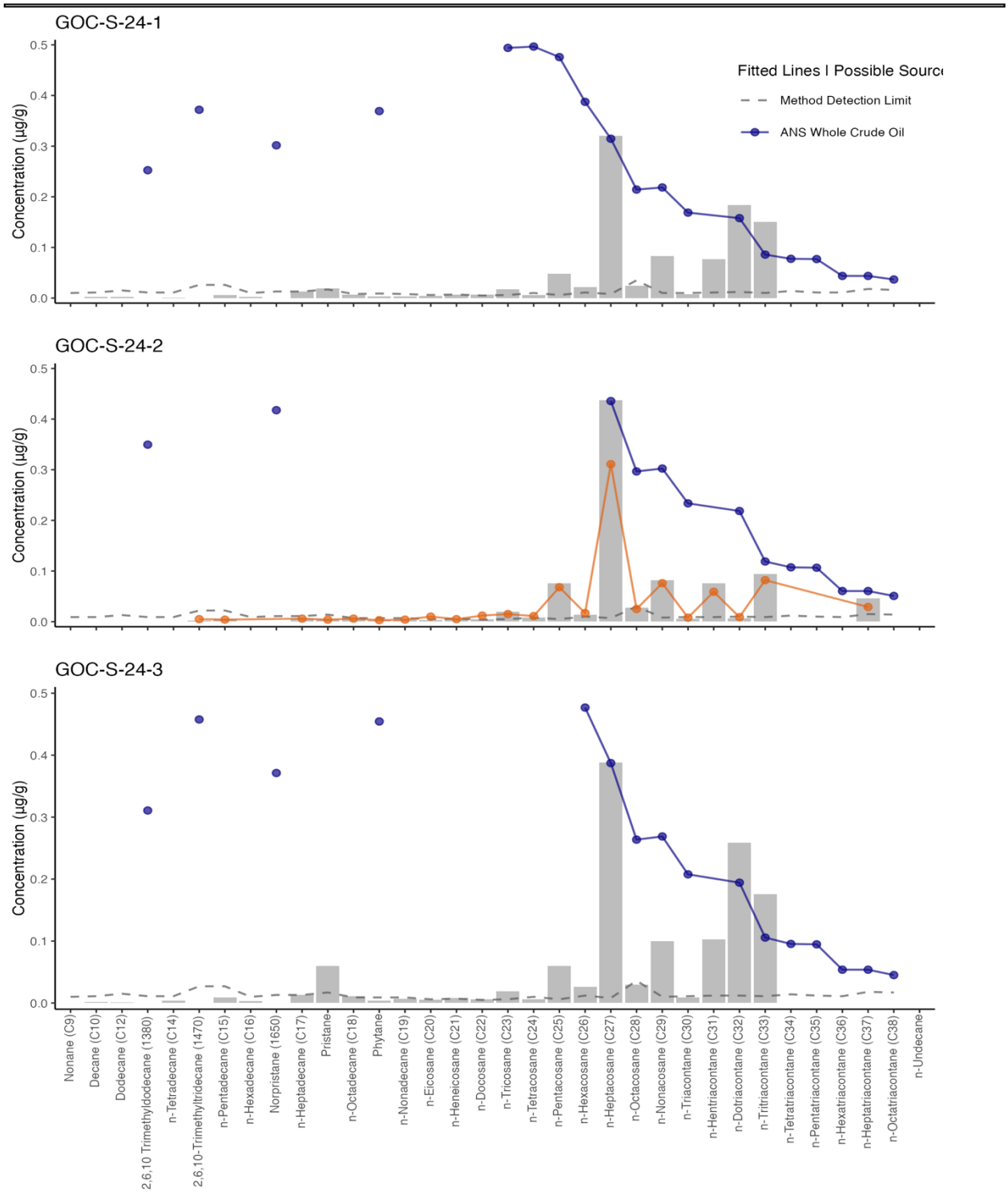

Figure 7. 2024 saturated hydrocarbon profiles from individual sediment samples at the Gold Creek (GOC) reference site with the ANS potential source profile, sample duplicate, and the analyte-specific method detection limit superimposed as different lines. ANS profile lines are scaled to n-Heptacosane (C27) and represent data only where points are present.

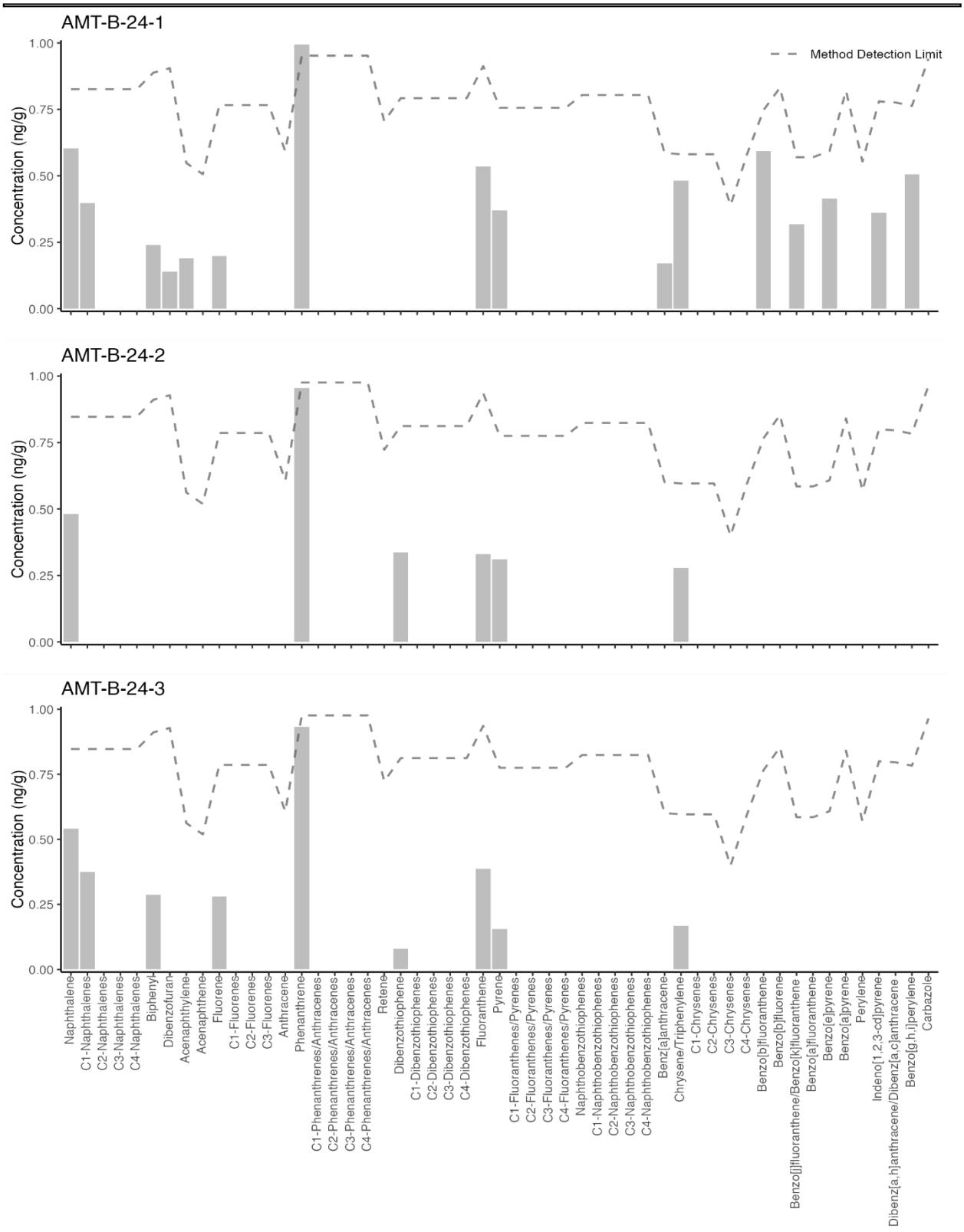

Figure 8. 2024 PAH profiles from individual tissue samples at the Valdez Marine Terminal (AMT) site with the analyte-specific method detection limit superimposed as a dotted line.

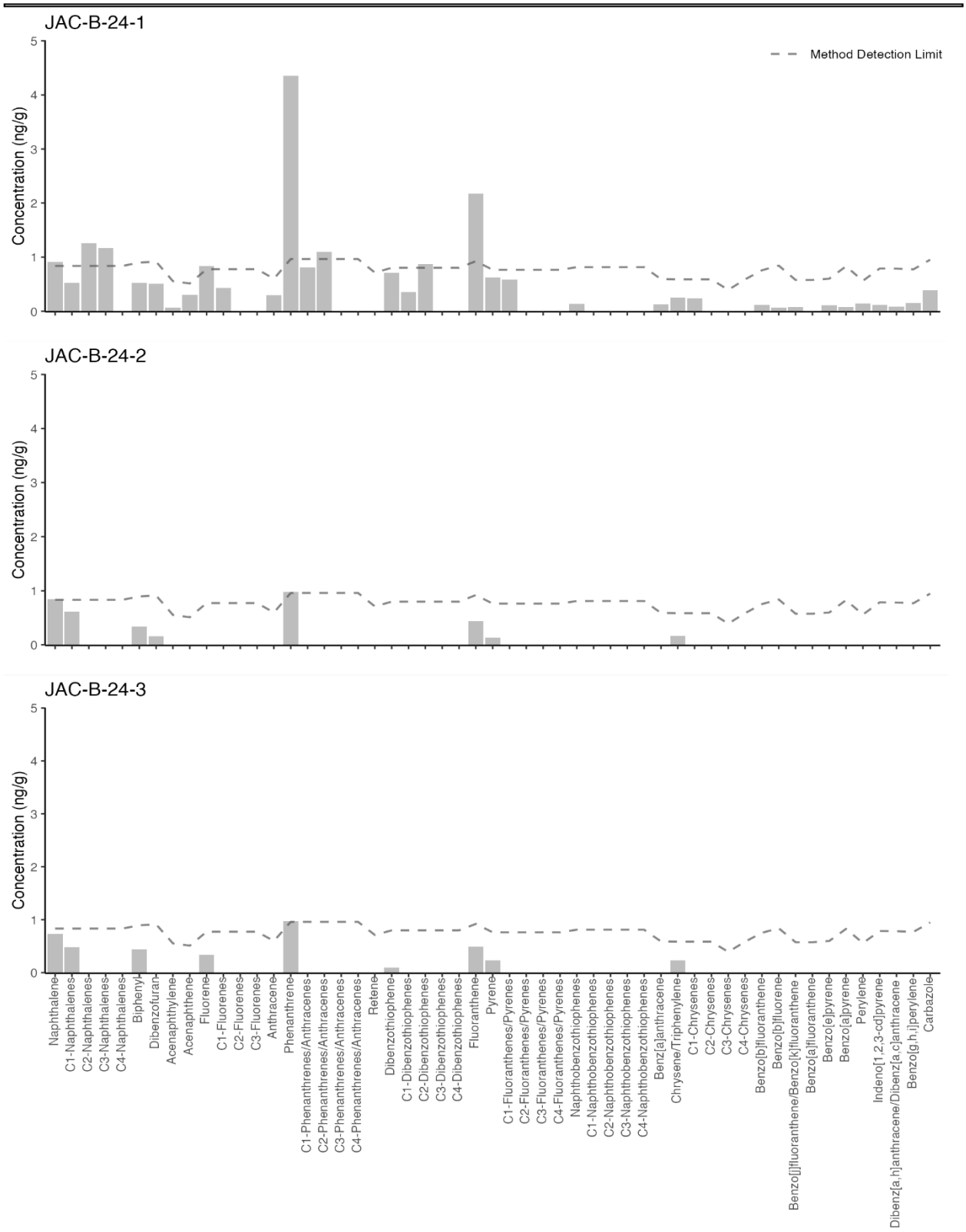

Figure 9. 2024 PAH profiles from individual tissue samples at the Jackson Point (JAC) site, near the Valdez Marine Terminal, with the analyte-specific method detection limit superimposed as a dotted line.

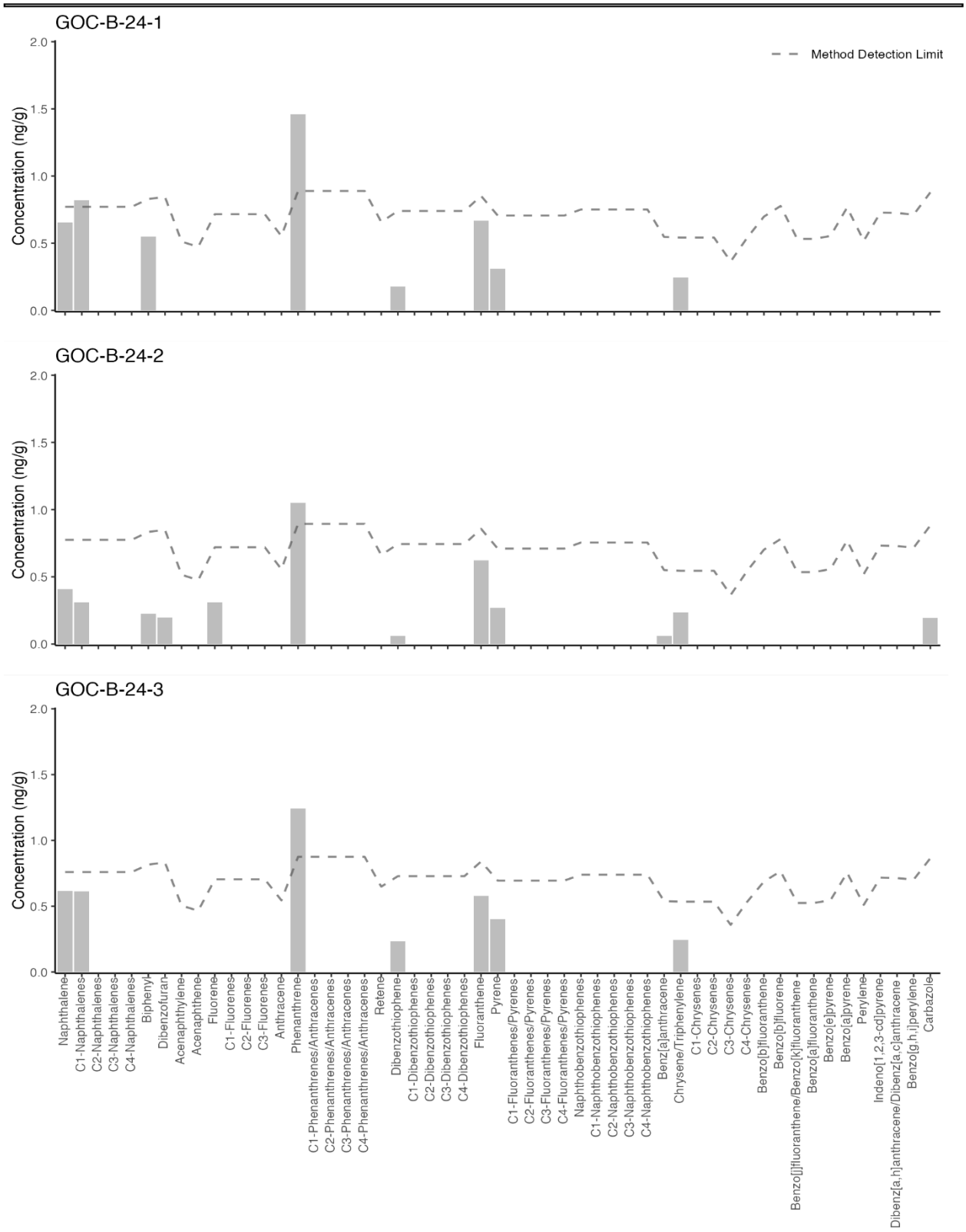

Figure 10. 2024 PAH profiles from individual tissue samples at the Gold Creek (GOC) reference site in Port Valdez with the analyte-specific method detection limit superimposed as a dotted line.

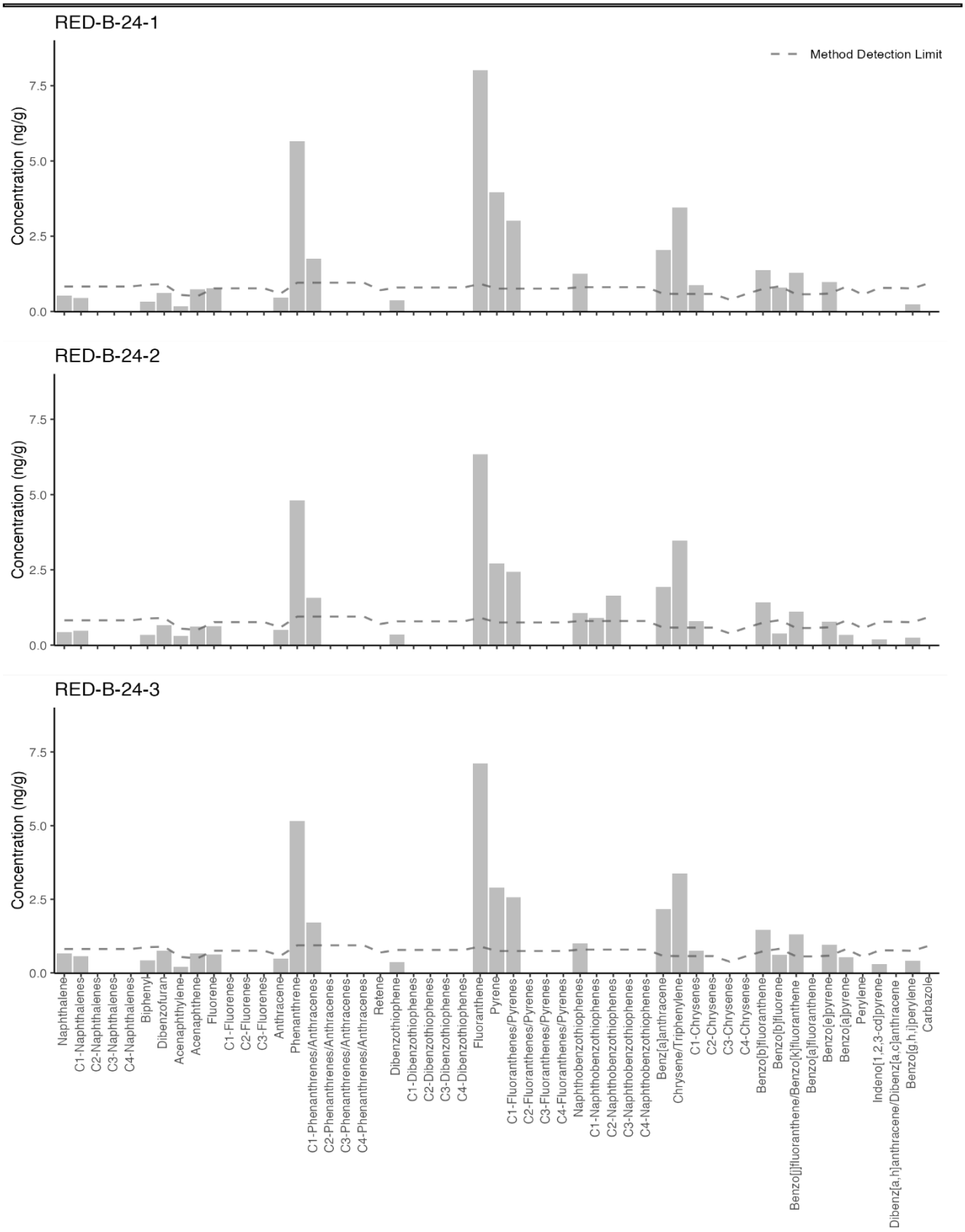

Figure 11.2024 PAH profiles from individual tissue samples at the entrance of the Valdez Small boat harbor (RED) site with the analyte specific method detection limit superimposed as a dotted line.

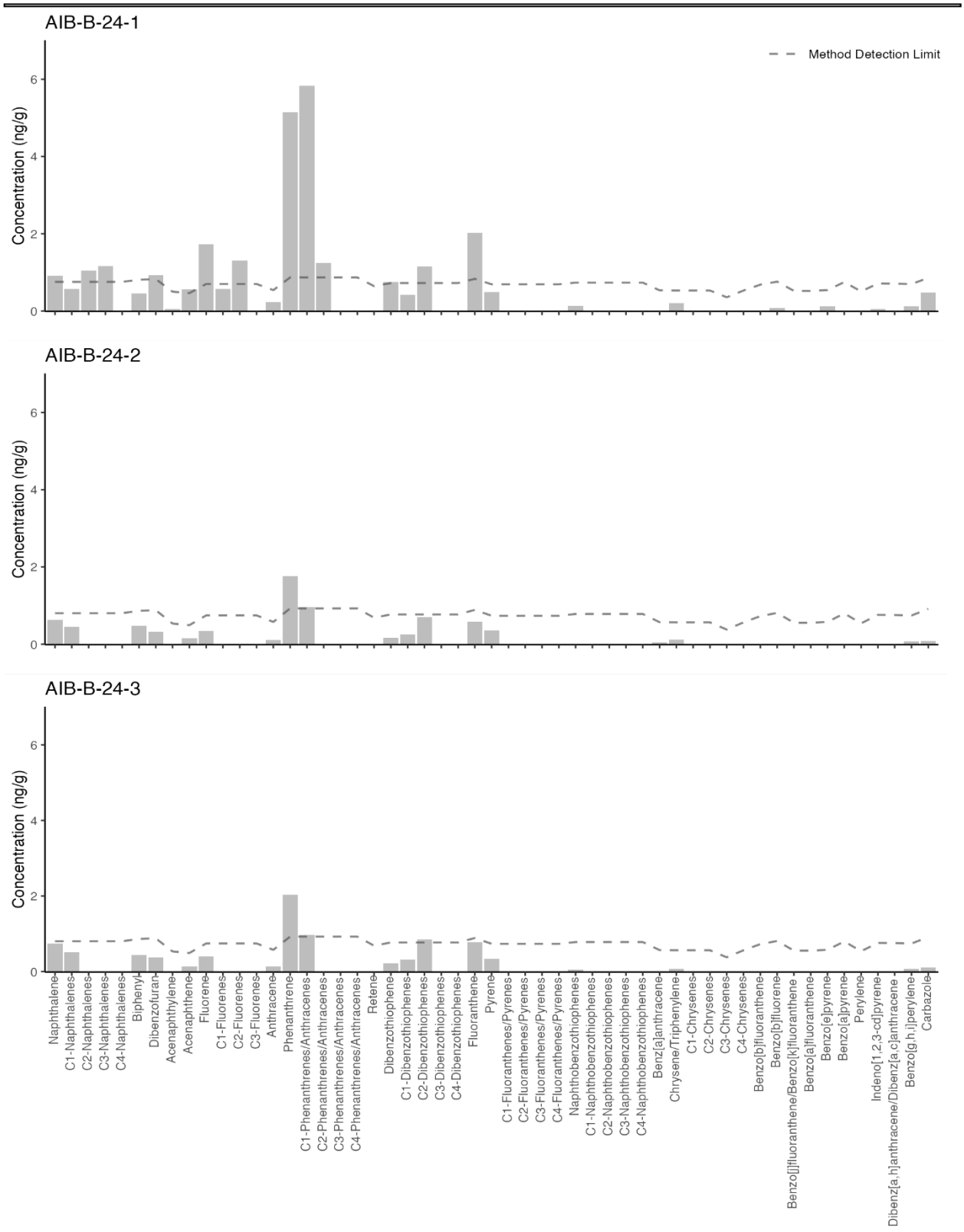

Figure 12. 2024 PAH profiles from individual tissue samples at the Aialik Bay (AIB) site, near the Valdez Marine Terminal, with the analyte specific method detection limit superimposed as a dotted line.

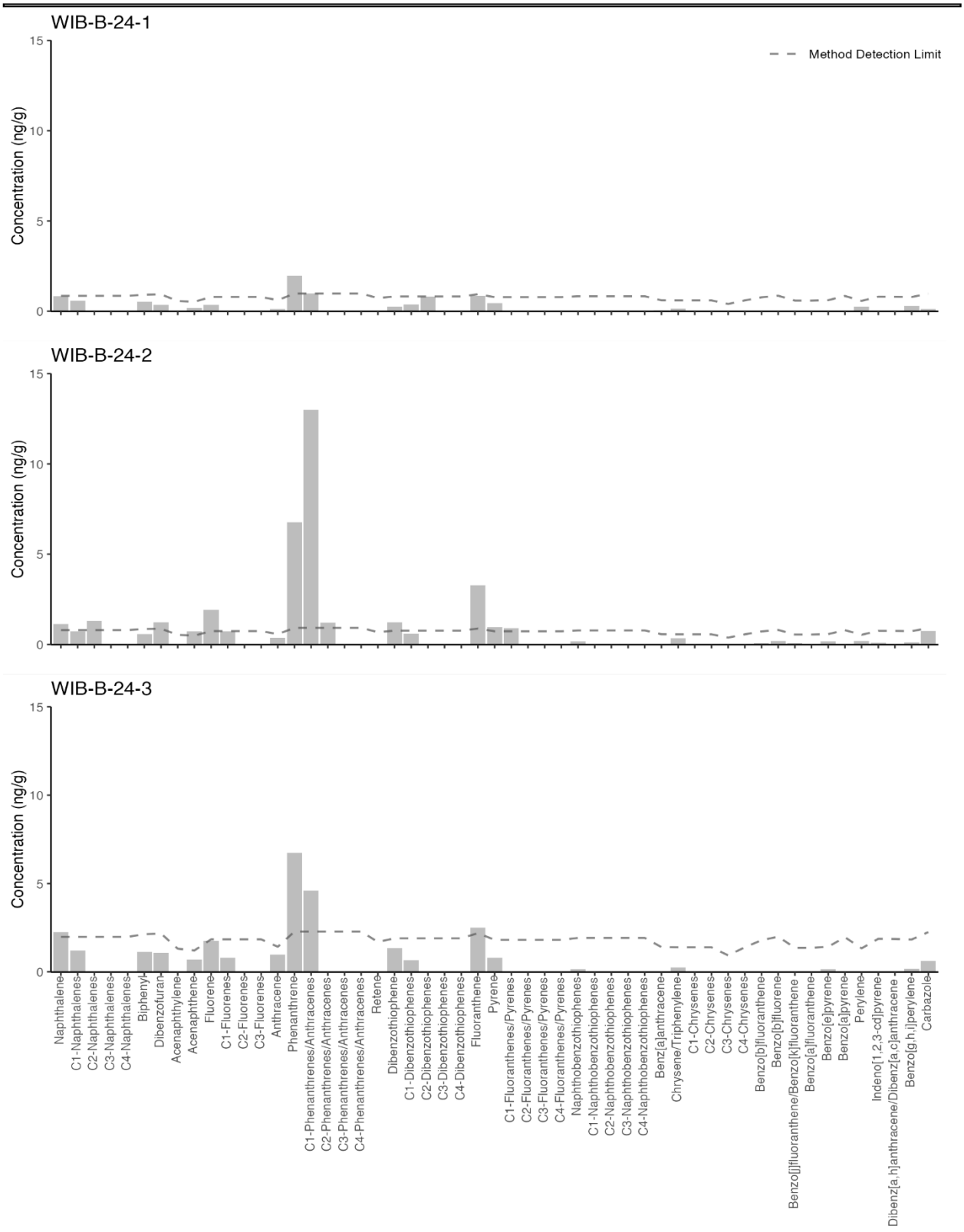

Figure 13. 2024 PAH profiles from individual tissue samples at the Windy Bay (WIB) site, near the Valdez Marine Terminal, with the analyte specific method detection limit superimposed as a dotted line.

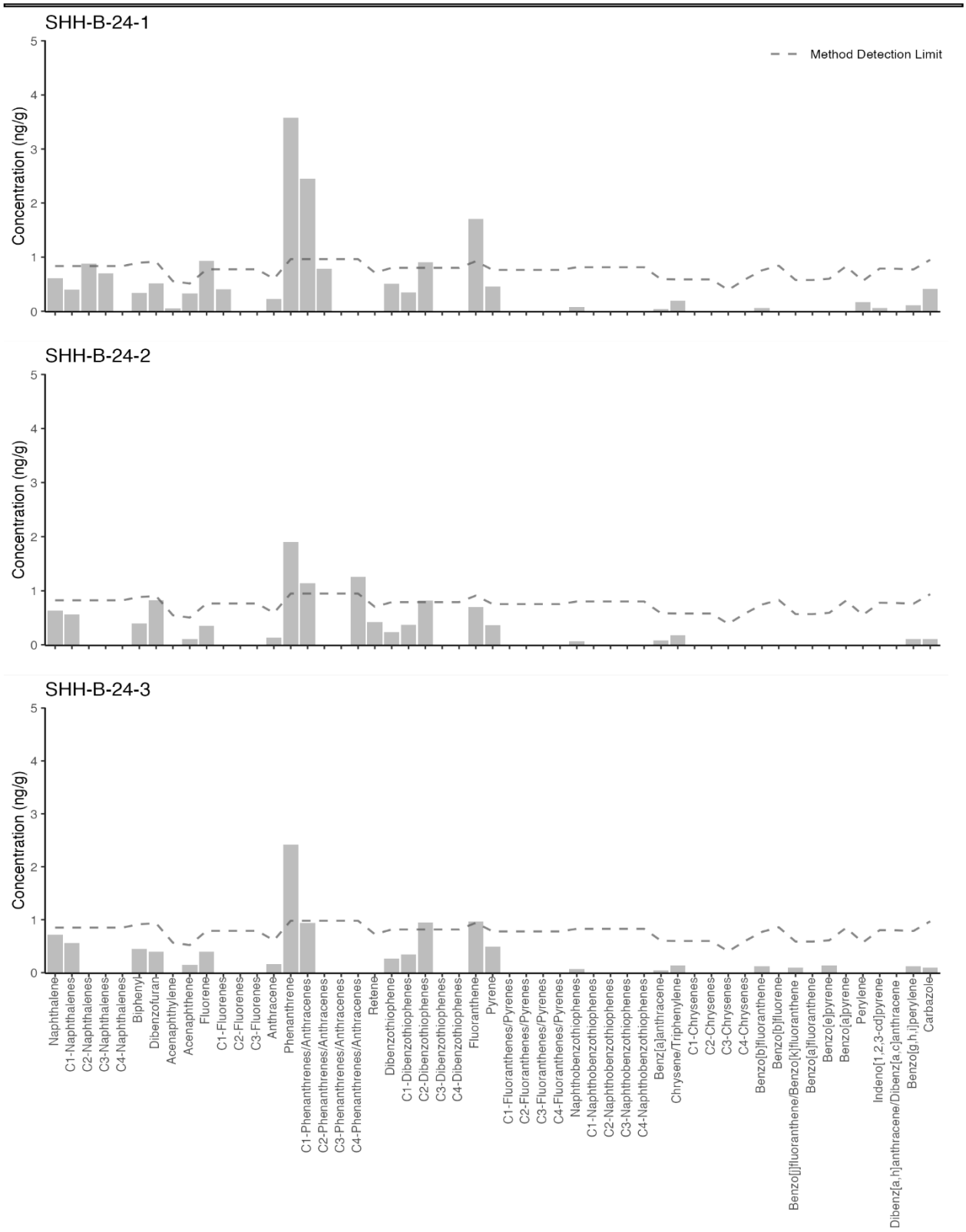

Figure 14. 2024 PAH profiles from individual tissue samples at the Shuyak Harbor (SHH) site, near the Valdez Marine Terminal, with the analyte specific method detection limit superimposed as a dotted line.

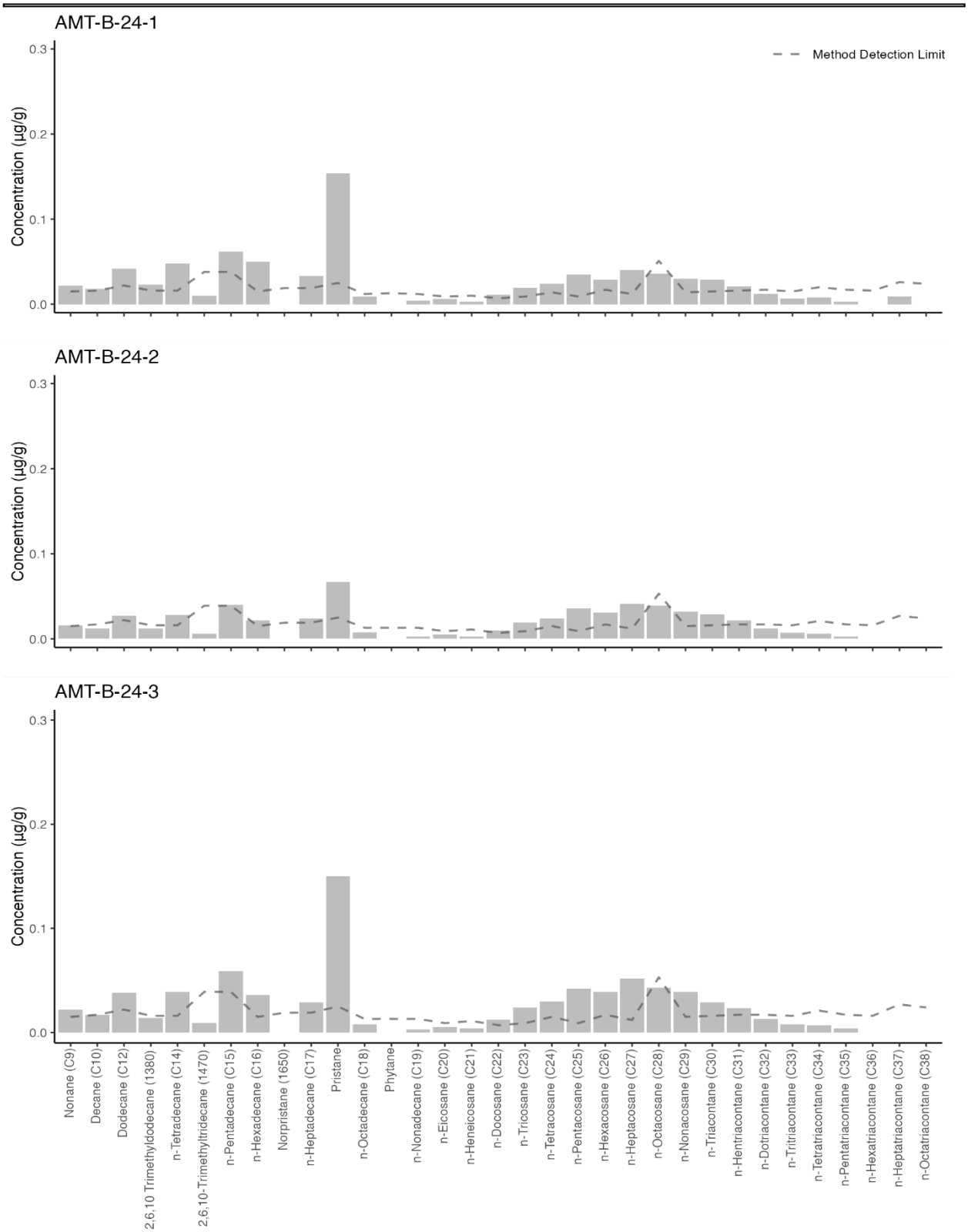

Figure 15. 2024 saturated hydrocarbon profiles from individual tissue samples at the Valdez Marine Terminal (AMT) site with the analyte-specific method detection limit superimposed as a dotted line.

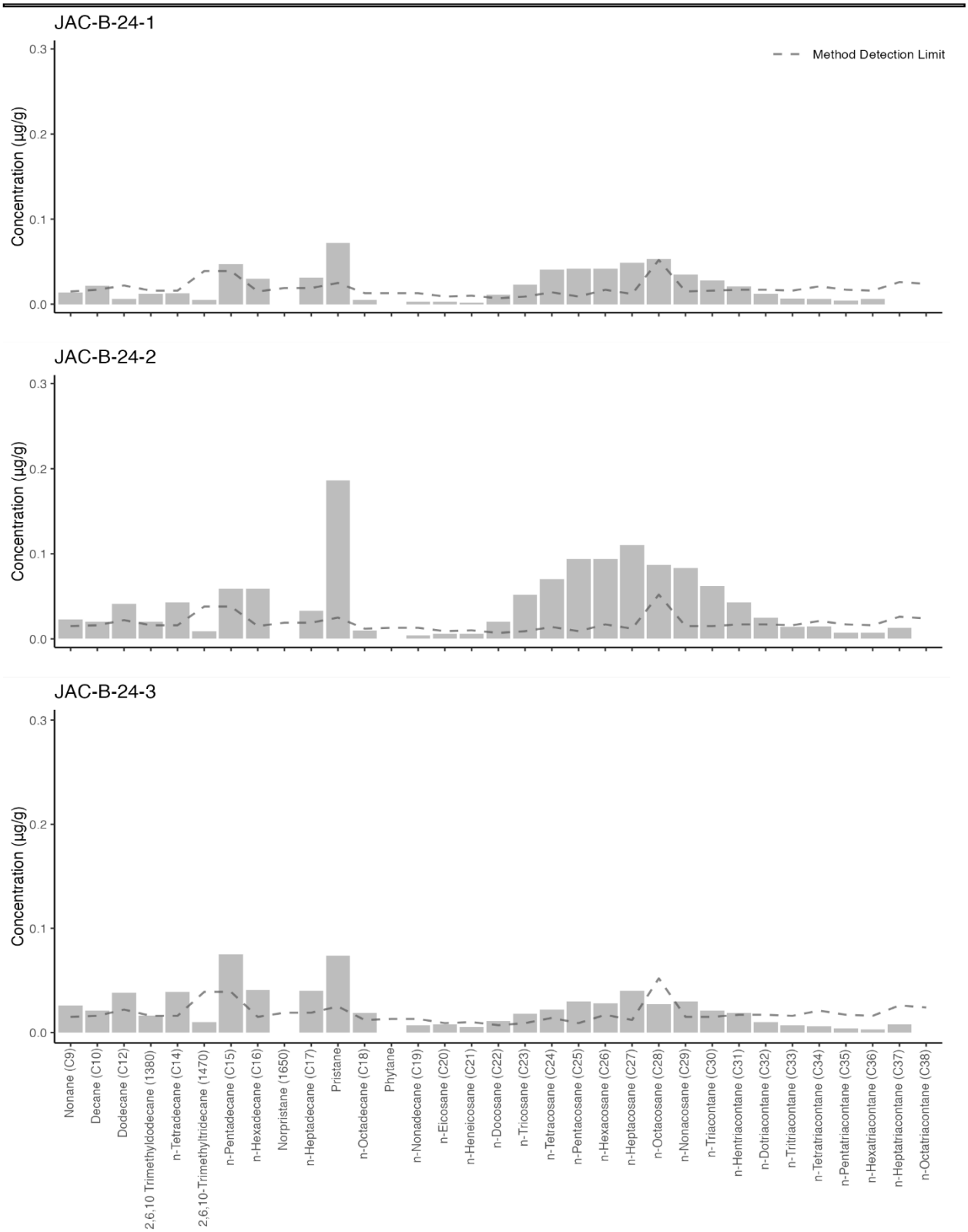

Figure 16. 2024 saturated hydrocarbon profiles from individual tissue samples at the Jackson Point (JAC) site with the analyte-specific method detection limit superimposed as a dotted line.

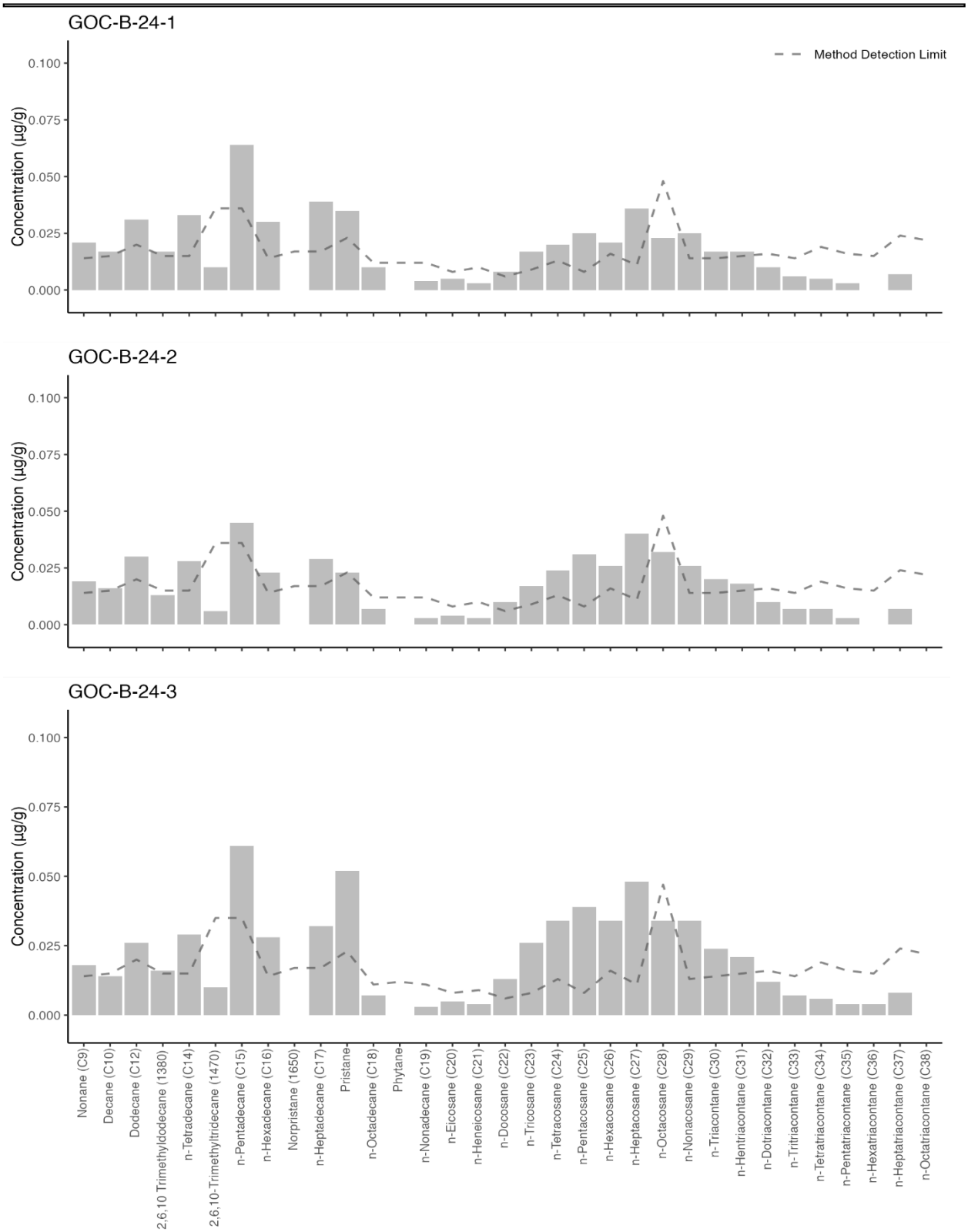

Figure 17. 2024 saturated hydrocarbon profiles from individual tissue samples at the Gold Creek (GOC) site with the analyte-specific method detection limit superimposed as a dotted line.

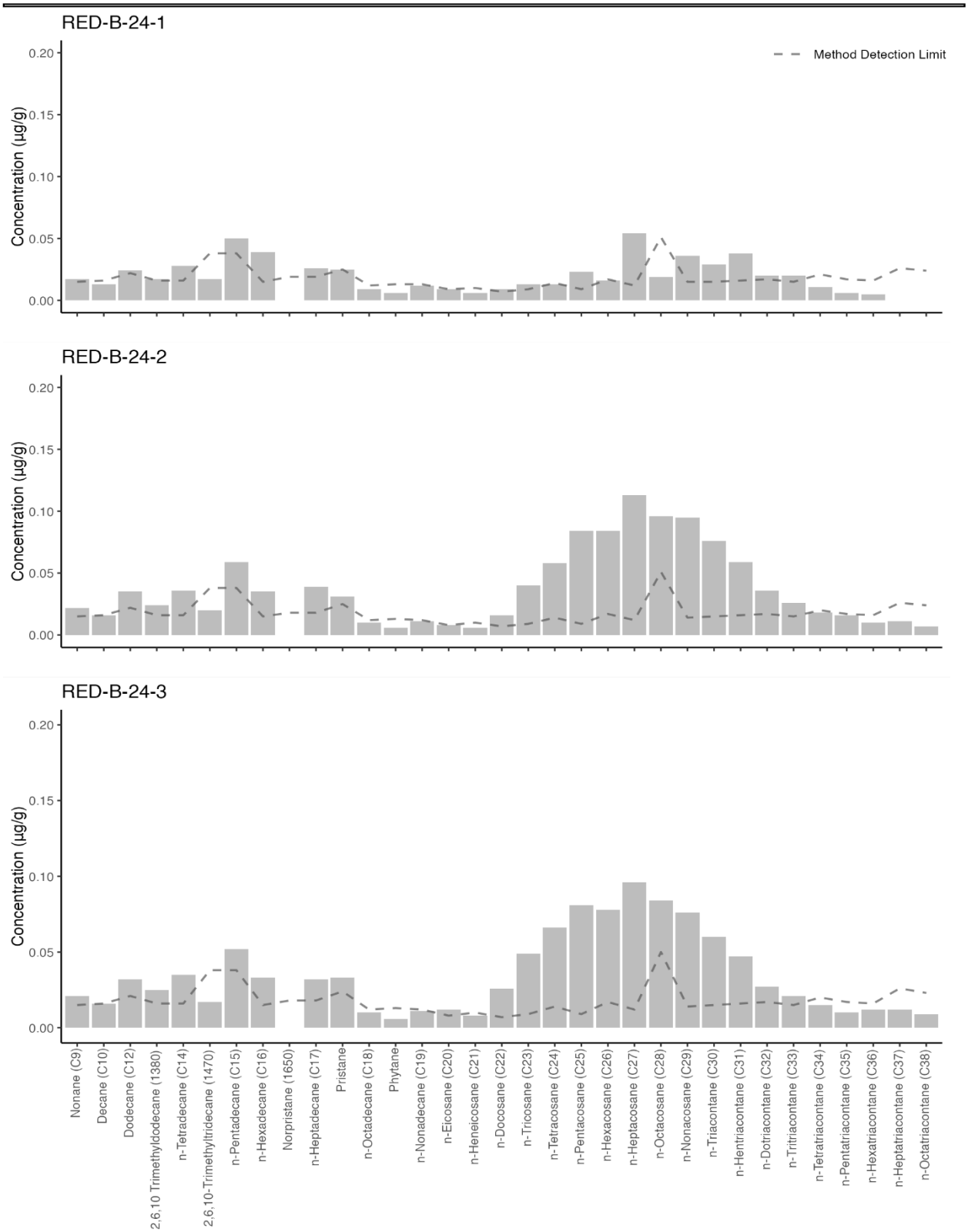

Figure 18. 2024 saturated hydrocarbon profiles from individual tissue samples at the entrance of the Valdez Small Boat Harbor (RED) site with the analyte-specific method detection limit superimposed as a dotted line.

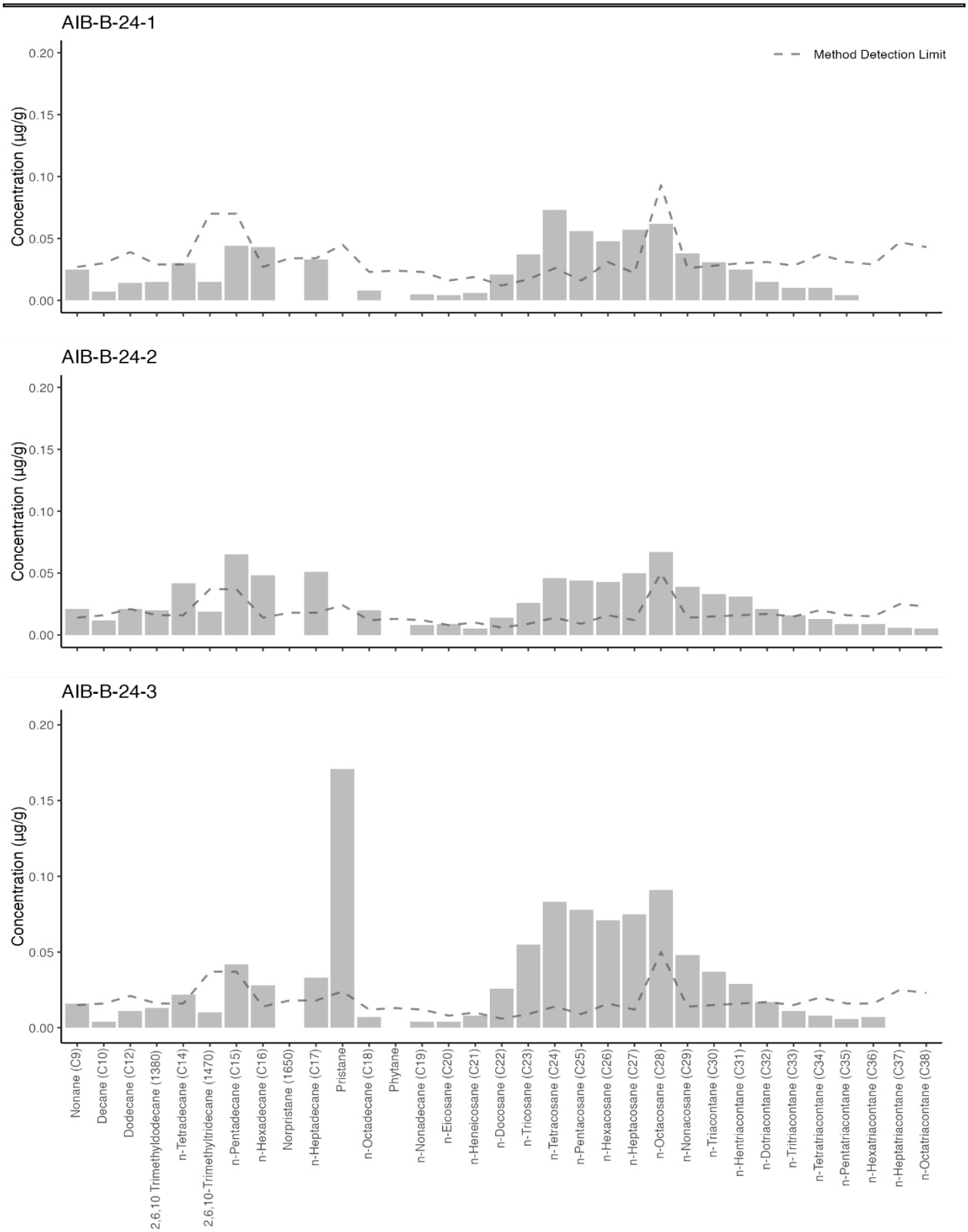

Figure 19. 2024 saturated hydrocarbon profiles from individual tissue samples at Aialik Bay (AIB) site with the analyte-specific method detection limit superimposed as a dotted line.

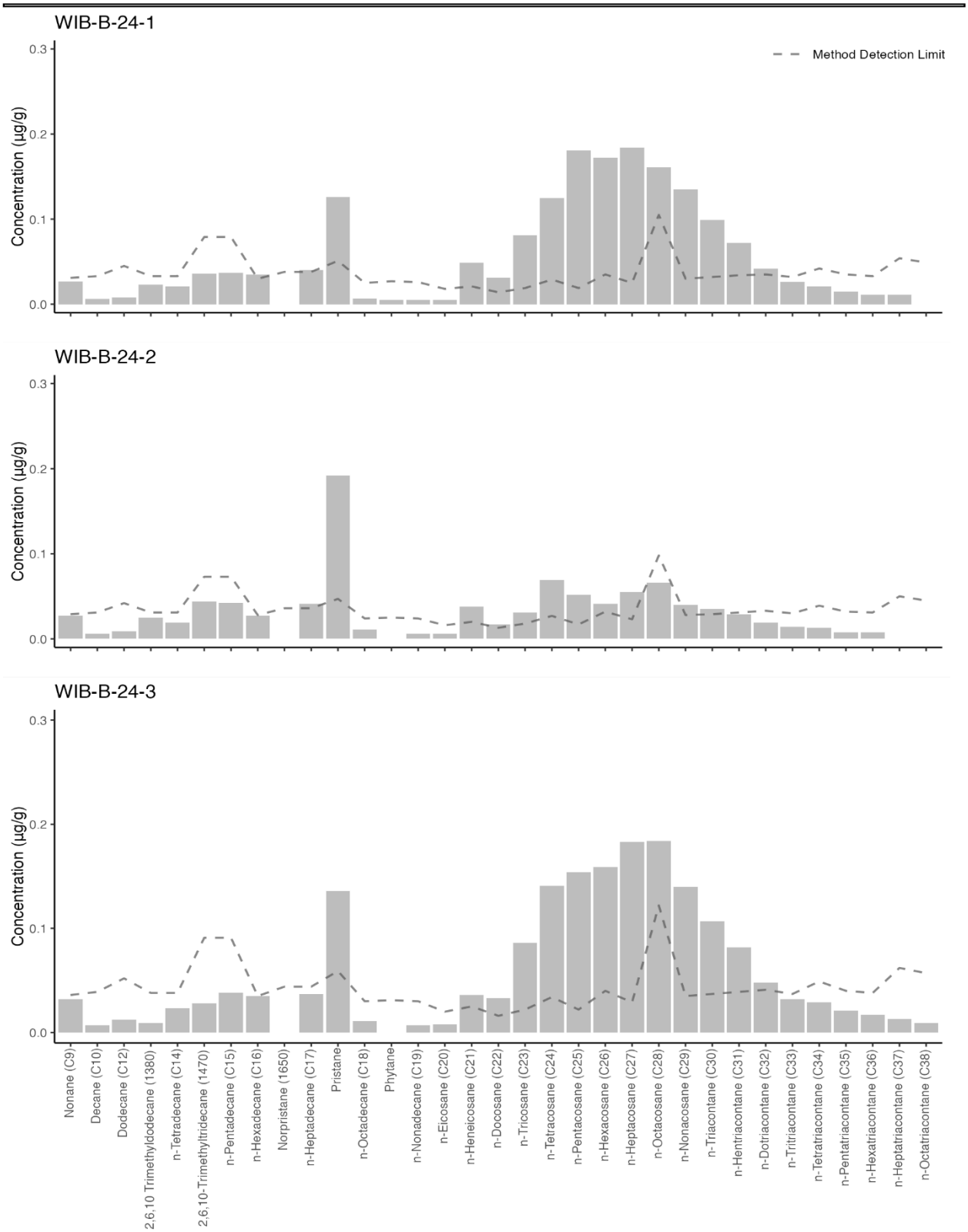

Figure 20. 2024 saturated hydrocarbon profiles from individual tissue samples at the Windy Bay (WIB) site with the analyte-specific method detection limit superimposed as a dotted line.

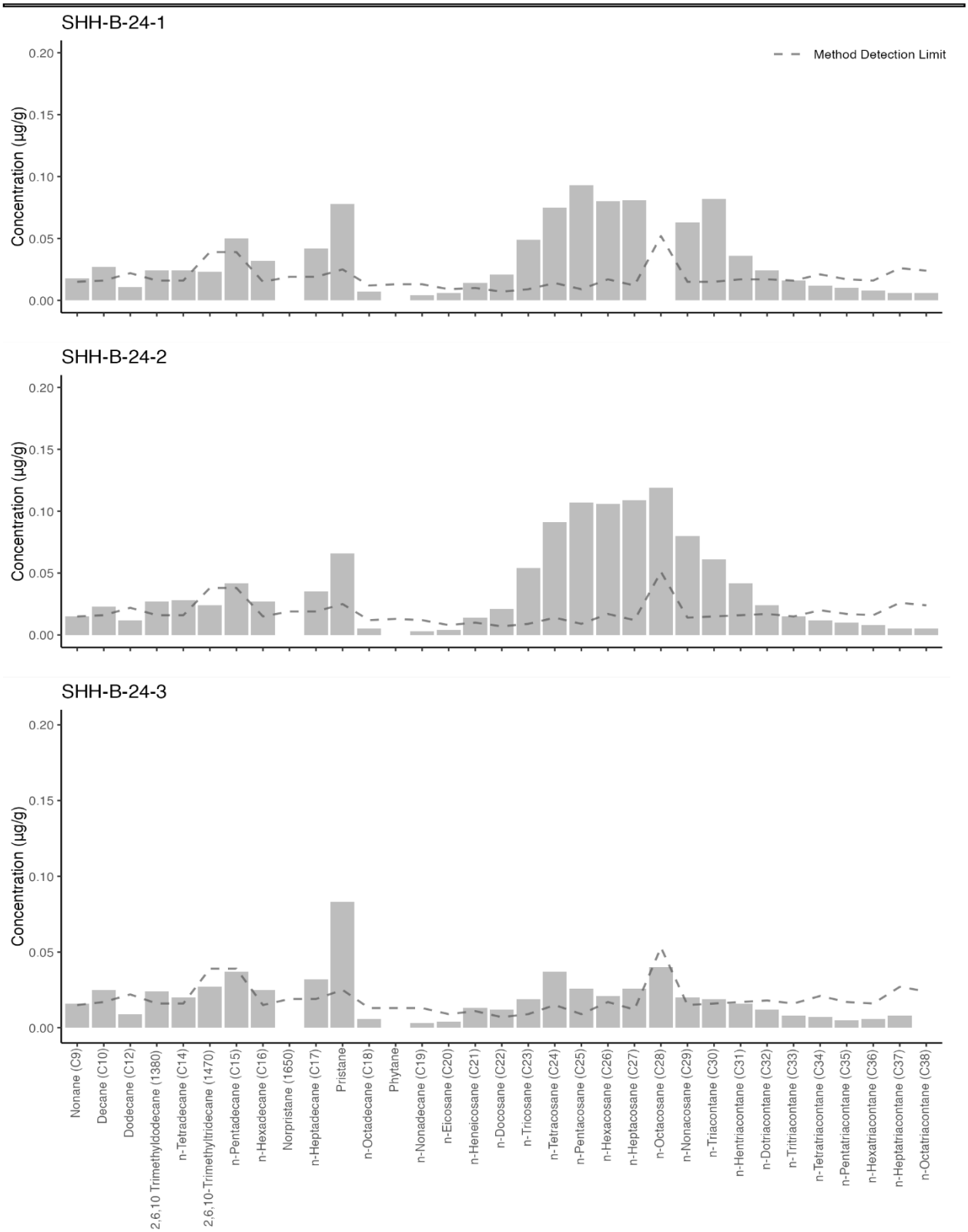

Figure 21. 2024 saturated hydrocarbon profiles from individual tissue samples at the Shuyak harbor (SHH) site with the analyte-specific method detection limit superimposed as a dotted line.

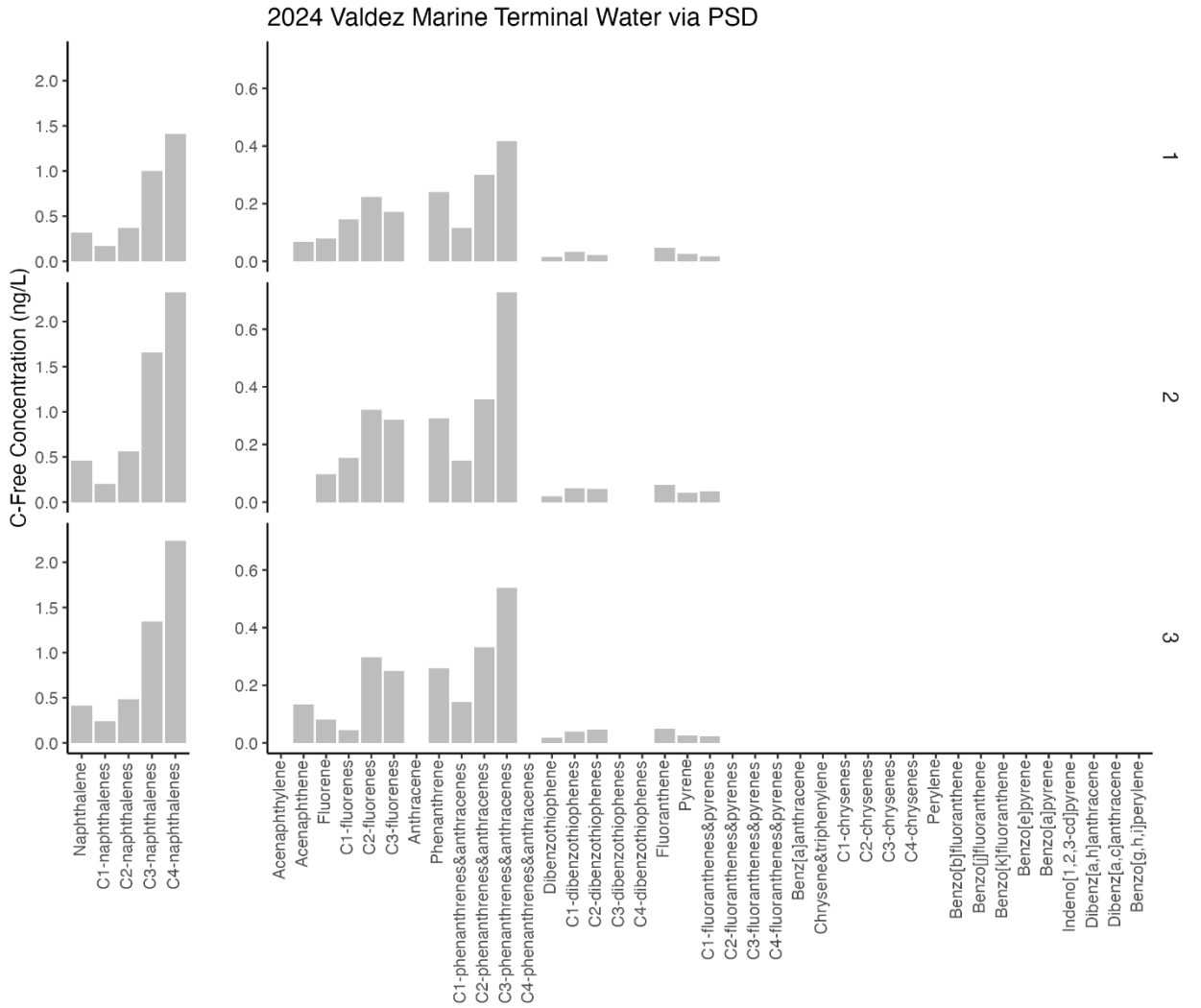

Figure 22. PAH profiles in seawater sampled via passive sampling devices placed at Valdez Marine Terminal in 2024. Values represent the reported values for the three replicates stacked vertically. Note the changes in scale between the Naphthalenes on the left and the other PAHs.

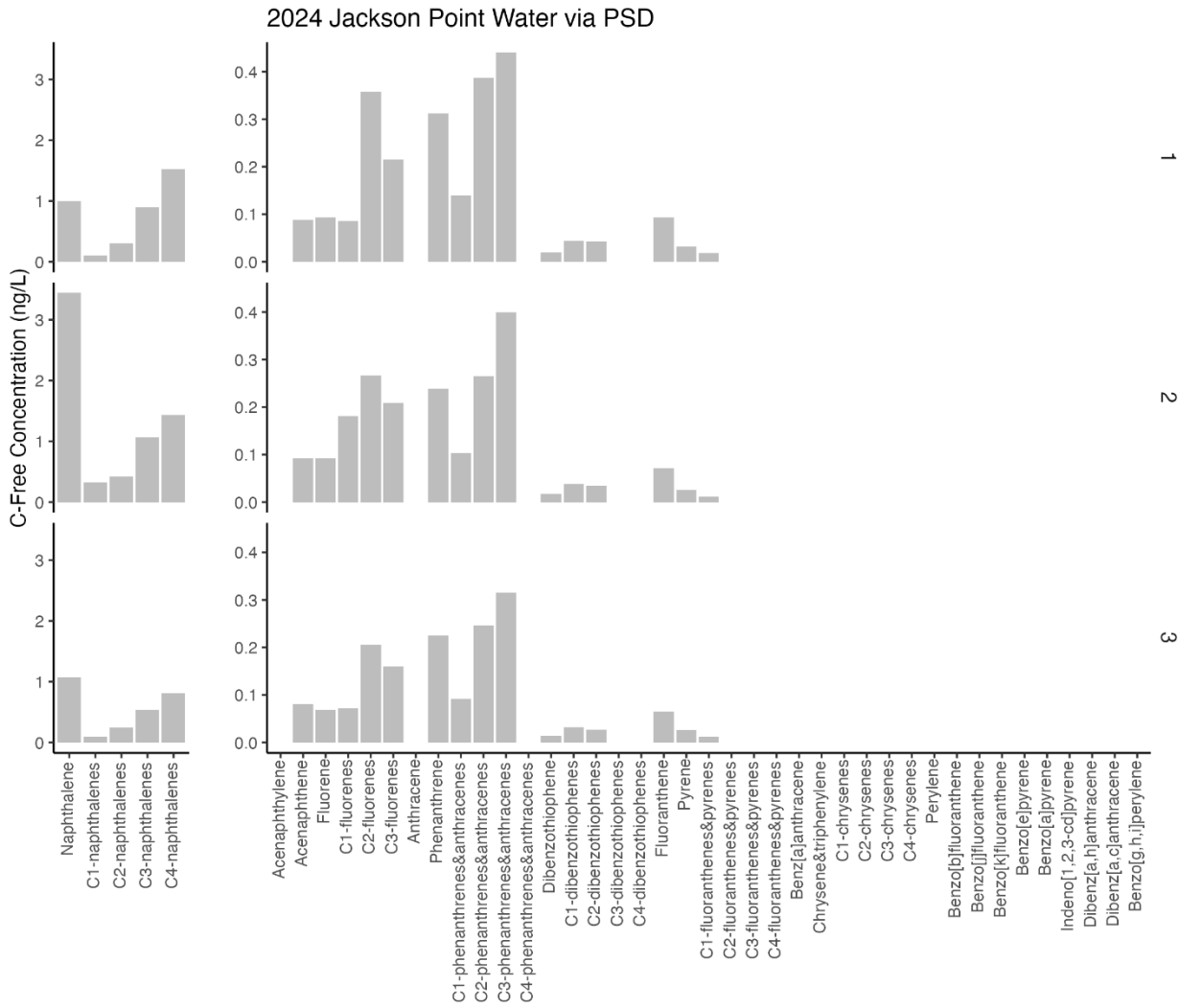

Figure 23. PAH profiles in seawater sampled via passive sampling devices placed at Jackson Point in 2024. Values represent the reported values for the three replicates stacked vertically. Note the changes in scale between the Naphthalenes on the left and the other PAHs.

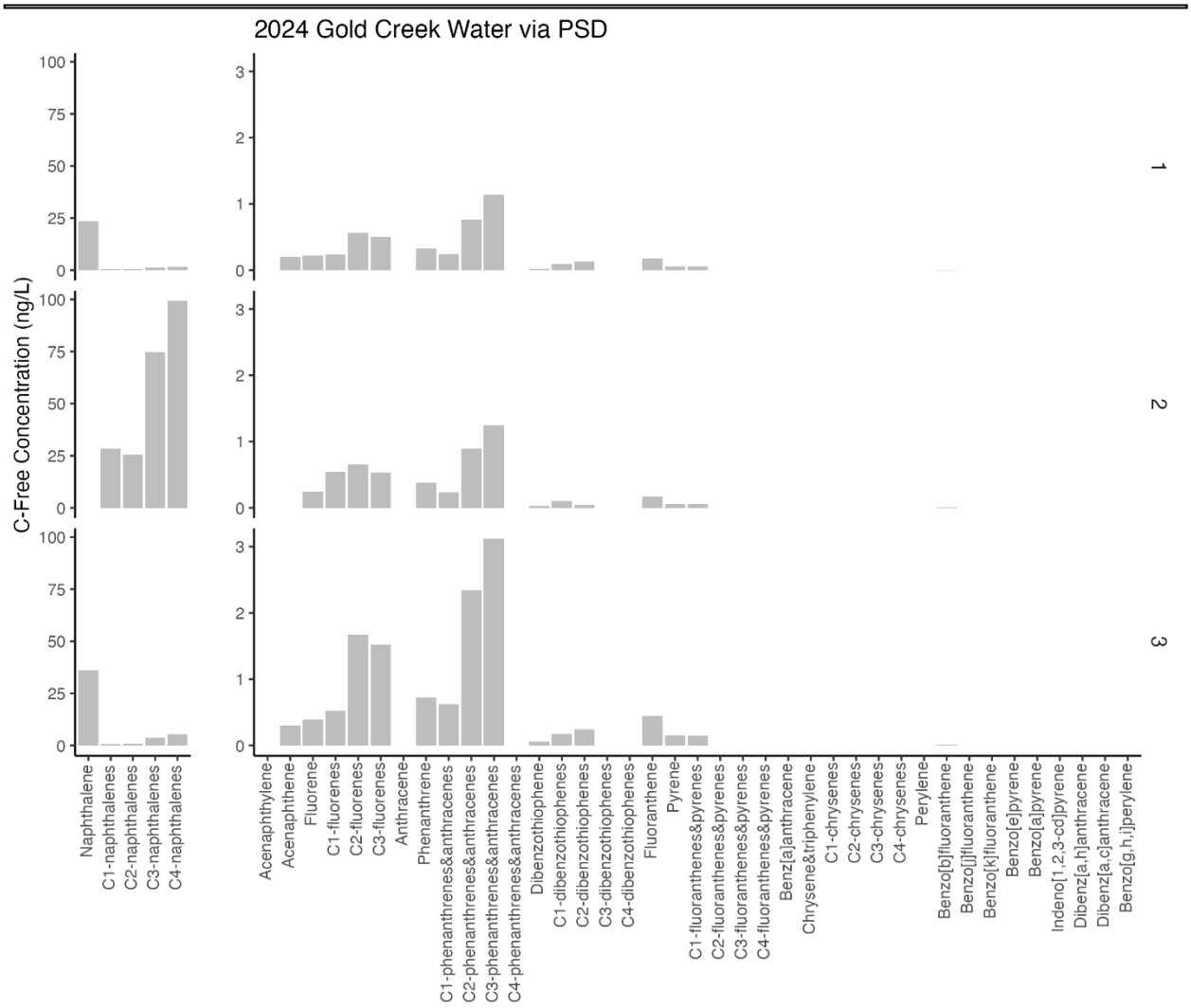

Figure 24. PAH profiles in seawater sampled via passive sampling devices placed at Gold Creek in 2024. Values represent the reported values for the three replicates stacked vertically. Note the changes in scale between the Naphthalenes on the left and the other PAHs.

fjord & fish sciences

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Final

2024 Sediment Metals Report

A pilot study of the Long-Term Environmental Monitoring Program

PREPARED FOR

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"The opinions expressed in this PWSRCAC commissioned report are not necessarily those of PWSRCAC. PWSRCAC Contract #9510.25.06."

Table of Contents

ACRONYMS AND ABBREVIATIONS

ADEC.....	Alaska Department of Environmental Conservation
AMT.....	Alyeska Marine Terminal, site name for Valdez Marine Terminal
ANS	Alaska North Slope
APDES.....	Alaska Pollutant Discharge Elimination System
BWTF	Ballast Water Treatment Facility
EPA.....	U.S. Environmental Protection Agency
ERL.....	Effects Range Low
ERM.....	Effects Range Medium
EVOS	Exxon Valdez Oil Spill
GOC	Gold Creek Reference Site
LTEMP.....	Long-Term Environmental Monitoring Program
NOAA.....	National Oceanic and Atmospheric Administration
PAHs	Polycyclic aromatic hydrocarbons
PPB	Parts Per Billion (ng/g [nanograms per gram] or µg/L [microgram/ liter])
PPM.....	Parts Per Million (mg/kg [milligram per kilogram])
PWSRCAC	Prince William Sound Regional Citizens' Advisory Council
SQG..... .	Sediment Quality Guidelines

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 to promote the environmentally safe operation at 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 has been conducted, focusing on crude oil-specific hydrocarbons. However, concern over the accumulation of metals, specifically zinc, in sediments from the terminal and tanker operations spurred investigations into sediment metal concentrations.

In 2024, we analyzed 23 different metals in sediments at the Valdez Marine Terminal (terminal), close to the outfall from the Ballast Water Treatment Facility and the Port Valdez reference site at Gold Creek. Twenty-two metals were detected at each site, ranging from 40,000 mg/kg dry-weight Iron in terminal sediments to less than 0.1 mg/kg mercury at the terminal and Gold Creek. The terminal sediments had significantly higher metal concentrations overall, and for 10 specific metals, than Gold Creek. Both sites exceed NOAA's sediment quality guidelines for the protection of benthic life for eight metals. Several metals known to be in Ballast Water Treatment Facility effluent from recent Council work were also found in higher concentrations at the terminal compared to Gold Creek. Of these metals with a suggested effluent origin, four metals—aluminum, copper, iron, and vanadium—exceeded the effect range thresholds, suggesting that terminal and tanker operations may be eliciting adverse effects on benthic organisms. These findings warrant further investigation into the extent of the metal accumulation, the sensitivity of benthic organisms in the area, and the source of high metal concentrations locally.

2. Introduction

The Long-Term Environmental Monitoring Program (LTEMP), managed by the Prince William Sound Regional Citizens' Advisory Council (Council), 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.

The 2024 LTEMP campaign also collected sediment samples to assess the degree of metal accumulation. In Spring 2024, the Council's Scientific Advisory Committee decided to include a pilot sampling campaign on sediment metals as recent studies by the University of New Orleans detected metals in water samples collected at the Valdez Marine Terminal's Ballast Water Treatment Facility (BWTF) (Harsha & Podgorski, 2023). There is a potential ecological risk associated with the discharge of metals from the BWTF, as metals are generally stable and do not degrade; thus, there is a possibility that metals accumulate in sediment, reaching toxic levels (Long et al., 1995). While not a part of the core LTEMP campaign, this additional sampling benefitted from piggybacking on the sampling, analysis, and data visualization of LTEMP's hydrocarbon analysis. The 2024 LTEMP campaign collected sediment samples from two sites in Port Valdez (i.e., Gold Creek and the BWTF's outfall at the Valdez Marine Terminal).

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

- The sediment metal concentrations and the level of variability at the Valdez Marine Terminal and the Gold Creek reference site.
- The potential bioavailability and ecotoxicological risk posed by the measured metal concentrations using protective sediment quality guidelines.
- The influence and potential effects of metals originating from the terminal and tanker activities.
- Recommendations for future monitoring of sediment metals at the terminal and in Prince William Sound.

3. Methods

Sediment samples were collected in early June of 2024, at LTEMP monitoring stations in Port Valdez, Alyeska's Valdez Marine Terminal, and Gold Creek (Figure 1). Sediment sampling was performed using a modified Van Veen grab deployed from a local fishing

vessel, Equinox. The top 5 cm of undisturbed sediment was scooped using a clean metal spoon and placed in a glass sampling jar. Triplicate grab samples were collected at each site. Samples were frozen until shipped to Pace Analytical Services in Mansfield, Massachusetts.

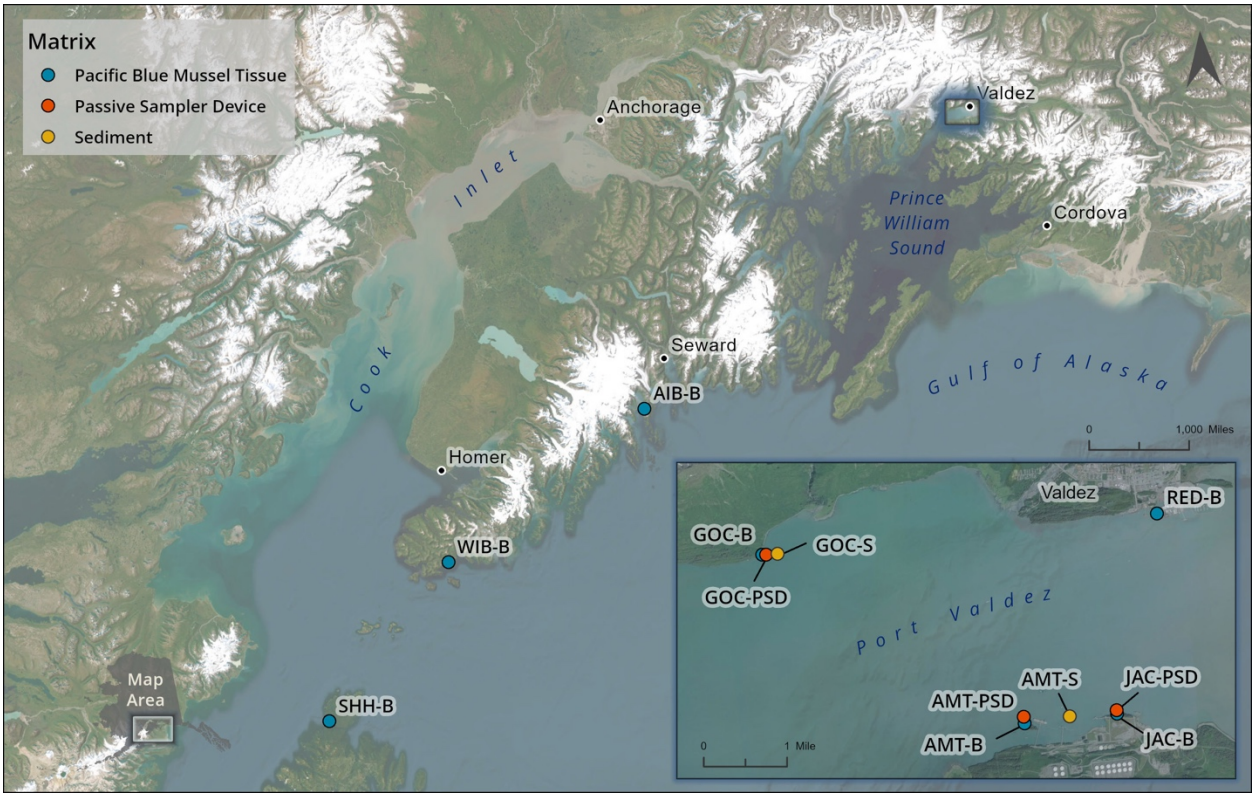

Figure 1. 2024 sampling sites for the Long-Term Environmental Monitoring Program in Port Valdez and the North Gulf of Alaska. The color of the points and labels represent differences in sampling matrices. Sediment metals samples were collected from the yellow-colored (S) sites only.

Samples were analyzed for 23 metals (Table 1) and the standard suite of LTEMP analytes (i.e., PAHs, saturated hydrocarbons, and geochemical petroleum biomarkers; Fjord & Fish, 2024). Sediment physical analyses included particle size (not reported herein) and total organic carbon content. Metals except mercury were quantified using the analytical method Environmental Protection Agency (EPA) 6020B (i.e., inductively coupled plasma). Mercury was quantified using EPA method 7474 to detect low-level mercury in ppb and ppm ranges. The results were of acceptable precision and accuracy based on laboratory quality control and quality assurance data.

Sediment quality guidelines (SQG) are numerical chemical concentrations intended to be either protective of biological resources, predictive of adverse effects on those resources, or both (Hübner et al., 2009). Here, we use the NOAA's SQGs for metals, expressed as effect ranges. Effect Range Low (ERL) is a threshold concentration below which effects should rarely be observed (i.e., in less than 10% exposure incidences; Long et al., 1995). It can be considered an appropriate sediment quality guideline that protects benthic organisms as it is based on the consensus value from 100s of rigorous exposure experiments conducted

across multiple laboratories and benthic taxa (Long et al., 1995). Effect Range Medium (ERM) was also used, indicating that adverse effects would frequently occur above this threshold (i.e., up to 95% of exposure incidences; Long et al., 1995). These SQGs are found to perform well at predicting primarily acute effects of contaminants in sediments on benthic organisms (Hübner et al., 2009).

Using R (R Core Team, 2024), metal concentrations were plotted as bar charts with mean concentrations and standard deviation across the three replicates. Statistical analysis between sites was done using a Two-Sample t-test for samples with equal variance (i.e., variance is less than an order of magnitude different between sites) and a Welch Two-Sample T-Test when variance was unequal. Statistical significance was set at alpha <0.05. Statistical parameters are presented (Table 2).

4. Results & Discussion

Twenty-two metals were detected at each site, with 21 found at both sites (Figure 2). Concentrations ranged from 40,000 mg iron /kg dry weight in terminal sediments to less than 0.1 mg mercury /kg at the terminal and Gold Creek. Iron, aluminum, magnesium, sodium, calcium, potassium, and magnesium exceeded 1000 mg/kg in the terminal and Gold Creek sediments. Meanwhile, antimony, beryllium, silver, cadmium, selenium, and thallium were estimated as concentrations under the reporting detection limit at both sites.

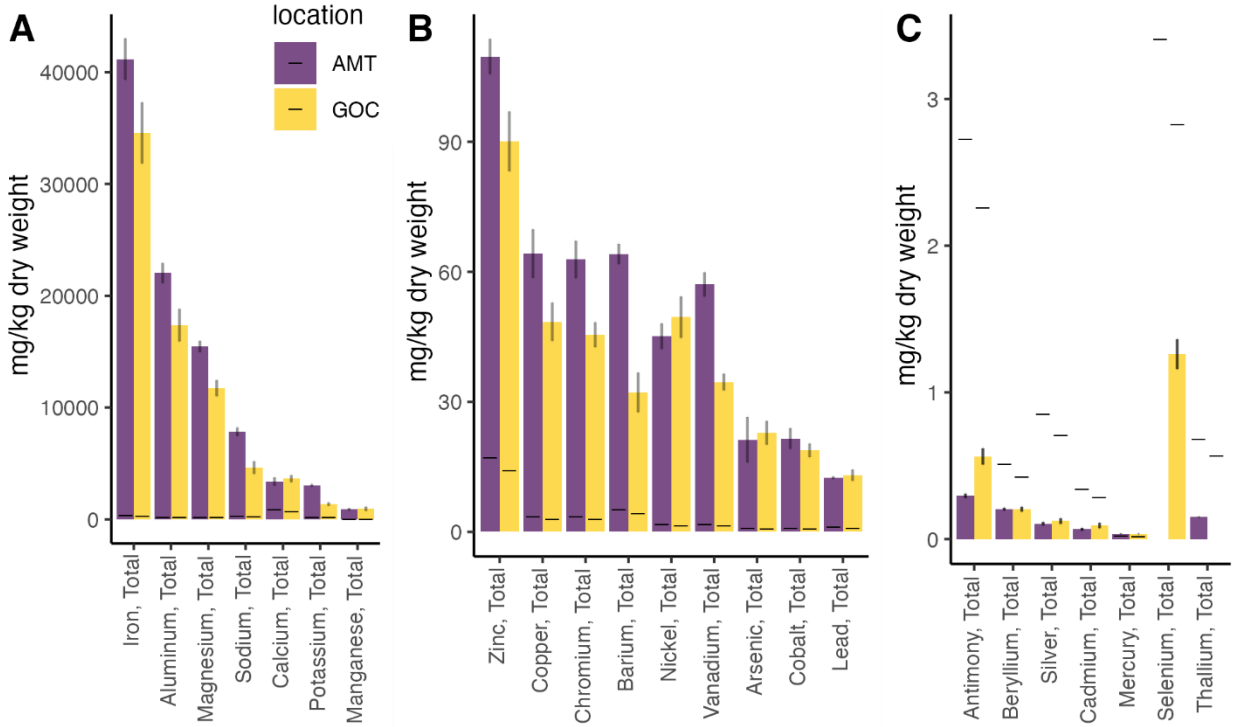

Figure 2. Sediment metal concentrations are displayed as a bar plot with mean ± standard deviation for Valdez Marine Terminal (AMT) in purple and Gold Creek (GOC) in yellow. Dashes represent the mean metal-specific reporting limit. Note that each panel has a different scale.

Were there differences between sites?

The terminal sediments had higher metal concentrations than Gold Creek, with statistically significantly higher concentrations of aluminum, barium, chromium, copper, iron, magnesium, potassium, sodium, vanadium, and zinc (Tables 1 and A1). Gold Creek had significantly higher concentrations of antimony compared to the terminal. Estimated selenium concentrations were detected at Gold Creek, while thallium was estimated at the terminal. The total organic carbon percentage was similar across both sites (0.50-0.52%), indicating similar metal bioavailability (Zhang et al., 2020).

Are these metal levels of concern for the ecosystem/biota?

Using the most protective empirically based sediment quality guidelines (e.g., Long et al. 1995), the ERL was exceeded at one or both stations for iron, vanadium, aluminum, arsenic, nickel, cobalt, copper, and selenium (Figure 3). The ERM was exceeded at in one replicate at Gold Creek for nickel (i.e. Nickel ERM set at 50 mg/kg and nickel values were 54.5, 49.1, and 45.0 mg/kg).

Zinc was one metal identified explicitly in the Harsha and Podgorski work, and Alaska Department of Environmental Conservation (ADEC) 2019 Alaska Pollutant Discharge Elimination System (APDES) permit renewal that is thought to be driving effluent toxicity. Here, we see that sediment zinc levels are, in fact, significantly higher at the terminal than at Gold Creek; however, these levels do not exceed the NOAA's protective effect thresholds for benthic life (i.e., ERM-L; Long et al., 1995). No other sediment toxicity thresholds were investigated in this pilot study.

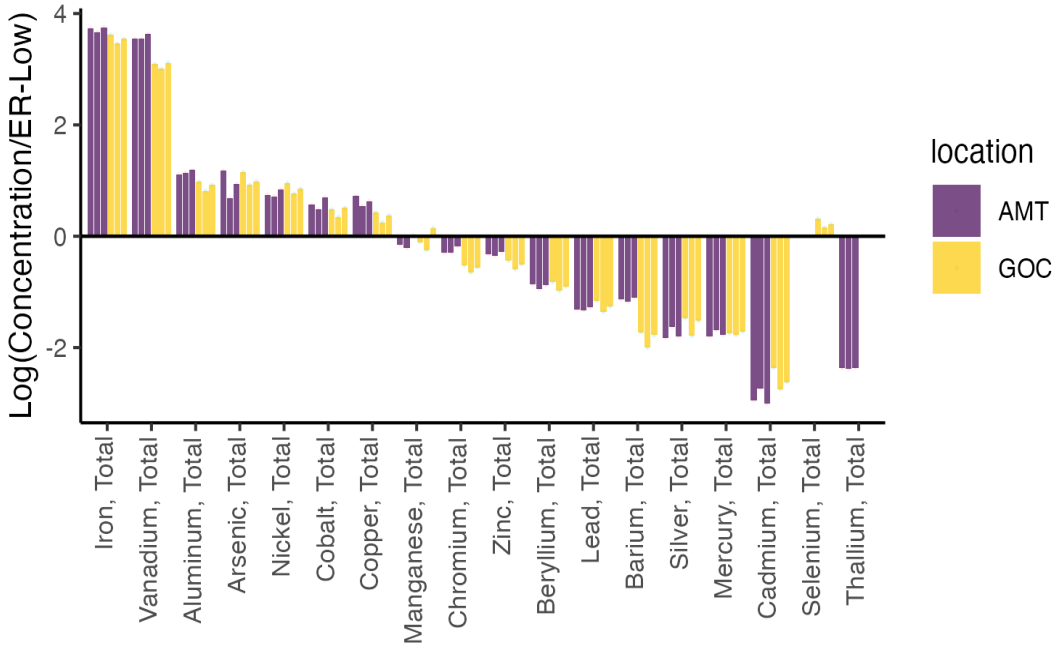

Figure 3. Sediment metal concentrations normalized to the Effect Range Low (ERL) value, shown on a log scale and organized by the degree of ERL threshold exceedance. Each sample replicate is displayed individually. Bar colors represent location. Metals that do not surpass the ERL threshold have negative values due to the log scale. Metals without an ERL threshold are excluded from the plot.

Are metals at the terminal likely related to terminal and tanker activity?

Of the metals found at concentrations > 1 µg/L in the BWTF effluent by Harsha and Podgorski (2023) (i.e., barium, zinc, magnesium, nickel, aluminum, mercury, arsenic, iron, copper), only nickel, mercury, and arsenic were not significantly enriched in the terminal sediments compared to Gold Creek. While found in low concentrations (i.e., < 1 µg/L) in the BWTF effluent, vanadium and potassium were significantly higher in the terminal sediments compared to Gold Creek.

Are metals likely contributed by terminal and tanker activity of environmental concern?

Four metals—aluminum, copper, iron, and vanadium—exceeded the effect range thresholds and are significantly elevated in the terminal sediments compared to Gold Creek. However, all of these metals exceed the effect range threshold at Gold Creek. No metal was found to only exceed the effect threshold at the terminal. This is most clearly seen in Figure 3.

Previous work by the EPA in Port Valdez conducted before and during the construction of the Valdez Marine Terminal and the Trans-Alaska Pipeline found widespread and comparable concentrations of metals, including vanadium, nickel, iron, chromium, and cobalt (EPA, 1976). Vanadium, for example, is a common naturally occurring element in the lithosphere but is also used intensely as an additive in the steel industry, with its rust-resistant properties making it highly valuable in shipbuilding and an emerging marine pollution concern (Tambat et al 2024). Other potential sources of metals are contemporary metal-based biocides used in antifouling paints, which contain copper and zinc (Torres and De-la-Torre, 2021).

5. Conclusion

The 2024 LTEMP sampling for hydrocarbons was complimented by sediment sampling for trace metals. The recent 2019 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). Aqueous input of metals, such as from the BWTF effluent, does not completely explain the presence and concentrations of the metals found in the terminal sediment; rather, the physical and chemical properties of individual metals and of the sediments themselves influence sediment metal concentrations (Zang et al 2020).

Our findings show that several metals in sediments at the terminal exceed protective sediment quality guidelines, possibly causing adverse effects in benthic organisms. Port Valdez is a metal-rich system with a history of copper and gold mining and several large, glacially-fed rivers entering within miles of the sampling locations. These local sources may explain regional patterns such as high iron concentration. This may also call into question the utility of the NOAA's Sediment Quality Guidelines for benthic organisms residing in Port Valdez. More effort could be put into framing these metal concentrations in the local and

regional background levels (e.g., values published in EPA's 1976 report titled The Sediment Environment of Port Valdez, Alaska), inputs from rivers and streams, LTEMP Hydrocarbon concentrations, or other areas with human activity and oil and gas transport.

Several metals are significantly elevated at the terminal, can be tied to BWTF effluent, and exceed protective guidelines. These metals accumulated in sediments near the terminal warrant further investigation, including understanding the specific sensitivity of local benthic organisms and the origin of metals detected using source identification techniques.

Table 1. A summary of sediment metal concentrations, analytical detection limits, sediment quality guidelines (Effect Range Low and Medium), exceedance of effect ranges, source of those effect ranges, and statistical test results of difference between stations.

Analysis	Valdez Marine Terminal (AMT)	Gold Creek (GOC)	Reporting Limit	Effects Range Low (ERL)	Effects Range Medium (ERM)	>ERL?	>ERM?	Source	Sign diff betwn sites?**
	Mean ± STD (mg/kg dry weight)			(mg/kg dry weight)					
Aluminum, Total	22033.33 ± 907.38	17366.67 ± 1464.01	141.33	7,000.00	-	yes	-	U.S. EPA, 2004	*
Antimony, Total	0.29 ± 0.02	0.56 ± 0.06	2.26	-	-	-	-		*
Arsenic, Total	21.27 ± 5.26	22.83 ± 2.75	0.71	8.2	70	yes	no	U.S. EPA, 2004	-
Barium, Total	64.1 ± 2.35	32.17 ± 4.57	4.24	200	-	no	-	Long et al., 1995	***
Beryllium, Total	0.2 ± 0.01	0.2 ± 0.02	0.42	0.5	3	no	no	Long et al., 1995	-
Cadmium, Total	0.07 ± 0.01	0.09 ± 0.02	0.28	1.2	4.2	no	no	Long et al., 1995	-
Calcium, Total	3386.67 ± 380.18	3643.33 ± 317.86	706	-	-	-	-		-
Chromium, Total	62.83 ± 4.3	45.47 ± 2.87	2.82	81	370	no	no	Long et al., 1995	**
Cobalt, Total	21.53 ± 2.38	18.8 ± 1.59	0.71	12	68	yes	no	Long et al., 1995	-
Copper, Total	64.2 ± 5.6	48.47 ± 4.41	2.82	34	197	yes	no	Long et al., 1995	*
Iron, Total	41166.67 ± 1858.31	34566.67 ± 2750.15	282.33	1,000.00	-	yes	-	U.S. EPA, 2004	*
Lead, Total	12.47 ± 0.31	13.07 ± 1.3	0.85	46	218	no	no	Long et al., 1995	-
Magnesium, Total	15466.67 ± 503.32	11733.33 ± 723.42	141.33	-	-	-	-		**
Manganese, Total	894.67 ± 110.75	947.33 ± 193.7	2.82	1,000.00	-	no	-	U.S. EPA, 2004	-
Mercury, Total	0.03 ± 0	0.04 ± 0	0.02	0.2	1	no	no	U.S. EPA, 2004	-
Nickel, Total	45.13 ± 2.99	49.53 ± 4.76	1.41	20.9	50	yes	some	Long et al., 1995	-
Potassium, Total	3043.33 ± 118.46	1360 ± 149.33	141.33	-	-	-	-		**
Selenium, Total	-	1.26 ± 0.1	2.82	1	9	yes	no	Long et al., 1995	
Silver, Total	0.1 ± 0.01	0.12 ± 0.02	0.71	0.6	7	no	no	Long et al., 1995	-
Sodium, Total	7836.67 ± 380.83	4623.33 ± 571.78	211.67	-	-	-	-		**
Thallium, Total	0.15 ± 0	-	0.57	1.6	-	no	-	U.S. EPA, 2004	
Vanadium, Total	57.07 ± 2.8	34.57 ± 1.93	1.41	1.6	-	yes	-	US EPA, 2004	***
Zinc, Total	109.67 ± 4.04	90.07 ± 6.92	14.13	150	410	no	no	Long et al 1995	*
Solids, Total (%)	56.4 ± 0.79	68.4 ± 2.69	0.1						
Total Organic Carbon (%)	0.52 ± 0.04	0.50 ± 0.03							
Total Metal Concentration	94343.52 ± 3033.14	74666.31 ± 5704.19							
Total Heavy Metals*	72446.47 ± 2522.56	57929.4 ± 4571.07							
*Total Heavy Metals (THM) by Harsha & Podgorski - Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V, and Zn									
**P-value conversion	"-" = Not Significant; * , α= 0.05-0.01; **, α = 0.01-0.001; ***, α <0.001								

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Table A1. A summary of the statistical test results for tests between sites for each metal.

Analysis	Valdez Marine Terminal (AMT)	Gold Creek (GOC)	Statistical Test	t Value	degrees of freedom	p-value
Mean ± STD (mg/kg dry weight)						
Aluminum, Total	22033.33 ± 907.38	17366.67 ± 1464.01	Welch 2 sample t test	4.69280	3.339	0.01435
Antimony, Total	0.29 ± 0.02	0.56 ± 0.06	Welch 2 sample t test	-8.01800	2.2907	0.01009
Arsenic, Total	21.27 ± 5.26	22.83 ± 2.75	Two Sample t-test	-0.45732	4	0.6712
Barium, Total	64.1 ± 2.35	32.17 ± 4.57	Two Sample t-test	10.75400	4	0.0004239
Beryllium, Total	0.2 ± 0.01	0.2 ± 0.02	Two Sample t-test	0.03049	4	0.9771
Cadmium, Total	0.07 ± 0.01	0.09 ± 0.02	Two Sample t-test	-2.10580	4	0.103
Calcium, Total	3386.67 ± 380.18	3643.33 ± 317.86	Two Sample t-test	-0.89711	4	0.4204
Chromium, Total	62.83 ± 4.3	45.47 ± 2.87	Two Sample t-test	5.81620	4	0.00435
Cobalt, Total	21.53 ± 2.38	18.8 ± 1.59	Two Sample t-test	1.65500	4	0.1733
Copper, Total	64.2 ± 5.6	48.47 ± 4.41	Two Sample t-test	3.82180	4	0.01875
Iron, Total	41166.67 ± 1858.31	34566.67 ± 2750.15	Two Sample t-test	3.44410	4	0.02619
Lead, Total	12.47 ± 0.31	13.07 ± 1.3	Two Sample t-test	-0.77748	4	0.4803
Magnesium, Total	15466.67 ± 503.32	11733.33 ± 723.42	Two Sample t-test	7.33740	4	0.001837
Manganese, Total	894.67 ± 110.75	947.33 ± 193.7	Two Sample t-test	-0.40883	4	0.7036
Mercury, Total	0.03 ± 0	0.04 ± 0	Two Sample t-test	-0.25000	4	0.8149
Nickel, Total	45.13 ± 2.99	49.53 ± 4.76	Two Sample t-test	-1.35510	4	0.2468
Potassium, Total	3043.33 ± 118.46	1360 ± 149.33	Two Sample t-test	15.29600	4	0.0001066
Selenium, Total	-	1.26 ± 0.1				
Silver, Total	0.1 ± 0.01	0.12 ± 0.02	Two Sample t-test	-1.35590	4	0.2466
Sodium, Total	7836.67 ± 380.83	4623.33 ± 571.78	Two Sample t-test	8.10140	4	0.001262
Thallium, Total	0.15 ± 0	-				
Vanadium, Total	57.07 ± 2.8	34.57 ± 1.93	Two Sample t-test	11.45900	4	0.000331
Zinc, Total	109.67 ± 4.04	90.07 ± 6.92	Two Sample t-test	4.23830	4	0.01328
Solids, Total (%)	56.4 ± 0.79	68.4 ± 2.69				
Total Organic Carbon (%)	0.52 ± 0.04	0.50 ± 0.03				
Total Metal Concentration	94343.52 ± 3033.14	74666.31 ± 5704.19				
Total Heavy Metals*	72446.47 ± 2522.56	57929.4 ± 4571.07				
*Total Heavy Metals (THM) by Harsha & Podgorski - Ag, Al, As, Ba, Cd, Co, Cr, C						
**P-value conversion	"-" = Not Significant; * , α= 0.05-0.01; **, α = 0.01					