From Tankers to Tissues – Tracking the Degradation and Fate of Oil Discharges in Port Valdez, Alaska

James R. Payne
Payne Environmental Consultants, Inc.
Encinitas, California
jrpayne@sbcglobal.net

William B. Driskell
Seattle, Washington

Joan F. Braddock, Justin Bailey
University of Alaska
Fairbanks, Alaska

Jeffrey W. Short
NOAA/NMFS
Auke Bay, Alaska

Lisa Ka'aihue, Thomas H. Kuckertz
Prince William Sound Regional Citizen's Advisory Council
Anchorage/Valdez, Alaska

Abstract

The Alyeska Pipeline Service Company (APSC) Ballast Water Treatment Facility (BWTF) at the terminus of the Trans-Alaska Pipeline in Port Valdez, Alaska, treats and discharges an average of nine million gallons per day of oil-contaminated ballast water offloaded from the tankers utilizing the Port. This study quantifies the fractions of benzene, toluene, ethylbenzene, and xylene(s) (BTEX), polycyclic aromatic hydrocarbons (PAH), and saturated hydrocarbons (SHC) being removed at different stages of treatment inside the terminal and evaluates the relative importance of abiotic (aeration) versus microbial processes. Evaporation is the dominant removal mechanism for BTEX, lower-molecular-weight SHC, and possibly the naphthalenes in the dissolved air flotation (DAF) cells/weirs and in the Splitter Box distributing DAF effluent to the biological treatment tanks (BTTs). Within the BTTs, microbial degradation of BTEX is very efficient and essentially complete midway through the tanks. During the warmer months, SHC biodegradation within the BTT tanks is also very rapid, but PAH biodegradation is only partially complete before the effluent is discharged into Port Valdez, a sill-constricted, subarctic fjord. Both SHC and PAH biodegradation are limited within the BWTF during colder months. Alkylated PAH homologues that make up the discharged oil signal have been tracked via mussel and sediment samples from the Long-Term Environmental Monitoring Program (LTEMP) that has detected accidental discharges as well as the seasonally-controlled transport of BWTF-sourced dissolved- and particulate/oil-phase fractions throughout the Port.

1 Introduction

During their return trip to Alaska, tankers transporting Alaska North Slope (ANS) crude oil along the west coast of the United States are loaded with seawater ballast. Segregated ballast tanks are being phased into the tanker fleet, but most still utilize the crude oil cargo tanks to hold the ballast water. Arriving at the Alyeska Marine Terminal (AMT) in Port Valdez, Alaska (Figure 1), the tankers de-ballast their oily-water into the Ballast Water Treatment Facility (BWTF). This facility typically treats and discharges 9,000,000 gallons of ballast water per day into Port Valdez.

This paper focuses on the results from two Prince William Sound Regional Citizens' Advisory Council (PWS RCAC) monitoring programs detailing changes in

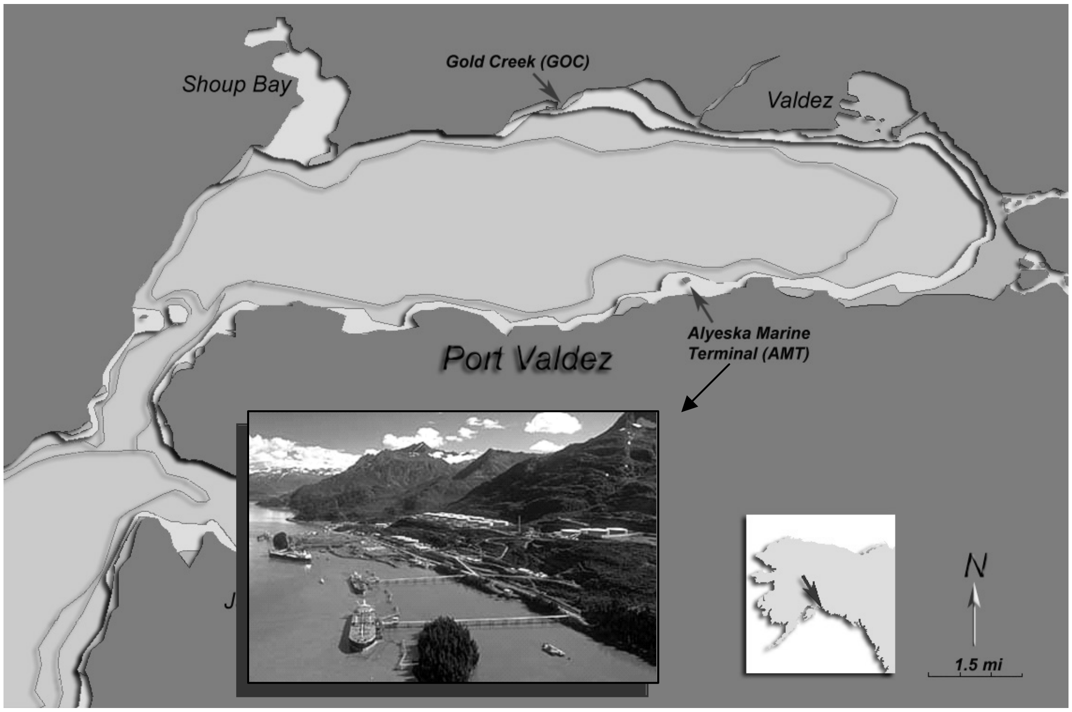

Figure 1. Map of Port Valdez sampling locations.

chemical composition of the treated ballast water as it moves from tankers through the facility, and subsequently traces the effluent hydrocarbons into the receiving environment of Port Valdez, a sill-constricted, subarctic fjord.

The treatment facility involves gravity separation (90s) tanks, dissolved air flotation (DAF) cells, and biological treatment tanks (BTT) as described further below. Effluent containing traces of volatile aromatics including benzene, toluene, ethylbenzene, and xylenes (BTEX), low levels of oil measured as total recoverable oil and grease (TROG), saturated hydrocarbons (SHC), and polycyclic aromatic hydrocarbons (PAHs) is being continuously discharged to Port Valdez (Payne et al., 2001, 2002a, 2003a; Salazar et al., 2002). Because of the extremely large average flow rate, even low concentrations can add up to a significant mass discharge. For example, an average flow of 9 million gallons per day (9 MGD) and an average TROG loading of only 2-6 mg/L imply a discharge of approximately 150-450 pounds (68-204 Kg) of oil per day. Assuming a specific gravity of 0.9, this is the equivalent of 0.5-1.4 barrels of oil being discharged daily into the Port. In addition, EPA's National Pollutant Discharge Elimination System (NPDES) Permit states that on average, approximately 580 pounds per day or 105 tons per year of BTEX is removed by the DAF system with much of this mass vented directly into the atmosphere. More recent studies estimate total BTEX discharge to the atmosphere at 43.4 tons per year (Imperial Oil Research, 2005).

1.1 Terminal Overview and BWTF Layout

In a plan view diagram of the BWTF, Figure 2 identifies sampling locations used in the PWS RCAC programs to evaluate treated ballast-water characteristics and process efficiencies. Brief descriptions of the different stages of the BWTF are presented below.

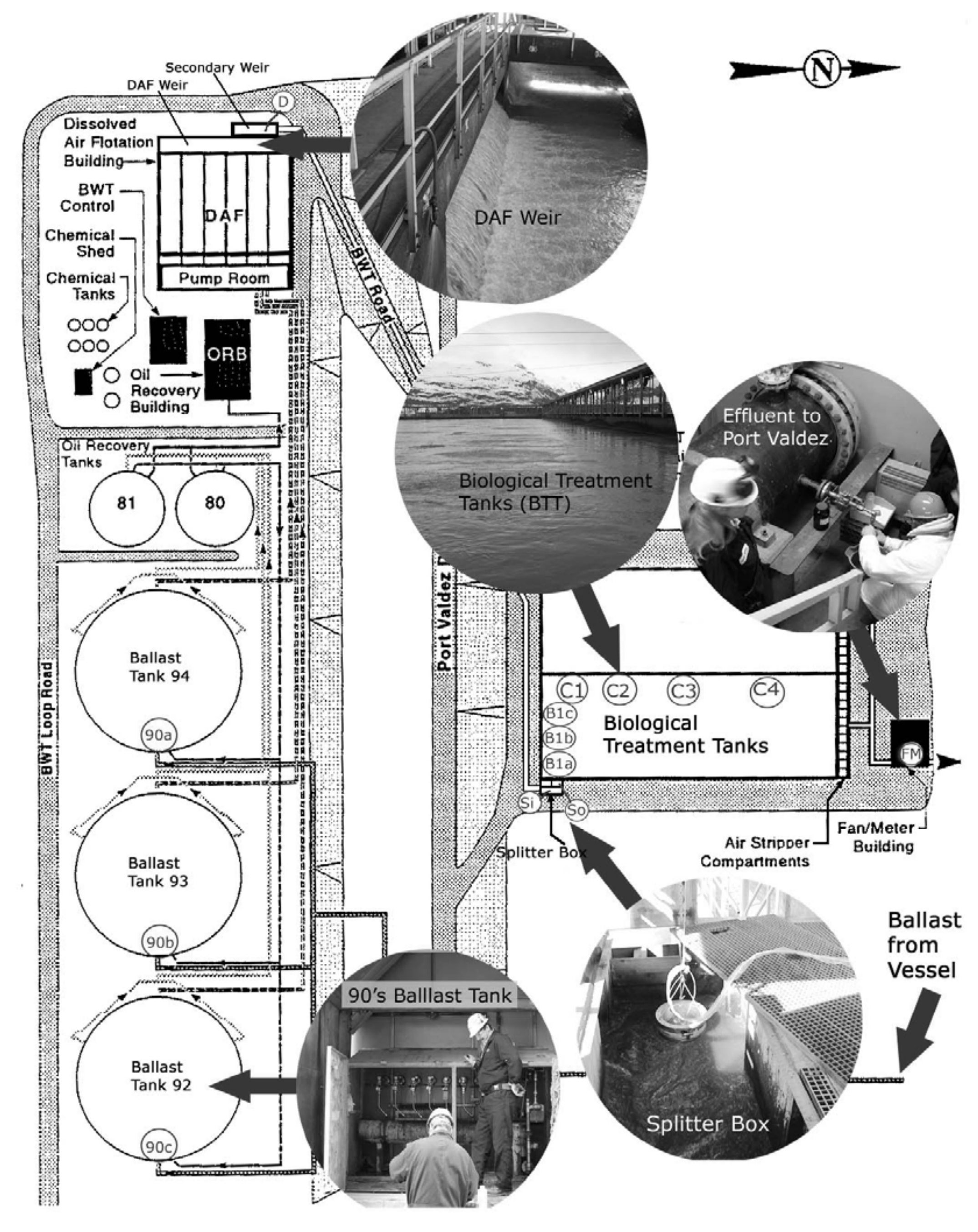

Figure 2. Alyeska Pipeline Service Company (APSC) Ballast Water Treatment Facility and project sampling locations (shown by the photos).

1.1.1 Oil/Water Separation Tanks

Ballast water is pumped from the ships into three large holding tanks used for initial settling and oil/water separation. These tanks are numbered as 92, 93, and 94 in Figure 2 and are referred to as the 90s tanks. Each of the three 90s tanks has a capacity of 430,000 barrels or approximately 18 million gallons. Typical operation of the 90s tanks consists of loading one tank with ballast water, while isolating the second tank for settling and oil/water separation, and draining the third tank to the DAF system. Each tank has a set of floating oil skimmers to remove the separated oil, which is drained by gravity to the two recovered oil tanks that are also known as the 80s tanks (see Figure 2). The estimated oil removal efficiency for the 90s tanks ranges from 95-99% with a holding or residence time of 1-3 hours and 99.5% removal after 4-6 hours (Imperial Oil Research, 2005).

1.1.2 Dissolved Air Floatation Cells

The ballast water next goes through a secondary treatment step for removal of oil in the dissolved air floatation (DAF) system. The system consists of 6 open-top tanks or cells operated in parallel (Figure 2). Each of the cells has a length of approximately 120 ft, a width of 24 ft, and a water depth of 12 ft. This yields a ballast-water holding capacity of approximately 240,000 gallons per cell, or 1,440,000 gallons total. Before entering the DAF cells, the ballast water is pressurized by air pumps to near the oxygen saturation point. As the pressurized and aerated water is released to the DAF tanks, small air bubbles are released from solution and rise through the water, collecting oil and suspended solids. The floated oil is then collected by one set of manually operated skimmers and one set of automatically operated skimmers. The additional oil removal and recovery efficiency in the DAF cells was estimated to be approximately 70-80% (Payne et al., 2002a; Imperial Oil Research, 2005. Recovered oil is pumped to the 80s tanks for further oil/water separation and is ultimately re-mixed with the crude oil loaded onto the tankers leaving the facility. At an average flow rate of 9 MGD, the residence time of the ballast water in the DAF cells is estimated to be about 4 hours.

In addition to removing oil, the DAF system vents BTEX into the atmosphere by volatilization, and this has been estimated at 7 tons per year (Imperial Oil Research, 2005). Exiting the DAF cells are a series of weirs that the ballast water flows over on its way to the Splitter Box and subsequently into one of the two Biological Treatment Tanks (Figure 2). The turbulence over the weirs further aerates the water, accelerating BTEX loss. Because there is currently no vapor collection or treatment system installed for either the DAF or Splitter Box areas, all of this volatilized BTEX is released into the atmosphere. At these sites, an estimated 27 and 9 tons per year of BTEX are lost to the atmosphere from the DAF weirs and Splitter Box, respectively (Imperial Oil Research, 2005). Both the DAF cells and the Splitter Box weirs are safety areas requiring personnel respirator protection.

1.1.3 Biological Treatment Tanks

Following the DAF system, the ballast water flows through the Splitter Box and into the Biological Treatment Tanks (BTT). The biological treatment system consists of two 5.5 million gallon open-air tanks operated in parallel (Figure 2). Microorganisms well-adapted to consuming petroleum hydrocarbons are already present in the untreated ballast water and do not require augmentation; however, nitrogen- and phosphorous-based nutrients are added to the ballast water near the overflow weirs at the end of the DAF system. The biological treatment is fully aerobic with additional air pumped through diffusers mounted along the bottom of the tanks.

In addition to the biological degradation, it had long been suspected that a significant portion of the BTEX may be removed by volatilization from the BTTs, but the results from this study and additional measurements completed by Imperial Oil Research (2005) clearly indicate that the major loss of BTEX from the BTTs is due to biodegradation. Less than three percent of the total annual volatile loss of BTEX is now believed to come from the BTTs. The temperature of the BWTF effluent varies between winter and summer months from approximately 8°C (47°F) to 15°C (59°F). This temperature drop in the colder months significantly reduces the biological treatment efficiency, and historical data indicate that the highest BTEX-loaded effluents occur in the winter and early spring months. These temperature variations also affect SHC and PAH removal, which is evaluated later in this paper.

The retention time in the biological treatment system is estimated to be approximately 1.2 days under the average daily flow rate of 9 MGD and could be less than 0.4 days at the maximum National Pollutant Discharge Elimination System (NPDES) permitted flow rate of 30 MGD. Over the last five years, however, Alyeska has limited the maximum flow rate to 22 MGD, and recently it has been clamped at 18 MGD, so actual retention times probably range from 15-30 hours (Imperial Oil Research, 2005). If one of the tanks were to be shut down for cleaning or maintenance then the retention time would be half of these values. The average BTT efficiencies for removal of oil and BTEX have been estimated as 55% and 99.7%, respectively (Payne et al. 2002a). Oil recovered from the BTTs is transferred to the 80s tanks where it is eventually re-injected into the ANS crude oil loaded into the tankers leaving the Port.

1.1.4 Air Stripper System

In the event of a failure in the biological treatment system, air stripper compartments are located at the end of the BTT (Figure 2) simply to reduce BTEX to a level to comply with NPDES permit limits. It is a last-resort system since it is intended to purposefully vent the BTEX into the ambient air rather than biodegrading the compounds in the BTT. According to Alyeska personnel and NPDES records, it has only been operated in need three times (in January/February 2004) since February 1999.

1.1.5 Fan/Meter Out

The Fan/Meter Out Building (Figure 2) has no functional role in treatment but serves as a process monitoring and sampling port for the final BWTF effluent.

1.2 PWS RCAC Port Valdez Studies

The Federally-mandated duties of Prince William Sound Regional Citizens' Advisory Council (PWS RCAC) include conducting a Long-Term Environmental Monitoring Program (LTEMP) for Alaska North Slope crude oil contamination at selected sites throughout Prince William Sound and the nearby Gulf of Alaska (KLI 2000 and references therein; Payne et al. 1998, 2001, 2003b, 2005). The program, started in 1993, is similar to the National Oceanic and Atmospheric Administration (NOAA) Mussel Watch and in Port Valdez includes seasonal sampling of intertidal mussels (*Mytilus trossulus*) and marine sediments (March and July, with an extra mussels-only collection in September). LTEMP and other data from PWS RCAC Port Valdez studies have shown that hydrocarbons released from the Alyeska Marine Terminal (AMT) Ballast Water Treatment Facility (BWTF) have accumulated in the subtidal sediments near the BWTF and in intertidal mussels as both oil-droplet and dissolved-phase fractions at several sites within the Port (KLI 2000, Payne et al., 2001, 2003a,b,c, 2005; Salazar et al., 2002).

2 Methods

2.1 Sampling and Analyses

Samples from the BWTF were collected on three occasions. In March 2004, a limited, pilot series of composite samples were collected from the DAF effluent, both BTTs, and the effluent to Port Valdez from a sampling port in the Fan/Meter Building. The second-round samples were collected from a wider suite of locations (shown in Figure 2) to obtain better resolution on process efficiencies between different stages of the BWTF, and were timed to evaluate seasonal biological process efficiencies. The average BTT effluent temperatures were 15.8 and 6.6 ^{o}C in September and January, respectively. In many of the figures presented in this paper we refer to BTT Cells 1, 2, 3, and 4, locations that roughly correspond to Stations C1, C2, C3, and C4, respectively, in Figure 2.

In addition to the grab samples for hydrocarbon analyses (acid quenched to $pH < 2$ upon collection), a BIORATE assay study was completed during both the September 2004 and January 2005 field programs to measure the degradation rates of BTEX, saturated hydrocarbons (SHC), and polycyclic aromatic hydrocarbons (PAH) under controlled temperature regimes where loss of components to evaporation was eliminated. Using procedures developed by Imperial Oil and Alyeska personnel (Imperial Oil Research, 2005), a series of thirty non-acidified composite samples of BTT ballast water in 60 mL septum-capped VOA vials was incubated in a constant-temperature bath at the BTT temperature, and then duplicate samples were systematically removed at specified time intervals (0.5, 1, 2, 4, and 8 hrs) and acid preserved (microbes quenched) by the addition of 6 N HCl through the septa of the VOA vials to lower the pH to < 2. The BIORATE composites were collected along the front wall of the BTT at stations B1a – B1c in September and between stations C1 and C2 in January (Figure 2).

In addition to the analyses of BTEX, the SHC and PAH were also analyzed to assess biodegradation processes (Payne et al., 1984; Payne and McNabb, Jr., 1984; NRC, 1985, 2003; Braddock et al., 1999, 2003). PAH and SHC data, and in particular, ratios of n-alkanes versus branched chain (isoprenoid) compounds in the BWTF samples, demonstrated the extent of hydrocarbon biodegradation that occurs in the tankers during transit versus that which occurs in various stages of the BWTF. In addition, because these higher-molecular-weight components are not subject to significant volatilization, the PAH and SHC data from the BWTF field samples and the BIORATE studies served to document the full effects of biodegradation in the system. Prior to this study, there were no available data on PAHs from the influent to the BTT to characterize the system's effectiveness in degrading PAHs.

During the September and January studies, most probable number (MPN) enumerations of microbes degrading benzene, naphthalene, phenanthrene, and whole ANS crude oil were completed on plates prepared and incubated at the Alyeska Marine Terminal by UAF personnel using miniaturized MPN techniques (Brown and Braddock, 1990; Brown et al., 1991; Braddock and Catterall 1999). MPNs were run in triplicate on the 9 samples collected across the system and on the composite samples collected for the BIORATE studies.

Table 1 lists the target analytes and abbreviations used in identifying individual components in the histogram plots and other figures presented in this paper. All analyses of the samples from the BWTF studies were completed by the Woods Hole Group Environmental Laboratories in Raynham, Massachusetts. Temperature- and acid-preserved samples were shipped under full chain-of-custody by Federal Express to the laboratory via overnight (or in one case, two-day) delivery, and all analyses followed published Woods Hole Group Standard Operating Procedures (Woods Hole Group SOPs O-004, O-008, and TPH-8100).

2.2 Sediments and Mussels

Since 1993, two stations have been occupied in Port Valdez by the LTEMP program. Seasonal collections include 3 replicates of intertidal mussels along a 30m transect and three replicates of subtidal sediments using a modified Van Veen grab. Mussels are currently sampled in spring, summer and fall; sediments in spring and summer only (see Payne et al., 2003b and 2005 for sampling protocols). Samples are currently analyzed by NMFS Auke Bay Laboratory for the list of analytes in Table 1.

Over the years, we've developed data analysis tools to help summarize and better understand the data trends. Of particular interest for tissue data is the Particulate to Dissolved Ratio (PDR), which allows quantification of the observed qualitative differences of particulate/oil-droplet vs. dissolved-phase components in the PAH histograms. The PDR is simply the ratio of the higher-molecular-weight PAH that have lower water solubilities and are generally associated with finite oil droplets, to the sum of the more water-soluble alkylated naphthalenes (Payne et al., 2003b).

$$\text{PDR} = (\text{Phenanthrenes} + \text{Dibenzothiophenes} + \text{Chrysenes})/\text{Naphthalenes} \qquad (1)$$

If a sample exhibits a PDR value greater than 2, the PAH pattern will show an accumulation of predominately the higher-molecular-weight alkylated components associated with particulate (finite) oil droplets, while a PDR value less than 1 will come from a sample where the naphthalenes (N) predominate. Samples with PDR values between 1 and 2 contain a mixture of components from both the dissolved and particulate phases.

Two other indices appear in this paper, the Mytilus Petrogenic index (MPI) and the CRUDE index. The MPI isolates the primary petroleum PAH groups. This summation would exclude most of the combustion products, a confounding signal in a PAH profile when looking for oiling trends.

$$\text{MPI} = \text{Naphthalenes} + \text{Fluorenes} + \text{Phenanthrenes} + \text{Dibenzothiophenes} \qquad (2)$$

The CRUDE index was developed to assess crude oil components in a profile by weighting various components of interest. It is, in both meanings of the term, a "crude" tool but it does effectively discriminate the crude oil components from within a Total PAH (TPAH) value and also weights various other oil indices into one term.

$$\text{CRUDE} = \text{MPI} + (\text{TSHC}/\text{CPI}^2) + \text{UCM} \qquad (3)$$

where MPI is defined in equation 2, TSHC is total SHC, UCM is the unresolved complex mixture of the aliphatic fraction, and $\text{CPI} = 2(C_{27} + C_{29})/(C_{26} + 2C_{28} + C_{30})$ (from Farrington and Tripp, 1977). The CRUDE index has been useful to track oil trends in the PWS RCAC dataset (see Payne et al., 1998 for full discussion and use).

Table 1. Polycyclic aromatic hydrocarbon (PAH) and saturated hydrocarbon (SHC) analytes measured in this study.

Analytes	**Abbreviation**	**Analytes**	**Abbreviation**
PAH			
Naphthalene	N	Benzo(e)pyrene	BEP
C1-Naphthalene	N1	Benzo(a)pyrene	BAP
C2-Naphthalene	N2	Perylene	PER
C3-Naphthalene	N3	Indeno(1,2,3-cd)pyrene	IP
C4-Naphthalene	N4	Dibenzo(a,h)anthracene	DA
Biphenyl	BI	Benzo(g,h,i)perylene	BP
Acenaphthylene	AC	Total PAH	TPAH
Acenaphthene	AE		
Fluorene	F	**SHC**	
C1-Fluorenes	F1	n-Decane	C10
C2-Fluorenes	F2	n-Undecane	C11
C3-Fluorenes	F3	n-Dodecane	C12
Dibenzothiophene	D	n-Tridecane	C13
C1-Dibenzothiophene	D1	n-Tetradecane	C14
C2-Dibenzothiophene	D2	n-Pentadecane	C15
C3-Dibenzothiophene	D3	n-Hexadecane	C16
C4-Dibenzothiophene	D4	n-Heptadecane	C17
Anthracene	A	Pristane	Pristane
Phenanthrene	P	n-Octadecane	C18
C1-Phenanthrene/Anthracene	P/A1	Phytane	Phytane
C2-Phenanthrene/Anthracene	P/A2	n-Nonadecane	C19
C3-Phenanthrene/Anthracene	P/A3	n-Eicosane	C20
C4-Phenanthrene/Anthracene	P/A4	n-Heneicosane	C21
Fluoranthene	FL	n-Docosane	C22
Pyrene	PYR	n-Tricosane	C23
C1-Fluoranthene/Pyrene	F/P1	n-Tetracosane	C24
C2-Fluoranthene/Pyrene	F/P2	n-Pentacosane	C25
C3-Fluoranthene/Pyrene	F/P3	n-Hexacosane	C26
C4-Fluoranthene/Pyrene	F/P4	n-Heptacosane	C27
Benzo(a)Anthracene	BA	n-Octacosane	C28
Chrysene	C	n-Nonacosane	C29
C1-Chrysenes	C1	n-Triacontane	C30
C2-Chrysenes	C2	n-Hentriacontane	C31
C3-Chrysenes	C3	n-Dotriacontane	C32
C4-Chrysenes	C4	n-Tritriacontane	C33
Benzo(b)fluoranthene	BB	n-Tetratriacontane	C34
Benzo(k)fluoranthene	BK	Total SHC	TSHC

3 Results

3.1 BWTF Characterization

3.1.1 BTEX Removal

Figure 3 presents the measured concentrations of BTEX at the nine sampling stations within the BWTF in September 2004 and January 2005. When examining these and other data presented in the following figures note that BTT Cells 1, 2, 3, and 4 correspond to the north sides of sampling stations C1, C2, C3 and C4, respectively, as shown in Figure 2.

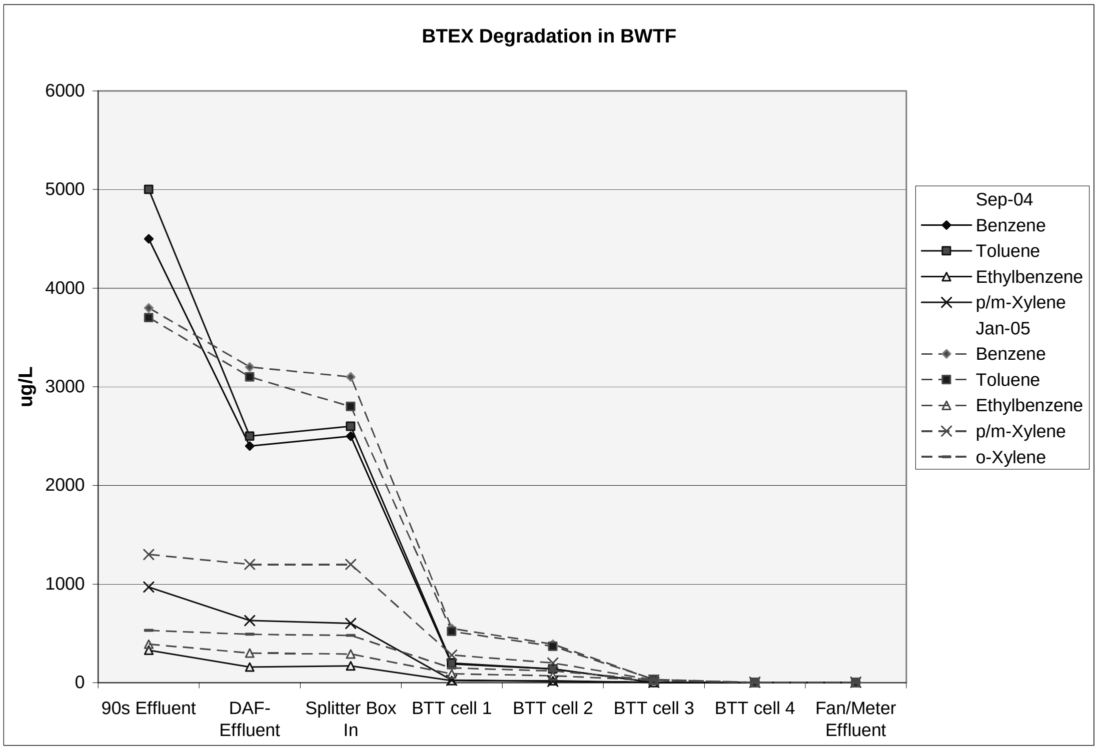

Figure 3. BTEX Degradation in BWTF, Sept 04 and Jan 05.

When the samples were collected in September 2004, the BWTF had been running at fairly low-flow rates (5,000 gallons per minute or approximately 7 MGD). The available data also suggest fairly high BTEX concentrations were present in the 90s tanks (4,700- 5,000 µg/L (ppb) (Figure 3). Under these low-flow conditions, the residence time in the DAF cells would be slightly longer and with these high initial BTEX loadings, significant decreases in BTEX concentrations (due primarily to volatilization and some biodegradation) are noted in the DAF effluent collected after the DAF weirs (Figure 3). As expected, the concentrations of BTEX in the Splitter Box sample are essentially unchanged from the DAF effluent, but there is a very significant drop in going from the Splitter Box to BTT Cell 1. Additional declines in BTEX concentration are observed in BTT Cells 2 and 3 while non-detect (< 2 ppb) concentrations were observed in BTT Cell 4 and the effluent to the Port collected from the Fan/Meter Building.

The large drop in BTEX concentration upon entering the BTT cells is due primarily to mixing of the Splitter Box effluent into the large volume (~5.5 million gallons) of the BTTs. The BTTs also recycle low hydrocarbon-concentration waters from the effluent end of the tank (by the Air Strippers – Figure 2) pumping them back to the front end, a process to ensure proper mixing, recirculate the microbes, and power the subsurface aspirators providing aeration to the BTTs. Furthermore, under these lower flow conditions, the residence time in the BTTs is such that the main volume is significantly depleted in BTEX due to prolonged microbial activity (see below). Once entering the BTT, the BTEX components from the Splitter Box effluent are rapidly degraded and almost completely eliminated by the time the treated ballast water is approximately half-way down the tank (Figure 3).

In contrast, during the January 2005 sampling, the BWTF had been running under variable flow conditions, but for approximately 16 hours the day before the samples were collected, it had been run at 11,000 gallons per minute (or 15.8 MGD). Under these high-flow conditions, the residence time in the DAF cells is much shorter and the BTEX "front" inside the BTTs is forced further down the tank. Under such high-flow conditions, we measured total BTEX at 890 µg/L in Cell 1, 640 µg/L in Cell 2, and 9.6 µg/L in Cell 3. The total BTEX concentration in a composite sample collected along the face of the south wall of the tank (at stations B1a, B1b, and B1c – Figure 2) was 690 µg/L. This is lower than the BTT Cell 1 levels due perhaps to immediate entrainment of less contaminated water pumped from the effluent end of the tank and released along the front end.

The January 2005 data (Figure 3) show that the overall BTEX concentrations in the effluent from the 90s tanks were initially lower compared to the summer samples (there is significant variability in BTEX and PAH/SHC loading to the 90s tanks from the different tankers in the fleet), and that less relative dilution was observed upon exiting the DAF cells and Splitter Box. Very significant declines were again observed, however, upon entering the BTT cells, and total BTEX concentrations dropped from 7,870 ppb in the Splitter Box to 1,590 ppb, 1,150 ppb, 141 ppb, and <12 ppb in Cells 1, 2, 3, and 4, respectively. The effluent to the Port collected from the Fan/Meter Building showed little BTEX, with all constituents < 2 µg/L.

The BIORATE tests conducted in both September 2004 and January 2005 demonstrated that the loss of BTEX in the BTT cells was the result of microbial degradation and not volatilization. As noted above, the September samples were collected along the south face of the BTT at Stations B1a-c (Figure 2) under low flow conditions. Unfortunately, the initial total BTEX concentrations were so low in that composite sample (< 14 µg/L), that all of the constituents were below the laboratory MDL (< 2 µg/L) by the first time-series sampling point at 0.5 hours (Figure 4).

As a result, we were not able to measure September biodegradation loss rates for BTEX, but PAH and SHC data (presented below) clearly showed the affects of microbial versus abiotic (volatilization) losses for those constituents. For the January 2005 BIORATE tests, we pre-screened the BTEX levels at various locations throughout the BTTs and chose our composite sample from between BTT Cells 1 and 2 to ensure there would be sufficient substrate for the bacteria to degrade. The results (Figure 4) showed very rapid biodegradation of all components in the sealed vials, with nearly complete elimination of benzene and toluene within 2 hours, and m/p-xylene, o-xylene, and ethylbenzene below the laboratory MDL (<2 µg/L per component) after 4 hours.

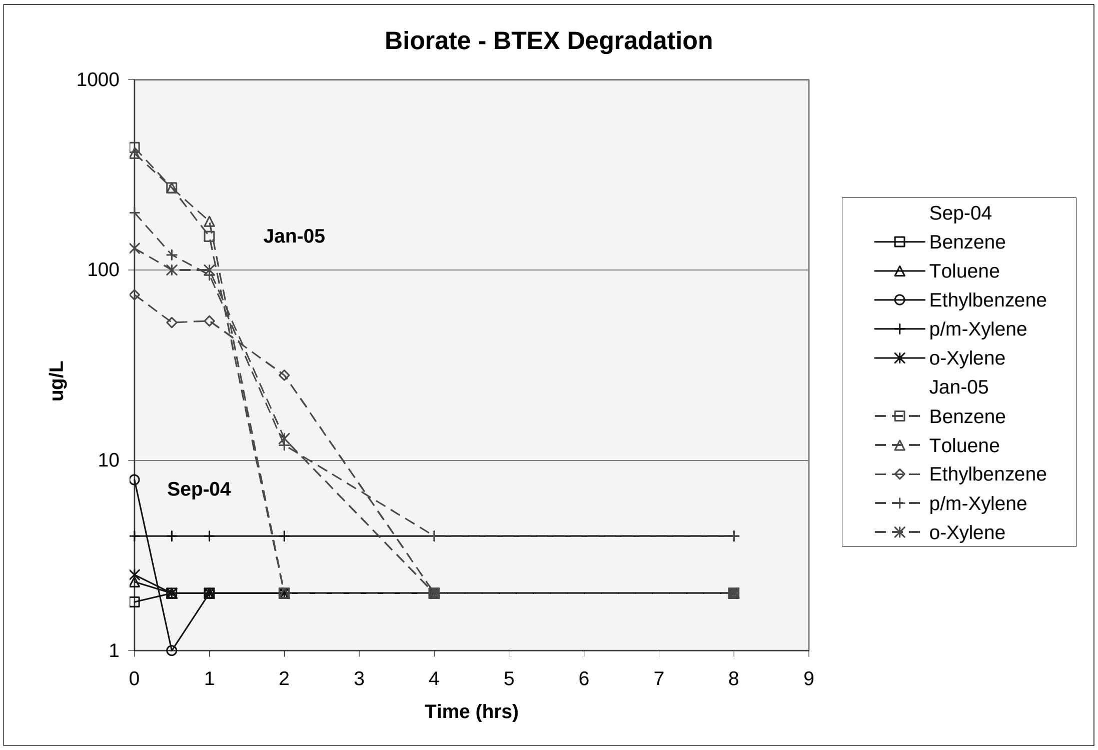

Figure 4. BIORATE BTEX Degradation, Sept 04 and Jan 05 (concentrations in µg/L).

3.1.2 PAH and SHC Removal

In September 2004, grab samples were taken for PAH and SHC from all nine BWTF field stations (Figures 5 and 6). At that time, the Ballast Water temperatures ranged from 15.9 to 16.3^o C. Quite clearly, the dissolved-phase naphthalenes dominate the PAH profiles in the 90s, DAF, and Splitter Box effluent samples, but there are also whole oil droplet-phase constituents as demonstrated by the presence of sparingly-water-soluble, higher-molecular-weight PAH components through the alkyl-substituted chrysenes and essentially insoluble, higher-molecular-weight n-alkanes. Based on the relatively invariant n-C_{17}/pristane and n-C_{18}/phytane ratios of 1.1-1.2 and 1.9-2.0, respectively, very little microbial degradation occurred while the oil-laden ballast water was in the tankers, in the 90s tanks (dissolved oxygen = 0.7 mg/L), or in transit through the DAF cells and Splitter Box.

Upon entering the BTT cells, however, the bacteria aggressively consumed the n-alkanes (n-C_{17}/pristane and n-C_{18}/phytane ratios drop to 0.1-0.5 and 0.1-0.7, respectively), while the PAH fractions show almost complete loss of the naphthalenes along with the parent and lower (C1 and C2) alkyl-substituted fluorenes, phenanthrenes/anthracenes, and dibenzothiophenes. Clearly, the grab samples from BTT Cells 1 (Figure 5) and BTT Cells 2, 3, and 4 (Figure 6) contain significant particulate/whole oil-phase residues as all the measured constituents have very limited water solubility. This signature reflects a combination of microbial degradation, evaporation weathering, and abiotic leaching of the more water-soluble constituents within each homologue group. The BIORATE tests (described below) clearly demonstrate that bacterial degradation of these components is occurring, but it is not possible to completely separate the effects of these complementary but competing processes.

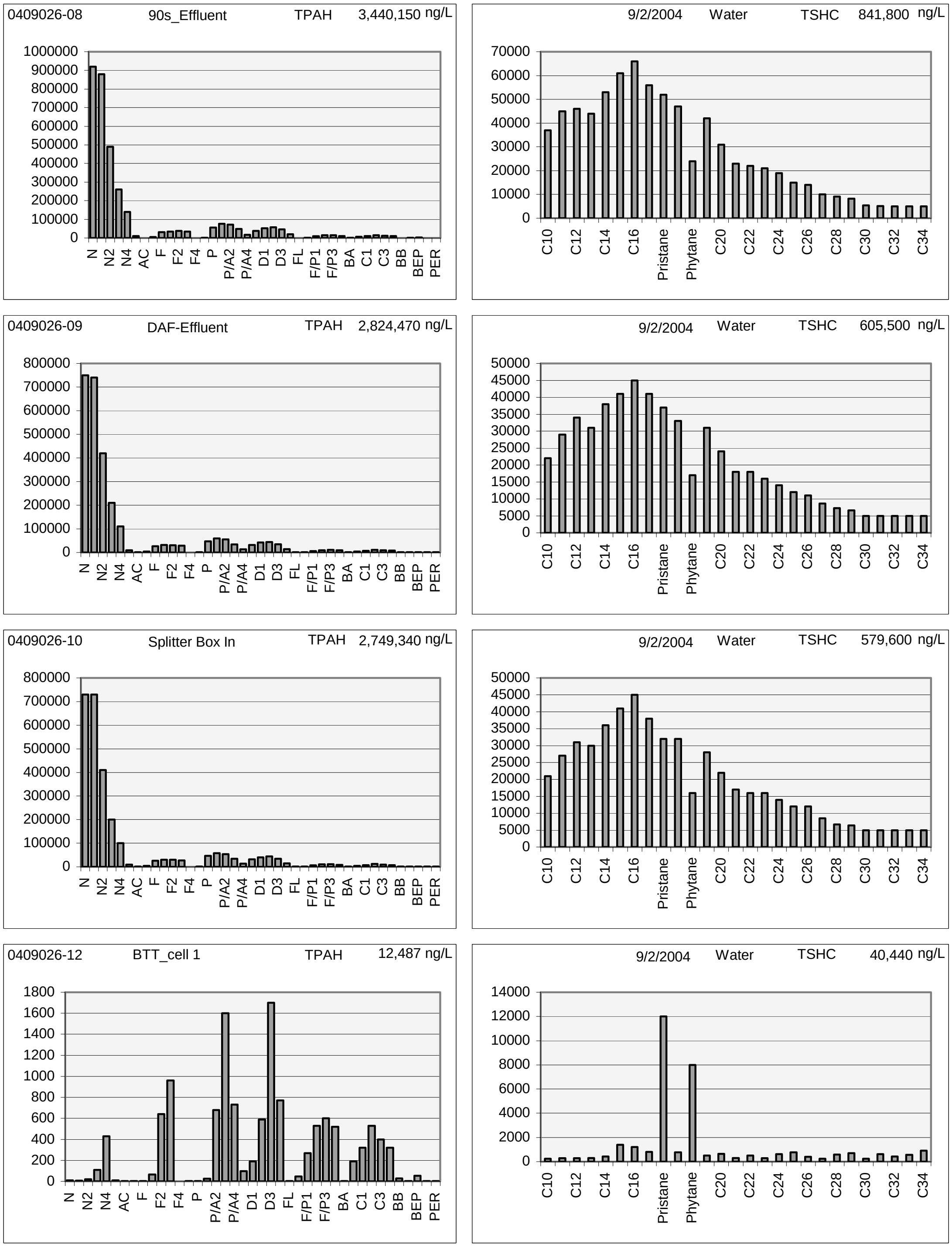

Figure 5. PAH and SHC histograms from 90s Tank effluent, DAF effluent, BTT Splitter Box effluent, and Cell 1, Sept 2004 (concentrations in ng/L).

The minor variability in TPAH and TSHC within the BTT is believed to reflect sample heterogeneity (i.e., inclusion of one or more microdroplets or tarballs can significantly affect the totals and the concomitant histogram profiles).

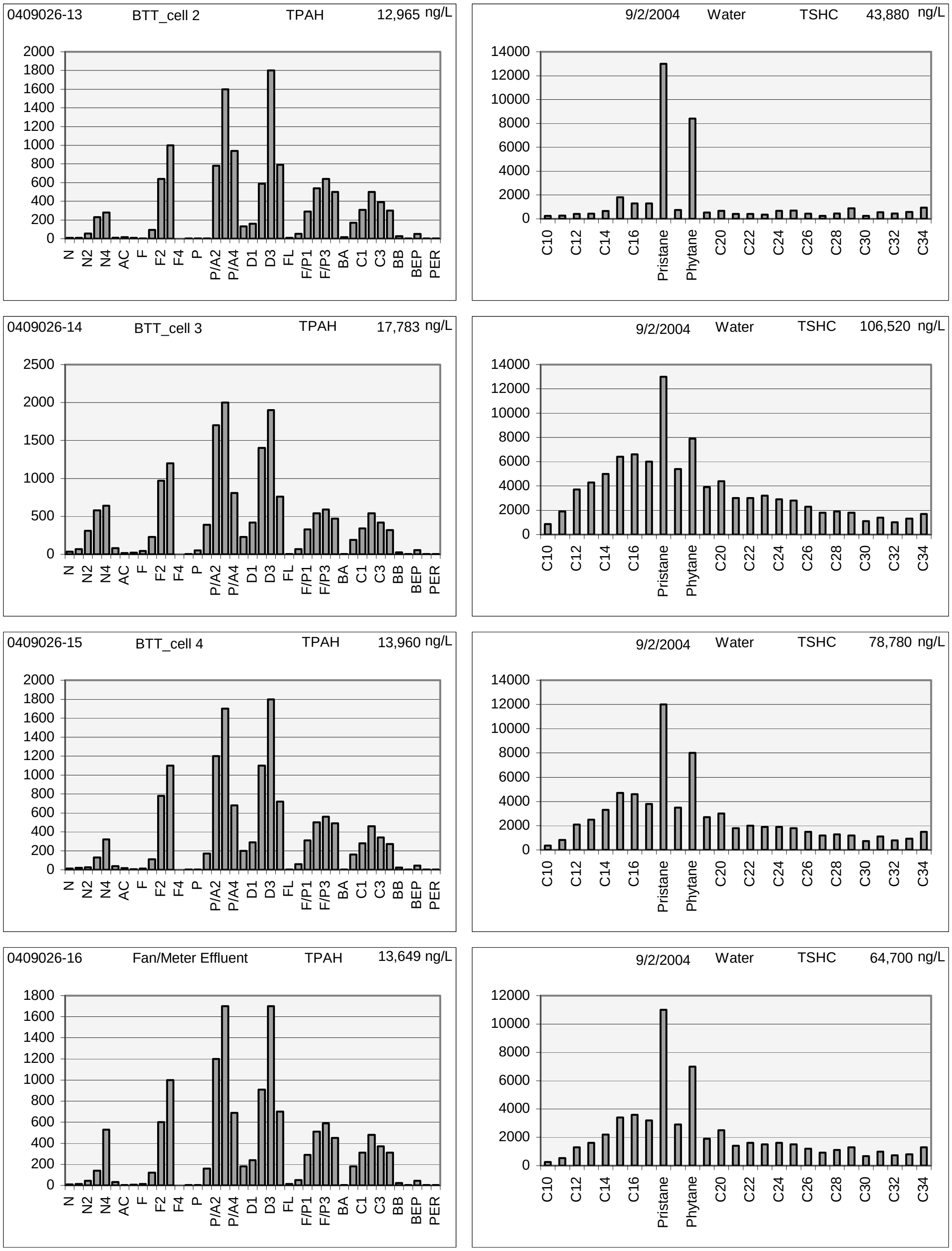

Figure 6. PAH and SHC histograms from BTT Cell 2, Cell 3, and Cell 4, and Fan/Meter effluent, Sept. 2004 (concentrations in ng/L).

In January 2005, PAH and SHC samples were again analyzed from the sequence of stations (Figures 7 and 8). At that time, Ballast Water temperatures ranged from 2.5 to 6.8^{o} C. As during the summer sampling period, dissolved naphthalenes dominate the PAH signals in the 90s tanks, the DAF cells, and the Splitter Box, but in the colder winter conditions, they also continue to be the most prominent components in the BTT Cells and BTT effluent collected from the Fan/Meter Building. As before,

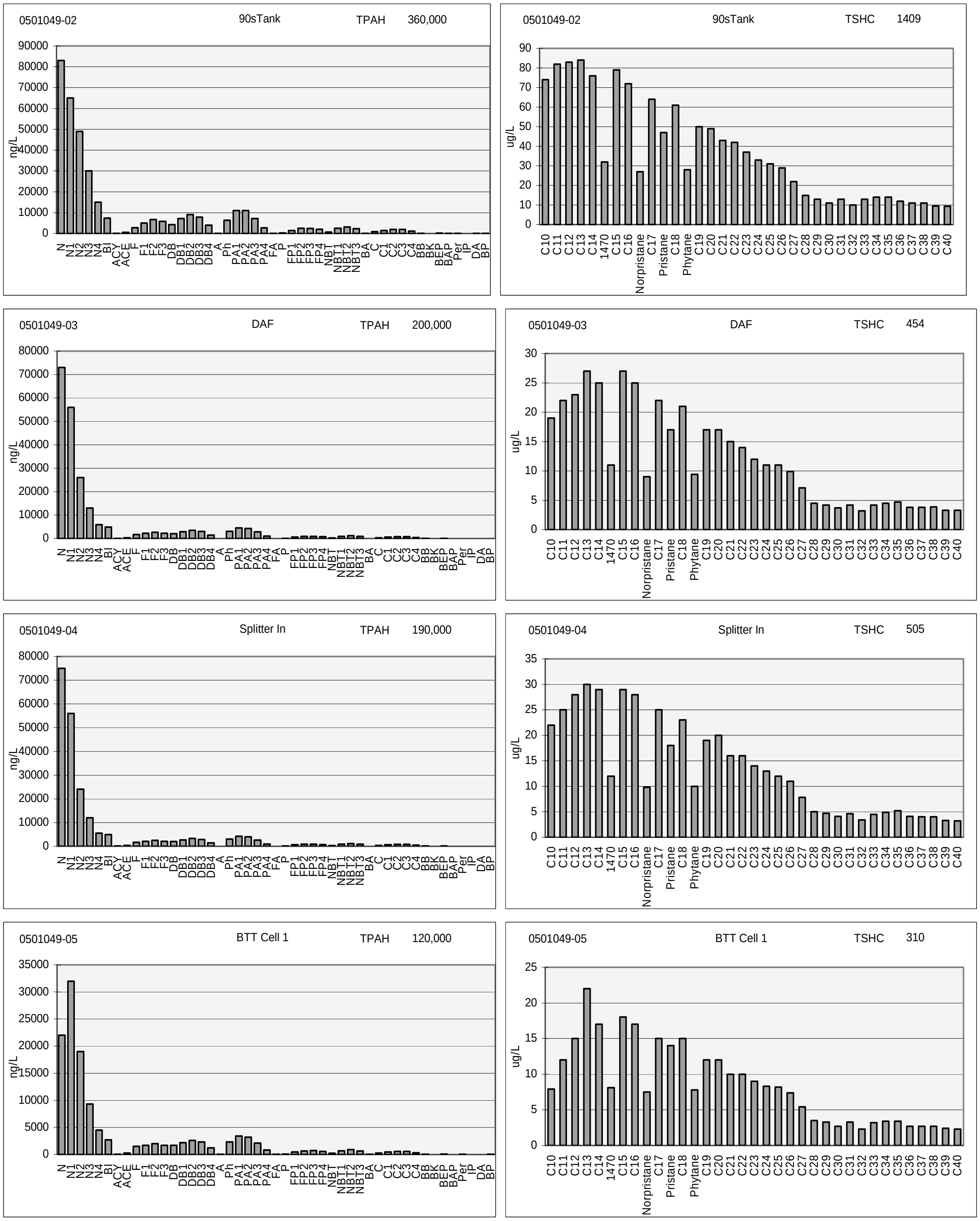

Figure 7. PAH and SHC histograms from 90s Tank effluent, DAF effluent, Splitter Box effluent, and BTT Cell 1, Jan. 2005 (PAH concentrations in ng/L; SHC concentrations in µg/L).

the presence of higher-molecular-weight PAH and n-alkanes demonstrates the inclusion of whole-oil microdroplets in the samples; however, during the colder winter conditions there is only minimal evidence of microbial degradation of the n-alkanes compared to the isoprenoid components, pristane and phytane. The

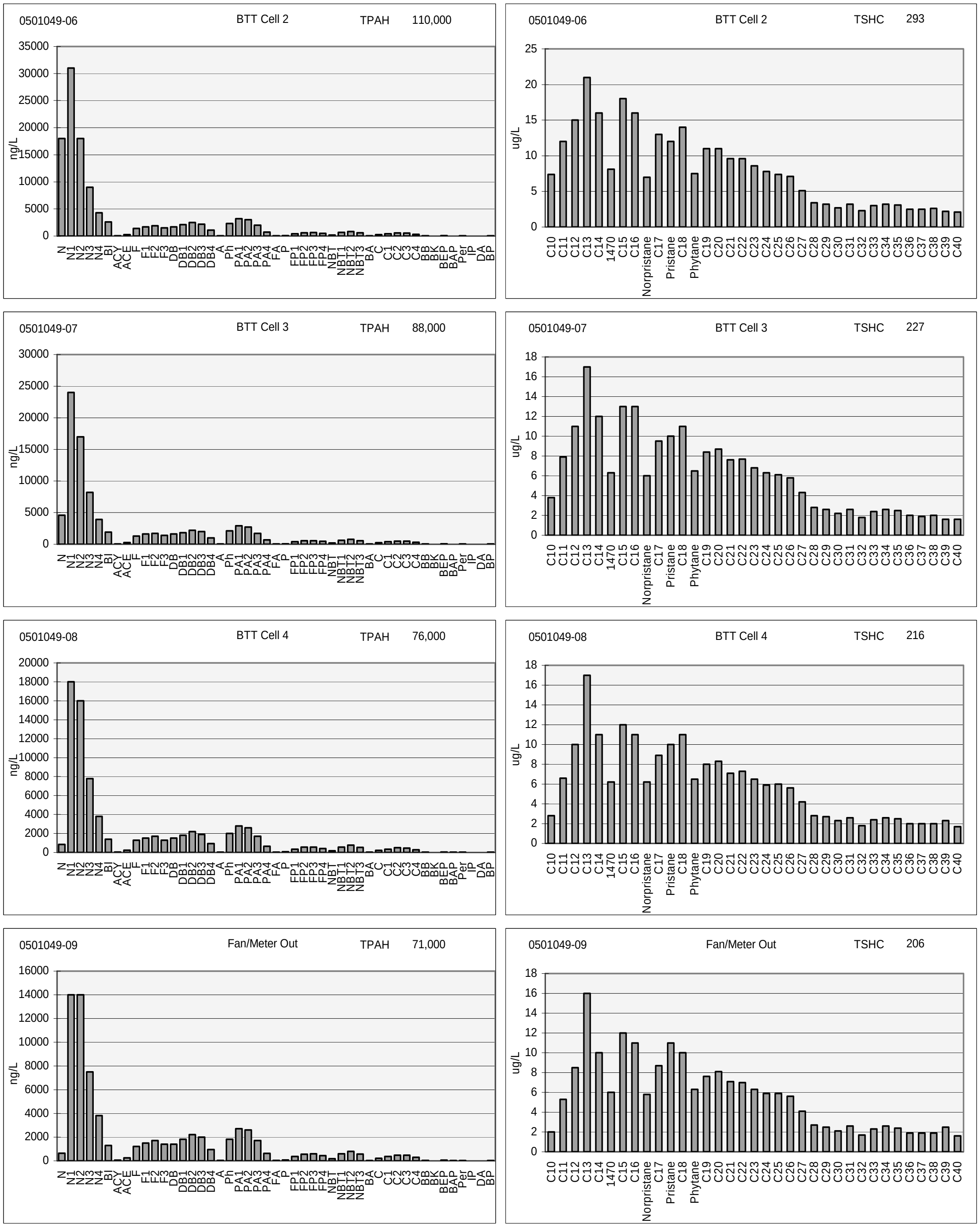

Figure 8. PAH and SHC from BTT Cell 2, Cell 3, and Cell 4, and Fan/Meter Out, Jan. 2005 (PAH concentrations in ng/L; SHC concentrations in µg/L).

respective n-C_{17}/pristane and n-C_{18}/phytane ratios are an invariant 1.3-1.4 and 2.2-2.3 in the 90s tanks, the DAF cells, and the Splitter Box, and they only drop to 0.8-1.1 and 1.6-1.9 in the BTT cells and effluent to the Port. Parent naphthalene is depleted in going from BTT Cell 1 to Cell 4, reflecting both abiotic dissolution and limited microbial degradation. As shown by the results of the BIORATE tests, naphthalene and several other parent PAH were slightly degraded by indigenous bacteria, but the rates were significantly depressed under the colder winter temperatures.

Consistent with the higher total BTEX concentrations measured in the summer, the initial total PAH levels were over an order of magnitude higher in the 90s tanks, the DAF cells, and the Splitter Box during the summer compared to the winter (Figure 9). Then, after being discharged into the BTTs there was a precipitous (three to four orders of magnitude) drop in the respective concentrations of naphthalenes, phenanthrene, anthracene, and dibenzothiophene along with C1-phenanthrene/ anthracene and C1-dibenzothiophene homologues. These concentration drops reflect both mixing with recirculated water from the effluent end of the BTTs (after the hydrocarbon components have already been subject to an estimated 38 hours of microbial degradation under the measured flow conditions) plus ongoing biodegradation. The concentration drops are greater for the PAH components in the summer because of the slower flow rate and warmer temperatures promoting more complete bacterial degradation within the BTTs. The BIORATE studies (discussed below) also showed microbial degradation of these constituents.

The summer concentration drops for the C-3 and C-4 alkylated dibenzothiophenes and all of the chrysenes are apparently due entirely to dilution/mixing as the Splitter Box dumps into the larger water body of the BTTs as there was no biological degradation of these components noted during the BIORATE tests. During the winter sampling, the PAH concentrations across all stations showed much more modest declines; results consistent with the higher flow rates and the slower bacterial degradation at the colder temperatures. In the winter samples, the minor (two or three fold) drop in most PAH concentrations in going from the 90's Tanks into the DAF cells and then upon being discharged into the BTTs is attributed to dilution because there is very little change in the relative distributions of PAH and SHC components. During the colder winter testing, we did not observe the major concentration declines for the lower-molecular-weight parent- and C1-alkylated PAH measured during the summer as the Splitter Box effluent enters the BTT cells because of the limited biodegradation for the majority of the PAH in the BTTs. The data suggest relatively constant and nearly steady-state concentrations for C-3 and C-4 alkylated phenanthrenes/anthracenes and dibenzothiophenes and all the chrysenes during both summer and winter conditions as the ballast water transits the BTT cells and enters Port Valdez.

During the summer BIORATE trials (Figure 10), naphthalene levels drop rapidly for the first hour and then fall below the MDL, while C1-naphthalene declines can be accurately measured through two hours and the C2-naphthalenes through four hours before dropping below the MDL. Likewise, phenanthrene and C1-phenanthrene drop below the MDL after eight hours. These rapid biodegradation rates validate the PAH profiles for the summer BTT cells (Figures 5 and 6), which show hundred-fold or greater declines for these components due to biodegradation in the BTT cells compared to input from the Splitter Box. The lack of significant changes in going from cell 1 to cell 4 are believed to reflect the fact that the BTTs are well mixed with re-circulated water from the effluent end. During the winter BIORATE studies (Figure 10), there is no evidence of significant PAH biodegradation (with the exception of limited removal of naphthalene and C-1 alkyl-substituted naphthalenes), a finding consistent with the PAH profiles for the winter BTT cells (Figures 7 and 8).

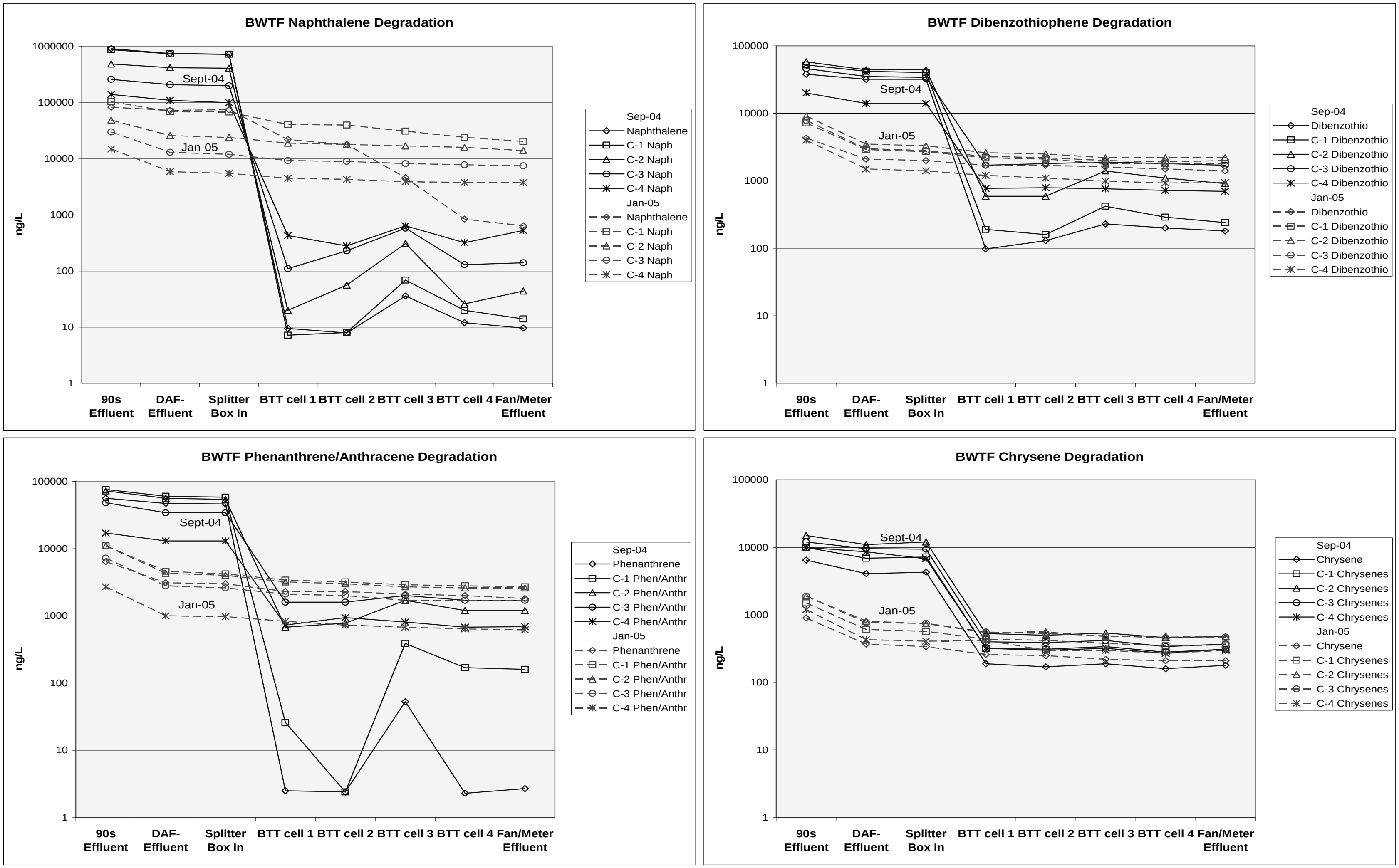

Figure 9. Selected PAH sequential degradation through the BWTF, Sept 2004 and Jan 2005 (all concentrations are ng/L).

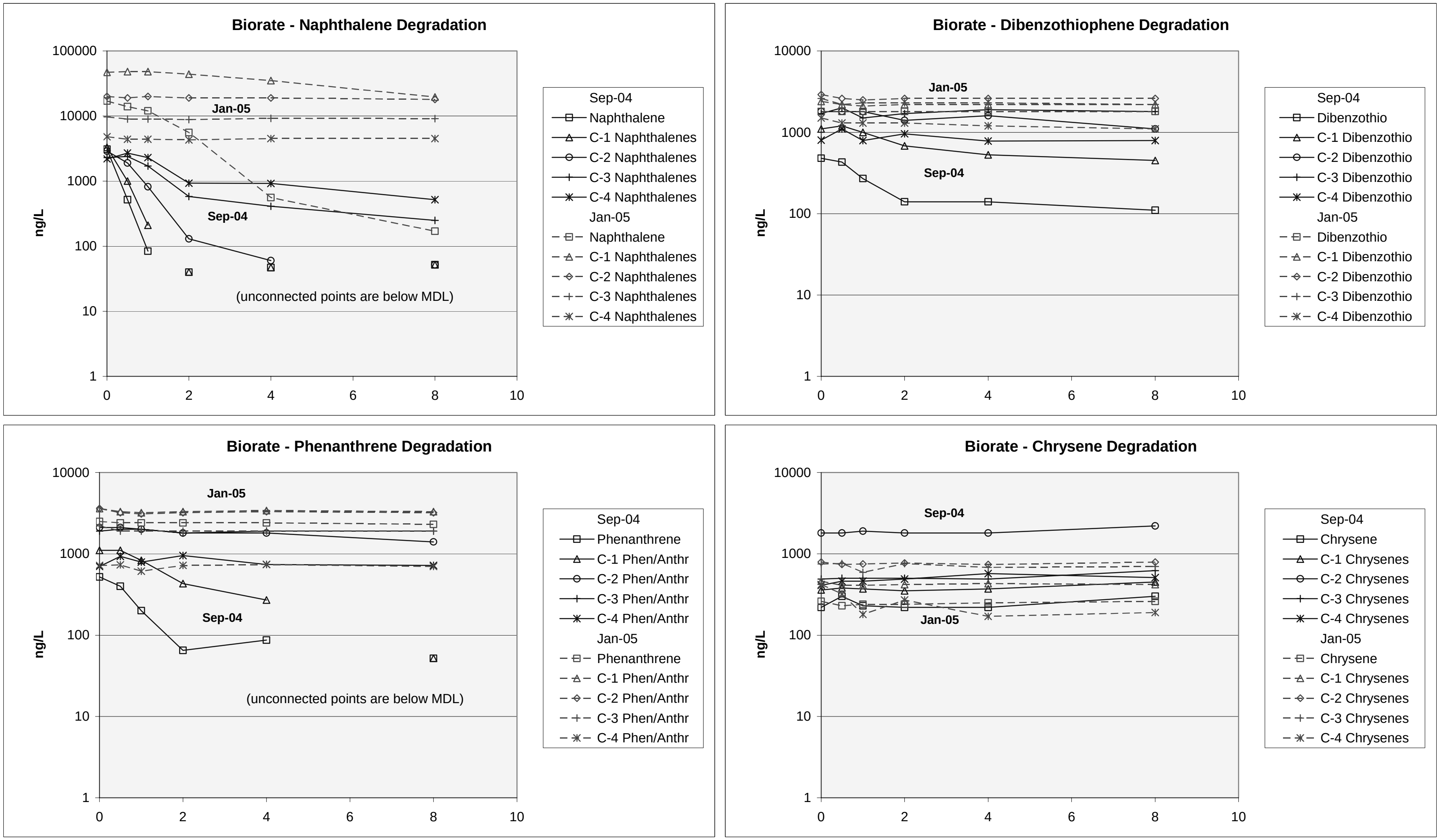

Figure 10. Selected PAH time series degradation (hrs) from BIORATE tests, Sept 2004 and Jan 2005 (all concentrations are ng/L).

During January 2005 sampling, the BTT effluent discharged to the Port was also sampled from the Fan/Meter Building with a Portable Large Volume Water Sampling System (PLVWSS) that allows differentiation of dissolved- and particulate/oil-phase fractions (Payne et al., 1999). The presence of the less water-soluble higher-molecular-weight PAH and SHC components is readily apparent in the particulate/oil-phase sample trapped on the glass-fiber filter of the PLVWSS (Figure 11). In the dissolved phase (filtrate), however, the naphthalenes clearly predominate over the other PAH, and the presence of the declining but slightly water-soluble C1- and C2-alkylated homologues is in direct contrast to the water-washed pattern obtained for the particulate/oil phase. Also, almost all of the n-alkanes are just barely above (or in most cases below) the MDL in the filtrate (dissolved phase) because of their limited water solubility. Naphthalene itself is essentially absent in both the particulate/oil-phase and dissolved-fractions (particularly compared to the initial Splitter Box concentrations shown in Figure 7) as a result of biodegradation and possibly evaporation processes. This resolution of dissolved- versus particulate/oil-phase fractions from the BWTF is discussed further below as it manifests itself in seasonally-controlled uptake in intertidal mussels throughout the Port.

3.2 Beyond the Pipe

Mussels collected by the LTEMP program in Port Valdez have demonstrated transient PAH patterns in their tissues that are clearly associated with known spill events such as the *T/V Eastern Lion* oil spill in 1994 and a BWTF sheening incident in 1997 (note 1994 Alyeska Marine Terminal spikes in MPI and the January 1997 increase in PDR in Figure 12) (Payne et al., 2003b,c). But these were acute events; the routine data are traceable to the BWTF discharge and tell of a subtler process.

On the ocean bottom at a depth of 65-75 m, 1200 m offshore from the Alyeska Marine Terminal, the BWTF effluent is released through a 60 m diffuser, and by regulation, is dissipated within the mixing zone without a visible plume reaching the surface. And as mentioned above, based on the average PAH and SHC concentrations and average flow, the discharge translates into approximately 300 pounds or roughly 0.95 barrels of oil per day. This effluent contains hydrocarbons in both the free oil-droplet and dissolved phases (Figure 11), with 10-20% of the PAH being contributed by the oil-droplet phase. Discriminating between the phase signals has provided clues as to the larger-scale transport processes of Port Valdez.

Relative to the receiving seawater, the BWTF effluent is warmer and less saline, so its behavior and dilution are controlled by the physical oceanography and water-column structure in the Port, a sill-constricted, subarctic fjord (Colonell 1980a,b; Woodward Clyde Consultants and ENTRIX 1987). During the period of stable water-column stratification in the Port (late spring, summer, and fall), the dispersed oil droplets released from the BWTF effluent are primarily entrained beneath the pycnocline (stratified layer) in the middle-water-column regions where they are advected and diluted into the receiving waters of Port Valdez without ever reaching the upper water column and surface layer to any significant extent. As a result, a predominantly dissolved-phase signal (PDR < 1; Figure 11) is observed in the LTEMP intertidal mussels collected in the summer period. During the winter and

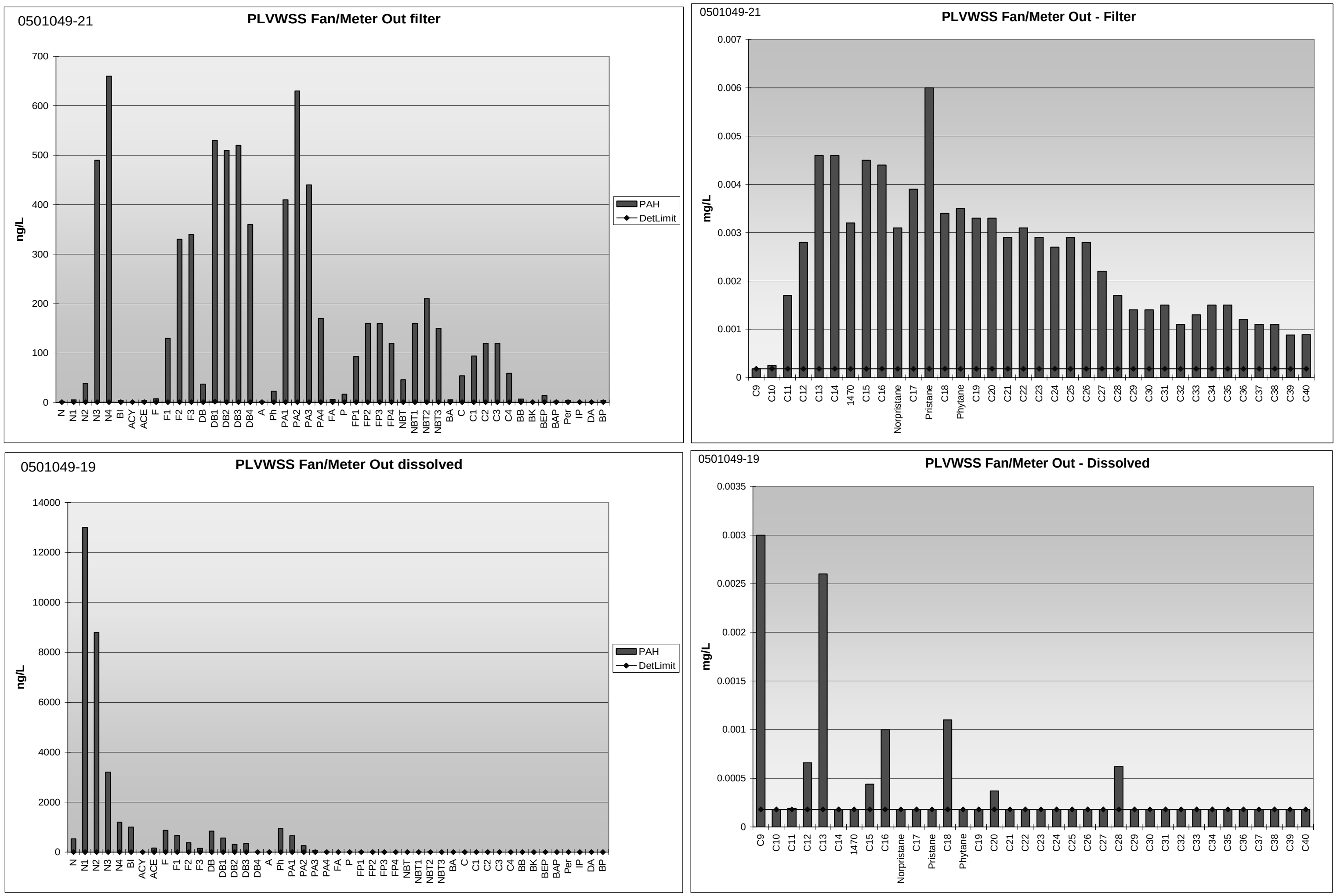

Figure 11. Particulate (filter) and dissolved (filtrate) PAH profiles of BWTF effluent, Jan 2005 (PAH concentrations in ng/L; SHC concentrations in mg/L). The solid line across the bottom of the SHC histograms represents the MDL.

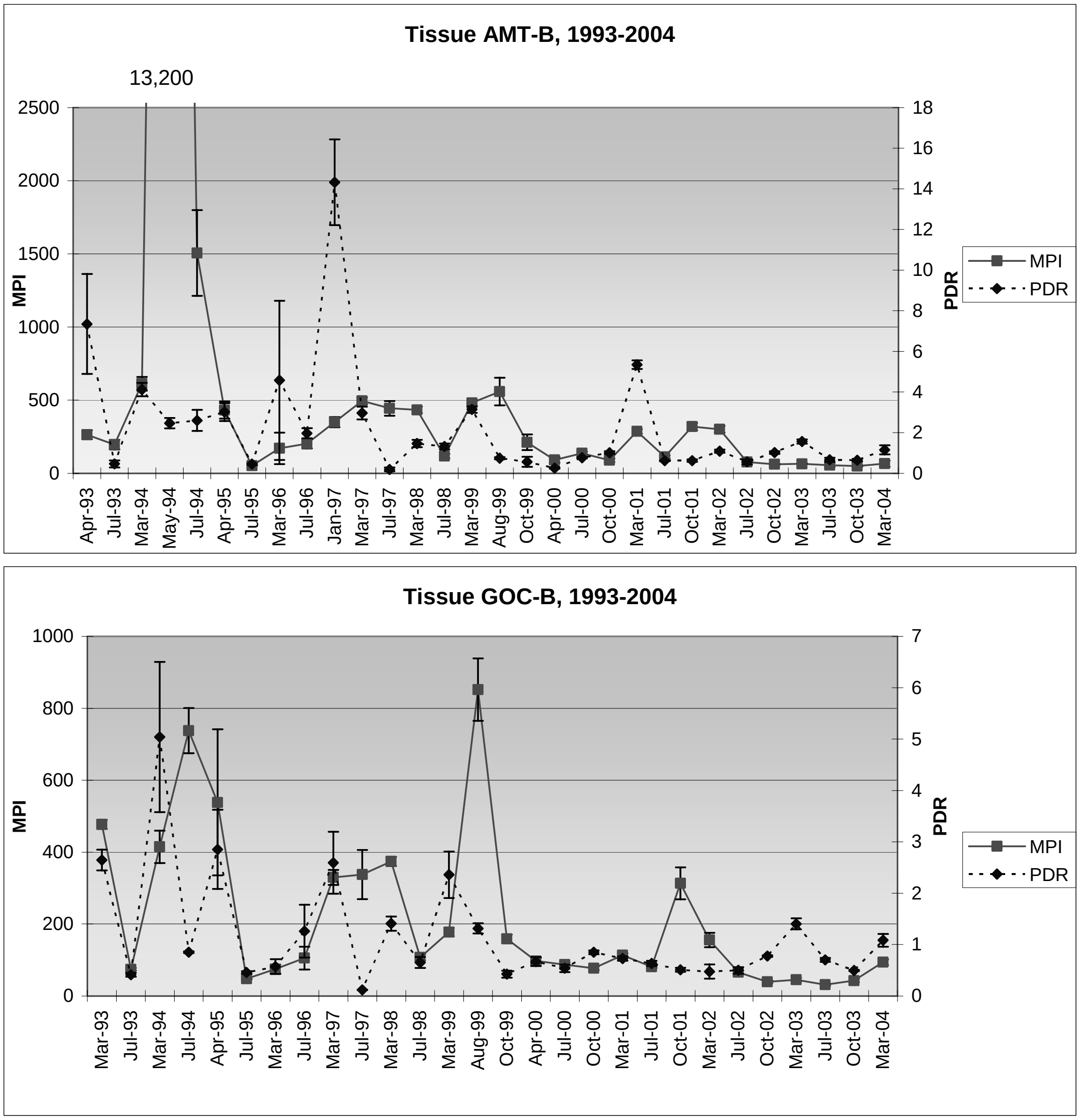

Figure 12. Mytilus Pollution Index (MPI) and Particulate/Dissolved Ratio (PDR) for Port Valdez intertidal mussel tissues, Alyeska Marine Terminal (AMT-B) and Gold Creek (GOC-B), 1993-2004 (± std error of means).

early spring, however, when the water column is not stratified, the warmer and less-saline BWTF effluent can reach the water surface where it is likely to form a surface microlayer (Hardy 1982; Hardy et al., 1987a,b, 1990; Cross et al., 1987) containing higher levels of weathered oil-droplet-phase SHC and PAH components. This effect results in the primarily oil-droplet-phase signals (PDR>2) observed in the intertidal mussels at Alyeska Marine Terminal and the Gold Creek (GOC) reference station 6 km across the port (Payne et al., 2001; Payne and Driskell, 2003). While these data are not absolutely consistent (i.e., over the first eight years of the LTEMP program there were occasionally samples in the spring that showed a dissolved-phase signal and there were occasionally samples in the summer that had an oil-droplet-phase signal), this summer vs. winter pattern of dissolved- vs. oil-droplet phases was highly significant (chi sq = 6.93, corrected for continuity; $p < 0.01$; Sokal and Rohlf 1969) for both the Alyeska Marine Terminal site and the control station across the Port.

Although the concentrations are very low, data from Alyeska Marine Terminal continue to indicate the accumulation of dissolved and particulate/oil-phase PAH components from the BWTF that are seasonally controlled by water-column stratification. In the 2002-2003 LTEMP report, we noted that this pattern appeared to be breaking down at Gold Creek after March 2000 with the overall decline in TPAH and MPI levels at the site (Figure 12; Payne et al. 2003b). The 2003-2004 data suggest, however, that water- column-stratification-controlled transport of dissolved PAH and particulate/oil-droplets may have reappeared at this site, although the dissolved-phase pattern clearly predominates (PDR<1). The data in Figure 12 plots Mytilus Petrogenic Index (MPI) rather than TPAH; as described earlier, MPI isolates the fossil fuel fraction of TPAH and eliminates pyrogenic components. Tissue PAH concentrations as reflected in TPAH and MPI plots appear to have declined at both Alyeska Marine Terminal and Gold Creek since October 2001 and March 2002, and this trend appears to be continuing with the 2003-2004 data (Payne et al., 2005).

Subtidal sediments also reflect the BWTF discharge. Sediments are collected seasonally from two shallow stations near the mussel sites in Port Valdez. Sediment TPAH concentrations at Alyeska Marine Terminal are low (generally below 600 ng/g dry wt.) and although highly variable, are primarily contaminated by a weathered ANS oil signal (Figure 13) consistent with BWTF-diffuser-sourced, dispersed oil-droplet/suspended-particulate-material (SPM) interactions and resulting sedimentation (Payne et al., 1989; 2003b,d).

Additional hydrocarbon sources in Alyeska Marine Terminal samples include combustion products (which may or may not be related to terminal activities) and biogenic marine and terrestrial SHC components. In contrast, at Gold Creek, the PAH components in the sediments are generally 5-10 times lower than those at Alyeska Marine Terminal, and do not show the same degree of petrogenic contamination or variability compared to the Alyeska Marine Terminal site (Figure 13). The PAH in Gold Creek sediments are derived primarily from combustion products. It is not possible to determine if the low-but-discernible petrogenic hydrocarbons in the Gold Creek sediments are from the BWTF and/or other activities at the Alyeska Marine Terminal, or if they represent input from other sources, including boat traffic; sewage and wastewater effluent; and surface/stormwater runoff from the city of Valdez.

The SHC in subtidal sediments at Alyeska Marine Terminal show a combination of biogenic and very weathered ANS oil signals (Figure 13), consistent with terrestrial and marine copepod fecal-pellet sources along with substantial oil-droplet/SPM interactions given the elevated levels of dispersed oil droplets introduced to the region from the BWTF diffuser. The SHC signals in the subtidal sediments at Gold Creek show a combination of marine and terrestrial biogenic input, with very little weathered-oil signal. Time series plots of sediment Crude index values show current annual trends to be stable at very low levels (Figure 14).

Double ratio plots of C-2 dibenzothiophene/C-2 phenanthrene versus C-3 dibenzothiophene/C-3 phenanthrene (D2/P2 vs. D3/P3; reviewed by Wang and Fingas, 2003) have been used to help identify ANS crude-derived sources for Alyeska Marine Terminal and Gold Creek sediments. The samples in Figure 15 are coded to reflect the sampling location including four weathered ANS crude oil samples from the Alyeska Ballast Water Treatment Facility (BWTF) effluent (Salazar et al., 2002, Payne et al., 2001, and this study). Quite clearly, most of the Alyeska

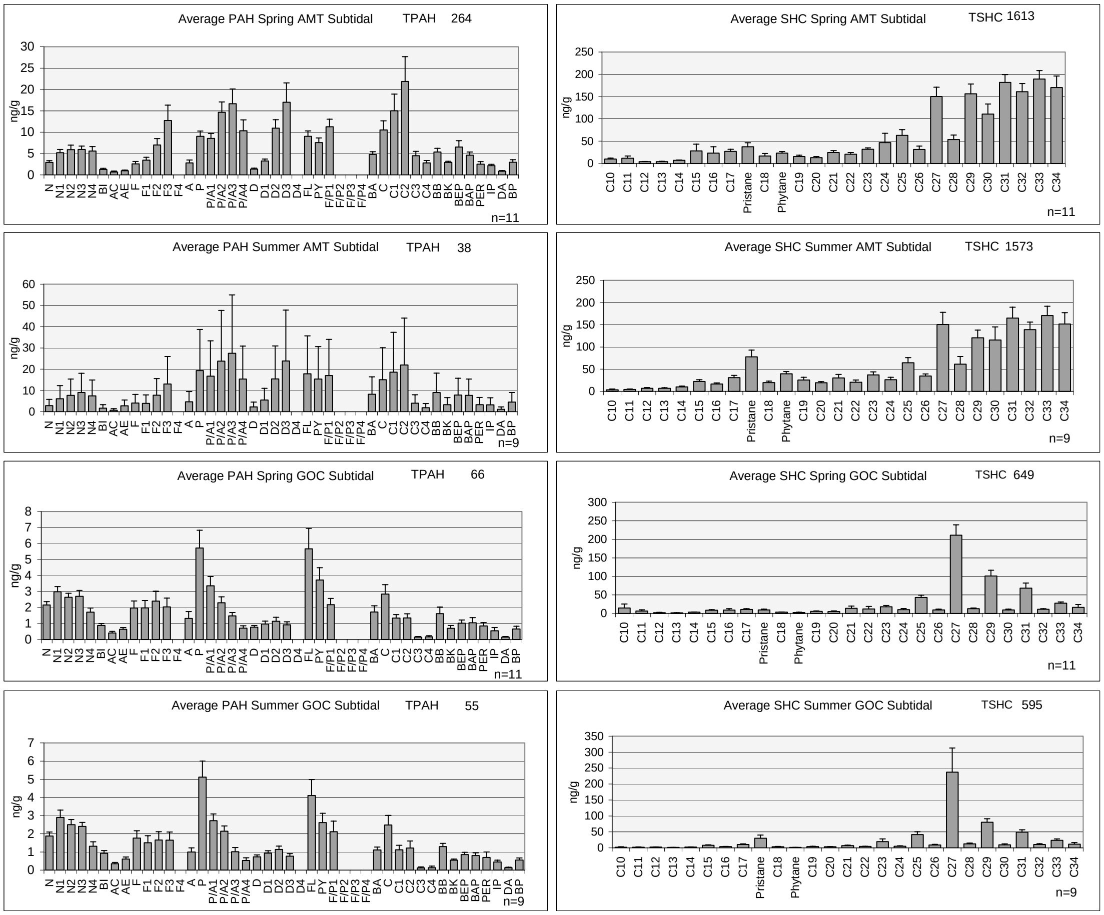

Figure 13. Average PAH and SHC histograms comparing seasonal subtidal sediment samples from Alyeska Marine Terminal and Gold Creek (concentrations in ng/g dry weight + std error of means).

Marine Terminal sediments cluster around the ANS source signals, although some of the Alyeska Marine Terminal samples also trend into the background signals observed at Gold Creek. The figure also distinguishes those samples that exhibited substantial pyrogenic source. These pyrogenic-dominated samples cluster much closer together showing a source that is not strongly correlated with ANS crude oil. For reference, a NIST reference sample for combustion soot is also presented on the figure. Not surprisingly, this combustion product profile is more closely associated with the samples from the background sediments collected at Gold Creek where the influence from the marine terminal is seldom observed.

4 Discussion

The LTEMP tissues and sediments from Port Valdez appear to routinely have persistent, but very low-levels of hydrocarbons directly attributable to the BWTF discharge. By way of comparison, however, the PAH burden in mussels at the most contaminated LTEMP monitoring site within Port Valdez (immediately adjacent to the Alyeska Marine Terminal) are usually lower by a factor of four or more compared to those from the clean-control reference site used for a similar monitoring program examining the Scope for Growth (SFG) in mussels (*Mytilus edulis*) conducted at

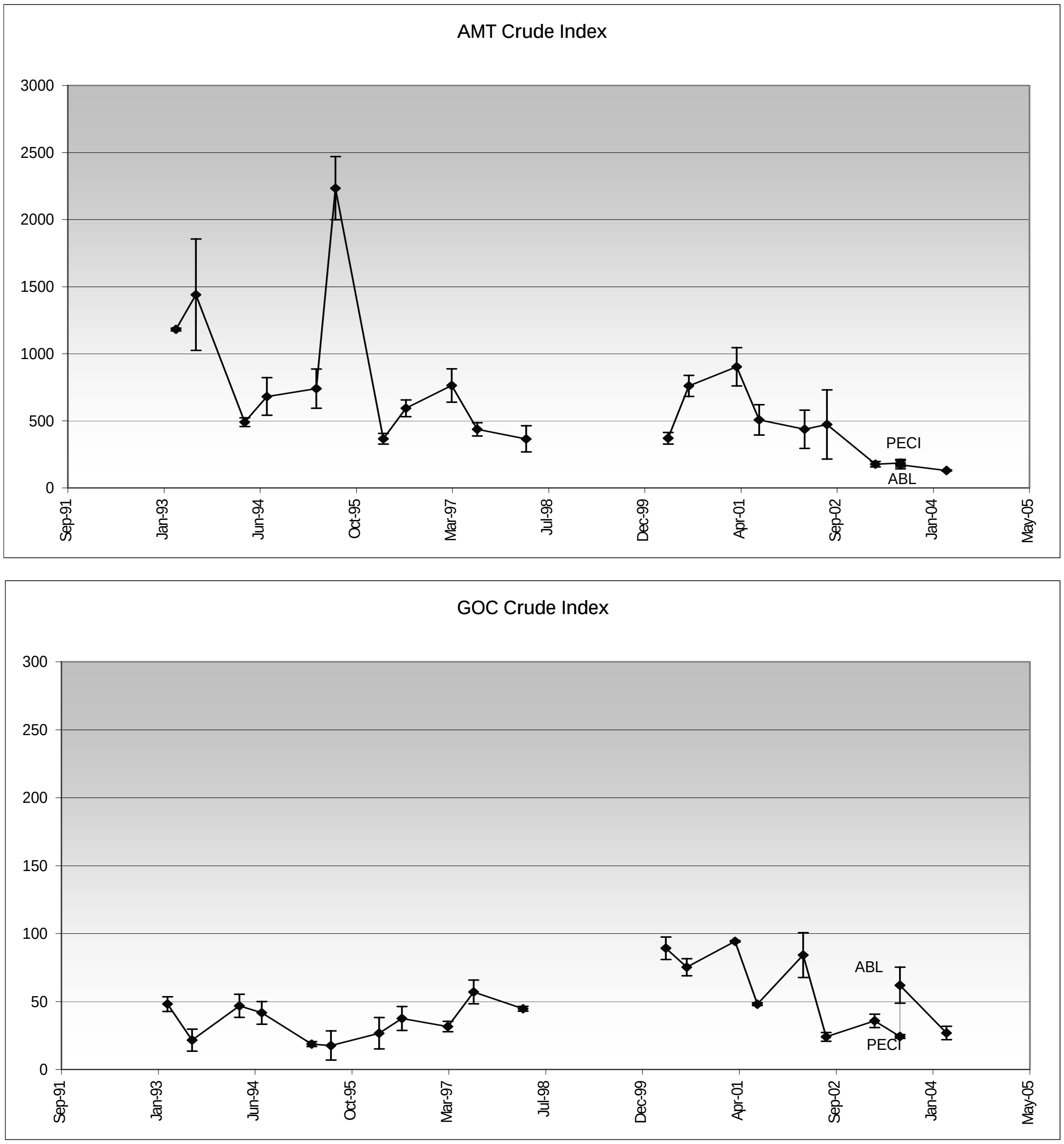

Figure 14. Hydrocarbon assessment index weighted for crude oil (CRUDE index) from AMT and GOC sediments samples, March 1993-2004 (± std error of means) (Payne et al. 2005).

Sullom Voe, one of the major oil terminals in the UK (Widdows et al. 1995). This has led us to conclude that the very high efficiency of oil removal in the BWTF and effective dispersion at the diffuser, result in remarkably little apparent impact of the discharged PAH on mussel populations within Port Valdez. This is especially noteworthy in light of the volume of oil transferred at the Alyeska Marine Terminal – approximately 20% of US oil consumption. Assuming the ballast water received at the BWTF contains at least 1% hydrocarbons (likely an underestimate) implies the overall hydrocarbon removal efficiency of the BWTF process is in excess of 99.9%, thus confirming the efficacy of the BWTF design and operation. In addition, further reductions in the environmental impact to receiving waters are realized by the

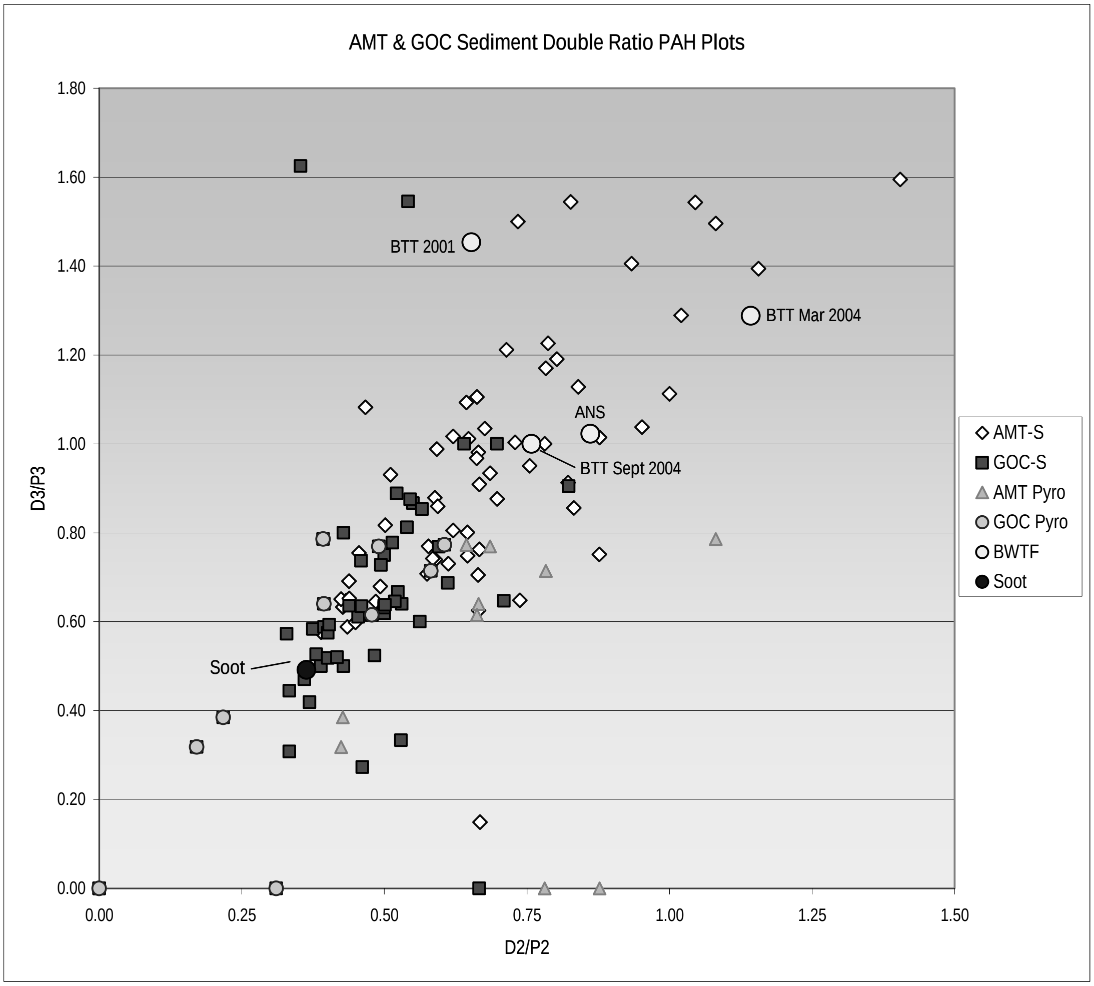

Figure 15. Double-ratio plot of C-2 dibenzothiophene/C-2 phenanthrene vs. C-3 dibenzothiophene/C-3 phenanthrene (D2/P2 vs. D3/P3) for LTEMP AMT & GOC sediment samples, 1993-2004 (Payne et al., 2005).

diffuser design, which disperses the oil that is discharged from the BWTF either as dissolved hydrocarbons or as oil microdroplets. These microdroplets have a very high surface area to volume ratio, which promotes the continued biological degradation processes within the water column.

From the discrimination of dissolved- and particulate/oil-phase signals, the proposed seasonally-mediated transport mechanisms and exposure routes discussed in this paper seem highly plausible, albeit untested. Data collected after the *Exxon Valdez* oil spill (EVOS) likewise reflect substantially different exposure routes for mussels versus herring and crab eggs following that event (Payne et al., 2001; Payne and Driskell, 2003). In 1989, the mussels clearly accumulated PAH and SHC primarily from the oil-droplet phases to which they were exposed. In contrast, the plots for the herring eggs collected in 1989 reflect the selective uptake of only the dissolved-phase (primarily the naphthalene homologues, which are the most water-soluble PAH derived from fresh ANS crude oil; Payne and McNabb, 1984; Payne et al., 1983, 1984, 1991a,b; French-McCay 2001, 2002). The SHC profiles for the exposed herring eggs show primarily lower-molecular-weight biogenic alkanes, which accumulate from the lipids in the phytoplankton (n-C_{15} and n-C_{17}) and calanoid copepods (pristane) that make up the majority of the diet of female herring before depositing their eggs (Cooney, 1993; Blumer et al., 1964).

By 1990 and 1991, the EVOS-impacted mussels were evidently no longer exposed to finite oil droplets as they were accumulating primarily dissolved-phase PAH (at significantly reduced overall concentrations) from the more water-soluble hydrocarbons still leaching from the intertidal zone. Likewise, the SHC profile for the mussel samples in 1990-1991 was characterized primarily by lower molecular weight biogenic components (n-C_{15}, n-C_{17}, and pristane) with little or no contribution of phytane and higher molecular weight n-alkanes from dispersed oil droplets.

In controlled laboratory experiments using gravel contaminated with lightly- and heavily-weathered ANS oil (where the naphthalenes and fluorenes had been significantly reduced), it has been confirmed that herring and salmon eggs exposed to the water fraction accumulated only components from the dissolved phase (Carls et al., 1999; Heintz et al., 1995, 1999; Marty et al., 1997). It was also shown that the same PAH patterns were obtained when salmon eggs were either exposed directly to the oiled gravel or only to the aqueous phase. The only shift in PAH accumulation occurred when more weathered oil was used in those studies. In those instances, the PAH distribution was skewed to the residual higher molecular weight components, which can still partition into the aqueous phase (although at slower rates) when seawater percolates through contaminated gravel.

PAH profiles from crab egg samples in the EVOS Trustees Database analyzed immediately following the spill revealed that PAH adsorption was again exclusively through the dissolved-phase, which is in agreement with more recent crab tissue results from the *M/V New Carissa* (Payne and Driskell 1999, 2000, 2001, 2003). After the *M/V New Carissa* oil spill near Coos Bay, Oregon in 1999, oysters, clams, and mussels were all observed to accumulate PAH and SHC signals from both the dissolved- and oil-droplet phases, while crabs picked up PAH only from the dissolved phase.

Based on the corroborating date from these other studies, there may still be potential concern for the very low-level dissolved-phase concentrations introduced into Port Valdez from the BWTF. Also, from another perspective, there is potential for photo-enhanced toxicity due to dissolved-component uptake into transparent organisms, e.g., eggs, larvae, and juveniles near the water surface (Barron and Ka'aihue, 2001; Pelletier et al., 1997, Duesterloh et al., 2002; Barron et al., 2003). Nevertheless, from the data available to date, it appears that the BWTF processes (and the effective dispersion of dissolved- and particulate/oil-phase components by the diffuser) result in minimal impact on biota, as indicated by the low concentrations of PAH that accumulate in mussels within the Port.

5 Conclusions

The Ballast Water Treatment Facility is effective in reducing BTEX to less-than NPDES permitted concentrations during both summer and winter conditions, but an estimated 26% is vented directly to the atmosphere annually. Microbial removal of SHC and selected PAH is effective in the BTTs during the summer; however, degradation of both hydrocarbon groups is significantly retarded during colder winter months. PAH components are detectable as dissolved- and particulate-phase signatures in the effluent.

The largest hydrocarbon pollution sources detected in samples from Port Valdez stations are correlated with an oil spill mishap at the terminal in 1994 and a sheen event from the Ballast Water Treatment Facility in January 1997. Apart from these events, concentrations from petrogenic sources are usually near or below the detection limits of the analytic methods, typically in the low parts per billion for individual PAH. But on a routine basis, an ANS oil signal attributed to the BWTF effluent is detectable in mussel tissues at both Alyeska Marine Terminal and Gold Creek stations, and sediments at Alyeska Marine Terminal.

From the hydrocarbon profiles, we are able to discriminate between particulate/oil-phase and dissolved-phase signals in the water column and then correlate those signals with seasonal uptake of hydrocarbons in mussels and from other studies, with potential absorption in herring and crab eggs. The results also suggest a surface microlayer mechanism may be responsible for seasonal transport of ANS weathered oil residues from the BWTF diffuser to intertidal zones to the north and west of the terminal. These findings give new insight into the transport and exposure pathways in Port Valdez. If surface microlayer concentration and transport of PAH components is occurring within the Port, then the potential for photo-enhanced toxicity to potentially exposed organisms and surface microlayer phenomena may warrant additional study.

6 Acknowledgements

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