Hydrocarbon Biodegradation in the Ballast Water Treatment Facility, Alyeska Marine Terminal

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cover photo "DAF cells"
by William Driskell, 2004

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Executive Summary

The Ballast Water Treatment Facility (BWTF) at the terminus of the Trans-Alaska Pipeline in Port Valdez, Alaska, currently 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. In the dissolved air flotation (DAF) cells/weirs and in the Splitter Box distributing DAF effluent to the biological treatment tanks (BTTs), evaporation is the dominant removal mechanism for BTEX, lower-molecular-weight SHC, and possibly the naphthalenes. Within the BTTs, microbial degradation of BTEX is very efficient in both summer and winter and essentially complete midway through the tanks. By the time the effluent reaches Port Valdez, all BTEX analytes were not detectable (< 12 ppb total BTEX).

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. During colder months, both SHC and PAH biodegradation are limited within the BWTF. In both seasons, the effluent signature is low level (< 300 ppb) but still appears in local mussel and sediment samples examined in the PWSRCAC Long Term Environmental Monitoring Program (LTEMP).

Concentrations and percent remaining at selected stages of treatment

		Concentration				Percent Remaining	
		90s Tanks	Splitter In	Fan/Meter Out	Units	Splitter	Fan/Meter
Sep-04	BTEX	11,320	6,230	< 12	µg/L	55%	< 0.1%
	TPAH	3,440	2,750	13.7	µg/L	80%	0.4%
	TSHC	842	580	65	µg/L	69%	8%
Jan-05	BTEX	9,750	7,900	< 12	µg/L	81%	< 0.1%
	TPAH	360	190	71	µg/L	53%	20%
	TSHC	1,409	505	206	µg/L	36%	15%

This study was conducted in parallel with a much larger Alyeska Pipeline Service Company (APSC) project to fully characterize the BWTF and in particular quantify losses of BTEX due to biodegradation versus evaporation to the atmosphere (Imperial Oil Research, 2005). As such, many of the measurements discussed in this PWSRCAC report serve as an independent quality assurance/quality control (QA/QC) validation of selected APSC data. Independent measurements of BTEX concentrations at various stages of the BWTF show remarkably close agreement in the APSC and PWSRCAC studies, and almost identical trends in degradation/loss are observed in side-by-side comparisons of the data. Likewise, independent BIORATE kinetics determinations of BTEX loss where evaporation was completely blocked,

generated very similar data. Thus, it appears that the measurement techniques utilized by both studies are valid, producing accurate and precise data. There may be an issue, however, with the manner in which the BTEX BIORATE data are interpreted; the PWSRCAC data from a single set of measurements suggest first-order kinetics (decay rate proportional to BTEX concentrations) while the APSC study assumed zero-order kinetics (rate thermally driven–independent of BTEX concentrations). As a result, APSC may have underestimated the biodegradation of BTEX in their current fate model.

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 ships 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). Currently, this facility typically treats and discharges 9,000,000 gallons of ballast water per day into Port Valdez.

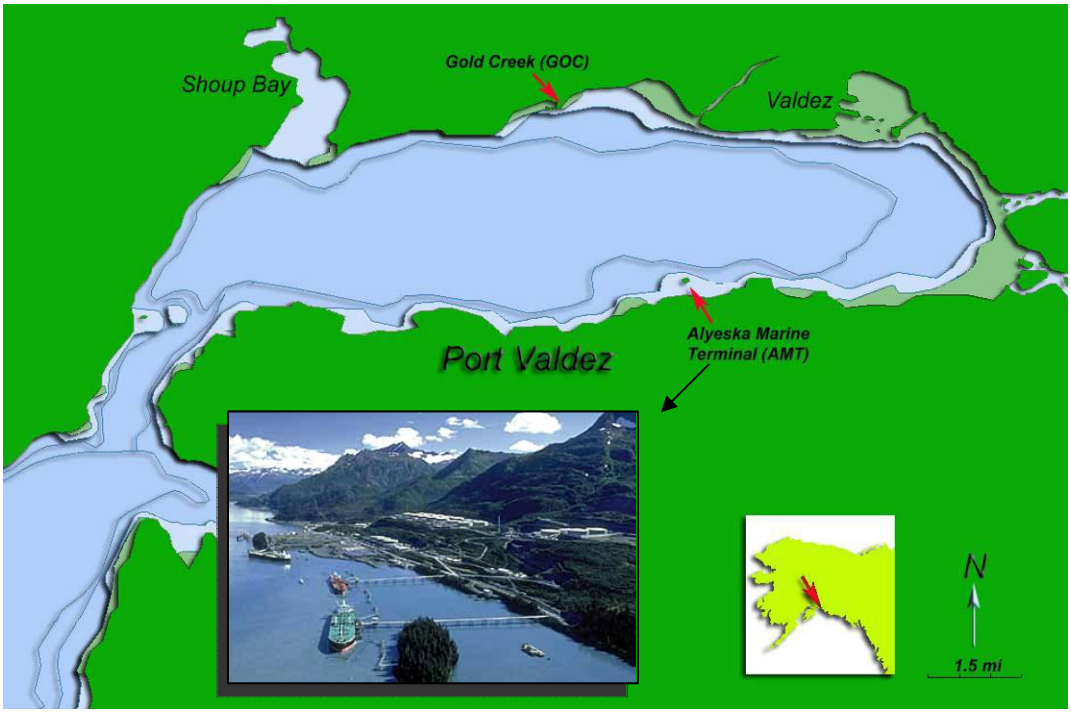


Figure 1. Map of Port Valdez sampling locations.

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, 2002, 2003a,b; 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 BWTF 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 from the BWTF plus another 55 tons per year from the 80s and 90s tanks (Imperial Oil Research, 2005).

1.1 BWTF Layout

In a plan view diagram, Figure 2 identifies BWTF sampling locations used in the PWSRCAC program to evaluate treated ballast-water characteristics and process efficiencies. Brief descriptions of the different stages of the BWTF follow.

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 and a polyelectrolyte polymer is added to aid in oil-flocculation and separation. 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 into 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.

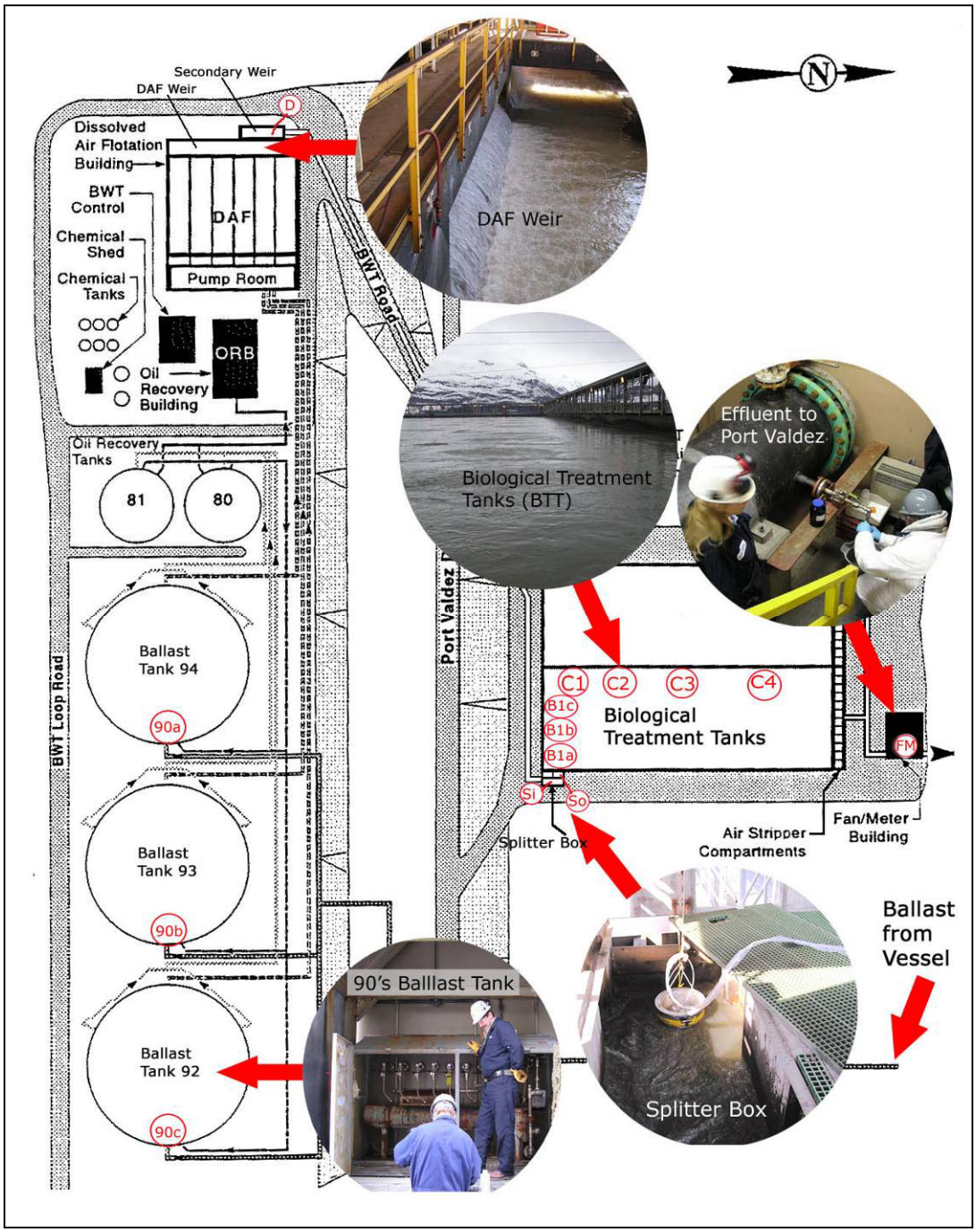


Figure 2. Alyeska Pipeline Service Company (APSC) Ballast Water Treatment Facility and PWSRCAC project sampling locations (shown by the photos).

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 from the BWTF 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 report.

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, APSC 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 BTTs (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.

2 Methods

Ballast water grab samples for hydrocarbon analyses were collected on three occasions from the BWTF (and acid quenched to pH < 2 upon collection to halt further biodegradation). 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 (60.4 and 43.9° F) in September 2004 and January 2005, respectively. In many of the figures presented in this report 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, BIORATE assay trials were 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 Research and APSC personnel (Imperial Oil Research, 2005), a non-acidified composite sample of BTT ballast water was poured into a series of thirty 60-mL septum-capped VOA vials that were incubated in a constant-temperature bath at the BTT temperature. Duplicate samples were then 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, 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 PAH data available 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; 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.

Once biodegradation begins, it proceeds at a particular rate based upon the kinetics of the microbial process in relation to substrate availability and the physiological state of the microbe among other factors. The form of the kinetic model is an important consideration for facility operators and designers in that it allows predictions of expected consumption, herein described best by the half-life of the decaying hydrocarbon. Although zero-order, three-half-order, and Michaelis-Menten (or Monod) kinetics have been used to define the biodegradation of a compound under some circumstances, first-order kinetics are commonly used as an approximation.

To empirically determine if the BTEX loss measured in our study followed zero-order kinetics (independent of BTEX concentration) or first-order kinetics (proportional to BTEX concentration), the data from the BIORATE tests were replotted so that the fit of the data versus model predictions could be evaluated and zero- or first-order rate constants determined from regression analyses of the plotted data. In the case of theoretical zero-order kinetics, a plot of $C_{x,0} - C_{x,t}$ versus time will yield a straight line through the origin with the slope equal to k, the zero-order, degradation-rate constant with units of mg/L/hr (Laidler, 1965; Imperial Oil Research, 2005). In our data, $C_{x,0}$ is the initial (time zero) concentration of benzene, toluene, ethylbenzene or xylene(s), and $C_{x,t}$ is the measured concentration of the individual constituent at time t (in hours). On the other hand, first-order degradation kinetics are evidenced by a plot of $-\ln(C_{x,t}/C_{x,0})$ versus time yielding a straight line through the origin with the slope equal to k, here, the first-order rate constant (with units of hrs^{-1}).

Tables 1 and 2 list the target analytes and abbreviations used in identifying individual components in the histogram plots and other figures presented in this paper. In addition to the analytes listed in Tables 1 and 2, the analytical methods employed look for additional components (shown in Tables 3 and 4); however, many of these constituents were not detected in any of the samples, so only those compounds actually found in the samples (and identified in Tables 1 and 2) are plotted in the figures. 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).

3 Results

3.1 BWTF Characterization

3.1.1 BTEX Removal

BTEX was measured at the eight sampling stations within the BWTF in September 2004 and January 2005 (Figure 3). Note that the BTT locations, Cells 1, 2, 3, and 4, used throughout this report correspond to the north sides of sampling stations C1, C2, C3 and C4, respectively, as shown in Figure 2.

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

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

Table 2. List of additional methods used and analytes of interest measured in this study.

EPA Method 8260	**EPA Method 8270**	**WHG PIANO 2**
Acetone	Phenol	Isopentane
Benzene	1,2-Dichlorobenzene	Pentane
Toluene	2-Pentanone, 4-hydroxy-4-methyl-	Cyclopentane
Ethylbenzene	2-Methylphenol	2-Methylpentane
p/m-Xylene	2-Propanol	3-Methylpentane
o-Xylene	2,4-Dimethylphenol	Hexane
Isopropylbenzene	Oleic Acid	Methylcyclopentane
n-Propylbenzene	Naphthalene	Cyclohexane
1,3,5-Trimethylbenzene	2-Methylnaphthalene	Benzene
tert-Butylbenzene	Dimethylphthalate	3-Methylhexane
1,2,4-Trimethylbenzene	Acenaphthylene	Heptane
sec-Butylbenzene	Acenaphthene	Methylcyclohexane
Naphthalene	Dibenzofuran	Toluene
	Diethylphthalate	Octane
	Fluorene	Ethylbenzene
	Phenanthrene	p/m-Xylene
	Anthracene	o-Xylene
	Di-n-butylphthalate	1-Methyl-3-ethylbenzene
	Fluoranthene	1-Methyl-4-ethylbenzene
	Pyrene	1,3,5-Trimethylbenzene
	Butylbenzylphthalate	1-Methyl-2-ethylbenzene
	Benz[a]anthracene	Undecane
	Chrysene	Dodecane
	bis(2-Ethylhexyl)phthalate	Naphthalene
	Di-n-octylphthalate	Tridecane
	Benzo[b]fluoranthene	2-Methylnaphthalene
	Benzo[k]fluoranthene	1-Methylnaphthalene
	Benzo[a]pyrene	
	Indeno[1,2,3-cd]pyrene	*See table 4 for full list of analytes*
	Dibenz[a,h]anthracene	
	Benzo[g,h,i]perylene	
	See table 3 for full list of analytes	

Table 3. Full list of EPA Method 8270 target analytes included in this study.

1,2,4-Trimethylbenzene	4-Nitrophenol	Dimethylphthalate	Nonadecane
1,2-Dichlorobenzene	9-Hexadecenoic acid	Di-n-butylphthalate	Nonadecane, 9-methyl-
1,3-Dichlorobenzene	9-Octadecenamide, (Z)-	Di-n-octylphthalate	Octadecane
1,4-Dichlorobenzene	Acenaphthene	Dodecane	Oleic Acid
2,4,5-Trichlorophenol	Acenaphthylene	Dodecane, 2-methyl-8-propyl-	Oxacyclotetradecan-2-one, 13-methy
2,4,6-Tribromophenol	Anthracene	Eicosane	Pentachlorophenol
2,4,6-Trichlorophenol	Benz[a]anthracene	Ethanol, 2-butoxy-	Pentadecane
2,4-Dichlorophenol	Benzene, (1-methylethyl)-	Fluoranthene	Pentadecane, 2,6,10,14-tetramethyl
2,4-Dimethylphenol	Benzene, 1,2,3,4-tetramethyl-	Fluorene	Phenanthrene
2,4-Dinitrophenol	Benzene, 1,2,3-trimethyl-	Heptadecane	Phenol
2,4-Dinitrotoluene	Benzene, 1-ethyl-2,4-dimethyl-	Heptadecane, 2-methyl-	Phenol, 2,3,6-trimethyl-
2,6-Dinitrotoluene	Benzene, 1-ethyl-2-methyl-	Hexachlorobenzene	Phenol, 2,4,6-trimethyl-
2-Chloronaphthalene	Benzene, 1-ethyl-4-methyl-	Hexachlorobutadiene	Phenol, 2,5-dimethyl-
2-Chlorophenol	Benzene, 1-methyl-4-(1-methylethyl	Hexachlorocyclopentadiene	Phenol, 2,6-dimethyl-
2-Fluorobiphenyl	Benzo[a]pyrene	Hexachloroethane	Phenol, 2-ethyl-
2-Fluorophenol	Benzo[b]fluoranthene	Hexadecane	Phenol, 4-ethyl-2-methyl-
2-Methylnaphthalene	Benzo[g,h,i]perylene	Hexadecane, 2,6,10,14-tetramethyl-	Phenol, 4-ethyl-3-methyl-
2-Methylphenol	Benzo[k]fluoranthene	Hexadecanoic acid	Phenol-d5
2-Nitroaniline	Benzyl alcohol	Indeno[1,2,3-cd]pyrene	Propanoic acid, 2-methyl-, 2,2-dim
2-Nitrophenol	bis(2-Chloroethoxy)methane	Isophorone	Pyrene
2-Pentanone, 4-hydroxy-4-methyl-	bis(2-Chloroethyl)ether	Naphthalene	Terphenyl-d14
2-Propanol, 1-(2-methoxy-1-methyl)	bis(2-chloroisopropyl)ether	Naphthalene, 1,4,6-trimethyl-	Tetracosane
3-Nitroaniline	bis(2-Ethylhexyl)phthalate	Naphthalene, 1,5-dimethyl-	Tetradecane
4,6-Dinitro-2-methylphenol	Butanoic acid, butyl ester	Naphthalene, 1,6-dimethyl-	Tetradecanoic acid
4-Bromophenyl-phenylether	Butylbenzylphthalate	Naphthalene, 1-methyl-	Thymol
4-Chloro-3-methylphenol	Chrysene	Naphthalene, 2,6-dimethyl-	Toluene
4-Chloroaniline	Cyclopentanone	Nitrobenzene	Tricosane
4-Chlorophenyl-phenylether	Dibenz[a,h]anthracene	Nitrobenzene-d5	Tridecane
4-Methylphenol	Dibenzofuran	n-Nitroso-di-n-propylamine	Tridecane, 7-hexyl-
4-Nitroaniline	Diethylphthalate	n-Nitrosodiphenylamine	

Table 4. Full list of Woods' Hole Group PIANO 2 method target analytes included in this study.

Isopentane	Heptane	1,2,4-Trimethylbenzene
1-Pentene	Methylcyclohexane	sec-Butylbenzene
2-Methyl-1-butene	2,5-Dimethylhexane	1-Methyl-3-isopropylbenzene
Pentane	2,4-Dimethylhexane	1-Methyl-4-isopropylbenzene
2-Pentene (trans)	2,2,3-Trimethylpentane	1-Methyl-2-isopropylbenzene
2-Pentene (cis)	2,3,4-Trimethylpentane	Indan
Tertiary butanol	2,3,3-Trimethylpentane	1-Methyl-3-propylbenzene
Cyclopentane/2,3-Dimethylbutane	3-Ethylhexane	1-Methyl-4-propylbenzene
2-Methylpentane	2-Methylheptane	n-Butylbenzene
MTBE	3-Methylheptane	1,2-Dimethyl-4-ethylbenzene
3-Methylpentane	Toluene	1,2-Diethylbenzene
1-Hexene	1-Octene	1-Methyl-2-propylbenzene
Hexane	Octane	1,4-Dimethyl-2-ethylbenzene
Diisopropyl Ether (DIPE)	1,2-Dibromoethane	Undecane
Ethyl Tertiary Butyl Ether (ETBE)	Ethylbenzene	1,3-Dimethyl-4-ethylbenzene
2,2-Dimethylpentane	p/m-Xylene	1,3-Dimethyl-5-ethylbenzene
Methylcyclopentane	1-Nonene	1,3-Dimethyl-2-ethylbenzene
2,4-Dimethylpentane	Nonane	1,2-Dimethyl-3-ethylbenzene
1,2-Dichloroethane	Styrene	1,2,4,5-Tetramethylbenzene
Cyclohexane	o-Xylene	Pentylbenzene
2-Methylhexane	Isopropylbenzene	Dodecane
Benzene	n-Propylbenzene	Naphthalene
2,3-Dimethylpentane	1-Methyl-3-ethylbenzene	Benzothiophene
Thiophene	1-Methyl-4-ethylbenzene	MMT
3-Methylhexane	1,3,5-Trimethylbenzene	Tridecane
TAME	1-Decene	2-Methylnaphthalene
1-Heptene/1,2-DMCP (trans)	1-Methyl-2-ethylbenzene	1-Methylnaphthalene
Isooctane	Decane	

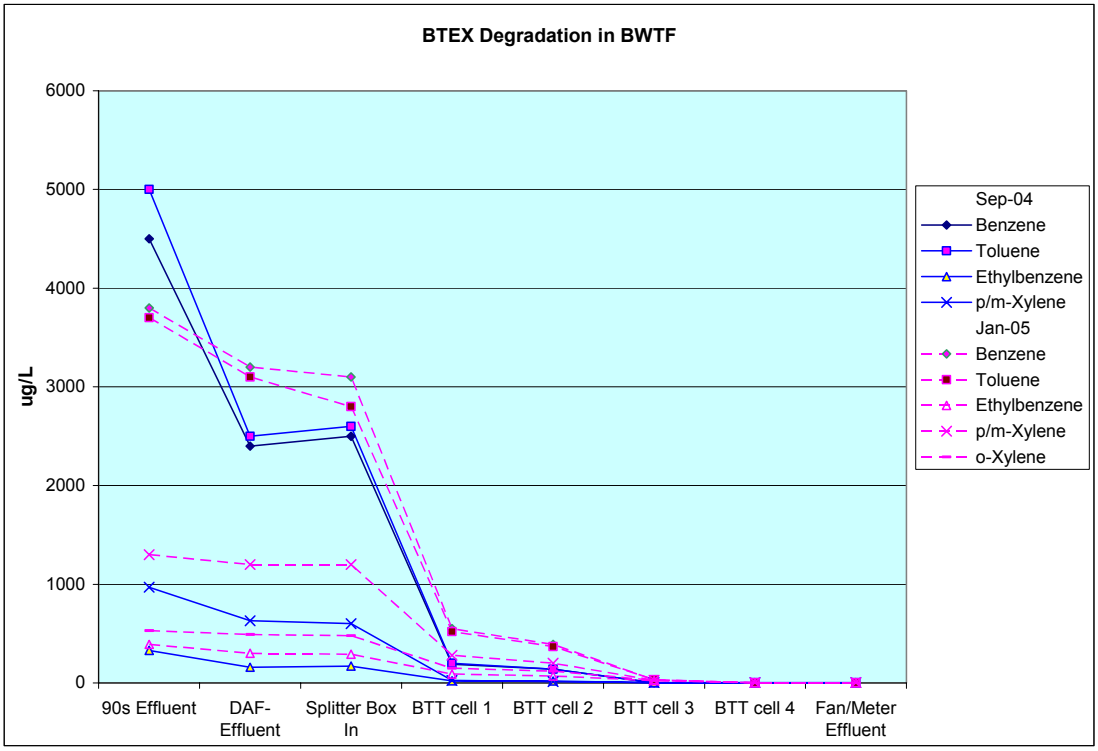


Figure 3. BTEX Degradation in BWTF, Sept 2004 and Jan 2005.

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 (within experimental error), 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. BTEX

degradation is also much slower at lower temperatures (see below), and 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 slightly 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 under the higher-flow conditions there was slightly less of a relative concentration drop in the DAF and Splitter box effluents. 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 no BTEX, with each constituent < 2 µg/L. In addition to collecting BTEX samples at each station, temperature and dissolved oxygen (D.O.) were measured *in situ*. The data in Table 5 illustrate the effects of initial hydrocarbon concentrations and flow rates on dissolved oxygen depression in the tanks. The D.O. concentrations in the 90s tanks are too low (0.7-0.8 mg/L) to support aerobic microbial degradation of either the volatile BTEX or the semivolatile SHC and PAH components in either the summer or winter. Microbial degradation can begin after the ballast water is oxygenated in the DAF cells, but during the higher hydrocarbon loadings and slower flow rates encountered during the warmer summer studies, the microbial degradation was sufficient to depress D.O. concentrations through the DAF cells, the splitter box, and part way down the BTTs. As described below, microbial degradation rates were significantly retarded during the colder winter studies, and under the higher-flow and colder conditions encountered in January, D.O. concentrations were relatively constant from the DAF weir effluent through the BTTs and in the final effluent discharged to the Port.

Table 5. Measured Temperatures and Dissolved Oxygen (D.O.) Concentrations

Station	**Temperature (^{o}C)**		**Dissolved Oxygen (mg/L)**	
	September '04	January '05	September '04	January '05
90s Tank	16.1	5.3	0.7	0.8
DAF Weir	16.3	4.8	4.8	8.0
Splitter Box	16.1	6.8	4.4	7.7
BTT Cell 1	15.8	2.8-6.4 [a]	5.8	8.2
BTT Cell 2	15.6	2.6-6.4 [a]	5.7	8.3
BTT Cell 3	15.5	2.5-6.1 [a]	6.9	8.4
BTT Cell 4	15.5	2.6-5.1 [a]	7.4	9.0
Fan/Meter Out	15.8	6.6	8.2	7.4

[a] The BTT temperatures were measured twice on January 11, 2005. Once around 1100 hrs (warmer readings) and later in the afternoon (between 1740 and 1810 hrs) after the air temperature dropped to around 6 ^{o}F (-14 ^{o}C) and the wind picked up to ~ 20-25 knots.

The BIORATE tests conducted in both September 2004 and January 2005 explicitly tested the loss rate of BTEX in the BTT cells from 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 unknowingly so low in the composite sample (< 14 µg/L), that all of the constituents of interest were consumed to below the laboratory MDL (< 2 µg/L) by the time the first time-series sample was taken (0.5 hours, Figure 4).

As a result, we were not able to measure September biodegradation loss rates for BTEX, but fortunately, the PAH and SHC data (presented below) were good and clearly showed the affects of microbial versus abiotic (volatilization) losses. For the January 2005 BIORATE tests, we prudently pre-screened the BTEX levels at various locations throughout the BTTs and then 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.

Calculations were made fitting the data to both zero- and first-order rate decay models (Figures 5 and 6). Unfortunately, there is enough noise in the non-replicated data to generate very good linear regression relationships for either zero-order or first order kinetics (r^2 values in Table 6), particularly so when some analytes fell below the method detection limits after only three sampling points (e.g., benzene and toluene). The APSC studies, on the other hand, utilized many more samples (sacrificed every 0.5 hrs) early in the BIORATE experiments, and their data led them to assume that the BTEX loss was zero-order. Consequently, they used that assumption in their fate modeling of BTEX throughout the BWTF (Imperial Oil Research, 2005). But there may be an issue with this assessment.

Based on the RCAC rate constants and calculated half-lives for the disappearance of individual components (albeit at a single temperature, 6.6^o C, 44^o F), the reactions from this single run strongly suggest first-order rather than zero-order kinetics. Specifically, the calculated half-life for ethylbenzene following zero-order kinetics is 23.6 hours versus 1.5 hours if the reaction is first-order (Table 6). Examination of the raw data (Figure 7) suggests that the loss of ethylbenzene, going from 74 µg/L to 37 µg/L, is closer to 1.5 hours, in agreement with the first-order calculation rather than zero-order's 23.6 hours (Table 6). This same comparison of calculated half-lives versus observed concentration drops for the other components (Figure 7 and Table 6), confirms our suspicion that, at least for the specific temperature and BTEX concentrations where we measured the BIORATE kinetics, the loss rate of BTEX appears to be first-order. This finding is also more in line with the literature because most bacterial processes are typically dependent on the substrate concentrations (Lehninger, 1976). PAH loss rates in this study (see below) were also determined to be first-order. We are perplexed to understand a process such that the degradation of BTEX would be independent of substrate concentration while PAH is dependent.

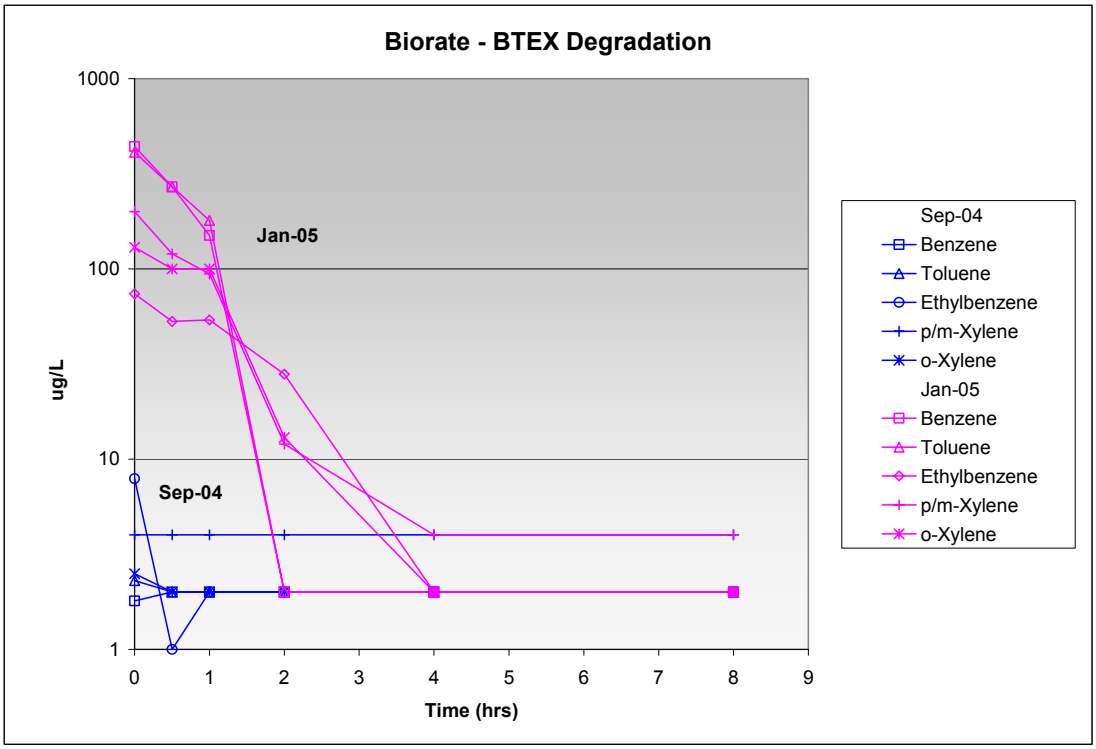


Figure 4. BIORATE BTEX Degradation, Sept. 2004 and Jan. 2005 (concentrations in µg/L).

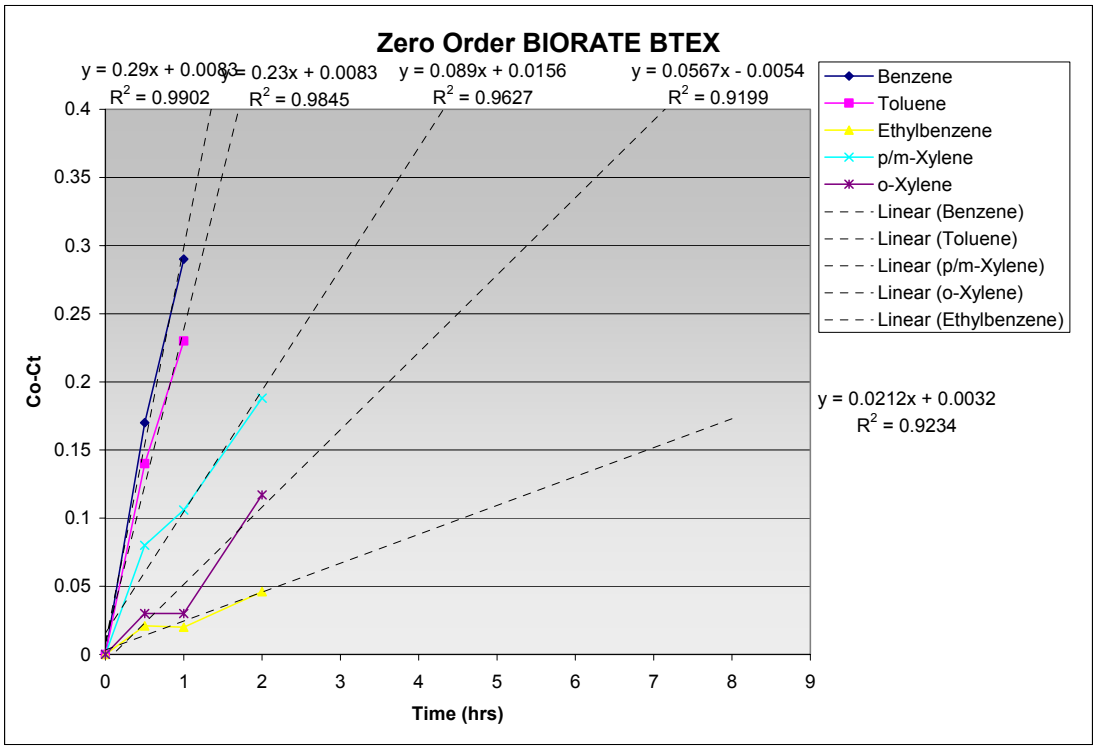


Figure 5. Plot of January 2005 PWS RCAC BIORATE data for BTEX showing zero-order kinetics.

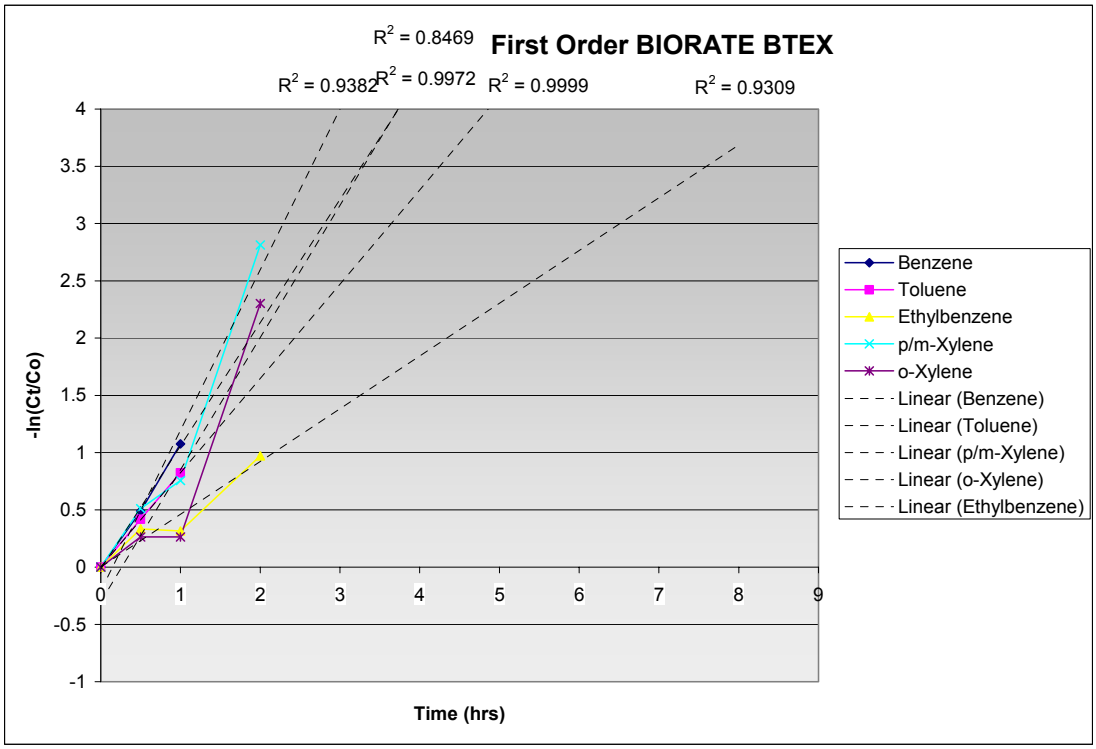


Figure 6. Plot of January 2005 PWS RCAC BIORATE data for BTEX showing possible first-order kinetics.

Table 6. Calculated half lives and rate constants for zero-order and first-order rate loss from PWS RCAC BIORATE BTEX trials in January 2005.

		Zero order model		First order model		
BTEX*	**Half life (hrs)**	**Rate Constant**	**r^2**	**Half Life**	**Rate Constant**	**r^2**
Benzene	1.724	0.2900	0.990	0.6441	1.0761	0.997
Toluene	2.174	0.2300	0.985	0.8420	0.8232	1.000
Ethylbenzene	23.58	0.0212	0.923	1.5049	0.4606	0.931
p/m-Xylene	5.618	0.0890	0.963	0.4942	1.4025	0.938
o-Xylene	8.818	0.0567	0.920	0.6005	1.1542	0.847

*Sample vials maintained at BTT ambient, 6.6° C (43.9° F)

3.1.2 PAH and SHC Removal

In September 2004, grab samples were taken for PAH and SHC from all eight BWTF field stations (Figures 8 and 9). At that time, the Ballast Water temperatures ranged from 15.9 to 16.3° C (Table 5). 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

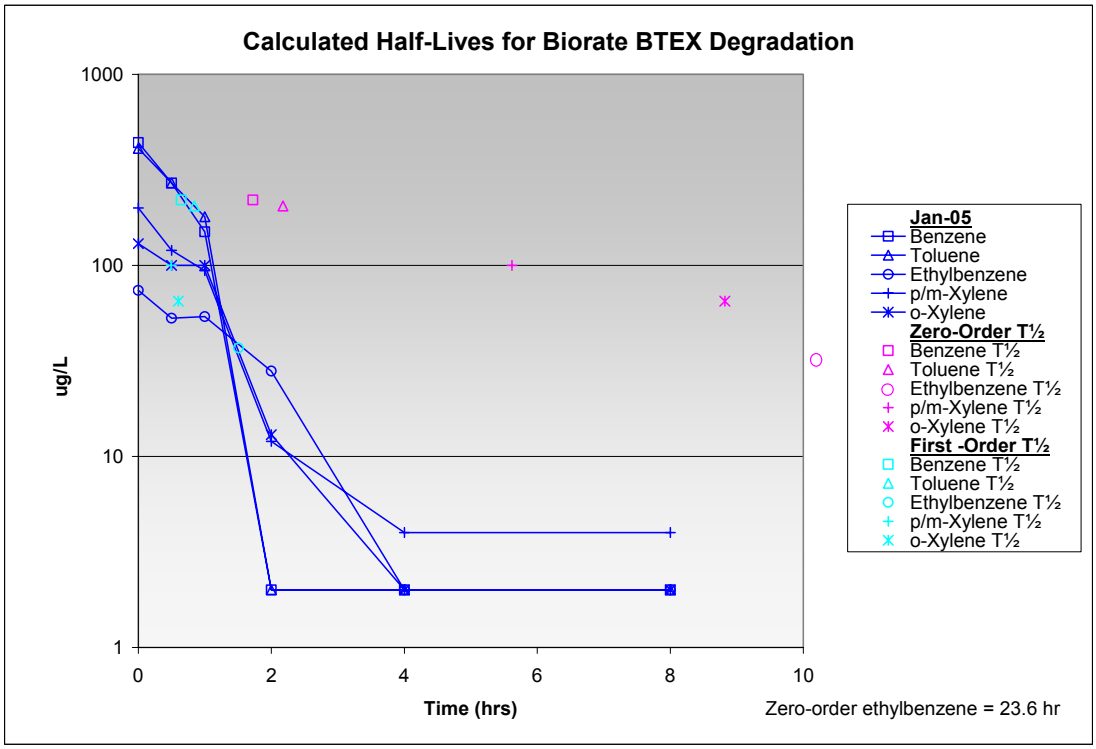


Figure 7. Comparison of calculated half-lives for zero- versus first-order kinetic models for BIORATE BTEX degradation. Half-lives for a first-order model more closely match the observed data.

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 (D.O. = 0.7 mg/L; Table 5), 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. Visually, the grab samples from BTT Cells 1 (Figure 8) and BTT Cells 2, 3, and 4 (Figure 9) 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 PAH 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. 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).

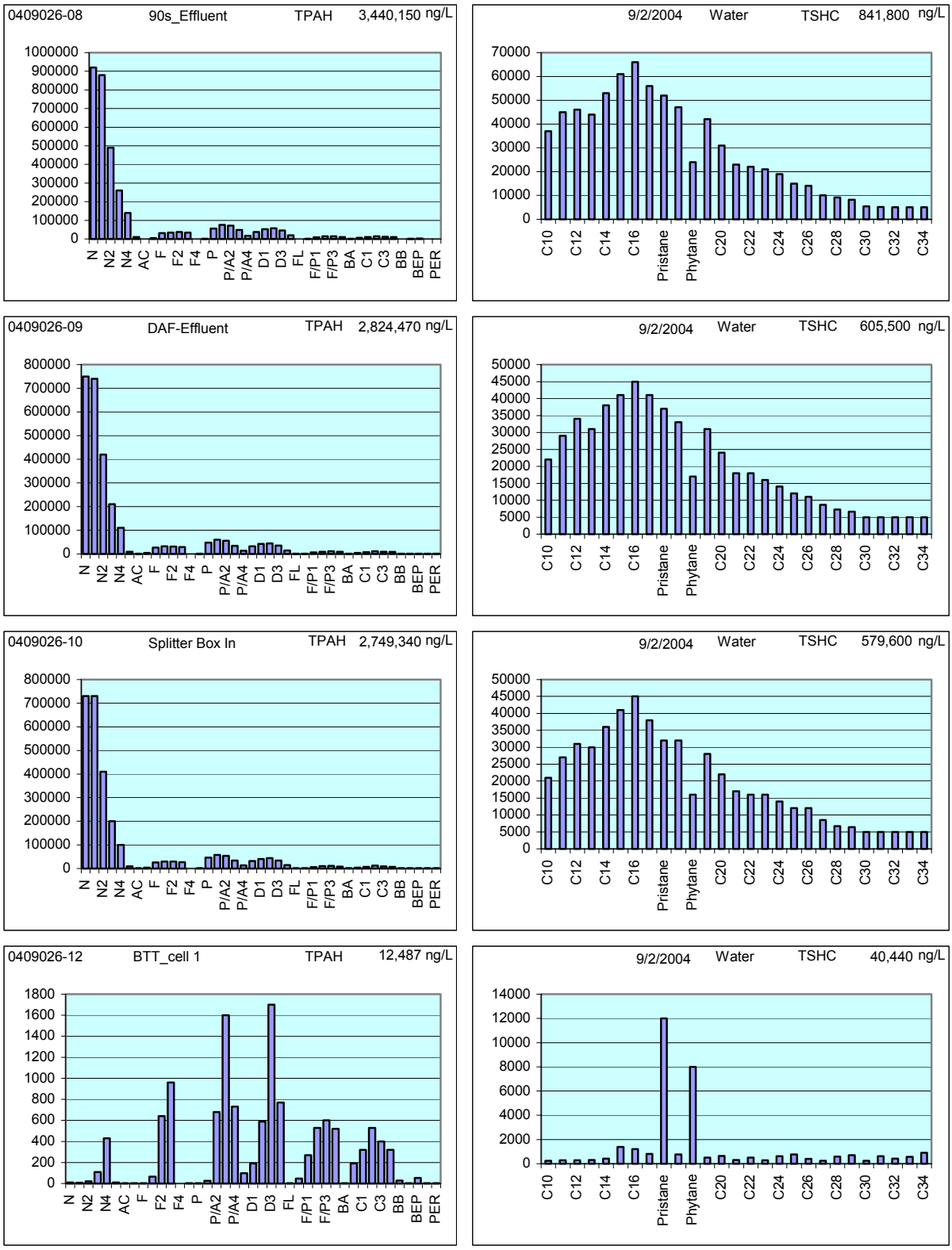


Figure 8. PAH and SHC histograms from 90s Tank effluent, DAF effluent, BTT Splitter Box effluent, and Cell 1, Sept 2004 (concentrations in ng/L).

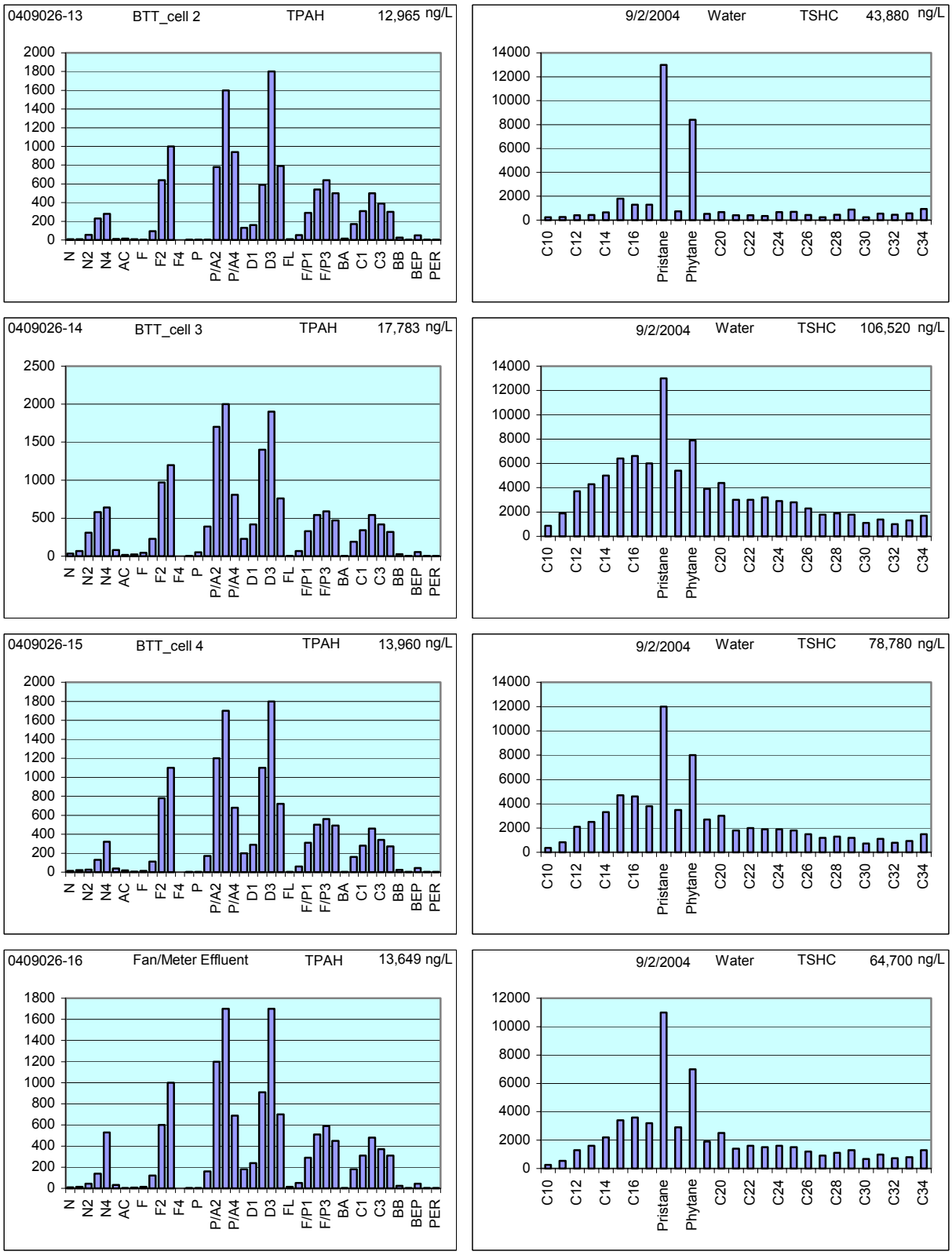


Figure 9. PAH and SHC histograms from BTT Cell 2, Cell 3, and Cell 4, and Fan/Meter effluent, Sept. 2004 (concentrations in ng/L).

In January 2005, PAH and SHC samples were again analyzed from the sequence of stations (Figures 10 and 11). At that time, Ballast Water temperatures ranged from 2.5 to 6.8^{o} C (Table 5). 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, 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 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 (see below), naphthalene and several other parent PAH were slightly degraded by indigenous bacteria, but the rates were significantly depressed (6 times lower for naphthalene and 140 times lower for phenanthrene) 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 12). 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 (Figure 12) 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.

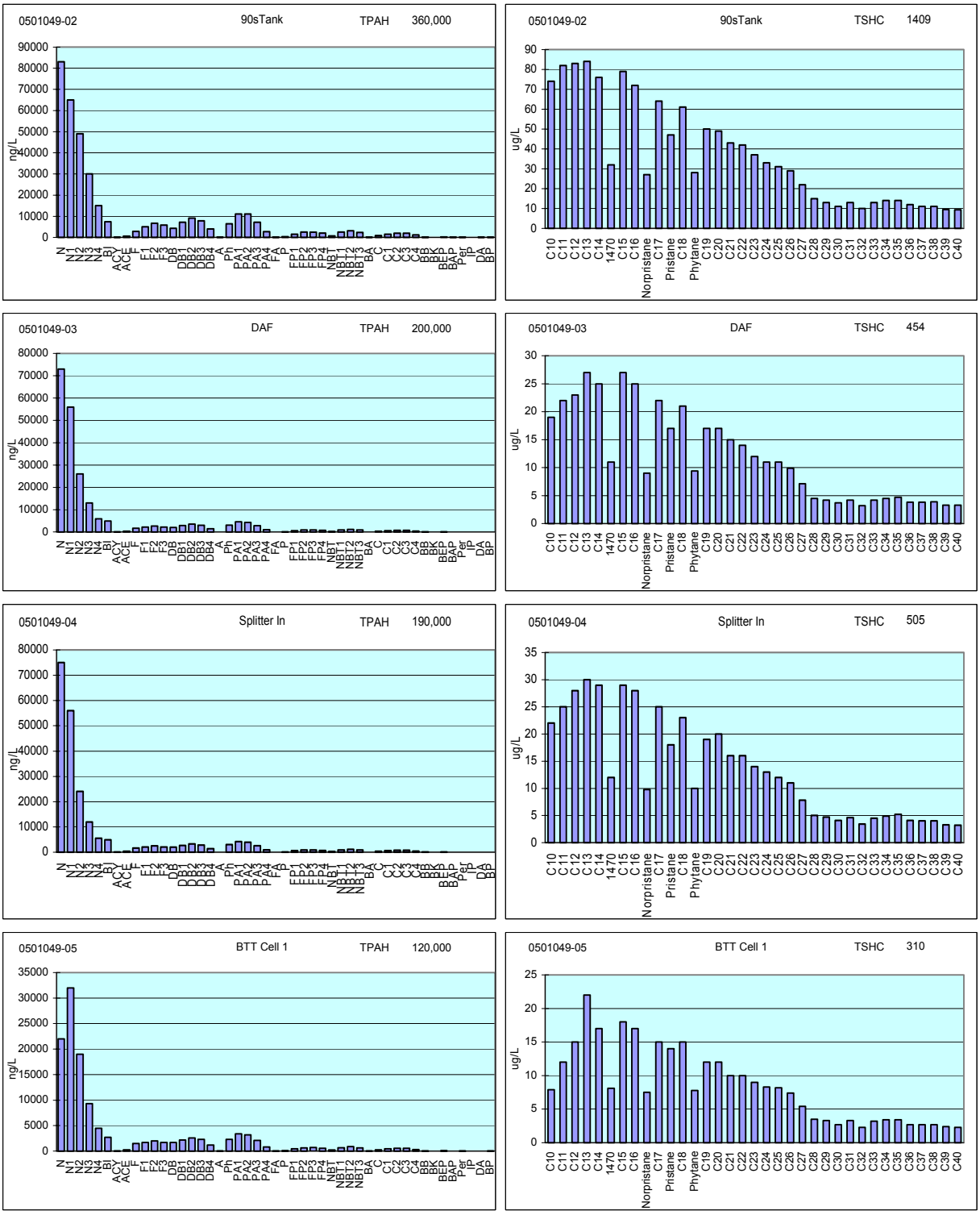


Figure 10. PAH and SHC histograms from 90s Tank effluent, DAF effluent, Splitter Box effluent, and BTT Cell 1, Jan. 2005 (PAH concentrations in ng/L; SHC concentrations in µg/L).

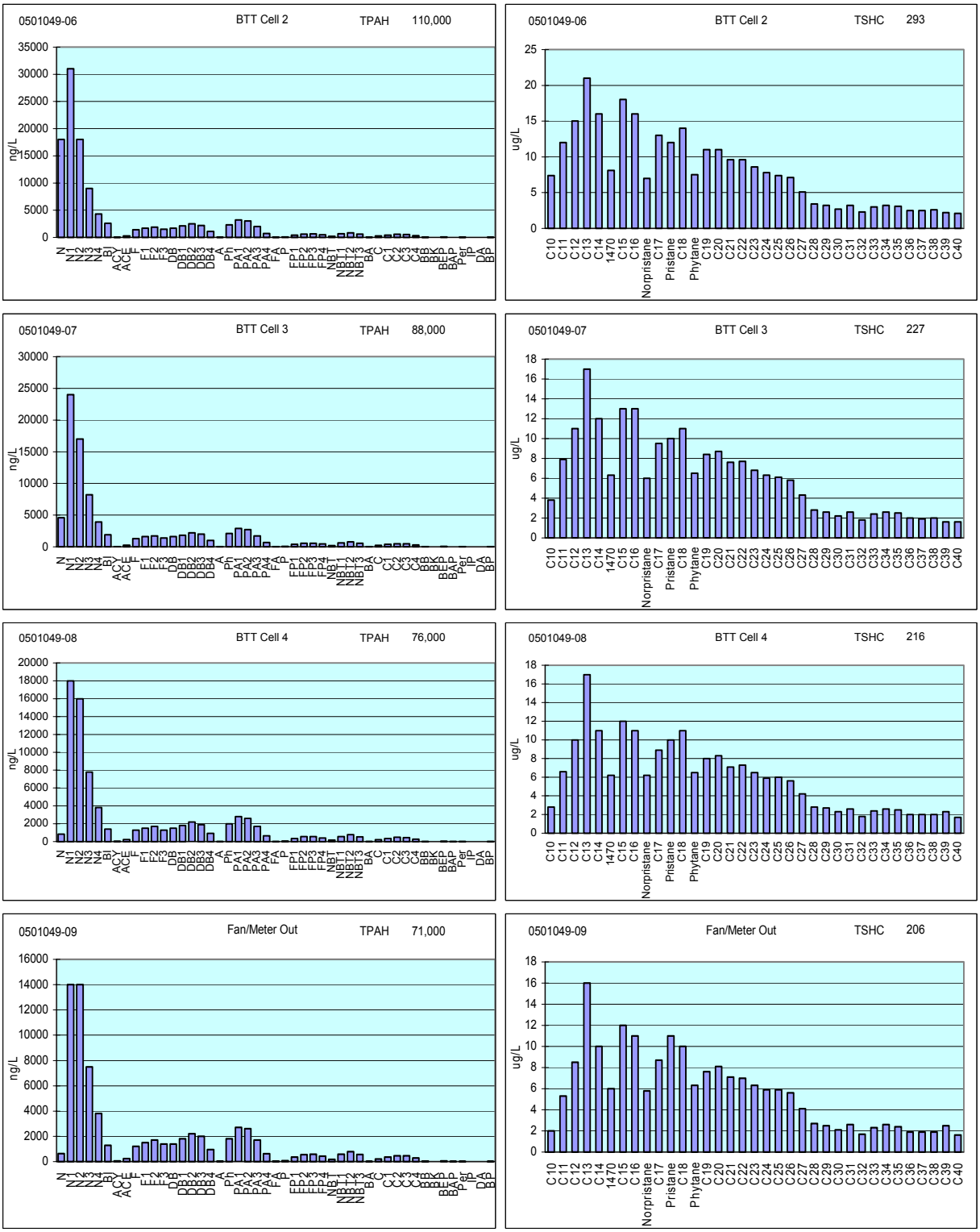


Figure 11. PAH and SHC from BTT Cell 2, Cell 3, and Cell 4, and Fan/Meter Out, Jan. 2005 (PAH concentrations in ng/L; SHC concentrations in µg/L).

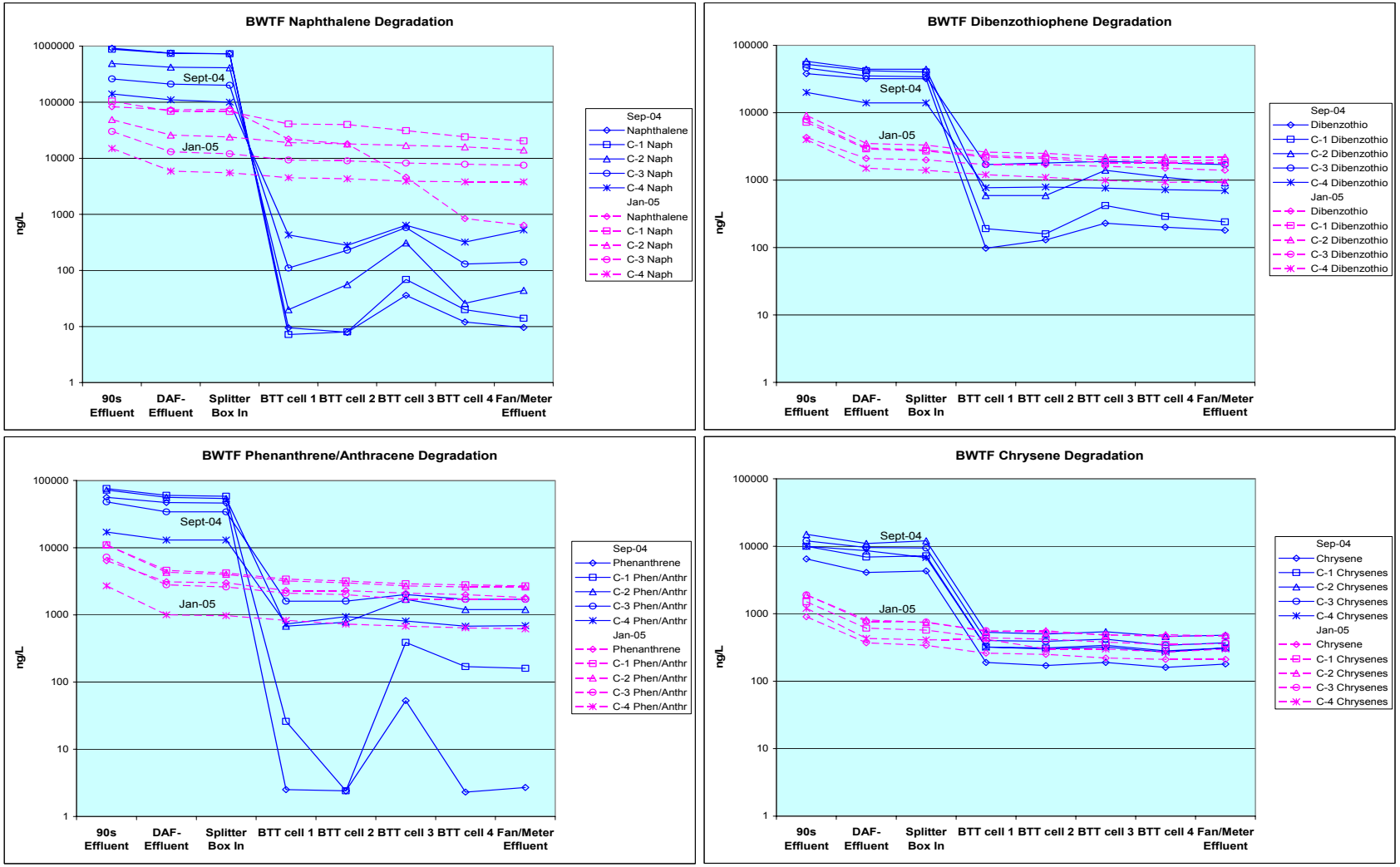


Figure 12. Selected PAH sequential degradation through the BWTF, Sept. 2004 and Jan. 2005 (all concentrations are ng/L).

Specifically, 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 in Figure 12 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 13), 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 8 and 9), 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 is 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 13), there is no evidence of significant PAH biodegradation (with the exception of limited removal of naphthalene and C1 and C2-alkyl-substituted naphthalenes), a finding consistent with the PAH profiles for the winter BTT cells (Figures 10 and 11).

As with the BTEX BIORATE studies, the PAH BIORATE data were replotted to determine if the rate-loss was zero-order or first-order. The naphthalene and C1- through C4-alkyl-substituted naphthalene data (Figure 14) clearly illustrates that the rate-loss for the PAH was first-order (proportional to the naphthalene concentrations). Similar plots were obtained for the other PAH that showed degradation during the summer, although the fits to the first-order rate equation weren't quite as good (r^2, Table 7). During the colder, winter BIORATE studies, however, only naphthalene, C1-naphthalene, C2-naphthalene, and phenanthrene showed first-order biodegradation. All other PAH either had zero slopes (first-order rate constants = 0) or the data were too noisy to obtain a reasonable plot. From the first order rate constants, it is possible to determine the half-life ($T_{1/2}$), the time for a given concentration of a PAH component to decrease by a factor of two (Table 7).

During January 2005 sampling, the BTT effluent discharged through the Fan/Meter Building to the Port was also sampled 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

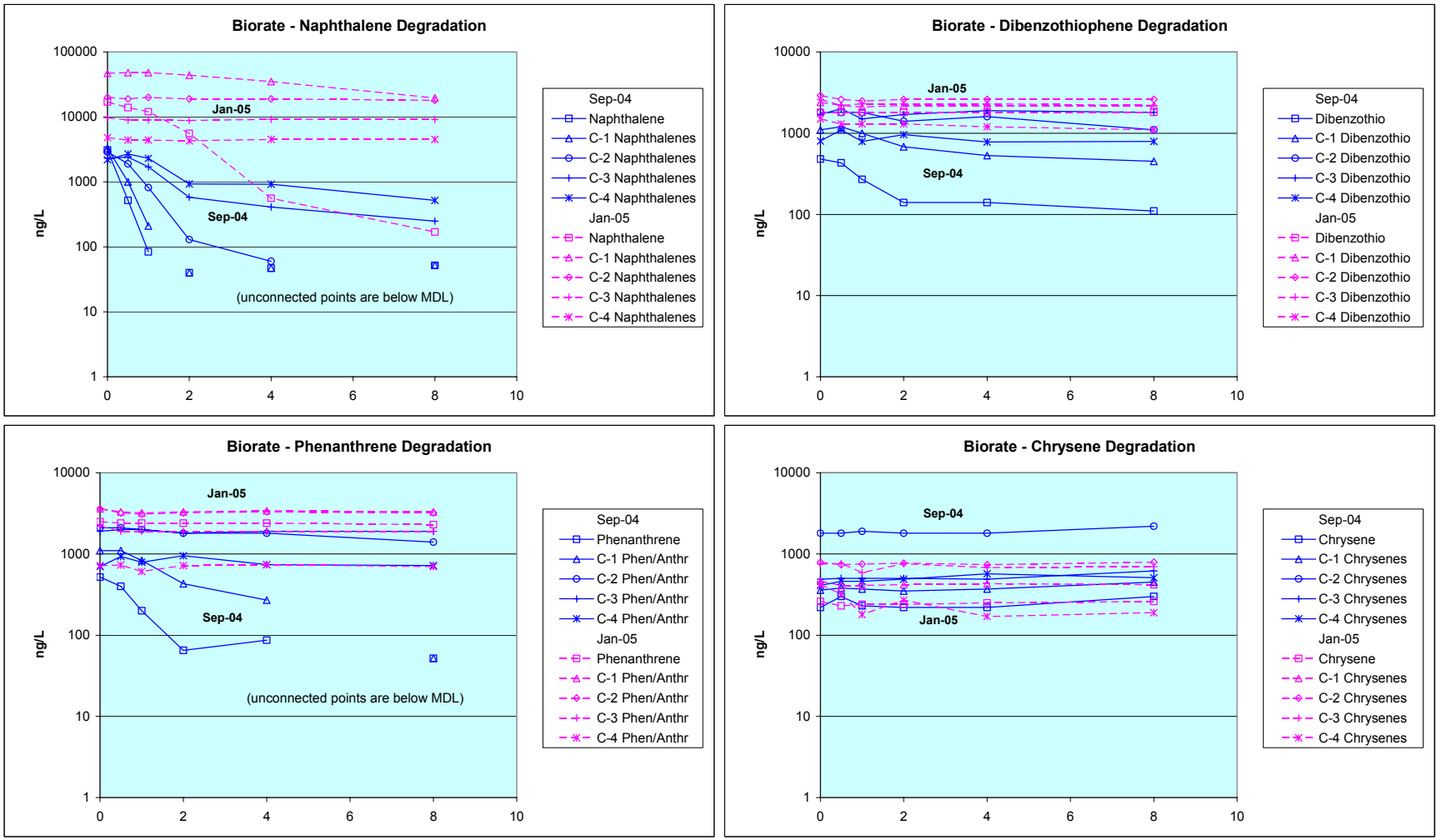


Figure 13. Selected PAH time series degradation (hrs) from BIORATE tests, Sept 2004 and Jan 2005 (all concentrations are ng/L).

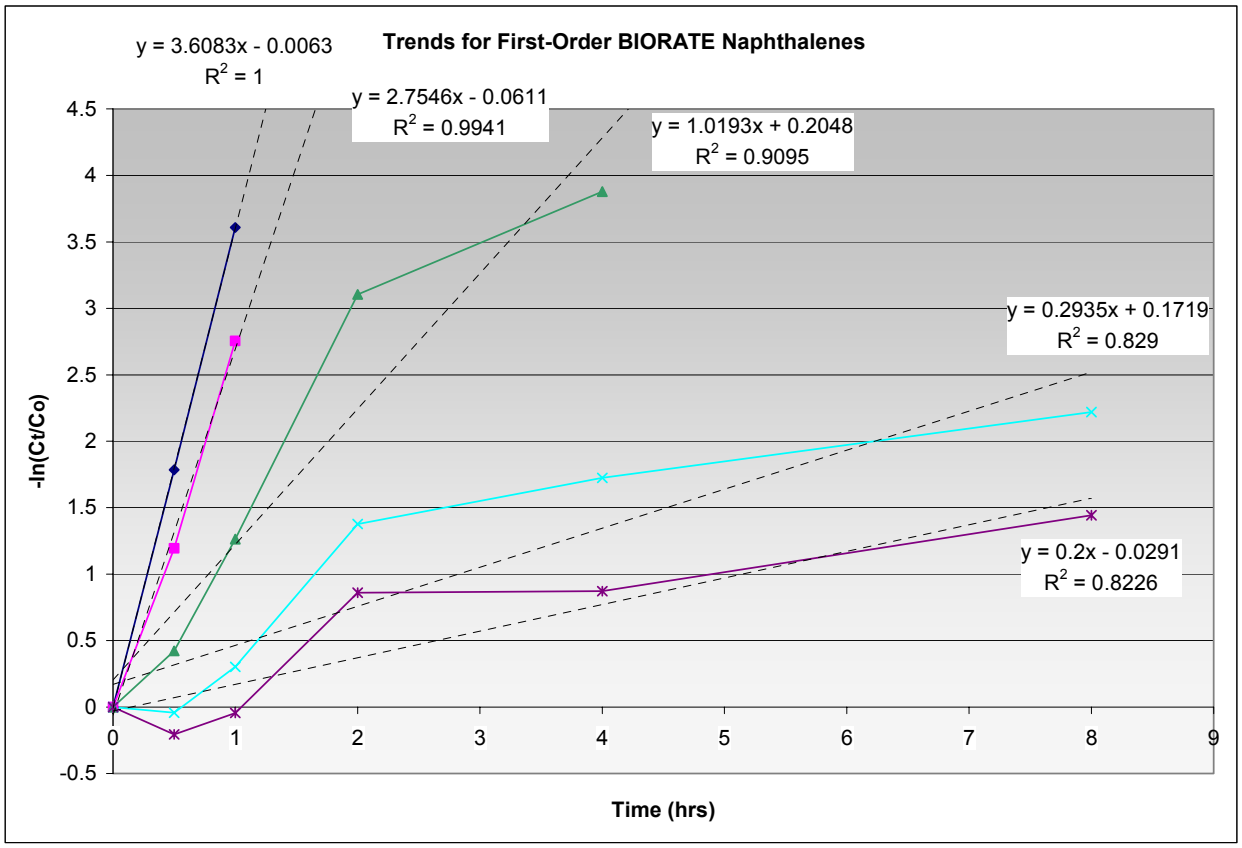


Figure 14. PWS RCAC September 2004 BIORATE data for decay of naphthalene homologues (PAH) showing derivation of first-order rate-loss kinetics (slope of trend line).

Table 7. Half-life and first-order rate decay of BTT PAH during BIORATE trials.

	Sept 2004			Jan 2005		
	Half-life (hrs)*	**Rate Constant**	**r^2**	**Half-life (hrs)***	**Rate Constant**	**r^2**
Naphthalene	0.19	3.6083	1.000	1.11	0.6232	0.941
C-1 Naphthalenes	0.25	2.7546	0.994	6.03	0.1149	0.963
C-2 Naphthalenes	0.68	1.0193	0.910	61.89	0.0112	0.728
C-3 Naphthalenes	2.36	0.2935	0.829	na	0.0020	0.032
C-4 Naphthalenes	3.47	0.2000	0.823	na	0.0013	0.010
Phenanthrene	0.64	1.0791	0.984	123.78	0.0056	0.807
C-1 Phen/Anthr	1.81	0.3840	0.948	na	-0.0025	0.122
C-2 Phen/Anthr	13.95	0.0497	0.952	na	-0.0025	0.123
C-3 Phen/Anthr	na	0.0035	0.070	na	1E-17	0.000
C-4 Phen/Anthr	na	0.0162	0.135	na	-0.0053	0.043

*Half-lives are not calculated for poor trend line fits (r^2).

particulate/oil-phase sample trapped on the glass-fiber filter of the PLVWSS (Figure 15). 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 10) as a result of biodegradation and possibly evaporation processes. This resolution of dissolved- versus particulate/oil-phase fractions from the BWTF manifests itself in seasonally-controlled transport and uptake in intertidal mussels throughout the Port (Payne et al., 2001; 2003b; 2005a,b; Payne and Driskell, 2003).

3.1.3 Microbial Populations

In both September 2004 and in January 2005, the numbers of microorganisms able to grow on various hydrocarbon substrates were estimated for samples from various parts of the ballast water treatment system (Figure 16). Interestingly, the numbers of microorganisms determined by the most probable number method (MPN) were generally somewhat higher in samples collected in January compared to those collected in September. This trend is particularly noticeable in BTT Cells 1-4 where numbers were one to two orders of magnitude greater in samples collected in January. While the ambient temperature was colder in January, the total concentrations of substrates were greater and the flow rate of the system faster. A likely explanation for the higher counts is that populations of microorganisms were responding rapidly to changing concentrations of substrate. Where substrate concentrations were very low and apparently biodegradation rates very high (e.g., the September sampling), populations of microorganisms were low due to lack of available substrate. In January when concentrations of substrate were high, the populations of microorganisms were also high although their activity was likely lower due to the decreased ambient temperature. This is consistent with lower apparent biodegradation rates as measured in the BIORATE studies.

At low substrate concentration, when microbial degradation is dependent on transport and metabolism of specific hydrocarbon substrates, reaction kinetics are likely to approximate first order with respect to substrate concentration. At high substrate concentration, when transport molecules and enzymes needed to degrade substrate are saturated, reaction kinetics will essentially be zero order with respect to substrate concentration. As noted earlier, this dual pattern of substrate-dependent kinetics has traditionally described enzymatic reactions (e.g. the Michaelis-Menten equation; Lehninger, 1976) and has also been shown to be a good approximation for microbial growth.

3.1.4 Other Analytes

As indicated in Section 2 and shown in Tables 2 through 4, a few selected samples were analyzed by EPA Method 8270 and the Woods Hold Group PIANO 2 Method for a variety of additional analytes besides PAH and SHC. Note that the analytical methods include a wider suite of components (Tables 3 and 4) but in the figures that follow, only the identified components listed in Table 2 are presented in an effort to maintain legibility. As in earlier component-specific histograms, the analytical method detection limit (MDL) for each component is shown by the blue diamonds and solid blue line along the bottom of the figure.

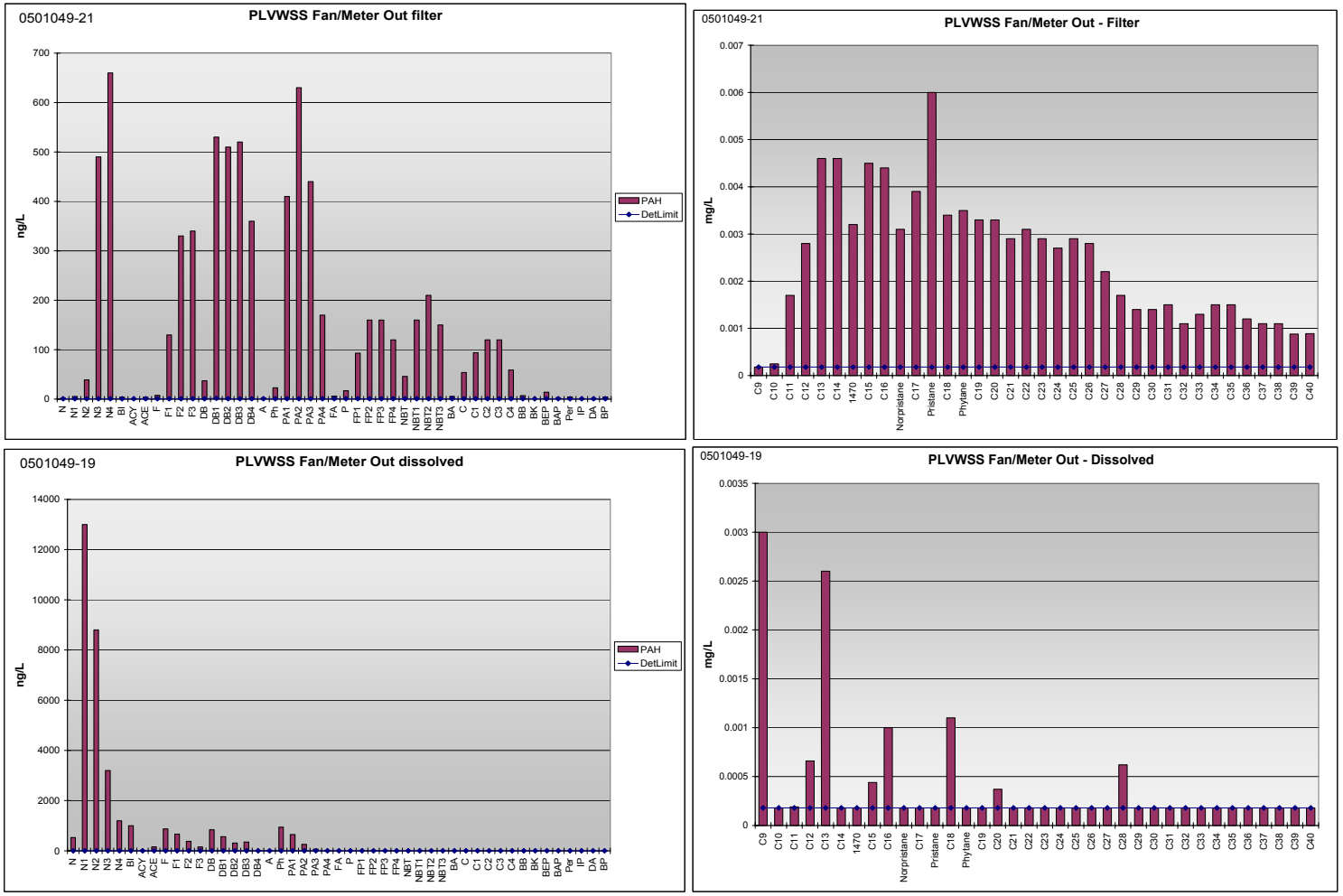


Figure 15. Particulate (filter) and dissolved (filtrate) PAH profiles of BWTF effluent, Jan 2005 (PAH concentrations in ng/L; SHC concentrations in mg/L). The solid line across the bottom of the SHC histograms represents the MDL.

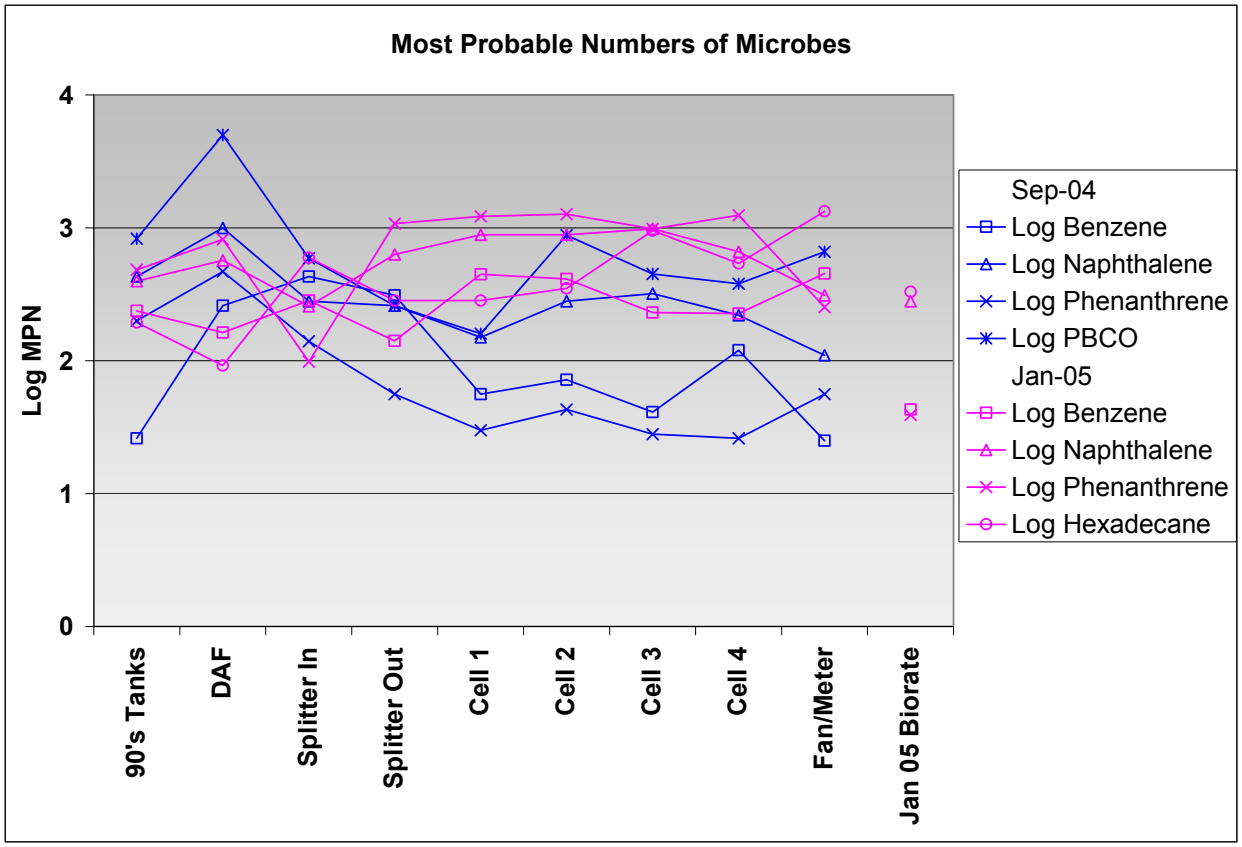


Figure 16. Most probable number (MPN) of microorganisms from selected stages of the BWTF, cultured on various hydrocarbon substrates. (PBCO = Prudhoe Bay Crude Oil)

In addition to the regulated BTEX components, there are a number of other volatile constituents associated with petroleum and the ballast water from the tankers. From the September 2004 90s tank effluent (Figure 17), these other components are five to six time less concentrated compared to benzene and toluene, but several (isopentane, pentane, methylcyclopentane, and cyclohexane) do exceed the measured concentration of ethylbenzene. It should also be noted that hexane, which was included along with naphthalene as a hazardous air pollutant (HAP) in APSC's study (Imperial Oil Research, 2005) is actually less concentrated than many of the other volatile components shown in the figure. None of these additional constituents were measured in the Fan/Meter Building effluent in September 2004 indicating they were removed by a combination of evaporation and microbial degradation processes.

The PIANO 2 analyses of the 90s tank effluent in January 2005, revealed many of the same components in the same relative proportions (Figure 18), but unlike the warmer-period samples, they were still detectable in the Fan/Meter Building effluent, although at significantly reduced concentrations compared to the 90s tank effluent. Interestingly, none of the BTEX constituents (which are also included in the PIANO 2 analyte list) were observed in the Fan/Meter building effluent (below MDL) suggesting that many of the PIANO 2 cyclic and branched components are somewhat more resistant to microbial degradation or that they were indeed lost to volatilization during the warmer summer study.

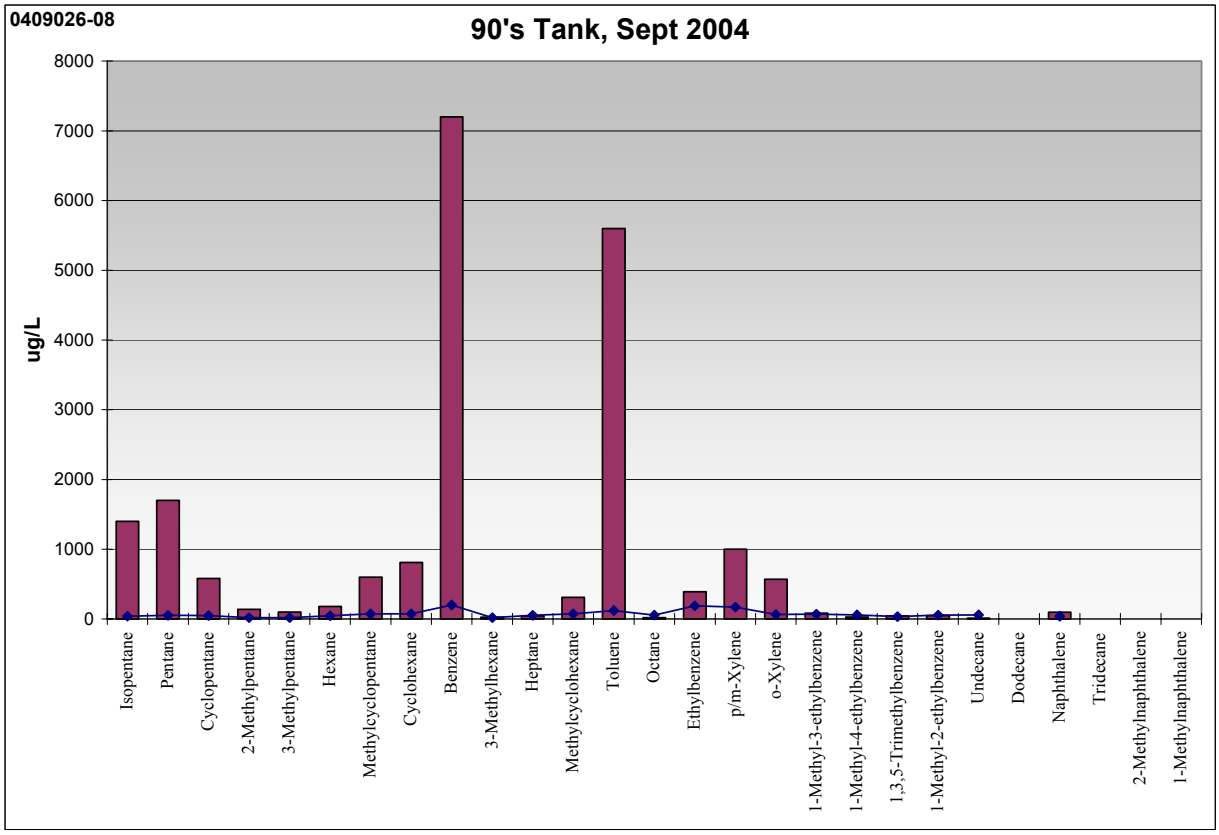


Figure 17. Other volatile components (PIANO 2) measured in 90's tank, Sept 2004.

In an effort to determine if we could identify any oxygenated intermediate metabolic products in the treated ballast water after undergoing extensive microbial degradation, grab samples from Cell 4 of the BTT and the effluent from the Fan/Meter Building were subjected to EPA Method 8270 analyses in both September 2004 and January 2005. EPA Method 8270 was selected and utilized because the standard target analyte list includes several alcohols and ketones, as well as phenol, numerous alkyl-substituted phenols, and aliphatic carboxylic acids (see Table 3). In addition, tentatively identified compound (TIC) scans could be run on the GC/MS data in an effort to identify other intermediate products that might be present. Unfortunately, the results from the September samples did not yield much information (Figure 19). Only 4-hydroxy-4-methyl-2-pentanone was identified at significant concentrations (>100 µg/L) with traces (<10 µg/L) of phenol, 2-methylphenol, oleic acid, and one other tentatively identified component detected. Most of these components were observed again in the January 2005 grab samples (Figure 20); however, phenol was present at a slightly higher concentration, oleic acid was not detected, and there were traces of fluorene and phenanthrene detected by the full-scan GC/MS method due to the more limited degradation of these components in the colder conditions. Notably, chlorinated hydrocarbon analytes were not detected by the EPA Method 8270 analyses during either the summer or winter sampling.

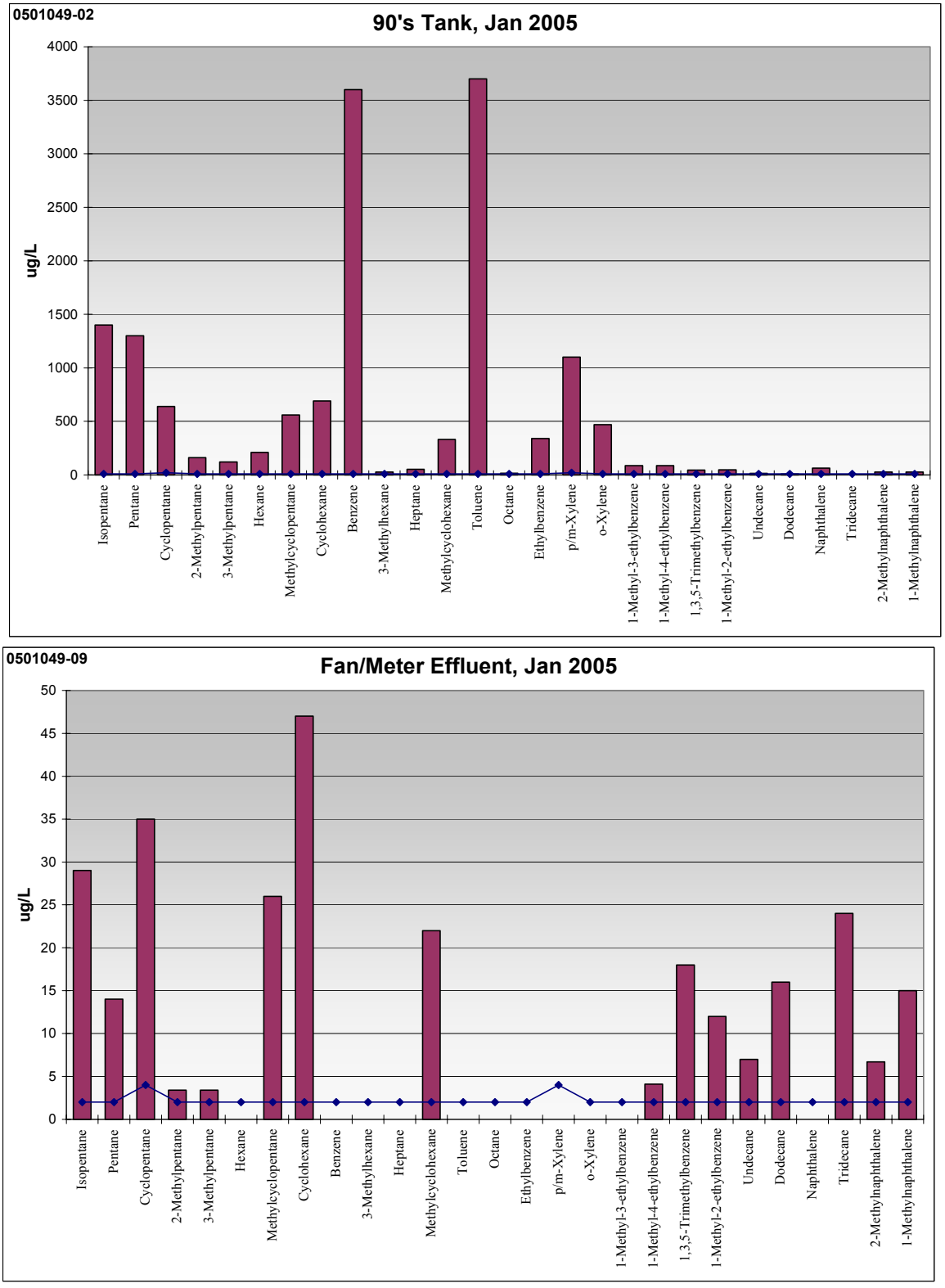


Figure 18. Other volatile components (PIANO 2) measured in BTT Cell 4 and Fan/Meter effluent, January 2005.

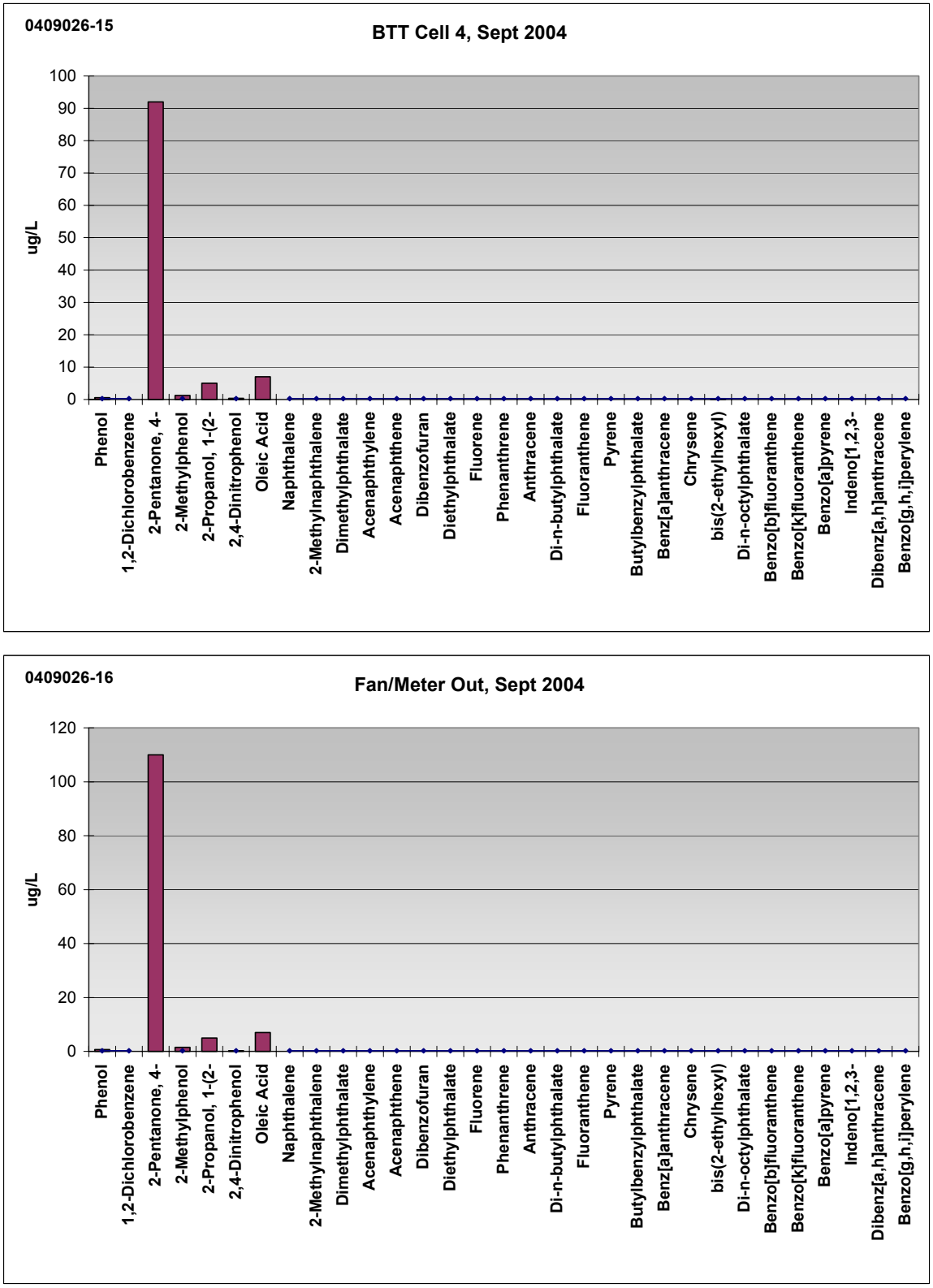
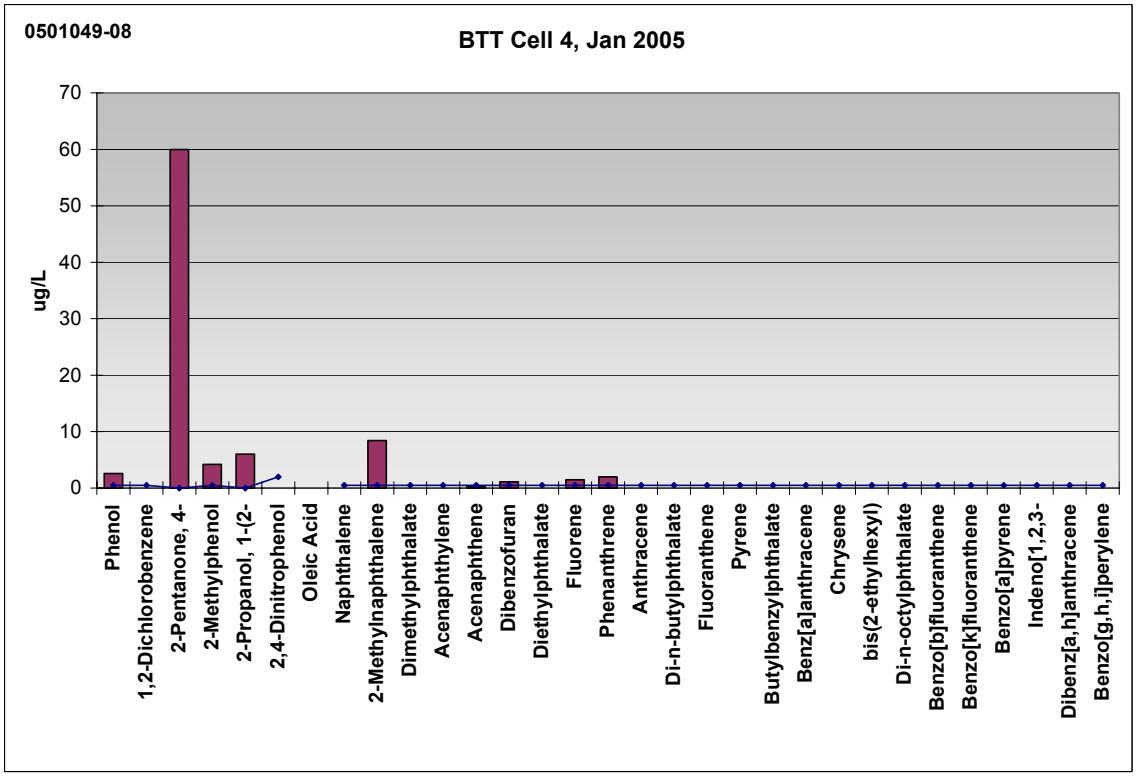


Figure 19. EPA Method 8270 analytes in the September 2004 BTT Cell 4 and Fan/Meter effluent grab samples.



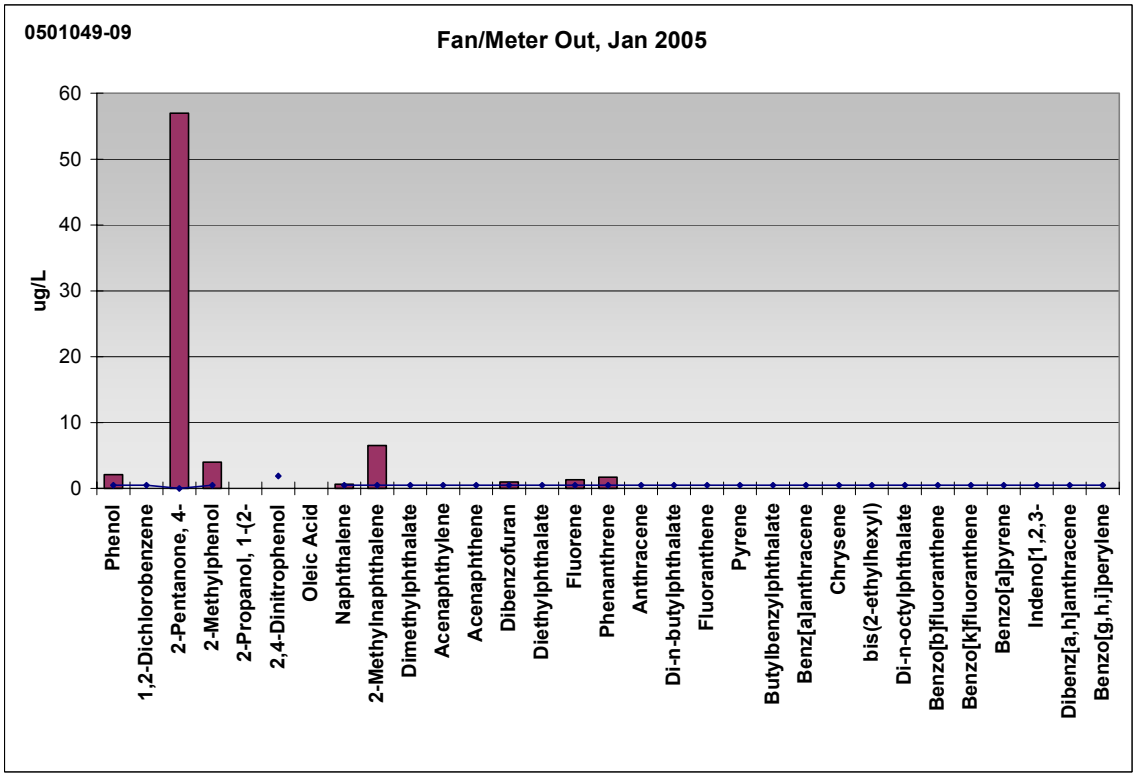


Figure 20. EPA Method 8270 analytes in the January 2005 BTT Cell 4 and Fan/Meter Building grab samples.

Information about the physical state (particulate/oil-phase vs. dissolved-phase) of these oxygenated components can be obtained from the PLVWSS samples collected from the Fan/Meter Building in January 2005 (Figure 21). Clearly, 4-hydroxy-4-methyl-2-pentanone and oleic acid tend to associate more with the particulate/oil-phase material trapped on the PLVWSS glass-fiber filter, while most of the other more water-soluble constituents are present in the dissolved phase. Detection of oleic acid in these samples (compared to the non-detect result from the 1L grab samples in Figure 20) is facilitated by the larger sample size (3.5 L) and thus, better detection limit obtained with the PLVWSS samples.

None of these additional analytes are regulated under the NPDES Permit for the BWTF discharge, and their impacts on the receiving waters of Port Valdez are completely unknown. They are discharged at concentrations in the same concentration range as the TPAH, but if they are truly intermediate products of microbial degradation they are likely to continue to degrade after discharge to the Port.

3.1.5 Beyond the Pipe

The RCAC LTEMP monitoring program routinely samples mussels and sediments from the terminal (AMT) and the Gold Creek reference site (GOC; Figure 1). Typically, the signals picked up in the samples reflect the effluent from the BWTF plus additional combustion and biogenic products (Figure 22).

Historically, the tissue data trends demonstrate that the sampled mussels have accumulated hydrocarbons and show PAH patterns specifically associated with known spill events such as the *T/V Eastern Lion* oil spill in 1994 and the BWTF sheening incident in 1997. More typically, tissue PAH concentrations are low but perceivable at both Alyeska Marine Terminal and Gold Creek (Figure 22). Since October 2001 and March 2002, tissue PAH concentrations appear to have declined at both sites, and this trend appears to be continuing with the 2003-2004 LTEMP samples (Table 8). Although the concentrations are low, Alyeska Marine Terminal mussels continue to accumulate dissolved and particulate/oil-phase PAH components from the BWTF that are seasonally controlled by water-column stratification although the dissolved-phase pattern clearly predominates (Payne et al., 2005a,b).

Sediment TPAH concentrations at Alyeska Marine Terminal are also low (generally below 600 ng/g dry wt, Table 9) but highly variable while the PAH and SHC profiles continue to indicate the accumulation of PAH and SHC components from the BWTF (and presumably other terminal operations) (Figure 23). Additional hydrocarbon sources at Alyeska Marine Terminal include combustion products (which may or may not be related to terminal activities) and biogenic marine and terrestrial SHC components. At Gold Creek, the PAH components in the sediments are generally 5-10 times lower than those at Alyeska Marine Terminal, and they do not show the same degree of petrogenic contamination or variability compared to the Alyeska Marine Terminal site (Figure 24). It is not possible to determine if the low-but-discernible petrogenic hydrocarbons in Gold Creek sediments are from the BWTF and/or other activities at the Alyeska Marine Terminal, or if they represent input from other sources, such as boat traffic, sewage and wastewater effluent, and surface/storm-water runoff from the city of Valdez. The SHC pattern in the Gold Creek sediments (Figure 24) clearly includes marine biogenic input and terrestrial-sourced plant wax components.

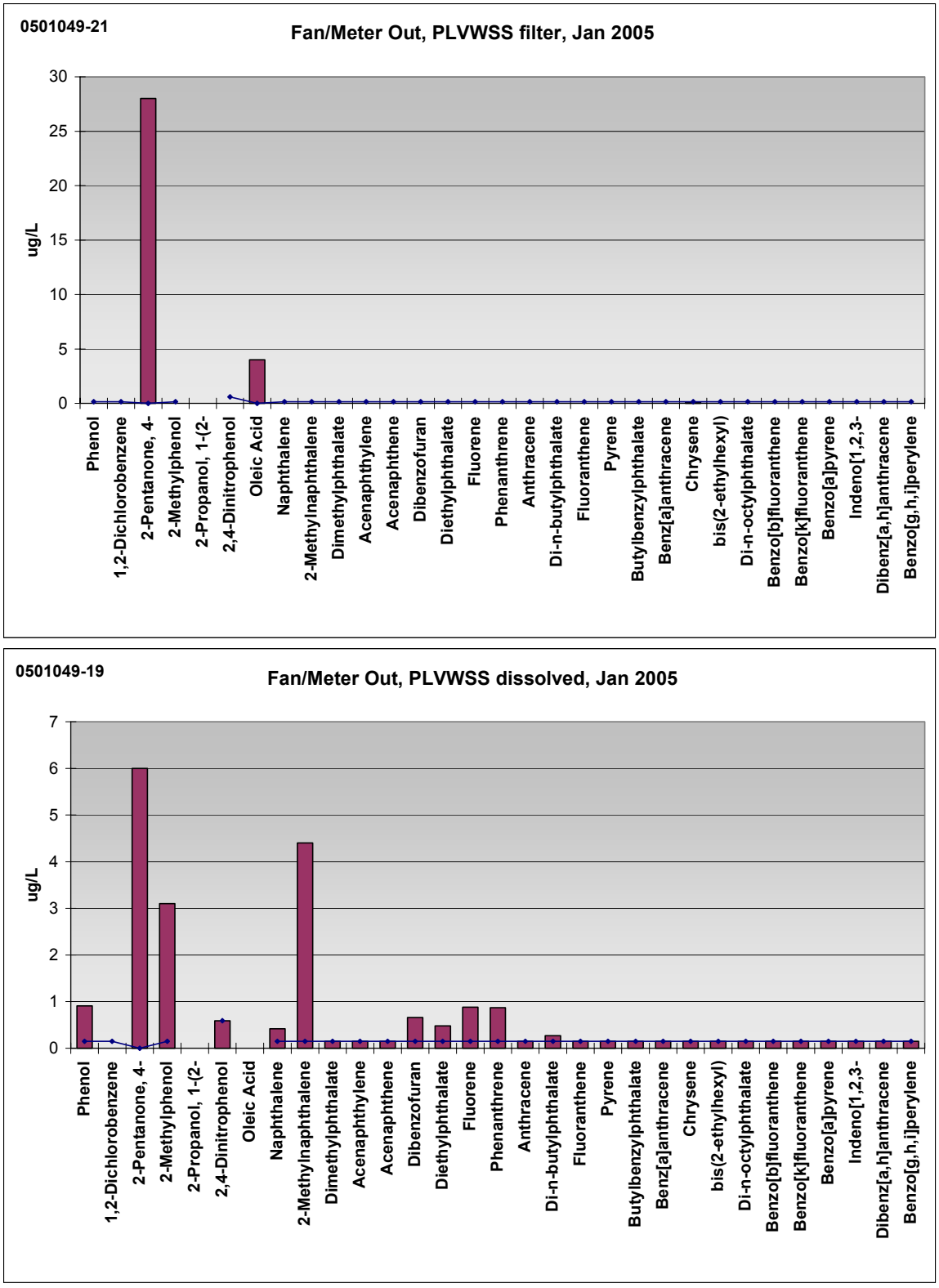
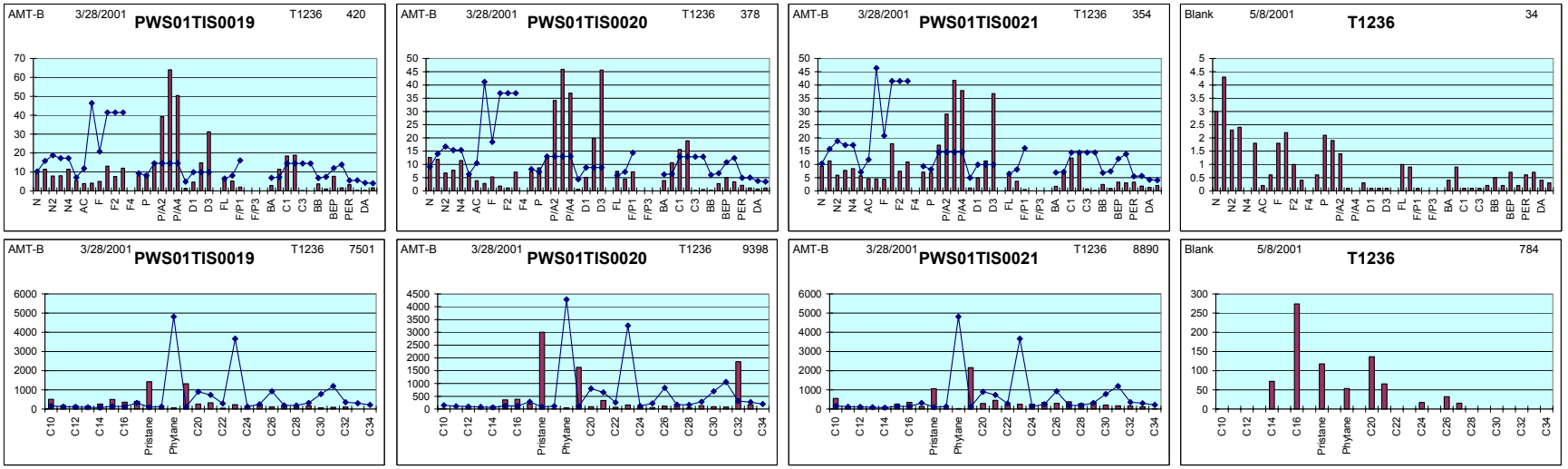


Figure 21. EPA Method 8270 analytes in the particulate and dissolved phase samples collected with the PLVWSS in the Fan/Meter Out effluent to Port Valdez.



Concentrations in ng/g dry wt.

Figure 22. PAH and SHC histograms for mussel tissues at AMT in March 2001 showing a particulate/oil-phase PAH signal and a primarily biogenic SHC pattern (from Payne et al., 2005a).

Table 8. LTEMP Tissue TPAH and TSHC for 2003-2004.

Sample ID	Sample Date	Total PAH*	Mean	Std Dev	CV	Total SHC*	Mean	Std Dev	CV
AMT-B-2-03-1	7/27/2003	90				860			
AMT-B-2-03-2	7/27/2003	61				433			
AMT-B-2-03-3	7/27/2003	45	65.2	22.58	34.63	347	546.64	275.06	50.32
GOC-B-2-03-1	7/27/2003	30				485			
GOC-B-2-03-2	7/27/2003	39				456			
GOC-B-2-03-3	7/27/2003	36	35.05	4.47	12.76	574	505.18	61.71	12.21
AMT-B-3-03-1	10/7/2003	46				310			
AMT-B-3-03-2	10/7/2003	64				311			
AMT-B-3-03-3	10/7/2003	66	58.68	10.91	18.58	406	342.14	55.05	16.09
GOC-B-3-03-1	10/7/2003	72				358			
GOC-B-3-03-2	10/7/2003	45				412			
GOC-B-3-03-3	10/7/2003	46	54.26	15.56	28.69	282	350.29	65.35	18.65
AMT-B-1-04-1	3/21/2004	120				94			
AMT-B-1-04-2	3/21/2004	53				0			
AMT-B-1-04-3	3/21/2004	39	70.92	43.48	61.31	24	39.27	48.98	124.71
GOC-B-1-04-1	3/21/2004	139				78			
GOC-B-1-04-2	3/21/2004	91				107			
GOC-B-1-04-3	3/21/2004	118	116.01	23.76	20.48	100	95.03	15.15	15.94

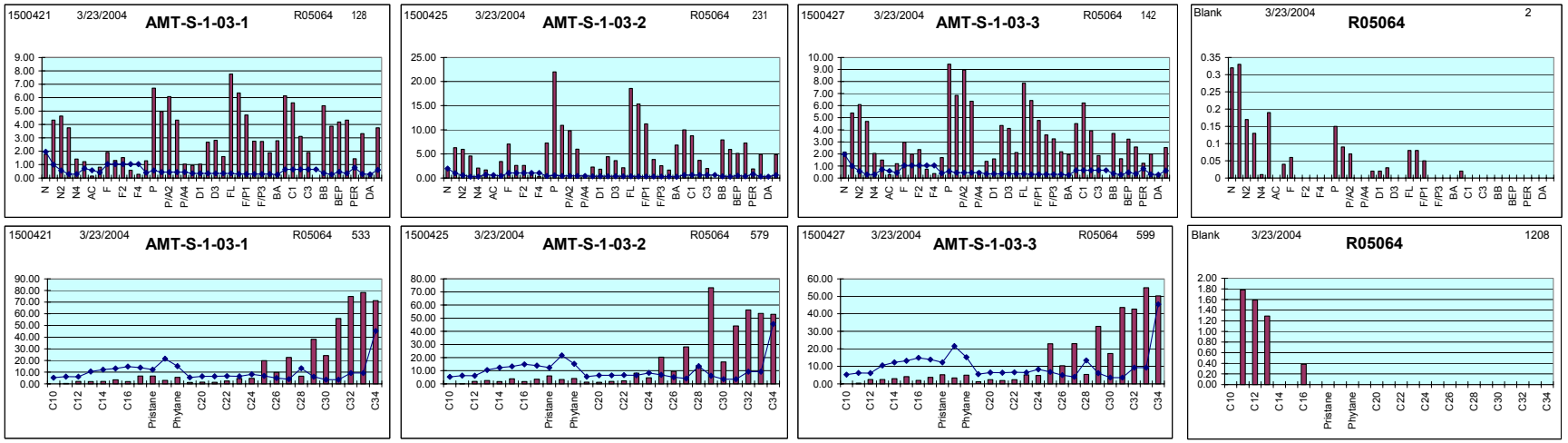
* concentrations in ng/g dry wt.

Table 9. LTEMP Sediment TPAH and TSHC for 2003-2004.

Sample ID	Date	Total PAH*	Mean	Std Dev	CV	Total SHC*	Mean	Std Dev	CV
AMT-S-2-03-1P	27-Jul-03	199				604			
AMT-S-2-03-2P	27-Jul-03	132				564			
AMT-S-2-03-3P	27-Jul-03	109	147	47	31.7	522	563	41	7.3
AMT-S-2-03-1A	27-Jul-03	230				791			
AMT-S-2-03-2A	27-Jul-03	286				701			
AMT-S-2-03-3A	27-Jul-03	144	220	71	32.4	496	663	151	22.8
AMT-S-1-03-1	23-Mar-04	128				451			
AMT-S-1-03-2	23-Mar-04	231				417			
AMT-S-1-03-3	23-Mar-04	142	167	56	33.6	352	407	50	12.3
GOC-S-2-03-1P	27-Jul-03	31				203			
GOC-S-2-03-2P	27-Jul-03	26				179			
GOC-S-2-03-3P	27-Jul-03	115	57	50	87.9	225	202	23	11.4
GOC-S-2-03-1A	27-Jul-03	32				283			
GOC-S-2-03-2A	27-Jul-03	31				306			
GOC-S-2-03-3A	27-Jul-03	33	32	1	2.1	219	269	45	16.8
GOC-S-1-03-1	23-Mar-04	33				193			
GOC-S-1-03-2	23-Mar-04	16				316			
GOC-S-1-03-3	23-Mar-04	36	28	11	38.7	132	214	94	43.8

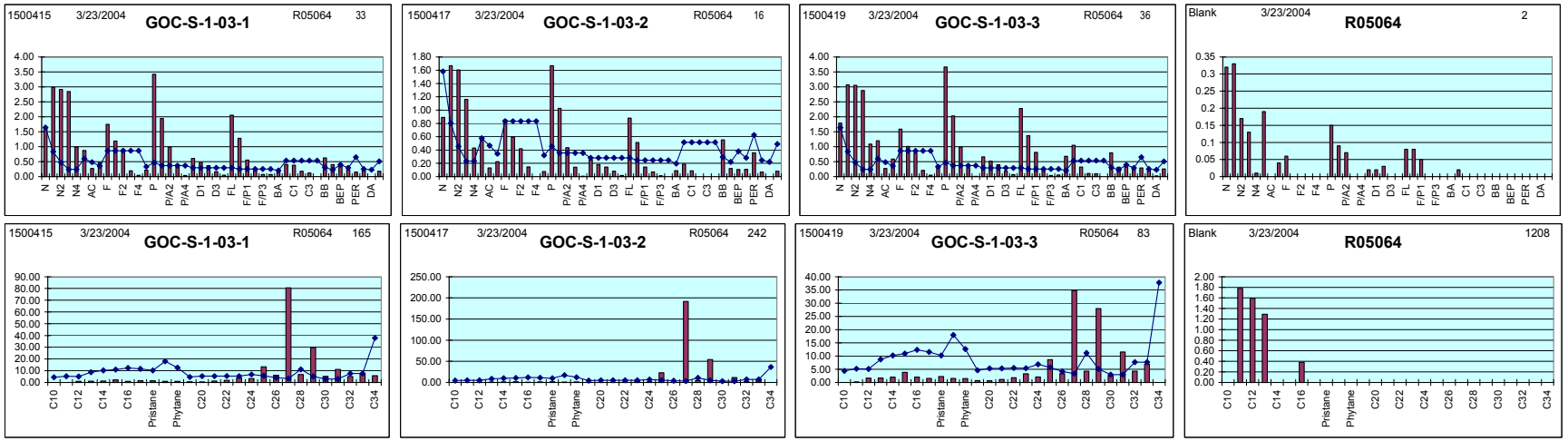
* concentrations in ng/g dry wt.

Note July sampling used two samplers (P & A suffixes) for sampler comparisons (see Payne et al., 2005a).



Concentrations in ng/g dry wt.

Figure 23. March 2004 sediment PAH and SHC profiles from Alyeska Marine Terminal and associated procedural blanks. These samples had very low PAH concentrations with significant combustion sources in addition to weathered oil. The SHC fractions showed below MDL traces of petroleum components plus significant levels of terrestrial plant wax components (from Payne et al., 2005a).



Concentrations in ng/g dry wt.

Figure 24. March 2004 sediment PAH and SHC profiles from Gold Creek and associated procedural blanks. These are among the lowest and least variable PAH measurements observed in the LTEMP to date, and the patterns reflect a mixture of a distillate product plus a very distinct combustion product profile from the fluorenes, phenanthrenes/anthracenes, fluoranthenes, and chrysenes, plus the BB to BP suite. The SHC profiles reflect primarily terrestrial plant waxes plus a trace of marine biogenic components (from Payne et al., 2005a).

4 Discussion

The dramatic changes in BTEX concentrations across the eight BWTF stations sampled in this study are illustrated by Figure 3 in Section 3.1.1, and Table 10 below lists the concentrations of total BTEX, TPAH and TSHC and the respective remaining percentages at selected stages of treatment. There were significant differences in the 90s tank's concentrations in September 2004 and January 2005, but these are attributed more to variation in BTEX and PAH/SHC loads in the tankers discharging to the tanks rather than seasonal differences. During the warmer months, losses of BTEX in the effluent sampled after the DAF cells/weirs are believed to be due to evaporation and some biodegradation (depending on the flow rate and residence time in the DAF cells). In the colder months and under conditions of higher flow, there is less of a drop observed in total BTEX in the DAF cells/weirs effluent, and it is believed to be almost entirely due to reduced volatilization. During both warm and cold conditions, the most significant declines in BTEX concentration are noted after the ballast water enters the BTTs and in the final effluent discharged through the Fan/Meter Building. PAH and SHC removals due to microbial degradation in the BTT (Fan/Meter) effluent are both noted to be retarded in the colder winter months. Intermediate stage (Splitter Box) percentage removals for PAH and SHC appear contrary to expectations (higher in winter) and probably reflect greater relative percent removal due to evaporation given the lower starting (90s tank) concentrations. The chemical fingerprints for the PAH and SHC indicated no microbial degradation in either the 90s tank or the DAF cells/weirs.

Table 10. Concentrations and percent remaining at selected stages of treatment.

		Concentration				Percent Remaining	
		90s Tanks	Splitter In	Fan/Meter Out	Units	Splitter	Fan/Meter
Sep-04	BTEX	11,320	6,230	< 12	µg/L	55%	< 0.1%
	TPAH	3,440	2,750	13.7	µg/L	80%	0.4%
	TSHC	842	580	65	µg/L	69%	8%
Jan-05	BTEX	9,750	7,900	< 12	µg/L	81%	< 0.1%
	TPAH	360	190	71	µg/L	53%	20%
	TSHC	1,409	505	206	µg/L	36%	15%

It is difficult to directly compare PWSRCAC measurements with those reported by APSC because the samples were collected during different time periods, and as noted above, there is significant variability in the BTEX and PAH/SHC loading in the ballast waters from different tankers. Nevertheless, in comparing the BTEX concentration profiles in Figure 3 with those reported by APSC (shown in Figure 25), it is apparent that the same general trends were observed in both studies. The BTEX concentrations are in the same general range in going from the 90s tanks through the DAF cells/weirs, and the same precipitous drops in BTEX concentrations were measured in replicated samples collected by different personnel and analyzed by two independent laboratories. Further BTEX concentration declines to non-detect (< 12 µg/L) concentrations were then observed in both studies as additional samples were

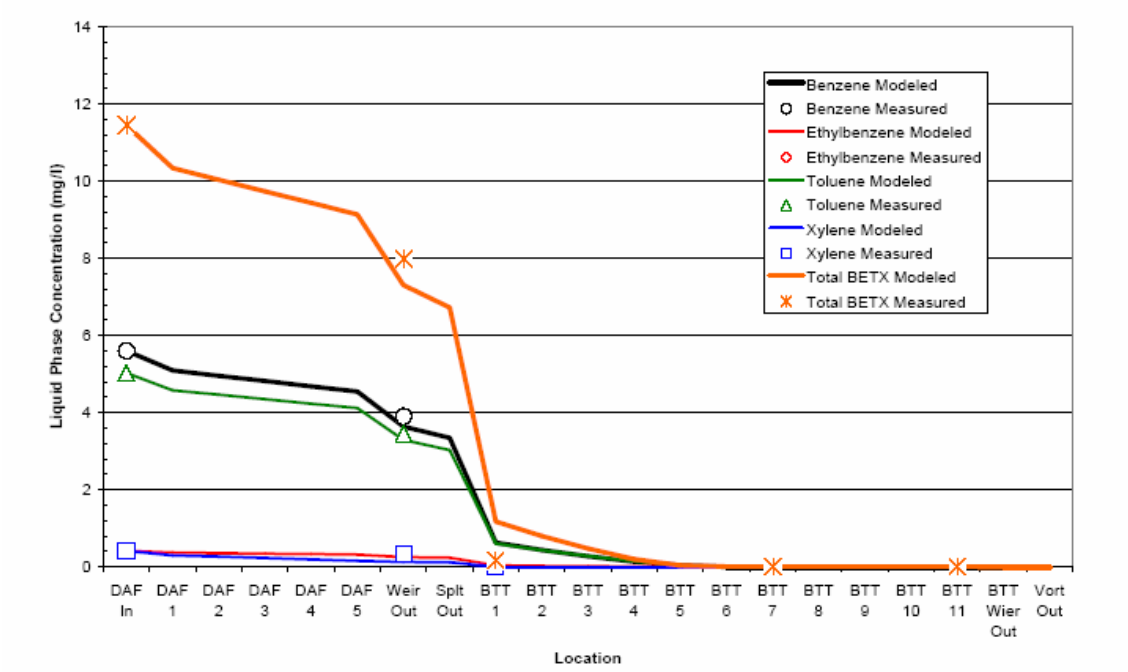


Figure 25. BWTF process concentrations and model predictions under average flow and average nutrient conditions, April 2004 (from Imperial Oil Research, 2005).

collected along the length of the BTTs. As a result of these finding, it is apparent that the two studies generated comparable data with similar precision and accuracy. Therefore, from a QA/QC perspective, we have no reason to question any of the BTEX measurements reported by APSC (Imperial Oil Research, 2005).

Regarding the selection of a BTEX zero-order rate model, the APSC study (Imperial Oil Research, 2005) measured the rate of BTEX biodegradation at higher initial concentrations (by compositing different blends of Splitter Box and BTT effluent) than those in the RCAC study. It is possible that at these higher concentrations, the BTEX may have been saturating (exceeding the bacteria's ability to transfer individual components through the cell walls) thus making it appear that the degradation rate was independent of concentration. Alternatively, the enzymatic degradation of BTEX within the bacterial cells is presumably following Michaelis-Menten kinetics, and this too would yield data that appear to be independent of concentration if the BTEX levels are above the Michaelis constant, K_m (Lehninger, 1976; Mahler and Cordes, 1968). This possibility may warrant further study.

Also, the APSC studies were conducted over a range of temperatures designed to span the majority of observed operating conditions between 1990-2003, and allow extrapolation to temperatures lower than those observed in the historic BWTF operation (Imperial Oil Research, 2005). Figure 26 shows the relationship between the APSC-measured, zero-order rate constants and temperature for benzene, toluene, ethylbenzene, and xylene(s), with the zero-order values obtained by our study (at 6.7^{o} C, 44 ^{o}F) superimposed in red. For the sake of comparisons and assuming zero-order kinetics are appropriate, then there is remarkably good agreement among the

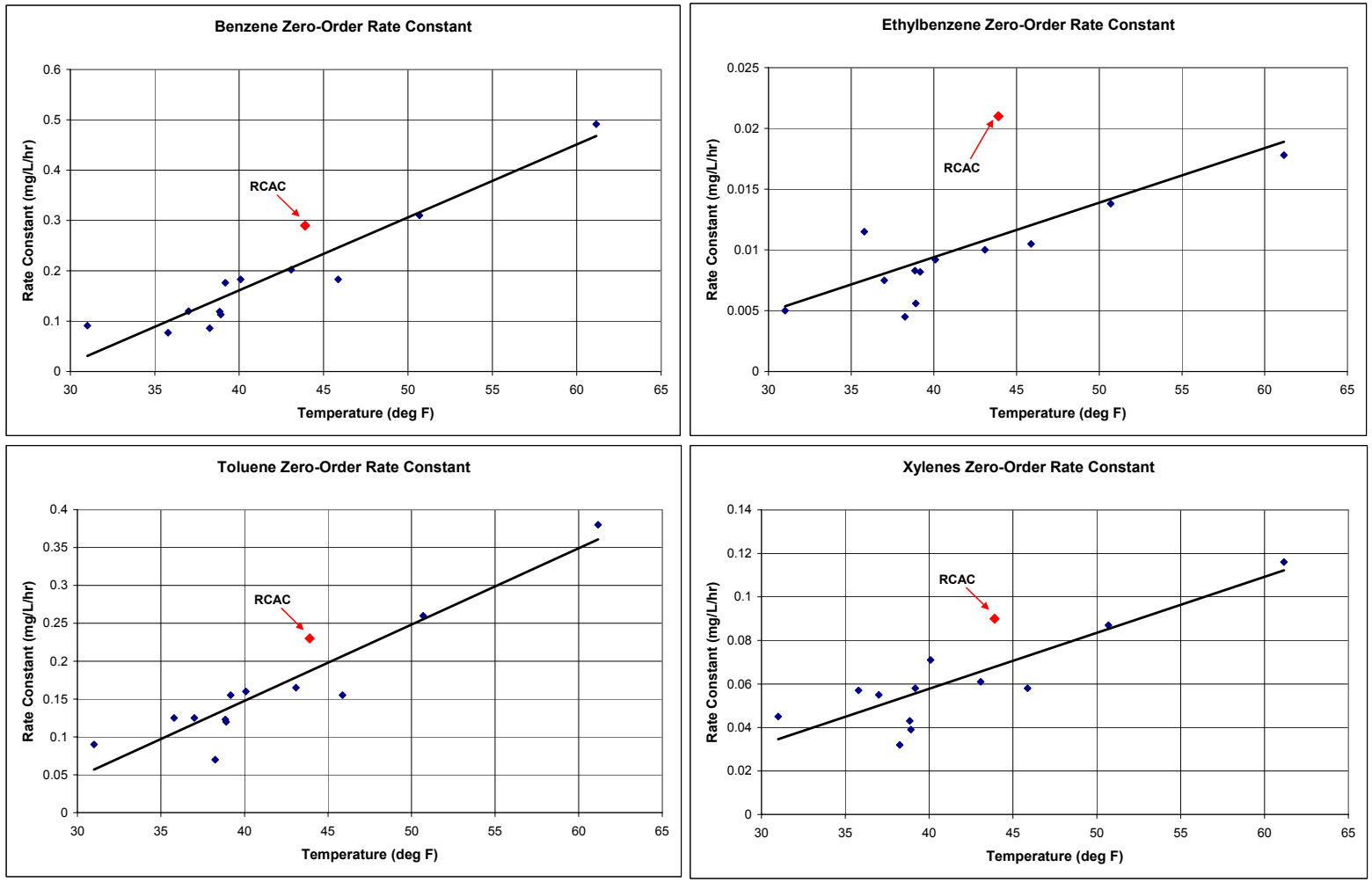


Figure 26. Zero-order rate constants' plots for BTEX compounds from January 2005 Imperial Oil Research BIORATE trials including PWSRCAC sample (modified from Imperial Oil Research, 2005).

RCAC values and the APSC results (Imperial Oil Research, 2005), with most of the rate constants agreeing within 15-20%. This is particularly noteworthy considering that the measurements were completed independently by two different laboratories and suggests that there were not any problems with the analytical chemistry or manner in which the kinetics measurements were completed. Thus, we conclude that the data generated in the BIORATE studies are probably fine, but that there may be an issue in fitting zero-order vs. first-order degradation rate models. If the APSC conclusion is wrong and the BTEX degradation is described more accurately first-order kinetics, then Imperial Oil Research may be under-estimating the rate of biodegradation in their model applications, and thus possibly over-estimating BWTF losses due to volatilization.

The APSC study also raises intriguing questions regarding how the future reduction of traffic, transition to double hulls, switching to heavy oil production, and strategic reconfiguration of the terminal will affect the effluent stream? Alyeska's study predicts 77% reduction of BTEX by 2009, which mainly reflects the general down-sizing of the BWTF operations. Obviously, the plant operators must and will somehow reconfigure the waste-flow to maintain plant efficiency and remain within required NPDES requirements, but those details are not currently available. On the plus side, it should be remarked that over the past few years of LTEMP monitoring, the samples have shown notably lower hydrocarbon concentrations, often near or below levels of detection.

Alyeska's study reported that the BTT is currently performing with high biological efficiency (i.e. 97-99% of the BTEX entering the BTT's from the splitter box is consumed biologically). Our data support that conclusion. Alyeska's study also reported that from modeling BTEX fates in 2003, 25% of the BWTF system's BTEX (43.3 tons/yr) was lost as air emission (Table 11). We have not attempted to validate this finding based on our sparse data set. Succinctly, our single run of BIORATE data confirms APSC's basic BTEX degradation findings prior to their being applied in further modeling but neither confirms or denies their modeling results.

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 25% 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 and in Port Valdez mussels and sediments analyzed as part of LTEMP.

Table 11. Modeled DAF and BTT BTEX Fate Path Summary for Calendar Year 2003 (from Imperial Oil Research, 2005).

Fate Path	Total BTEX	Benzene	Ethylbenzene	Toluene	Xylene
DAF Air Emissions	6.54	2.69	0.21	2.65	1.00
DAF Weir Air Emissions	27.01	11.42	0.87	10.55	4.17
Splitter Box Air Emissions	8.64	3.65	0.28	3.38	1.33
BTT Air Emissions	1.23	0.46	0.08	0.48	0.22
Total Air Emissions	***43.43***	***18.21***	***1.43***	***17.06***	***6.72***
DAF Bio and Float	29.99	14.00	0.60	11.49	3.90
BTT Bio	97.94	41.51	3.06	38.31	15.06
Total Biological	***127.92***	***55.51***	***3.66***	***49.80***	***18.96***
BTT Outlet Water	0.17	0.04	0.05	0.04	0.04
Total Water Effluent	***0.17***	***0.04***	***0.05***	***0.04***	***0.04***
Total	***171.52***	***73.76***	***5.14***	***66.90***	***25.72***

*These emission rates are not applicable to future years' emissions as those emissions will be lower than in 2003.

6 Acknowledgements

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