

# **An Evaluation of the Composition, and Potential Environmental Fate and Toxicity of Heavy Venezuelan Crude Oil Released into the Delaware River During the *M/T ATHOS I* Oil Spill**

*Prepared for:*

**Aquatic Technical Work Group for *ATHOS I* Spill**

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**Michael C. Donlan<sup>1</sup>, Gregg Douglas<sup>2</sup>, and Donald D. MacDonald<sup>3</sup>**

**<sup>1</sup>Project Manager**

**Industrial Economics Inc.**

2067 Massachusetts Avenue

Cambridge, Massachusetts 02140

**<sup>2</sup>Technical Consultant**

**New Fields Environmental Forensics Practice LLC.**

100 LedgeWood Place, Suite 302

Rockland, Massachusetts 02370

**<sup>3</sup>Technical Consultant**

**MacDonald Environmental Sciences Ltd.**

#24 - 4800 Island Highway North

Nanaimo, British Columbia V9T 1W6

# Table of Contents

<b>List of Tables</b> .....	<b>ii</b>
<b>List of Figures</b> .....	<b>iii</b>
<b>List of Appendices</b> .....	<b>iv</b>
<b>List of Appendices Figures</b> .....	<b>iv</b>
<b>Executive Summary</b> .....	<b>v</b>
<b>1.0 Introduction</b> .....	<b>1</b>
<b>2.0 Physical and Chemical Properties of Crude Oil Released into the Delaware River</b> .....	<b>2</b>
2.1 Physical Properties .....	2
2.2 Chemical Composition .....	3
2.2.1 Monocyclic Aromatic Hydrocarbons (MAHs) .....	4
2.2.2 Polycyclic Aromatic Hydrocarbons (PAHs) .....	5
2.2.3 Trace Metals .....	6
<b>3.0 Potential Environmental Fate of Oil Released from the <i>M/T ATHOS I</i></b> .....	<b>7</b>
<b>4.0 Potential Toxicity of Source Oil Released from the <i>M/T ATHOS I</i></b> .....	<b>8</b>
4.1 Toxicity of Crude Oils - Overview .....	8
4.2 Toxicity of Constituents of Crude Oils .....	10
4.2.1 Monocyclic Aromatic Hydrocarbons .....	11
4.2.2 Polycyclic Aromatic Hydrocarbons .....	13
4.2.3 Trace Metals .....	15
4.2.4 Alkanes .....	18
4.2.5 Other Constituents of Crude Oil .....	18
<b>5.0 Preliminary Screening Evaluation of Aquatic Field Data Collected During the <i>M/T ATHOS I</i> Spill Response</b> .....	<b>20</b>
<b>6.0 Summary</b> .....	<b>22</b>
<b>7.0 References Cited</b> .....	<b>24</b>

## List of Tables

<b>Table 1</b>	Physical and chemical properties of source oil from the <i>M/T ATHOS I</i> . . . . .	T-1
<b>Table 2</b>	Concentrations of mono aromatic substances in source oil from the <i>M/T ATHOS I</i> . . . . .	T-2
<b>Table 3</b>	Concentrations of PAHs in source oil from the <i>M/T ATHOS I</i> (Polaris Applied Sciences, Inc 2005) . . . . .	T-3
<b>Table 4</b>	Concentrations of PAHs in source oil from the <i>M/T ATHOS I</i> (GERG 2005) . . . . .	T-5
<b>Table 5</b>	Concentrations of metals in source oil from the <i>M/T ATHOS I</i> (Columbia Analytical Services 2005) . . . . .	T-7
<b>Table 6</b>	Relative impact of weathering processes on crude oils and heavy distillates (National Research Council 2003) . . . . .	T-8
<b>Table 7</b>	Log $K_{ow}$ , freshwater solubility, and estimated acute and chronic toxicity of PAH frequently found in crude and refined petroleum. Solubility and toxicity values are micrograms per liter ( $\mu\text{g/L}$ ppb). Log $K_{ow}$ values and solubilities are from Mackay <i>et al.</i> (1992), Neff and Burns (1996), and Ran <i>et al.</i> (2002). Table taken directly from Neff <i>et al.</i> (2005) . . . . .	T-9
<b>Table 8</b>	Toxicity thresholds for surface water (freshwater and saltwater) . . . . .	T-11
<b>Table 9</b>	Toxicity thresholds for freshwater and saltwater sediments . . . . .	T-13
<b>Table 10</b>	Calculated ESB-TUs for whole-sediment samples collected in the Delaware River in December, 2004 (From R. Greene, Delaware DNREC) . . . . .	T-14
<b>Table 11</b>	Screening evaluation of potential polycyclic aromatic hydrocarbon (PAH) toxicity: Athos water samples . . . . .	T-15
<b>Table 12</b>	Screening evaluation of potential polycyclic aromatic hydrocarbon (PAH) toxicity: Athos sediment samples . . . . .	T-16

## List of Figures

<b>Figure 1</b>	Total ion chromatogram of the <i>M/T ATHOS I</i> Venezuelan crude oil . . .	F-1
<b>Figure 2</b>	Alkane (ion 85) extracted ion plot of the <i>M/T ATHOS I</i> Venezuelan crude oil . . . . .	F-2
<b>Figure 3</b>	GC/FID chromatogram of North Slope crude oil . . . . .	F-3
<b>Figure 4</b>	PAH distribution in <i>M/T ATHOS I</i> and North Slope crude oils . . . . .	F-4
<b>Figure 5</b>	South Delaware River subtidal sediment sample locations and total PAH concentrations . . . . .	F-5
<b>Figure 6</b>	North Delaware River subtidal sediment sample locations and total PAH concentrations . . . . .	F-6
<b>Figure 7</b>	Track lines for the V-SORS highlighting the percent of visual oil coverage on the snares . . . . .	F-7
<b>Figure 8</b>	South Delaware River water sample locations and total PAH concentrations . . . . .	F-8
<b>Figure 9</b>	North Delaware River water sample locations and total PAH concentrations . . . . .	F-9
<b>Figure 10</b>	Delaware River oyster sample locations and total PAH concentrations . . . . .	F-10
<b>Figure 11</b>	Delaware River fish tissue sample locations and total PAH concentrations . . . . .	F-11

## List of Appendices

<b>Appendix 1 A Preliminary Evaluation of Delaware Department of Natural Resources and Environmental Conservation Assessment of Injuries Associated with the <i>M/T ATHOS I</i> Oil Spill in the Delaware River</b> .....	<b>A-1</b>
<b>A1.0 Introduction</b> .....	<b>A-1</b>
A1.1 Assessment of Risks to Human Health .....	A-1
A1.2 Assessment of Sediment Toxicity .....	A-2
A1.3 Assessment of Sediment Quality Conditions .....	A-3
<b>Appendix 2 Preliminary Evaluation of the Potential for Injury to Sediment-dwelling Organisms Associated with Releases of Venezuelan crude oil to the Delaware River from the <i>M/T ATHOS I</i></b> .....	<b>A-7</b>

## List of Appendices Figures

<b>Figure A1.1</b> Acute toxicity units for PAHs in sediment pore water (From R. Greene, Delaware DNREC) .....	<b>A-4</b>
<b>Figure A1.2</b> Chronic Toxicity units for PAHs in Sediment pore water (From R. Greene, Delaware DNREC) .....	<b>A-5</b>
<b>Figure A1.3</b> 10-day percent survival of <i>Leptocheirus plumulosus</i> (From R. Greene, Delaware DNREC) .....	<b>A-6</b>

## Executive Summary

This report summarizes available information on the composition of the crude oil released to the Delaware River during the *M/T ATHOS I* oil spill. In addition, it evaluates the potential fate and toxicity of that oil to enhance understanding of the potential effects of spilled oil on aquatic organisms and aquatic dependent wildlife.

In this Executive Summary, however, we provide our preliminary view of what the information in this report (along with other information known about the spill) suggests with respect to future actions that could be taken by the Aquatic Technical Work Group to move the assessment of aquatic resource injuries forward.

In our view, there is potential for ongoing impacts to sediment-dwelling organisms associated with accumulation of spill-related PAHs in Delaware River sediments. First, while the rate of weathering is dependent on many factors, and the more soluble and volatile hydrocarbons (e.g., naphthalenes) may be lost within days to weeks after an oil spill, the heavier 3-6 ring PAH compounds (e.g., chrysenes) can persist for years.

While non-polar narcosis is the primary mode of toxicity for PAH with three or fewer aromatic rings, many higher molecular weight PAHs may also be associated with mutagenic, carcinogenic, and teratogenic effects (Eisler 1987). In particular, methyl-substituted PAHs tend to be much more mutagenic than the parent compound (Environment Canada and Health Canada 1994). In addition, the metabolic degradation products of HMW-PAHs, particularly epoxide derivatives, tend to be highly mutagenic (NRCC 1983). These metabolites tend to be much more electrophilic and reactive than the parent compound, which increases the likelihood that they will bind covalently to DNA, RNA, and other cellular proteins (Varanasi 1989). In turn, these complexes may be associated with alterations in normal cellular processes (e.g., cell division, protein synthesis). Such alterations may be expressed by tumour formation, developmental abnormalities, and/or other related effects in aquatic animals (Heidelberger 1976; Larson *et al.* 1976; 1977).

We recognize that high molecular weight PAHs can be more tightly bound to sediments and, therefore, less available to aquatic organisms. For this reason, certain low molecular weight PAHs can be more toxic to sediment-dwelling organisms than high molecular weight PAHs, as evidenced by the sediment quality guidelines that have been established for these substances. For example, the consensus-based probable effect concentrations (PECs) for low molecular weight PAHs range from 561 to 845 ug/kg DW, while comparable PECs for high molecular weight PAHs range from 1050 to 2230 ug/kg DW (MacDonald *et al.* 2000). Nevertheless, in our view it would be unreasonable to simply assume that spill-related, persistent high molecular weight PAHs potentially present in Delaware river sediments are sufficiently bound by sediments to eliminate their potential toxicity.

Also relevant to our evaluation is the very preliminary, desk-top calculations we performed (see Appendix 2) to get a rough idea of the potential magnitude of spill-associated sediment PAH concentrations. These preliminary calculations, while generally based on conservative (i.e., damage-increasing) assumptions, suggest that total PAH concentrations could potentially be on the order of 830 to 1430 mg/kg OC (assuming TOC concentrations of three percent in Delaware River sediments). These concentrations fall between the total PAH threshold effect concentration (393 mg/kg OC) and LC<sub>50</sub> (2114 mg/kg OC) of total PAHs (Swartz 1999). The survival of amphipods exposed to sediments with these concentrations could be on the order of 50%, based on the results of 28-d toxicity tests (MacDonald *et al.* 2003).

However, several assumptions underlying these calculations are conservative. In addition, PAH degradation over time would reduce the potential for ongoing impacts. For discussion purposes, if we assume that at least 50 percent of the PAHs are either no longer present in the sediments or biologically unavailable one year after the spill (a plausible scenario in our view), then potential ongoing concentrations approach the threshold effects level, suggesting modest (but not zero) potential for ongoing injury to sediment-dwelling biota.

We readily acknowledge the substantial uncertainty inherent in the calculations described above. While these calculations and underlying assumptions certainly could be refined and improved with additional effort, in our view the "take-home" message is unlikely to change: spill-associated PAHs pose a potential ongoing risk to sediment-dwelling biota, although this risk is likely modest/moderate. This general message also appears consistent with the chronic toxicity units calculations performed by Rick Greene based on the limited subtidal sediment sample data available and toxicity testing information (from three locations) indicative of toxicity potentially associated with the spill near its origin, but not in locations further downstream. Comparison of available subtidal sediment data collected during spill response activities and toxicity thresholds identified in the technical literature also suggest that PAHs are present in spill-exposed sediments in concentrations sufficient to cause injury, although the relative contributions of spill and non-spill sources requires further investigation. However, existing data do not provide a sufficient basis for assessing the extent and severity of potential sediment injury.

In practical terms, this suggests to us that it would be prudent to undertake the targeted collection of sediment samples in a few known depositional areas in the vicinity of the spill origin and downstream where biological receptors of concern are present (or likely to be present). We would suggest collection of a few hundred grab samples, each of which would be photographed, described by field personnel, and analyzed for total PAHs using field testing kits (i.e., UV fluorescence techniques). A subset of those samples (potentially samples with the highest PAH measurements and some covering the range of concentrations) would be sent for laboratory analysis to: a) confirm PAH concentrations (and provide a scaling factor to adjust field measurements if needed); and b) provide information needed to help ascertain the source of observed PAHs.

We also considered the potential for toxicity associated with other components of the oil. MAHs, including but not limited to benzene, toluene, ethylbenzene and xylenes (BTEX), are volatile, and soluble low molecular-weight organic compounds. In the environment, they typically partition from oil and quickly evaporate into the air or dissolve into water. Among these chemicals, benzene is considered to be the most environmentally-significant COPC because of its potential risk to human and ecological receptors (ATSDR 1997). However because of benzene's intrinsic volatility, solubility and biodegradability, it generally does not persist in crude oils released to the environment (National Research Council 2003). In fact, benzene and the other BTEX compounds are among those chemicals with the shortest residence times in the shoreline/water/sediments when crude oil is released in the environment (Hayes *et al.* 1992). In most marine oil spills, these compounds are lost within hours to days after the oil spill (National Research Council 2003).

In our view, it would be reasonable to compare MAH water column measurements immediately after the spill to relevant effects thresholds for short term effects. While field observations do not provide evidence of significant kills of conspicuous aquatic biota (excluding birds, which are addressed by another technical working group), and the MAH content of the source oil is low (0.02%), it is not reasonable to rule out the potential for some short-term water-column impacts from this class of compounds. Further, comparison of existing water column MAH concentration data to effects thresholds would be relatively simple and cost-effective to perform.

Alkanes are a class of aliphatic hydrocarbons that is characterized by open chains of carbon with only single bonds between adjacent carbon atoms. Simple alkanes include the substances with one to eight carbon atoms, including methane, ethane, propane, butane, pentane, hexane, heptane, and octane. More complicated alkanes have larger numbers of carbon atoms, branched structures (such as phytane and pristane), or aromatic structures. Because simple alkanes are highly volatile, they are among the first substances that are lost when oil is subject to weathering. This volatility limits the potential for long-term toxicity associated with exposure to these substances.

Overall, in our view alkanes are unlikely to contribute substantially to the toxicity of oil spilled into the Delaware River, with the possible exception of acute toxicity to water column species immediately following the spill. As a group, alkanes have low to moderate aquatic toxicity (Irwin *et al.* 1997). For example, the acute LC<sub>50</sub>s of pentane, hexane, and octane to the water flea, *Daphnia magna*, were reported to be 135, 45, and 3.3 mg/L, respectively (Irwin *et al.* 1997). Decane was more toxic to this species, as indicated by the acute LC<sub>50</sub> of 0.2 mg/L. By comparison, the Bureau of Reclamation (2002) reported acute toxicity thresholds of 3.9, 0.37, and 0.028 mg/L for hexane, octane, and decane, respectively, based on the results of 48-h toxicity tests with water fleas. Together, these data suggest that the toxicity of alkanes tends to increase with increasing numbers of carbon in the molecule. Cyclopentane and cyclohexane had similar toxicities to water fleas as did the linear forms of these substances (i.e., 150 and 45 mg/L, respectively; Irwin *et al.* 1997). The Bureau of Reclamation (2002) reported 48-h LC<sub>50</sub>s for water fleas of 3.8 and 1.5 mg/L for cyclohexane and

methylcyclohexane. No data were available to evaluate the toxicity of simple or more complex alkanes in sediment. In the Delaware River, any simple alkanes present in the source oil would contribute to acute toxicity, adding to the toxicity exhibited by the MAHs.

While various trace metals are present in the source oil, we do not believe that they pose toxicity risk given their low concentrations and generally low bioavailability.

The vast majority of the oil (95%+) is comprised of thousands of compounds that are not individually quantified, but referred to generally as the unresolved complex mixture (UCM). Information on the toxicity of UCMs is limited in the literature, although there is some toxicological data that suggests that these substances may contribute to the toxicity of crude oil. For example, Neff *et al.* (2000) evaluated the effects of weathering on the toxicity of three crude oils to various marine fish and invertebrates species. The results of these toxicity tests indicated that the acute toxicity of the water-accommodated fractions (WAFs) of fresh and weathered oils to six species of temperate and tropical animals varied substantially, ranging from non-toxic to about 11% WAF [i.e., toxic (greater than 50% mortality) if present in the water column at 11% (or greater) strength].

In fresh oils, the MAHs were considered to be the most important contributors to the acute toxicity of the WAFs. However, PAHs contributed substantially to the toxicity of the WAFs prepared from weathered oils. While MAHs, PAHs, and phenols accounted for the majority of the toxicity of WAFs from condensate or light crude oil, these substances could not account for all of the toxicity of the WAFs from middle-weight crude oil. Accordingly, Neff *et al.* (2000) concluded that the components in the UCM and polar substances (i.e., resins) contributed to the toxicity of the WAFs from heavier oil.

Several studies on mussels, *Mytilus edulis*, confirm that unresolved aromatic hydrocarbon mixtures can be toxic to aquatic organisms. More specifically, Donkin *et al.* (2001) reported that exposure to an aromatic UCM isolated from a North Sea crude oil results in a 40% reduction in feeding rates of mussels in 24-h. Similarly, feeding rates of juvenile mussels were reduced by 70% when exposed to a mono aromatic UCM (Donkin *et al.* 2003). However, later-eluting fractions containing aromatic UCMs (i.e., higher molecular weight substances) produced smaller depressions in feeding rate. These results suggest that the lighter-weight fractions in the UCMs are primarily responsible for observed toxicity. The results of an earlier study indicated that saturated hydrocarbons had not effect on the feeding rate of mussels (Thomas *et al.* 1995). In a related study, 6-cyclohexyltetralin, 7-cyclohexyl-1-methyltetralin, and 7-cyclohexyl-1-propyltetralin were all shown to be toxic to mussels, however (Smith *et al.* 2001).

However, given variability in UCM content and toxicity from oil to oil, the tendency for high molecular weight UCM components to remain associated with oil globules, and the limited toxicological data available in the literature, in our view it is unlikely that UCM-based injury thresholds could be developed.

It is possible that physical effects (e.g., smothering) associated with the UCM could arise. Some simple HEA calculations, however, suggest that there would have to be a relatively substantial area affected by such material before significant restoration requirements would arise. For example, if one assumes the complete loss of benthic services due to smothering from one acre (4,840 yd<sup>2</sup>) of river bottom for three years, and restoration (perhaps oyster reef or wetland creation) that provides benefits for 15 years at a level twice as productive per unit area as the baseline condition of river bottom habitat, the restoration requirement would total only 600 yd<sup>2</sup> of new habitat.

How likely is it that there is one or more acres of river bottom habitat affected by residual *M/T ATHOS I* oil in this way? While the possibility can't be ruled out, in our view the likelihood is low that ongoing effects of this magnitude are present. However, a few days of VSORS monitoring potentially would be a useful, cost-effective check to see if relatively large patches of residual oil are still present. If significant hits of oil occur, further sampling could be undertaken to address sourcing issues.

## 1.0 Introduction

Crude oil is a complex mixture of thousands of chemical compounds that can be broadly grouped as either hydrocarbons or non-hydrocarbons (Tissot and Welte 1984). The former consists of both saturate hydrocarbons, including straight chain alkanes (e.g., hexane), branched alkanes (e.g., pristane), cyclic alkanes (methylcyclohexane), and aromatic hydrocarbons (e.g., benzene), while the latter consists of various nitrogen, sulfur, and oxygen (NSO) or metal (e.g., V and Ni) containing compounds. The hydrocarbons in petroleum may range from highly volatile compounds (e.g., propane) to compounds with low volatility with as many as 100+ carbon atoms. The proportion of compound classes (e.g., saturate versus aromatic hydrocarbons) and oil volatility is a function of the source and type of petroleum. The non-hydrocarbons typically present in crude oil include low molecular weight heteroatom compounds (e.g., the sulfur containing dibenzothiophenes), as well as heavier, more complex compounds called asphaltenes and resins.

Crude oils from around the world vary widely in the relative abundance of saturate hydrocarbons, aromatic hydrocarbons, and non-hydrocarbons. Much of this variation reflects the combined effects of: (1) the character of the ancient organic matter in the oil's source rock(s), (2) the thermal maturity of the oil's source rocks, and (3) any alteration after accumulating in an oil reservoir (e.g., biodegradation; Seifert *et al.* 1984; Sofer 1984; Mackenzie 1984; Moldowan *et al.* 1985). It is important to adequately characterize these features of the oil, so scientifically defensible conclusions can be reached regarding the origin, behavior, toxicity and fate of the crude oil in the environment. To document these features in the *M/T ATHOS I* oil, physical (e.g., viscosity), and chemical (e.g., volatile hydrocarbons) measurements were performed (Table 1).

This report was prepared to summarize the available information on the composition of the crude oil released to the Delaware River during the *M/T ATHOS I* oil spill. In addition, an evaluation of the potential fate and toxicity of that oil was conducted to enhance understanding of the potential effects of spilled oil on aquatic organisms and aquatic-dependent wildlife.

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## 2.0 Physical and Chemical Properties of Crude Oil Released into the Delaware River

The physical and chemical characteristics of crude oil have a major influence on the transport and ultimate fate of the oil once released to the environment. Light crude oils will evaporate more quickly, whereas heavy oils will tend to persist for longer periods of time in the environment. Most crude oil contains tens of thousands of compounds that on a "bulk" level can be broadly grouped as either hydrocarbons or non-hydrocarbons. Bulk composition analysis of crude oils generally includes API Gravity, % topped oil (approximately all hydrocarbons lost to evaporation up to  $n\text{-C}_{12}$  to  $n\text{-C}_{14}$ ), and saturate, aromatic, resins and asphaltenes (SARA). Measurement of these "bulk" chemical parameters provide the compositional information required to understand, and, in some cases, predict the environmental behavior of a crude oil.

### 2.1 Physical Properties

The product from the *M/T ATHOS I* is a heavy *biodegraded* (in the oil reservoir) Venezuelan crude oil. Two samples of the source oil from hold No. 7 center were analyzed for select physical characteristics and a broad range of chemical characteristics. The general physical and chemical properties of the spilled oil are provided in Table 1. The density of the oil samples was 0.97 and 0.98 grams per milliliter (g/mL), respectively. The density of fresh water is 1.00 g/mL, and oceanic seawater is 1.025 g/ml, therefore, the oil is lighter than both fresh water and seawater. The viscosity of the source oil is greater than 5,000 centistokes (cSt) at 100°F and at ambient water temperature greater than 50,000 cSt, meaning that the oil is very viscous and has a relatively high pour point. Michel *et al.* (2005) reported that the source oil had viscosity similar to cold honey at ambient water temperatures. In addition, visual observation by Michel *et al.* (2005) observed that the oil is very viscous and did not form a stable emulsion even when exposed to high wave energy.

Conventional crude oil flows naturally or can be pumped without being heated or diluted. Crude oil is commonly classified as light, medium or heavy, referring to its gravity as measured on the American petroleum Institute (API) scale. The API gravity is measured in degrees and is calculated using the formula:

$$\text{API Gravity} = (141/\text{specific gravity}@60^\circ\text{F}) - 131.5$$

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Light crude oil is defined as having an API gravity higher than 31.1°, medium oil as having an API gravity between 22.3° and 31.1°, and heavy oil as having an API gravity below 22.3°. Oil that does not flow, or cannot be pumped, without being heated or diluted is called bitumen, and generally has an API gravity of around 8°. The API gravity for the source oil is low (approximately 13), which is consistent with heavy Venezuelan crude.

## 2.2 Chemical Composition

The source oil released from the *M/T ATHOS I* was comprised of four major classes of compound, including aromatics (49.2% by weight), saturated hydrocarbons (i.e., aliphatics; 35.9% by weight), resins/NSO (3%), and asphaltenes (12.9% by weight; Table 1). Oil from this source also includes relatively smaller quantities of several other substances, including but not limited to metals and non-saturated organics.

The total ion chromatogram (TIC) for the spilled oil is provided in Figure 1. The chromatogram indicates that the oil is a heavily biodegraded crude oil, depleted in lower molecular weight hydrocarbons and n-alkanes. Alkanes are a class of aliphatic hydrocarbons that is characterized by open chains of carbon with only single bonds between adjacent carbon atoms. Simple alkanes include the substances with one to eight carbon atoms, including methane, ethane, propane, butane, pentane, hexane, heptane, and octane. More complicated alkanes have larger numbers of carbon atoms, branched structures (such as phytane and pristane), or aromatic structures. Traces of alkanes were observed in the more analytically-sensitive alkane extracted ion plot (ion 85; Figure 2) and are indicative of a secondary, less degraded product, possibly a gas-oil diluent added to improve the flow properties of the oil.

The visual differences between the biodegraded heavy Venezuelan crude (Figure 1) and a medium API Gravity Alaska North Slope crude oil (Figure 3) indicate that, relative to North Slope crude oil, the Venezuelan crude oil is depleted in light hydrocarbons and alkanes, dominated by the unresolved complex mixture (UCM), and exhibits a much heavier hydrocarbon maximum in the  $n\text{-C}_{20}+$  range. The UCM is comprised of compounds that fall into several categories, including branched alkanes and cycloalkanes, complex aromatics, resin/NSO compounds, and asphaltenes (Frysiner *et al.* 2003).

Three specific sub-classes of chemicals of potential concern (COPCs) have been quantified in the source oil by laboratory analysis, including:

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- Monocyclic aromatic hydrocarbons (MAHs), primarily including benzene, toluene, ethylbenzene and xylenes (collectively identified as BTEX compounds);
- Polycyclic aromatic hydrocarbons (PAHs); and,
- Trace metals.

While the following discussion is focused on these chemical classes, the source oil also consists of myriad other substances that have not been quantified, such as simple alkanes (i.e., butane to octane), branched alkanes, cycloalkanes, resins/NSO compounds, and asphaltenes.

### **2.2.1 Monocyclic Aromatic Hydrocarbons (MAHs)**

The MAHs, including but not limited to benzene, toluene, ethylbenzene and xylenes (BTEX), are volatile, and soluble low molecular weight organic compounds. In the environment, they typically partition from oil and quickly evaporate into the air or dissolve into water. Among these chemicals, benzene is considered to be the most environmentally-significant COPC because of its potential risk to human and ecological receptors (ATSDR 1997). However because of benzene's intrinsic volatility, solubility and biodegradability, it generally does not persist in crude oils released to the environment (National Research Council 2003). In fact, benzene and the other BTEX compounds are among those chemicals with the shortest residence times in the shoreline/water/sediments when crude oil is released in the environment (Hayes *et al.* 1992). In most marine oil spills, these compounds are lost within hours to days after the oil spill (National Research Council 2003).

Recently, Rixey (2001) reported the benzene content of 69 unweathered crude oils from around the world. The crude oils in this study spanned a broad API Gravity range, from heavy (8.8 API) to very light (46 API) crude oil. The benzene content measured in these oils ranged from not detected (<~1 ppm) to a maximum of 5,900 ppm, with a mean and median of 1,340 ppm and 780 ppm respectively. The concentrations of BTEX in the *M/T ATHOS I* oil were 14, 33, 50, and 128 ppm respectively (Table 2). Compared to the mean and median of crude oils examined from around the world, these concentrations would be considered low (MAH = 0.02%) and are consistent with a highly viscous heavy Venezuelan crude oil.

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## 2.2.2 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons are a diverse class of organic compounds that contain two or more fused benzene, or aromatic rings. The PAHs with fewer than four rings are termed low molecular weight PAHs (LMW PAHs), while those with four or more rings are termed high molecular weight PAHs (HMW PAHs). Polycyclic aromatic hydrocarbons are ubiquitous in the environment and arise from naturally-occurring and man-made sources. They can be found in substances such as crude oil, distillate fuels, coal, coal tar pitch, creosote, roofing tar, and asphalt used in road construction. PAHs are found throughout the environment in the air, water, and soil. They can occur in the air, either attached to dust particles or as solids in soil or sediment. Combustion of fossil fuels through residential wood burning, forest fires and industrial activities (e.g., coal burning and coal tar manufacturing) represents the major sources of PAHs to the environment (ATSDR 1995; Neff 1979).

The United States Environmental Protection Agency (USEPA) has identified 16 priority pollutant PAHs that may pose an adverse ecological or human health risk (USEPA 2003). The USEPA 16 priority pollutant PAH are generally only a small percentage of crude oil - typically less than 0.1% (Neff 1979; Douglas *et al.* 1994). In contrast, alkylated PAHs are the major PAHs contained in crude oil (National Research Council 2003)<sup>1</sup>. The PAHs (parent PAH, alkylated PAHs, and dibenzothiophenes) were measured in the *M/T ATHOS I* source oil using gas chromatography with mass spectrometry following a modified EPA Method 8270 (Figure 4; Table 3 and 4).

The PAH distributions in the source oil are consistent with those observed from oils collected from around the world (Kerr *et al.* 2001). Figure 4 is a plot of the PAH distributions in the *M/T ATHOS I* source oil versus North Slope crude oil, a medium API gravity oil. The concentrations and relative distributions of the parent PAH and associated alkyl homologs are similar with the exception of the lower molecular weight naphthalenes. These more water soluble/volatile PAHs are greatly reduced in the source oil and account for 40% lower total PAH content in the source oil versus the North Slope Crude oil (0.6 % *M/T ATHOS I* source oil versus approximately 1% for North Slope crude oil; Douglas *et al.* 1994). The lower molecular weight hydrocarbons (e.g., butane through *n*-C<sub>15</sub>) act as solvents within the

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<sup>1</sup>Alkylated PAHs are parent PAHs that have additional carbon side chains attached to them. For example, naphthalene is a parent PAH, and C1-naphthalenes are the alkylated PAHs because they have one additional carbon group (alkyl group) attached to it. For each parent PAH, there is a homologous series of alkylated PAHs with increasing number of attached carbon molecules. For example, the naphthalene PAH series measured in petroleum includes naphthalene, C1-naphthalenes, C2-naphthalenes, C3-naphthalenes, and C4-naphthalenes (Douglas *et al.* 2004). In addition to parent and alkylated PAHs, selected source specific heterocyclic compounds are also measured in petroleum. Dibenzothiophene is an example of a heterocyclic compound where a sulfur molecule is exchanged with one of the carbon molecules in the aromatic ring. For clarity, the PAHs, alkylated PAHs, and dibenzothiophenes are identified in this report as PAHs.

petroleum and their reduced concentration in the source oil is consistent with a viscous heavy crude oil. Overall, the proportion of measured PAH to total aromatic hydrocarbons concentration in the oil is low. These additional aromatic compounds (not identified by the PAH analysis) are more likely to be higher molecular weight complex aromatic compounds present in the UCM [e.g., alkyltetralins (Warton *et al.* 1999), complex monocyclic aromatic hydrocarbons (Donkin *et al.* 2003)].

### 2.2.3 Trace Metals

All crude oils contain low levels of naturally-occurring trace metals. Metals in crude oils arise from the metals present in the ancient depositional environment oil source rock and are typically incorporated into naturally-occurring metal-containing organic molecules, such as chlorophyll during oil's genesis. The complexation (formation of chemical bonds between the metal and large organic molecules) of these metals in crude oil generally reduces their bioavailability (and toxicity to marine biota). Trace metals are also naturally-occurring constituents in the environment, found in appreciable concentrations in rocks, soil, and modern organic matter. Some metals, such as chromium, selenium and zinc, are essential for life. Certain metals such as lead, mercury, and cadmium may pose adverse risk to humans and the environment.

As part of the effort to characterize the chemical composition of the *M/T ATHOS I* source oil, the concentrations of 18 trace metals were measured in the reference oil samples using Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry, following EPA Method 6010B. The metals and their measured concentrations in the source oil are listed in Table 5. The metals with the highest concentrations in the source oil sample were vanadium and nickel (averaging 445 ppm and 57 ppm, respectively; n=2), a result consistent with the literature (Tissot and Welte 1984).

Aluminum, barium, calcium, chromium, copper, iron, magnesium, manganese, sodium and zinc were present at low part per million levels. The remaining metals were not detected at their associated detection limits (Table 6).

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### **3.0 Potential Environmental Fate of Oil Released from the M/T ATHOS I**

Upon release into the environment, the chemical and physical properties of the M/T ATHOS I oil will change depending on a number of environmental fate processes. Collectively, these changes in the properties of the source oil are termed weathering. The major weathering factors for marine crude oil spills are the initial chemical and physical properties of the spilled oil, spreading, evaporation, dispersion, emulsification, dissolution, oxidation, sedimentation and biodegradation. Given the viscosity of the oil, spreading over the water surface, dispersion, and emulsification appear to play a minor role in the water column. Oil was observed to pool in subsurface trenches at the spill site where the crude oil was apparently injected into the sediments from the penetrated hull. Under these conditions, the oil exhibited some adhesive properties in the sediments that prevent remobilization even though the density of the oil was less than that of the overlying water column.

Overall, based on the physical and chemical properties of the oil, its persistence in the environment is likely more similar to a heavy distillate/residual oil than that of a medium to high API Gravity crude oil. A rough ranking of weathering factors for crudes and heavy distillate oils is provided in Table 6.

To evaluate the potential for evaporative weathering of the source oil, the fresh source oil was heated to 90°C under vacuum and evaporative losses measured over a four hour period. The results of this study indicated that less than 3% of the source oil was lost by evaporation after 4 hours (termed % topped oil; Table 1). Application of the National Oceanic and Atmospheric Administration (NOAA) oil weathering model ADIOS further indicates that up to 13% of the oil could have evaporated within 5 days of the release (Michel *et al.* 2005). Based on the low concentrations of MAH and naphthalenes, and after reviewing the GC/MS total ion chromatogram (TIC), it is highly probable that evaporative losses from this oil were minor because of the relatively low proportion of these compounds in the oil.

The behavior of oil-borne PAHs in the environment is generally well understood. Once released into the environment, the concentration of total PAH in the oil will decrease due to various environmental weathering processes that include volatilization, dissolution (transport of soluble hydrocarbons from the oil to the water column), and biodegradation (National Research Council 2003; Stout *et al.* 2002). The rate of weathering is dependent on many factors (discussed earlier); however, the more soluble and volatile hydrocarbons (e.g,

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naphthalenes) may be lost within days to weeks after an oil spill, whereas the 3-6 ring PAH compounds (e.g., chrysenes) may persist for months to years.

## **4.0 Potential Toxicity of Source Oil Released from the *M/T ATHOS I***

This brief review of relevant information on the constituents of crude oil from this source and the associated toxicity of those substances (based on the published literature) indicates that certain constituents of *M/T ATHOS I* source oil are toxic to aquatic organisms, both in acute and chronic exposures. While such compounds may occur in *M/T ATHOS I* source oil at lower levels than is the case for some other oils, there is still the potential for acute/chronic effects in short and long term, depending on concentration of oil in sediments/water column and duration of exposure. These issues are discussed in more detail in the following sections of this document.

### **4.1 Toxicity of Crude Oils - Overview**

No information on the toxicity of heavy Venezuelan crude oil to freshwater or estuarine biota was located in the published literature. For this reason, a cursory review of the scientific literature was conducted to generally assess the toxicity of crude oils to aquatic organisms, with the goal of evaluating the relative toxicity of these constituents and identifying those substances that should be considered for evaluation in a NRDA of the *M/T ATHOS I* oil spill. A wide variety of studies have been conducted to assess the toxicity of crude oils to aquatic organisms and aquatic-dependent wildlife. In general, these toxicity tests are conducted to evaluate the toxicity to aquatic organisms exposed to the water soluble fraction (WSF) of one or more types of oil, rather than evaluating the toxicity of the entire oil matrix. As such, these toxicity tests are intended to simulate the effects of oil released into freshwater or marine ecosystem through dissolution of water-soluble substances.

Exposure to the WSFs of various crude oils has resulted in a variety of adverse effects on aquatic organisms. For example, short-term exposure to WSF from crude oils have been shown to adversely affect the survival, growth, and/or reproduction of crustaceans (*Cancer magister*; Caldwell *et al.* 1977), polychaetes (*Nereis* spp.; Lee *et al.* 1981), echinoderms

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(*Patiria miniata*; Davis *et al.* 1981), and leaches (*Johanssonia arctica*; Khan and Kiceniuk 1989). In addition, oiling of substrate materials has been shown to adversely affect microbial communities, benthic invertebrates, and fish (Lock *et al.* 1981; Spies *et al.* 1988; Paine *et al.* 1991). Ingestion of crude oil is also known to cause mortality and reproductive failure in aquatic-dependent wildlife (Vangilder and Peterle 1980; Peterson 2001).

The acute toxicity of crude oil has been demonstrated to be primarily associated with the concentrations of MAHs and PAHs in the oils (Neff *et al.* 2000). Bioavailability is also an important factor, and generally decreases with increasing molecular weight. The exposure of sensitive marine organisms to water-accommodated fractions (WAF) of the fresh and artificially-weathered crude oils are used to determine acute toxicity (National Research Council 2003). This approach incorporates the concentration of the COPCs in the oil with the bioavailability of the COPCs in the water. The major chemical classes of compounds most commonly measured in crude oil WAF studies are MAHs, PAHs, and phenols (Neff *et al.* 2000)<sup>2</sup>.

Environmental processes that reduce the concentrations of MAHs, PAHs and phenols in the crude oil will also reduce the acute toxicity of the oil to marine organisms. The two weathering processes that will have the greatest impact on these lower molecular weight water soluble compounds are evaporation and solubilization. These processes occur at the oil/water or oil/air interface, and the compound must diffuse from the oil to the adjacent medium in order to be removed. Based on initial evaporation and oil modeling studies (Table 1), overall hydrocarbon losses due to volatilization are likely to be minor in the source oil from the *M/T ATHOS I* (although significant for MAHs, which comprise only 0.02% of the source oil).

Within the water column/sediment environment the MAH compounds in the crude oil will eventually be lost. The rate is dependent on the thickness of the oil, concentration of the hydrocarbon in oil, temperature of the water/oil, and the velocity of the water in contact with the oil. For surface oils, this rate is generally rapid; however, for subsurface oils the rate of loss may be slower. The most soluble PAH compounds will also migrate into the water based on their solubility and concentration in the source oil. Within the PAH class of hydrocarbons, dissolution generally decreases with increased alkylation (within a homologous series) and number of aromatic rings (e.g., 2 ring > 3 ring > 4 ring > 5 ring).

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<sup>2</sup>Crude oil may also adversely affect aquatic biota through physical impacts (e.g., smothering).

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Neff *et al.* (2000) evaluated the acute toxicities of three Australian crude oils. The crude oil with the lowest WAF toxicity contained 0.53% PAH and 1.2% MAH (versus 0.6% PAH and 0.02% MAH in the *M/T ATHOS I* oil). In their study, they reported that this crude oil was slightly toxic to silverside minnows and shrimp and the WAFs of the weathered fractions of the oil were practically non-toxic to all of the test organisms (clownfish, silverside minnows, mysids, shrimp, urchin, echinoderm) but the mysids. Given that the *M/T ATHOS I* crude oil PAH concentration is similar, and the toxic MAH compounds are approximately two orders of magnitude lower than the Neff crude oil, the acute toxicity of the *M/T ATHOS I* oil to freshwater and estuarine biota may be low. However, as the chemical composition of the WSF depends on the physical and chemical properties of the source oil, information on the toxicity of the WSF of other (particularly lighter) crude oils, comparisons between oils needs to be undertaken cautiously.

Finally, recent studies (Neff *et al.* 2000; Donkin *et al.* 2003) have suggested that oil toxicity may also be associated with the complex aromatic hydrocarbons present in the oil UCM. Given the high aromatic content of this crude oil and the dominance of the UCM in the oil, the potential for aquatic toxicity may require further evaluation. These issues are discussed in more detail below.

Various studies provide information on the effects of weathering on the toxicity of crude oils. For example, Carls *et al.* (1999) reported that herring eggs (*Clupea pallasii*) exposed to the WSF of weathered and less weathered oil exhibited similar effects, including malformations, genetic damage and mortality. However, the lowest observed effect concentrations (LOECs) were higher for the less weathered oil (i.e., 9.1 ug/L vs. 0.4 ug/L). These differences in the LOECs were considered to reflect the lower levels of high molecular weight PAHs in the less weathered oil. Such differences were not observed when mature herring, rather than ova, were exposed to the WSF of weathered and less weathered oil, however (Carls *et al.* 2000). These results emphasize the importance of considering the effects of PAH exposures via multiple routes and evaluating sensitive, sub-lethal endpoints (Peterson 2001; Peterson *et al.* 2003).

## 4.2 Toxicity of Constituents of Crude Oils

The following sections of this document provide summaries of the readily-available data on the toxicities of the following crude oil constituents:

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- Monocyclic aromatic hydrocarbons;
- Polycyclic aromatic hydrocarbons;
- Metals;
- Alkanes; and
- Other substances.

#### 4.2.1 Monocyclic Aromatic Hydrocarbons

While specific receptors discussed below may be more or less relevant for the Delaware River and Delaware Bay, it is clear that MAHs have the potential to harm aquatic biota. Because MAHs are typically quick to degrade, they are likely to be most important in terms of their potential for toxicity to water column species immediately following the spill. While the MAH content of the *M/T ATHOS I* source oil may be low relative to other oils, in our view it is not reasonable to rule out the possibility of short-term impacts. If field measurements are available for these constituents, observed concentrations could be compared to injury thresholds. Based on the information presented below, and further discussions with the Trustees about receptors of concern in the Delaware River, we could develop thresholds for determining injury associated with MAHs.

As indicated previously, the principal MAHs contained in crude oil include benzene, ethylbenzene, toluene, and xylene. Summaries of the available information on the toxicity of these substances to aquatic organisms are provided below.

Information on the acute and chronic toxicity of benzene is available for numerous species representing a variety of receptor groups and was summarized in Environment Canada and Health Canada (1993a). These data suggest that aquatic plants are not particularly sensitive to the effects of benzene, with a 3-h  $EC_{50}$  for inhibition of photosynthesis of 312 mg/L reported for the alga, *Chlorella vulgaris*. Freshwater invertebrates appear to be more sensitive, with 48-h  $LC_{50}$ s of 10 mg/L, 15 mg/L and 31 mg/L reported for damselflies (*Ischnura elegans*) and two species of water fleas (*Daphnia pulex* and *Daphnia magna*), respectively. Toxicity thresholds for rainbow trout (*Orcorhynchus mykiss*) and coho salmon (*O. kisutch*) were even lower, as evidenced by the 96-h  $LC_{50}$ s that have been reported for these species (5.3 and 9 mg/L, respectively). Leopard frogs (*Rana pipiens*) were among the most sensitive species tested, with a 9-d  $LC_{50}$  of 3.7 mg/L reported. A chronic toxicity threshold of 1.4 mg/L for rainbow trout has also been reported for benzene (Bureau of Reclamation 2002).

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No information was located on the toxicity of benzene to sediment-dwelling organisms (i.e., from spiked-sediment toxicity tests). Nevertheless, various USEPA regions have established benchmarks for benzene in sediments. The geometric mean of the reported benchmarks was calculated and used to establish toxicity thresholds of 0.12 and 0.11 mg/kg DW (at 1%OC) for freshwater and marine sediments, respectively.

The available data on the toxicity of ethylbenzene to aquatic organisms were summarized by CCME (1999). These data indicate that freshwater fish, invertebrates, and plants have similar sensitivities to ethylbenzene. Estimates of the acute toxicity of ethylbenzene (i.e., 96-hr LC<sub>50</sub>s) range from 4.2 mg/L for rainbow trout to 210 mg/L for channel catfish (*Ictalurus punctatus*). For freshwater invertebrates, toxicity thresholds range from 1.8 mg/L (48-h EC<sub>50</sub> immobilization) to 77 mg/L (24-h LC<sub>50</sub>) for the water flea, *D. magna*. Chronic toxicity studies on fish were not located in the literature. For marine organisms, acute toxicity thresholds range from 0.49 mg/L for bay shrimp (*Crago franciscorum*) to 360 mg/L for sheepshead minnows (*Cyprinodon variegatus*). The 16-h EC<sub>50</sub> for growth of 0.114 mg/L for 13 species of bacteria is the lowest observed effect level in the literature.

No information was located on the toxicity of ethylbenzene to sediment-dwelling organisms (i.e., from spiked-sediment toxicity tests). Nevertheless, various USEPA regions have established benchmarks for ethylbenzene in sediments. The geometric mean of the reported benchmarks was calculated and used to establish toxicity thresholds of 0.47 and 0.32 mg/kg DW (at 1%OC) for freshwater and marine sediments, respectively.

A review of the available data on the toxicity of toluene to aquatic organisms indicates that aquatic plants, aquatic invertebrates, and fish exhibit similar sensitivities to this substances (Environment Canada and Health Canada 1992). For example, several studies on the effects of toluene on the growth of freshwater algae indicated that acute toxicity thresholds are on the order of 10 mg/L. Similarly, short term (i.e., 48 to 96-h) LC<sub>50</sub>s for freshwater and marine invertebrates ranged from 11.5 mg/L for the water flea, *D. magna*, to 28 mg/L for the crab, *Cancer magister*. Salmonids appear to be the most sensitive fish species, with 96-hr LC<sub>50</sub>s of 5.5 to 5.8 mg/L reported in the literature for coho trout and rainbow salmon. The results of long-term studies indicate that chronic toxicity thresholds for freshwater and marine species tend to be lower, as evidenced by continuous exposure LC<sub>50</sub>s of 0.02 mg/L for rainbow trout, 0.39 mg/L for leopard frogs, and 0.85 mg/L for salamanders (*Ambystoma gracile*).

No information was located on the toxicity of toluene to sediment-dwelling organisms (i.e., from spiked-sediment toxicity tests). Nevertheless, various USEPA regions have established

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benchmarks for toluene in sediments. The geometric mean of the reported benchmarks was calculated and used to establish toxicity thresholds of 0.58 and 0.48 mg/kg DW (at 1%OC) for freshwater and marine sediments, respectively.

There are three isomers of xylenes (ortho or o-xylene, meta- or m-xylene, and para or p-xylene), each of which is toxic to aquatic organisms. Based on the results of a review of the available toxicological literature (Environment Canada and Health Canada 1993b), it appears that the toxicity of the three isomers is similar. For example, 72-h EC<sub>50</sub>s for growth of the alga, *Selenastrum capricornutum*, ranged from 3.2 to 4.9 mg/L for the three xylene isomers. For the waterflea, *D. magna*, 24-h LC<sub>50</sub>s ranged from 1.0 mg/L for o-xylene to 4.7 mg/L for m-xylene. Bay shrimp showed similar levels of sensitivity, with 96-h LC<sub>50</sub>s ranging from 1.1 mg/L for o-xylene to 3.2 mg/L for m-xylene. Rainbow trout was the most sensitive freshwater fish represented in the toxicological data set, with 96-h LC<sub>50</sub>s of 2.6, 7.6, and 8.4 for the p-, o-, and m- isomers, respectively. The acute toxicity thresholds reported for striped bass (*Morone saxatilis*) were similar to those for rainbow trout (i.e., 1.7 to 9.7 mg/L). Continuous exposure LC<sub>50</sub>s of 3.5 and 3.8 mg/L were reported for leopard frogs and rainbow trout, respectively.

No information was located on the toxicity of toluene to sediment-dwelling organisms (i.e., from spiked-sediment toxicity tests). In addition, none of the USEPA regions polled have established benchmarks for xylenes in sediments.

#### **4.2.2 Polycyclic Aromatic Hydrocarbons**

Overall, in our view, PAHs are of potential concern with respect to short term water column impacts and short and long term effects on sediment dwelling biota. While the PAH content of the source oil is low relative to other crude oils, impacts could still occur from exposure to the source oil. Further, PAHs can persist in the environment for months/years. While their bioavailability can vary, in our view there is still a toxicity risk associated with this class of compounds. Differences in the size and structure of the individual PAHs result in substantial variability in their physical, chemical, and toxicological properties.

Exposure to PAHs has been associated with a wide range of effects in aquatic organisms, including effects on survival, growth, reproduction, metabolism, and health. The responses of aquatic biota to PAH exposures vary significantly among taxonomic groups and depend, at least in part, on the organism's ability to metabolize and excrete PAHs. In addition, biological responses may be affected by duration of exposure to the PAHs, by the substance

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or group of substances under consideration, and ambient environmental conditions. Overall, because of their persistence and toxicity, in our view, PAHs have the potential to exert toxic effects on sediment-dwelling organisms.

The acute toxicity of PAHs is primarily associated with their action as non-polar narcotics. That is, PAHs tend to enter the organism and bind irreversibly to lipophilic sites within the cell. Binding to sites on cell membranes tend to disrupt surface membrane processes, inhibition and gas exchange, and increase the movement of water across the membrane. In fish, hypoxia and osmotic imbalances may result from impaired membrane function. In tissues, changes in membrane permeability can disrupt neurological and muscular function. Together, these effects can lead to metabolic dysfunction, immobility, and death.

In water column exposures, the acute toxicity of PAHs increases with increasing molecular weight, with HMW-PAHs being much more toxic than LMW-PAHs (Table 7). This increased toxicity is related to the relative hydrophobicity and persistence of HMW-PAHs in aquatic organisms. However, this pattern may not be always be obvious for sediment-associated PAHs. Differences in the physicochemical properties (e.g., solubility) of individual PAHs could significantly affect the observed toxicity of these substances in sediments. That is, HMW-PAHs may be more tightly bound to sediments and, therefore, less available to aquatic organisms. Therefore, certain LMW-PAHs can be more toxic to sediment-dwelling organisms than are HMW-PAHs, as evidenced by the sediment quality guidelines that have been established for these substances. For example, the consensus-based probable effect concentrations (PECs) for LMW-PAHs range from 561 to 845 ug/kg DW, while comparable PECs for HMW-PAHs range from 1050 to 2230 ug/kg DW (MacDonald *et al.* 2000). Such concentrations of LMW-PAHs and HMW-PAHs are frequently associated with toxicity to sediment-dwelling organisms. That sediment-associated PAHs are toxic to aquatic organisms is emphasized by the results of studies conducted in Eagle Harbor, WA, which showed high toxicity to amphipods exposed to creosote-contaminated sediment (Swartz *et al.* 1989). English sole from this area also had a high incidence of hepatic lesions (Malins *et al.* 1985). Table 9 presents the freshwater and marine toxicity thresholds that have been established based on the benchmarks that are currently being used in various USEPA regions in screening level ecological risk assessments.

While non-polar narcosis is the primary mode of toxicity for PAH with three or fewer aromatic rings, many HMW-PAHs may also be associated with mutagenic, carcinogenic, and teratogenic effects (Eisler 1987). For example, terata have been observed in fish exposed to naphthalene (239 ug/L for 7-d), phenanthrene (85 ug/L for 27-d), and benzo(a)pyrene (0.2 ug/L for 36-d). In addition, genotoxic and neoplastic effects have been reported in

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vertebrates and invertebrates from metabolism of certain PAHs, including naphthalene, phenanthrene, and benzo(a)pyrene (Environment Canada and Health Canada 1994). Both water-borne and sediment-associated PAHs elicited these types of effects. Methyl-substituted PAHs tend to be much more mutagenic than the parent compound (Environment Canada and Health Canada 1994). Interestingly, however, PAHs with longer alkyl-substitution tend to be less toxic due to their decreased ability to cross cell membranes (NRCC 1983). In addition, the metabolic degradation products of HMW-PAHs, particularly epoxide derivatives, tend to be highly mutagenic (NRCC 1983). These metabolites tend to be much more electrophilic and reactive than the parent compound, which increases the likelihood that they will bind covalently to DNA, RNA, and other cellular proteins (Varanasi 1989). In turn, these complexes may be associated with alterations in normal cellular processes (e.g., cell division, protein synthesis). Such alterations may be expressed by tumour formation, developmental abnormalities, and/or other related effects in aquatic animals (Heidelberger 1976; Larson *et al.* 1976; 1977). In plants, PAH metabolites may bind with various components of the chloroplast and, thereby, inhibit photosynthesis (Neff 1979).

#### **4.2.3 Trace Metals**

Vanadium and nickel are the metals that occur at the highest concentrations in crude oil. However, several other trace metals and metalloids have also been measured at concentrations in excess of 1.0 mg/L in crude oils (i.e., aluminum, barium, calcium, chromium, copper, iron, magnesium, manganese, sodium, and zinc). Of the metals that were measured in *M/T ATHOS I* source oil, chromium, copper, nickel, and zinc are the most toxic to aquatic organisms. Nevertheless, summaries of the available information on the toxicity of these substances to aquatic organisms are provided below, while freshwater and marine toxicity thresholds for trace metals in water and sediments are presented in Table 8 and 9, respectively. Overall, in our view metals are an unlikely source of toxicity from this spill, due to their low levels in the source oil and limited bioavailability.

Trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI), are the two principal forms of chromium in the environment. The fate of chromium in aquatic systems varies depending on the form of the metal that is released and the environmental conditions in the receiving water system. Generally, Cr(III) forms associations with sediment, while Cr(VI) remains in the water column. Both forms of chromium are toxic to aquatic organisms, with Cr(VI) being the more toxic of the two forms. Water-borne chromium is highly toxic to aquatic plants and invertebrates, with short- and longer-term exposures causing effects on the survival, growth,

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and reproduction. Exposure to sediment-associated chromium causes acute and chronic toxicity to sediment-dwelling organisms.

Exposure to elevated levels of water-borne chromium is known to adversely affect aquatic organisms, with toxicity influenced by chromium species present, water hardness, and pH (CCREM 1987). Of the species tested, crustaceans (water fleas, *Daphnia magna* and *Ceriodaphnia dubia*) appear to be among the most sensitive to the effects of chromium, with acute toxicity thresholds (i.e., 96-h LC<sub>50</sub>s) as low as 15.3 ug/L reported for Cr(VI) and 2000 reported for Cr(III) (Eisler 1986). In long-term toxicity tests, exposure to concentrations as low as 2.5 ug/L of Cr(VI) resulted in impaired reproduction, growth, and/or survival of water fleas (Call *et al.* 1981). Chronic toxicity thresholds for Cr(III) were somewhat higher in these species, however (i.e., 66 to 445 ug/L; USEPA 1985a). Algae appear to be nearly as sensitive to the effects of chromium as are water fleas (CCREM 1987). Although the available data from spiked-sediment toxicity tests are limited, it is apparent that sediment-associated chromium is acutely toxic to sediment-dwelling organisms (CCME 1999). In freshwater sediments, 48-h LC<sub>50</sub>s for water fleas of 195 and 167 mg/kg DW have been reported for trivalent and hexavalent chromium, respectively (Dave 1992). In marine sediments, 24 week exposure of blue mussels, *Mytilus edulis*, to 150 mg/kg DW of chromium caused reduced filtration rates. In the long-term, reduced filtration rates are likely to translate into reduced growth rates in bivalves.

Water-borne copper is highly toxic to aquatic organisms, causing effects on the survival, growth, and reproduction of fish, invertebrates, and plants. The results of laboratory studies indicate that copper salts are acutely toxic to aquatic plants, invertebrates, and fish, with LC<sub>50</sub>s as low as 6.5 ug/L reported in the literature (CCREM 1987). In long-term exposures, copper has been shown to adversely affect the behavior, growth, reproduction, and survival of aquatic organisms, with copper concentrations as low as 3.9 ug/L were found to be toxic to fish (Spear and Pierce 1979; CCREM 1987; Sauter *et al.* 1976). Even lower concentrations of copper (i.e., 1 ug/L) inhibited the growth of plant species USEPA (1980a; 1985b).

Sediment-associated copper can acutely or chronically toxic to sediment-dwelling organisms. In freshwater sediments, 10-d LC<sub>50</sub>s of 380 to 1078 mg/kg DW have been reported for the amphipod, *Hyalella azteca* (Cairns *et al.* 1984; Milani *et al.* 1996). The midge, *Chironomus tentans*, appears to less sensitive to the effects of this substance, with 10- to 14-d LC<sub>50</sub>s of 857 to 2296 mg/kg DW reported (Cairns *et al.* 1984; Milani *et al.* 1996). Adverse effects on the growth of these species have been noted at copper concentrations of 89.8 and 496 mg/kg DW, respectively (Milani *et al.* 1996). In marine sediments, long-term exposure (i.e., to 48-

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d) to copper-spiked sediments (13.6 to 38.2 mg/kg DW) resulted in delayed predator avoidance response (i.e., increased reburial time) and reduced survival rates in clams, *Protothaca staminea* and *Mya arenaria* (Phelps *et al.* 1983; 1985).

The toxicity of water-borne nickel varies depending on the species and life stage tested, duration of exposure, and water hardness (USEPA 1980b). Overall, acute and chronic toxicity thresholds for nickel ranged from 24 to 10,000 ug/L (Environment Canada 1994). In short-term toxicity tests (i.e., 96-hr) in soft waters, median lethal concentrations (i.e., LC<sub>50</sub>s) of 102 ug/L and 190 ug/L were reported for the snail, *Juga plicifera*, and the mussel, *Anodonta imbecilis*, respectively (Environment Canada 1994). Exposure to water-borne nickel for longer periods of time caused an avoidance response in rainbow trout (*Oncorhynchus mykiss*; i.e., at 24 ug/L; Giattina *et al.* 1982), reduced longevity in water fleas (*Daphnia magna*; i.e., at 40 ug/L; Munzinger 1990), impaired growth in algae (*Scenedesmus acuminatus*; i.e., at 50 ug/L; Stokes 1981), and reduced embryo survival in rainbow trout, and toads (*Gastrophryne carolinensis*; i.e., at 50 ug/L; Birge 1978). Therefore, exposure to water-borne can adversely affect the survival, growth, and reproduction of aquatic organisms. The toxicity of nickel to aquatic organisms tend to increase with decreasing water hardness.

No data from spiked-sediment toxicity tests were available to assess the effects of sediment-associated nickel on benthic invertebrates (Long and Morgan 1991; Environment Canada 1994; CCME 1999). Nevertheless, data from field studies have been used to derive sediment quality guidelines for nickel. Collectively, these sediment quality guidelines suggest that sediments with nickel concentrations in excess of roughly 50 mg/kg DW are likely to be toxic to sediment-dwelling organisms (MacDonald *et al.* 2000).

Water-borne zinc is highly toxic to aquatic organisms, with the respiratory organs being the primary site of toxic action (Eisler 1993). The toxicity of water-borne zinc varies depending on the species and life stage tested, duration of exposure, and the physical and chemical characteristics of the water. According to Eisler (1993), freshwater fish tend to be more sensitive than marine species and embryos and larvae are the most sensitive development stages. For fish and aquatic invertebrates, acute toxicity thresholds ranged from 90 to 58,100 ug/L (CCREM 1987). While acute toxicity to zinc is modified by water hardness (i.e., zinc is more toxic in soft water than in hard water), chronic toxicity is not (USEPA 1980). Zinc is also more toxic at low dissolved oxygen concentrations, high sodium levels, low levels of organic complexing agents, and low pH. The results on long-term toxicity tests indicate that zinc toxicity increases with duration of exposure. Adverse effects on the survival, growth, and reproduction of aquatic organisms start at roughly 30 ug/L to 70 ug/L, depending on the life stage and species tested.

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Exposures to sediment-associated zinc can be toxic to sediment-dwelling organisms. In freshwater sediments, an LC<sub>25</sub> of 3531 mg/kg DW was reported for the amphipod, *Hyaella azteca* (Borgmann and Norwood 1997). By comparison, Oakden *et al.* (1994) reported >50% mortality in amphipods, *Rhepoxynius abronius*, exposed to 613 mg/kg DW of zinc for 72-h in marine sediments. Swartz *et al.* (1988) reported a 10-d LC<sub>50</sub> of 276 mg/kg DW for the same species of amphipod. Collectively, these data suggest the toxicity of zinc may vary depending on the species tested, duration of exposure, and the physical-chemical characteristics of the receiving water.

#### 4.2.4 Alkanes

Because simple alkanes are highly volatile, they are among the first substances that are lost when oil is subject to weathering. This volatility limits the potential for long-term toxicity associated with exposure to these substances. Overall, alkanes are unlikely to contribute substantially to the toxicity of oil spilled into the Delaware River, with the possible exception of acute toxicity to water column species immediately following the spill.

As a group, alkanes have low to moderate aquatic toxicity (Irwin *et al.* 1997). For example, the acute LC<sub>50</sub>s of pentane, hexane, and octane to the water flea, *D. magna*, were reported to be 135, 45, and 3.3 mg/L, respectively (Irwin *et al.* 1997). Decane was more toxic to this species, as indicated by the acute LC<sub>50</sub> of 0.2 mg/L. By comparison, the Bureau of Reclamation (2002) reported acute toxicity thresholds of 3.9, 0.37, and 0.028 for hexane, octane, and decane, respectively, based on the results of 48-h toxicity tests with water fleas. Together, these data suggest that the toxicity of alkanes tends to increase with increasing numbers of carbon in the molecule. Cyclopentane and cyclohexane had similar toxicities to water fleas as did the linear forms of these substances (i.e., 150 and 45 mg/L, respectively; Irwin *et al.* 1997). The Bureau of Reclamation (2002) reported 48-h LC<sub>50</sub>s for water fleas of 3.8 and 1.5 mg/L for cyclohexane and methylcyclohexane. No data were available to evaluate the toxicity of simple or more complex alkanes in sediment.

#### 4.2.5 Other Constituents of Crude Oil

As indicated throughout other portions of this document, crude oil consists of a wide range of substances, only a few of which have been definitively quantified by laboratory analysis (i.e., various simple alkanes, MAHs, PAHs, and metals). The higher molecular weight substances in the UCM are likely to remain associated with oil globules in the environment

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and, hence, are less likely to be toxic to aquatic organisms. Nevertheless, ingestion of these oil globules could result in toxicity to benthic organisms and/or wildlife species.

Although little information is available on the toxicity of UCMs, there is some toxicological data available that suggests that these substances may contribute to the toxicity of crude oil. For example, Neff *et al.* (2000) evaluated the effects of weathering on the toxicity of three crude oils to various marine fish and invertebrates species. The results of these toxicity tests indicated that the acute toxicity of the water-accommodated fractions (WAFs) of fresh and weathered oils to six species of temperate and tropical animals ranged from not toxic (i.e., LC<sub>50</sub> of >100% WAF) to highly toxic (i.e., LC<sub>50</sub> of about 11% WAF). In fresh oils, the MAHs were considered to be the most important contributors to the acute toxicity of the WAFs. However, PAHs contributed substantially to the toxicity of the WAFs prepared from weathered oils. While MAHs, PAHs, and phenols accounted for the majority of the toxicity of WAFs from condensate or light crude oil, these substances could not account for all of the toxicity of the WAFs from middle-weight crude oil. Accordingly, Neff *et al.* (2000) concluded that the components in the UCM and polar substances (i.e., resins) contributed to the toxicity of the WAFs from heavier oil.

Several studies on mussels, *Mytilus edulis*, confirm that unresolved aromatic hydrocarbon mixtures can be toxic to aquatic organisms. More specifically, Donkin *et al.* (2001) reported that exposure to an aromatic UCM isolated from a North Sea crude oil results in a 40% reduction in feeding rates of mussels in 24-h. Similarly, feeding rates of juvenile mussels were reduced by 70% when exposed to a mono aromatic UCM (Donkin *et al.* 2003). However, later-eluting fractions containing aromatic UCMs (i.e., higher molecular weight substances) produced smaller depressions in feeding rate. These results suggest that the lighter-weight fractions in the UCMs are primarily responsible for observed toxicity. The results of an earlier study indicated that saturated hydrocarbons had not effect on the feeding rate of mussels (Thomas *et al.* 1995). In a related study, 6-cyclohexyltetralin, 7-cyclohexyl-1-methyltetralin, and 7-cyclohexyl-1-propyltetralin were all shown to be toxic to mussels, however (Smith *et al.* 2001).

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## 5.0 Preliminary Screening Evaluation of Aquatic Field Data Collected During the *M/T ATHOS I* Spill Response

During the days and weeks following the spill (November 27 to December 11, 2004), subtidal sediment samples were collected from locations along a more than 60 mile stretch of the mainstem Delaware River (and associated tributaries). Subtidal sampling locations and total PAHs concentrations are identified in Figures 5 and 6. As shown in the figures, total PAH concentrations observed in these samples range from 209 to 23,985 ug/kg.

V-SORS were towed in a wide range of locations that were identified as likely areas of subsurface oil. The highest oil recovery was in the vicinity of Tinicum Island. The oil encounter of the V-SORS tows near Tinicum Island is shown in Figure 7. Most of the oil recovered by the V-SORS was from the subtidal areas south of Tinicum Island.

A total of 80 water samples were collected in the Delaware River to quantify the PAH concentrations in water from the vicinity of the spill. Figures 8 and 9 show the results for total PAH at locations of water quality samples collected in the Delaware River from November 27 to December 8, 2004. Total PAH in the samples ranged up to 4987 ng/L total PAH. The toxicity threshold for benzo(a)pyrene was exceeded in only two of these samples; no other exceedances of the toxicity thresholds for PAHs were observed (Table 11).

Limited sampling was conducted to evaluate the levels of PAHs in the tissues of aquatic organisms. Concentrations of total PAHs found in oyster tissue sampled December 7 and 9, 2004 are shown in Figure 10. Oyster tissue PAH ranged from 15.7 to 28.5 ng/g wet weight. Concentrations of total PAHs found in catfish, perch and shad tissue samples collected December 9 and 16, 2004 are illustrated on Figure 11. Perch filet samples in the lower Bay ranged from 17 to 23.5 ng/g wet weight on December 9, 2004. Perch carcass samples in the lower Bay ranged from 36.5 to 73 ng/g wet weight on December 9, 2004. Perch filets samples in the Delaware River ranged from 72 to 239 ng/g wet weight on December 16, 2004. Perch carcass samples in the Delaware River ranged from 205 to 1143 ng/g wet weight on December 16, 2004. None of the tissue samples had PAH concentrations (i.e., benzo(a)pyrene) sufficient to adversely affect piscivorous wildlife (Sample *et al.* 1996).

Available chemistry data also include measurements of individual PAHs and trace metals (see the Preassessment Data Report for these data). For screening-level evaluation purposes, we compared measured concentrations of individual PAHs in water and sediment samples to toxicity thresholds identified in Tables 8 and 9 of this document. In addition, total PAH

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concentrations for subtidal sediment samples were compared to consensus effects range low (4000 ug/kg) and probable effects levels (23,000 ug/kg) identified in the technical literature (Long and Morgan 1991; MacDonald *et al.* 2000). The results of these comparisons are shown below.

Several subtidal sediment samples exceed individual and/or total PAH toxicity thresholds, including some close to the spill origin (e.g., SED-MAN-03 [19,735 ug/kg total PAH] and SED-TN-01 [12,847 ug/kg total PAH]). However, total PAH variability among all samples is relatively high (spanning two orders of magnitude), even within some subgroups of samples collected in relatively close proximity (e.g., SED-TN-01 [12,847 ug/kg total PAH] and SED-TN-02 [459 ug/kg total PAH]). In addition, some samples collected in areas distant from the spill have PAH concentrations that exceed toxicity thresholds, (e.g., SED-PTB-02 [11,786 ug/kg total PAH]), suggesting that pre-spill concentrations of PAHs may be substantial in some locations. Overall, we believe that additional collection and analysis of subtidal sediment data is warranted given observed exceedences of toxicity thresholds in spill affected areas and the need to better define spatial gradients of contamination within the relatively large area potentially affected by the spill (tens of river miles) and evaluate the potential contributions of spill and non-spill sources of PAHs. Existing data do not provide a sufficient basis for assessing the extent and severity of potential sediment injury.

Our screening level comparisons of water sample data suggest a relatively low likelihood of acute impacts from PAH contamination to water column biota. However, no data were located on the water column concentrations of mono aromatic hydrocarbon or other substances present in the source oil. Oysters are present only in locations more than 40 miles distant from the spill origin, and so of limited utility in this screening level evaluation. The potential implications of available fish tissue data are unclear given difficulties linking tissue contamination levels to particular sources of contamination, arising in part from their mobility, longevity and ability to metabolize PAHs. While the toxicity threshold for benzo(a)pyrene was not exceeded in any fish tissue samples, it is important to note that toxicity thresholds were not available for most of the substances that could accumulate in fish tissues.

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## 6.0 Summary

Several of the constituents present in the crude oil released during the *M/T ATHOS I* oil spill have the potential to have toxic effects on aquatic biota. MAHs are present in the source oil at low concentrations (approximately 0.02%) relative to other oils and typically are lost within hours to days after an oil spill. For these reasons, this class of compounds is of potential significance with respect to toxicity to water-column species immediately following the spill. PAHs are associated with a wide range of effects in aquatic organisms, and comprise approximately 0.6% of the source oil. Once released into the environment, the concentration of total PAH in the oil will decrease due to various environmental weathering processes that include volatilization, dissolution, and biodegradation. The rate of weathering is dependent on many factors, however the more soluble and volatile hydrocarbons (e.g. naphthalenes) may be lost within days to weeks after an oil spill, whereas the 3-6 ring PAH compounds (e.g., chrysenes) may persist for months to years. While the PAH content of the source oil is low relative to other oils, if present in sufficient concentrations it could have toxic effects. Thus, PAHs are of potential longer-term (i.e., months to a few years) toxic concern to sediment dwelling biota.

While various trace metals are present in the source oil, in our view their potential for toxicity is low given their low concentrations and limited bioavailability.

A wide variety of alkanes are present in the source oil. The simple alkanes (i.e., butane to octane) are highly volatile and moderately toxic, making them of greatest concern immediately following the spill. Only low levels of simple alkanes were measured in the source oil, however. The more complex, branched and aromatic alkanes are more likely to be persistent, possibly remaining associated with the oil matrix for months. As their bioavailability is typically low, they are of lower concern from a toxicological perspective than are the MAHs or PAHs. The unresolved complex mixture (UCM) is comprised of compounds that fall into several categories, including branched alkanes, cycloalkanes, and complex aromatics, resins/NSO compounds, and asphaltenes. Although little information is available on the toxicity of UCMs, there is some toxicological data available that suggests that these substances may contribute to the toxicity of crude oil. However, given variability in UCM content from oil to oil the tendency for high molecular weight UCM components to remain associated with oil globules, and the limited toxicological data available, in our view it is unlikely that UCM-based injury thresholds could be developed.

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Ultimately, the presence, severity and duration of aquatic biota impacts from this spill will depend on the magnitude and duration of actual exposure to the spilled oil, which we do not attempt to evaluate in this memo. While we summarize information from the literature on threshold levels at which acute and chronic effects have been observed for a variety of aquatic biota, we would need to engage in discussions with the trustees to improve our understanding of particular receptors of concern before attempting to establish specific injury thresholds for use in NRD assessment activities.

Finally, we were asked to review a presentation from Rick Green (Delaware Department of Natural Resources and Environmental Control). Our initial comments are provided in the attached Appendix. We would welcome further discussion on related issues, either in response to our comments and/or to brainstorm potential approaches for evaluating aquatic injuries caused by the *M/T ATHOS I* spill.

## 7.0 References Cited

- ATSDR (Agency for Toxic Substances and Disease Registry). 1995. Toxicological profile for polycyclic aromatic hydrocarbons. United States Department of Health and Human Services. Public Health Service. Agency for Toxic Substances and Disease Registry. Atlanta, Georgia.
- ATSDR (Agency for Toxic Substances and Disease Registry). 1997. Toxicological profile for benzene. United States Department of Health and Human Services. Public Health Service. Agency for Toxic Substances and Disease Registry. Atlanta, Georgia.
- Birge, W.J. 1978. Aquatic toxicology of trace elements of coal and fly ash. *In: Energy and Environmental Stress in Aquatic Systems*. J.H. Thorp and J.W. Gibbons, Eds.. Department of Energy Symposium Series (CONF-771114). Washington, District of Columbia. (As cited in Environment Canada 1994).
- Borgmann, U., and W.P. Norwood. 1997. Toxicity and bioaccumulation of zinc and copper in *Hyalella azteca* exposed to metal-spiked sediments. *Canadian Journal of Fisheries and Aquatic Science* 54(5):1046-1054.
- Bureau of Reclamation. 2002. Final environmental assessment Animas-La Plata Project, Ridges Basin Dam and Reservoir pre-construction facilities relocation. (Appendix A, Petroleum Products Spill Analysis). United States Department of the Interior Bureau of Reclamation. Upper Colorado Region.
- Cairns, M.A., A.V. Nebeker, J.H. Gakstatter, and W.L. Griffis. 1984. Toxicity of copper-spiked sediments to freshwater invertebrates. *Environmental Toxicology and Chemistry* 3:435-445.
- Caldwell, R.S., E.M. Caldarone, and M.H. Mallon. 1977. Effects of a seawater-soluble fraction of cook inlet crude oil and its major aromatic components on larval stages of the Dungeness crab, *Cancer magister*. *In: Fate and Effects of Petroleum Hydrocarbons in Marine Ecosystems and Organisms*. D.A. Wolfe, Ed. Pergamon Press. New York, New York.
- Call, D.J., L.T. Brooke, N. Ahmad, and D.D. Vaishnav. 1981. Aquatic pollutant hazard assessments and development of a hazard prediction technology by quantitative structure activity relationships. Second Quarterly Report to the USEPA Center for Lake Superior Environmental Studies. University of Wisconsin. Superior, Wisconsin. (As cited in CCREM 1987).
-

- Carls, M.G., S.D. Rice and J.E. Hose. 1999. Sensitivity of fish embryos to weathered crude oil: Part I. Low-level exposure during incubation causes malformations, genetic damage, and mortality in larval Pacific herring (*Clupea pallasii*). *Environmental Toxicology and Chemistry* 18(3):481-493.
- Carls, M.G., J.E. Hose, R.E. Thomas, and S.D. Rice. 2000. Exposure of Pacific herring to weathered crude oil: Assessing effects of ova. *Environmental Toxicology and Chemistry* 19(6):1649-1659.
- CCME (Canadian Council of Ministers of the Environment). 1999. Canadian environmental quality guidelines. Guidelines and Standards Division. Environment Canada. Winnipeg, Manitoba.
- CCREM (Canadian Council of Resource and Environment Ministers). 1987. Canadian Water Quality Guidelines. Prepared by the Task Force on Water Quality Guidelines, Canadian Council of Resource and Environment Ministers.
- Columbia Analytical Services. 2005. Lab sheets for the concentrations of metals in Source Oil from the M/T Athos 1.
- Dave, G. 1992. Sediment toxicity in lakes along the river Kolbacksan, central Sweden. *Hydrobiologia* 235/236:419-433. (As cited in CCME 1999).
- Davis, P.H., T.W. Schultz, and R.B. Spies. 1981. Toxicity of Santa Barbara seep oil to starfish embryos: Part 2 - The growth bioassay. *Marine Environmental Research* 5:287-294.
- Donkin, P., E.L. Smith, and S.J. Rowland. 2003. Toxic effects of unresolved complex mixtures of aromatic hydrocarbons accumulated by mussels, *Mytilus edulis*, from contaminated field sites. *Environmental Science & Technology* 37(21):4825-4830.
- Douglas, G.S., R.C. Prince, E.L. Butler, and W.G. Steinhauer. 1994. Use of internal chemical indicators in petroleum and refined products to evaluate the extent of biodegradation. *In: Hydrocarbon Bioremediation*. Hinchee, R.E., Alleman, B.C., Hoepfel, R.E., Miller, R.N., Eds. Lewis Publishers. Ann Arbor, Michigan.
- Douglas, G.S., W.A. Burns, A.E. Bence, D.S. Page, and P.B. Boehm. 2004. Optimizing detection limits for the analysis of petroleum hydrocarbons in complex samples. *Environmental Science and Technology* 38(14):3958-3964.
- Eisler, R. 1986. Chromium hazards to fish, wildlife, and invertebrates: A synoptic review. *Biological* 85(1.6). Contaminant Hazard Reviews Report Number 6. Fish and Wildlife Service. United States Department of the Interior. Laurel, Maryland.
-

- Eisler, R. 1987. Polycyclic aromatic hydrocarbon hazards to fish, wildlife, and invertebrates: A synoptic review. Biological Report, Publication No. 85(1.11). Contaminant Hazard Reviews Report No. 11. United States Department of the Interior. Fish and Wildlife Service. Patuxent Wildlife Research Center. Laurel, Maryland.
- Eisler, R. 1993. Zinc hazards to fish, wildlife, and invertebrates: A synoptic review. Biological Report 10. Contaminant Hazard Reviews Report 26. United States Fish and Wildlife Service. Laurel, Maryland.
- Environment Canada. 1994. Canadian Sediment Quality Guidelines for Polycyclic Aromatic hydrocarbons. Environment Canada. 195. Guidelines Division. Evaluation and Interpretation Branch. Ecosystem Conservation Directorate. Environment Canada
- Environment Canada and Health Canada. 1992. Canadian Environmental Protection Act. Toluene. Priority Substances List Assessment Report. ISBN 0-662-19950-2. 26 pp. Government of Canada. Ottawa, Ontario.
- Environment Canada and Health Canada. 1993a. Canadian Environmental Protection Act. Benzene. Priority Substances List Assessment Report. ISBN 0-662-20434-4. 39 pp. Government of Canada. Ottawa, Ontario.
- Environment Canada and Health Canada. 1993b. Canadian Environmental Protection Act. Xylenes. Priority Substances List Assessment Report. ISBN 0-662-21040-9. 32 pp. Government of Canada. Ottawa, Ontario.
- Environment Canada and Health Canada. 1994. Canadian Environmental Protection Act. Polycyclic aromatic hydrocarbons. Priority Substances List Assessment Report. ISBN 0-662-22209-1. 61 pp. Government of Canada. Ottawa, Ontario.
- Fryzinger, G.S., R.B. Gaines, L. Xu, and C.M. Reddy. 2003. Resolving the unresolved complex mixture in petroleum-contaminated sediments. Environmental Science and Technology 37(8):1653-1662.
- GERG (Geochemical and Environmental Research Group). 2005. Lab sheets for PAH concentrations in Source Oil from the M/T Athos I.
- Giattina, J.D., R.R. Garton, and D.G. Stevens. 1982. Avoidance of copper and nickel by rainbow trout as monitored by a computer-based data acquisition system. Transactions of the American Fisheries Society 111:491-504. (As cited in Government of Canada 1994).
- Hayes, M.O., R. Hoff, J. Michel, D. Scholz, and G. Shigenaka. 1992. Introduction to coastal habitats and biological resources for Oil Spill Response. HMRAD-92-4. Coastal Monitoring and Bioeffects Assessment Division. National Oceanic and Atmospheric Administration. Seattle, Washington.
-

- Heidelberger, C. 1976. Studies on the mechanisms of carcinogenesis by polycyclic aromatic hydrocarbons and their derivatives. *In: Carcinogenesis - A Comprehensive Survey*, Vol. 1. Polycyclic Aromatic Hydrocarbons. R. Freudenthal and P.W. Jones (Eds.). New York, New York. Raven Press.
- Irwin, R.J., M. Van Mouwerik, L. Stevens. M.D. Seese and W. Basham. 1997. Environmental contaminants encyclopaedia (alkanes entry). National Parks Service. Water Resources Division. Fort Collins, Colorado.
- Kerr, J.M., S.J. McMillen, R.I. Magaw, R.H. Melton, and G. Naughton. 2001. Risk-based soil screening levels for crude oil: The role of polyaromatic hydrocarbons. *In: Risk-Based Decision-Making for Assessing Petroleum Impacts at Exploration and Production Sites*. S.J. McMillen, R.I. Magaw, and R.L. Carovillano (Eds.). ISBN 0-9717288-0-1. Department of Energy and PERF.
- Khan, R.A. and J.W. Kiceniuk. 1989. Sublethal effects of crude oil on a cold-water marine leech, *Johanssonia arctica*, following chronic exposure. *Bulletin Environmental Contamination and Toxicology* 43:590-596.
- Larson, R.A., D.W. Blankenship, and L.L. Hunt. 1976. Toxic hydroperoxides: photochemical formation from petroleum constituents. pp. 298-308. *In: Sources, Effects and Sinks of Hydrocarbons in the Aquatic Environment*. Washington, District of Columbia. American Institute of Biological Sciences.
- Larson, R.A., L.L. Hunt and D.W. Blankenship. 1977. Formation of toxic products from a #2 fuel oil by photooxidation. *Environmental Science and Technology* 11:492-496.
- Lee, R.F., J. Stolzenbach, S. Singer, and K.R. Tenore. 1981. Effects of crude oil in growth and mixed function oxygenase activity in polychaetes, *Nereis* sp. *In: Biological Monitoring of Marine Pollutants* 323-334.
- Lock, M.A., R.R. Wallace, D.R. Barton and S. Charlton. 1981. The effects of synthetic crude oil on microbial and macroinvertebrate benthic river communities - Part I: Colonisation of Synthetic Crude Oil Contaminated Substrata. *Environmental Pollution (Series A)* 24:207-217.
- Long, E.R. and L.G. Morgan. 1991. The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52. National Oceanic and Atmospheric Administration. Seattle, Washington. pp. 175 + appendices.
- MacDonald, D.D., C.G. Ingersoll, and T.A. Berger. 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology* 39:20-31.
-

- MacDonald D.D., R. Gale, W. Brumbaugh, C.G. Ingersoll, D.E. Smorong, S. Hamilton, and Y. Muirhead. 2005. Guidance on the Selection of analytical detection limits for generating water chemistry, sediment chemistry, and tissue residue data for use in aquatic risk assessments. Draft. Prepared for Office of Environmental Policy and Compliance. Natural Resources Trust and Response Team. Department of the Interior. Washington, District of Columbia and Emergency Response Team. United States Environmental Protection Agency. Edison, New Jersey.
- MacKay, D., W.Y. Shiu, and K.C. Ma. 1992. Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. Polynuclear aromatic hydrocarbons, polychlorinated dioxins, and dibenzofurans. Chelsea, Michigan, U.S.A.: Lewis. 597 p. (As cited in Neff *et al.* 2005).
- Mackenzie, Andrew S. 1984. Applications of biological markers in petroleum geochemistry. *In: Advances in Petroleum Geochemistry.* J. Brooks and D. Welte, Eds. Academic Press, London.
- Magaw, R.I., S.J. McMillen, W.R. Gala, J.H. Trefry and R.P. Trocine. 2001. Risk evaluation of metals in crude oil. *In: Risk-Based Decision-Making for Assessing Petroleum Impacts at Exploration and Production Sites.* S.J. McMillen, R.I. Magaw, and R.L. Carovillano (Eds.). ISBN 0-9717288-0-1 Department of Energy and PERF.
- Malins, D.C., M.M. Krahn, M.S. Myers, L.D. Rhodes, D.W. Brown, C.A. Krone, B.B. McCain and S-L Chan. 1985. Toxic chemicals in sediments and biota from a creosote-polluted harbor: relationships with hepatic neoplasms and other hepatic lesions in English sole (*Parophrys vetulus*). *Carcinogenesis* 6:1463-1469.
- McCoy, D.L., J.M. Jones, J.W. Anderson, M. Harmon, I. Hartwell, and J. Hameedi. 2002. Distribution of cytochrome P4501A1-inducing chemicals in sediments of the Delaware River-Bay system, USA. *Environmental Toxicology and Chemistry* 21(8):1618-1627
- Michel, J., D. Simecek-Beatty, E. Levine, W. Lehr, G. Ott, V. Trumbull, C. Pfeifer, M. Ploen, and J. Elliott. 2005. Submerged oil assessment and recovery at the ATHOS oil spill. Proceedings of the 2005 International Oil Spill Conference. Miami Beach, Florida. May 2005.
- Milani, D., K.E. Day, D.J. McLeay, and R.S. Kirby. 1996. Recent intra- and interlaboratory studies related to the development and standardization of Environment Canada's biological test methods for measuring sediment toxicity using freshwater amphipods (*Hyalella azteca*) or midge larvae (*Chironomus riparius*). Environmental Protection Service. Environment Canada. Burlington, Ontario.
- Moldowan, J.M., W.K. Seifert, and E.J. Gallegos. 1985. Relationship between petroleum composition and depositional environment of petroleum source rocks. *Bulletin of the American Association of Petroleum Geology* 69:255-1268.
-

- Munzinger, A. 1990. Effects of nickel on *Daphnia magna* during chronic exposure and alterations in the toxicity to generations pre-exposed to nickel. *Water Research* 24:845-852. (As cited in Government of Canada 1994).
- National Research Council. 2003. *Oil in the Sea III*. The National Academies Press. Washington, District of Columbia.
- Neff, J.M. 1979. *Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*. Applied Science Publishers Ltd., London.
- Neff, J.M. and W.A. Burns. 1996. Estimation of polycyclic aromatic hydrocarbon concentrations in the water column based on tissue residues in mussels and salmon: An equilibrium partitioning approach. *Environmental Toxicology and Chemistry* 15:2240-2253. (As cited in Neff *et al.* 2005).
- Neff, J.M., S. Ostazeski, W. Gardiner, and I. Stejskal. 2000. Effects of weathering on the toxicity of three offshore Australian crude oils and a diesel fuel to marine animals. *Environmental Toxicology and Chemistry* 19(7):1809-1821.
- Neff, J.M., S.A. Stout, and D.G. Gunster. 2005. Ecological risk assessment of polycyclic aromatic hydrocarbons in sediments: Identifying sources and ecological hazard. *Integrated Environmental Assessment and Management* 1(1):22-33.
- NRCC (National Research Council of Canada). 1983. *Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Formation, Sources, Fate and Effects on Aquatic Biota*. NRC Associate Committee on Scientific Criteria for Environmental Quality. Publication No. NRCC 18981. 209 pp.
- Oakden, J.M., J.S. Oliver, and A.R. Flegal. 1984. Behavioural responses of a phoxocephalid amphipod to organic enrichment and trace metals in sediments. *Marine Ecology-Progress Series* 14:253-257.
- Paine, M.D., W.C. Leggett, J.K. McRuer, and K.T. Frank. 1991. Effects of incubation in oiled sediment on emergence of capelin (*Mallotus villosus*) larvae. *Canadian Journal of Fish and Aquatic Sciences* 48(11):2228-2239.
- Peterson, C.H. 2001. The "Exxon Valdez" oil spill in Alaska: Acute, indirect and chronic effects on the ecosystem. *Advances in Marine Biology* 39:1-103.
- Peterson, C.H., S.D. Rice, J.W. Short, D. Esler, J.L. Bodkin, B.E. Ballachey, and D.B. Irons. 2003. Long-term ecosystem response to the Exxon Valdez oil spill. *Science* 302:2082-2086.
- Phelps, H.L., J.T. Hardy, W.H. Pearson, and C.W. Apts. 1983. Clam burrowing behaviour: Inhibition by copper-enriched sediment. *Marine Pollution Bulletin* 14(12):452-455.
-

- Phelps, H.L., W.H. Pearson, and J.T. Hardy. 1985. Clam burrowing behaviour and mortality related to sediment copper. *Marine Pollution Bulletin* 16(8):309-313.
- Polaris Applied Sciences, Inc. 2005. Lab sheets for the concentrations of polycyclic aromatic hydrocarbon data in Source Oil from the M/T Athos I.
- Ran, Y., Y. He, G. Yang, J.L. H. Johnsib, and S.H. Yalkowsky. 2002. Estimation of aqueous solubility of organic compounds by using the general solubility equation. *Chemosphere* 48:487-509. (As cited in Neff *et al.* 2005).
- Rixey, W.G. 2001. An evaluation of benzene risk. *In: Risk-Based Decision-Making for Assessing Petroleum Impacts at Exploration and Production Sites.* S.J. McMillen, R.I. Magaw, and R.L. Carovillano, Eds. ISBN 0-9717288-0-1. Department of Energy and PERF.
- Sample, B., D. Opresko, and G. Suter II. 1996. Toxicological benchmarks for wildlife: 1996 Revision. ES/ER/TM-86/R3. Prepared by the Risk Assessment Program, Health Sciences Research Division, Oak Ridge, Tennessee. Prepared for the United States Department of Energy. (As cited in CDM 1999.)
- Sauter, S., K.S. Buxton, K.J. Macek, and S.R. Petrocelli. 1976. Effects of exposure to heavy metals on selected freshwater fish. Toxicity of copper, cadmium, chromium, and lead to eggs and fry of seven fish species. EPA-600/3-76-105. United States Environmental Protection Agency. Duluth, Minnesota. (As cited in CCREM 1987).
- Seifert, W.K., J.M. Moldowan, and G.J. DeMaison. 1984. Source correlation of biodegraded oils. *Organic Geochemistry* 6:633-643.
- Smith, E., E. Wraige, P. Donkin, and S. Rowland. 2001. Hydrocarbon humps in the marine environment: Synthesis, toxicity and aqueous solubility of monoaromatic compounds. *Environmental Toxicology and Chemistry* 20(11):2428-2432.
- Sofer, Z. 1984. Stable carbon isotope compositions of crude oils: Application to source depositional environments and petroleum alteration. *Bulletin of the American Association of Petroleum Geology* 68:31-49.
- Spear, P.A. and R.C. Pierce. 1979. Copper in the Aquatic environment: Chemistry, distribution, and toxicology. NRCC No. 15454. Associate Committee on Scientific Criteria for Environmental Quality. National Research Council of Canada. Ottawa, Ontario.
- Spies, R.B., D.D. Hardin, and J.P. Toal. 1988. Organic enrichment or toxicity? A comparison of the effects of kelp and crude oil in sediments on the colonization and growth of benthic infauna. *Journal Exp. Mar. Biol. Ecol.* 124(3):261-282.
-

- Stokes, P.M. 1981. Multiple Metal Tolerance in Copper-tolerant Green Algae. *Journal of Plant Nutrition*. 3:667-678. (As cited in Government of Canada 1994).
- Stout, S.A., A.D. Uhler, K.J. McCarthy, and S.D. Emsbo-Mattingly. 2002. Chemical fingerprinting of hydrocarbons. *In: Introduction to Environmental Forensics*. B. Murphy and R. Morrison, Eds. Academic Press.
- Swartz, R.C., P.F. Kemp, D.W. Schults and J.O. Lamberson. 1988. Effects of mixtures of sediment contaminants on the marine infaunal amphipod, *Rhepoxynius abronius*. *Environmental Toxicology and Chemistry* 7:1013-1020.
- Swartz, R.C., P.F. Kemp, D.W. Schults, G.R. Ditsworth and R.J. Ozretich. 1989. Acute toxicity of sediment from Eagle Harbor, Washington, to the infaunal amphipod *Rhepoxynius abronius*. *Environmental Toxicology and Chemistry* 8:215-222.
- Thomas, K.V., P. Donkin and S.J. Rowland. 1995. Toxicity enhancement of an aliphatic petrogenic unresolved complex mixture (UCM) by chemical oxidation. *Water Research* 29(1):379-382.
- Tissot, B.P. and D.H. Welte. 1984. *Petroleum Formation and Occurrence*. Springer-Verlag. New York, New York.
- USEPA (United States Environmental Protection Agency). 1980a. Ambient water quality criteria for copper. EPA-440/5-80-036. Criteria and Standards Division. Office of Regulations and Standards. Washington, District of Columbia.
- USEPA (United States Environmental Protection Agency). 1980b. Ambient water quality criteria for nickel. EPA-440/5-80-060. Criteria and Standards Division. Office of Regulations and Standards. Washington, District of Columbia. (As cited in CCREM 1987).
- USEPA (United States Environmental Protection Agency). 1985a. Ambient water quality criteria for chromium - 1984. EPA-440/5-84-029. Criteria and Standards Division. Office of Regulations and Standards. Washington, District of Columbia.
- USEPA (United States Environmental Protection Agency). 1985b. Ambient water quality criteria for copper - 1984. EPA-440/5-84-031. Criteria and Standards Division. Office of Regulations and Standards. Washington, District of Columbia.
- USEPA (United States Environmental Protection Agency). 2003. Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: PAH Mixtures. EPA-600-R-02-013. Office of Research and Development. Washington, District of Columbia.
-

- Vangilder, L.D., Peterle, T. J. 1980. South Louisiana Crude oil and DDE in the diet of mallard hens: Effects on reproduction and duckling survival. *Bulletin of Environmental Contamination and Toxicology*. 25(1):23-28.
- Varanasi, U. (Ed.). 1989. *Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*. CRC Press Inc., Boca Raton, Florida. 341 pp.
- Warton, B., R. Alexander, and R.I. Kagi. 1999. Characterization of the ruthenium tetroxide oxidation products from the aromatic unresolved complex mixture of a biodegraded crude oil. *Organic Geochemistry* 30:1255-1272.

**Table 1. Physical and chemical properties of source oil from the *M/T ATHOS I*.**

Measurement	Result	Units	Source
<b>Visual Observations</b>	Heavy degraded crude oil, tar like, viscosity like cold honey, does not appear to form emulsions		Michel <i>et al.</i> (2005)
<b>General Physical Properties</b>			
Viscosity	50,000	cSt@ambient	Michel <i>et al.</i> (2005)
Oil density	0.973-0.978	g/mL	Michel <i>et al.</i> (2005)
API Gravity (estimated)	13		
% lost to topping <sup>1</sup>	2.5	% oil	GERG
<b>General Chemical Properties</b>			
GC/FID Chromatogram	Oil carbon range from n-C7 through n-C40. Oil is a biodegraded crude oil with a dominant UCM.	NA	GERG, B&B
GC/MS Total Ion Chromatogram			
Saturates	35.9	% oil	GERG
Aromatics	49.2	% oil	GERG
Resins/NSO <sup>2</sup>	3	% oil	GERG
Asphaltenes	12.9	% oil	GERG
<b>Compound Specific Measurements</b>			
MAH (BTEX)	225	mg/kg oil	Lancaster
Total Reported Volatile HCs	660	mg/kg oil	Lancaster
16 Priority Pollutant PAH	338-343	mg/kg oil	GERG, B&B, Lancaster
Total PAH	6460-6546	mg/kg oil	GERG, B&B
Metals			Columbia Analytical Services

<sup>1</sup>The amount of volatile hydrocarbons lost from the oil when heated to 90 oC, for 4 hours under a vacuum. This analysis provides an estimate of the amount of oil that may be lost due to evaporation.

<sup>2</sup>May be underestimated, color remained on separation column after resins fraction collected. Mass balance for SARA compounds 69%, data subsequently normalized to 100%.

**Table 2. Concentrations of mono aromatic substances in source oil from the *M/T ATHOS I*.**

Analyte	Units	Sample Result (4419595)	Method Detection Limit
Methyl t-Butyl Ether	µg/kg	ND	1,000
Benzene	µg/kg	14,000	1,000
Toluene	µg/kg	33,000	1,000
Ethylbenzene	µg/kg	50,000	1,000
m,p-Xylene	µg/kg	100,000	2,000
o-Xylene	µg/kg	28,000	1,000
Isopropylbenzene (Cumene)	µg/kg	58,000	1,000
n-Propylbenzene	µg/kg	39,000	1,000
1,3,5-Trimethylbenzene	µg/kg	50,000	1,000
tert-Butylbenzene	µg/kg	ND	30,000
1,2,4-Trimethylbenzene	µg/kg	94,000	1,000
sec-Butylbenzene	µg/kg	65,000	1,000
p-Isopropyltoluene	µg/kg	48,000	1,000
n-Butylbenzene	µg/kg	81,000	1,000

**Table 3. Concentrations of PAHs in source oil from the *M/T ATHOS I* (Polaris Applied Sciences, Inc. 2005).**

Target Compounds [Surrogate Corrected Concentration (ng/mg)]	Sample: ETX3872.D Sample 1 Tank Center 7	Sample: ETX3872D.D Duplicate Sample 1 Tank Center 7
Naphthalene	61.3	63.1
C1-Naphthalenes	93.5	96.1
C2-Naphthalenes	314	343
C3-Naphthalenes	373	401
C4-Naphthalenes	306	331
Benzothiophene	4.1*	4.4*
C1-Benzothiophenes	25.4	27.7
C2-Benzothiophenes	69.2	74.0
C3-Benzothiophenes	125	122
Biphenyl	14.5	16.3
Acenaphthylene	<10	<10
Acenaphthene	14.7	16.2
Dibenzofuran	10.3	9.5*
Fluorene	36.6	37.9
C1-Fluorenes	78.5	81.0
C2-Fluorenes	188	204
C3-Fluorenes	187	197
Carbazole	<10	<10
Anthracene	<10	<10
Phenanthrene	158	147
C1-Phenanthrene/Anthracenes	392	370
C2-Phenanthrene/Anthracenes	538	499
C3-Phenanthrene/Anthracenes	572	535
C4-Phenanthrene/Anthracenes	334	316
Dibenzothiophene	54.9	50.8
C1-Dibenzothiophenes	245	225
C2-Dibenzothiophenes	513	474
C3-Dibenzothiophenes	564	562
Fluoranthene	4.1*	4.5*
Pyrene	16.0	16.4
C1-Fluoranthenes/Pyrenes	93.3	84.7
C2-Fluoranthenes/Pyrenes	132	122
C3-Fluoranthenes/Pyrenes	73.8	74.6
Naphthobenzothiophene	54.0	55.8
C1-Naphthobenzothiophenes	163	155
C2-Naphthobenzothiophenes	253	264
C3-Naphthobenzothiophenes	194	184
Benz(a)anthracene	6.8*	6.8*
Chrysene	27.4	27.5
C1-Chrysenes	74.4	75.6

**Table 3. Concentrations of PAHs in source oil from the *M/T ATHOS I* (Polaris Applied Sciences, Inc. 2005).**

Target Compounds [Surrogate Corrected Concentration (ng/mg)]	Sample: ETX3872.D Sample 1 Tank Center 7	Sample: ETX3872D.D Duplicate Sample 1 Tank Center 7
C2-Chrysenes	91.0	93
C3-Chrysenes	43.5	43.8
C4-Chrysenes	5.6*	5.4*
Benzo(b)fluoranthene	9.6*	10.0
Benzo(k)fluoranthene	1.3*	1.2*
Benzo(e)pyrene	14.1	15.1
Benzo(a)pyrene	3.5*	3.7*
Perylene	9.8*	10.2
Indeno(1,2,3-c,d)pyrene	1.2*	1.1*
Dibenzo(a,h)anthracene	0.8*	0.7*
Benzo(g,h,i)perylene	2.0*	2.1*
Total PAHs	6546	6460

\*<Method Detection Limit

**Table 4. Concentrations of PAHs in source oil from the *M/T ATHOS I* (GERG 2005).**

Analyte	Sample Identifier (GERG ID)				
	C45279	W44253	W44254	W44259	W44260
<i>Polycyclic Aromatic Hydrocarbons</i>					
Naphthalene	60.24	58.3	61.3	61.3	63.7
C1-Naphthalenes	129.62	132.8	137.8	130.8	135.5
C2-Naphthalenes	254.17	264.6	271.9	266.3	274.7
C3-Naphthalenes	263.56	296.2	299.3	301.7	309.1
C4-Naphthalenes	188.07	212.3	201.9	206.2	216.0
Biphenyl	13.27	13.1	13.7	11.2	12.6
Acenaphthylene	8.64*	7.8*	8.9*	7.7*	8.7*
Acenaphthene	21.45	17.9	18.9	18.4	18.6
Fluorene	50.78	46.6	46.7	46.2	49.3
C1-Fluorenes	120.08	119.5	127.9	116.3	131.1
C2-Fluorenes	227.34	219.0	220.8	216.7	238.4
C3-Fluorenes	271.21	287.7	287.9	288.4	336.5
Phenanthrene	87.19	86.0	91.6	84.2	94.4
Anthracene	8.86*	6.7*	7.2*	7.6*	8.6*
C1-Phenanthrenes/Anthracenes	228.96	222.4	246.3	225.1	260.5
C2-Phenanthrenes/Anthracenes	338.85	314.7	333.7	328.2	358.1
C3-Phenanthrenes/Anthracenes	282.08	275.8	287.8	290.0	316.3
C4-Phenanthrenes/Anthracenes	208.45	240.5	230.5	255.0	258.5
Dibenzothiophene	40.98	36.4	42.6	38.3	42.1
C1-Dibenzothiophenes	162.97	127.3	138.0	125.5	146.4
C2-Dibenzothiophenes	367.72	348.6	369.4	365.9	408.4
C3-Dibenzothiophenes	373.04	346.5	373.2	369.2	406.8
Fluoranthene	3.95*	3.1*	4.1*	3.0*	4.7*
Pyrene	16.44	14.3	17.5	16.0	18.6
C1-Fluoranthenes/Pyrenes	84.53	78.1	79.8	83.7	87.8
C2-Fluoranthenes/Pyrenes	123.87	124.0	137.3	131.1	152.0
C3-Fluoranthenes/Pyrenes	139.00	173.4	168.5	184.6	207.6

**Table 4. Concentrations of PAHs in source oil from the *M/T ATHOS I* (GERG 2005).**

Analyte	Sample Identifier (GERG ID)				
	C45279	W44253	W44254	W44259	W44260
<i>Polycyclic Aromatic Hydrocarbons</i>					
Benzo(a)anthracene	10.40	5.3*	6.3*	7.1*	6.0*
Chrysene	36.91	32.8	38.8	38.7	41.0
C1-Chrysenes	79.65	82.8	94.1	90.5	95.5
C2-Chrysenes	90.14	123.4	144.6	135.4	141.8
C3-Chrysenes	47.12	36.8	48.1	45.8	45.4
C4-Chrysenes	9.84*	11.2	5.7*	10.8	14.4
Benzo(b)fluoranthene	7.86*	8.0*	8.3*	8.1*	8.6*
Benzo(k)fluoranthene	2.07*	1.1*	1.2*	1.0*	0.3*
Benzo(e)pyrene	14.92	12.9	15.5	13.1	14.7
Benzo(a)pyrene	6.82*	5.5*	3.4*	5.3*	3.8*
Perylene	8.90*	18.1	12.6	16.6	16.4
Indeno(1,2,3-c,d)pyrene	4.99*	4.4*	2.7*	3.3*	2.7*
Dibenz(a,h)anthracene	7.27*	5.2*	5.2*	3.7*	4.2*
Benzo(g,h,i)perylene	8.25*	6.2*	4.9*	5.9*	4.5*
2-Methylnaphthalene	70.02	71.8	74.4	70.3	73.8
1-Methylnaphthalene	59.60	60.9	63.4	60.4	61.7
2,6-Dimethylnaphthalene	139.18	132.1	140.7	129.2	143.8
1,6,7-Trimethylnaphthalene	101.52	95.5	100.7	94.7	107.5
1-Methylphenanthrene	65.53	58.2	66.9	60.2	69.7

All samples were from Tank Center 7.

\*<Method Detection Limit of 10.0

**Table 5. Concentrations of metals in source oil from the *M/T ATHOS I* (Columbia Analytical Services 2005).**

Analyte	Sample	Duplicate	Analytical Method
<i>Metals (mg/kg wet weight)</i>			
Aluminum	8.6	7.2	USEPA Method 6010B
Antimony	<5.0	<5.0	USEPA Method 6010B
Barium	1.3	1.3	USEPA Method 6010B
Beryllium	<0.5	<0.5	USEPA Method 6010B
Cadmium	<0.5	<0.5	USEPA Method 6010B
Calcium	41.8	40.9	USEPA Method 6010B
Chromium	1.5	<1.0	USEPA Method 6010B
Cobalt	<1.0	<1.0	USEPA Method 6010B
Copper	1.7	1.3	USEPA Method 6010B
Iron	43.0	37.6	USEPA Method 6010B
Lead	<10	<10	USEPA Method 6010B
Magnesium	18.4	16.3	USEPA Method 6010B
Manganese	1.1	1.0	USEPA Method 6010B
Nickel	54.8	59.3	USEPA Method 6010B
Potassium	<200	<199	USEPA Method 6010B
Silicon	<50	<50	USEPA Method 6010B
Silver	<1.0	<1.0	USEPA Method 6010B
Sodium	34.7	33.4	USEPA Method 6010B
Tin	<10	<10	USEPA Method 6010B
Vanadium	440	453	USEPA Method 6010B
Zinc	3.8	3.8	USEPA Method 6010B

**Table 6. Relative impact of weathering processes on crude oils and heavy distillates  
(National Research Council 2003).**

<b>Process</b>	<b>Crude Oils</b>	<b>Heavy Distillates</b>
Persistence	Months	Years
Evaporation	Moderate	Low
Emulsification	Moderate	Moderate > Low
Dissolution	Moderate	Low
Oxidation	Moderate	Low
Horizontal Transport	Moderate	High
Vertical Transport	Moderate	Low
Sedimentation	Moderate	High
Shoreline Stranding	High	High
Tarballs	Moderate	High

**Table 7. Log  $K_{ow}$ , freshwater solubility, and estimated acute and chronic toxicity of PAH frequently found in crude and refined petroleum. Solubility and toxicity values are micrograms per liter ( $\mu\text{g/L}$  ppb). Log  $K_{ow}$  values and solubilities are from Mackay *et al.* (1992); Neff and Burns (1996); and Ran *et al.* (2002). Table taken directly from Neff *et al.* (2005).**

Polycyclic Aromatic Hydrocarbon	Log $K_{ow}$	Freshwater Solubility	Acute Toxicity	Chronic Toxicity
Naphthalene	3.37	33720	4870	970
C <sub>1</sub> -Naphthalenes	3.87	27160	1420	284
C <sub>2</sub> -Naphthalenes	4.37	4725	410	81
C <sub>3</sub> -Naphthalenes	4.90	2100	130	17
C <sub>4</sub> -Naphthalenes	5.55	NV <sup>a</sup>	42	4.1
Biphenyl	3.95	7728	1420	250
Acenaphthylene	4.07	16688	1181	180
Acenaphthene	3.92	16908	1360	270
Dibenzofuran	4.12	4225	860	135
Fluorene	4.18	2045	730	150
C <sub>1</sub> -Fluorenes	4.97	1090	96	19
C <sub>2</sub> -Fluorenes	5.2	NV	56	11
C <sub>3</sub> -Fluorenes	5.5	NV	16	5.3
Anthracene	4.54	79.6	300	60
Phenanthrene	4.46	1100	367	55
C <sub>1</sub> -Phenanthrenes	5.14	272	64	13
C <sub>2</sub> -Phenanthrenes	5.51	NV	26	5.1
C <sub>3</sub> -Phenanthrenes	6.0	NV	7.4	1.5
C <sub>4</sub> -Phenanthrenes	6.51	NV	2.0	0.40
Dibenzothiophene	4.49	1136	350	70
C <sub>1</sub> -Dibenzothiophenes	4.86	NV	140	28
C <sub>2</sub> -Dibenzothiophenes	5.5	NV	27	5.4
C <sub>3</sub> -Dibenzothiophenes	5.73	NV	16	3.1
Fluoranthene	5.22	261	55	11
Pyrene	5.18	134	61	12
C <sub>1</sub> -Fluoranthenes/pyrenes	5.72	NV	15	3.1
Benz[a]anthracene	5.91	14.7	9.8	2.0
Chrysene	5.86	6.0	11	2.2
C <sub>1</sub> -Chrysenes	6.42	62.2	2.7	0.53
C <sub>2</sub> -Chrysenes	6.88	25.0	0.8	0.16
C <sub>3</sub> -Chrysenes	7.44	NV	0.2	0.04
C <sub>4</sub> -Chrysenes	8.0	NV	0.06	0.01
Benzo[b]fluoranthene	5.8	4.1	14	2.9
Benzo[k]fluoranthene	6.0	0.8	8.6	1.7
Benzo[e]pyrene	6.04	4.0	7.6	1.5
Benzo[a]pyrene	6.04	1.4	7.6	1.5

**Table 7. Log  $K_{ow}$ , freshwater solubility, and estimated acute and chronic toxicity of PAH frequently found in crude and refined petroleum. Solubility and toxicity values are micrograms per liter ( $\mu\text{g/L}$  ppb). Log  $K_{ow}$  values and solubilities are from Mackay *et al.* (1992); Neff and Burns (1996); and Ran *et al.* (2002). Table taken directly from Neff *et al.* (2005).**

Polycyclic Aromatic Hydrocarbon	Log $K_{ow}$	Freshwater Solubility	Acute Toxicity	Chronic Toxicity
Perylene	6.25	0.4	4.3	0.86
Indeno[1,2,3-cd]pyrene	7.0	6	0.64	0.13
Dibenz[a,h]anthracene	6.75	0.5	1.3	0.25
Benzo[g,h,i]perylene	6.5	0.3	2.4	0.49

<sup>a</sup> NV = No solubility value could be found.

**Table 8. Toxicity thresholds for surface water (freshwater and saltwater).**

<b>Class/Analyte Name</b>	<b>Chemical Abstracts Number</b>	<b>Freshwater Toxicity Threshold (<math>\mu\text{g/L}</math>)<sup>1</sup></b>	<b>Saltwater Toxicity Threshold (<math>\mu\text{g/L}</math>)<sup>2</sup></b>
<i>Metals</i>			
Aluminum	7429-90-5	88.4	1900
Arsenic	7440-38-2	154	42
Cadmium	7440-43-9	0.39	9.17
Chromium_III	16065-83-1	79.2	548
Chromium_VI	18540-29-9	10.8	50
Copper	7440-50-8	4.17	3.04
Iron	7439-89-6	887	158
Lead	7439-92-1	1.16	7.07
Mercury	7439-97-6	0.182	0.291
Methylmercury	22967-92-6	0.00277	0.0029
Molybdenum	7439-98-7	395	298
Nickel	7440-02-0	60.5	8.67
Selenium	7782-49-2	4.96	70.5
Silver	7440-22-4	0.098	0.142
Thallium	7440-28-0	9.85	58.4
Tin	7440-31-5	84.8	0.854
Uranium	7440-61-1	2.6	2.6
Vanadium	7440-62-2	17.7	156
Zinc	7440-66-6	60.8	68.6
<i>Polycyclic Aromatic Hydrocarbons</i>			
2-Methylnaphthalene	91-57-6	31.2	69
Acenaphthene	83-32-9	21.9	62.8
Acenaphthylene	208-96-8	168	300
Anthracene	120-12-7	0.391	3.4
Benz(a)anthracene	56-55-3	0.0754	0.469
Benzo(a)pyrene	50-32-8	0.014	0.0345
Benzo(b)fluoranthene	205-99-2	0.495	300
Benzo(g,h,i)perylene	191-24-2	7.64	300
Benzo(k)fluoranthene	207-08-9	0.027	300
Biphenyl	92-52-4	14	14
Chrysene	218-01-9	0.172	300
Dibenz(a,h)anthracene	53-70-3	0.367	300
Fluoranthene	206-44-0	8.35	7.65
Fluorene	86-73-7	4.23	23.6
Indeno(1,2,3-cd)pyrene	193-39-5	0.341	300
Naphthalene	91-20-3	23.9	105
Phenanthrene	85-01-8	11.5	7.9
Pyrene	129-00-0	1.3	27.8

*footnotes continued on next page...*

**Table 8. Toxicity thresholds for surface water (freshwater and saltwater).**

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<b>Class/Analyte Name</b>	<b>Chemical Abstracts Number</b>	<b>Freshwater Toxicity Threshold (µg/L)<sup>1</sup></b>	<b>Saltwater Toxicity Threshold (µg/L)<sup>2</sup></b>
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CAS = chemical abstracts; NBA = no benchmark available; USEPA United States Environmental Protection Agency.

<sup>1</sup>The toxicity threshold is the geometric mean of the Draft Freshwater Benchmarks by USEPA Region (MacDonald *et al.* 2005)

<sup>2</sup>The toxicity threshold is the geometric mean of the Draft Saltwater Benchmarks by USEPA Region (MacDonald *et al.* 2005)

<sup>3</sup>Indicates that the Toxicity Threshold is a Water Quality Guideline (WQG) developed by the Canadian Council of Ministers of the Environment (CCME 1999). These WQGs were selected for substances for which a EPA Regional Benchmark was not available.

**Table 9. Toxicity thresholds for freshwater and saltwater sediments.**

<b>Class/Analyte Name</b>	<b>Chemical Abstracts Number</b>	<b>Freshwater Toxicity Threshold<sup>1</sup></b>	<b>Saltwater Toxicity Threshold<sup>2</sup></b>
<b><i>Metals (mg/kg DW)</i></b>			
Arsenic	7440-38-2	7.15	7.95
Cadmium	7440-43-9	0.991	1.31
Chromium	7440-47-3	20.2	25
Copper	7440-50-8	25.2	28.7
Lead	7439-92-1	35.3	41.3
Mercury	7439-97-6	0.158	0.145
Nickel	7440-02-0	18.7	19.5
Zinc	7440-66-6	124	142
<b><i>Polycyclic Aromatic Hydrocarbons (µg/kg DW)</i></b>			
2-Methylnaphthalene	91-57-6	114	72.8
Acenaphthene	83-32-9	98.3	35.6
Acenaphthylene	208-96-8	78.3	44
Anthracene	120-12-7	151	142
Benzo(a)anthracene	56-55-3	132	226
Benzo(a)pyrene	50-32-8	205	342
Benzo(b)fluoranthene	205-99-2	4740	2640
Benzo(g,h,i)perylene	191-24-2	252	327
Benzo(k)fluoranthene	207-08-9	139	240
Biphenyl	92-52-4	1100	1100
Chrysene	218-01-9	195	313
Dibenzo(a,h)anthracene	53-70-3	59.6	77.9
Fluoranthene	206-44-0	505	502
Fluorene	86-73-7	84.1	41.3
Indeno(1,2,3-cd)pyrene	193-39-5	193	257
Naphthalene	91-20-3	176	145
Phenanthrene	85-01-8	234	266
Pyrene	129-00-0	360	506

CAS = chemical abstracts; NBA = no benchmark available; DW = dry weight.

<sup>1</sup>The toxicity threshold is the geometric mean of the Draft Freshwater Sediment Benchmarks (MacDonald *et al.* 2005) Benchmarks that were expressed on an organic carbon (OC) normalized basis were converted to units on a dry weight basis at 1% OC prior to calculating the geometric mean.

<sup>2</sup>The toxicity threshold is the geometric mean of the Draft Marine Sediment Benchmarks (MacDonald *et al.* 2005). Benchmarks that were expressed on an organic carbon (OC) normalized basis were converted to units on a dry weight basis at 1% OC prior to calculating the geometric mean.

**Table 10. Calculated ESB-TUs for whole-sediment samples collected in the Delaware River in December, 2004 (From R. Greene, Delaware DNREC).**

<b>Client Sample ID</b>	<b>GERG ID</b>	<b>Sediment T.U. (Acute)</b>	<b>Sediment T.U. (chronic)</b>
SED-RC-01	C45280	0.100	0.511
SED-RC-02	C45281	0.094	0.481
SED-RC-03	C45282	0.089	0.453
SED-TI-01	C45283	0.437	2.225
SED-TI-02	C45284	0.523	2.663
SED-TI-03	C45285	0.328	1.671
SED-TP-01	C45286	0.011	0.058
SED-CW-01	C45287	0.113	0.575
SED-PP-01	C45291	0.016	0.081
SED-PP-02	C45292	0.015	0.078
SED-PP-03	C45293	0.025	0.129

ESB-TUs - equilibrium partitioning sediment benchmark-toxic units.

**Table 11. Screening evaluation of potential polycyclic aromatic hydrocarbon (PAH) toxicity: Athos water samples.**

<b>Chemical</b>	<b>Units</b>	<b>Toxicity Threshold</b>	<b>Frequency of Exceedance</b>
Naphthalene	ng/L	105,000	0 of 80 samples
Biphenyl	ng/L	14,000	0 of 80 samples
Acenaphthylene	ng/L	300,000	0 of 80 samples
Acenaphthene	ng/L	62,800	0 of 80 samples
Fluorene	ng/L	23,600	0 of 80 samples
Anthracene	ng/L	3,400	0 of 80 samples
Phenanthrene	ng/L	7,900	0 of 80 samples
Fluoranthene	ng/L	7,650	0 of 80 samples
Pyrene	ng/L	27,800	0 of 80 samples
Benz(a)anthracene	ng/L	469	0 of 80 samples
Chrysene	ng/L	300,000	0 of 80 samples
Benzo(b)fluoranthene	ng/L	300,000	0 of 80 samples
Benzo(k)fluoranthene	ng/L	300,000	0 of 80 samples
Benzo(a)pyrene	ng/L	35	2 of 80 samples
Indeno(1,2,3-c,d)pyrene	ng/L	300,000	0 of 80 samples
Dibenz(a,h)anthracene	ng/L	300,000	0 of 80 samples
Benzo(g,h,i)perylene	ng/L	300,000	0 of 80 samples
2-Methylnaphthalene	ng/L	69,000	0 of 80 samples

**Table 12. Screening evaluation of potential polycyclic aromatic hydrocarbon (PAH) toxicity: Athos sediment samples.**

<b>Chemical</b>	<b>Units</b>	<b>Toxicity Threshold</b>	<b>Frequency of Exceedance</b>
Naphthalene	ug/kg	145	14 out of 27 samples
Biphenyl	ug/kg	1,100	0 out of 27 samples
Acenaphthylene	ug/kg	44	13 out of 27 samples
Acenaphthene	ug/kg	35.6	8 out of 27 samples
Fluorene	ug/kg	41.3	14 out of 27 samples
Anthracene	ug/kg	142	7 out of 27 samples
Phenanthrene	ug/kg	266	8 out of 27 samples
Fluoranthene	ug/kg	502	9 out of 27 samples
Pyrene	ug/kg	506	8 out of 27 samples
Benz(a)anthracene	ug/kg	226	14 out of 27 samples
Chrysene	ug/kg	313	10 out of 27 samples
Benzo(b)fluoranthene	ug/kg	2,640	0 out of 27 samples
Benzo(k)fluoranthene	ug/kg	240	4 out of 27 samples
Benzo(a)pyrene	ug/kg	342	7 out of 27 samples
Indeno(1,2,3-c,d)pyrene	ug/kg	257	2 out of 27 samples
Dibenz(a,h)anthracene	ug/kg	77.9	2 out of 27 samples
Benzo(g,h,i)perylene	ug/kg	327	1 out of 27 samples
2-Methylnaphthalene	ug/kg	72.8	17 out of 27 samples
Total PAH (Effects Range Low)	ug/kg	4,000	17 out of 27 samples
Total PAH (Probable Effects Level)	ug/kg	23,000	1 out of 27 samples

Figure 1. Total ion chromatogram of the *M/T ATHOS I* Venezuelan crude oil.

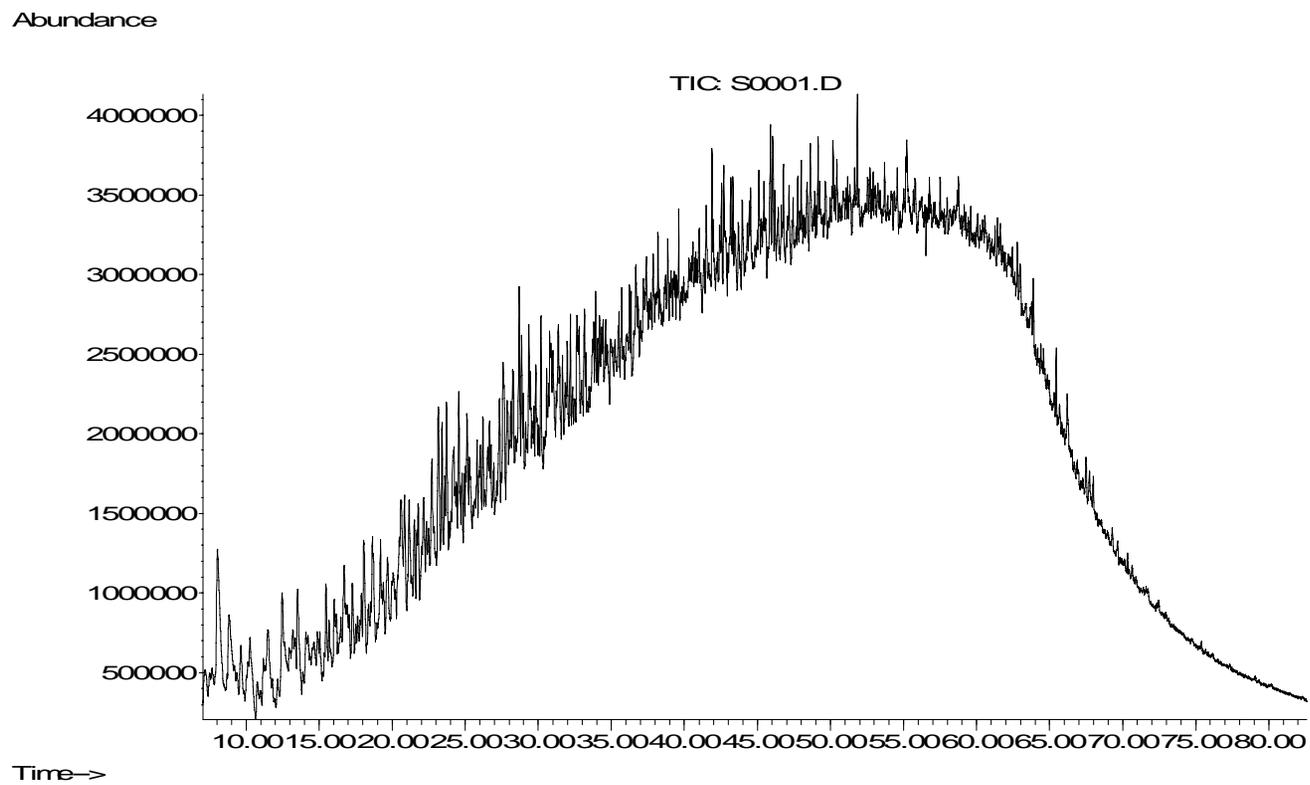


Figure 2. Alkane (ion 85) extracted ion plot of the *M/T ATHOS I* Venezuelan crude oil.

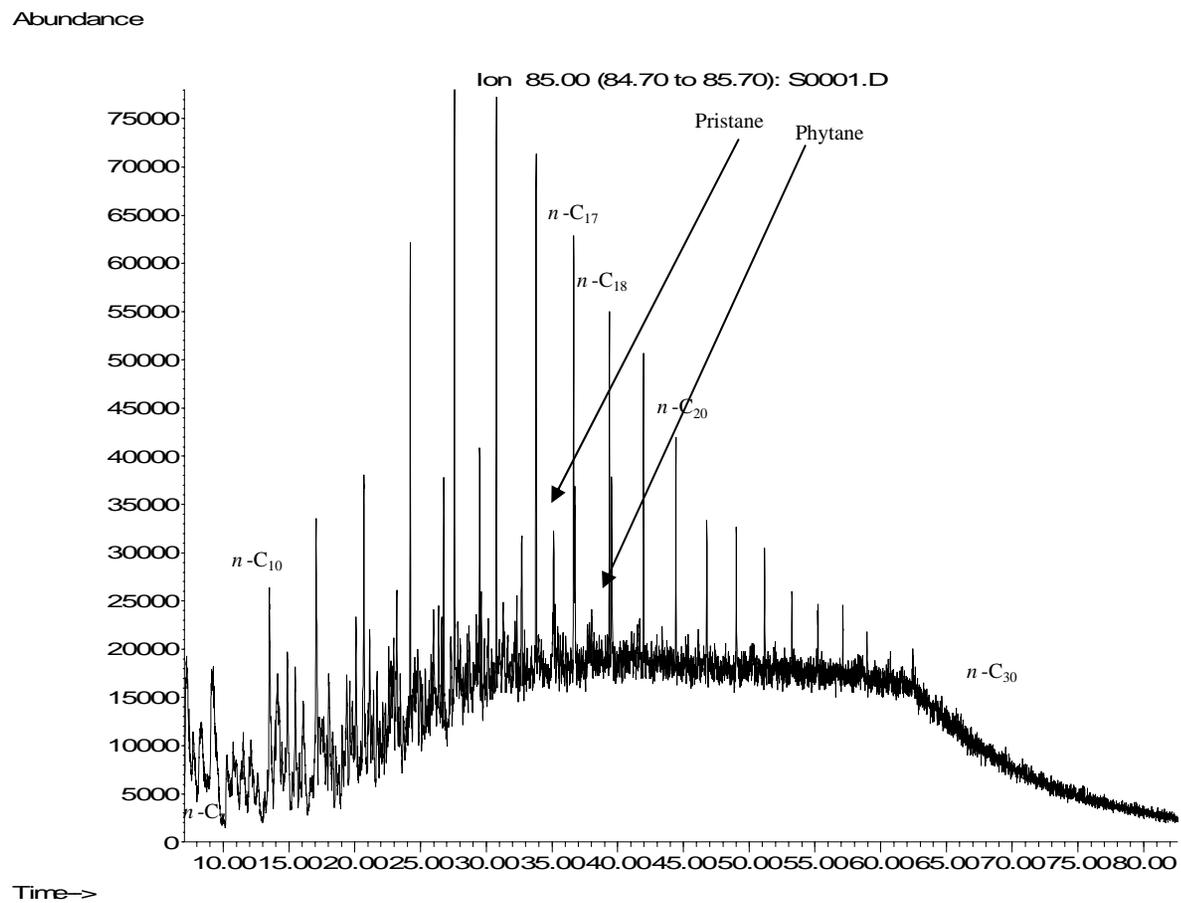


Figure 3. GC/FID chromatogram of North Slope crude oil.

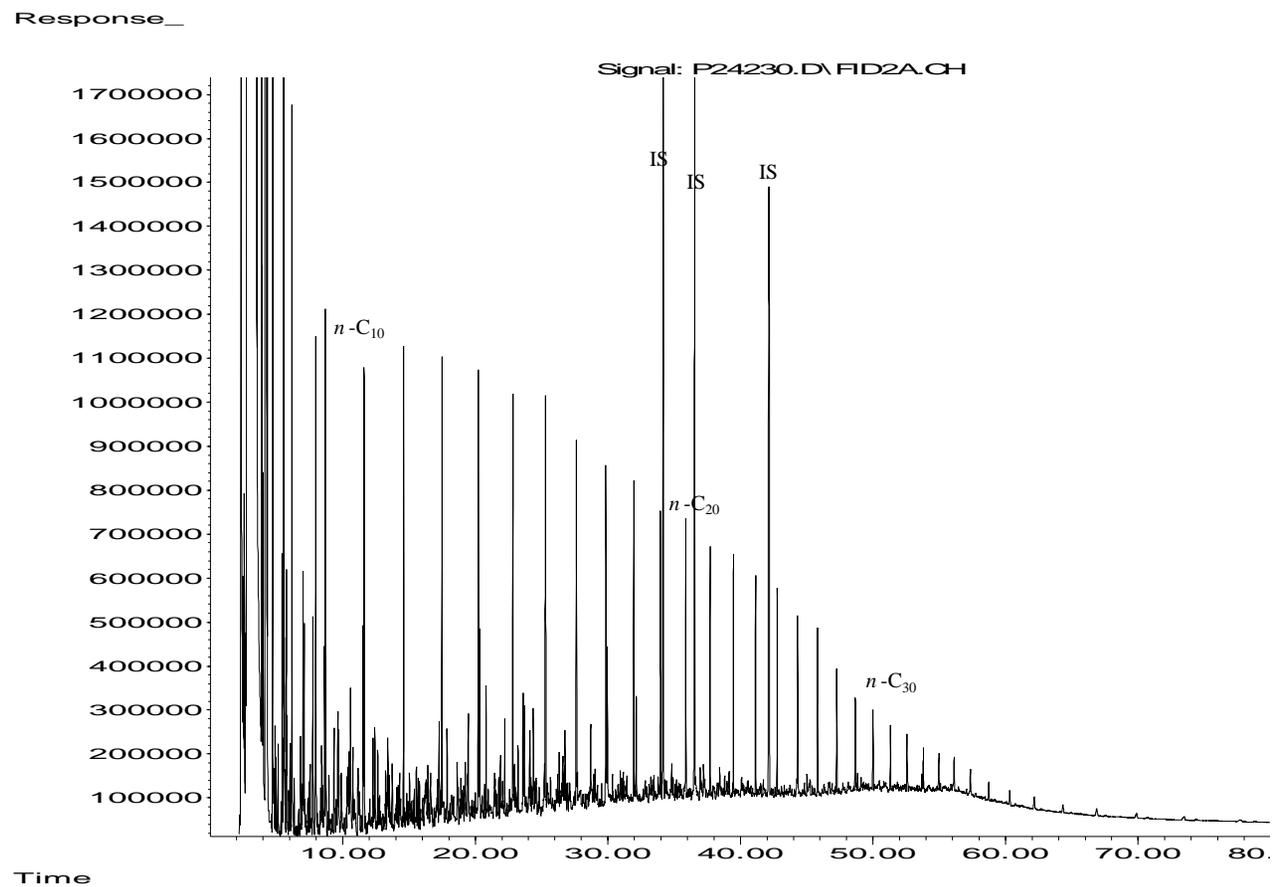


Figure 4. PAH distribution in *M/T ATHOS I* and North Slope crude oils.

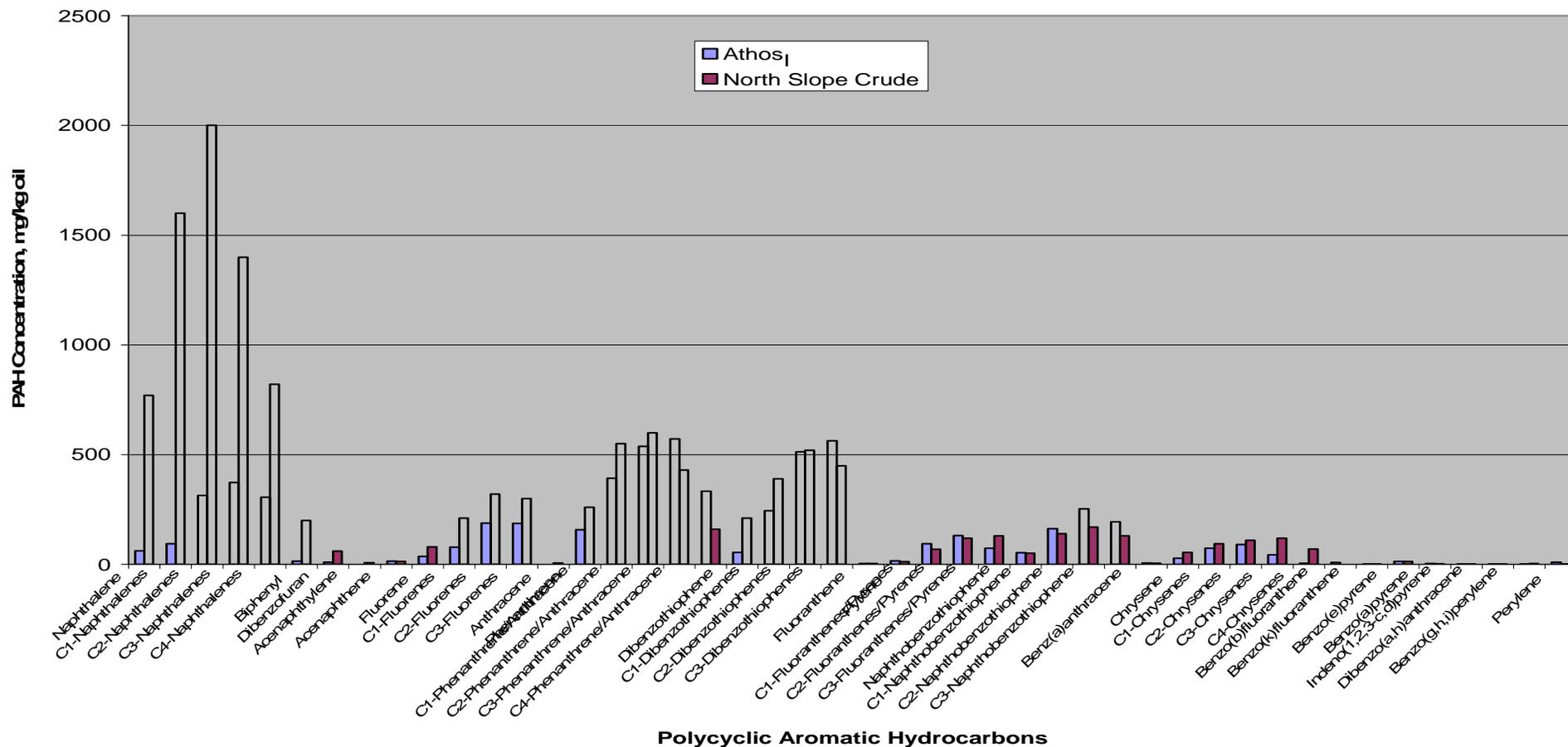


Figure 5. South Delaware River Subtidal sediment sample locations and total PAH concentrations.

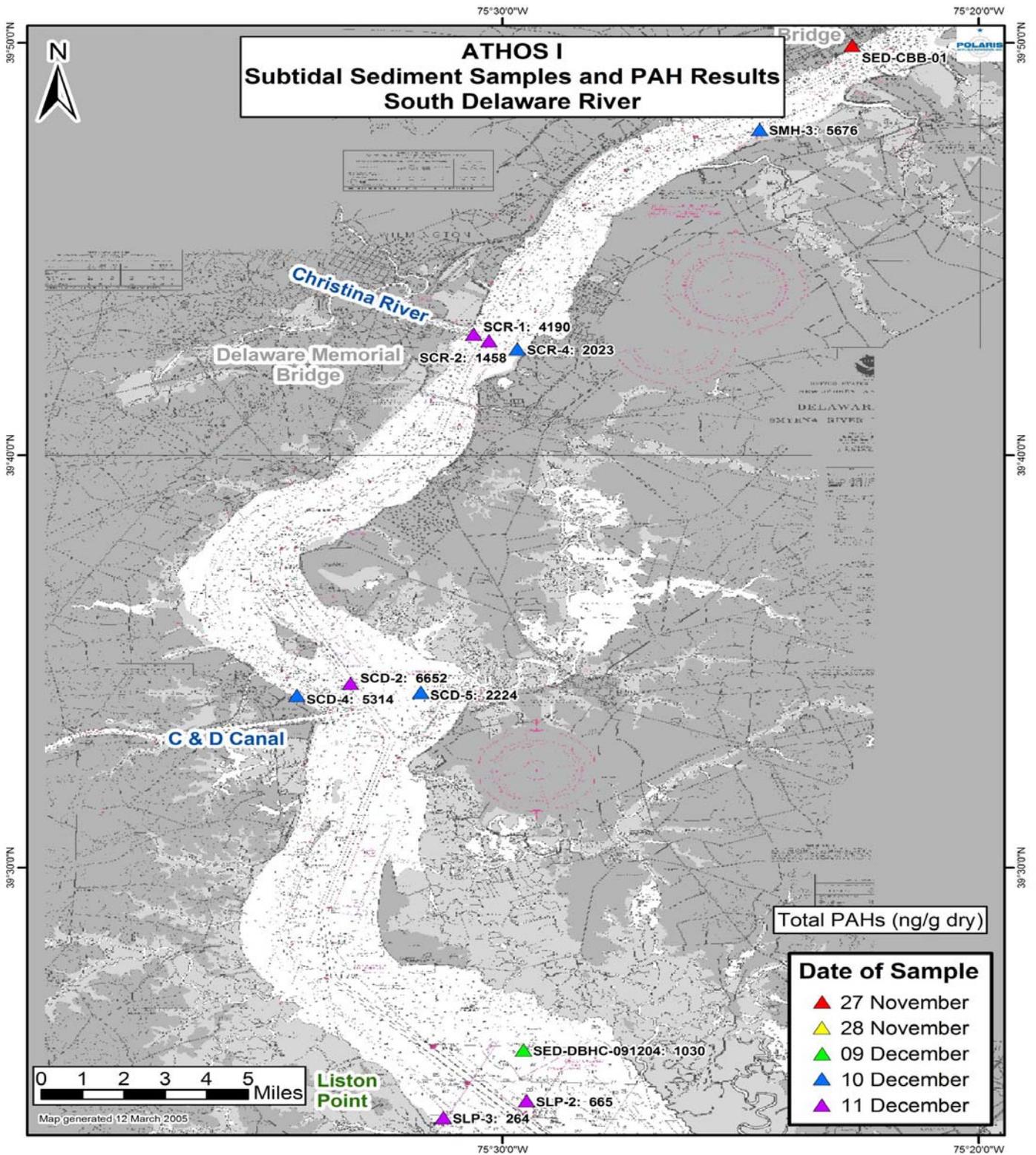


Figure 6. North Delaware River Subtidal sediment sample locations and total PAH concentrations.

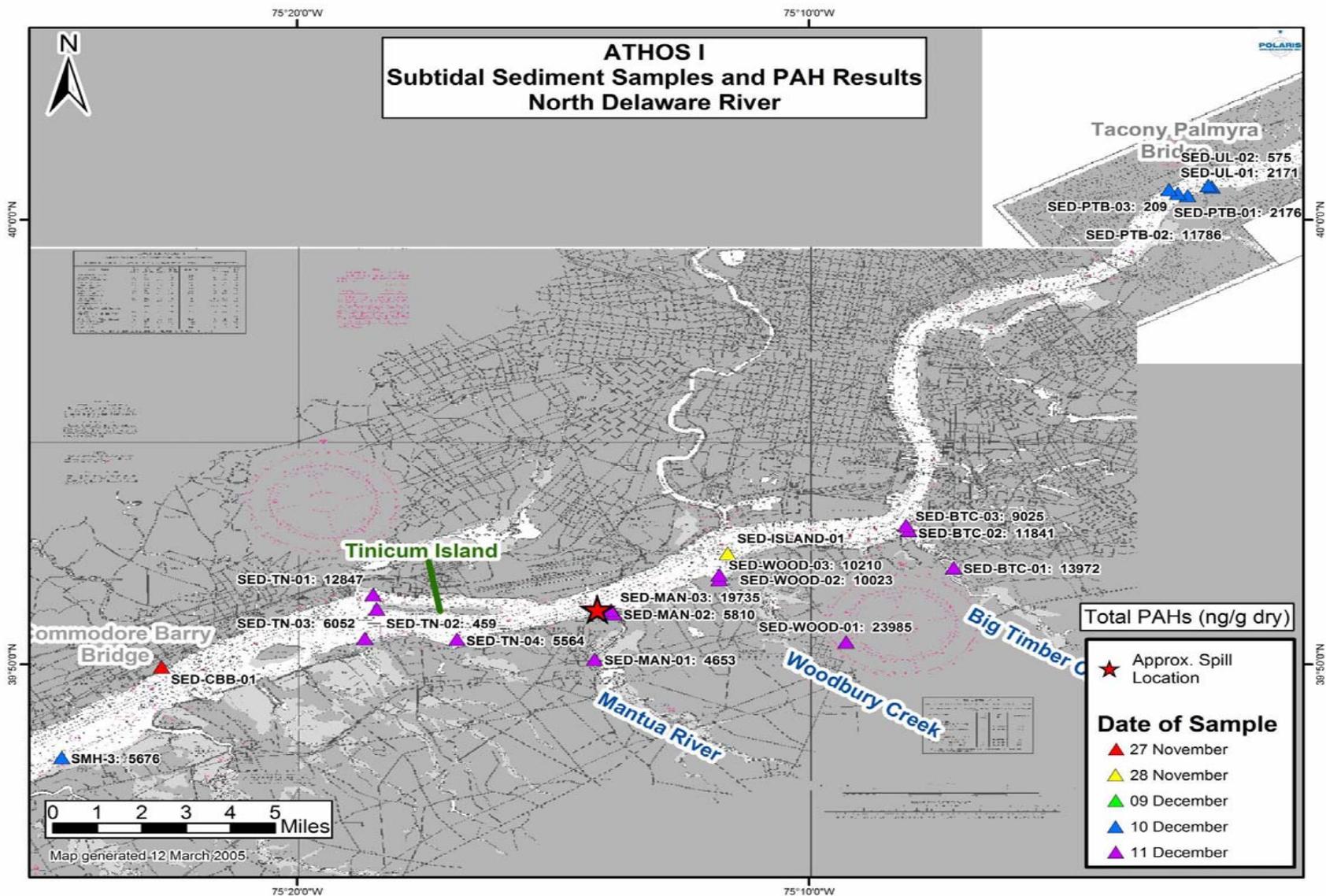


Figure 7. Track lines for the V-SORS highlighting the percent of visual oil coverage on the snares.

### M/V Athos I, Delaware River, NJ/PA

VSORS  
created by NOAA  
USE ONLY AS A GENERAL REFERENCE

12/06/04 through 12/10/04

Graphic does not represent precise amounts or locations of oil

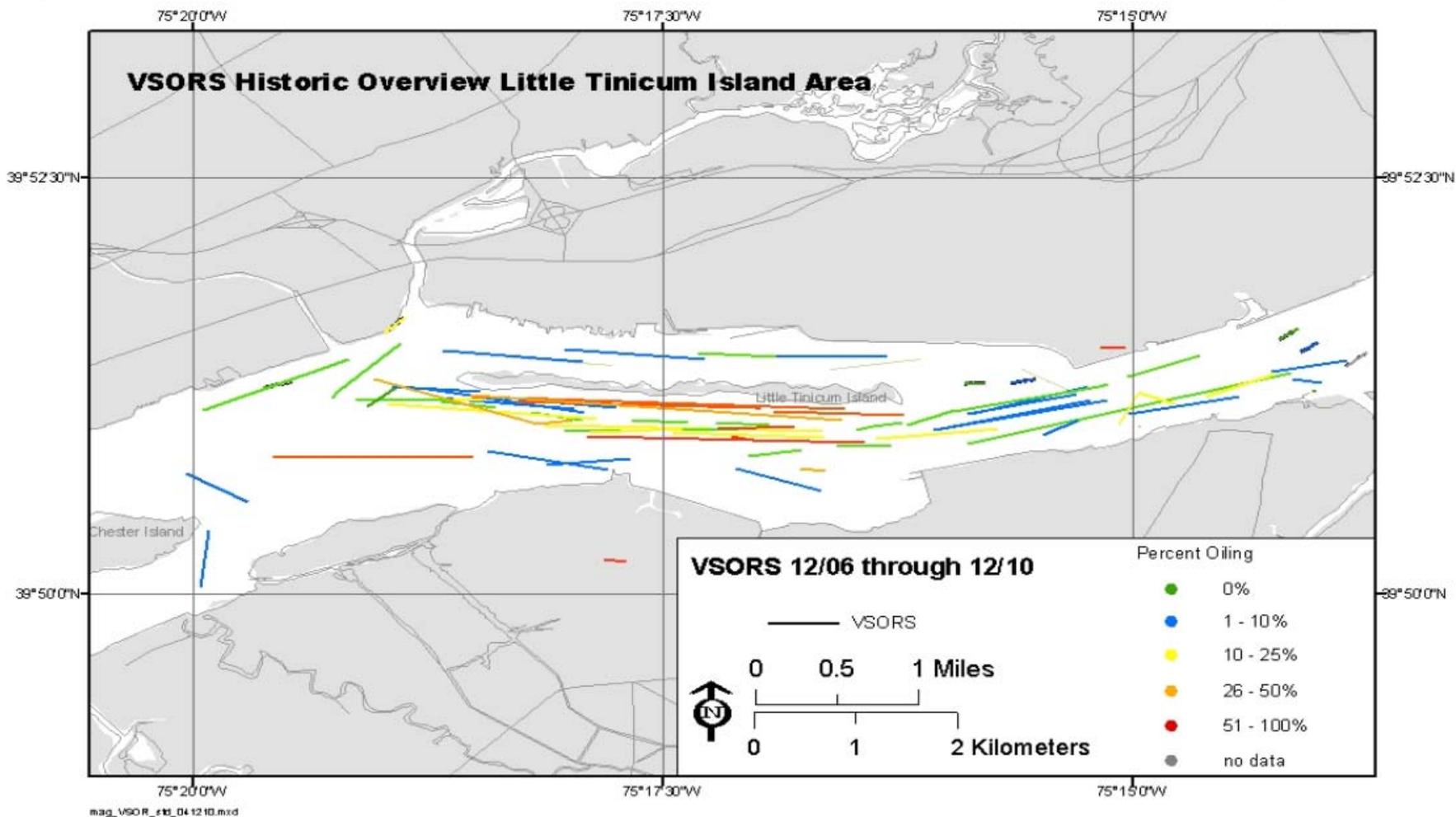


Figure 8. South Delaware River water sample locations and total PAH concentrations.

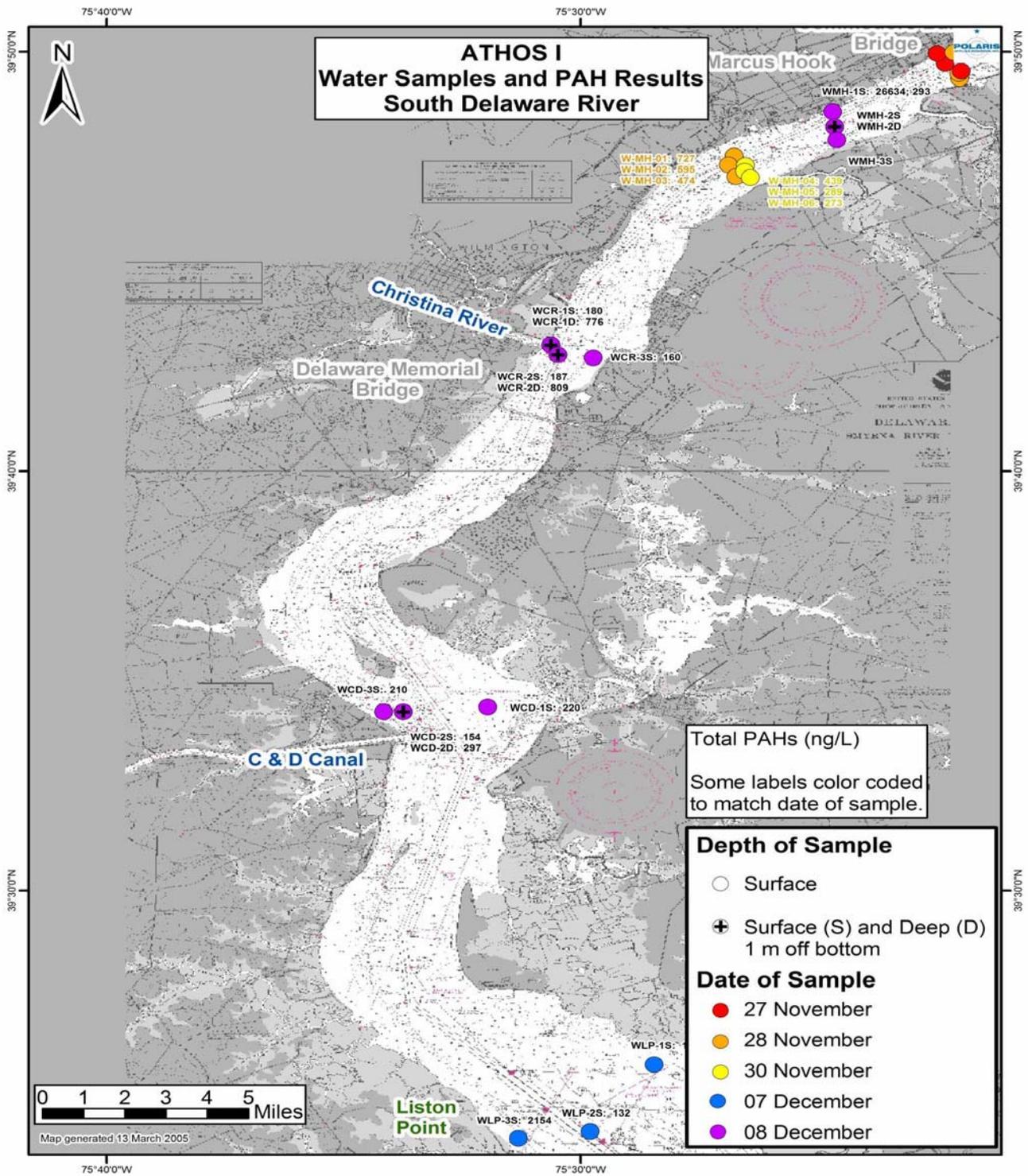


Figure 9. North Delaware River water sample locations and total PAH concentrations.

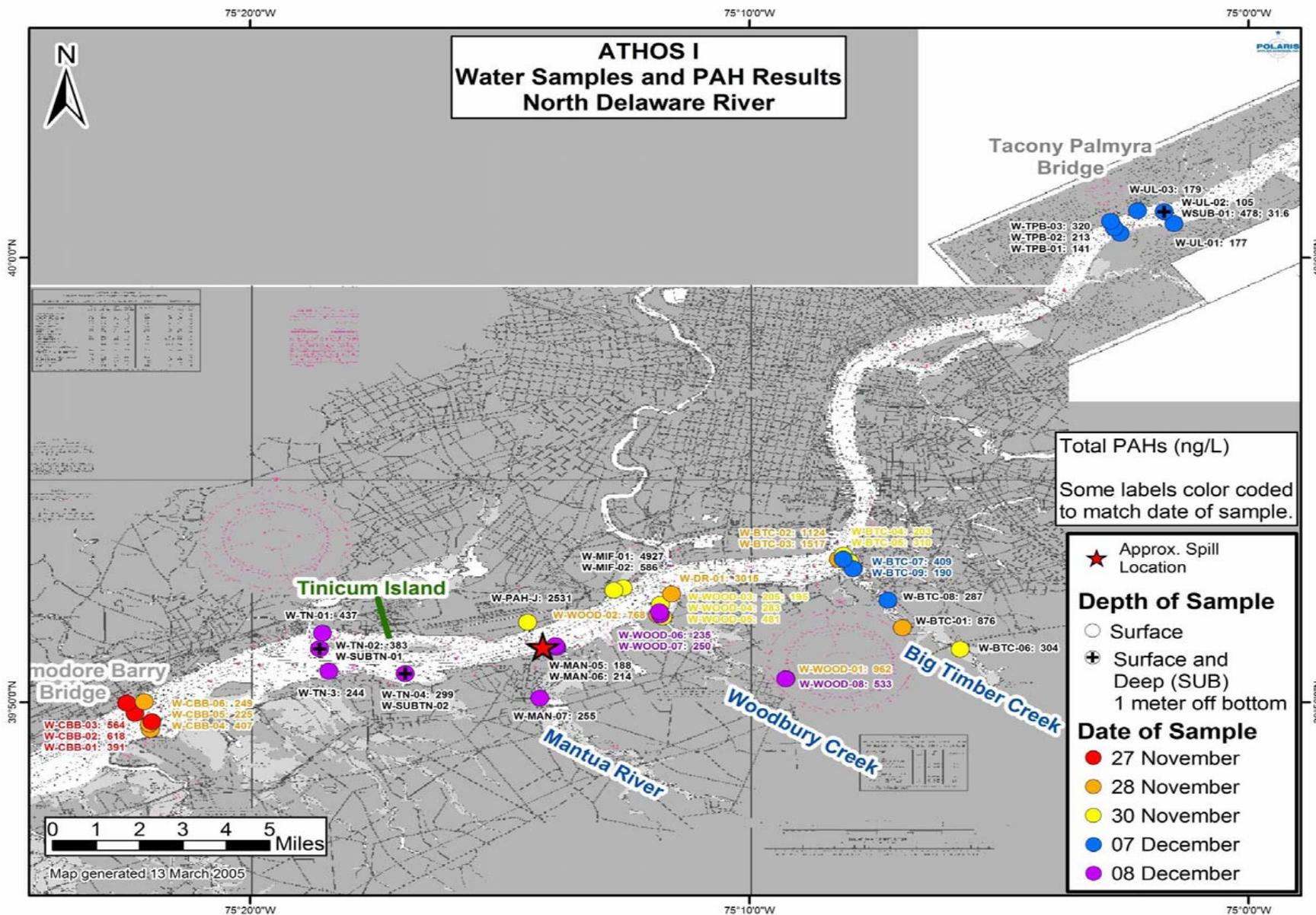


Figure 10. Delaware River oyster sample locations and total PAH concentrations.

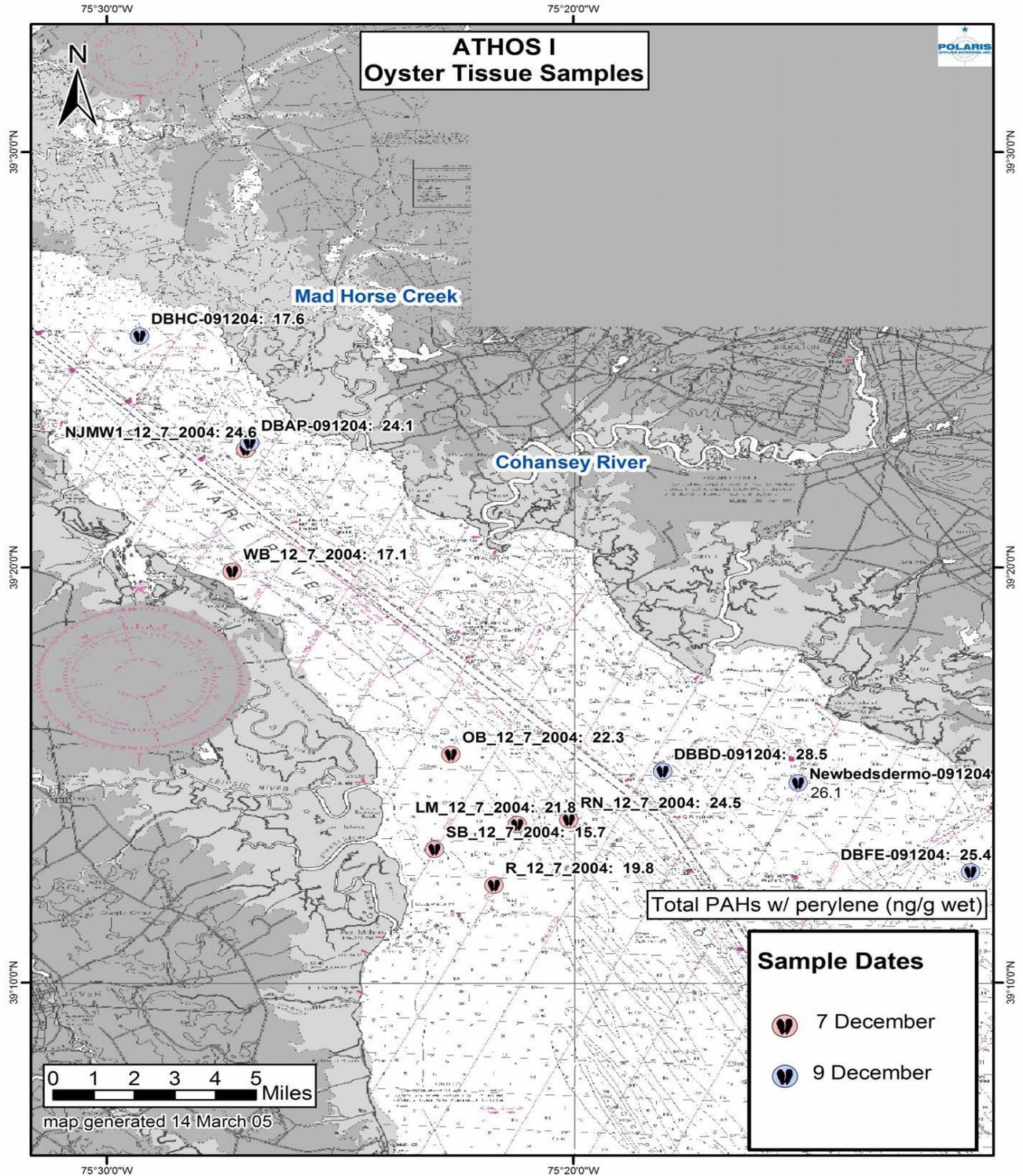
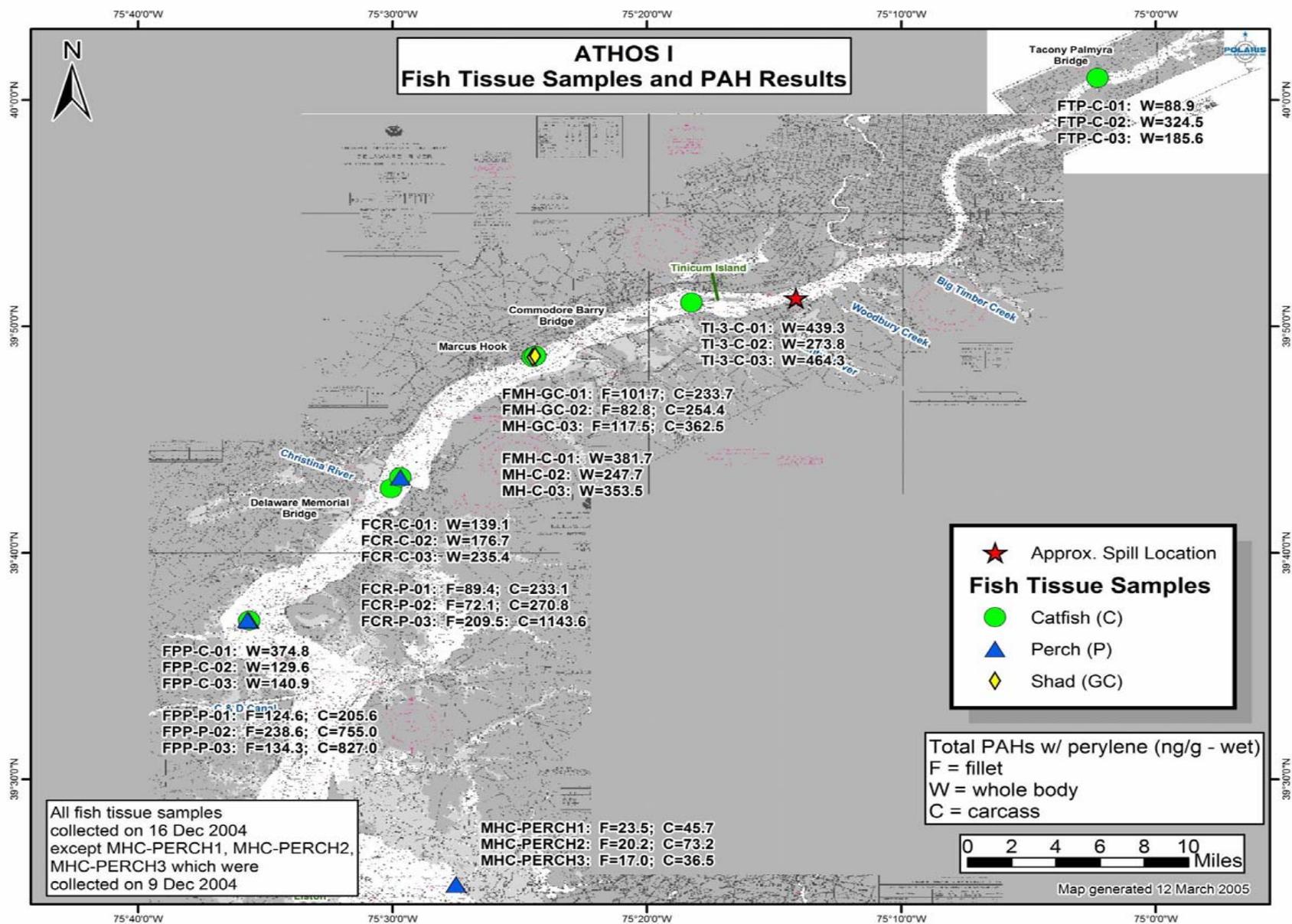


Figure 11. Delaware River fish tissue sample locations and total PAH concentrations.



# **Appendix 1 A Preliminary Evaluation of Delaware Department of Natural Resources and Environmental Conservation Assessment of Injuries Associated with the *M/T ATHOS I* Oil Spill in the Delaware River**

## **A1.0 Introduction**

In April, 2005, Delaware Department of Natural Resources and Environmental Control (DDNREC) presented the results of a preliminary assessment of injuries to natural resources associated with the *M/T ATHOS I* oil spill in the Delaware River (Greene 2005). This assessment consisted of three main elements, including:

- An assessment of risks to human health associated with exposure to benzo(a)pyrene in oysters and fish;
- An assessment of sediment toxicity using the equilibrium-based sediment benchmark toxic units model (ESB-TUs); and,
- An assessment of sediment quality conditions using the sediment quality triad.

This appendix provides a preliminary review of these three assessments with respect to the assessment of damages to natural resources associated with the *M/T ATHOS I* oil spill.

### **A1.1 Assessment of Risks to Human Health**

The assessment of risks to human health was conducted using data on the concentrations of benzo(a)pyrene (BaP) in the edible tissues of oysters and fish from Delaware Bay. More specifically, data on the concentrations of BaP in fish and invertebrate tissues were used to calculate BaP toxic equivalents for each tissue sample. This information was then considered in conjunction with daily seafood consumption rates, consumer body weights, and BaP potency to calculate lifetime cancer risk associated with consumption of fish and shellfish from Delaware Bay. While the results of this assessment should prove to be valuable for a variety of purposes, risks to human health are not claimable under NRD OPA regulations.

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## A1.2 Assessment of Sediment Toxicity

An assessment of sediment toxicity using the equilibrium-based sediment benchmark toxic units model (ESB-TUs) was also conducted by DDNREC. Briefly, USEPA (2003) developed a procedure for assessing the toxicity of sediment-associated PAHs based on predicted pore-water concentrations and associated acute- and chronic-narcotic toxicity thresholds. This procedure results in the calculation of equilibrium-based sediment benchmark toxicity units (ESB-TUs). Sediments with calculated ESB-TUs of greater than one are predicted to be acutely- or chronically-toxic, depending on whether acute- or chronic-toxicity thresholds were used in the calculations. Based on the calculations conducted by Rick Greene (DDNREC), acute ESB-TUs for the 11 Delaware River sediment samples ranged from 0.011 to 0.523, assuming these sediment contain roughly 2% organic carbon (Figure A1.1). By comparison, chronic ESB-TUs for the same 11 Delaware River sediment samples ranged from 0.058 to 2.66, assuming these sediment contain roughly 2% organic carbon (Figure A1.2). Three of the samples were predicted to be chronically toxic to sensitive sediment-dwelling organisms, based on calculated ESB-TUs exceeding 1.0. All of these samples were collected in the vicinity of Tinicum Island.

The approach that was used by DDNREC is technically-valid and represents one of the lines of evidence that could be pursued to assess injury to sediments and sediment-dwelling organisms. As indicated in the presentation, the reported results will be enhanced by substituting sample-specific TOC values for the assumed TOC values. In addition, better spatial coverage would be beneficial to identify the locations where PAHs are elevated in the vicinity of the oil spill. It is important to note that NOAA conducted a sediment-quality investigation of the Delaware River in 1997 and that the results of this survey showed that sediments in this water body were contaminated by various COPCs, including PAHs (McCoy *et al.* 2002). Therefore, it is unclear whether the measured concentrations of PAHs or the measured toxicity were directly associated with the *M/T ATHOS I* oil spill. As noted by Greene (2005), fingerprinting will be required to determine what portion of the PAHs likely originated from the *M/T ATHOS I* oil spill. It may also be useful to evaluate the narcotic potential of the source oil (i.e., to determine what concentrations of the source oil would be toxic to sediment-dwelling organisms).

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### A1.3 Assessment of Sediment Quality Conditions

To support the assessment of injury to sediment-dwelling organisms, DDNREC collected whole-sediment samples at three locations in the Delaware River basin. More specifically, sediment samples were collected from the vicinity of Tinicum Island, Claymont/Oldmans Point, and Pea Patch Island on November 29, 2004, December 15, 2004, and February 17, 2005 (Note: the Tinicum Island site was not sampled on November 29, 2004). A sediment quality triad approach was used to assess sediment quality conditions at each the site, which included:

- Measuring PAH and TOC concentrations in whole-sediment samples;
- Evaluating the toxicity of whole-sediment samples to the amphipod, *Leptocheirus plumulosus*, in 10-d toxicity tests; and,
- Assessing benthic invertebrate community structure.

Additional sampling at these locations was to be conducted in mid-April, 2005.

The sediment quality triad approach represents a robust procedure for assessing sediment quality conditions in freshwater and estuarine ecosystems. Interestingly, the results of the toxicity tests indicated that the sediment samples collected in the vicinity of Tinicum Island were toxic to amphipods on both dates (December 15, 2004 and February 17, 2005; i.e., based on control-adjusted survivals of <80%; Figure A1.3). None of the other sediment samples were found to be toxic to this species. While these data will support an assessment of sediment injury, should one be undertaken in the future, the data that have been collected are unlikely to provide sufficient spatial coverage to evaluate the extent of injury to sediment-dwelling organisms. In addition, it would be advisable to include measurements of other COPCs (e.g., metals, SEM, AVS, ammonia, hydrogen sulfide, PCBs, pesticides) to provide a basis for determining which COPCs are associated with the observed biological effects. Ian Hartwell (NOAA) should be consulted relative to the interpretation of the benthic invertebrate community structure data. Finally, it is important to note that the results of the 1997 NOAA study showed that sediments in this water body were contaminated by various COPCs, including PAHs. Therefore, the extent to which the measured concentrations of PAHs or the measured toxicity were directly associated with the *M/T ATHOS I* oil spill is unclear.

Figure A1.1. Acute toxicity units for PAHs in sediment pore water (From R. Greene, Delaware DNREC).

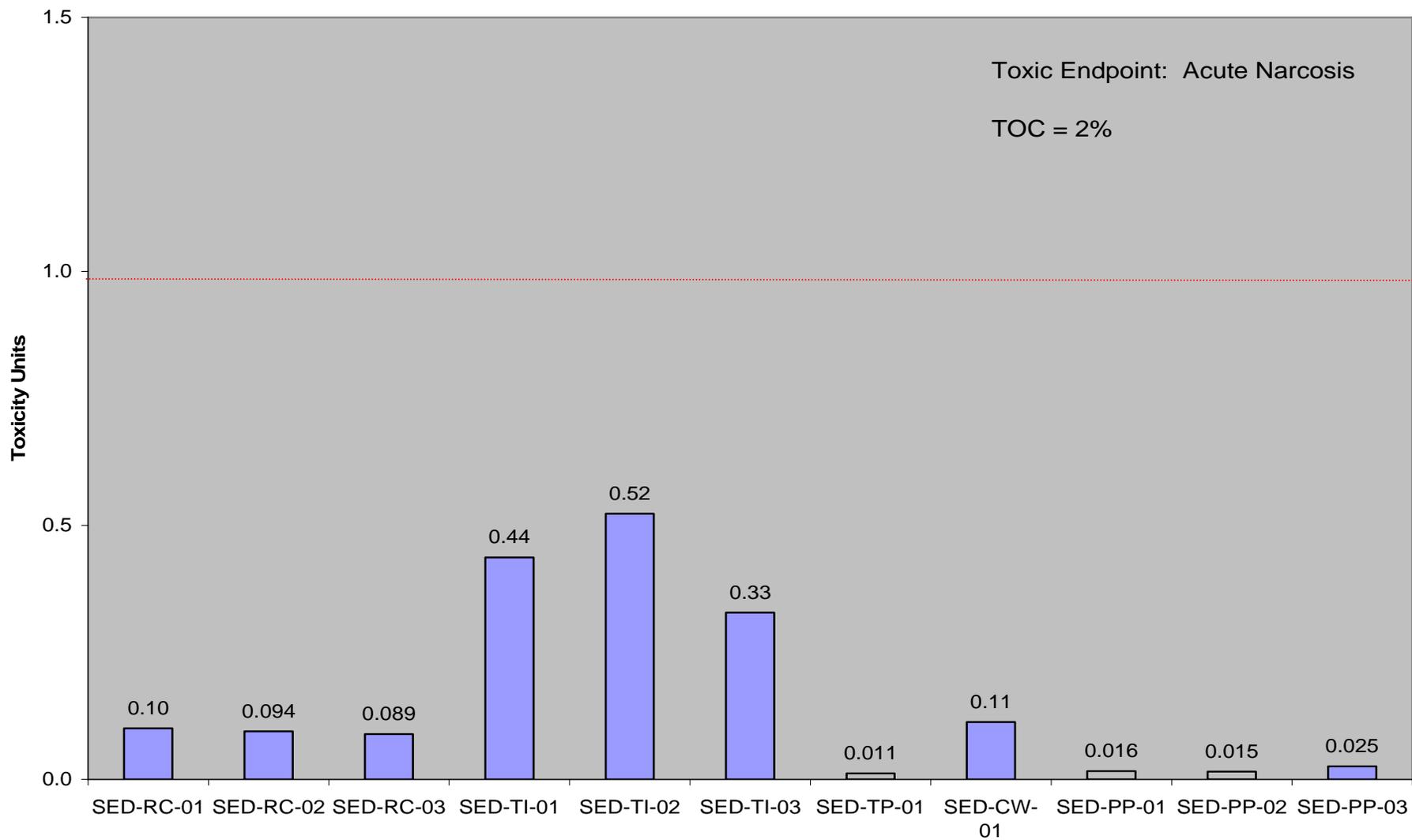


Figure A1.2. Chronic toxicity units for PAHs in sediment pore water (From R. Greene, Delaware DNREC).

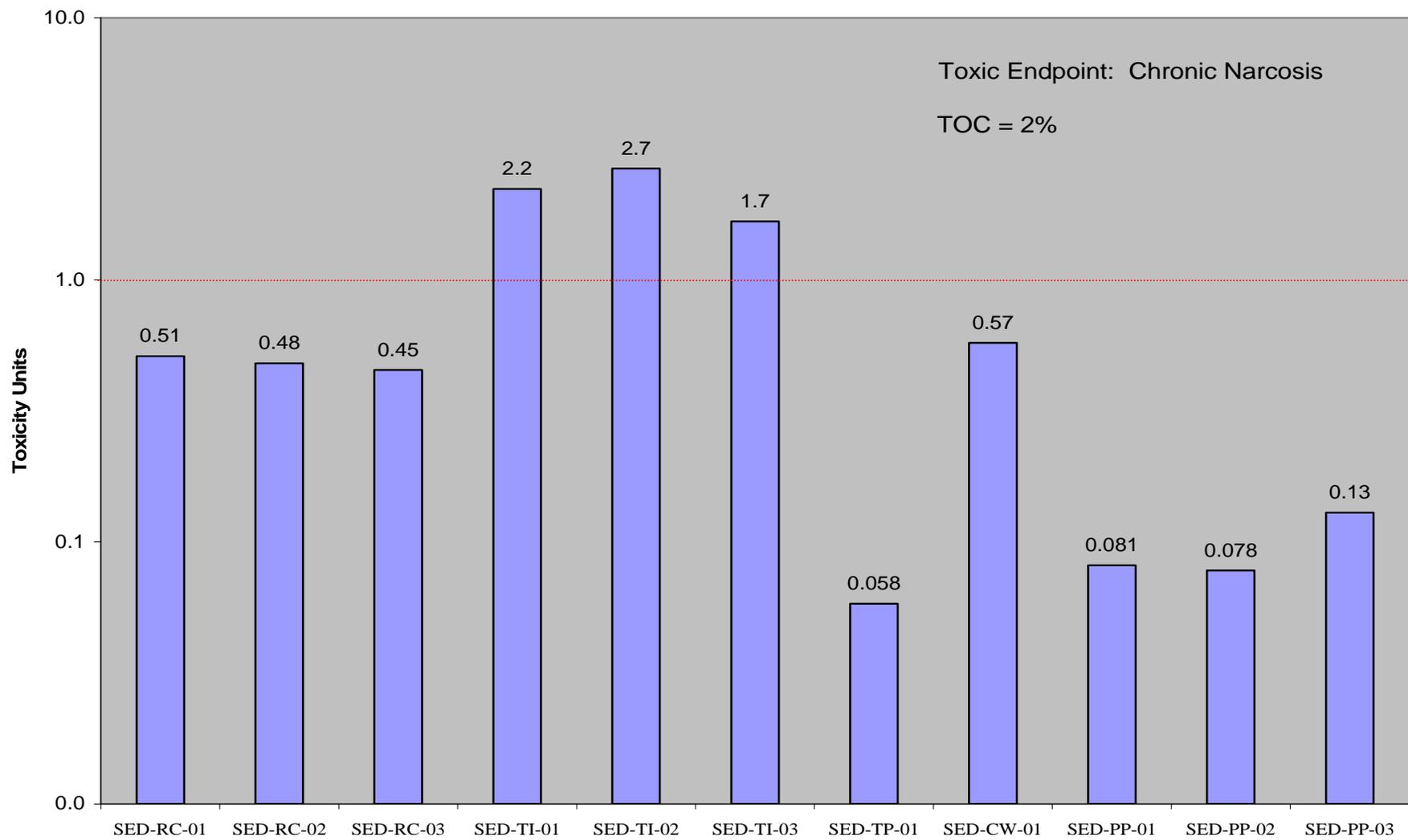
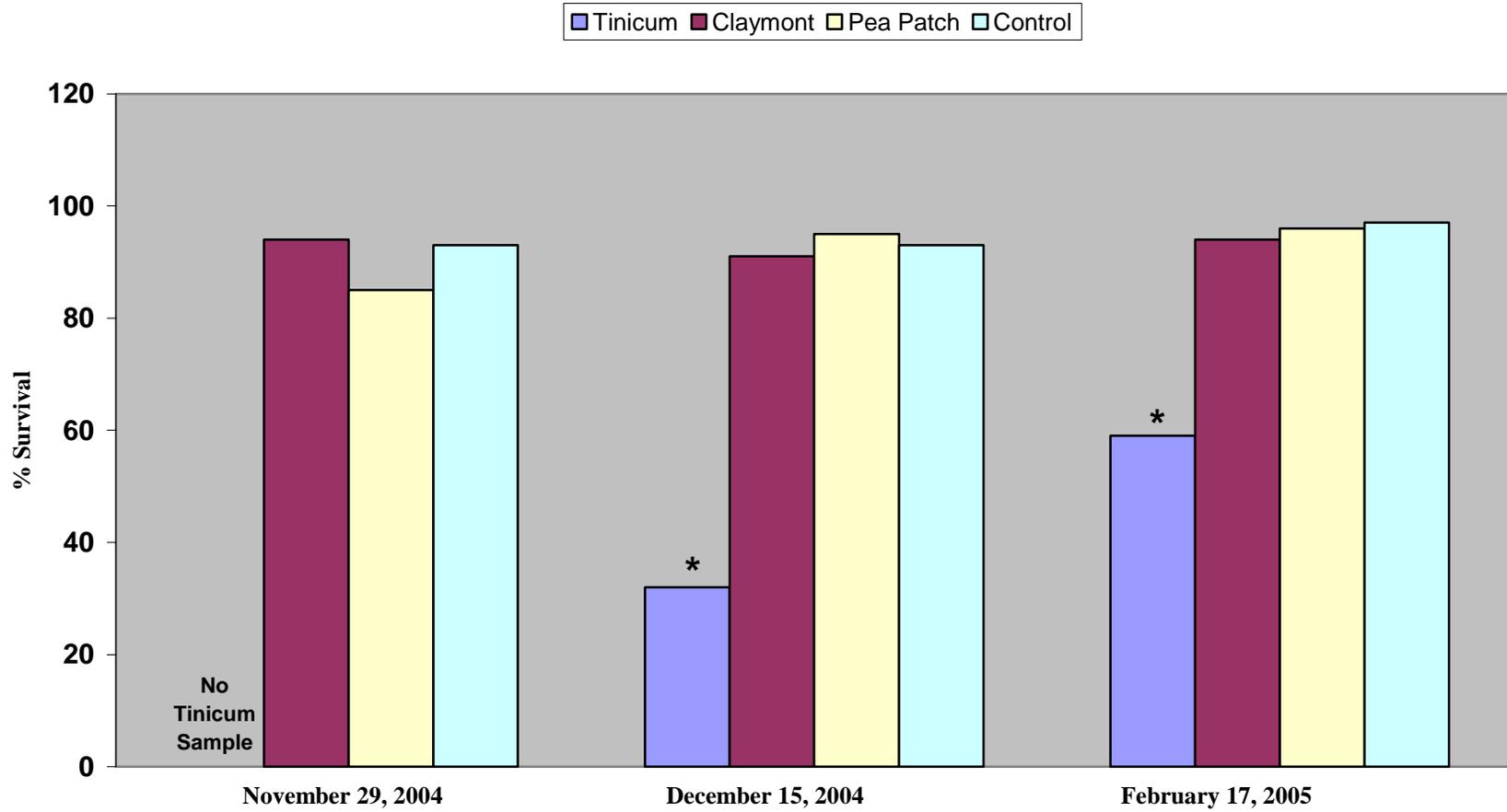


Figure A1.3. 10-day Percent survival of *Leptocheirus plumulosus* (From R. Greene, Delaware DNREC).



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## **Appendix 2 Preliminary Evaluation of the Potential for Injury to Sediment-dwelling Organisms Associated with Releases of Venezuelan crude oil to the Delaware River from the *M/T ATHOS I***

As a follow-up to our recent discussions regarding the potential for injury to sediment-dwelling organisms associated with releases of Venezuelan crude oil to the Delaware River from the *M/T ATHOS I*, I have conducted some back-of-the envelope calculations to determine if PAHs in sub-tidal sediments following the oil spill could, potentially, occur at harmful concentrations. By their very nature, these types of calculations are dependent on a series of assumptions regarding the amount of oil spilled, the composition of that oil, the fate of the following release into the river, the bioavailability of the substances present in the oil, the location and nature of depositional environments, and baseline levels of chemicals of potential concern (COPC), to name but a few. Nevertheless, the results of such calculations can be instructive, particularly when the underlying assumptions tend to be conservative and the results suggest that the potential for adverse effects is limited. The following sections of this memorandum document the key assumptions and report the results of the injury calculations.

- Assumption 1: 265,000 gallons (1,003,134 L) of crude oil was spilled in the Delaware River in the vicinity of Mantua Creek on November 26, 2004 (PASI 2005);
- Assumption 2: As of March 10, 2005, 129,436 gallons (489,969 L) of oil and oily liquid and 13,428 tons of oil solids were recovered/collected from the river (PASI 2005);
- Assumption 3: Approximately, one-half of the oil (i.e., 132,500 gallons or 501,566 L) that was released into the river was not recovered and, hence, remained in the Delaware River;
- Assumption 4: The density of the oil was, on average, 0.975 kg/L (PASI 2005);
- Assumption 5: The mass of oil that was released to the Delaware River was on the order of 489,026 kg (i.e., 501,566 L x 0.975 kg/L);
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- Assumption 6: PAHs represent the primary COPCs relative to the potential for longer-term toxic effects on sediment-dwelling organisms, because the lighter oil fractions would have quickly volatilized (i.e., 3% of the mass in 4 hours; Michel *et al.* 2005) and the heavier oil fractions are comprised largely of substances with relatively low solubilities in water (i.e., alkanes; asphaltenes);
- Assumption 7: PAHs represented approximately 0.6546% of the oil, by mass (PASI 2005);
- Assumption 8: Approximately 3201 kg of total PAHs were released into the river and lost following the oil spill (i.e., 489,026 kg x 0.006546);
- Assumption 9: All of the PAHs that were lost following the oil spill were incorporated into Delaware River sediments within the first 10 miles (16 km) downstream of the spill site (i.e., between Mantua Creek and the Commodore Barry Bridge);
- Assumption 10: On average, the reach of the river from Mantua Creek and the Commodore Barry Bridge is approximately 1.5 km in width (excluding intertidal areas; estimated from maps);
- Assumption 11: The area of the reach of the river from Mantua Creek and the Commodore Barry Bridge is approximately 24 km<sup>2</sup> (i.e., 16 km in length x 1.5 km in width);
- Assumption 12: Approximately 10% of the area of the reach of the river from Mantua Creek and the Commodore Barry Bridge are depositional habitats (i.e., 2.4 km<sup>2</sup> or 2,400,000 m<sup>2</sup>);
- Assumption 13: All of the PAHs that were incorporated into Delaware Bay sediments were deposited in the top 2.5 cm of sediment within the depositional habitats of this reach;
- Assumption 14: The PAHs were deposited in a sediment volume of 60,000 m<sup>3</sup> (i.e., 2,400,000 m<sup>2</sup> x 0.025 m);
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- Assumption 15: The density of Delaware River sediments is on the order of 2200 kg/m<sup>3</sup> (assumes relatively low moisture content);
- Assumption 16: The PAHs were deposited in a sediment mass of 132,000,000 kg (i.e., 60,000 m<sup>3</sup> x 2000 kg/m<sup>3</sup>);
- Assumption 17: Equal distribution of 3201 kg of total PAHs within 132,000,000 kg of Delaware River sediment would augment total PAH concentrations by approximately 24.25 mg/kg;
- Assumption 18: Background (pre-oil spill) concentrations of total PAHs in Delaware River sediments within the selected reach may range from 0.4 to 18.1 mg/kg (averaging 8 mg/kg; i.e., for site 13, 14, and 15 of McCoy *et al.* 2002 study);
- Assumption 19: Total PAH concentrations in sediments within the selected reach of the Delaware River could range from 25 to 43 mg/kg (i.e., background plus oil spill contribution);
- Assumption 20: The probability of observing toxicity to amphipods in 10-d toxicity tests is less than 50% in sediments with such concentrations of PAHs, based on comparisons to the ER-M for total PAHs (i.e., 44.8 mg/kg DW; Long *et al.* 1995).
- Assumption 21: Assuming that Delaware River sediments within the selected reach has TOC concentrations average at least 3% (i.e., for site 10 and 11 of Costa and Sauer 1993 study), then total PAH concentrations would be on the order of 830 to 1430 mg/kg OC (i.e., 25 to 43 mg/kg ÷ 0.03). These concentrations fall between the  $\Sigma$ PAH threshold effect concentration (393 mg/kg OC) and LC<sub>50</sub> (2114 mg/kg OC) of total PAHs (Swartz 1999). Therefore, amphipod survival in 10-d toxicity tests would be predicted to be on the order of 65 to 85% in these sediments.
- Assumption 22: The survival of amphipods exposed to sediment with 25 to 43 mg/kg could be on the order of 50%, based on the results of 28-d toxicity tests (MacDonald *et al.* 2003).
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Overall, the results of these back-of-the-envelope calculations indicate that exposure to PAHs from oil released from the *M/T ATHOS I* oil spill could result in toxicity to sensitive sediment-dwelling organisms (i.e., amphipods) if all of the PAHs were incorporated into sediments within depositional habitats located in the 10 miles downstream of the spill site. However, visual observations and snare sampling results indicate that oil from the *M/T ATHOS I* spill was transported to areas located further downstream in the river (PASI 2005). In addition, whole-sediment chemistry data collected in the vicinity of the spill site (i.e., downstream to the Commodore Barry Bridge; PASI 2005) indicate that total PAH concentrations rarely exceed the toxicity threshold of 22.8 mg/kg (MacDonald *et al.* 2000). These observations indicate that the scenario described in the above assumptions is probably overly conservative and that adverse effects on sediment-dwelling organisms are possible, but unlikely to be extensive.

### References Cited

- Costa, H. and T. Sauer. 1993. Characterization of chemical contaminants and assessment of toxicity in Delaware Estuary sediments Draft Report. Submitted to USEPA and Delaware River Basin Commission (Reference 42976-00). Arthur D. Little, Inc. Acorn Park. Cambridge, Massachusetts.
- Green, R. 2005. Preliminary evaluation of the risks posed by oil released from the MT Athos to the Delaware River. As presented at the April 12, 2005 meeting of the Aquatic Technical Working Group. Delaware Department of Natural Resources and Environmental Control. Dover, Delaware.
- Long, E.R., D.D. MacDonald, S.L. Smith, and F.D. Calder. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management* 19:81-97.
- MacDonald, D.D., C.G. Ingersoll, and T.A. Berger. 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology* 39:20-31.
- MacDonald, D.D., R.L. Breton, K. Edelmann, M.S. Goldberg, C.G. Ingersoll, R.A. Lindskoog, D.B. MacDonald, D.R.J. Moore, A.V. Pawlitz, D.E. Smorong, and R.P. Thompson. 2003a. Development and evaluation of preliminary remediation goals for selected contaminants of concern at the Calcasieu Estuary cooperative site, Lake Charles, Louisiana. Prepared for United States Environmental Protection Agency, Region 6. Dallas, Texas.
-

- McCoy, D.L., J.M. Jones, J.W. Anderson, M. Harmon, I. Hartwell, and J. Hameedi. 2002. Distribution of cytochrome P4501A1-inducing chemicals in sediments of the Delaware River-Bay system, USA. *Environmental Toxicology and Chemistry* 21(8):1618-1627.
- Michel, J., D. Simecek-Beatty, E. Levine, S. Lehmann, W. Lehr, G. Ott, V. Trumbull, C. Pfeifer, M. Ploen and J. Elliott. 2005 (In press). Submerged oil assessment and recovery at the ATHOS oil spill. *Proceedings of the 2005 International Oil Spill Conference*. Miami, Florida. May 2005.
- PASI (Polaris Applied Sciences, Inc.). 2005. Preassessment data report MT/Athos I oil spill, Delaware River, New Jersey, Pennsylvania and Delaware. Prepared for US Department of Commerce-National Oceanic and Atmospheric Administration, US Department of the Interior-US Fish and Wildlife Service, State of New Jersey-Department of Environmental Regulation, State of Delaware-Department of Natural Resources and Environmental Control, and Commonwealth Pennsylvania-Department of Conservation and Natural Resources. Prepared by Polaris Applied Sciences Inc. Kirkland, Washington.
- Swartz, R.C. 1999. Consensus sediment quality guidelines for polycyclic aromatic hydrocarbon (PAH) mixtures. *Environmental Toxicology and Chemistry* 18(4):780-787.
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