

Preassessment Data Report #3

Selendang Ayu oil risk to early life stage salmon

COMMENTS OF THE RESPONSIBLE PARTY

Page 1; Paragraph 1; Introduction

“Polynuclear aromatic hydrocarbons (PAH) from the Selendang Ayu oil spill were biologically available at detrimental concentrations in 1 of 14 streams examined, likely placing resident juvenile fish and possibly embryos at risk.”

Replace *“likely placing resident juvenile fish and possibly embryos at risk.”* with *“possibly exposing resident juvenile fish to PAHs.”*

“Although bioavailable PAH in bays was widely distributed, only the water of Skan Bay posed a risk to emigrant juvenile pink salmon during the sampling period.”

A risk is argumentative. “Potentially exposed” is more accurate.

The use of the word “risk” is inappropriate here. “Exposed” would be more consistent with the purpose of a preassessment data report.

Page 1; Paragraph 2; Introduction

*“The impacted area included 19 streams utilized by pink salmon (*Oncorhynchus gorbuscha*)...”*

Replace with *“Nineteen streams empty into these bays and are utilized by pink salmon (*Oncorhynchus gorbuscha*)”*

“Long term follow-up studies demonstrated that low part per billion level exposures (1 to 18 µg/L) were effective in causing both short term (Marty et al 1997, and long term effects, including reductions in adult returns after embryonic exposures (Heintz et al. 1999, 2000; Carls et al. 2005).”

Replace *“demonstrated”* with *“have suggested”*

What is being referred to as *“part per billion”*? Is the measurement *“(1 to 18 µg/L)”* referring to TPAH?

Page 1; Paragraph 3; Introduction

“This caused considerable concern because the Exxon Valdez experience demonstrated significant multi-year negative effects in pink salmon when banks of streams were contaminated with oil.”

Replace with “This caused considerable concern because studies in the Exxon Valdez spill area have suggested that significant multi-year negative effects in pink salmon result when banks of streams in Prince William Sound were contaminated with crude oil.

Page 1; Paragraph 3; Introduction

“This caused considerable concern because the Exxon Valdez experience demonstrated significant multi-year negative effects in pink salmon when banks of streams were contaminated with oil. Dye studies in Prince William Sound (PWS) after the Exxon Valdez oil spill demonstrated gravity-driven groundwater flow from contaminated intertidal substrate into stream channels, including the hyporheic zone utilized by developing pink salmon embryos (Carls et al. 2003). Sensitive passive samplers (low-density polyethylene membrane devices (PEMDs) detected a PAH concentration gradient in at least one affected stream a decade after the Exxon Valdez spill, demonstration of the long, slow release from stranded intertidal oil (Carls et al. 2004a). Consistent with drainage of PAH into stream systems, cytochrome P4501A (CYP1A) was induced in pink salmon alevins (1989 to 1991; Wiedmer et al. 1996). All of these observations in PWS explain the elevated pink salmon egg mortality that persisted for 4 years in oiled PWS streams (Bue et al. 1998).”

The dye studies of Carls et al (2003) do not demonstrate that weathered oil from the Exxon Valdez (EVO) that accumulated in intertidal boulder/cobble/gravel sediments and anadromous stream banks (named stream deltas by Carls et al., 2003) migrated into the tidally-influenced reaches of streams where a fraction of Prince William Sound pink salmon redds are located. Buried, weathered crude oil in stream delta sediments does not behave like a water-soluble dye. The weathered oil was highly viscous and nearly insoluble and its presence substantially decrease sediment permeability, decreasing water flow through the sediment and partitioning of hydrocarbons, including PAH, from the oil phase into sediment pore water. Brannon et al. (1995) measured only low concentrations of petroleum PAH in intertidal spawning sediments of oiled streams in August 1989 and April 1990. An exception was the steam emptying into Sleepy Bay on the north shore of Latouche Island where TPAH concentrations in stream gravels were elevated, probably due to seasonal, storm induced changes in the position of the lower stream channel, and the extremely high level of contamination of the shore in Sleepy Bay.

As the authors reveal later in the report, the conditions under which these studies were conducted do not exist within the Unalaska Island streams studied. Therefore, this comment is irrelevant and should be deleted.

Page 2; Paragraph 1; Introduction

“Sensitive passive samplers (low-density polyethylene membrane devices (PEMDs) detected a PAH concentration gradient in at least one affected stream a decade after the Exxon Valdez spill, demonstration of the long, slow release from stranded intertidal oil (Carls et al. 2004a).”

Replace “*demonstration of the*” with “indicating that at that site there was a”

Add “crude” before “oil”

The contaminated stream was the one in Sleepy Bay, alluded to above. The entire intertidal zone of the region of Sleepy Bay where the stream was heavily oiled with EVO and shoreline cleanup was delayed until later summer, 1989. Substantial amounts of oil penetrated the coarse boulder/cobble sediments and accumulated as subsurface oil deposits. Seasonal storms have periodically changed the course of the lower stream channel, probably exposing sequestered subsurface oil deposits. Highest PAH concentrations determined by PEMDs were in the lowest tidal zone examined (+2 m above MLLW).

“All of these observations in PWS explain the elevated pink salmon egg mortality...”

Replace with “Some scientists believe that these observations in PWS are related to elevated pink salmon egg mortality...”

Page 2; Paragraph 2; Introduction

“Experience and sampling strategy developed in the study of the Exxon Valdez spill was applied to the Selendang Ayu spill, including division of ...”

Not relevant to this PADR and should be deleted.

Deployment of passive samplers (PEMDs) to detect oil began 3 months after the Selendang Ayu spill, a technology developed after the Exxon Valdez oil spill (Huckins et al. 1990; Carls et al. 2004b).”

Delete “*a technology developed after the Exxon Valdez oil spill (Huckins et al. 1990; Carls et al. 2004b).*” This is not relevant to this PADR.

Page 2; Paragraph 3; Introduction

“...6) to evaluate the risk to salmonids in oil-affected streams...”

Delete “to”.

Page 3; Paragraph 6; Methods: Assessment of nearshore marine habitat

“These PEMDs were deployed in March, April, May, and August; sampler loss in this high energy environment was relatively frequent, resulting in discontinuous sampling.”

Add “of 2005” after “August”.

Page 4; Paragraph 1; Methods: PEMD preparation and quality assurance

“The PEMDs were buried about 3 to 6 cm below the stream bed during the first installation.”

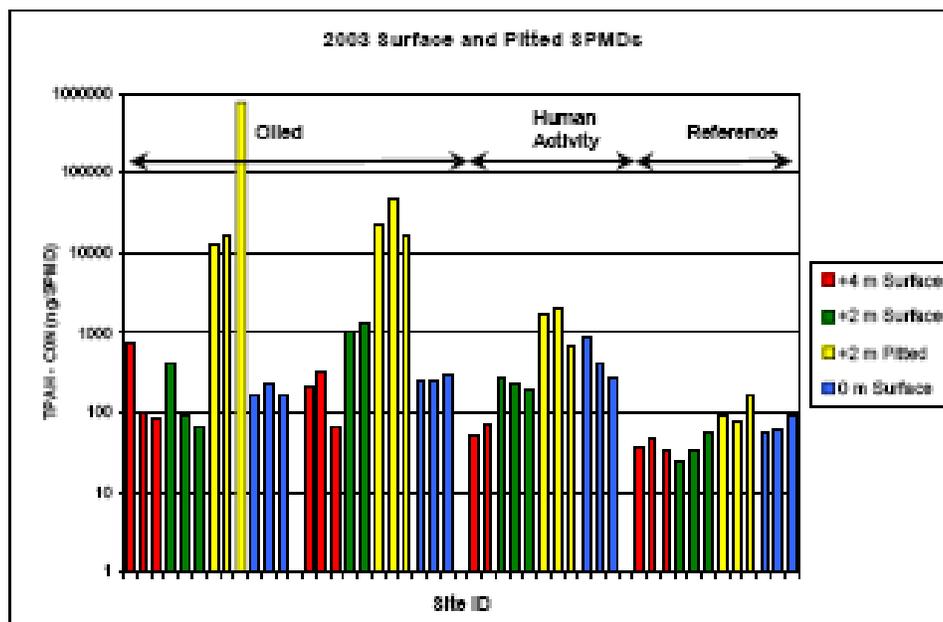
Carls et al. (2007) used passive samplers, low-density polyethylene membrane devices (PEMDs) to document PAH from lingering subsurface oil (SSO) and seepage from stream-bank sediments in salmon streams in the spill zone. As in oil bioavailability studies in Prince William Sound, Carls et al. (2007) buried PEMDs (or semi permeable membrane devices (SPMDs)) in oil-contaminated stream-bed and intertidal sediments to demonstrate that the oil was “bioavailable” (and therefore, potentially toxic) (Short et al., 2005; Springman et al., 2005). This provided meaningless data.

PEMDs resemble the more widely used and validated semi permeable membrane devices (SPMDs: Huckins et al., 2000) except that they lack the lipid, triolein inside the membrane tube. The conceptual model of the SPMD is that non-polar organic chemicals, such as PAH, partition across the 86 µm thick low-density polyethylene membrane and accumulate in the lipid, mimicking the partitioning of chemicals across biological membranes into lipid phases in tissues. In the PEMD, the non-polar organic chemicals adsorb or are absorbed by the membrane itself, where they are relatively persistent (Carls et al., 2004b). This difference makes PEMDs more susceptible than SPMDs to physical contamination with oil when the membranes are buried in sediment.

Although PEMDS and SPMDS can be used effectively in monitoring organic contaminants in water, particularly where bivalves are not available, oil spill studies present some unique challenges in estimating the concentrations of bioavailable fractions of oil PAH in the water and shoreline sediments as part of bioavailability and exposure assessments. Shea et al., (2007) have studied the use of SPMDs in oil spill studies and found that while SPMDs can be used to estimate bioavailable PAH when “source oil is not visible” they found that “...SPMDs...are an inappropriate means of estimating bioavailable PAHs in the

presence of crude oil". In effect, direct contact of SPMD membranes with crude oil caused a gross (300+ fold) overestimation of bioavailability of petroleum PAH compared to results obtained from mussels resident at the sites of SPMD deployment. Boehm et al. (2005) found that burial or partial burial of SPMDs in pits on beaches with known SSO residues produces artificially elevated levels of EVOS PAH residues adsorbed on and absorbed in the SPMDs membranes (Figure 1).

Figure 1. Total PAH concentrations in SPMDs deployed in pits and at the sediment surface at three tide heights at several oiled, unoled human activity, and unoled reference sites in Prince William Sound, AK (Data from Boehm et al., 2005).



A better approach would have been to analyze tissues of intertidal animals, such as clams, mussels, crabs, or salmon embryos/alevins (Brannon et al., 1995, 2007; Neff et al., 2006). This gives a much better and more accurate estimate of potential exposure to and bioavailability of intertidal oil residues to intertidal animals.

Mussels were collected from several oiled and unoled shores on Unalaska Island in 2005 and 2006 and analyzed for PAH (Table 1). Total PAH concentrations in mussels collected from the most heavily oiled bays (North Skan Bay and South Skan Bay) were higher than in mussels from lightly oiled or unoled bays. Mean TPAH concentrations in mussels collected in North Skan Bay on April 25, 2005 (4 months after the spill) was 9625 ng/g dry wt (parts per billion). By May 24, 2006 (13 months later), the mean TPAH concentration in mussel tissues had dropped by 94% to 540 ng/g. In South Skan Bay, mean TPAH concentrations in mussels dropped by 86% from 1114 ng/g on April 25, 2005 to 159 ng/g on May 26, 2006. The PAH residues in the mussel tissues can be considered to reflect the bioavailable fraction of PAH from intertidal sediments. TPAH concentrations in

Table 1. Total PAH ($\mu\text{g}/\text{kg}$) in blue mussels collected over time in the *Selendang Ayu* spill area.

Date	SCAT segment	Sample ID	Total PAH ($\mu\text{g}/\text{kg}$)	Notes
Volcano Bay				
5-26-06	VLC-05	MU-VLC05-26May06	2.85	
Cannery Bay				
8-29-05	CNB-17	MU-CNB17-8-29-05-01	8.4	
9-23-05	CNB-19	MU-CNB-19-9-23-05-01	86	Same location as 8-29 – Segment misidentified
9-23-05	CNB-19	MU-CNB-19-9-23-05-02	9.4	Same location as 8-29 – Segment misidentified
Anderson Bay				
8-29-05	AND-02	MU-AND2-8-29-05-01	7.1	
North Skan Bay				
4-25-05	SKN-11	SKN-11 (North) Rep 1	8706	
4-25-05	SKN-11	SKN-11 (North) Rep 2	12411	
4-25-05	SKN-11	SKN-11 (South)	7759	
9-23-05	SKN-11	MU-SKN-11-9-23-05	6079	
5-24-06	SKN-11	SKN-11 North 5-24-06	613.02	
5-24-06	SKN-11	SKN-11 South 5-24-06	467.31	
South Skan Bay				
4-25-05	SKS-04	SKS-4 (South)	642	
4-25-05	SKS-04	SKS-4 (North)	1009	
4-28-05	SKS-04	SKS-4N	1692	
8-27-05	SKS-06	MU-SKS06-8-27-05-01	257	Close to SKS-04
8-28-05	SKS-17	MU-SKS17-8-28-05-01	537	South of SKS-04 and SKS-06
9-23-05	SKS-04	MU-SKS-04-9-23-05-01	479	
9-23-05	SKS-04	MU-SKS-04-9-23-05-02	800	
5-26-06	SKS-04	MU-SKS04-26May06	158.76	
Makushin Bay				
8-28-05	MKS-11	MU-MKS-11-8-28-05-01	18	
9-23-05	MKS-11	MU-MKS-11-9-23-05	91	
5-26-06	MKS-11	MU-MKS11-26May06	51.45	
Kashega Bay				
8-31-05	KSB-07	MU-KSB7-8-31-05	19	
5-26-06	KSB-08	MU-KSB08-26May06	3.12	Same location as 2005; Segment misidentified
Kismaliuk Bay				
8-31-05	KMK-07	MU-KMK7-8-31-05	70	
5-26-06	KMK-28	MU-KMK28-26May06	14.24	Note different segment location

stream-bed sediments and associated mussels undoubtedly were much lower than in middle and lower intertidal sediments and mussels. Thus, even shortly after the

spill, concentrations of petroleum PAH in spawning redds of spill-path streams on Unalaska Island probably were very low.

Page 5; Paragraph 1; Methods: Interpreting PAH concentrations in PEMDs

“A summary oil-identification model comprised of multiple oil-identification models was used to determine if PAH composition in PEMDs and tissue was consistent with a petrogenic source, presumptively Selendang Ayu oil, the only known and largest potential source of oil (Carls 2006).”

A confounding factor in assessing long-term exposure to and effects of the *Selendang Ayu* oil spill early life stages of pink salmon and other fish that use coastal waters is that the coastal waters were and still are not free from chronic petroleum contamination. More than 4000 ships per year pass near Unalaska Island along routes similar to that of the *Selendang Ayu*. Releases of oil in bilge or ballast discharges are not unusual in the area. Although the *Selendang Ayu* spill was the major source of petroleum PAH in streams and coastal waters for several months after the spill, as time after the *Selendang Ayu* spill increases it becomes more difficult to attribute any evidence of exposure to oil to the heavy fuel oil spilled from the *Selendang Ayu*.

Page 5; Paragraph 6; Study Area: Oiled area

“In June 2005, numerous adult salmon carcasses, apparently pink salmon, were observed partially buried in fine bottom sediments in this area.”

Were these carcasses spawned out?

Page 6; Paragraph 1; Study Area: Oiled area

“Stream SKN14 supports a salmon run (mean 12,000 fish, n = 3; Appendix 2).”

Pink salmon?

Page 7; Paragraph 4; Results: Oil and spawning habitat distribution

“There was little overlap between oiled habitat and pink salmon spawning habitat in most streams.” and “There was no evidence of intertidal spawning at any stream (examined with hydraulic pumping); the habitat in the Aleutians was not similar to the intertidal habitat in PWS. Tides are significantly smaller in the Aleutians and beaches and stream mouths are typically subjected to higher energy surf. In addition, stream gradients in the lower reaches above the surf zone are often too low to provide spawning gravels. Observed oiling was generally confined to beach areas and usually did not extend upstream to spawning habitat.”

These large differences in the characteristics of pink salmon spawning habitat between Prince William Sound and the Bering Sea coast of Unalaska Island as well as the differences in the physical, chemical, and toxicological properties of the *Selendang Ayu* heavy fuel oil and North Slope mid-weight crude oil make it inappropriate to extrapolate from the *Exxon Valdez* pink salmon studies to the *Selendang Ayu* salmon studies to predict effects or even design studies for the latter spill.

Page 8; Paragraph 1; Results: Oiling and spawning habitat distributions

“A tributary in the vicinity of site 3 was prime spawning habitat; alevins were abundant. The lower portion of this tributary was oiled for about 35m. Juvenile coho and Dolly Varden...”

What species would use this habitat? Was the area where the alevins were abundant above or below the oiled area?

Page 8-9; Results: Potential biological availability of PAH, measured in PEMD surrogates and Page 11; Paragraph 3; Discussion.

Throughout this section (pages 8-9), PAH concentrations in PEMDs are quoted as “total PAH concentrations in marine water” (Page 8, Paragraph 4). This is patently incorrect; the data are concentrations of PAH in PEMDs. The data in Carls et al. (2004b) are not sufficient to estimated concentrations of bioavailable PAH in water from concentrations of PAH in PEMDs, as is done routinely for SPMDs (Huckins et al., 1993), contrary to the statement on page 11 (“*A rough, order-of-magnitude estimate of aqueous TPAH in Unalaska streams is possible by comparison of PAH concentrations in PEMDs to data from a controlled laboratory experiment.*”). In addition, physical contamination of PEMD membranes by direct contact with buried oil during deployment, as discussed above, would produce gross overestimates (by 300-fold or more according to Shea et al., 2007) of the actual TPAH concentration in the water.

Page 8; Paragraph 3; Results: Potential biological availability of PAH, measured in PEMD surrogates

“SKN4: oil was observed only near the mouth and in the intertidal berm, consistent with SCAT observations (Fig. 1). “

No figures were included with our copy of this PADR. We reserve our right to provide additional comment at that time.

Page 8; Paragraph 6; Results: Potential biological availability of PAH, measured in PEMD surrogates; Comparison of oiled bays and oiled streams

“This relationship is clear in SKN14 where initial and final TPAH concentrations in stream water were high and the oil was fresh (Fig. 3 and Appendix 4).”

No appendices were provided with our copy of this PADR. We reserve our right to provide additional comment at that time.

Page 9; Paragraph 6; Discussion: Pink salmon embryo exposure and risk

“Polynuclear aromatic hydrocarbons (PAH) from the Selendang Ayu oil spill were biologically available at detrimental concentrations in 1 of 14 streams examined (SKN14), likely placing resident juvenile fish and possibly embryos at risk.”

The PEMD data do not document that PAH from the *Selendang Ayu* oil spill were biologically available at detrimental concentrations in any streams. As discussed above, the PEMD data can not be used to estimate concentrations of bioavailable PAH in the water and any estimates would be overestimates of actual concentrations because of physical contamination of PEMD membranes with oil during burial in stream-bed and bank sediments. In addition, because, as Carls et al., 2007 attest, pink salmon do not spawn in the intertidal reaches of oiled streams where elevated concentrations of petroleum PAH were accumulated in PEMDs; therefore, pink salmon embryos in oiled Unalaska Island streams are not at risk of harm from exposure to *Selendang Ayu* heavy fuel oil. Juvenile fish that utilize the stream mouths during summer are much more tolerant to weathered oil than pink salmon embryos, and would not be harmed by exposure to weathered *Selendang Ayu* heavy fuel oil in the water column. Water samples were collected on 12/13/04, slightly more than one month after the spill, in several bays where oil from the *Selendang Ayu* drifted. The highest TPAH concentration measured (2.6 ppb) was in a water sample from the west fork of Skan Bay, an area considered by Carls et al. (2007) to have salmon streams. This concentration is lower than concentrations of petroleum PAH considered toxic to juvenile fish.

Page 10; Paragraph 3; Discussion: Pink salmon embryo exposure and risk

“Salmonids were at risk in stream SKN14, where oil...”

Replace with “Salmon alevin were exposed to oil in stream SKN14, where oil...”

Page 10; Paragraph 4; Discussion: Pink salmon embryo exposure and risk

“Given the physical nature of the bunker oil spilled, persistence of the oil is virtually guaranteed in the freshwater environment for several months².”

Add at end of sentence: “if not removed from the environment”.

Page 11; Paragraph 1; Discussion: Pink salmon embryo exposure and risk

“Composition of the biologically available PAH from Selendang oil (IFO 380, a refinement residue) was so similar to biologically available PAH from Exxon Valdez crude oil that the highly discriminatory first-order loss-rate model of Short and Heintz (1997) generally failed to distinguish the two³. Not only was PAH composition about the same, it also followed the weathering patterns observed for crude oil (more rapid loss of smaller molecular weight PAH). Similar effects in the Selendang spill could be expected if exposure concentrations and conditions (similar exposure periods, comparable life stages and species) were similar to the Exxon Valdez crude oil spill.”

We believe the similarity of the *Selendang Ayu* fuel compared to *Exxon Valdez* (Alaska North Slope) crude is overstated. A detailed explanation can be found in the Attached Appendix 1.

Page 11; Paragraph 3; Discussion: Pink salmon embryo exposure and risk

“A rough, order-of-magnitude estimate of aqueous TPAH in Unalaska streams is possible by comparison of PAH concentrations in PEMDs to data from a controlled laboratory experiment. The consistent overall pattern was an exponential TPAH decline in the heavily oiled SKN14 stream. A similar decline was evident in PEMDs serially deployed in a laboratory experiment where measured aqueous concentrations were falling exponentially (Carls et al. 2004b; 2005a). The PAH composition, temperature, and deployment times were similar in both.”

This experiment used Alaska North Slope crude. We believe the similarity of the *Selendang Ayu* fuel compared to *Exxon Valdez* (Alaska North Slope) crude is overstated. A detailed explanation can be found in the Attached Appendix 1.

Page 11; Paragraphs 3 and 4; Discussion: Pink salmon embryo exposure and risk

“With this approach, we estimate that 1,000,000 ng/g in PEMDs corresponds to roughly 20 µg/L in water and 100,000 ng/g corresponds to roughly 2 µg/L.”

“Based on these approximations, fish in portions of stream SKN14 were at risk for a portion of the sampling period; this risk probably extended back to the oiling event and was probably even greater in the months prior to sampling. PAH are highly toxic to fish embryos (0.4 to 23 µg/L TPAH; Marty et al. 1997; Carls et al. 1999; Heintz et al. 1999,

2000; Barron et al. 2003; Colvaecchia et al. 2004; Rhodes et al. 2005) and concentrations in this range and above represent a risk. Aqueous concentrations in SKN14 may have ranged up to about 10 µg/L at the lowest sample elevation and up to 1 µg/L at other oiled sites (March-April), placing developing embryos and other young salmon at risk, particularly in the lowest reaches of the stream⁵.”

Again, these conclusions are based on “approximations” that are not based on data or an analytical method that is described in the report. Such speculation should be deleted.

We suggest this section be extensively rewritten or deleted.

Page 12; Paragraph 4; Discussion: Risk to juvenile salmonids in freshwater and marine environments

“After the 1989 Exxon Valdez oil spill, wild juvenile pink salmon in PWS were exposed to roughly 1 to 3 µg/L TPAH in saltwater⁷ and growth was reduced (Wertheimer et al. 1996; Willette et al. 1996; Short & Harris 1996a,b; Carls et al. 2002).”

⁷ Exact estimates are not available. Total PAHs in mussel tissue were analyzed as site-specific surrogates of exposure; mean concentrations at oiled sites ranged from 3772 to 8282 ng/g (Carls et al. 1996b). Assuming peak concentrations in water and peak concentrations in mussels observed in two specific areas where mussel and aqueous TPAH data were collected concurrently (Short & Harris 1996a,b; Carls et al. 2002) provide a reasonable measure of bioaccumulation by PWS mussels (mean 2652 times), then aqueous exposure concentrations ranged from about 1.4 to 3.1 µg/L. This estimate is within the directly observed range of aqueous TPAH concentrations (range of means 0.9 to 6.2 µg/L) observed elsewhere in the slick area in 1989 (Short and Harris 1996a). The derived bioaccumulation factor is far lower than theoretically possible in mussels (2×10^5 ; Livingstone 1991); bioaccumulations this high would imply aqueous TPAH concentrations less than 0.1 µg/L, i.e., background concentration. This concentration is too low to explain the observed significant CYP1A induction in the juvenile pink salmon fry in PWS and too low to explain the significant TPAH differences in mussel tissue between reference and oiled areas of PWS (Carls et al. 1996b, Carls et al. 2005a).”

Estimation of concentrations of TPAH in water based on comparisons of PAH concentrations in water samples and caged mussels, collected at approximately the same time and location has little scientific merit. PAH residues in tissues of mussels that have been deployed in cages for approximately one month are proportional to the time integrated mean PAH concentration in the ambient water, whereas, the water samples give a snapshot of the concentration at one time and location in the water column. Neff and Burns (1996) described a method based on well established equilibrium partitioning theory for estimating average PAH concentrations in the water from tissue residues in caged or natural populations of mussels. An extensive database of PAH concentrations in the water column of Prince William Sound, including spill path and non-spill path areas was

summarized by Neff and Stubblefield (1995), Neff and Burns (1996), and more recently by Boehm et al. (2007). This data synthesis and review included the water quality data from Short and Harris (1996a,b) for water samples and caged mussel samples, respectively, as well as other water quality and estimated water PAH from mussel tissue data from several Exxon studies.

Boehm et al (2007) reviewed possible exposure of herring and pink salmon to PAH residues from the North Slope crude oil spilled from the *Exxon Valdez* and concluded: “Most pink salmon fry emerged from salmon streams in PWS in April and May 1989 (Cooney et al., 2001). However, only about 30 of the approximately 1300 wild-stock pink salmon streams (2.3% of the total) in PWS suffered significant oiling in tidally influenced reaches after the spill (Brannon et al., 1995; Maki et al., 1995). In addition, hatchery managers delayed release of salmon fry from the hatcheries in 1989 until late April and early May because of the spill. This delayed release avoided the highest concentrations of dispersed and dissolved oil in the water column, which probably coincided with the storm that began 3 days after the spill (Wolfe et al., 1994). Juvenile pink salmon in coastal waters were exposed to low concentrations, generally 0.1–1 ppb TPAH, with a few higher values observed (Fig. 2) in April through July 1989. The juveniles moved to offshore waters in July 1989 (Cooney et al., 2001) where TPAH concentrations were lower (<0.1 ppb). By 1990, exposure to Exxon Valdez-related TPAH was consistent with that occurring in the range of pre-spill or background exposures.”

Thus, although some of the salmon alevins incubating in oiled streams in the spring of 1989 (about 2.3% of pink salmon streams in PWS were oiled by the spill) probably were exposed to harmful concentrations of *Exxon Valdez* oil and could have been killed or suffered sublethal effects, wild-run and hatchery salmon fry migrating to nearshore waters within the spill path probably were not exposed to high enough concentrations of petroleum PAH to cause harm. Measured TPAH concentrations in tissues of pink salmon fry and juveniles collected in April and June 1989 from 4 spill path areas of the sound were significantly higher (181 ± 28 ng/g) than in tissues of juvenile pink salmon from four unoiled reference areas (54 ± 8 ng/g) (Carls et al., 1996b). Only about one-third of the juvenile pink salmon collected in 1989 actually contained PAH from spilled EVC (Bence and Burns, 1995), and many of the PAH were associated with skin or gut contents of the fish and had not actually been bioaccumulated. Some of the PAH in the fish tissues were from other sources (diesel fuel, seep oil, and pyrogenic sources).

Residues of PAH in salmon tissues tended to decrease with time after the spill. In 1990, PAH concentrations in soft tissues of pink salmon fry from spill path and reference areas of the sound were the same (51 ± 7 ng/g) (Carls et al., 1996b). There was no evidence of bioaccumulation of EVC PAH by juvenile salmon in 1990.

There was cytochemical evidence of induction of cytochrome P450 enzymes in tissues of juvenile salmon from spill path, but not unoiled reference areas of the western sound in late spring and early summer of 1989 (Carls et al., 1996b; Willette, 1996). In 1990, there was not a significant difference in MFO activity between spill path and reference area juvenile salmon. The tissue residue and cytochemical staining data are consistent in showing that pink salmon fry and juveniles in spill path areas of the sound were exposed to low levels of PAH in the spring and early summer of 1989, but not in 1990.

Measured concentrations of TPAH in tissues of juvenile salmon in 1989 were in equilibrium with estimated concentrations of less than 0.2 µg/L TPAH in solution in the water column (Neff and Burns, 1996), well below concentrations that might be toxic to juvenile marine fish.

Pink salmon do not spawn in tidally-influenced reaches of anadromous streams on Unalaska Island, but restrict spawning to the upstream freshwater portions of low gradient streams, areas that received minimal oiling from the *Selendang Ayu* spill. By spring of 2005, several months after the spill, when pink salmon fry out-migrated from streams into coastal waters, it is highly likely that PAH concentrations in the well-mixed, high energy coastal waters of western Unalaska Island had returned to near background levels. Thus, it is highly unlikely that significant numbers of pink salmon eggs, alevins, fry, or juveniles were exposed to harmful concentrations of PAH from the heavy fuel oil released from the *Selendang Ayu*.

We believe the similarity of the *Selendang Ayu* fuel compared to *Exxon Valdez* (Alaska North Slope) crude is overstated. A detailed explanation can be found in the Attached Appendix 1.

Page 13; Paragraph 2; Discussion: Risk to juvenile salmonids in freshwater and marine environments

“Juvenile salmon in bays affected by the Selendang Ayu were potentially placed at risk.”

Delete “*placed*”

Page 13; Paragraph 3; Discussion: Oil persistence

“The oil in Skan Bay was persistent; the highest observed TPAH concentration was in a cove south of SKN14 in September, perhaps a result of disturbances caused by ongoing shoreline cleanup activities. Evidence from other spills suggests that not all intertidal oil will be removed by cleanup activity and that remaining oil will be a persistent source of biologically available hydrocarbons for many years.”

Because of the physical/chemical properties of the heavy fuel oil spilled from the *Selendang Ayu* and the high energy of coastal waters around Unalaska Island, the oil is not expected to penetrate and accumulate in intertidal sediments to the same extent as the middle-weight North Slope crude oil spilled from the *Exxon Valdez*. Surface oil that does persist will weather to solid, toxicologically inert residues, similar to the Monterey heavy oil spilled in the 1964 earthquake (Kvenvolden et al., 1995). Persistent subsurface oil residues will have low bioavailability and toxicity and, so, will not pose a risk to intertidal organisms and coastal fish. These topics were discussed in detail in a report “Composition, Environmental Behavior, and Toxicity of Heavy Fuel Oils” attached as Appendix 1.

Page 13; Paragraph 4; Discussion: Oil persistence

“Contaminated prey and disturbance of oiled substrate during feeding activities explains the failure of sea otter and harlequin duck populations to recover in oiled areas of PWS for more than a decade (Esler et al. 2000; Bodkin et al. 2002). For both species, chronic exposure to oil (elevated cytochrome P4501A) and struggling populations in the most heavily oiled areas of Prince William Sound were observed in the decade after the spill (Esler et al. 2000; Bodkin et al. 2002). Salt marsh fiddler crabs (Uca pugnax) populations, feeding rates, and burrowing have been affected by buried oil for greater than 30 years in a West Falmouth marsh (Culbertson et al. 2005). In a review of seven well-studied oil spills, Teal and Howarth (1984) conclude that oil effects can persist for at least 6 to 12 years in sediment.”

This text has nothing to do with exposure to salmon. The discussion should not be part of this Preassessment report.

References

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APPENDIX 1

Composition, Environmental Behavior, and Toxicity of Heavy Fuel Oils

Jerry M. Neff

Neff & Associates LLC

Duxbury, MA 02332

Summary

Heavy fuel oils, such as the IFO-380 fuel oil released from the *Selendang Ayu* are dense, viscous oils with high pour points. Pour point (the temperature below which the oil will not flow) of heavy fuel oils often is near ambient air and water temperatures, particularly in cold environments, such as the site of the *Selendang Ayu* spill. Spilled heavy fuel oil on the cold sea surface is very viscous and tends to fragment into discrete patches, globules, and patties, rather than forming a thin oil slick. By comparison, the middle weight Alaskan North Slope crude oil released from the *Exxon Valdez* formed a massive slick that spread through Prince William Sound and into the Gulf of Alaska. When it washed ashore on sand/gravel beaches, it often seeped below the surface and accumulated as subsurface oil deposits. On the shore, heavy fuel oils may migrate laterally by gravity-driven flow until the pour point is reached, at which point, flow ceases. The heavy, viscous fuel oil does not penetrate sand/gravel sediments, but may be buried, usually in the upper intertidal storm berm, by storm-induced sediment redistribution on the shore. Heavy fuel oils on the shore often weather to a solid asphalt pavement, sometimes containing an inner layer of less weathered, viscous oil. These deposits do not weather away rapidly by erosion from tidal water-washing or biodegradation by hydrocarbon-degrading microbes.

Heavy fuel oils, produced from residual oil with added hydrocarbon diluents, have a different chemical composition than crude oils. They often contain higher concentrations of PAH than crude oils do. The IFO-380 heavy fuel oil from the *Selendang Ayu* contained substantially higher concentrations of PAH, including 4- through 6-ring PAH, than the North Slope crude oil released from the *Exxon Valdez*. However, heavy fuel oils have a much lower aqueous solubility than most crudes, including North Slope crude. The low solubility of hydrocarbons, including PAH, from heavy fuel oil is caused by the low surface to volume ratio of the heavy oil globules and their high viscosity which slows mixing of hydrocarbons to the surface of the oil mass where they can partition into the ambient water. As a result, bioavailability of PAH from weathered heavy fuel oils is much lower than bioavailability of PAH from weathered crude oils, such as North Slope crude oil.

The aquatic toxicity of heavy fuel oils often appears to be higher than that of crude oils, when the dose is measured as the concentration of total petroleum hydrocarbons (TPH) or PAH in the exposure water. However, these are an inappropriate measures of exposure concentration from an environmental perspective, because TPH and PAH are not the sole contributors to oil toxicity, particularly after weathering has reduced concentrations of lower molecular weight, more soluble hydrocarbons. When exposure concentration or

dose is measured as the mass of oil added to the water or the percent of the water accommodated fraction at which toxicity occurs, heavy fuel oils nearly always are much less toxic than crude oils.

The soluble/finely dispersed fraction of weathered North Slope crude oil is enriched in phenanthrenes and dibenzothiophenes compared to the aqueous fraction of weathered *Selendang Ayu* heavy fuel oil collected from Skan Bay about one month after the oil spill. Water samples from oiled bays in the spill zone of Unalaska Island contained lower TPAH concentrations than those of North Crude oil required to harm pink salmon embryos. Thus, the weathered *Selendang Ayu* heavy fuel oil probably was much less toxic to marine animals, including pink salmon embryos, than the weathered North Slope crude oil from the *Exxon Valdez* spill. Therefore, because of the differences in physical/chemical properties and resulting environmental behavior and toxicity of heavy fuel oils and middle weight crude oils, such as North Slope crude oil, it is not appropriate to use data from the extensive studies of the *Exxon Valdez* oil spill to predict long term effects of the *Selendang Ayu* heavy fuel oil on the Bering Sea environment.

Environmental Behavior of Heavy Fuel Oils

Physical Properties and Environmental Persistence of Heavy Fuel Oils

Density, viscosity, pour point, and surficial tension are interrelated physical properties that affect the environmental behavior of heavy fuel oils. Density (as measured by API gravity) is the defining physical property of heavy fuel oils. The weight of crude, refined, and residual oils usually is measured as API gravity ($^{\circ}$ API), which is related to specific gravity (density) as follows:

$$^{\circ}\text{API} = (141.5/\text{SG}) - 131.5$$

where SG is the specific gravity (g/cm^3) at 15°C . API gravity decreases as oil density increases. Heavy fuel oils are defined as oils with an $^{\circ}$ API less than 20 (density $> 0.93 \text{ g}/\text{cm}^3$).

Most heavy fuel oils (e.g., No. 6 fuel oil, Bunker C, IFO-380) have a fairly narrow range of $^{\circ}$ API, with a median of about 12 $^{\circ}$ API, corresponding to a density of $0.986 \text{ g}/\text{cm}^3$ at 15°C (Table 1). Heavy fuel oils are made from the residues from refining of crude oil feed stocks. Atmospheric and vacuum distillation residues (bottoms), also called heavy ends, are the products of distillation of a crude oil stock at temperatures up to 345°C (Boduszynski et al., 1998). The atmospheric residue is composed primarily of high molecular weight hydrocarbons and related NSO compounds ($>300 \text{ MW}$, $>\text{C}20$). The 455 to 540°C vacuum gas oil fraction from a 21 $^{\circ}$ API crude oil has a nominal molecular weight range of 190 to 760. By comparison, a mid-weight crude oil, such as an Alaskan North Slope crude oil similar to that released in the *Exxon Valdez* spill, has a higher $^{\circ}$ API, 26.6 – 30.9, corresponding to a density of $0.866 - 0.895 \text{ g}/\text{cm}^3$ at 15°C (Table 1).

Heavy fuel oils usually are quite viscous, some even being solids at ambient temperatures. The viscosity of oil increases as temperature decreases. Thus, at a specific temperature, i.e., the pour point, the viscosity is so high that the oil will not flow at all. ‘Fresh’¹ and weathered heavy fuel oils often have high pour points, ranging from +26°C to -9°C (Table 1). These high pour points (as compared to conventional crude oils and most other fuels) require that heavy oils be handled, transported, and stored under heated conditions. The environmental implication of this is that heavy fuel oils will flow slowly, or not at all, when spilled at most ambient temperatures, particularly the low ambient water temperatures at the site of the *Selendang Ayu* spill (~ 5°C). On the shore, heavy fuel oils may migrate laterally by gravity-driven flow until the pour point temperature is reached, at which point, flow would cease. In cold climates, such as the eastern Aleutians, the pour point often is reached quickly and lateral flow is retarded. At sea, where low ambient air and surface water temperatures are typical, such as in the Bering Sea, spilled heavy fuel oil on the sea surface is very viscous and tends to fragment into discrete patches, globules, and patties (rather than forming a thin, continuous film/slick) that do not disperse by wave action or from application of chemical dispersants.

Table 1. Physical properties of several heavy fuel oils from throughout the world, compared to properties of Alaskan North Slope crude oil similar to that released from the *Exxon Valdez*. From Neff et al., 2003.

Fuel Oil	°API	Density (g/cm ³)	Pour Point (°C)	Viscosity @ 20°C (cSt)
No 5 Fuel Oil	11.55	0.988	-19	1410
No 6 Fuel Oil	10.3	0.998	-6	
No 6 Fuel Oil	8.1	1.013	-9	
No 6 Fuel Oil	4.6	1.040	-6	
Bunker C Fuel	7	1.022	26	>650
Bunker C Fuel	11	0.993	10	>3000
Bunker C Fuel	12.3	0.984	15	Solid
Bunker C (Alaska)	11.4	0.989	-2	8706
IF-30-Bunker Fuel	19.7	0.936	6	236
Heavy Fuel Oil 6303	11.47	0.989	-1	22800
IFO-180	12.5	0.983	4 – 15	>1000
IFO-180	14.7	0.967	-10	6650
IFO-280	12	0.986	4 – 15	>1700
IFO-300	11.9	0.986	-6	53770
IFO-380	11.5	0.990	4 – 15	>2400
IFO-380	16.1	0.959		
Residual Oil #6	12	0.986	15	>45,000
Alaska North Slope Crude	27.5	0.881	-18	32
Alaska North Slope Crude (2002)	30.9	0.866	-32	11.5
Prudhoe Bay Crude (2004)	26.6	0.895		38.9

¹ Use of the term ‘fresh’ is intended to imply unweathered due to environmental weathering.

By comparison, a mid-weight crude oil, such as the North Slope crude oil released in the *Exxon Valdez* spill, has a low pour point, -18 to -32°C, and viscosity 11.5 – 38.9 cSt @ 20°C (Table 1). This oil spreads readily on the sea surface as thin slicks, readily disperses as fine droplets in the water column, and spreads on the shore, penetrating medium to coarse-grained sediments (Wolfe et al., 1994).

The pour point (the temperature below which oil will not flow) of heavy fuel oils is extremely variable, ranging from +26°C to -9°C (Table 1). Most heavy oils with API gravity <20 have pour points above 0°C, but a few have lower pour points. Waxes, resins, and asphaltenes all increase the pour point of heavy crude and fuel oils. The IFO-380 fuel oil released from the *Selendang Ayu* had a density of 0.988 to 0.990 g/cm³ and a pour point between 4 and 15°C. By comparison, Alaskan North Slope crude oil (a crude oil similar to that released from the *Exxon Valdez*) has a density of about 0.893 and a pour point of -10°C (Kucklick, 1994).

Heavy fuel oil pour point and viscosity often are correlated. Usually, fuel oils with pour points >~5°C have kinematic viscosities² >~2,000 cSt (Carlson et al., 1998). The pour point and viscosity of a heavy oil have a profound effect on its behavior if spilled in the environment and the methods that can be used to recover or remediate it (Europa, 2003). Heavy oils with high pour points and viscosities are extremely difficult to disperse effectively with chemical dispersants or wash from shorelines with “beach cleaners.” The heavy, viscous oil disperses in the water column as large droplets that quickly coalesce and return to the surface or remain suspended in the water column as large globules. High wax and asphaltene content tends to stabilize water in oil emulsions, formed when water droplets are physically dispersed into the heavy oil phase, forming water-in-oil emulsions, sometimes called chocolate mousse. However, because heavy oil residues remain as thick layers or mousse on the water surface or on the shoreline, they may be easy to recover mechanically.

Density, pour point and viscosity increase as heavy fuel oils weather in the environment (Table 2). Density of some heavy fuel oils increases with extended weathering to the point that the oil is denser than sea water (SG ~ 1.1 g/cm³). These dense, weathered fuel oils sink or remain suspended as large patties in the water column, where they are difficult to recover. The IFO-300 heavy fuel oil in Table 2 and most other heavy fuel oils are unlikely to weather to a density equal to or greater than that of sea water. They contain relatively low concentrations of volatile hydrocarbons that evaporate from the oil during weathering, increasing oil density only slightly. However, if they mix with large amounts of silt/sand, they may become more dense than seawater and sink (Michel and Galt, 1995).

² Kinematic viscosity (cSt) = dynamic viscosity (cP) divided by density. Since most heavy fuels have a density near 1.0, cSt ≈ cP.

Table 2. Change in physical properties of an IFO 300 heavy fuel oil and an Alaska North Slope Crude Oil during artificial weathering. From Environment Canada, 2006.

% Evaporation	Density @ 0°C	Pour Point (°C)	Viscosity @ 0°C (cP)	Interfacial Tension @ 0°C (mN/m)
IFO 300 Heavy Fuel Oil				
0	0.996	-6	128,600	72.9
5	1.010	12	3,350,000	Immobile
North Slope Crude Oil				
0	0.878	-32	23.2	22.5
10	0.905	-20	76.7	25.3
22.5	0.930	-9	614	26.8
30.5	0.946	-6	4230	30.1

Environmental weathering of these heavy fuel oils causes a gradual change in their physical state; they become highly viscous, solid to semi-solid masses that are difficult to disperse, but may be easier to recover from the sea surface or the shore.

Changes in physical properties of a mid-weight crude oil, such as an Alaskan North Slope crude oil similar to that released in the *Exxon Valdez* spill, are much less dramatic than those for a heavy fuel oil (Table 2). Density, pour point, viscosity, and interfacial tension all increase during weathering, but the increases are relatively small. The crude oil remains liquid and can be dispersed as small droplets into the water column. North Slope crude oil forms stable mousse, containing about 70% water. Mousse formed from heavy fuel oils and North Slope crude oil are resistant to dissolution and microbial degradation, and so are persistent (Irvine et al., 1999).

The fraction of oil boiling at less than 200°C and the fraction boiling above about 370°C are good indicators of the fraction that will evaporate quickly from spilled oil and the residual fraction that may be resistant to evaporation, dissolution, and biodegradation, respectively. Heavy fuel oils contain very little low-boiling fraction (usually 3 – 24 percent: ITOPF, 2003) and a large high-boiling fraction and so are likely to be persistent in the environment if spilled.

Finally, interfacial tension³ also usually is higher in heavy fuel oils than in a mid-weight crude oil and often increases with weathering (Table 2). Interfacial tension controls the tendency of a non-miscible liquid, such as a heavy fuel oil, to spread on the water surface. There is an inverse relationship between interfacial tension and oil spreading and droplet formation. Thus, as oil weathers and interfacial tension increases, it spreads more slowly on the sea surface and becomes more difficult to disperse into the water column. Heavy fuel oils, such as those released from the *Selendang Ayu*, spread poorly on the sea surface and tend to form thick patties, globules, or tar balls on the sea surface and on the shore. North Slope crude oil has a low interfacial tension that increases only slightly

³ def. - the attractive force between two immiscible liquids.

during evaporative weathering. In the *Exxon Valdez* spill, it spread as thin slicks on the sea surface (Wolfe et al., 1994).

Heavy fuel oils blended from vacuum residua require the addition of a less dense ‘cutter’ stock to meet heavy fuel oil specifications (Michel et al., 1995). Heavy residual fuels are derived from the refinery distillation bottoms (residua). Because of the high density and viscosity of the starting material, they are carefully blended with lighter petroleum products to achieve viscosity, flash point, pour point, vanadium, and sulfur specifications (Table 3) and, at the same time, produce a homogeneous and stable product that is free of excess particles (unsettled asphaltenes and Conradson carbon residues). Toward this end, it is common practice to “cut” refinery residua (e.g., vacuum distillation residua) with 20 to 40 percent lighter petroleum fractions such as diesel fuel, marine diesel, kerosene, or cycle oil and, in some instances, even crude oil. The best practice is to blend in an aromatic-enriched cracked distillate (e.g., cat-cracked heavy gas oil, desulfurized gas oil) to minimize asphaltene precipitation in the blended residual fuel (Schmidt, 1969).

Table 3. Specifications for marine residual fuel oils and fuel oil #6. (From ASTM D-2069-98 and D-396-02a).

Category ISO-F-	Property and Limit											
	Density at 15°C, g/ml	Gravity (°API)	Kinematic Viscosity at 100°C, cSt	Flash Point, °C	Pour Point (upper), °C	Winter Quality	Summer Quality	Carbon Residue, % mass	Ash, % mass	Water, % vol.	Sulfur, % mass	Vanadium, mg/kg
	Max.	Min.	Max.	Min.	Max.		Max.	Max.	Max.	Max.	Max.	
RMA 10	0.975	13.6	10	60		0	6	10	0.1	0.5	3.5	150
RMB 10	0.991	11.3	10	60		24	24	10	0.1	0.5	3.5	150
RMC 10	0.991	11.3	10	60		24	24	14	0.1	0.5	3.5	300
RMD 15	0.991	11.3	15	60		30	30	14	0.1	0.8	4	350
RME 25	0.991	11.3	25	60		30	30	15	0.1	1	5	200
RMF 25	0.991	11.3	25	60		30	30	20	0.2	1	5	500
RMG 35	0.991	11.3	35	60		30	30	18	0.2	1	5	300
RMH 35	0.991	11.3	35	60		30	30	22	0.2	1	5	600
RMK 35	35	60		30	30	22	0.2	1	5	600
RML 35	35	60		30	30	...	0.2	1	5	600
RMH 45	0.991	11.3	45	60		30	30	22	0.2	1	5	600
RMK 45	45	60		30	30	22	0.2	1	5	600
RML 45	45	60		30	30	...	0.2	1	5	600
RMH 55	0.991	11.3	55	60		30	30	22	0.2	1	5	600
RML 55	55	60		30	30	...	0.2	1	5	800
Fuel Oil #6			50	60		15*				2.0**		

* Value for “low pour”-type fuel oil #6, “high pour”-type has no maximum

** Water plus sediment, % vol.

Chemical Composition of Heavy Oils

The chemical compositions of heavy fuel oils affect their persistence in the environment, toxicity, and ability to be degraded by sunlight and microbial activity (Neff, 1990). Crude oil was formed over millions of years in sedimentary strata deep in the earth by the natural decay and chemical rearrangement of ancient organic matter, mostly marine and freshwater plants (Tissot and Welte, 1984). As a result, crude oil is composed of a complex mixture of thousands of organic chemicals and smaller numbers of inorganic compounds; no two crude oils are exactly alike. Instead, they vary tremendously in chemical composition, depending on the species composition and geologic age of the organisms that formed the original building blocks of the oil, the temperature and pressure conditions under which the oil was formed and has resided in the formation, and the physical, chemical, and biological transformations it has undergone during formation, migration, and storage in the reservoir.

The refined and residual oils produced from crude oil refining also are composed of a complex, variable mixture of hydrocarbons, reflecting the composition of the starting crude oil feed stock. Each refined product contains the hydrocarbons within a defined boiling point range. Residual oil is the heavy fraction, boiling above about 345°C, remaining after the refined products are removed. Heavy fuel oils usually are cut with 20 to 40 percent middle distillate oil or light crude oil to reduce viscosity, and so contain some light hydrocarbons boiling below 345°C.

Heavy fuel oils often contain smaller amounts of saturated hydrocarbons, especially the more biodegradable n-paraffins, than conventional crude oils (Table 4). Thus, heavy fuel oils often are preferentially enriched in aromatic hydrocarbons, NSO compounds, and polars/resins/asphaltenes compared to conventional oils, such as North Slope crude oil. Saturated hydrocarbons usually comprise less than 25% of heavy fuel oils. Conventional crude oils (°API > 20) usually contain more than 50 percent saturated hydrocarbons (Tissot and Welte, 1984). Aromatic hydrocarbons and benzothiophene derivatives (which are not easily separated from aromatics and therefore often are reported as aromatics) usually represent more than 35 percent of heavy fuel oils. Conventional crude oils contain an average of 28.6 percent aromatic hydrocarbons. Different samples of Prudhoe Bay crude oil and North Slope crude oil (similar to the oil released from *Exxon Valdez*) contain 15 – 37 percent aromatic hydrocarbons. Resins, asphaltenes and polars comprise 15 to 50 percent of most heavy fuel oils, compared to an average of 14.2 percent in conventional crude oils (Tissot and Welte, 1984).

Hydrocarbons

The most abundant chemicals in petroleum are hydrocarbons, organic compounds composed of just carbon and hydrogen. Most crude oils contain 50 to 98 percent hydrocarbons (National Academy of Sciences, 1985). The two main types of hydrocarbons in crude and refined petroleum are saturated (also called aliphatic, paraffin, or alkane) and aromatic hydrocarbons. Small amounts of alkenes or olefins, hydrocarbons

with one or more double bonds between carbon atoms, are present in many heavy fuel oils (Frolov and Smirnov, 1994).

Resolved (by GC) aromatic hydrocarbons usually account for about 1 to 20 percent of the total hydrocarbons in crude and residual oils (Spears and Whitehead, 1969; Tissot and Welte, 1984). Much of the aromatic hydrocarbons in crude and residual oils are insoluble, naphtho-aromatics (complex hydrocarbons with fused saturated and aromatic ring structures) and high molecular weight polycyclic aromatic hydrocarbons (PAH). These high molecular weight aromatic structures are not resolved by conventional gas chromatography and are of little environmental concern because of their insolubility. Volatile and soluble monocyclic aromatic hydrocarbons (alkyl-benzenes) are present in heavy fuel oils, usually at low concentrations (George et al., 2002). Highly alkylated, branched and linear alkyl benzenes may be abundant in some heavy fuel oils (Sutton et al., 2005). Resolved 2- through 6-ring PAH and related heterocyclic hydrocarbons usually represent less than 5 percent of the total aromatic hydrocarbons in crude oils and heavy fuel oils.

Table 4. Bulk compositions of heavy fuel oils and Alaskan North Slope crude oils. From Ostazeski et al., 1995, 1997; Environment Canada, 2006.

Oil	API Gravity	Saturates (wt%)	Aromatics (wt%)	Resins/Asphaltenes (wt%)
No 5 Fuel Oil	11.55	44.2	39.5	16.4
No 6 Fuel Oil	10.1	11.2	54.5	34.2
Heavy No 6 Fuel Oil	4.6	9.0	71.3	19.8
Bunker C Fuel Oil	14.1	21.1	34.2	44.7
Bunker C (Alaska)	11.4	25	47	28
Heavy Fuel Oil 6303	11.47	42.5	29	28.5
IFO-180	14.7	29	51	21
IFO-300	11.9	26	52	22
IF-30 Bunker Fuel	19.7	19.0	63.4	17.6
Prudhoe Bay Crude Oil	27	61.2	35.6	3.1
Alaska North Slope Crude Oil	27.5	53	37	10
Alaska North Slope Crude Oil (2002)	30.9	75	15	10.1
Prudhoe Bay Crude Oil (2004)	26.6	60.8	28.3	10.9

The aromatic hydrocarbons in heavy crude oils are of particular interest because they are considered the most toxic components of crude and refined oils (Neff, 1979, 2002). The most abundant aromatic hydrocarbons in most crude and refined oils are the monocyclic aromatic hydrocarbons, particularly benzene, toluene, ethylbenzene, and xylenes (BTEX) (Neff, 2002). However, heavy oils are substantially depleted in volatile (and soluble) hydrocarbons (George et al., 2002) and the concentrations of monocyclic aromatic

hydrocarbons, such as benzene are very low. Several heavy fuel oils listed by Environment Canada (2006) contained 1290 to 1787 mg/L total C₀- through C₃-benzenes. By comparison different samples of North Slope crude oil contained 21,920 to 22,400 mg/L total C₀- through C₃- benzenes. Because most of the volatile and slightly soluble monocyclic aromatic hydrocarbons are lost rapidly from heavy oils by evaporation, and water washing, PAH usually are the most abundant resolved aromatic hydrocarbons in heavy fuel oils and conventional crude oils following release to the environment.

The PAH composition of residual fuel oils is highly variable and depends on the composition of the refinery feed stock and where the residua came from in the refinery stream. The residual fraction from a catalytic cracker often is enriched in higher molecular weight 4- through 6-ring PAH. The TPAH concentrations in 49 unweathered, residual fuel oils (Bunker C and fuel oil #6) surveyed by Stout et al. (2001) ranged from 8,660 to 48,200 mg/kg, but most samples contained from 20,000 and 30,000 mg/kg TPAH (average 27,450 mg/kg; Figure 1). The TPAH concentration of most conventional crude oils is lower than that of many heavy fuel oils. The higher concentrations of PAH in heavy fuels is not unexpected, given the blending stocks that include refinery residua from which they are formulated. Nearly all the PAH in the residual fuel oils are 2-ring (naphthalenes; 18.1-78.6% of TPAH) and 3-ring (fluorenes, phenanthrenes, and dibenzothiophenes) PAH.

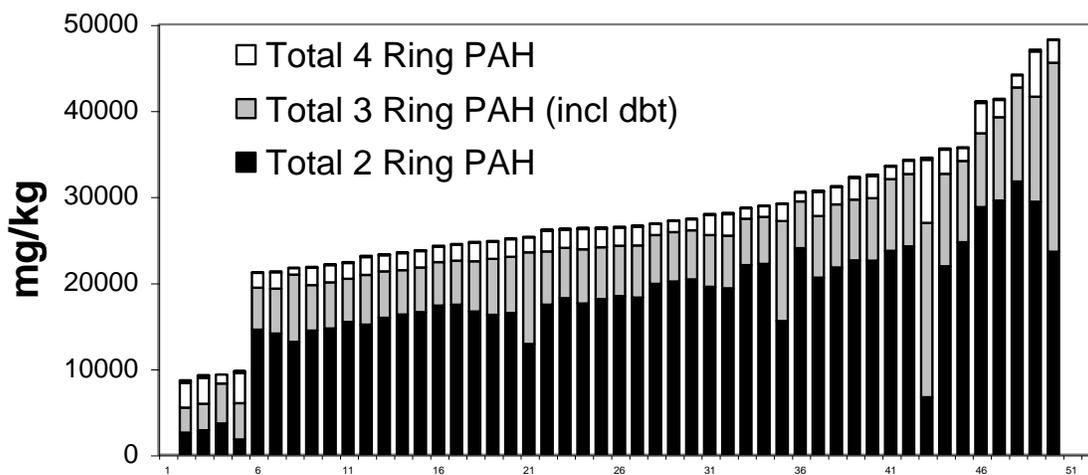


Figure 1. Histogram showing the concentrations and ring number proportions for 49 residual fuel oils. From Stout et al., 2001 (dbt – dibenzothiophenes).

Heavy fuel oils from the *Selendang Ayu* contain 13,302 – 41,101 mg/L total resolved PAH, compared to 12,410 mg/L TPAH in an Alaskan North Slope crude oil similar to that released in the *Exxon Valdez* spill (Table 5). As with most heavy fuel oils, the most abundant PAH in the *Selendang Ayu* oils are alkyl naphthalenes and alkyl phenanthrenes. These also are the most abundant PAH in Alaskan North Slope crude oil. Concentrations of alkyl chrysenes and most other 4- and 5-ring PAH also are more abundant in the heavy fuel oils than in North Slope crude oil.

The PAH fraction of the heavy fuel oil on the sea surface weathered slowly after the spill, because of the low ambient temperatures and the high viscosity of the oil. Naphthalene and alkyl naphthalenes were depleted most in the weathered oils (Table 6). There was little loss of higher molecular weight 3- through 5-ring PAH. Alaskan North Slope crude oil lost low molecular weight PAH more rapidly than the *Selendang Ayu* heavy fuel oils did during the first few weeks after the *Exxon Valdez* spill (Bence et al., 1996).

Table 5. Concentrations of resolved PAH in Alaskan North Slope crude oil (ANSC) and five samples of heavy fuel oil from the *Selendang Ayu*.

Analyte	ANSC	PST-5A/B	PST-12-C	PST-11-C	RMG-35	IF-038
Naphthalene	730	1000	1800	100	1800	1700
C1-Naphthalene	1500	2400	4100	290	4500	4500
C2-Naphthalene	1700	3000	6100	600	5700	6000
C3-Naphthalene	1200	2200	4600	840	4400	4400
C4-Naphthalene	610	980	2300	730	2200	2200
Biphenyl	180	69	120	25	120	120
Dibenzofuran	56	52	94	10	100	98
Acenaphthylene	7.4	3	8	1.8	8.8	9.2
Acenaphthene	12	89	150	21	160	160
Fluorene	86	160	210	50	230	230
C1-Fluorene	210	360	600	170	580	610
C2-Fluorene	310	540	990	350	960	990
C3-fluorene	260	560	1100	390	1100	1100
Anthracene	0	62	78	17	93	92
Phenanthrene	280	540	790	160	770	780
C1-Phenanthrene	630	1800	2500	520	2500	2500
C2-Phenanthrene	640	2100	3300	700	3400	3300
C3-Phenanthrene	430	1200	2100	600	2300	2200
C4-Phenanthrene	150	460	740	320	830	790
Dibenzothiophene	220	210	310	75	360	340
C1-Dibenzothiophene	440	620	950	460	1000	1000
C2-Dibenzothiophene	560	1000	1700	1100	1800	1700
C3-Dibenzothiophene	470	820	1400	1300	1500	1400
C4-Dibenzothiophene	230	340	610	950	640	610
Benzo(b)fluorene	0	19	28	5.6	33	31
Fluoranthene	3.9	27	41	8.8	48	47
Pyrene	13	190	250	72	290	280
C1-Fluoranthene/Pyrene	78	420	600	220	740	700
C2-Fluoranthene/Phrene	130	400	600	290	730	700
C3-Fluoranthene/Pyrene	150	260	360	250	440	420
C4-Fluoranthene/Pyrene	95	87	140	180	160	150
Naphthobenzothiophenes	59	54	75	84	90	86
C1-Naphthobenzothiophenes	150	120	180	370	190	180
C2-Naphthobenzothiophenes	180	120	190	570	200	190
C3-Naphthobenzothiophenes	130	80	130	480	130	120
C4-Naphthobenzothiophenes	95	51	72	300	63	59
Benz(a)anthracene	3.6	26	46	19	48	47
Chrysene	49	52	92	45	96	97
C1-Chrysene	80	130	240	140	240	240
C2-Chrysene	98	140	240	170	230	240
C3-Chrysene	100	110	190	170	180	180
C4-Chrysene	60	42	90	94	74	70
Benzo(b)fluoranthene	5.7	4.4	8.2	4.9	8.1	8.8
Benzo(k)fluoranthene	0.78	1.1	2.2	1.1	2	2.6
Benzo(a)fluoranthene	0	0.7	1.2	1	0.89	0.96
Benzo(e)pyrene	12	9.1	17	18	16	16
Benzo(a)pyrene	1.1	7.8	14	11	14	13
Perylene	0	3.1	6.7	4.1	6.4	6.1
Indeno(123cd)pyrene	0	1.3	2.7	2	2.6	2
Dibenz(ah)anthracene	0.87	1.7	2.4	1.8	2.3	2.3
Benzo(ghi)perylene	3.4	8.6	16	9.6	15	15
Total PAH	12409.75	22930.8	40284.4	13301.7	41101.09	40732.96

Table 6. PAH composition and concentrations in two samples of *Selendang Ayu* heavy fuel oil collected from the sea surface near the spill site six days and 31 days after the spill. The spill occurred on 12/09/04. Concentrations are mg/kg oil.

Analyte	Surface Oil (12/15/04)	Surface Oil (1/09/05)
Naphthalene	230	70
C1-Naphthalene	1000	520
C2-Naphthalene	2000	1300
C3-Naphthalene	1900	1500
C4-Naphthalene	1200	1000
Biphenyl	38	21
Dibenzofuran	30	18
Acenaphthylene	3	1.8
Acenaphthene	52	31
Fluorene	88	60
C1-Fluorene	290	240
C2-Fluorene	560	500
C3-fluorene	620	600
Anthracene	40	28
Phenanthrene	360	270
C1-Phenanthrene	1200	1000
C2-Phenanthrene	1600	1400
C3-Phenanthrene	1100	1000
C4-Phenanthrene	460	480
Dibenzothiophene	150	120
C1-Dibenzothiophene	610	560
C2-Dibenzothiophene	1200	1200
C3-Dibenzothiophene	1200	1300
C4-Dibenzothiophene	680	830
Benzo(b)fluorene	15	12
Fluoranthene	22	17
Pyrene	140	110
C1-Fluoranthene/Pyrene	370	320
C2-Fluoranthene/Phrene	420	380
C3-Fluoranthene/Pyrene	300	310
C4-Fluoranthene/Pyrene	160	180
Naphthobenzothiophenes	81	86
C1-Naphthobenzothiophenes	290	330
C2-Naphthobenzothiophenes	410	540
C3-Naphthobenzothiophenes	390	480
C4-Naphthobenzothiophenes	240	360
Benz(a)anthracene	25	25
Chrysene	58	58
C1-Chrysene	150	160
C2-Chrysene	180	220
C3-Chrysene	170	220
C4-Chrysene	86	150
Benzo(b)fluoranthene	6	6.4
Benzo(k)fluoranthene	1.2	2.3
Benzo(a)fluoranthene	0.65	0.99
Benzo(e)pyrene	17	20
Benzo(a)pyrene	10	11
Perylene	4.7	4.8
Indeno(123cd)pyrene	2.2	2.8
Dibenz(ah)anthracene	1.8	2
Benzo(ghi)perylene	10	12
Total PAH	20,172	18,070

Toxicity of Heavy Fuel Oils

Toxicity of Oil in Water

Very little information is available about the toxicity of heavy fuel oils to terrestrial and aquatic plants and animals. Heavy oils are difficult to work with in toxicity and ecological effects studies. Oil toxicity to marine organisms usually is evaluated by exposing the organisms in laboratory aquaria to dispersions or aqueous extracts (called water soluble fractions [WSF] or water accommodated fractions [WAF]) of the fresh, weathered, or chemically dispersed oil (Anderson et al., 1974; Rice et al., 1979; Markarian et al., 1994). The incidence of adverse biological effects or mortality is recorded for one or more days (usually 48 or 96 hours) and toxic response is recorded as the median lethal or effects concentration (the concentration causing 50 percent mortality or sublethal effect in the specified time).

Anderson et al. (1974) evaluated the composition and toxicity of four crude and refined oils, including a Bunker C residual fuel oil, to six species of marine animals. The oils had API gravities ranging from 7.3 to 34.5 (Table 7). The water soluble fractions (WSF) of the oils contained 1.4 to 23.8 mg/L total resolved hydrocarbons and 1.3 to 13.9 mg/L total aromatics (by gas chromatography). The Bunker C WSF contained the lowest concentration of hydrocarbons, but was the most toxic (lowest LC₅₀ concentration) to all six species, based on total petroleum hydrocarbon concentrations in the exposure water, measured by infrared spectrometry (EPA Method 418.1). However, the IR method measures mainly aliphatic hydrocarbons, which probably did not contribute much to the toxicity of any of the oils (Neff et al., 2000). If Bunker C toxicity is measured as the amount of oil added or the percent WSF, it is less toxic than the other refined and crude oils. The low solubility of the Bunker C residual oil indicates that exposure concentrations in the water column after a spill are likely to be low, probably below lethal concentrations.

Environment Canada has collected data on the physical properties, composition, and toxicity of crude and refined oils, particularly those produced or used extensively in Canada (Bobra and Callaghan, 1990). Physical, chemical, and toxicity data for 4 crude and refined oils evaluated by Bobra and Callaghan (1990) are summarized in Table 8. The 100% WSFs of the Bunker C and heavy lube oil were not toxic, because of their low aqueous solubilities. The Tarsuit crude oil (°API = 23.3) was more toxic than Prudhoe Bay crude oil (°API = 27) when toxicity was measured as initial TPH concentration in the lethal dilution of the WSF. TPH concentration is not a good indication of the toxicity of the WSF because most of the hydrocarbons measured as TPH contribute little to oil WSF toxicity.

The best indication of the toxicity of an oil WSF to aquatic animals is a comparison of the “solubility” of the oil (the initial concentration of total petroleum hydrocarbons in the 100 percent WSF) and the LC₅₀ concentration. Environmental toxicity (the potential toxicity to water column organisms after a spill) is roughly inversely proportional to the LC₅₀/solubility ratio (Bobra et al., 1983). In the examples in Table 8, the Tarsuit crude oil and Prudhoe Bay crude oil have LC₅₀/solubility ratios of 0.75-0.80 and 0.22-0.47,

respectively. LC₅₀/solubility ratios of the two heavy refined/residual products are >1, indicating little or no acute toxicity to water column organisms. When expressed this way, North Slope crude oil has a higher acute toxicity to water column organisms than does Tarsuit crude oil or the heavy fuel and lube oil. Likewise, the heavy fuel from the *Selendang Ayu*, with its low aqueous solubility, probably is much less toxic than fresh or weathered North Slope crude oil. Weathering of these oils will tend to decrease the concentration of aromatic hydrocarbons in the WSF, decreasing toxicity further.

Table 7. Toxicity of the water soluble fraction (WSF) of four oils, including a heavy Bunker C fuel oil to six species of marine animals. Median lethal concentrations of the WSF (concentration causing 50% mortality after 96 hours of exposure) are in mg/L of total petroleum hydrocarbons (TPH) measured by IR analysis. API gravity of each oil and the initial concentration of resolved hydrocarbons (by GC) in the WSF are included. From Anderson et al. , 1974; and Pancirov, 1974.

Property/Species	S. Louisiana Crude	Kuwait Crude	No. 2 Fuel Oil	Bunker C Residual Oil
API Gravity	34.5	31.4	31.6	7.3
Initial Total Resolved HC in WSF	23.8	21.6	5.3	1.4
Initial Resolved Saturates in WSF	9.9	11.6	0.54	0.08
Initial Resolved Aromatics in WSF	13.9	10.0	5.7	1.3
Mysid <i>Mysidopsis almyra</i>	8.7	6.6	0.9	0.9
Grass Shrimp <i>Palaemonetes pugio</i>	>16.8	>10.2	3.5	2.6
Shrimp larvae <i>Penaeus aztecus</i>	>19.8	Not tested	4.9	1.9
Sheepshead Minnow <i>Cyprinodon variegates</i>	>19.8	Not tested	6.3	3.1
Silverside <i>Menidia beryllina</i>	5.5	6.6	3.9	1.9
Mumichog <i>Fundulus heteroclitus</i>	16.8	>10.4	3.9	1.7

Table 8. Relationship of physical/chemical properties of two crude and two refined oils to the toxicity (48 hr LC₅₀) of their water soluble fractions (WSF) to the freshwater water flea *Daphnia* sp. The samples are in order of API gravity. (From Bobra and Callaghan, 1990).

Oil	°API	Viscosity (cP)	Aromatics (%)	Solubility (mg/L TPH)	48 hr LC ₅₀ (mg/L TPH)
Bunker C	7.3 – 15.5	48,000	25 – 54	4.4	>0.4 - >4.5
Heavy Lube Oil	14 - 25	975	---	0.8 – 2.3	>0.8 - >2.3
Tarsiut Crude	23.3	7.4	7.4	2 – 8.5	1.6 – 6.4
Prudhoe Bay Crude	27.0	33	9.9 – 36	20 – 42	9.4

During weathering of crude and refined oil on the water surface or on the shore, volatile and slightly soluble hydrocarbons are lost by evaporation; dissolution, biodegradation, and photooxidation. This causes the solubility of the WSF to decrease (Bobra et al., 1983; Shiu et al., 1990; Neff et al., 2000). The light alkanes and monocyclic aromatics (BTEX), which contribute most to the toxicity of unweathered crude and refined oils, are lost most rapidly. Higher molecular weight alkanes and PAH are lost more slowly. Because PAH and their degradation products appear to be the most toxic fraction of crude and refined oils (Neff et al., 2000), it is unclear if toxicity increases or decreases during oil weathering. Bobra et al. (1983) measured the composition and toxicity of WSF of four fresh and weathered crude oils and a gas condensate. As expected, the solubility of the oils decreased as they weathered. Toxicity appeared to increase, (LC₅₀ measured as TPH by GC at the LC₅₀ concentration decreased) as the oils weathered. However, the ratio of the lethal concentration to the solubility (LC₅₀/solubility) increased as the oils weathered, indicating that more weathered than fresh oil was required to cause toxicity. WSFs of weathered Prudhoe Bay crude oil were not acutely toxic. It is likely that the toxicity of heavy fuel changes in the same way during weathering.

Neff et al., (2000) examined the weathering and toxicity of several crude oils and a diesel fuel from Australia. The toxicity of the fresh oil WSFs was caused mainly by monocyclic aromatic hydrocarbons. These were lost during evaporative weathering. Toxicity of the weathered oil WSFs was caused mainly by low molecular weight PAH. LC₅₀, measured as total PAH, seemed to increase with weathering. However, if the toxic dose was measured as percent WSF or the LC₅₀/solubility ratio, toxicity decreased during weathering. Higher oil loading was required to produce a lethal dose. Solubility of the WSF decreased markedly with weathering. These results confirm the conclusion of Bobra et al. (1983) that toxicity of crude and refined oils to aquatic organisms is limited by the amount of petroleum hydrocarbons that are dissolved or finely dispersed from the spilled oil into the water column. Heavy fuel oils, because of their high viscosity and low solubility and dispersibility, usually are less toxic (based on mass of oil required to cause toxic effect) than lighter, more soluble crude and refined oils.

Field Studies of the Toxicity of Heavy Fuel Oils

Field studies after heavy oil spills confirm that toxicity of heavy oils decrease as they weather naturally in sediments. In 1970, the tanker *Arrow* grounded and spilled 2000 m³ of Bunker C heavy fuel oil into coastal waters of Chedabucto Bay, Nova Scotia, Canada. Shortly after the spill, planktonic copepods were observed to have ingested dispersed heavy oil droplets (Conover, 1971). As much as 10% of the oil became associated with zooplankton, and nearly 20% sedimented to the bottom as zooplankton fecal pellets. Ingestion of the Bunker C droplets apparently had no adverse effects on the copepods. Samples of intertidal sediments contaminated with the weathered residual fuel from the *Arrow* were collected from the shore after the spill and evaluated for evidence of aquatic toxicity (Lee et al., 2003). The weathered oil had only a limited ability to induce cytochrome P450 activity in winter flounder (*Pleuronectes americanus*) and was not toxic in the Microtox[®] assay. Although pore water was not toxic in sensitive Microtox[®] and echinoderm larval tests, the whole sediment was slightly toxic to benthic amphipods. Thus, both fresh and highly weathered residual fuel oil had a low toxicity in a realistic field exposure.

These observations explain why it is difficult to correlate the aquatic toxicity of fresh and weathered oil to TPH or PAH concentrations in the exposure water. Most of the toxicity of oils, particularly heavy poorly soluble oils, probably is caused by polar oxidation products of the aromatic and aliphatic hydrocarbons. However, these polar, slightly soluble degradation products rapidly leach out of the oil on the sea surface or on the shore, or react with other oil components to produce less soluble high molecular weight products characteristic of weathered oil. As a result, the toxicity of weathered oil decreases with time as it loses soluble toxic components and becomes more viscous. The toxicity of the remaining hydrocarbons, including 3- through 5-ring PAH and their oxidation products tends to decrease with time through weathering of the crude oil to a physical form from which the PAHs and oxidation products do not readily leach into the interstitial water (Page et al., 2002); the PAH in the viscous weathered oil have a low bioavailability (they leach slowly from the viscous oil phase into the ambient water) which limits their toxicity to marine animals. Because heavy fuel oils weather rapidly to very viscous, semisolid residues, hydrocarbons, including PAH, in them partition very slowly from the oil to the water phase. Although many heavy fuel oils, including the IFO-380 fuels released from the *Selendang Ayu*, contain higher concentrations of total PAH than middle weight crudes, such as the North Slope crude oil released from the *Exxon Valdez* (Table 5), the solubility and, therefore, the bioavailability of PAH from the weathered heavy fuel oils is much less than from the weathered North Slope crude oil.

Page et al.(2002) showed that weathered North Slope crude oil from the *Exxon Valdez* spill in intertidal sediments of Prince William Sound, Alaska, decreased as it weathered. In 1993, four years after the spill, the threshold concentrations of total PAH in intertidal sediments causing toxicity in sediment-dwelling amphipods (Page et al., 2002), or altering intertidal sediment biological community structure (Gilfillan et al., 1995), was 2.6 mg/kg TPAH in dry sediment. By 2002, the oil residues buried in intertidal sediments

were in a form and location where they were no longer bioavailable to intertidal animals and, therefore, were no longer toxic (Neff et al., 2006).

On November 19, 2002, the tank vessel *Prestige* sank off the coast of Galicia, Spain, and spilled a large volume of a heavy Russian fuel oil (similar to the fuel oil released from the *Selendang Ayu*). Large amounts of heavy fuel oil came ashore along the north coast of Spain and the Atlantic coast of southern France. Four years after the spill, Morales-Caselles et al. (2007) measured the bioavailability and toxicity of the heavy fuel oils in sediments off the Spanish coast. Concentrations of total petroleum hydrocarbons and TPAH in sediments decreased in the four years after the spill. The oil-contaminated sediments collected four years after the spill were not toxic in the Microtox[®] test, a 10-day sediment bioassay with sediment-dwelling amphipods, and a 10 day polychaete toxicity test. At the end of the exposure period, the polychaetes, a deposit-feeding species, *Arenicola marina*, were analyzed for PAH as an indication of hydrocarbon bioavailability. TPAH concentrations in test sediments ranged from 38 to 323 mg/kg dry wt in 2005-2006, down from 390 to 2120 mg/kg in 2003-2004. The sediments collected in 2005-2006 were not toxic in any of the sediment bioassays. The polychaetes bioaccumulated small amounts of TPAH during exposure for 10 days to some oil/contaminated sediments.

Bioaccumulation indices (TPAH in worms exposed to oiled sediments/TPAH in worms exposure to unoiled reference sediments) ranged from 1.0 (no bioaccumulation) to 1.6, indicating that the TPAH in the oiled sediments had a very limited bioavailability to the deposit-feeding worms (Morales-Caselles et al., 2007). Thus, PAH from heavy fuel oil released from the *Prestige* had a low bioavailability and no toxicity to sediment dwelling animals within four years after the spill. Studies of both the *Arrow* and *Prestige* spills of heavy fuel oils show that the heavy oils in sediments weather to a state where they have a low bioavailability and little or no toxicity to sediment-dwelling organisms. It is highly probable that the heavy fuel oil from the *Selendang Ayu* will behave similarly.

There are no aquatic toxicity data available for the heavy fuel oils spilled from the *Selendang Ayu*. However, the solubility of fresh and weathered heavy fuel oils, including the *Selendang Ayu* fuel oil, is lower than that of fresh and weathered North Slope crude oil, as discussed above. Since the dissolved hydrocarbons, particularly the PAH, are the most bioavailable and toxic fractions of oil, heavy fuel oils usually are less toxic than mid-weight crude oils.

Water samples were collected on 12/13/04, less than a week after the spill, in several bays where oil from the *Selendang Ayu* drifted. The highest TPAH concentration measured (2.6 ppb) was in a water sample from the west fork of Skan Bay (Figure 2), an area considered by Carls et al. (2007) to have salmon streams. The PAH composition of the weathered *Selendang Ayu* oil in water was different from that of the effluent toxic to embryos of pink salmon from a column containing 29 mg/kg weathered North Slope crude oil on gravel (Heintz et al., 1999). The column effluent water was enriched in alkyl phenanthrenes and dibenzothiophenes (the PAH Heintz et al. identified as the main toxicants in the weathered North Slope crude oil) compared to the *Selendang Ayu* crude

oil. In addition, the concentration range of TPAH in water samples collected shortly after the *Selendang Ayu* spill was lower than the concentrations of TPAH in column effluents associated with toxicity to pink salmon embryos (Heintz et al., 1999). Brannon et al. (2006) showed that the column effluents in the laboratory studies of Heintz et al. (1999) contained dispersed as well as dissolved hydrocarbons that contributed to their toxicity. The *Selendang Ayu* oil, because of its high viscosity, is much less likely to form fine oil in water dispersions than the weathered North Slope crude oil that Heintz et al. (1999) evaluated. Therefore, it is likely that the weathered *Selendang Ayu* fuel oil is substantially less toxic to marine animals, including early life stages of salmon, than the weathered North Slope crude oil.

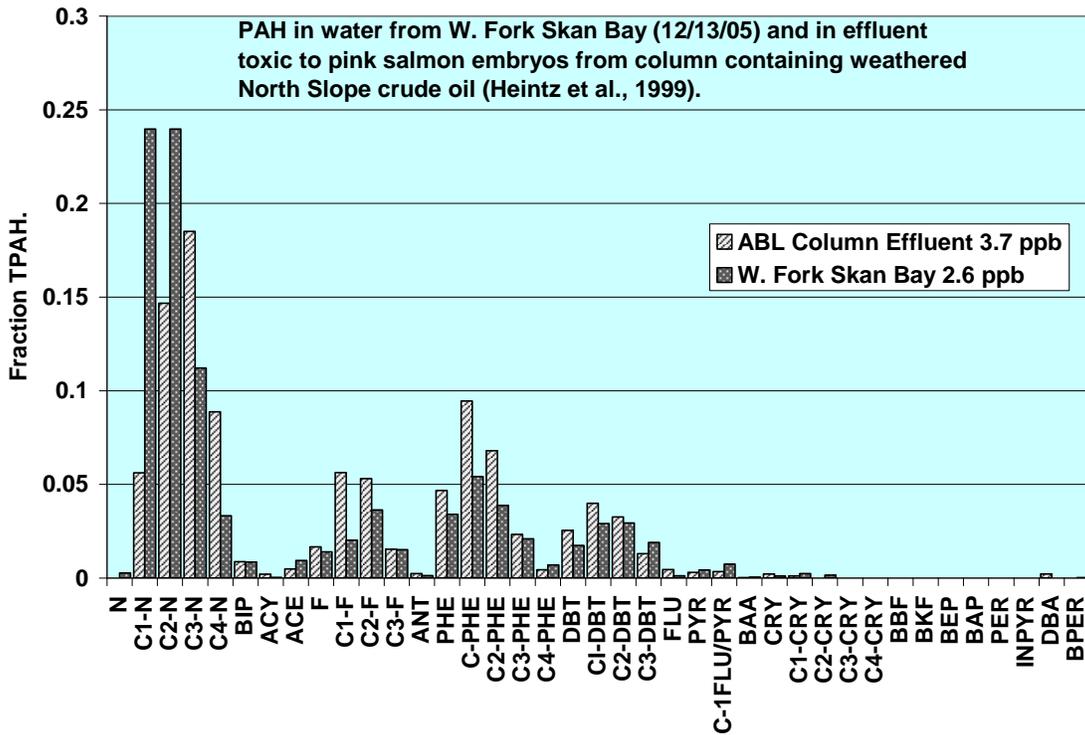


Figure 2. The composition of the PAH (expressed as fraction TPAH) in an effluent toxic to pink salmon embryos from a column containing 29 mg/kg weathered Alaska North slope crude oil (Heintz et al., 1999) and in a water sample collected on 12/13/05 from the west fork of Skan Bay (a bay heavily contaminated by heavy fuel oil from the *Selendang Ayu* oil spill).

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