OPERATIONAL SCIENCE ADVISORY TEAM SUMMARY REPORT FOR FATE AND EFFECTS OF REMNANT OIL REMAINING IN THE BEACH ENVIRONMENT

Annex K: Aquatic Toxicity

Potential for Aquatic Toxicity from the MC252 Oil Remaining On or Near Sand Beaches

Numerous studies have shown that crude oil and weathered crude oil is toxic to aquatic life (Carls and Meador 2009, Incardona et al. 2005, Morales-Caselles et al. 2008). As crude oil weathers, the biologically available and more acutely toxic monoaromatic and light alkane fractions are lost. The weathered oil becomes a complex mixture of PAHs and other high molecular weight compounds, which are more chronically toxic than the monoaromatic and light alkane fractions but are less biologically available (Di Toro et al. 2007). Research has shown that overall toxicity of crude oil is reduced as the oil weathers. The focus of this evaluation is on the potential impacts of the weathered MC 252 crude oil residues to aquatic receptors.

The scope of the OSAT 2 report focuses on three types of residual oil from MC252: supratidal buried oil (SBO), small surface residue balls (SSRBs), and submerged oil mats (SOMs). By definition, SBOs are located in generally dry areas and not assumed to be in direct contact with the aquatic environment, and therefore should have a minimal impact on aquatic receptors. As a result, the aquatic toxicity section focuses on the SSRBs and the SOMs, although the results from the SBO Water Accommodated Fractions (WAFs; see below) are used because the compositions of the different types of oil on a given beach are fairly similar. Further information on this observation is provided in the "Weathering and Depletion of Oil" section of the OSAT 2 report.

At the start of the OSAT 2 effort, no data were available to the OSAT 2 team that were believed to be applicable to assessing the potential for the SOMs or SSRBs to cause adverse effects to aquatic organisms or intertidal or subtidal beach invertebrates. Most of the intertidal beach invertebrates (e.g. ghost shrimp, ghost crabs or mole shrimp) are associated with moist environments. Therefore, it was determined that for this evaluation the intertidal and subtidal organisms would be assessed for potential risk as a single group. This approach was taken because the bulk of the exposure of these surf zone invertebrates to oil residues was assumed to be from dissolved oil residues originating from the residual oil deposits such as buried SSRBs. Therefore, aquatic toxicity to subtidal receptors such as fish, mysid shrimp, etc. and toxicity to intertidal organisms such as ghost shrimp, ghost crabs, mole shrimp, etc. was estimated using the

same procedure. Potential risks to aquatic receptors such as marine mammals and a discussion of ghost crabs in the supratidal areas are presented in Annex L of the OSAT 2 report.

In order to assess the potential aquatic toxicity of the SOMs and SSRBs, it is necessary to understand the types and concentrations of chemicals that are likely to dissolve into the water that comes into contact with these deposits, because these dissolved compounds are what the organisms would be exposed to. Given the short time frame available to collect data, the OSAT 2 team decided that a Water Accommodated Fraction (WAF) approach would provide the best estimate of what may solubilize from the oil into the overlying water. Recent studies usually report WAF preparation and/or toxicity results as milligram (mg) of total oil compounds measured per liter of WAF solution, often reported as total petroleum hydrocarbons (TPH). This approach can be useful for an estimate of the potential for environmental effects if water samples are collected from the environment being assessed, because the concentrations of the oil compounds in the water would be directly measured. If water samples are not collected from the environment, then the WAF data are of limited utility because the extrapolation of chemical concentrations in the WAF to concentrations in the aquatic environment is problematic at best and is generally not recommended. Given the OSAT 2 time constraints, however, the collection of WAF data was the only option for obtaining information about what may be dissolving from the oil residues.

The methods reported in the literature to produce the WAFs are varied. Singer and others (2000, 2001) have noted a number of factors that influence the type and concentrations of constituents in the WAF, such as initial amount of oil used in the WAF preparation, mixing and settling time, mixing energy and the type of oil used in the WAF preparation. The different preparation methods can result in different toxicities in WAFs prepared from similar oils, and the literature notes the difficulties of comparing results of WAF toxicity tests from various researchers. It is believed, however, that reported WAF toxicity testing results can be used to provide a rough estimate of the potential toxicity of WAFs that have not been tested for toxicity by comparing the chemistries of tested and untested WAFs.

WAF Preparation Overview

Samples of SBO, SSRBs and tar balls (representing SOMs) were collected from four areas along the Gulf. The areas are Grand Isle, Louisiana; Petit Bois Island, Mississippi; Bon Secour National Wildlife Refuge, Alabama; and Fort Pickens, Florida (Figure K-1). For each WAF, an amount of oil residue was added to a glass vessel at a fixed oil loading of approximately 5 g of oil per liter of water. This required adding approximately 50-200 g of SSRB, SBO or SOM material because much of the residual oil deposits consisted of sand (oily material mixed with sand). A total of 1.5 liters of artificial sea water (32 parts per thousand salinity) was then added

to the vessel and the water/oil residue combination was slowly stirred (60 RPM with no vortex formation) for 24 hours to create a WAF. The aqueous WAF was drawn off, centrifuged (at about 1500 RPM), and then analyzed by gas chromatography/flame ionization detection (GC/FID) and gas chromatography/mass spectrometry (GC/MS) to determine the concentrations of oil compounds present. It should be noted that in most cases the SSRB, SBO and SOM material completely broke up into sand particles and an oily phase material. The centrifugation was generally sufficient to eliminate particulate oil (e.g., micelles); however, in some cases the analytical results indicated that non-dissolved oil particles remained in the water phase and these WAFs were not considered for the WAF calculations, because they were not representative of a true WAF due to the presence of the non-dissolved phase oil material.

WAF Chemical Analysis Results

The results of the chemical analyses of the WAFs are provided in Table K-1. The raw data are available at the National Oceanic and Atmospheric Administration's (NOAA) Environmental Response Management Application (ERMA) website. As shown in Table K-1, many of the WAFs were not used in the risk calculations, because oil concentrations in the water were calculated to be greater than would be predicted to be possible given the solubility of the compounds. It was surmised that despite the slow stirring of the WAF during preparation and the centrifugation to remove suspended oil droplets and particulates, particulate-associated or otherwise non-dissolved oil was present in the WAFs. For a chemical to exert a toxic (rather than physical) effect on an aquatic organism, the chemical generally needs to be dissolved in the water. Inclusion of non-dissolved constituents would overestimate the potential for the solution to cause chemical toxicity. Therefore the WAFs that apparently contained non-dissolved oil were not considered for use in the aquatic toxicity evaluation. It is postulated that colloidal clays may have remained suspended in the aqueous solution due to the centrifugation speed used, and that oil associated with those particles may have been the cause for the presence of the oil in excess of its solubility. The solid material, especially the SBO, often disintegrated while the WAF was being prepared, resulting in a sandy mix at the bottom of the vessel and an oil residue on top of the water. The disintegration of the SBO, SSRB or SOM could have been the source of the colloidal clays.

In addition to the tabular presentation of data in Table K-1, the PAH results also are presented graphically for SOMs in Figure K-2. SOMs were chosen as the example to display because the exposure of aquatic organisms to SOMs is likely to be higher than to SSRBs and certainly compared to SBO. Not surprisingly, the WAF PAH profile from each site is generally similar to the PAH profile measured in the parent material for each site (see Annex C, "Weathering and Degradation").

WAF Toxicity Estimation

In this OSAT 2 effort, the potential aquatic toxicity of the WAFs was assessed using two different types of toxicity measures or benchmarks. One comparison was performed by using the PAH concentrations measured in the WAFs to calculate acute and chronic Sum Toxic Units for each WAF. The other comparison was performed by comparing the TPH (total petroleum hydrocarbon) concentrations measured in the MC252 WAFs to literature-derived WAF TPH acute toxicity benchmarks.

PAH Toxicity Benchmark Comparison

The U.S. Environmental Protection Agency (USEPA 2003) describes a methodology to assess the potential toxicity from bioavailable PAHs in water or sediment; this approach is based on narcosis theory. Narcotic toxicants frequently demonstrate additive toxicity; that is, the effects of individual narcotic toxicants can be added together to predict the total amount of toxicity present in a mixture of such chemicals. It has been observed that this additivity can occasionally over-estimate toxicity (i.e., result in a conservative and overly-protective estimate of risk).

The effects endpoints used to calculate toxic units in USEPA (2003) are the PAH final chronic values (FCVs). The FCVs for over 60 PAHs, including most of the PAHs presented in Table K-2, are reported in Table 3-4 of USEPA (2003). To estimate the total effect of the mixture of PAHs in a WAF sample, the measured concentration of each compound in the WAF is divided by a "potency divisor" (Table K-2) to give an individual toxic unit for that compound. The potency divisors are used in the calculation to represent the concentration of an individual chemical that can cause an adverse effect. Dividing the measured concentration by the potency divisor provides the individual compound's potential to cause toxicity and thus its contribution to the overall PAH mixture's toxicity. The potential for toxic effects of the mixture is then calculated by adding the fractional toxicity contributions (individual "toxic units") of all components of the mixture.

As stated, these toxic units can be used to estimate whether or not toxicity for the entire mixture could be expected. If the sum of the toxic units exceeds a value of 1.0, toxicity to aquatic receptors could be expected. As noted above, estimates of the bioavailable amounts of PAHs in the water cannot exceed PAH solubility. If PAH solubility is exceeded, a non-aqueous phase liquid may form and observed toxicity may be due to physical mechanisms such as coating of respiratory membranes with oil droplets.

The Sum Toxic Unit approach used in this effort was also used during the MC 252 oil spill to assess water samples for potential PAH-related toxicity. A modification used in this assessment was the addition of 9 additional compounds (5 of those being the heterocyclic dibenzothiophenes) to those PAHs that were assessed during the spill. These 9 additional compounds were found in the WAFs and are considered appropriate to include in the toxic unit calculation. In all calculations, only analytes that were detected were used for calculation purposes and a value of "zero" was used for analytes that were not detected in the analysis (per decisions made in OSAT 1).

The Sum Toxic Units using final (externally verified to reflect laboratory reports) and draft (not yet verified) data for the MC252 WAFs ranged from 0.20 - 0.85 for the acute (short term exposure) toxicity calculation and 0.85 - 3.53 for the chronic (long term exposure) toxicity calculation. See Table K-3 for a summary of the WAF analytical and toxicological results. These calculated results imply that acute (short term exposure) toxicity from exposure to the WAFs would not be expected due to PAHs, but chronic (long term exposure) toxicity would be possible.

TPH Toxicity Benchmark Comparison

WAF toxicity results have been reported in the literature as grams of oil loading per liter of water to allow predictions of disssolved concentrations of oil constituents and their effects on aquatic organisms during a spill. Recent work has reported WAF toxicity results as milligrams (mg) of total oil compounds measured per liter of solution, often reported as total petroleum hydrocarbons (TPH). This can provide general toxicity information that can be used to compare different WAFs regarding the potential for aquatic toxicity. The results of the WAF analyses generated in this effort were compared with TPH toxicity values that were obtained from literature sources. The literature was searched and references reviewed in an effort to obtain a representative group of papers containing WAF toxicity information. Table 4 summarizes the literature used for the review and the toxicity information for various crude oil WAFs.

The residual oil in the SBO, SSRBs and SOMs is weathered crude oil. The literature acquired reported tests on WAFs from both weathered and fresh crude. Using WAF data only from weathered crude oil would have been preferred, but due to the relatively small number of weathered crude studies, all available and applicable WAF literature that was identified was considered.

Various authors have noted the large differences in chemical composition as well as toxicity that can be observed from preparing WAFs using different crude oils. For this analysis, it was decided that the focus would be on the literature toxicity results obtained from WAFs prepared with South Louisiana Crude Oil (SLCO), because this crude is likely to be most similar to the oil released from MC252. The intent was to minimize uncertainty in this assessment as much as possible.

There were only three studies identified using SLCO (Table K-4). Bryne and Calder (1976) reported toxicity as percent WSF (Water Soluble Fraction) in the test solution, measured by gravimetric analysis. It was not believed appropriate to compare the information from this paper to the data generated by the OSAT 2 effort, because the method of gravimetric measurement of the TPH in the WSF used by Bryne and Calder (1976) was deemed not comparable to the more modern analyses performed for the OSAT 2 study. The remaining toxicity studies with SLCO WAF (Rossi et al. 1976, Barron et al. 1999) reported the acute toxicity as mg/L TPH or mg/L THC (Total Hydrocarbons). The toxicity values reported were 4 to 6 day LC50s. The LC50 is a lethal concentration to 50% of the test organisms. It is generally preferable to use an endpoint with a lower severity of effect as a benchmark. These were the only WAF toxicity values identified for South Louisiana crude oil, however, and they do provide some range for comparison. The LC50 range for the selected studies was 7.10 mg/L to 15.2 mg/L TPH or THC. The MC252 WAF TPH concentrations (using draft and final data) ranged from 0.143 mg/L to 0.900 mg/L. This comparison implies that substantial acute aquatic toxicity from the WAFs would not be expected based on the TPH measured. As noted previously, TPH is a crude measure for estimating potential aquatic toxicity, but it does provide an additional input to the general assessment.

Discussion

As stated above, it is generally not recommended to try to relate a WAF concentration or toxicity to an environmental setting. However, given that these were the only data available, the WAF data were used to inform our predictions of potential risk to aquatic receptors from the SSRBs and SOMs. The WAF concentrations are believed to provide an idea of a possible worst case scenario for potential oil compound concentrations in water that is in close association with the SSRB and SOM surfaces. The petroleum concentrations in the water in a beach setting would be expected to decline quickly with distance from an oil residue surface (see Figure K-3 for more discussion of this dilution phenomenon). The WAF data imply that elevated petroleum concentrations might be found in pores in the sand right next to an SSRB, or within a few millimeters of the surface of a SOM, but the dynamic nature of the surf zone and subtidal areas and the associated water movement in these areas are expected to rapidly dilute petroleum concentrations as the water is moved away from the oil deposit's surface. Therefore for water

along the beaches, any significantly elevated petroleum concentrations would be expected to be localized to the oil mat or tar ball surface.

Additionally, the WAFs had 24 hours to come to equilibrium, which is unlikely to occur in a dynamic beach environment as the water is constantly moving. Therefore it is not anticipated that concentrations of petroleum products would have time to reach equilibrium concentrations in water next to the oil residue before the water was moved away from the oil deposit, so that the WAF-level concentrations are not expected unless an unusually stagnant situation occurs on the beach.

Lastly, the Sum Toxic Unit PAH WAF petroleum concentrations exceeded chronic toxicity benchmarks but did not exceed acute benchmarks. This implies a receptor would need to be exposed to the WAF concentration in the environment for multiple days to be adversely affected. This is not considered to be reasonably possible in an environment as dynamic as a beach, again except in an unusually stagnant situation. Given these considerations, it is not believed that the SSRBs in the intertidal zone or the SOMs in the subtidal areas are likely to pose a significant risk to aquatic organism populations along the sand beaches.

The exception to this is the potential for impact to the environment upon which a tar mat would be laying. The area under the mat could experience elevated petroleum concentrations as well as low dissolved oxygen concentrations, which would cause an adverse impact to the subtidal area covered by the oil mat. This impact would be localized to the "footprint" of the mat, and the overall extent of the impact would be directly dependent on how much of the subtidal area along the Gulf coast is covered by oil mats.

There are a number of uncertainties associated with this assessment. The major uncertainties and their potential impacts have been tabulated in Table K-5.

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Table K-1. Measured concentration of PAHs and TPHs in all WAFs prepared for OSAT-2.

Low molecular weight PAHs (LPAH) included 2-3 ring analytes (Naphthalene to C-4 Dibenzothiophene). High molecular weight PAHs (HPAH) included 4-6 ring analytes (Fluoranthene to Benzo[g,h,I]perylene). Oil types: supratidal buried oil= SBO; submerged oil mats= SOMs; small surface residue balls= SSRBs.

Oil	Sample Name	LPAH	HPAH	TPH	Valid	
Туре		(ng/L)	(ng/L)	(µg/L)	$\mathbf{W}\mathbf{A}\mathbf{F}^1$	
	Grand Isle					
SBO	TC-20110104-WAF1-002 SUPRATIDAL	5482	504	209	YES	
SBO	TC-20110104-WAF1-002 SUPRATIDAL DUP	5473	568	254	YES	
SOM	TC-20110104-WAF1-003 SUBTIDAL	6471	856	525	YES	
SOM	TC-20110104-WAF1-003 SUBTIDAL DUP	7481	706	326	YES	
SSRB	TRB-20110104-WAF1-001 SSRB	10123	743	350	YES	
SSRB	TRB-20110104-WAF1-001 SSRB DUP	8197	519	345	YES	
	Petit Bois					
SBO	TRB-20110106-WAF1-001 SUPRATIDAL	1906	2688	3087	NO	
SBO	TRB-20110106-WAF1-001 SUPRATIDAL DUP	2443	3901	4673	NO	
SOM	TRB-20110106-WAF1-002 SUBTIDAL	5794	1149	1598	NO	
SOM	TRB-20110106-WAF1-002 SUBTIDAL DUP	7768	1842	3072	NO	
SSRB	TRB-20110106-WAF1-003 SSRB	928	322	617	YES	
SSRB	TRB-20110106-WAF1-003 SSRB DUP	5311	428	900	YES	
Bon Secour						
SBO	TC-20110108-WAF1-002 SUPRATIDAL	644	1428	1324	NO	
SBO	TC-20110108-WAF1-002 SUPRATIDAL DUP	984	1762	1996	NO	
SOM	TC-20110108-WAF1-001 SUBTIDAL	4199	495	143	YES	
SOM	TC-20110108-WAF1-001 SUBTIDAL DUP	6043	717	204	YES	
SSRB	TRB-20110108-WAF1-003 SSRB	1067	233	202	YES	
SSRB	TRB-20110108-WAF1-003 SSRB DUP	1822	114	297	YES	
	Fort Pickens	5				
SBO	TC-20110105-WAF1-002 SUPRATIDAL	22341	13726	16281	NO	
SBO	TC-20110105-WAF1-002 SUPRATIDAL DUP	13718	7548	9101	NO	
SOM	TC-20110105-WAF1-003 SUBTIDAL	3315	259	56	YES	
SOM	TC-20110105-WAF1-003 SUBTIDAL DUP	3469	326	43	YES	
SSRB	TRB-20110105-WAF1-001 SSRB	3018	4687	4549	NO	
SSRB	TRB-20110105-WAF1-001 SSRB DUP	4029	5261	4869	NO	

¹ WAFs suspected to be contaminated with suspended particulates were not included in this analysis.

		Aquatic 7	Coxicity Benchma	rk
Oil-Related Organic Compounds	CAS#	Acute Potency Divisor (ug/L)	Chronic Potency Divisor (ug/L)	Source
Naphthalene	91-20-3	803	193	1
C1-Naphthalenes		340	81.7	1
C2-Naphthalenes		126	30.2	1
C3-Naphthalenes		46.1	11.1	1
C4-Naphthalenes		16.9	4.05	1
Biphenyl	92-52-4	985.6	190.0	2
Acenaphthylene	208-96-8	1,280	307	1
Acenaphthene	83-32-9	232	55.8	1
Dibenzofuran	132-64-9	846	170.0	2
Fluorene	86-73-7	164	39.3	1
C1-Fluorenes		58.1	14.0	1
C2-Fluorenes		22.0	5.30	1
C3-Fluorenes		7.99	1.92	1
Anthracene	85-01-8	86.1	20.7	1
Phenanthrene	120-12-7	79.7	19.1	1
C1-Phenanthrenes/Anthracenes		31.0	7.44	1
C2-Phenanthrenes/Anthracenes		13.3	3.20	1
C3-Phenanthrenes/Anthracenes		5.24	1.26	1
C4-Phenanthrenes/Anthracenes		2.33	0.559	1
Dibenzothiophene	132-65-0	136	33	3
C1-Dibenzothiophenes		47.27	11.359	3
C2-Dibenzothiophenes		18.08	4.345	3
C3-Dibenzothiophenes		6.81	1.637	3
C4-Dibenzothiophenes		7.80	1.875	3
Fluoranthene	206-44-0	29.6	7.11	1
Pyrene	129-00-0	42.0	10.1	1
C1-Fluoranthenes/Pyrenes		20.3	4.89	1
C2-Fluoranthenes/Pyrenes		4.5	1.09	4*
C3-Fluoranthenes/Pyrenes		2.6	0.63	5*
Benz(a)anthracene	56-55-3	9.28	2.23	1
Chrysene	218-01-9	8.49	2.04	1
C1-Chrysenes/Benz(a)anthracene		3.56	0.856	1
C2-Chrysenes/Benz(a)anthracene		2.01	0.483	1
C3-Chrysenes/Benz(a)anthracene		0.699	0.168	1

Table K-2. Aquatic toxicity benchmarks/potency divisors used in the Sum Toxic Unit procedure to assess the potential risk of WAFs to aquatic invertebrates.

C4-Chrysenes/Benz(a)anthracene		0.294	0.0706	1
Benzo(b)fluoranthene	205-99-2	2.82	0.677	1
Benzo(k)fluoranthene	207-08-9	2.67	0.642	1
Benzo(e)pyrene	192-97-2	3.75	0.901	1
Benzo(a)pyrene	50-32-8	3.98	0.957	1
Perylene	198-55-0	3.75	0.901	1
Indeno(1,2,3-cd)pyrene	193-39-5	1.14	0.275	1
Dibenz(a,h)anthracene	53-70-3	1.17	0.282	1
Benzo(g,h,i)perylene	191-24-2	1.83	0.439	1

Source:

^{1.} http://www.epa.gov/bpspill/water-benchmarks.html

In Bold: Not in the above link, but generated from other sources:

² USEPA (2008) model for non-PAHs U.S. EPA. 2008. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms. Compendium of Tier 2 Values for Nonionic Organics. Office of Research and Development, EPA/600/R-02/016. PB2008-107282. March 2008.

http://www.epa.gov/NHEERL/publications/files/ESB_Compendium_v14_final.pdf ^{3.} Calculated using the guidance document (See 5)

- ^{4.} Dave Mount, USEPA, Pers. Comm., January 2011.

^{5.} USEPA (2003) model for PAHs U.S. EPA. 2003. Draft Technical Basis for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Non-Ionic Organics. EPA-600-R-02-014. Office of Research and Development. Washington, DC. http://www.epa.gov/nheerl/publications/files/PAHESB.pdf

Site	TPAH ¹ (ng/L)	$\sum TU_{acute}^{1,2}$	∑TU _{chronic} ^{1,2}	TPH ¹ (µg/L)	Sample size
Grand Isle	5986-10866	0.43-0.77	1.79-3.22	209-525	3
Petit Bois	1250-5740	0.26-0.61	1.08-2.52	617-900	2
Bon Secour	1300-6760	0.20-0.55	0.85-2.30	143-297	4

1.29-1.43

43-56

2

Table K-3. Toxicity comparison results used to characterize the risk of the three forms of oil to aquatic organisms.

¹ The non-detected compounds were assigned a value of "0" for the calculations, per the decisions made in OSAT 1.

0.31-0.34

 $^{2}\Sigma TU$ is the Sum Toxic Unit.

3574-3796

Fort Pickens

Test Organism	WAF Crude Source	Test Type	Toxicity Endpoint	Constituent Measure	Reference
Sand Crab	Weathered SLCO	6-d static renewal	LC50	7.1 mg/L TPH	Barron and others (1999)
Quahog clam embryo	SLCO	48h static	LC50	5.7 ppm WSF	Bryne and Calder (1977)
Quahog clam larvae	SLCO	10-day static renewal	LC50	2.1 ppm WSF	Bryne and Calder (1977)
Quahog clam larvae	SLCO	10-day static renewal	EC50 - growth	1.1 ppm WSF	Bryne and Calder (1977)
Polychaetes - juvenile	SLCO	96h static	TL _m	15.2 ppm THC (77% WSF)	Rossi and others (1976)
Polychaetes - adults	SLCO	96h static	TL _m	12.5 ppm THC (61% WSF)	Rossi and others (1976)
Fish – Atlantic silver side	KCO - PCCO	16-d – flow through	EC50 - growth	12.42 mg/L TPH	Al-Yakoob and others (1996)
Mysid shrimp	Guadalupe Crude	7-d static renewal	LC50	0.57 mg/L TPH	Cleveland and others (2000)
Mysid shrimp	Guadalupe Crude	7-d static renewal	NOEC – mean biomass	0.31 mg/L TPH	Cleveland and others (2000)
Mysid shrimp	Guadalupe Crude	7-d static renewal	LOEC – mean biomass	0.57 mg/L TPH	Cleveland and others (2000)
Ghost crab - reproducing	КСО	96h flow through	LC50	0.19 mg/L TPH	Jackson and others (1981)
Ghost crab – non reproducing	КСО	96h flow through	LC50	1.35 mg/L TPH	Jackson and other (1981)
Fish – Tidewater silversides	Weathered California oil field crude	7d static renewal UV enhanced	LC50	0.93 mg/L TPH	Little and others (2000)

Table K-4. Summary of WAF literature reviewed for this evaluation.

Test Organism	WAF Crude Source	Test Type	Toxicity Endpoint	Constituent Measure	Reference
Fish – Atlantic herring	CE-Weathered South	24h	EC50	8.5 mg/L	McIntosh and others
embryos	American crude			ТРАН	(2010)
Fish - salmon	Cook Inlet Crude	4 d flow through	LC50	0.7 mg/L TAH	Moles (1998)
Crustacean - shrimp	Cook Inlet Crude	4 d flow through	LC50	1.4 mg/L TAH	Moles (1998)
Echinoderm – starfish	Cook Inlet Crude	4 d flow through	LC50	>1.3 mg/L TAH	Moles (1998)
Mollusk - scallop	Cook Inlet Crude	4 d flow through	LC50	2.0 mg/L TAH	Moles (1998)
Fish - silverside	Wonnich Crude (Australia)	96h static	LC50	0.14 mg/L PAH	Neff and others (2000)
Mysid	Wonnich Crude (Australia)	96h static	LC50	0.21 mg/L PAH	Neff and others (2000)
Sea urchin larvae	Wonnich Crude (Australia)	96h static	LC50	0.20 mg/L PAH	Neff and others (2000)
Fish - silverside	Weathered Wonnich Crude (Australia)	96h static	LC50	1.08 mg/L PAH	Neff and others (2000)
Mysid	Weathered Wonnich Crude (Australia)	96h static	LC50	0.58 mg/L PAH	Neff and others (2000)
Sea urchin larvae	Weathered Wonnich Crude (Australia)	96h static	LC50	0.50 mg/L PAH	Neff and others (2000)
Fish - silverside	Agincourt Crude (Australia)	96h static	LC50	0.002 mg/L PAH	Neff and others (2000)
Shrimp	Agincourt Crude (Australia)	96h static	LC50	0.002 mg/L PAH	Neff and others (2000)
Mysid	Weathered Agincourt Crude (Australia)	96h static	LC50	0.04 mg/L PAH	Neff and others (2000)
Mysid	PBCO	96h continuous flow	LC50	14.23 mg/L THC	Singer and others (2001)
Fish - Topsmelt	РВСО	96h continuous flow	LC50	9.35 mg/L THC	Singer and others (2001)
Fish - Silverside	РВСО	96h continuous flow	LC50	11.83 mg/L THC	Singer and others (2001)

Test Organism	WAF Crude Source	Test Type	Toxicity Endpoint	Constituent Measure	Reference
Mysid	Weathered PBCO	96h continuous flow	LC50	0.95 mg/L THC	Singer and others (2001)
Fish - Topsmelt	Weathered PBCO	96h continuous flow	LC50	>1.6 mg/L THC	Singer and others (2001)
Mysid	CE-PBCO	96h continuous flow	LC50	9.46 mg/L THC	Singer and others (2001)
Fish - Topsmelt	CE-PBCO	96h continuous flow	LC50	7.27 mg/L THC	Singer and others (2001)
Fish - Silverside	CE-PBCO	96h continuous flow	LC50	32.47 mg/L THC	Singer and others (2001)
Mysid	CE-Weathered PBCO	96h continuous flow	LC50	5.72 mg/L THC	Singer and others (2001)
Fish - Topsmelt	CE-Weathered PBCO	96h continuous flow	LC50	16.86 mg/L THC	Singer and others (2001)
Fish - Silverside	CE-Weathered PBCO	96h continuous flow	LC50	20.28 mg/L THC	Singer and others (2001)
Notes:					

ANSCO	Alaska North Shore Crude Oil	ppm	pa	arts per million
CE	chemically enhanced		PBCO	Prudhoe Bay crude oil
d	day		PCCO	partially combusted crude oil
h	hour		SLCO	South Louisiana crude oil
EC50	effective concentration for 50 percent of test organisms		TAH	total aromatic hydrocarbons
KCO	Kuwait crude oil		THC	total hydrocarbons compounds
LC50	lethal concentration for 50 percent of test organisms		TPH	total petroleum hydrocarbons
LOEC	lowest observed effect concentration		WSF	water soluble fraction
mg/L	milligram per liter		WAF	water-accommodated fraction
NOEC	no observed effect concentration			
ppm	parts per million			

Uncertainties/Sources	Underestimate	Overestimate	Unknown	Comments
Sampling Data			X	SSRB and SOM samples used in this analysis were collected from only 4 locations throughout the entire area impacted by releases from MC252. It is assumed that since the SSRB and SOM evaluated at locations have the same source they should be representative, but additional sampling over a larger geographical area would be needed to substantiate this assumption. Initial indications are that the oil residues from different sites are weathering at different rates.
Exposure Concentrations		Х		Exposure concentrations for aquatic receptors are based on WAF concentrations. The WAF chemical concentrations are a likely overestimation of potential concentrations in the aquatic environment, except for a very limited set of conditions.
Exposure Duration		Х		Due to the limited occurrences of SSRBs and SOMs in the environment and the movement of most aquatic receptors in the environment, constant long term (days) exposure of aquatic receptors to these sources by most aquatic receptors is expected to be limited. Those sessile organisms located on or immediately adjacent to these oil deposits will have the highest duration of exposure.
Toxicity Evaluation	Х	Х	Х	Bulk chemistry results for WAF samples can overestimate the bioavailable fraction of each constituent. In addition, site-specific screening values were not developed based on site-specific taxa, which could be more or less sensitive than the organisms used to generate the benchmarks. The WAFs were not tested for aquatic toxicity but rather the toxicity was estimated from literature values. This leads to uncertainty about the WAFs actual potential for toxicity.
Sum Toxic Unit Calculation	х			The concentrations for non-detected compounds in the PAH Sum Toxic Unit calculation were assumed to be zero. This could have underestimated the risks from

Table K-5. Uncertainties and their potential impacts associated with this assessment.

Dissolved versus Suspended X Oil Exposures	Because the gentle stirring in the WAFs caused the disintegration of the oil mat or tarballs for some samples, there may be potential for the surf to cause disintegration of some oil mats, resulting in suspended oil as was seen in the WAFs that could result in some physical fouling of aquatic organisms.

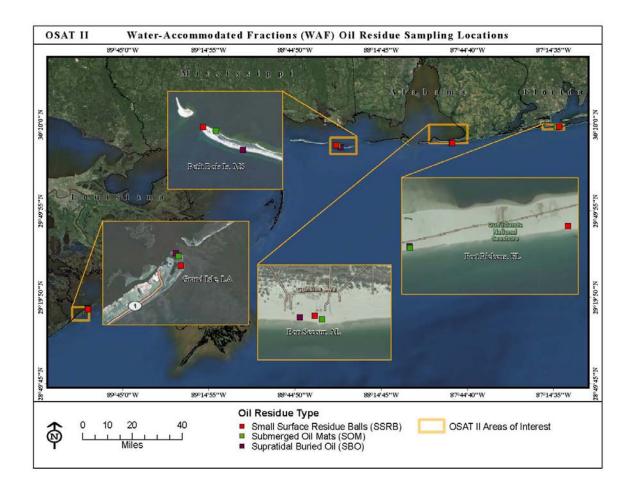


Figure K-1. Locations along the Gulf Coast where the oil residue samples used in WAF preparation were taken.

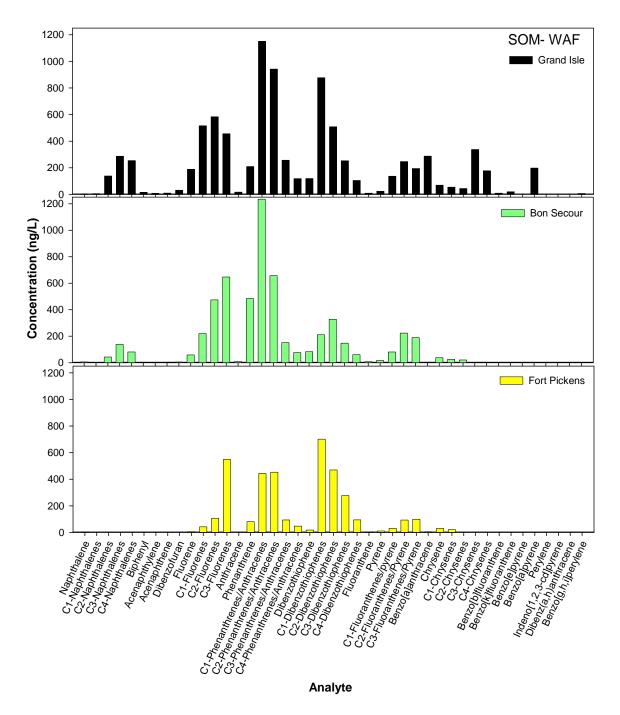


Figure K-2. Comparison of the PAH composition in water accommodated fraction (WAF) from submerged oil mat (SOM) samples collected at three locations. Petit Bois SOM was excluded because of particulate contamination of the WAF.

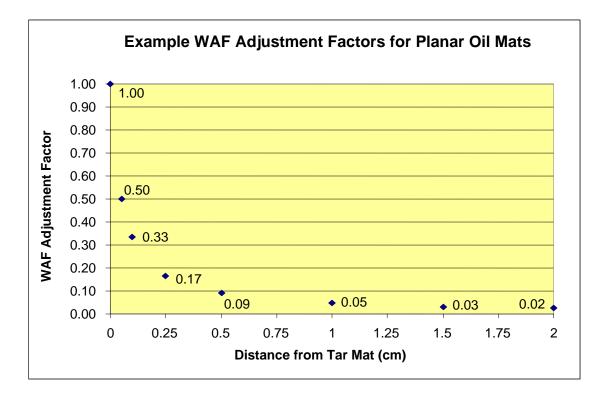


Figure K-3. Example dilution estimates for water near oil mat surfaces.

<u>Discussion</u>: WAF data simulate water concentrations in a closed system (no circulation) where equilibrium between the hydrocarbons in the sediment and water has had time to establish. As such, it represents concentrations expected in very close proximity to an oil mat or SSRB where mixing of intertidal water is minimal and where water/sediment contact is long enough for quasi-equilibrium to exist. This condition only exists in the thin layer of sand on the perimeter of the tarry material.

While WAF data may represent dissolved concentrations in the immediate vicinity of an oil mat, the concentrations will exponentially decline as a function of distance from the mat. This exponential decline is, at a minimum, based on geometric considerations. Water circulation and mixing further amplify the decline but the geometric factor alone is used in this analysis to portray the limited area over which WAF applies for benthic toxicity. Assume a flat oil mat having an outer shell of fine sand grains with an average diameter of 250 microns. The micro-layer has a thickness of perhaps 2 sand grains. At a distance of 1 cm from the micro-layer, the ratio of the cylindrical volume (on a per unit area basis) in the micro-layer relative to the volume in the 1 cm high cylinder is only 5%. This exponential decline simulates the decrease in potential toxicity as benthic organisms move away from an oil mat.