



Appendix I

Ecological Effects Evaluation

1. Ecological Effects Evaluation

Soil, sediment, and surface water data in the downstream areas was analyzed for a variety of constituents including volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), and metals, as described in Section 2 of the Downstream Areas Data Assessment Report (main report). The data collected was evaluated by comparison to background as well as based on effects on ecological receptors consistent with the Downstream Areas Remedial Sampling Plan (DARSP; ARCADIS 2013), as discussed in Section 5 of the main report. The ecological evaluation involved comparison of data to ecological screening values (ESVs) as well as calculating sample-specific toxic units (TUs) to evaluate the combined effect of PAHs in sediment and surface water on aquatic receptors. This appendix provides the technical basis for the selection of ESVs as well as the methods used to estimate the TUs. Examples are also provided to illustrate the TU calculations.

1.1 Ecological Screening Values

ESVs are constituent concentrations in environmental media below which risk to ecological receptors exposed to those media is considered *de minimus* (i.e., if there are no exceedances of the ESV, the constituent(s) being screened is eliminated from any further risk evaluation). However, the reverse is not true; concentrations exceeding ESVs do not necessarily imply that ecological risk exist, rather, it indicates that additional ecological risk evaluation is warranted. ESVs were identified from literature sources based on the hierarchy recommended by the Arkansas Department of Environmental Quality (ADEQ) as described in the DARSP (ARCADIS 2013), which was approved by the ADEQ on July 12, 2013. ESVs were identified for individual constituents where available and are summarized in Table 5-2 of the report. Further, as discussed in the DARSP (ARCADIS 2013), the ecotoxicity of PAHs as a mixture was evaluated. This is because PAHs occur in the environment as mixtures rather than individual constituents, and they generally act through a common mechanism of action (i.e., non-specific narcosis). Narcosis “results in the degradation of cell membranes, which could result in mild toxic effects or mortality, depending upon the exposure,” and the effects of narcotic compounds are approximately additive (USEPA 2009). Therefore, the ecological toxicity of PAHs is the result of the cumulative effects of the various PAHs in a mixture. To evaluate PAH mixture, consistent with agency recommendations (USEPA 2001, 2007a), PAHs were summed based on their molecular weight into two groups: low-molecular weight (LMW) PAHs to include PAHs with three or less benzene rings and high-molecular weight (HMW) PAHs to include PAHs with four or more benzene rings. PAHs that were not detected in a particular sample were not included in the sums.

Many PAHs were analyzed for in the downstream area, therefore it was imperative to identify those that will be used in PAHs sums for comparison to ESVs for sums. A list 43 PAH compounds were analyzed for in soil and subsurface sediment samples; while a list of 88 PAH compounds was analyzed for in surface sediment samples. Over half of these PAHs are heterocyclic PAHs that contain sulfur, nitrogen, or oxygen atoms in their rings—and were analyzed for forensic purposes only. The heterocyclic PAH derivatives are not used in the sums that were compared to ESV based on sums as the ESVs were based on non-heterocyclic PAHs. Table 5-3 of the report lists the PAHs used in the summations for soils and sediments.

For soils and subsurface sediments, the summations include 38 PAH compounds: the priority pollutant list of PAH compounds (16), two additional non-alkylated PAHs (or parent compounds), and 20 alkylated forms of parent PAH compounds. For surface sediments, the summations include 40 PAH compounds: the priority pollutant list of PAH compounds (16), four additional non-alkylated PAHs (or parent compounds), and 20 alkylated forms of parent PAH compounds. USEPA guidance (USEPA 2001, 2007a, 2009) does not define the specific PAHs or the number of PAHs to be included in the PAH summations. It is noteworthy, the available ESVs for LMW, HMW, and total PAHs were derived using data for a relatively low number of PAH compounds. To be conservative, this screen was conducted by comparing (to the ESVs) the sums of substantially larger numbers of PAHs than those for which the ESVs were developed. The remaining sections describe the identification of ESVs by medium.

1.1.1 Soil

Soil ESVs were obtained from the following sources in order of hierarchy, consistent with the DARSP (ARCADIS 2013):

1. USEPA Ecological Soil Screening Levels (EcoSSLs; USEPA 2013a), including those for PAHs (USEPA 2007a)
2. USEPA Region 4 Screening Values¹ (USEPA 2011)
3. USEPA Region 5 Screening Values (USEPA 2003a)
4. National Oceanic and Atmospheric Administration (NOAA) Screening Quick Reference Tables (SQiRTs; Buchman 2008)
5. Canadian Council of Ministers of the Environment (CCME [2008])

ESVs for soil are summarized in Table 5-2 of the main report. The ESVs for VOCs were identified from either Region 4 or 5. These ESVs were based on various endpoints; however, they are considered conservative. For metals (except for mercury) and for PAHs, the soil ESVs were obtained from the most current USEPA EcoSSLs, available on the EcoSSL website (USEPA 2013a). USEPA EcoSSLs are available for the protection of up to four endpoints: plants, soil invertebrates, bird, and mammals (USEPA

¹ The USEPA Region 4 soil ESVs used in this evaluation are the October 2011 values provided to ARCADIS by the agency referenced herein as USEPA 2011. ARCADIS was notified that USEPA Region 4 is in the process of revising the ESVs to reflect more recent recommendations by USEPA. The revised USEPA Region 4 ESVs default to USEPA EcoSSLs where available. The revised ESVs also contain updated ESVs for some organic compounds. Attached to this report is the current USEPA Region 4 ESV table provided to ARCADIS, along with the associated correspondence.

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2013a). The lowest EcoSSL value, from those for the four endpoints, was selected as the ESV for each constituent, as shown in Table 5-2 of the report.

The EcoSSLs that were used for the protection of plants and invertebrates are conservative. They were derived from plant and soil invertebrate chronic toxicity test data (USEPA 2005a) from studies where the bioavailability of the constituents is higher than what would be expected in a natural setting. For example, the data used to derive the plant EcoSSL for nickel are all from studies where the soil bioavailability index was 2, which corresponds to “relatively high or very high bioavailability” (USEPA 2007b).

Likewise, the assumptions used to derive EcoSSLs for the protection of avian and mammalian species are also conservative. EcoSSLs for those species are calculated by combining dietary uptake models and conservative toxicity thresholds (i.e., toxicity reference values [TRVs]) that rely on generic receptor exposure assumptions that may not reflect site receptors or conditions. For example, the EcoSSL for vanadium is based on vanadium effects on birds (USEPA 2005b), and the TRV used to calculate that EcoSSL is based on toxicity studies with the domestic chicken (*Gallus domesticus*), which has been shown to be more sensitive to vanadium than naturally-occurring species observed at the site such as mallard ducks (*Anas platyrhynchos*) (Rattner et al. 2006).

Bioaccumulation factors used to derive EcoSSLs for wildlife are selected to be conservative as well. For example, the HMW PAH EcoSSL (USEPA 2007a), which was based on mammalian receptors, uses a bioaccumulation factor of 2, which is 2 orders of magnitude higher than what is generally seen in the field (Jager et al. 2003). Where such high bioaccumulation models have been used to estimate risk adverse effects were not documented in the field when concentrations exceeded the EcoSSLs (Kapustka 2004). In addition, the EcoSSLs currently available from USEPA (2013a) do not account for bioavailability, although it has become clear that bioavailability plays an important role in uptake and toxicity (Interstate Technology & Regulatory Council [ITRC] 2011) and efforts are underway to update the EcoSSLs (Sample et al. 2013) to incorporate bioavailability among other recent technical advances. Currently EcoSSLs assume that bioavailability from food and incidentally ingested soil to be 100%. This is highly conservative because it has been shown that the relative bioavailabilities of constituents are typically lower. For example, the relative bioavailability of vanadium in soil is approximately 8% (United States Department of Defense 2003), and as such, the Vanadium EcoSSL that uses 100% is very conservative.

To evaluate the combined ecotoxicological contributions of PAHs in soil, total LMW PAH and total HMW PAH concentrations in site soil data² were compared to the LMW and HMW PAH ESVs. Although the ESVs

²Naphthalene and pyrene were analyzed by USEPA Method 8260 and the Modified Method 8270 SIM. For the calculation of the sums and the toxic units, data from Method 8260 were used because it is the more precise method for those analytes.

for both LMW and HMW PAHs are based on single compound toxicity studies, USEPA (2007a) recommends these values to screen PAHs in soil. For conservatism, the initial soil screen was conducted on the sum of 16 priority pollutant PAHs, two additional non-alkylated PAHs not included in the priority pollutant list (benzo(e)pyrene and perylene), and 20 alkylated PAHs. The PAHs are presented in what is referred to as the Long List in Table 5-3 of the report which sums 40 PAHs for surface sediments and 38 PAHs for subsurface sediments and soils since benzo(a)fluoranthene and benzo(b)fluorene were not analyzed.

1.1.2 Sediment

Sediment ESVs were obtained from the following sources in order of hierarchy, consistent with the DARSP (ARCADIS 2013):

1. USEPA Region 4 Sediment Screening Levels (USEPA 2001)
2. USEPA Region 3 Freshwater Sediment Screening Values (USEPA 2006)
3. USEPA Region 5 Screening Values (USEPA 2003a)
4. USEPA ECOTOX Thresholds (USEPA 2013b)
5. NOAA SQUIRTs (Buchman 2008)
6. CCME (2008)

The ESVs for sediment are summarized in Table 5-2 of the report. There are some detected constituents for which sediment ESVs were not available from the sources listed above and therefore, are not evaluated herein: barium, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 2-phenylbutane, n-butylbenzene, n-propylbenzene, and p-isopropyltoluene (Cymene).

For PAH mixtures, the sediment ESVs from Region 4 are based on practical quantitation limits for LMW PAHs. There is a high degree of uncertainty associated with the available sediment ESVs from Region 4 for PAHs; the 330 µg/kg ESV for individual PAHs and total LMW PAHs is based on a PQL (i.e., does not have ecological significance), and the 655 µg/kg ESV for total HMW PAHS is based on a toxic effect level (TEL). TELs are derived from associations observed between measures of adverse biological effects and the concentrations of analytes measured in sediments that may contain multiple constituents. Using a TEL to derive an ESV may not reflect a constituent-specific response threshold due to unknown co-contaminant and constituent mixture issues, and does not incorporate site-specific factors that influence bioavailability (MacDonald et al. 2000; DiToro et al. 1991). Specifically, the Region 4 ESV for HMW PAHs is based on a TEL measured in estuarine sediment where six of the non-alkylated HMW PAHs were measured and summed (USEPA 2001, MacDonald 1994). Because PAHs are present in mixtures, it is likely that the same sediment in which those six PAHs were measured could have contained many more individual PAHs. In

addition, if the PAHs had been measured and summed, the TEL would likely have been higher. Therefore, the use of the sediment ESVs from Region 4 leads to some uncertainty.

Sediment ESVs were used as a first conservative step in screening site sediment data for potential toxicological effects. PAH data were summed in two ways to compare to the ESVs. First, a conservative approach was conducted using the sum of priority pollutants, four additional alkylated PAHs that are not on the priority pollutant list, and the 20 alkylated PAHs for a total of 40 PAHs (referred to hereafter as the long list). A second approach summed the priority pollutant list plus 1- and 2-methylnaphthelene for a total of 18 PAHs (referred to hereafter as “Priority+2” List). The methylnaphthalenes were included in this shorter list for conservatism. Table 5-3 of the report lists the PAHs used in each sum³. Both of these sums are conservative since the ESVs were based on data for a much shorter list of PAHs.

1.1.3 Surface Water

Surface water data collected concurrently with the soil and sediment data per the DARSP are presented in this report. Surface water data collected per the DASRP were compared to surface water ESVs. Surface water ESVs were identified using the following hierarchy:

1. Arkansas Pollution Control and Ecology Commission Regulation No. 2 Standards dated August 26, 2011.
2. USEPA National Recommended Water Quality Criteria for Freshwater Aquatic Life Chronic Continuous Criteria (USEPA 2013c)
3. USEPA Region 4 Screening Values (USEPA 2001)
4. USEPA Region 3 Freshwater Screening Values (USEPA 2006)
5. USEPA Region 5 Screening Values (USEPA 2003a)
6. NOAA SQuiRTs (Buchman 2008)
7. CCME (2008)
8. Oak Ridge National Laboratory (Suter and Tsao 1996)

³ Naphthalene and pyrene were analyzed for via two USEPA Method 8260 and also the Modified Method 8270 SIM. In the calculation of the sums and the toxic unit, data from Modified Method 8270 SIM were used.

Surface water ESVs used in the ecological screen are presented in Table 5-2 of the report. An ESV was not available for carbazole which was detected in surface water; however, carbazole was not detected in the crude oil and therefore, eliminated from further evaluation.

1.2 Toxic Unit Calculations

In addition to comparing PAH mixtures to the ESVs, the mixtures in sediment and surface water were evaluated by estimating sample TUs based on USEPA's guidance for evaluating the toxicity of PAH mixtures (USEPA 2003b). This guidance provides methods to evaluate PAHs by estimating TUs using equilibrium partitioning (EqP) and identifies benchmarks that are causally linked to specific PAHs, applicable across various geochemical environments and appropriately protective of benthic organisms. Thus, using TUs to evaluate PAHs is considered to have less uncertainty than the ESV comparison discussed above (i.e., those based on a PQL or TEL). Using a TU approach allows for evaluating the additive effect of PAHs. Since it is well understood that toxicity of PAHs is attributable to the concentration of PAHs in water or interstitial porewater, the TU can be calculated by comparing the water or porewater concentrations of PAHs to their final chronic values (FCVs), which are protective of aquatic life. FCVs developed using the National Water Quality Criteria Guidelines are provided for 34 individual PAHs⁴ (USEPA 2003b) and therefore the TU were calculated for those PAHs as seen in equation below:

$$TU = \frac{[PAH_1]}{FCV_1} + \frac{[PAH_2]}{FCV_2} + \dots + \frac{[PAH_n]}{FCV_n}$$

The TU is analogous to a hazard quotient (HQ). If the HQ (total TU) is equal to or less than one in a given sediment sample, potential risk from concentration of the PAH mixture in that sample is considered acceptable for the protection of benthic organisms (USEPA 2003b, 2009, 2012). If the TU exceeds one, potential risk from concentration of the PAH mixture in that sample may not be acceptable for the protection of benthic organisms and may need further evaluation.

1.2.1 Sediment

It has been well established that PAH toxicity is related to the amount of organic carbon in sediment, which governs the bioavailability of PAHs to benthic organisms (Swartz 1999; USEPA 2003b, 2012). Based on this, the organic-carbon normalized sediment concentration is a reasonable approximation of the interstitial concentration. USEPA (2003b) provide methods for estimating the interstitial/dissolved water concentrations using what is referred to as a one-carbon model that relies on the binding capacity of organic carbon in sediment for PAHs. In this model, all organic carbon is treated equally, or as a single type of carbon. More

⁴ While USEPA (2003b) presents FCVs for 34 PAHs, site data for 35 PAHs were used because data for 1-methylnaphthalene and 2-methylnaphthalene were reported individually in addition to C1-methylnaphthalene.

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recently, USEPA issued guidance to provide a summary of procedures for determining the freely dissolved concentrations of nonionic organic chemicals (including PAHs) for deriving sediment TUs (USEPA 2012). The 2012 guidance specifically addressed how interstitial water dissolved concentrations can be measured or estimated. It discusses estimation methods based on the one-carbon model, previously described by USEPA (USEPA 2003b), as well as a two-carbon model.

The one-carbon partitioning model incorporates the partitioning of PAHs to naturally occurring organic carbon (OC) and can be used to estimate the dissolved concentration (C_d) of each PAH ($[PAH_x]$) using the measured PAH bulk sediment concentration (C_{sed}) of individual PAHs. OC is a measure of natural organic carbon such as vegetative debris, humic and fulvic acids, and decayed remains of plants and animals. However, it has become widely recognized that various types of carbon have differing capacity for binding PAHs (and other narcotic chemicals; USEPA 2012). One such type of carbon that has been shown to have a significant binding capacity is black carbon (BC) such as coke, charcoal, and soot, which originates from combustion sources and are known to have extremely high sorption capacities (USEPA 2012; Accardi-Dey and Gschwend 2002, 2003; Burgess 2009, Ghosh 2007, Hauck et al. 2007, Hawthorne et al. 2007, ITRC 2011, Lohmann et al. 2005). Therefore, whereas the one-carbon partitioning model is useful to assess PAHs in sediment, the presence of BC in sediments may make this approach overly conservative because estimated dissolved concentrations will be higher than what actually occur. Alternatively, the two-carbon model can accommodate the presence of both natural OC and BC and more accurately estimate dissolved concentrations in the presence of BC.

To assess sediment in the downgradient area of the site, PAHs in surface sediment (i.e., the biologically active zone) were evaluated based on their cumulative effects and bioaccessibility to benthic invertebrates consistent with USEPA guidance (USEPA 2003b, 2012). Sample-specific TUs were initially calculated using the one-carbon model for all sediment samples. Where a specific PAH was not detected, its concentration was set at zero. If the TU result using the one-carbon model was below one, the sample was not further evaluated. If the TU was at or above one, the TU using the two-carbon model was calculated. The models are presented below and sample calculations for sediment are presented in Tables I-1 and I-2 for the one- and two-carbon models respectively.

One-carbon model

In the one-carbon model, the C_d of each PAH ($[PAH_x]$) is estimated using the equation presented below (USEPA 2003b):

$$C_d = C_{sed} / f_{OC}$$

Where:

C_{sed} = concentration of each PAH in sediment (micrograms per kilogram dry weight [dw]; measured value)

C_d = concentration of freely dissolved PAH in pore water (micrograms per liter; estimated value)

f_{OC} = fraction of organic carbon (set at total organic carbon [TOC]; measured value)

Two-carbon model

The two-carbon model can be used to better estimate the C_d of each PAH ([PAH_x]) using the following relationship (USEPA 2012; Accardi-Dey and Gschwend 2002):

$$C_{sed}/C_d = f_{OC} \times K_{OC} + f_{BC} \times K_{BC} C_{pw}^{n-1}$$

Where:

C_{sed} = concentration of each PAH in sediment (micrograms per kilogram dw; measured value)

C_d = concentration of freely dissolved PAH in pore water (micrograms per liter; estimated value)

f_{OC} = fraction of organic carbon exclusive of BC in sediment (kilogram [kg] OC/kg dw); f_{OC} exclusive of BC calculated from the difference between TOC and BC (from measured values)

f_{BC} = fraction of BC in sediment (kg BC/kg dw) (measured value)

K_{BC} = BC – pore water partition coefficient (liters per kilogram [L/kg] BC) for each individual PAH. PAH-specific K_{BC} s were calculated based on a regression equation from Koelmans et al. 2006 ($\text{Log}K_{BC} = 0.6997\text{Log}K_{ow} + 2.8219$). This regression equation was selected because it was derived using values from various laboratory and field studies obtained from the literature

K_{OC} = OC – water partition coefficient (L/kg OC) for each individual PAH (USEPA 2003b)

n = Freundlich coefficient for sorption to BC (unitless) (0.7; Hauck et al. 2007)

The equation is used, via an iterative approach, to estimate the freely dissolved PAH concentration by solving for C_d .

1.2.2 Surface Water

To evaluate the combined toxic contributions of PAHs in a mixture in surface water, the sum of the quotients of the actual measured PAH concentrations in surface water to the water FCVs for each individual PAH (i.e., the TU) was calculated. A sample calculation TU calculation for surface water is presented in Table I-3.

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Tables

Table I-1
Example for Calculating the Toxic Unit in Sediment Using the One-Carbon Model

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Analyte	Final Chronic Value (FCV) ¹ (µg/g _{oc})	SED-DA-045 Concentration (µg/kg)	TU ²
Total Organic Carbon (%)	--	4.64	--
PAHs - Non-alkylated			
Acenaphthene	491	26.8	0.001
Acenaphthylene	452	30.7	0.001
Anthracene	594	38	0.001
Benzo(a)anthracene	841	60	0.002
Benzo(a)pyrene	965	90.9	0.002
Benzo(b)fluoranthene	979	142	0.003
Benzo(e)pyrene	967	171	0.004
Benzo(g,h,i)perylene	1095	189	0.004
Benzo(j)+(k)Fluoranthene	981	41.4	0.001
Chrysene/Triphenylene	844	275	0.007
Dibenz(a,h)anthracene	1123	32.6	0.001
Fluoranthene	707	126	0.004
Fluorene	538	179	0.007
Indeno[1,2,3-cd]pyrene	1115	50.8	0.001
Naphthalene	385	44.6	0.002
Perylene	967	133	0.003
Phenanthrene	596	669	0.02
Pyrene	697	193	0.006
PAHs - Alkylated			
1-Methylnaphthalene	446	371	0.02
2-Methylnaphthalene	447	492	0.02
C1-Chrysenes	929	922	0.02
C1-Fluoranthenes/Pyrenes	770	1032	0.03
C1-Fluorenes	611	714	0.03
C1-Phenanthrenes/Anthracenes	670	2302	0.07
C2-Chrysenes	1008	1336	0.03
C2-Fluorenes	686	2021	0.06
C2-Naphthalenes	510	2538	0.1
C2-Phenanthrenes/Anthracenes	746	4461	0.1
C3-Chrysenes	1112	1095	0.02
C3-Fluorenes	769	2244	0.06
C3-Naphthalenes	581	4265	0.2
C3-Phenanthrenes/Anthracenes	829	4853	0.1
C4-Chrysenes	1214	753	0.01
C4-Naphthalenes	657	4045	0.1
C4-Phenanthrenes/Anthracenes	913	3212	0.08
Total TU³			1

Notes:

¹ FCVs from USEPA 2003.

² The analyte-specific TU is calculated by dividing the TOC-normalized concentration by the FCV.

³ The sample total TU is the summation of all analyte-specific TU values. A TU equal to 1 or less indicates that risk to benthic receptors is not likely. A TU above 1 indicates that more evaluation is necessary to evaluate potential risk to the benthic receptors.

-- = not applicable

FCV = final chronic value

µg/g_{oc} = micrograms per gram of organic carbon

µg/kg = micrograms per kilogram

PAH = polycyclic aromatic hydrocarbon

TOC = total organic carbon

TU = toxic unit

USEPA = United States Environmental Protection Agency

Reference:

USEPA. 2003. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks for the Protection of Benthic Organisms: PAH Mixtures. Environmental Protection Agency, Office of Research and Development. EPA-600-R-02-013. November 2003.

Table I-2
Example for Calculating the Toxic Unit in Sediment Using the Two-Carbon Model

Downstream Areas Data Assessment Report
ExxonMobil Environmental Services Company
Mayflower Pipeline Incident Response, Mayflower, Arkansas

Analyte	Final Chronic Value (FCV) ¹ (µg/L)	Analyte-Specific Physical Parameters				Solubility [C _{OC,PAHI,MAXI}] (µg/g _{OC})	SED-DA-045 Concentration (µg/kg)	Estimated Pore Water PAH Concentration (µg/L)	TU ²
		USEPA log K _{OW}	USEPA log K _{OC}	Log K _{BC}					
Total Organic Carbon (%)	--	--	--	--	--	4.64	--	--	
Black Carbon (%)	--	--	--	--	--	0.24	--	--	
Organic Carbon (%)	--	--	--	--	--	4.4	--	--	
PAHs - Non-alkylated									
Acenaphthene	55.85	4.0	3.9	5.6	33400	26.8	0.0050	0.0001	
Acenaphthylene	306.9	3.2	3.2	5.1	24000	30.7	0.037	0.0001	
Anthracene	20.73	4.5	4.5	6.0	1300	38	0.0024	0.0001	
Benzo(a)anthracene	2.227	5.7	5.6	6.8	4153	60	0.00033	0.0001	
Benzo(a)pyrene	0.9573	6.1	6.0	7.1	3840	90.9	0.00022	0.0002	
Benzo(b)fluoranthene	0.6774	6.3	6.2	7.2	2169	142	0.00028	0.0004	
Benzo(e)pyrene	0.9008	6.1	6.0	7.1	4300	171	0.00048	0.001	
Benzo(g,h,i)perylene	0.4391	6.5	6.4	7.4	648	189	0.00023	0.001	
Benzo(j)+(k)fluoranthene	0.6415	6.3	6.2	7.2	1220	41.4	0.000049	0.0001	
Chrysene/Triphenylene	2.042	5.7	5.6	6.8	826	275	0.0024	0.001	
Dibenz(a,h)anthracene	0.2825	6.7	6.6	7.5	2389	32.6	0.000013	0.00005	
Fluoranthene	7.109	5.1	5.0	6.4	23870	126	0.0036	0.001	
Fluorene	39.3	4.2	4.1	5.8	26000	179	0.043	0.001	
Indeno[1,2,3-cd]pyrene	0.275	6.7	6.6	7.5	--	50.8	0.000024	0.0001	
Naphthalene	193.5	3.4	3.3	5.2	61700	44.6	0.046	0.0002	
Perylene	0.9008	6.1	6.0	7.1	967	133	0.00034	0.0004	
Phenanthrene	19.13	4.6	4.5	6.0	34300	669	0.11	0.01	
Pyrene	10.11	4.9	4.8	6.3	9090	193	0.0092	0.001	
PAHs - Alkylated									
1-Methylnaphthalene	75.37	3.8	3.8	5.5	165700	371	0.26	0.004	
2-Methylnaphthalene	72.16	3.9	3.8	5.5	154800	492	0.37	0.01	
C1-Chrysenes	0.8557	6.1	6.0	7.1	--	922	0.0044	0.01	
C1-Fluoranthenes/Pyrenes	4.887	5.3	5.2	6.5	--	1032	0.036	0.01	
C1-Fluorenes	13.99	4.7	4.6	6.1	--	714	0.082	0.01	
C1-Phenanthrenes/Anthracenes	7.436	5.0	5.0	6.3	--	2302	0.18	0.02	
C2-Chrysenes	0.4827	6.4	6.3	7.3	--	1336	0.0037	0.01	
C2-Fluorenes	5.305	5.2	5.1	6.5	--	2021	0.10	0.02	
C2-Naphthalenes	30.24	4.3	4.2	5.8	--	2538	1.1	0.04	
C2-Phenanthrenes/Anthracenes	3.199	5.5	5.4	6.6	--	4461	0.16	0.05	
C3-Chrysenes	0.1675	6.9	6.8	7.7	--	1095	0.00089	0.01	
C3-Fluorenes	1.916	5.7	5.6	6.8	--	2244	0.038	0.02	
C3-Naphthalenes	11.1	4.8	4.7	6.2	--	4265	0.67	0.1	
C3-Phenanthrenes/Anthracenes	1.256	5.9	5.8	7.0	--	4853	0.060	0.05	
C4-Chrysenes	0.07062	7.4	7.2	8.0	--	753	0.00021	0.003	
C4-Naphthalenes	4.048	5.3	5.2	6.5	--	4045	0.20	0.05	
C4-Phenanthrenes/Anthracenes	0.5594	6.3	6.2	7.2	--	3212	0.014	0.03	
Total TU³								0.4	

Notes:

1. FCV obtained from USEPA 2003.

2. Porewater concentrations were estimated using the equation: $C_{sed}/C_{pw} = f_{OC} \times K_{OC} + f_{BC} \times K_{BC} C_{pw}^{n-1}$

where:

C_{sed} = sediment concentration

C_{pw} = estimated porewater concentration

f_{BC} = fraction black carbon

f_{OC} = fraction organic carbon

K_{BC} = BC – pore water partition coefficient for each individual PAH (liters per kg BC; Koelmans et al. 2006)

K_{OC} = Organic carbon – water partition coefficient for each individual PAH (liter per kg organic carbon; USEPA 2003)

n = freundlich coefficient (0.7; Hauck et al. 2007)

3. The sample total toxic unit is the summation of all analyte-specific toxic unit values. A TU equal to 1 or less indicates that risk to benthic receptors is not likely. A TU above 1 indicates that more evaluation is necessary to evaluate potential risk to the benthic receptors.

-- = not available or not applicable

C_{OC,PAHI,MAXI} = Aqueous solubility of a given PAH

FCV = final chronic value

K_{ow} = Octanol-Water Partition Coefficient

Table I-2
Example for Calculating the Toxic Unit in Sediment Using the Two-Carbon Model

Downstream Areas Data Assessment Report
ExxonMobil Environmental Services Company
Mayflower Pipeline Incident Response, Mayflower, Arkansas

$\mu\text{g/g}_{\text{OC}}$ = micrograms per gram of organic carbon

$\mu\text{g/kg}$ = micrograms per kilogram

$\mu\text{g/L}$ = microgram per liter

PAH = polycyclic aromatic hydrocarbon

TOC = total organic carbon

TU = toxic unit

USEPA = United States Environmental Protection Agency

References:

Koelmans, A.A., M.T.O. Jonker, G. Cornelissen, T.D. Buchelli, P.C.M. Van Noort, and Ö. Gustafsson. 2006. Black Carbon: the reverse of its dark side. *Chemosphere* 63:365-377.

Hauck, M, M.A.J. Huijbregts, A.A. Koelmans, C.T.A. Moermond, M.J. Van Den Heuvel-Greve, K. Veltman, A.J. Hendriks, and A.D. Vethaak. 2007. Including Sorption to Black Carbon in Modeling Bioaccumulation of Polycyclic Aromatic Hydrocarbons: Uncertainty Analysis and Comparison to Field Data. *Environ. Sci. Technol.*, 41:2738-2744.

USEPA. 2003. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks for the Protection of Benthic Organisms: PAH Mixtures. Environmental Protection Agency, Office of Research and Development. EPA-600-R-02-013. November 2003.

Table I-3
Example for Calculating the Toxic Unit in Surface Water

Downstream Areas Data Assessment Report
ExxonMobil Environmental Services Company
Mayflower Pipeline Incident Response, Mayflower, Arkansas

Analyte	Final Chronic Value (FCV) ¹ (µg/L)	WS-027DA Concentration (µg/L)	TU ²
PAH - Non-alkylated			
Acenaphthene	55.85	10.88	0.0002
Acenaphthylene	306.9	15.34	0.00005
Anthracene	20.73	28.84	0.001
Benzo(a)anthracene	2.227	24.58	0.01
Benzo(a)pyrene	0.9573	39.48	0.04
Benzo(b)fluoranthene	0.6774	100.66	0.1
Benzo(e)pyrene	0.9008	65.24	0.07
Benzo(g,h,i)perylene	0.4391	54.74	0.1
Benzo(j)+(k)fluoranthene	0.6415	31.31	0.05
Chrysene/Triphenylene	2.042	62.62	0.03
Dibenz(a,h)anthracene	0.2825	5.31	0.02
Fluoranthene	7.109	90.01	0.01
Fluorene	39.3	24.87	0.001
Indeno[1,2,3-cd]pyrene	0.275	48.14	0.2
Naphthalene	193.5	31.01	0.0002
Perylene	0.9008	136.81	0.2
Phenanthrene	19.13	61.62	0.003
Pyrene	10.11	59.38	0.006
PAH - Alkylated			
1-Methylnaphthalene	75.37	23.41	0.0003
2-Methylnaphthalene	72.16	28.63	0.0004
C1-Chrysenes	0.8557	< 1.8 U	0
C1-Fluoranthenes/Pyrenes	4.887	49.73	0.01
C1-Fluorenes	13.99	32.12	0.002
C1-Phenanthrenes/Anthracenes	7.436	111.31	0.01
C2-Chrysenes	0.4827	< 1.8 U	0
C2-Fluorenes	5.305	< 1.9 U	0
C2-Naphthalenes	30.24	92.46	0.003
C2-Phenanthrenes/Anthracenes	3.199	161.29	0.05
C3-Chrysenes	0.1675	< 1.8 U	0
C3-Fluorenes	1.916	< 1.9 U	0.0000
C3-Naphthalenes	11.1	127.75	0.01
C3-Phenanthrenes/Anthracenes	1.256	< 3.5 U	0
C4-Chrysenes	0.07062	< 1.8 U	0
C4-Naphthalenes	4.048	< 6.7 U	0
C4-Phenanthrenes/Anthracenes	0.5594	< 3.5 U	0
Total TU³			0.9

Notes:

¹ FCVs from USEPA 2003.

² The analyte-specific toxic unit is calculated by dividing the concentration in water by the FCV.

³ The sample total TU is a summation of all analyte-specific toxic unit values. A TU equal to 1 or less indicates that risk to benthic receptors is not likely. A TU above 1 indicates that more evaluation is necessary to evaluate potential risk to the benthic receptors.

< = less than the limit of quantitation

FCV = final chronic value

µg/kg = micrograms per kilogram

µg/L = micrograms per liter

PAH = polycyclic aromatic hydrocarbon

TOC = total organic carbon

TU = toxic unit

USEPA = United States Environmental Protection Agency

Reference:

USEPA. 2003. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks for the Protection of Benthic Organisms: PAH Mixtures. Environmental Protection Agency, Office of Research and Development. EPA-600-R-02-013. November 2003.



Attachment I-1

USEPA Region 4 ESV Table

FW Ecological Screening Levels Email.txt

From: Brett Thomas [mailto:Thomas.Brett@epamail.epa.gov]
Sent: Tuesday, July 03, 2012 8:22 AM
To: Fontenot, Lance
Cc: Meredith Anderson
Subject: Fw: Ecological Screening Levels

Lance,

Sorry for the delay in response. I think the hierarchy you have below should be good. I am forwarding a link to our Region 4 Guidelines, as they moved, and an updated Region 4 soil screening table, as this has not yet been incorporated into the online RAGS version. The update was to incorporate the Eco SSL screening values. So I guess at this point, use the Region 4 values where they are available, and then move down the hierarchy for compounds not covered by the Region 4 guidelines. Sounds like that is what you are proposing.

<http://www.epa.gov/region04/superfund/programs/riskassess/ecolbul.html>

Also, the soil screening table has been revised but not yet included in the Guidelines document. Here is the revised Table:

(See attached file: Revised Region 4 screening values for soil Oct 2011.xlsx)

Thanks. Hope all is well there.

Brett Thomas, Ph.D.
Ecological Risk Technical Support
Superfund Division, EPA Region 4
61 Forsyth Street, SW
Atlanta, GA 30303
(T) (404) 562-8751
(F) (404) 562-8896

Hi Brett. I am adding some minor revisions to the work plan for Hattiesburg and wanted to check with you to see current Region 4 preference for surface water, sediment and soil screening levels. Will the hierarchy below work? Any suggestions would be appreciated. I also noticed that Region 5 actually has a much larger selection of soil screening values for wildlife. Do you think the Region 5 values would suffice for our screening effort of the numerous Appendix 9 constituents?
Thanks,
Lance

* ?USEPA Region 4 "Ecological Risk Assessment Bulletins - Supplement to RAGS" website (USEPA 2001b); and
* ?USEPA Ecological Soil Screening Levels website; and
* ?USEPA Region 5 Ecological Screening Levels.

Table 4. Recommended Ecological Screening Values for Soil (mg/kg dry weight)

CONSTITUENT	CAS #	TAL	TCL	Ecological Screening Value	Source	Receptor
INORGANIC COMPOUNDS						
Aluminum	7429-90-5	•		Narrative statement	[1]	
Antimony	7440-36-0	•		0.27	[1]	a
Arsenic	7440-38-2	•		18	[1]	b
Barium	7440-39-3	•		330	[1]	c
Beryllium	7440-41-7	•		21	[1]	a
Boron	7440-42-8			0.5	[2]	b
Cadmium	7440-43-9	•		0.36	[1]	a
Chromium III (total)	16065-83-1	•		26	[1]	d
Chromium VI (hexavalent)	18540-29-9			130	[1]	a
Cobalt	7440-48-4	•		13	[1]	b
Copper	7440-50-8	•		28	[1]	d
Iron	7439-89-6	•		Narrative statement	[1]	
Lanthanum	7439-91-0			50	[2]	d
Lead	7439-92-1	•		11	[1]	d
Lithium	7439-93-2			2	[2]	b
Manganese	7439-96-5	•		220	[1]	b
Mercury (total)	7439-97-6	•		0.1	[2]	c
Methyl mercury(1+), Ion	22967-92-6			0.67	[3]	f
Molybdenum	7439-98-7			2	[2]	b
Nickel	7440-02-0	•		38	[1]	b
Selenium	7782-49-2	•		0.52	[1]	b
Silver	7440-22-4	•		4.2	[1]	d
Technetium	7440-26-8			0.2	[2]	b
Thallium	7440-28-0	•		1	[4]	f
Tin	7440-31-5			50	[2]	b
Titanium	7440-32-6			1000	[2]	e
Tungsten	7440-33-7			400	[2]	e
Uranium	7440-61-1			5	[2]	b
Vanadium	7440-62-2	•		7.8	[1]	d
Zinc	7440-66-6	•		46	[1]	d
PESTICIDES						
Aldrin	309-00-2		•	0.00006	[4]	f
Atrazine	1912-24-9		•	0.0002	[4]	f
Azinphos-methyl	86-50-0			0.000005	[4]	f
a-BHC	319-84-6		•	0.003	[4]	f
b-BHC	319-85-7		•	0.009	[4]	f
g-BHC (Lindane)	58-89-9		•	0.00005	[4]	f
BHC total (a-BHC/b-BHC/g-BHC)	--			0.01	[4]	f
Carbaryl	63-25-2			0.00003	[4]	f
Carbofuran	1563-66-2			0.00002	[4]	f
Chlordane	57-74-9		•	0.00003	[4]	f
DDD	72-54-8		•	see total		
DDE	72-55-9		•	see total		
DDT	50-29-3		•	see total		
DDT/DDE/DDD (total)	--		•	0.021	[1]	a
Dieldrin	60-57-1		•	0.0049	[1]	a
Endrin	72-20-8		•	0.00004	[4]	f

Drins total (aldrin/dieldrin/endrin)	--			0.005	[4]	f
Endosulfan	115-29-7		•	0.00001	[4]	f
Heptachlor	76-44-8		•	0.0007	[4]	f
Heptachlor epoxide	1024-57-3		•	0.0000002	[4]	f
Maneb	12427-38-2			0.002	[4]	f
Organotin compounds	--			0.001	[4]	f
MCPA (4-chloro-2-methyl phenoxy acetic acid)	94-74-6			0.00005	[4]	f

POLYCHLORINATED BIPHENYLS (PCBs)

PCB toxic equivalents (TEQ)				0.000004	[5]	f
PCBs (sum)	1336-36-3		•	0.02	[4]	f

SEMIVOLATILE ORGANIC COMPOUNDS (SVOCs)

2-Chloroacetamide	79-07-2			2	[2]	c
3-Chlorophenol	108-43-0			7	[2]	b
3,4-Dichlorophenol	95-77-2			20	[2]	b,c
2,4,5-Trichlorophenol	95-95-4		•	4	[2]	b
2,4,6-Trichlorophenol	88-06-2		•	10	[2]	c
2,3,4,5-Tetrachlorophenol	4901-51-3			20	[2]	c
Phenol	108-95-2		•	0.05	[4]	f
Pentachlorophenol (PCP)	87-86-5		•	2.1	[1]	d
Chlorophenols ¹ (each)	--			0.05	[5]	f
Nonchlorinated phenols ² (each)	--			0.1	[5]	f
Chlorophenols (sum)	--		•	0.01	[4]	f
Cresol (3-methylphenol)	1319-77-3			0.05	[4]	f
Cresols (sum)	--			0.05	[4]	f
4-Nitrophenol	100-02-7		•	7	[2]	c
2,4-Dinitrophenol	51-28-5		•	20	[2]	b
Nonylphenol (and its ethoxylates)	25154-52-3			5.7	[5]	f
Monochloroaniline				0.005	[4]	f
Dichloroaniline				0.005	[4]	f
3-Chloroaniline (3-Aminochlorobenzene)	108-42-9			20	[2]	b
Hexachlorobenzene	118-74-1		•	0.05	[5]	f
Pentachlorobenzene	608-93-5			0.05	[5]	f
Hexachlorocyclopentadiene	77-47-4		•	10	[2]	b
2,4-Dichloroaniline	554-00-7			100	[2]	c
3,4-Dichloroaniline	95-76-1			20	[2]	c
2,4,5-Trichloroaniline	634-93-5			20	[2]	bc
2,3,5,6-Tetrachloroaniline	3481-20-7			20	[2]	bc
Pentachloroaniline	527-20-8			100	[2]	c
1,1'-Biphenyl	92-52-4		•	60	[2]	b
N-Nitrosodiphenylamine	86-30-6		•	20	[2]	b
Nitrobenzene	98-95-3		•	40	[2]	c

POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

2-Methylnaphthalene*	91-57-6		•	See LMWPAHs		
Acenaphthene*	83-32-9		•	See LMW PAHs		
Acenaphthylene*	208-96-8		•	See LMW PAHs		
Anthracene*	120-12-7		•	See LMW PAHs		
Benzo(a)anthracene**	56-55-3		•	See HMWPAHs		
Benzo(a)pyrene**	50-32-8		•	See HMWPAHs		
Benzo(b)fluoranthene**	205-99-2		•	See HMWPAHs		
Benzo(k)fluoranthene**	207-08-9		•	See HMWPAHs		
Benzo(ghi)perylene**	191-24-2		•	See HMWPAHs		

Chrysene**	218-01-9		•	See HMWPAHs
Dibenzo(a,h)anthracene**	53-70-3		•	See HMWPAHs
Fluoranthene**	206-44-0		•	See HMWPAHs
Fluorene*	86-73-7		•	See LMW PAHs
Indeno(1,2,3-cd)pyrene**	193-39-5		•	See HMWPAHs
Naphthalene*	91-20-3		•	See LMW PAHs
Phenanthrene*	85-01-8		•	See LMW PAHs
Pyrene**	129-00-0		•	See HMWPAHs
TOTAL PAHs				
Low Molecular Weight (LMW)* PAHs	130498-29-2	NA	29	[1] c
High Molecular Weight (HMW)** PAHs	130498-29-2	NA	1.1	[1] a
PHTHALATE ESTERS				
Diethylphthalate	84-66-2		•	100 [2] b
Dimethylphthalate	131-11-3		•	200 [2] c
Di-n-butyl phthalate	84-74-2		•	200 [2] b
Phthalates (sum)	--			0.1 [4] f
VOLATILE ORGANIC COMPOUNDS				
Acrylonitrile	107-13-1			0.000007 [4] f
Vinyl chloride	75-01-4		•	0.01 [4] f
Dichloromethane (Methylene chloride)	75-09-2		•	0.4 [4] f
Trichloromethane (chloroform)	67-66-3		•	0.02 [4] f
Tetrachloromethane (Carbon tetrachloride)	56-23-5		•	0.4 [4] f
1,1-Dichloroethane	75-34-3		•	0.02 [4] f
1,2-Dichloroethane	107-06-2		•	0.02 [4] f
1,1-Dichloroethene	75-35-4		•	0.1 [4] f
1,2-Dichloroethene	540-59-0		•	0.2 [4] f
1,1,1-Trichloroethane	71-55-6		•	0.07 [4] f
1,1,2-Trichloroethane	79-00-5		•	0.4 [4] f
Dichloropropane	78-87-5		•	0.002 [4] f
1,2-Dichloropropane	78-87-5		•	0.1 [5] f
Cis-1,4-dichloro-2-butene	1476-11-5			1,000 [2] e
Trans-1,4-dichloro-2-butene	110-57-6			1,000 [2] e
Trichloroethene	79-01-6		•	0.1 [4] f
Tetrachloroethene	127-18-4		•	0.002 [4] f
Aliphatic chlorinated hydrocarbons ³ (each)	--			0.1 [5] f
Aliphatic nonchlorinated (each)	--			0.3 [5] f
Cyclohexanone	108-94-1			0.1 [4] f
Benzene	71-43-2		•	0.01 [4] f
Chlorobenzenes ⁴ (each)				0.05 [5] f
Chlorobenzene	108-90-7		•	0.1 [5] f
1,2-Dichlorobenzene	95-50-1		•	0.1 [5] f
1,3-Dichlorobenzene	541-73-1		•	0.1 [5] f
1,4-Dichlorobenzene	106-46-7		•	0.1 [5] f
Ethylbenzene	100-41-4		•	0.03 [4] f
Chlorobenzenes (sum)			•	0.03 [4] f
Catechol (o-Dihydroxybenzene)	120-80-9			0.05 [4] f
Resorcinol (m-Dihydroxybenzene)	108-46-3			0.05 [4] f
Hydroquinone (p-Dihydroxybenzene)	123-31-9			0.05 [4] f
Styrene (Vinyl benzene)	100-42-5		•	0.3 [4] f
Toluene	108-88-3		•	0.01 [4] f
Pyridine	110-86-1			0.1 [4] f
Furan	110-00-9			NA [2] b

Tetrahydrofuran	109-99-9			0.1	[4]	f
Tetrahydrothiophene	110-01-0			0.1	[4]	f
Xylenes	1330-20-7		•	0.1	[3,4]	f
OTHER CHEMICALS						
Bromide				20	[4]	bc
Bromine (total)	7726-95-6			10	[2]	c
Fluoride				500	[4]	bc
Fluorine (total)	7782-41-4			30	[2]	e
Iodine	7553-56-2			4	[2]	b
Sulfur (elemental)	7704-34-9			500	[5]	f
Cyanide (free)	57-12-5		•	0.9	[5]	f
Cyanide, complex (total)	--		•	5	[4]	f
Phthalic acid esters (each)				30	[5]	f
Quinoline	91-22-5			0.1	[5]	f
Thiophene	110-02-1			0.1	[5]	f
Thiocyanates (sum)	--			1	[4]	f
Ethylene glycol	107-21-1			960	[5]	f
Mineral oil	8042-47-5			50	[4]	f
pH (standard units)				6 - 8	[5]	f

Notes:

The ecological screening value (ESV) is the lowest value reported for the protection of ecological receptors

a = ESV for the protection of mammalian wildlife

b = ESV for the protection of terrestrial plants

c = ESV for the protection of soil invertebrates

d = ESV for the protection of avian wildlife

e = ESV for the protection of microbes

f = ESV for the protection of all ecological receptors

*LMWPAHs have less than 4 rings

**HMWPAHs have 4 or more rings

CAS = Chemical abstracts service

NA = No data available

TAL = Target analyte list (inorganics)

TCL = Target compound list (organics)

¹Chlorophenols include:

chlorophenol isomers (ortho, meta, para)

dichlorophenols (2,6- 2,5- 2,4- 3,5- 2,3- 3,4-)

trichlorophenols (2,4,6- 2,3,6- 2,4,5- 2,3,4- 3,4,5-)

tetrachlorophenols (2,3,5,6- 2,3,4,5- 2,3,4,6-)

³Aliphatic chlorinated hydrocarbons include:

chloroform

dichloroethane (1,1- 1,2-), dichloroethene (1,2- 1,2-)

dichloromethane

1,2-dichloropropane, 1,2-dichloropropene (cis and trans)

1,1,2,2-tetrachloroethane, tetrachloroethene

carbon tetrachloride

trichloroethane (1,1,1- 1,1,2-), trichloroethene

² Nonchlorinated aliphatic compounds include:

2,4-dimethylphenol

2,4,-dinitrophenol

2-methyl 4,6-dinitrophenol

phenol

cresol

⁴ Chlorobenzenes include:

all trichloroebnzene isomers

all tetrachlorobenzene isomers

pentachlorobenzene

Sources:

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