

**SITE ASSESSMENT FOR PROPOSED COKE  
POINT DREDGED MATERIAL CONTAINMENT  
FACILITY AT SPARROWS POINT  
BALTIMORE COUNTY, MARYLAND**

**APPENDIX F**

**Sediment Sorption Calculations**

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## APPENDIX F. SEDIMENT SORPTION CALCULATIONS

Chemical species that are in contact with two different physical phases, when given time to equilibrate, split into these phases according to some constant partitioning ratio. Hydrophobic constituents like polycyclic aromatic hydrocarbons and volatile organic compounds tend to partition preferentially out of the water and into the hydrophobic portions of solid materials. Their partitioning ratio therefore depends not only on the nature of the specific compound of interest, but also on the amount of organic matter present in the sediment.

By looking at the ratio of naphthalene and benzene concentrations in the offshore sediments and the groundwater, it is possible to evaluate whether they are at equilibrium (i.e. in the expected ratio), and thus if the contaminants in the sediment are likely derived from the groundwater.

### F.1 CALCULATIONS OF EXPECTED EQUILIBRIUM VALUES

The measured concentrations of benzene and naphthalene in shallow aquifer groundwater (URS2005a) were used to calculate the corresponding concentrations of these chemicals that should be present in equilibrium with associated offshore sediments, using the equilibrium partitioning ratio,  $K_d$ .

The partitioning ratio was calculated using the Eqn (1), where  $K_d$  is the expected sediment:aqueous ratio of the target species (mL/g),  $K_{oc}$  is the known organic carbon-water partitioning coefficient for that species (mL/g), and  $f_{oc}$  is the fraction of organic matter in the sediment.

$$K_d = K_{oc} * f_{oc} \quad (1)$$

Literature values of 83.2 and 549.5, respectively, were used for the  $K_{oc}$  of benzene and naphthalene (Suthersan 1997). The fraction of organic matter for natural river bottom sediments was calculated using the total organic carbon measurements for sediments that were determined in the field to be unimpacted by contaminants, based on visual and olfactory analysis and PID measurements (Table F-1). The average value was 1.37 percent. For the slag deposits, no unimpacted offshore samples were available, and an organic matter content of 5 percent was estimated based on total organic carbon measurements of onshore slag deposits.

A summary of the  $K_d$  calculations is shown in Table F-2.

These  $K_d$  values were multiplied by the contaminant concentrations in nearby groundwater ( $C_w$ ) to calculate the expected sediment concentrations in equilibrium with that groundwater ( $C_{seq}$ ).

$$C_{seq} = K_d * C_w \quad (2)$$

This calculation was performed for benzene and naphthalene at near-shore sampling sites, where the groundwater has the potential to most directly impact the sediments, and where benzene and naphthalene concentrations in the sediments were measured. To estimate groundwater

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concentrations  $C_w$  at given near-shore locations, measured values in the shallow aquifer were extrapolated to the coastline near the given sediment sampling site.

The site locations, groundwater concentrations,  $K_d$  values, resulting calculations of the sorbed quantity in equilibrium with the groundwater, and actual solids calculations (for comparison) are shown in Tables F-3 and 4.

## **F.2 COMPARISON OF EQUILIBRIUM TO ACTUAL VALUES**

A comparison of actual solid-phase concentrations to calculated equilibrium concentrations allows evaluation of the likelihood that the offshore sediment contamination is derived from groundwater. If the calculated and actual values are similar, then the sediment is in apparent equilibrium with the groundwater with respect to the contaminant of interest. This suggests that the sediment-associated contaminant originated in the groundwater, and partitioned onto the sediment according to the expected sorption equilibrium. If the actual concentrations are higher than the equilibrium values, this implies that there is or has been another source of contaminant to the sediment.

A number of assumptions are made in comparing the two values. In using groundwater concentrations from onshore measurements for the calculated values, it is assumed that the contaminant is not diluted when groundwater enters the offshore environment, over the distance from the shoreline to the sampling site. This also requires an assumption that it is not degraded biologically, or volatilized, over this distance. The comparison also requires the assumption that the rate of sorption is faster than the rate of water flow through the sediments, which would allow equilibrium to be reached.

Based on these assumptions, the calculated values represent a maximum estimate of the amount of sorbed contaminant. This is what allows the conclusion that another source must be present where actual values exceed this maximum estimate. Meanwhile, in cases where the actual value is lower than the calculated equilibrium value, it is likely that one or more of these assumptions have proven false.

### **F.2.1 Benzene**

The comparison of actual concentrations of benzene to the calculated equilibrium values (Table F-3) shows that, on average, actual values are lower than equilibrium values. However, there is wide variation in this relationship, with actual values sometimes much higher than equilibrium values. These data indicate that the assumptions were not valid for benzene, which is volatile and relatively easily biodegradable. It is possible that, in the cases where the actual value exceeds the calculated value, another source of benzene is indeed present. However, it is difficult to make conclusions about benzene sources because of the inconsistencies between sites.

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## **F.2.2 Naphthalene**

Actual concentrations of naphthalene in the sediments consistently exceed the calculated equilibrium values in the northwestern and western portion of the Peninsula, in both slag material and river bottom sediments (Table F-4). This relationship is also seen off the southeast corner of the Peninsula. Actual values average 400 times the calculated equilibrium values, with one sample reaching 3,000 times the calculated value. Thus sorption from groundwater cannot account for naphthalene concentrations in sediments around these large portions of the Peninsula.

Offshore from the Coal Tar Storage area, calculated naphthalene concentrations in most cases exceed the actual values. This relationship is most pronounced for the sites estimated to have very high naphthalene concentrations, and suggests that one or more of the assumptions do not hold true in this area. For example, the high-naphthalene groundwater in this area may become more diluted in the local hydrologic conditions, causing it to become more diluted offshore. Or the sediments may have just not reached equilibrium with such high concentrations.

## **F.3 SUMMARY**

Comparison of expected sediment concentrations of benzene and naphthalene to their actual values was inconclusive for benzene, but suggested that an additional source of naphthalene, in addition to nearby groundwater, is present along the western and southeastern coasts of Sparrows Point.

**Table F-1. Calculation of Average Fraction Organic Carbon**  
**Coke Point Peninsula, Sparrows Point Site Assessment (2009), Baltimore, Maryland**

Location	Sample ID	Water Depth (feet below water surface)	Top of Sample Interval(s) (feet below sediment line)	Stratigraphic Determination	Description	Contaminant Impacted <sup>1</sup> (Y/N)	Total Organic Carbon <sup>2</sup> (mg/L)	Total Organic Carbon (%)
BH-SED-01	BH-SED-01-8	22.5	8	Slag Fill Material	Black, wet coal slag with silt. Hydrocarbon odor. Small sheer observed.	Y	311000	31.1
BH-SED-03C	BH-SED-03C-2	14.75	0	Slag Fill Material	Black, wet silt with fine grain sand. Coal tar odor. Sheen visible.	Y	73900	7.39
BH-SED-03B	BH-SED-03B-2	11.5	2	River Bottom Sed.	Dark gray, moist clay with very fine grain sand. Slight plasticity. Coal tar odor. Sudan IV = positive	Y	43000	4.3
BH-SED-06	BH-SED-06-6	15.5	6	River Bottom Sed.	Black, moist silty clay with very fine sand. Medium gray, moist clay at bottom. Slight plasticity. Sudan IV = negative	Y	77300	7.73
BH-SED-12	BH-SED-12-4	14.5	4	River Bottom Sed.	Medium gray, wet fine grained sand clay. No plasticity. Shell material.	Y	37900	3.79
BH-SED-03A	BH-SED-03A-TOC	5.5	16	River Bottom Sed.	Medium gray, moist clay with shell hash near bottom. Medium plasticity. No odor.	N	16000	1.6
BH-SED-03E	BH-SED-03E-TOC	18	18	River Bottom Sed.	Medium gray, moist soft clay. Slight plasticity. No odor.	N	11900	1.19
BH-SED-10	BH-SED-10-TOC	7	24	River Bottom Sed.	Medium gray, moist soft clay. Medium plasticity. No odor.	N	14800	1.48
BH-SED-11	BH-SED-11-TOC	11	20	River Bottom Sed.	Medium gray, moist clay. Medium plasticity. No odor.	N	14900	1.49
BH-SED-13A	BH-SED-13A-TOC	9	24	River Bottom Sed.	Medium gray, moist stiff clay. Moderate plasticity.	N	10800	1.08
BH-SED-13B	BH-SED-13B-TOC	19	24	River Bottom Sed.	Medium gray, stiff clay. Moderate plasticity. No odor.	N	15800	1.58
BH-SED-13C	BH-SED-13C-TOC	12.5	20	River Bottom Sed.	Medium gray, moist stiff clay, slight plasticity. No odor.	N	11600	1.16

<sup>1</sup>Based on field observations and PID analysis.

<sup>2</sup>Data from Test America

**Table F-2. Calculation of Kd Values**  
**Coke Point Peninsula, Sparrows Point Site Assessment (2009), Baltimore,**  
**Maryland**

		Benzene	Naphthalene
	$K_{oc}^1$	83.2	549.5
	$f_{oc}$	$K_d$	
River Bottom Sediment	0.0137	<b>1.14</b>	<b>7.53</b>
Slag Fill Material	0.05	<b>4.16</b>	<b>27.48</b>

<sup>1</sup> Values from Sunderson 1997.

**Table F-3. Comparison of Actual and Estimated Benzene Concentrations  
Coke Point Peninsula, Sparrows Point Site Assessment (2009), Baltimore, Maryland**

	Sample ID	Estimated Benzene in Groundwater ( $\mu\text{g/L}$ )	$K_d$	Benzene in Sediments ( $\mu\text{g/kg}$ )	
				Equilibrium	Actual
<b>Slag Fill Material</b>	BH-SED-01-8	10000	4.16	41,588	11
	BH-SED-02-4	2000	4.16	8,318	36,000
	BH-SED-03A-12	25	4.16	104	490
	BH-SED-03C-2	25	4.16	104	720
	BH-SED-13A-6	540	4.16	2,246	490
	BH-SED-13C-6	520	4.16	2,163	64
	Mean			9,087	6,296
Max			41,588	36,000	
Min			104	11	
<b>River Bottom Sediment</b>	BH-SED-03B-2	25	1.14	28	200
	BH-SED-04-8	1000	1.14	1,138	53
	BH-SED-05-4	100	1.14	114	10
	BH-SED-06-6	18	1.14	20	630
	BH-SED-07-6	62	1.14	71	11
	BH-SED-08-10	4	1.14	5	11
	BH-SED-09-12	100	1.14	114	8.1
	BH-SED-10-2	6.4	1.14	7	11
	BH-SED-11-2	7.5	1.14	9	10
	BH-SED-12-4	180	1.14	205	8.9
	BH-SED-13B-8	540	1.14	615	10
	BH-SED-14-8	100	1.14	114	21
	BH-SED-15-2	540	1.14	615	8.6
	Mean			235	76
	Max			1,138	630
Min			5	8	

**Table F-4. Comparison of Actual and Estimated Naphthalene Concentrations**  
**Coke Point Peninsula, Sparrows Point Site Assessment (2009), Baltimore, Maryland**

	Sample ID	Estimated Naphthalene in Groundwater ( $\mu\text{g/L}$ )	$K_d$	Naphthalene in sediments (mg/kg)	
				Equilibrium	Actual
<b>Slag Fill Material</b>	BH-SED-01-8	100	27.5	2.7	28
	BH-SED-02-4	150	27.5	4.1	290
	BH-SED-03A-12	580	27.5	16	29
	BH-SED-03C-2	580	27.5	16	2,800
	BH-SED-13A-6	5700	27.5	157	2.4
	BH-SED-13C-6	340	27.5	9.3	8.4
	Mean			34	526
	Max			157	2,800
	Min			2.7	2
<b>River Bottom Sediment</b>	BH-SED-03B-2	580	7.52	4.4	51
	BH-SED-04-8	1000	7.52	7.5	4,400
	BH-SED-05-4	140	7.52	1.1	590
	BH-SED-06-6	31	7.52	0.23	62
	BH-SED-07-6	95	7.52	0.71	10
	BH-SED-08-10	99	7.52	0.75	17
	BH-SED-09-12	68	7.52	0.51	0.024
	BH-SED-10-2	21	7.52	0.16	32
	BH-SED-11-2	100	7.52	0.75	2,400
	BH-SED-12-4	940	7.52	7.1	1.9
	BH-SED-13B-8	5700	7.52	43	0.0076
	BH-SED-14-8	100	7.52	0.75	6.1
	BH-SED-15-2	5700	7.52	43	3.2
	Mean			8	583
	Max			43	4,400
Min			0.16	0.0076	