# SITE ASSESSMENT FOR PROPOSED COKE POINT DREDGED MATERIAL CONTAINMENT FACILITY AT SPARROWS POINT

## **BALTIMORE COUNTY, MARYLAND**

# **APPENDIX E**

## **Mass Flux Calculations and Surface Water Modeling**

Prepared for:



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#### APPENDIX E: MASS FLUX CALCULATIONS AND SURFACE WATER MODELING

Groundwater chemistry data from the Nature and Extent report (URS 2005a) was used to calculate the flux of constituents from the aquifers of the Coke Point Peninsula to the surrounding surface water.

#### E.1 MASS FLUX

Fluxes of indicator species (*i*) were calculated across discrete shoreline boundary sections of interest along the coast of the peninsula. The groundwater mass flux (*J*) in grams/second from each aquifer through each section was calculated using Eqn. (1), where  $C_i$  is the concentration of species *i* at the boundary in  $\mu$ g/L.

$$J_i = n v C_i A \tag{1}$$

The groundwater velocity v in ft/day was calculated using Eqn. (2), from the hydraulic conductivity (k) in ft/day, the porosity of the aquifer (n), and the hydraulic gradient (dh/dl).

$$v = \frac{k}{n} \cdot \frac{dh}{dl} \tag{2}$$

Cross-sectional area (A) (in  $ft^2$ ) of each boundary section was calculated from the length of the section in map view (L) and the average thickness of the given aquifer (b), both in feet (Eqn. 2)

$$A = Lb \tag{3}$$

#### **E.1.1** Sections of Interest and Concentrations

Sections of interest for calculating mass flux were identified based on elevated concentrations of indicator species in near-shoreline samples from the aquifers. Each section was divided into subsections and segments as necessary to accurately portray the lateral variability of constituent concentrations in each aquifer. Benzene and naphthalene were selected as indicator organic compounds representative of VOCs and PAHs respectively. Vanadium was chosen as an indicator metal, because of its high mobility and particularly elevated levels in groundwater.

**Benzene and naphthalene** - For benzene and naphthalene, the key sections for plume migration into surface water were (1) the northwest portion of the Peninsula, down-gradient of the Benzol Processing area, and (2) the eastern side of the Peninsula, down-gradient of the Coal Tar Storage area. Both the shallow and intermediate aquifers flow westward from the Benzol Processing area, and both show high chemical concentrations associated with the NAPL plume. Therefore, both were considered in mass flux calculations for the northwest section. However, chemical concentrations were much lower in the intermediate aquifer in the eastern section, where it flows primarily to the northwest. Therefore, only the shallow aquifer was considered in calculations for the eastern section. The deep aquifer was omitted from analyses because of negligible mass of target analytes.

Subsections within the sections were chosen using concentration isocontours for benzene and naphthalene in the shallow and intermediate aquifers, produced by URS as part of the Nature and

Extent report (URS 2005a). The main subsections were BN1-BN3 in the northeast and BN4 in the east (Figure E-1). In some cases, subsections were divided up further into segments to better capture variations in chemical concentrations. Concentrations within segments were calculated as the average ( $C_{avg}$ ) of the bounding minimum and a maximum values ( $C_{min}$  and  $C_{max}$ ). For segments with uniform concentrations,  $C_{max}$  was equivalent to  $C_{avg}$ . Conservative professional judgment was used to reconcile/adjust concentration profiles as needed based on nearest well concentrations.

The length of each segment was measured in inches along the shore on the concentration isocontour maps and converted to feet based on the appropriate scale. A weighted average concentration was then calculated for each subsection, based on the fraction of total length represented by each of its constituent segments.

*Vanadium* – Plumes of elevated vanadium are also present in the northwest and eastern sections, associated with the Benzol Processing and Coal Tar Storage areas. Therefore, the same large sections were used, although the subsections within each section were customized to reflect variability of this constituent. The primary subsections for the vanadium mass flux calculation were V1-V2 in the northwest and V3 in the east (Figure E-2).

In the eastern section, where a concentrated near-shore vanadium plume is present, segments were determined based on approximated concentration isocontours for vanadium. Average concentrations for each segment were determined as described for benzene and naphthalene. In sections of diffuse, relatively low-level contamination, insufficient data was available for contour construction, and conservative professional judgment was used in estimating average concentrations over larger subsections.

*Arsenic* – Because arsenic was only present in the intermediate aquifer along the northwest shore of the peninsula, its mass flux was only modeled in this region. Only three data points for arsenic in this aquifer and section were available, and an average concentration was estimated for the section based on the distribution of these measurements.

#### E.1.2 Groundwater Velocity

*Hydraulic gradient* – The hydraulic gradient dh/dl was calculated from groundwater flow contours for the shallow aquifer in the northwest section (westerly direction) and in the eastern section (easterly direction), as the change in water table height (dh) in feet divided by the surface distance in feet between two points (dl). Calculations were performed for multiple timepoints in each section, and were found to be very similar. Lateral variability within each section also appeared to be minimal. Therefore an average of the calculated values was used for each section. Table E-1 shows the hydraulic gradient calculations, as well as the input information, for the following timepoints: December 2003 (URS 2005a), June 2004 (URS 2005a), and August 2006 (URS 2006).

Using the groundwater isocontour figures cited, the hydraulic gradients were determined between pairs of points perpendicular to the isocontours from the center of the 6-foot isocontour lines to wells CO29, CO26 and CP16 for Sections 1, 2, and 3 respectively. Change in water

height dh was defined as difference between the 6-foot height (defined by the contour) and the water table height for a given well. Negative water table heights in the shallow aquifer were assumed to have a value of 0 ft, relative to mean sea level. The change in distance dl was defined as the length between the two points measured in the respective groundwater flow contour map and converted from feet to inches based on the scale given. Hydraulic gradients were averaged for the three timeframes, yielding values of 0.0016 and 0.0025, respectively, for the northwestern and eastern sections of the shallow aquifer.

The hydraulic gradients were similarly determined for the intermediate aquifer, for which input information is also displayed in Table E-1 (URS 2005a, URS 2006). Groundwater in the intermediate aquifer flows out to sea in the westerly direction, more specifically towards the graving dock, and is therefore only significant in Section 1. As noted previously, the groundwater flow in the intermediate aquifer was significantly influenced by pumping in the graving dock (URS 2005a). The diversion of flow into the graving dock is evident in December 2003 and August 2006, in comparison to June 2004 during which the pump was not operational. The hydraulic gradients in the intermediate aquifer were calculated only for timeframes in which the graving dock pump was operational (December 2003 and August 2006), between wells CO07 and CO27. Hydraulic gradients were averaged for the two timeframes yielding a final value of 0.0016.

**Porosity** –Porosities were estimated based on literature values for similar geologic materials (Fetter 1994). In the shallow aquifer, a soil porosity value of n = 0.25 was assumed based on the moderate to large grain size and poor sorting of the slag. In the intermediate aquifer, a porosity value of n = 0.3 was assumed based on the average porosity for sand and silt.

*Hydraulic conductivity* – Hydraulic conductivities of k = 149 ft/day and k = 23.2 ft/day were previously calculated for the shallow and intermediate aquifers respectively, based on piezometer testing and subsequent modeling with calibration based on observed hydrology (CH2M-Hill 2001). Hydraulic conductivities had also been determined using slug tests (URS 2005a), but the results were highly variable due to the heterogeneity of the aquifers. Therefore, the modeled results were used for the mass flux calculations.

**Groundwater velocity** – Groundwater velocity v was calculated from Eqn. (2) to be 0.96 and 1.50 ft/day in the shallow aquifer of the northwestern and eastern sections, respectively. Groundwater velocities and input information are available in Table E-2. In the intermediate aquifer in the northwest, the groundwater velocity was 0.12 ft/day. Groundwater velocity values were used in the mass flux calculations for the respective aquifer and section.

#### E.1.3 Aquifer Cross-Sectional Area

The cross-sectional area A of the shallow and intermediate aquifer through which chemical mass flux passes was determined for individual subsections within the northwest and east sections and calculated based on Eqn. (3). Lengths of subsections were measured on maps and converted to feet using the scale provided. Aquifer thicknesses b were reported from the cross-sections as 30 and 40 ft respectively for the shallow aquifer and intermediate aquifers respectively (URS

2005a). This shallow aquifer thickness reflects average slag depth. These thicknesses were approximated as constant for each aquifer.

#### E.1.4 Mass Flux

The mass flux J of each constituent in g/s for a given subsection and aquifer was calculated using Eqn. (1) (Table E-3) based on groundwater velocity in ft/day, the average concentration in  $\mu$ g/L, subsection lengths in feet, average aquifer depth in feet, and porosity. Mass fluxes for a given constituent in the shallow and intermediate aquifer were summed to yield the total mass flux discharged from a given subsection. The percent contributions of chemical discharge of the shallow and intermediate aquifers were calculated for each subsection.

The resulting mass flux calculations by region is provided in Table E-3. The mass flux was evenly distributed over the shoreline model cells in each region, and the benzene flux in region 1 was 100 times greater than that of naphthalene, while benzene in regions 2 and 3 were respectively 6.6 and 11.4 times greater than naphthalene. East towards the turning basin, the naphthalene mass flux was 8.9 times greater than that of benzene. Totaled over the four regions, the total benzene mass flux was 11.8 times greater than naphthalene.

#### **E.2 SURFACE WATER MODELING**

#### E.2.1 Model and Inputs

A tidally dynamic model was developed to examine the mixing of the constituent mass flux of groundwater from the shoreline surrounding Sparrows Point into Baltimore Harbor. The US Army Corps models RMA2 (hydrodynamics) and RMA4 (water quality) were used. Both are finite element numerical models. RMA2 calculates fluid flow velocities within a 2-dimensional grid system, and RMA4 uses the solutions to calculate movement of mass through the grid, based on advection and diffusion processes. These models were executed within the framework provided by the Surfacewater Modeling System (SMS). The downstream end of the model domain has a tidal boundary at a transect between North Point and Rock Point (Figure E-3). The model included all of Baltimore Harbor and Bear Creek upstream of this location. A lower resolution model grid was used for much of Baltimore Harbor, while a more refined grid was used in the vicinity of Sparrows Point. The objective for including Baltimore Harbor was to represent the upstream intertidal volume such that the tidal reversing flows in the vicinity of Sparrows Point would be properly represented. The model included 3,664 cells and 10,660 nodes.

An average flow of 250 cubic feet per second (cfs) was applied where the Patapsco River enters Middle Branch as an upstream boundary condition. A 1.1 ft sinusoidal tide curve with a 12.4 hr period was applied at the downstream model boundary. The model was executed with a 0.5 hour time step and output saved every hour. The hydrodynamic output file from RMA2 is used as an input file to RMA4. The groundwater mass flux at the Sparrows Point shoreline (see Section E.1 above) was modeled as a conservative tracer. Thus the model only represents physical processes affecting chemical transport and mixing, and does not include any chemical effects. A zero background concentration was used for all constituents, such that the model only represents chemical concentrations resulting from the calculated fluxes from Coke Point. The model was executed for 2,400 hours (100 days) to approach an equilibrium concentration at nodes in the vicinity of Sparrows Point. The build-up of naphthalene is illustrated in Figure E-4 at three representative model nodes.

#### E.2.2 Results

The modeled concentration isocontours for benzene, naphthalene, and vanadium are shown in Figures E-5 to E-7. The spacing of the isocontours reflects the large differences in mass flux for the different species (Table E-3). The 1  $\mu$ g/L benzene contours are located near the farthest extents of the model grid, as much as 4 miles from the primary benzene flux, whereas the 1  $\mu$ g/L contours for naphthalene are close offshore from the Coke Point peninsula, and those for vanadium occur within the turning basin. The EPA's recommended water quality criterion for benzene in seawater from which organisms are harvested for human consumption is 51  $\mu$ g/L, and the model predicts concentrations in excess of this value within the graving dock, where the highest benzene fluxes from groundwater occur (USEPA 2009b). Criteria for naphthalene and vanadium in surface water are not available.

The modeled values of benzene and naphthalene can be compared to those measured in the surface waters around Coke Point; equivalent comparison is not possible for vanadium, as levels of this metal in surface water were not measured. The modeled concentrations of benzene are generally on the same order of magnitude as the measured concentrations, except in the graving dock, where modeled concentrations are as much as 10 times higher than actual. The agreement is closer for naphthalene, for which all modeled concentrations are within a factor of 2-3 of the measured concentrations. This agreement is notable, given that this model includes no other chemical sources and no chemical sinks, and suggests that hydrodynamic mixing of constituents from Coke Point groundwater is a primary determinant of VOC and PAH concentrations in the vicinity of Coke Point.



Figure E-1. Near Field Model Grid and Shoreline Regions Associated with Groundwater Mass Flux



Figure E-2. Near Field Model Grid and Shoreline Regions Associated with Groundwater Flux for Vanadium



Figure E-3. Baltimore Harbor Model Grid





Figure E-5. Modeled Benzene Concentrations (µg/L) in Surface Water

	Feet	
0	2,000	4,000



Figure E-6. Modeled Naphthalene Concentrations (µg/L) in Surface Water

### Site Assessment for Proposed Coke Point Dredged Material Containment Facility at Sparrows Point

#### <u>Legend</u>

#### Naphthalene Isoconcentration Contour

Sources ESRI, i-cubed, GeoEye, 2009 Tele Atlas North America Inc., ESRI, 2006



		Feet		
0		1,000		2,000
	1		I	





Figure E-7. Modeled Vanadium Concentrations (µg/L) in Surface Water

### Site Assessment for Proposed Coke Point Dredged Material Containment Facility at Sparrows Point

#### <u>Legend</u>

#### Vanadium Isoconcentration Contour

Sources ESRI, i-cubed, GeoEye, 2009 Tele Atlas North America Inc., ESRI, 2006



		Feet		
0		1,000		2,000
	I		I	



## Table E-1. Hydraulic Gradient Calculation Coke Point Penisula, Sparrows Point Site Assessment (2009), Baltimore, Maryland

			December 2003			June 2004			August 2006			Average
Aquifer Section	Direction	Water table height	Distance	Hydraulic gradient	Water table height	Distance	Hydraulic gradient	Water table height	Distance	Hydraulic gradient	Hydraulic gradient	
			dh (ft)	dl (ft)	dh/dl	dh (ft)	dl (ft)	dh/dl	dh	dl (ft)	dh/dl	dh/dl
Shallow East	Northwest	Westerly	6	3500	0.0017	5.72	3500	0.0016	5.11	3500	0.0015	0.0016
	Easterly	4.73	1890	0.0025	4.54	1750	0.0026	5.19	2100	0.0025	0.0025	
Intermediate	Northwest	Graving dock (pump on)	1.22	1225	0.0010				2.73	1225	0.0022	0.0016

Aquifer	Section	Direction	Average hydraulic gradient	Porosity	Hydraulic conductivity (ft/day)	Groundwater velocity (ft/day)		
Aquiter Section		Direction	dh/dl	п	k	v = k/n(dh/dl)		
Shallow	Northwest	Westerly	0.0016	0.25	149	0.96		
Shallow	East	Easterly	0.0025	0.25	149	1.50		
Intermediate	Northwest	Graving dock (pump on)	0.0016	0.3	23.2	0.12		

# Table E-2. Groundwater Velocity Coke Point Penisula, Sparrows Point Site Assessment (2009), Baltimore, Maryland

Analyte	Aquifer	Section	Sub-Section	Groundwater Velocity (ft/day)	Length (ft)	Average Depth (ft)	Cross- sectional area (ft <sup>2</sup> )	Porosity	Average Concentration (µg/L)	Mass Flux (g/s)	% Contribution to Total Mass Flux	Sub-Section Mass Flux (g/s)	Total Mass Flux								
				v	L	D	Α	n	Cavg	J	%	J	J								
	Shallow		BN1	0.96	2331	30	69941	0.25	8051	4.41E-02	13.6	2.79E-01									
	Intermediate		DIVI	0.12	2331	40	93255	0.3	205213	2.35E-01	72.4	2.79E-01									
	Shallow	Northwest	BN2	0.96	1128	30	33850	0.25	216	5.73E-04	0.2	6 04E 04									
Benzene	Intermediate	Northwest	DINZ	0.12	1128	40	45134	0.3	219	1.21E-04	0.0	6.94E-04	0.32								
	Shallow		BN3	0.96	1230	30	36912	0.25	14513	4.19E-02	12.9	4.19E-02									
	Intermediate		DINS	0.12	1230	40	49216	0.3	4	2.47E-06	0.0	4.19E-02									
	Shallow	East	BN4	1.50	3188	30	95640	0.25	222	2.62E-03	0.8	2.62E-03									
	Shallow	Northwest									BN1	0.96	2331	30	69941	0.25	313	1.71E-03	6.2	2.81E-03	
	Intermediate		DINI	0.12	2331	40	93255	0.3	964	1.10E-03	4.0	2.01E-05									
	Shallow		BN2	0.96	1128	30	33850	0.25	365	9.67E-04	3.5	1.08E-03									
Naphthalene	Intermediate		BIN2	0.12	1128	40	45134	0.3	197	1.09E-04	0.4	1.08E-03	0.028								
	Shallow		BN3	0.96	1230	30	36912	0.25	1228	3.55E-03	12.9	3.55E-03									
	Intermediate		BINS	0.12	1230	40	49216	0.3	11	6.64E-06	0.0	3.33E-03									
	Shallow	East	BN4	1.50	3188	30	95640	0.25	1709	2.01E-02	73.0	2.01E-02									
	Shallow	Northwest	V1	0.96	2769	30	83077	0.25	13	8.13E-05	1.5	1.67E.04									
Vanadium	Shallow	Northwest	V2	0.96	346	30	10385	0.25	105	8.53E-05	1.6	1.67E-04									
	Shallow	East	V3	1.50	940	30	28212	0.25	1518	5.28E-03	96.5	5.28E-03									
	Intermediate	Northwest	V1	0.12	2769	40	110769	0.3	18	2.38E-05	0.4	2.67E.05									
	Intermediate	Northwest	V2	0.12	346	40	13846	0.3	18	2.97E-06	0.1	2.67E-05	0.0055								
Arsenic	Intermediate	Northwest	A1	0.12	4038	40	161538	0.3	140	2.77E-04	100.0	2.77E-04	0.00028								

## Table E-3. Mass Flux Calculations Coke Point Penisula, Sparrows Point Site Assessment (2009), Baltimore, Maryland