APPENDIX C

CAP AMENDMENT ISOTHERM DEVELOPMENT
(ADDENDUM 2)

PARSONS

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To: Caryn Kiehl-Simpson

         Parsons

From: Danny Reible and Anthony Smith, University of Texas

Re: Phase IV Addendum 2 Report —Isotherm Experiments with Organic Contaminants of Concern with Sand, Organoclay and Peat and for Mercury with Sand, Organoclay, Peat, and Activated Carbon

1.0 Executive Summary

Isotherm testing on Organoclay, Sand, Peat, and Activated Carbon (for mercury) was conducted in compliance with the Phase IV Pre-Design Investigation (PDI) Addendum 2 Work Plan (Work Plan) with changes as described below (Parsons, 2008). Isotherm testing for organics on activated carbon is included in a separate report (Lowry, 2008). Representative porewater was generated from sediments in Sediment Management Unit (SMU) 1 and a composite of SMUs 6 and 7. These studies were performed at the University of Texas under the direction of Dr. Danny Reible.

Partitioning of selected organic and inorganic contaminants to various sorbents was measured under conditions corresponding to both SMU 1 and SMU 6/7 porewater. The contaminants and sorbent media evaluated in these studies are shown below in Table 1. Organic contaminants sorption onto sand, organophyllic organoclays PM-199 and XB-1, and peat were studied. Mercury sorption was studied on these materials with the exception of organoclay XB-1. Mercury sorption onto mercury sorbing organoclays MR2/MR4 and activated carbon was also studied.

Table 1 – Sorbents and contaminants included in isotherm studies reported herein

Contaminant	Sand	Organoclay PM-199/XB-1	Organoclay MR2/MR4	Peat	Activated Carbon
Organic	X	X		X	
Mercury	X	X	X	X	X

Effective partition coefficients defined as the ratio of solid phase to water phase concentration for each contaminant of interest and each sorbent were estimated over a range of initial solution concentrations.

1.1 Organic Contaminant Sorption Isotherm Experiments

Experimental Procedure

Sparged site water from SMUs 1 and 6/7 were received from TestAmerica as described in the Work Plan and stored at 4°C. Sorptive media (Organoclays PM-199 and XB-1 from Cetco, Peat provided by Parsons) was added to 50-mL vials, which were then filled with site water. With large masses of solids, this volume was less than 50 mL, and the actual volume was documented for computation of the contaminant mass balance. Tests with 10 g of organoclay were done in 55-mL vials while tests with all other masses of organoclay were done in 50-mL vials. In each vial, aqueous volumes were negligibly reduced by the presence of the solids (<5%), so 50 mL was assumed for partitioning computations. As peat is less sorptive than organoclay, larger masses of solids were required to achieve target equilibrium concentrations which reduced aqueous volumes to less than 50 mL in some isotherm vials, and the actual volume was documented for computation of the contaminant mass balance. Vials were then capped with Mininert™ valves. The contaminant spike solution (AccuStd, Inc.) was diluted in purge-and-trap grade methanol (Sigma-Aldrich), and the diluted spike solution was added to the sample vial. Vials were tumbled at 12°C for 7 days then centrifuged at room temperature for 15 minutes at 2000 rpm. Caps were removed and aqueous samples were decanted directly to either 20-mL or 40-mL VOA vials. Forty-mL vials were provided with 0.5 mL of 1:1 HCl, but 20-mL vials were provided without preservative. Concentrated HCl (0.1 mL) was added to 20-mL vials before samples were decanted. VOA vials were then stored at 4°C until picked up for analysis by DHL Analytical, Round Rock, TX. Samples were analyzed using purge and trap GC/MS by a commercial lab (SW5030B/8260B).

Experiment Set-up

Isotherm experiments were conducted using spike dilutions and volumes and sorptive media masses tabulated in Table 2. Two types of blanks were included, each in duplicate: site water was added directly from storage bottles to VOA vials to verify site water residual concentration, and site water was added to vials and tumbled for 7 days along with samples to demonstrate consistency in concentration before and after tumbling. Control vials consisted of site water spiked with the same diluted spike solution and volume used for samples. These controls were used to confirm spike concentration and to account for losses to volatilization or sorption to the vial. For analysis of sample vials, C0 was assumed

to be equal to the average concentration measured in the control vials with the same spike dilution and volume. Partition coefficients were then computed for each compound in each sample by equations 4 – 7. Data and analysis of samples are presented in Appendix B. Similar Kd values were computed with SMU1 and SMU7 porewaters which had DOC concentrations of 760 and 70 mg/L, respectively. This result suggested that sorbent fouling by organic carbon was not a concern for organoclay and peat and testing with organic free water was not pursued.

Table 2a: Sorbent mass, spike dilutions and aqueous volumes in isotherm sample vessels – SMU 1

SMU 1 Sample	Media	MassOC (mg)	Spike Soln Diln (1/x)	SpikeVol (mL)	Aq Vol (mL)
SMU1V1	PM-199	10000	100	0.1	50
SMU1V2	PM-199	1000	100	0.1	50
SMU1V3	PM-199	1000	100	1	50
SMU1V4	PM-199	100	100	1	50
SMU1V1	PM-199	100	20	1	50
SMU1V5	XB-1	1000	100	0.1	50
SMU1V6	XB-1	1000	100	1	50
SMU1V7	XB-1	1000	100	0.1	50
SMU1V8	XB-1	1000	100	1	50
SMU1V9	XB-1	10000	100	0.1	50
SMU1V10	XB-1	1000	100	0.1	50
SMU1V11	XB-1	1000	100	1	50
SMU1V12	XB-1	100	100	1	50
SMU1V9	Peat	10000	400	0.1	31.5
SMU1V10	Peat	2000	400	0.1	50
SMU1V11	Peat	1000	400	1	47
SMU1V12	Peat	2000	400	1	47
SMU1V13	Peat	500	20	1	50
SMU1V20	Peat	2000	3	0.1	50
SMU1V21	Peat	500	3	0.1	50

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Table 2b: Sorbent mass, spike dilutions and aqueous volumes in isotherm sample vessels – SMU 6/7

SMU 6/7 Sample	Media	MassOC (mg)	Spike Soln Diln (1/x)	SpikeVol (mL)	Aq Vol (mL)
SMU6V19	PM-199	10000	100	0.1	50
SMU6V20	PM-199	1000	100	0.1	50
SMU6V21	PM-199	1000	100	1	50
SMU6V22	PM-199	100	100	1	50
SMU6V1	PM-199	100	3	0.1	50
SMU6V23	XB-1	1000	100	0.1	50
SMU6V24	XB-1	1000	100	1	50
SMU6V25	XB-1	1000	100	0.1	50
SMU6V26	XB-1	1000	100	1	50
SMU6V27	XB-1	10000	100	0.1	50
SMU6V28	XB-1	1000	100	0.1	50
SMU6V29	XB-1	1000	100	1	50
SMU6V30	XB-1	100	100	1	50
SMU6V23	Peat	10000	400	0.1	31.5
SMU6V24	Peat	1000	400	0.1	50
SMU6V25	Peat	2000	3	0.01	47
SMU6V26	Peat	2000	3	0.1	47
SMU6V27	Peat	500	3	0.1	50

Determination of Solid Masses and Contaminant Concentrations

Literature values for contaminant soil partitioning coefficients (Koc) and contaminant concentrations in site water sparged for 15 minutes and measured by TestAmerica-Pittsburgh are reported in Table 3. These partitioning coefficients were used for experimental design of the isotherm testing of organoclays PM-199 and XB-1. The magnitude of the solid-water partitioning coefficient (Kd,clay) was expected to be approximately equal to literature estimates of Koc (eqn. 1). For peat, the water content and fraction organic matter were measured by loss on ignition (data and calculations in Appendix A). The organic carbon fraction of peat (foc,peat) was calculated to be 30% by mass. Values of Kd,peat were expected to be equal to the product of the fraction organic carbon and Koc (eqn. 2).

Table 3: Contaminants of Interest, their log-K_{oc} values, and concentrations measured in site porewater by TestAmerica-Pittsburgh

		Porewater	
		SMU 1	SMU 6/7
Compound	log Koc[b]	Conc (mg/L),	Conc (mg/L)
Benzene	1.92	0.50	0.013
Toluene	2.48	0.29	0.044
ethylbenzene	3.04	0.07	0.036
p-xylene[a]	2.38	0.29	0.009
chlorobenzene	2.52	1.20	0.050
1,2-DCB	3.23	0.55	0.091
naphthalene	2.97	2.70	0.120
m-Xylene[a]	2.48	0.29	0.009
o-Xylene	2.41	0.26	0.010
1,3-DCB	3.23	< 0.20	0.033
1,4-DCB	3.23	0.49	0.022

[a] m-xylene and p-xylene eluted simultaneously, so each compound was assumed to contribute one half of the peak area

[b] Reible. D.D. Fundamentals of Environmental Engineering. Lewis Publishers. 1999

$$K_{d,clay} \approx K_{oc} \qquad \text{(eqn. 1)}$$

$$K_{d,peat} \approx f_{oc} \times K_{oc} \qquad \text{(eqn. 2)}$$

In order to estimate appropriate sorbent masses and contaminant spike concentrations to give the desired range of equilibrium aqueous phase concentrations, approximate partitioning coefficientswere used to compute theoretical aqueous phase concentrations at equilibrium with the sorptive media by a contaminant mass balance. The total contaminant mass in the vial (M_{total}) was given by the product of the spike solution concentration (C_{spike}) and volume (V_{spike}) plus the product of the residual contaminant concentration in the site water (C_{sw}) and the aqueous phase volume (V_{aq}) (eqn. 3). The initial aqueous phase concentration (C0) is the total mass divided by the aqueous phase volume (the addition of the spike solution changed the aqueous volume less than 2%) (eqn. 4). C0 or M_{total} are used only to indicate the total mass in the system. For isotherm calculations, only the aqueous concentration and mass sorbed to the solid at the end of the equilibration time are relevant. After seven days, the mass was allowed to settle (centrifuged for peat to aid solid separation) and the unfiltered equilibrium aqueous phase concentration (Ce) was measured, and the contaminant mass in the aqueous phase ($M_{aq,equil}$) was found by the product of Ce with V_{aq} (eqn. 5). The difference between the total contaminant mass and the mass in the aqueous phase was assumed bound to the solid. The sorbed contaminant mass was

divided by the mass of dry solid sorptive media ($M_{solidMedia}$) to give the contaminant weight fraction of the solid media (W_{solid}) (eqn. 6). The observed partitioning coefficient was computed by the quotient of w_{solid} and Ce (eqn. 7). Filtration of the water samples was not conducted because the sorbent settled rapidly in the equilibration vessels

$$M_{total} = C_{spike} \times V_{spike} + C_{sw} \times V_{aq} \qquad \textbf{(eqn. 3)}$$

$$CO = M_{total} / V_{aq} \qquad \textbf{(eqn. 4)}$$

$$M_{aq,equil} = Ce * V_{aq} \qquad \textbf{(eqn. 5)}$$

$$w_{solid} = (M_{total} - M_{aq,equil}) / M_{solidMedia} \qquad \textbf{(eqn. 6)}$$

$$K_d = w_{solid} / Ce \qquad \textbf{(eqn. 7)}$$

Sorbent masses and contaminant spike volumes and concentrations were selected to produce equilibrium contaminant concentrations of approximately 10^{-3}, 10^{-2}, 10^{-1}, 1, and 10 mg/L. The concentrations in the undiluted spike solution are reported in Table 4.

Table 4: Analyte concentrations in spike solution

Compound	Spike Concentrations (mg/L)
benzene	1001
toluene	10000
ethylbenzene	30001
p-xylene	29910
chlorobenzene	30075
1,2-DCB	29955
naphthalene	29940
m-Xylene	30030
o-Xylene	29970
1,3-DCB	29955
1,4-DCB	30034

Results

A summary of computed partition coefficients is presented in Table 5, isotherm data and calculations are presented in Appendix B. Sorption isotherms were linear with linear regression coefficients generally in excess of 0.9. This was observed for both formulations of organoclay (i.e. PM-199 and XB-1) as well as peat. Standard errors for peat samples were large presumably due to sample heterogeneity. The two organoclay formulations performed comparably. There were also minimal differences between the sorption characteristics from SMU 1 and SMU 6/7 porewater with organoclay PM-199. This suggests that partitioning of the contaminants of concern was minimally influenced by the high dissolved organic matter concentrations in the SMU 1 water, owing to the relatively low hydrophobicity of the contaminants Sorption to Organoclay XB-1, was different between SMU 1 and SMU 7 but showed sorption equivalent to or less than PM-199.

Table 5: Results of linear regression from isotherm data

SMU1	PM-199 Linear Isotherm			XB1 Linear Isotherm			Peat Linear Isotherm		
COI	K_d	Std Error	R^2	K_d	Std Error	R^2	K_d	Std Error	R^2
Bz	64.9	9.7	0.919	50.1	2.4	0.984	16.1	5.7	0.572
Tol	161.1	4.4	0.997	127.1	3.3	0.995	23.6	9.2	0.523
EtBz	290.2	5.8	0.998	278.6	8.3	0.993	23.7	6.6	0.683
Xyl[q]	394.2	14.1	0.995	355.5	10.6	0.994	27.7	6.7	0.742
ClBz	447.0	21.4	0.991	447.4	14.3	0.993	28.2	6.0	0.787
12DCB	2412.3	96.2	0.994	3228.2	121.2	0.990	47.9	6.5	0.902
Naph	4140.7	150.9	0.995	3041.5	365.2	. 0.908	59.2	8.2	0.897
13DCB	777.4	10.2	0.999	1084.3	22.8	0.997	42.1	5.9	0.894
14DCB	218.1	4.9	0.998	384.6	13.5	0.992	36.1	6.2	0.869

Table 5: Results of linear regression from isotherm data (Cont.)

SMU 6/7	PM-199 Linear Isotherm			XB1 Linear Isotherm			Peat Linear Isotherm		
COI	K_d	Std Error	R^2	K_d	Std Error	R^2	K_d	Std Error	R^2
Bz	59.3	4.8	0.974	26.2	7.3	0.649	11.9	2.4	0.865
Tol	166.6	20.0	0.945	71.2	6.6	0.942	17.7	1.6	0.969
EtBz	231.3	31.6	0.930	110.4	9.2	0.954	20.0	0.5	0.997
Xyl[a]	332.6	4.8	0.999	178.5	5.6	0.993	20.9	0.4	0.999
ClBz	357.5	31.4	0.970	273.9	5.0	0.998	25.8	1.6	0.984
12DCB	1611.3	120.0	0.978	1404.4	9.4	1.000	69.9	3.4	0.991
Naph[b]	1949.9	108.5	0.988	454.3	299.1	0.248	61.2	5.5	0.968
13DCB	576.6	55.6	0.964	356.6	13.8	0.990	69.2	4.4	0.984
14DCB	212.8	31.6	0.919	92.0	14.2	0.857	71.4	4.5	0.984

[a] Total xylenes measured by DHL – isomers were not detected individually

[b] In many organoclay samples sorption of naphthalene was so high that it was undetected in the aqueous phase. The values reported for PM-199 and XB1 were computed by assuming that the aqueos phase concentration was equal to the reporting limit for naphthalene.

Initial assumptions of the sorption capacity of the organoclays and peat were tested by computing the ratio of K_d and K_{oc} for each compound with the organoclays and peat (Table 6). The ratios are near unity for the organoclays and around 0.05 for peat. These ratios are consistent with the fact that the organoclays can absorb significantly more than expected from their organic carbon content (~35%) while peat sorption is in approximate proportion to a fraction of its organic carbon content (~30% organic carbon, 70% organic matter). This difference is due to the synthetic nature of the organic sorbent matter in organoclay and the natural organic matter source of organic matter in the peat.

Table 6: Ratio of observed partition coefficient (K$_d$) to organic-carbon based partition coefficient (K$_{oc}$) (Table3).

Compound	SMU1			SMU6/7		
	PM-199	XB-1	Peat	PM-199	XB-1	Peat
Bz	0.94	0.89	0.19	0.92	0.74	0.56
Tol	0.89	0.85	0.55	0.90	1.35	0.50
EtBz	0.81	0.80	0.45	0.78	0.67	0.43
Xyl	1.05	1.03	0.58	1.02	0.91	0.53
ClBz	1.05	1.05	0.57	1.01	0.97	0.56
12DCB	1.05	1.09	0.52	0.99	0.97	0.57
Naph	1.22	1.17	0.59	NA	NA	0.60
13DCB	1.17	1.22	0.65	1.11	1.03	0.74
14DCB	0.94	1.04	0.63	0.94	0.79	0.75

Porewaters with greater aromaticity may exhibit greater fouling of activated carbon and organoclay sorbents (Sharma, 2008). The aromatic content of the site waters was determined by specific ultraviolet absorbance (SUVA, EPA Method 415.3). Absorbance of the standard, potassium hydrogen phthalate (KHP), was maximal at 275 nm rather than the 254 nm detailed in the EPA method, but literature suggests that absorbance at this wavelength is appropriate for measuring phenolic content (Traina et al., 1990). DOC in SMU1 and SMU6/7 porewaters was calculated to have 5.1% and 11.6% aromatic content, respectively. The procedure is described in Appendix C. This was found to have limited impact on the organoclay as a sorbent for the compounds of interest.

1.2 Mercury (Hg^{2+}) Sorption

Experimental Procedure

CETCO MR-2, CETCO MR-4, CETCO PM-199, peat, sand, and activated carbon were chosen as sorbents in mercury isotherm experiments. The MR-2 and MR-4 formulations of organoclay are designed specially to absorb mercury from water while the PM-199 was selected as typical of a sorbent that might be used to absorb organic contaminants of interest. Peat and sand were employed as per the organic contaminant isotherm experiments. Filtrasorb F-400 was included to evaluate mercury sorption of activated carbon. To prevent any artifacts from heterogeneity of sorbents, peats and sand were homogenized by using 2 mm and 425 um sieve, respectively.

The other sorbents were not sieved because the particle size distributions were relatively homogeneous.

Sparged site water from SMUs 1 and 6/7 were received from TestAmerica as described in the Work Plan and stored at 4°C. Midway through the experiment it was determined that the analytical method employed for mercury on the isotherm samples from SMU 6/7 was not appropriate for the concentrations levels observed. Initially mercury was being analyzed at Test America by low level method 1631, this was modified to method 7471 and analysis was conducted at the University of Texas as described below. This modification did result in the loss of SMU 6/7 porewater volume. As such artificial porewater was generated by dissolving salts ($CaCl_2$, $MgCl_2$, $NaCl$, Na_2SO_4, KCl, $(Na)_2CO_3$, $NaHCO_3$) to target the similar pH and concentrations of ions(calcium, potassium, magnesium, sodium, sulfate and chloride) as measured in the SMU 6/7 porewater (See Table 7). Dissolved organic carbon was not recreated in the artificial porewater since the concentration was only 10% of the DOC actually employed in the SMU 1 tests.

Table 7 – SMU 1 and SMU 6/7 porewater characteristics (as measured by Test America)

	SMU1		SMU6/7	
	sparged	unsparged	sparged	unsparged
total alkalinity (mg/L)	2760	2730	1860	1950
DOC (mg/L)	795	761	69	69
TOC (mg/L)	776	755	76.9	73.7
chloride (mg/L)	2060	2060	2360	2080
nitrate as N (mg/L)	0	0.24	10.6	0
potential (mV)	-81	-94	77	53
pH	12	12	7.5	7.5
phosphate as P (mg/L)	0	0	0	0
sulfate (mg/L)	276	279	16.2	18.6
TDS (mg/L)	8430	8460	3580	5580
Calcium (ug/L)	2100000	681000	212000	433000
Iron (ug/L)	22500	0	0	1210
Potassium (ug/L)	285000	392000	18200	36600
magnesium (ug/L)	117000	11.4	135000	159000
manganese (ug/L)	1760	0	116	887
sodium (ug/L)	1590000	1870000	925000	1090000

The site porewater has high concentration of dissolved organic carbon ($DOC_{SMU1} \approx 761$ mg/L, $DOC_{SUM6/7} \approx 69$ mg/L) and most of the water borne mercury (particularly in SMU 1) is expected to be associated with DOC. In light of this, glass bottles were used to prevent mercury losses due to adsorption of DOC to the bottle material.

All glassware was cleaned by soaking in a detergent (Alconox®), rinsing with distilled water, soaking again 1 M HNO_3 and rinsed with ultra high purity water. Glassware was then dried sequentially at room temperature and at 90°C in an oven. Preliminary experiments ensured that this cleaning process removed any residual mercury in the bottles to less than 2 ~ 5 ng/L.

The isotherm experiments were conducted with 100 mg sorbent in 50 mL of porewater which yields 2 g/L suspension concentrations. Mercury stock solution (1000 ppm) was made by dissolving mercury nitrate in 1M HNO_3 and further diluted to 1 and 100 mg/L in 0.1M HNO_3 for spiking. The mercury stock for SMU 1 and the SMU 6/7 porewater was added volumetrically to each 50 mL glass tube. Equal volumes of 0.1 M NaOH were added to neutralize acid added by the mercury stock.

Post-equilibration concentrations in isotherm vials with SMU 6/7 porewater were initially in the 100-5,000 µg/L range, well above the actual concentration range for mercury in SMU 6/7 porewaters. The high concentrations resulted in relatively low effective partition coefficients, likely associated with nonlinear sorption at these high concentrations. Experiments were repeated using SMU 6/7 artificial porewaters (eliminating residual Hg which was present in the actual sediment pore water) and allowed for complete experimental control of the amount of Hg in each vial. Spiking vials with amounts of Hg lower than those in the experiment with actual porewater (see column titled "Spiked Concentration" in Appendix D) yielded more realistic post-equilibration concentrations (with the exception of sand) in the 0.001-100 µg/L range were obtained. Results for organoclay and peat in SMU 6/7 were generated using the artificial porewater and are discussed below and in Table 8. The post-equilibrium concentrations for sand were 0.59-1,800 ug/L in the APW and 3.6-217 in the actual porewater. To best capture the lower end of the concentrations range the APW and actual porewater results were used for sand in SMU 6/7, results are summarized below and in Figure 1. Post-equilibration concentrations in SMU 1 porewaters were in the 3-300 µg/L range. The mercury and sorbent were mixed in an end-over-end tumbler for one day at 12°C. A preliminary kinetics experiment showed that sorption equilibrium was reached within one day. After equilibration, particles were allowed to settle for one hour before filtering the overlying water through a 0.5 um glass fiber to remove any residual particles.

Analysis

The high concentrations in the SMU 1 and in the initial SMU 6/7 samples led to inconsistent concentrations measured by Test America by EPA Method 1631E for dissolved low level Hg. The low level mercury method required several thousand fold dilution of samples (up to a dilution by a factor of 10000) and the resulting estimated concentrations were in error by as much as a factor of 100 based upon simultaneous measurements by both TestAmerica and the University of Texas using a high concentration method (EPA 7470) more appropriate for those concentrations. The several thousand fold dilution required for analysis of the samples at

TestAmerica apparently led to the introduction of substantial error compared with results obtained at the University of Texas using much smaller sample dilution factors. Results from TestAmerica were consistent with low level contamination of the diluted samples that when multiplied by the large dilution factor to estimate actual concentration gave unrealistically high estimated sample concentrations. These results are not included in the isotherm results discussed below, but, for completeness, data are included in Appendix D and labeled "from TestAmerica".

All subsequent analyses were performed at the University of Texas. Concentrations above approximately 1 µg/L were analyzed by cold vapor atomic absorption (AA), (EPA Method 7470A) as modified by AA manufacturer (Perkin Elmer)'s recommendation which included use of sodium borate rather than stannous sulfate to reduce the sample immediately prior to analysis. Required dilutions for analysis within the linear range of the AA instrument were no higher than a factor of 10 in most samples. For SMU 1 samples, processing with excess $KMnO_4$ oxidant to digest dissolved organic matter was compared to samples processed with no $KMnO_4$. A small but not significant effect of oxidant was noted providing confidence that sufficient oxidant was added. Low concentration (< 0.1 µg/L mercury) samples from SMU 6/7 porewater were analyzed at University of Texas by Method 1631, a low level mercury method involving oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS).

Results

The measured linear sediment-water partition coefficient for SMU 1 and 6/7 is shown in Table 8. The partition coefficient is shown in log units ± a standard deviation. The standard deviation gives an indication of uncertainty in the partition coefficient and indirectly indicates the appropriateness of the assumption of a linear isotherm (constant partition coefficient). Results from individual measurements are shown in the Appendix D.

Table 8 –Average Mercury (Hg²⁺) sorbent water partition coefficient, L/kg (logarithmic units) ± log standard deviation . SMU specific partition coefficients are shown in bold. The range of concentrations shown below the partition coefficient represent the range of the measured post-equilibration concentrations Standard deviations give an indication of variation in the data and since most averages were based upon 4 data points, this also represents the approximate estimated standard error of the mean.

Type of sorbent	SMU1		SMUs 6/7	
	Actual Porewater		Artificial Porewater	
	Log Kd ± STDEV	Equilibrium Concentration Range, µg/L	Log Kd ± STDEV	Equilibrium Concentration Range, µg/L
Sand	**2.90 ± 0.28**	22.9 – 314	See below	See below
Organoclay PM-199	**2.99 ± 0.28**	17.2 – 291	**4.01 ± 0.22**	0.005 - 130
Organoclay MR-2	**4.54 ± 0.47**	3.0 – 5.5	**4.21 ± 0.64**	0.009 - 148
Peat	**4.09 ± 0.62**	7.6 - 131	**4.01 ± 0.69**	0.006 - 475
Activated carbon	**3.73 ± 0.32**	7.3 - 125	**4.69 ± 0.84**	3.3 - 265

Isotherms for sand were generated using both the APW and the actual porewater. In doing so additional data points at the low end of the concentration range were incorporated into parameter development. Given the limited sorption capacity of sand compared to the other amendments evaluated a Freundlich isotherm was generated for the data which allows a better estimate of the Kd at the lower concentrations observed in porewater in SMU 6 and 7, see Figure 1.

Figure 1 – Mercury Isotherm for Sand

Figure 1 – Mercury Isotherm for Sand
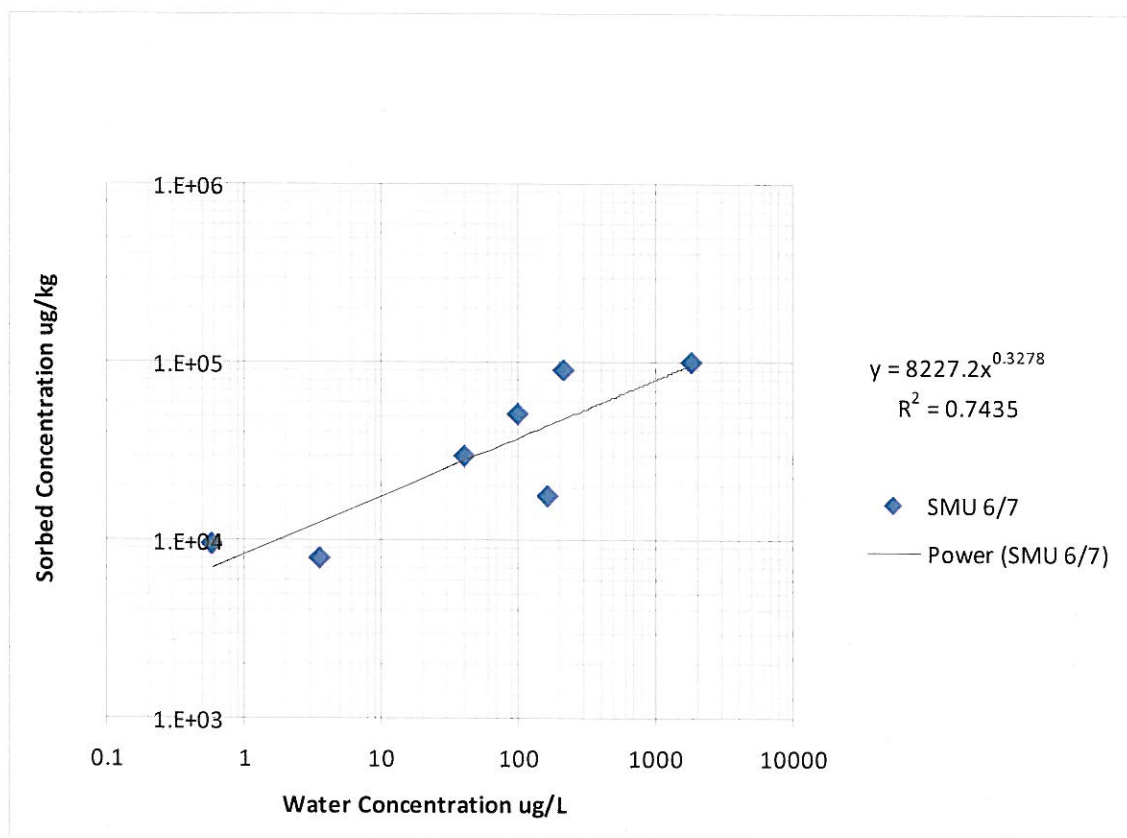
Discussion

Sorption onto the sand was weakest with an effective sand-water partition coefficient in SMU 1 of 794 L/kg (=$10^{2.9}$) and SMU 6/7 of 8227 L/kg at 1 ug/L. Due to the comparatively low sorption onto sand, the post-equilibrium water concentrations were all > 22 µg/L in SMU 1 porewaters and >0.59 µg/L in SMU 6/7 porewaters. At higher concentrations, the comparatively small number of sites for sorption onto sand are expected to be nearly saturated and nonlinear sorption isotherms would be expected to result. Reflecting this behavior, the sorption onto the sand from SMU 6/7 porewaters is far greater at 0.59 µg/L than at the higher concentrations (K_d=$10^{4.2}$(=15,800 L/kg). Thus use of the Kd at 1 ug/L is expected to be conservative estimate of sorption onto sands in SMU 6/7 outside of the ILDW where the dissolved mercury concentrations are generally low, the maximum mercury concentration from the PDI is 1.5 ug/L with an average concentration 0.13 ug/L.

Sorption of mercury onto organoclay, peat and activated carbon all showed mercury partition coefficients generally in excess of 10,000.   Lower sorption of mercury onto activated carbon and organoclay PM-199 in SMU 1 as compared with SMUs 6/7 outside the ILDW is likely

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associated with the high dissolved organic matter load in those waters as well as the relatively high concentrations of mercury evaluated in the SMU 1 porewaters. The sorption of mercury onto these materials is likely associated with the sorption of the organic matter to which it is complexed. The somewhat greater sorption of mercury onto the MR-2 organoclay in SMU 1 waters compared to SMU 6/7 may be the result of direct mercury sorption as well as organic sorption in this formulation.

2.0 Deviations from Work Plan

Cetco organoclays PM-199 and XB-1 were tested, not PM-200. PM-200 uses an identical chemical formulation as PM-199 although the particle size is larger. Thus equilibrium sorption is expected to be identical.

The organic contaminant spike solution was the same standard used for the activated carbon isotherms not the concentrations described in Table 8 of the Work Plan. Mercury analyses were conducted at the University of Texas as opposed to at TestAmeria as discussed in Analysis Section above.

Preliminary testing with organic free water was not conducted. Similar K_d values were computed with SMU1 and SMU7 porewaters which had DOC concentrations of 760 and 70 mg/L, respectively. This result suggested that sorbent fouling by organic carbon was not a concern for organoclay and peat and testing with organic free water was not pursued.

3.0 Future Work

No additional isotherm work is recommended. Column Studies are currently underway on sediments mercury specific columns from SMU 1, 4, and 7. The results from the isotherm studies will be compared to the column studies results to develop a final recommended partitioning coefficient for mercury.

4.0 Conclusions

A review of the measured sorption isotherms shows that organoclays adsorb organic contaminants with a $K_d \sim K_{oc}$ with very little difference between the PM-199 (or PM-200) and XB-1. Peat was somewhat less sorbing with an average $K_d \sim 55\%$ of the K_{oc}. Sorption isotherms for both sorbents were effectively linear over the concentration range studied although some variability was noted with peat, presumably due to sample heterogeneity. Mercury sorption to sand was best described by a Freundlich isotherm

Mercury was effectively sorbed by all cap materials but especially by organoclays, peat, or activated carbon.

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5.0 References

EPA Method 415.3. Determination of total organic carbon and specific UV absorbance at 254 nm in source and drinking water. Revision 1.1, February, 2005.

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Reible, D.D. Fundamentals of Environmental Engineering. Lewis Publishers. 1999

Sharma, B., Evaluation Of Reactive Cap Sorbents For In-Situ Remediation Of Contaminated Sediments, Ph D Dissertation, University of New Hampshire (2008)

Standard Method 5910B: Ultraviolet Absorption Method. In *Standard Methods for the Examination of Water and Wastewater*, Eaton, AD, Clesceri LS, Greenberg AE, Eds.; American Public Health Association, DC, 1995, 10th ed.

Traina S.J., Novak J, Smeck NE (1990). An Ultraviolet Absorbance Method of Estimating the Percent Aromatic Carbon Content of Humic Acids. J. Environ. Qual. 19:151-153.

Appendix A: Loss on Ignition for Determination of Water and Organic Carbon Content of Peat

The moisture content of the peat was determined by measuring the mass lost from three peat samples after drying in a 105 °C oven for five days. The volatile fraction was determined by measuring the loss on ignition for the dry samples after ignition in a

550 °C oven for six hours. The volatile fraction is assumed to be organic matter of the formula CH_2O (MW = 30 g/mol). The carbon fraction of organic matter was computed by the product of the volatile fraction with the ratio of molecular weights of C and CH_2O (i.e. 12/30 = 0.4). Results are reported in Table A1.

Table A1. Moisture content and volatile fraction of peat

Sample	Peat (g)	Dry peat (g)	Fixed solids (g)	Moisture Content	Volatile Fraction	f_{oc}
1	8.8412	3.1002	0.6552	64.9%	0.789	0.316
2	10.1024	3.5294	0.7744	65.1%	0.781	0.312
3	10.1254	3.5354	0.8044	65.1%	0.772	0.309
Average	-	-	-	65.0%	0.781	0.312

Appendix B: Isotherm Data and Calculations

Aqueous Phase Concentrations were reported by DHL-Austin. COI weight fraction on the sorbent (w, mg/kg) was computed as described in equations 3-7. Contaminant concentrations at T=0 were determined by averaging the spike controls for the same dilution factor and spike volume (e.g., The average of spike controls receiving 0.1 mL of a 1/100 dilution was 1.09 mg/L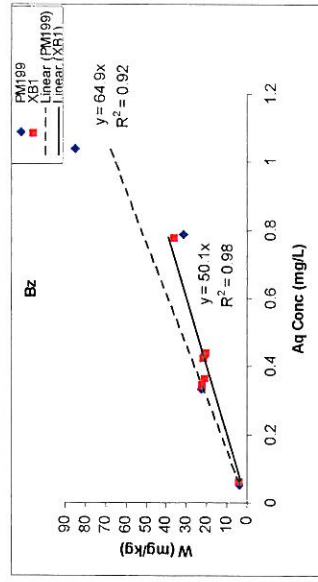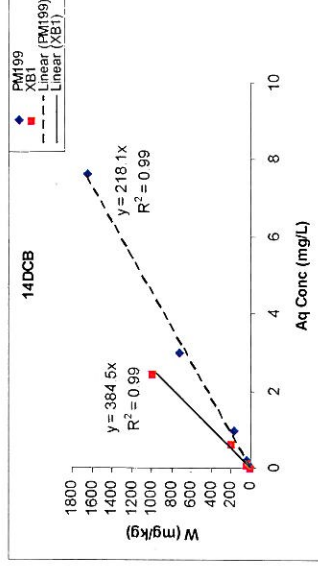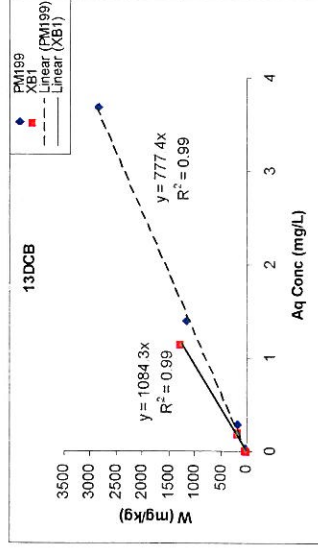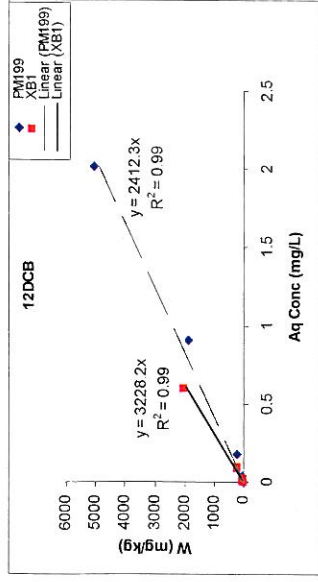 of 1,2-DCB, so the starting 1,2-DCB concentration in vials with organoclays receiving 0.1 mL of a 1/100 dilution is assumed to be 1.09 mg/L).

SMU 1, Organoclays PM-199 and XB-1

Type	Name	Date	OC	MassOC	Spike Soln Diln (1/x)	SpikeVol (mL)	Days Tumbled	12DCB C (mg/L)	12DCB w (mg/kg)	13DCB C (mg/L)	13DCB w (mg/kg)	14DCB C (mg/L)	14DCB w (mg/kg)	Bz C (mg/L)	Bz w (mg/kg)	MCB C (mg/L)	MCB w (mg/kg)	EtBz C (mg/L)	EtBz w (mg/kg)	Naph C (mg/L)	Naph w (mg/kg)	Xyl C (mg/L)	Xyl w (mg/kg)	Tol C (mg/L)	Tol w (mg/kg)
Sample	SMU1V1	7/14/2008	PM-199	10000	100	0.1	7	0.00368	5.4316	0.00316	2.0217	0.0217	4.9415	0.0518	3.661	0.0312	10.194	0.00998	2.6326	ND	NA	0.0374	12.663	0.0206	3.052
Sample	SMU1V2	7/14/2008	PM-199	1000	100	0.1	7	0.0391	52.545	0.0309	18.83	0.204	40.3	0.335	22.45	0.291	88.95	0.0912	22.265	0.0972	188.39	0.374	109.8	0.168	23.15
Sample	SMU1V3	7/14/2008	PM-199	100	100	1	7	0.18	222	0.292	169.65	0.965	173.25	0.428	21.125	0.934	255.8	0.822	180.65	0.181	369.95	2.25	602.5	0.609	73.3
Sample	SMU1V4	7/14/2008	PM-199	100	100	1	7	0.906	1867	1.4	1142.5	2.99	720	0.788	31.25	3.5	1275	2.87	782.5	0.888	3346	8.48	2910	1.6	237.5
Sample	SMU1V1	10/1/2008	PM-199	100	20	1	7	2.02	5040	3.68	2845	7.62	1640	1.04	85	7.76	3620	6.48	1910	1.73	7385	18.3	7450	3.61	595
Sample	SMU1V5	7/14/2008	XB-1	1000	100	0.1	2	0.024	53.3	0.0205	19.35	0.13	44	0.349	21.75	0.23	92	0.087	22.475	0.105	188	0.347	111.15	0.173	22.9
Sample	SMU1V6	7/14/2008	XB-1	1000	100	1	2	0.11	225.5	0.203	174.1	0.618	190.6	0.438	20.625	0.749	265.05	0.785	182.5	0.189	369.55	2.08	611	0.634	72.05
Sample	SMU1V7	7/14/2008	XB-1	1000	100	0.1	4	0.0287	53.065	0.0196	19.395	0.138	43.6	0.366	20.9	0.252	90.9	0.0868	22.485	0.1	188.25	0.351	110.95	0.18	22.55
Sample	SMU1V6	7/14/2008	XB-1	1000	100	1	4	0.0994	226.03	0.191	174.7	0.62	190.5	0.427	21.175	0.727	266.15	0.766	183.45	0.165	370.75	2.02	614	0.613	73.1
Sample	SMU1V9	7/14/2008	XB-1	10000	100	0.1	7	0.0098	5.401	ND	NA	ND	NA	0.0948	3.596	0.0338	10.181	0.0096	2.6345	0.299	17.83	0.033	12.685	0.0257	3.0265
Sample	SMU1V10	7/14/2008	XB-1	1000	100	0.1	7	0.019	53.55	0.016	19.575	0.113	44.85	0.345	21.95	0.21	93	0.0772	22.965	ND	NA	0.291	113.95	0.164	23.35
Sample	SMU1V11	7/14/2008	XB-1	1000	100	1	7	0.0992	226.04	0.198	174.35	0.637	189.65	0.444	20.325	0.752	264.9	0.797	181.9	0.161	370.95	2.16	607	0.647	71.4
Sample	SMU1V12	10/1/2008	XB-1	100	100	1	7	0.604	2008	1.15	1267.5	2.46	965	0.779	35.75	3.14	1455	2.81	812.5	0.951	3309.5	8.24	3030	1.64	217.5
SpikeControl	SMU1V13	7/14/2008	none	0	100	0.1	2	1.08	NA	0.407	NA	1.01	NA	0.783	NA	2.06	NA	0.536	NA	3.67	NA	2.57	NA	0.624	NA
SpikeControl	SMU1V14	7/14/2008	none	0	100	1	7	4.42	NA	3.5	NA	4.23	NA	0.807	NA	5.74	NA	4.15	NA	7.44	NA	13.5	NA	1.94	NA
SpikeControl	SMU1V15	7/14/2008	none	0	100	0.1	2	1.1	NA	0.408	NA	1.01	NA	0.785	NA	2.08	NA	0.537	NA	4.06	NA	2.57	NA	0.638	NA
SpikeControl	SMU1V16	7/14/2008	none	0	100	1	2	4.82	NA	3.87	NA	4.63	NA	0.894	NA	6.35	NA	4.72	NA	7.72	NA	15.1	NA	2.21	NA
SpikeControl	SMU1V15	10/1/2008	None	0	400	0.1	7	0.710	NA	0.107	NA	0.671	NA	0.804	NA	1.65	NA	0.148	NA	3.25	NA	1.38	NA	0.504	NA
SpikeControl	SMU1V16	10/1/2008	None	0	400	1	7	1.73	NA	1.01	NA	1.64	NA	0.818	NA	2.46	NA	0.909	NA	4.46	NA	3.71	NA	0.751	NA
SpikeControl	SMU1V17	10/1/2008	None	0	20	1	7	12.1	NA	9.37	NA	10.9	NA	1.21	NA	15.0	NA	10.3	NA	16.5	NA	33.2	NA	4.60	NA
Blank(TA)	SMU1BL1	6/27/2008	none	0	0	0	0	0.550	NA	ND	NA	0.490	NA	0.500	NA	1.200	NA	0.065	NA	2.700	NA	0.840	NA	0.290	NA
Blank	SMU1BL2	7/14/2008	none	0	0	0	0	0.658	NA	ND	NA	0.576	NA	0.572	NA	1.4	NA	0.0494	NA	2.97	NA	0.911	NA	0.342	NA
Blank	SMU1V17	10/12/2008	none	0	0	0	0	0.548	NA	ND	NA	0.486	NA	0.499	NA	1.21	NA	0.041	NA	3.84	NA	0.753	NA	0.298	NA
Blank	SMU1V18	10/12/2008	none	0	0	0	0	0.658	NA	0.0427	NA	0.637	NA	0.714	NA	1.53	NA	0.0678	NA	3.32	NA	1.09	NA	0.430	NA
Blank	SMU1V19	10/12/2008	none	0	0	0	0	0.610	NA	ND	NA	0.594	NA	0.699	NA	1.47	NA	0.0598	NA	6.35	NA	1.04	NA	0.425	NA
BlankControl	SMU1V17	7/14/2008	none	0		0	7	0.608	NA	ND	NA	0.554	NA	0.712	NA	1.49	NA	0.0594	NA	3.01	NA	1.05	NA	0.413	NA
BlankControl	SMU1V18	7/14/2008	none	0		0	7	0.599	NA	ND	NA	0.548	NA	0.714	NA	1.5	NA	0.0602	NA	3.92	NA	1.05	NA	0.424	NA
MediaControl	SMU1V2	10/1/2008	PM-199	100	0	0	7	0.140	NA	0.0138	NA	0.414	NA	0.714	NA	0.934	NA	0.0448	NA	0.534	NA	0.662	NA	0.371	NA

SMU 1, Organoclays PM-199 and XB-1

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SMU 6/7, Organoclays PM-199 and XB-1

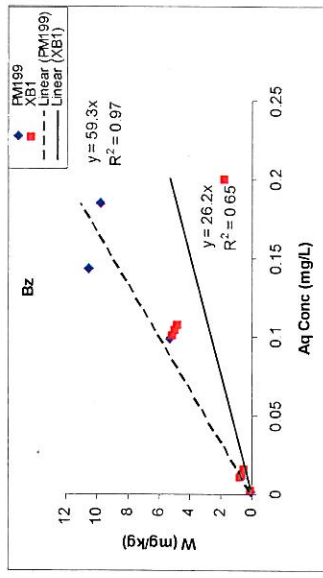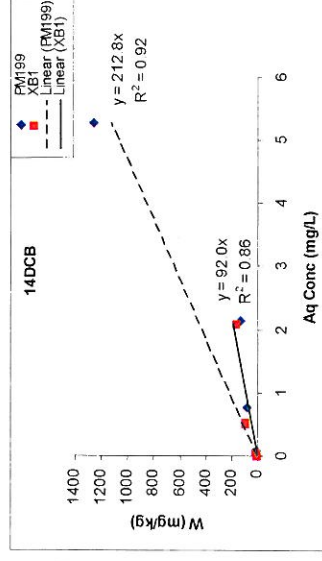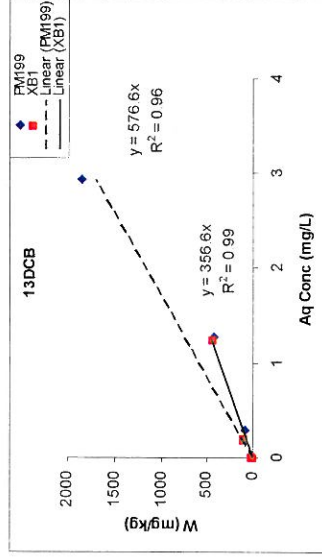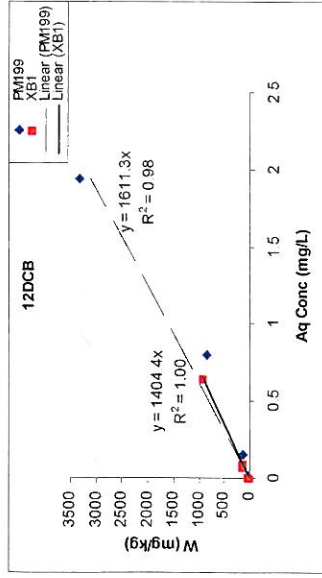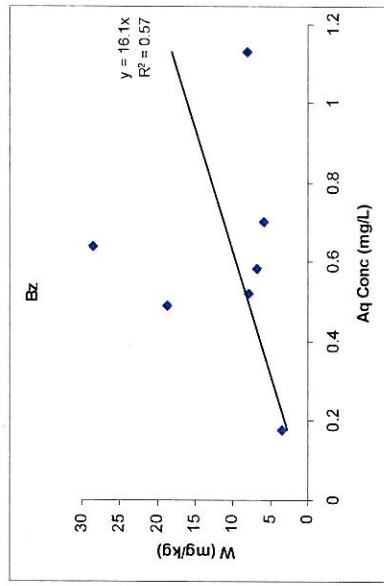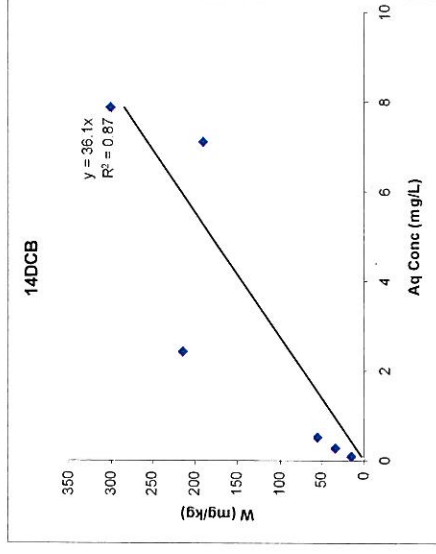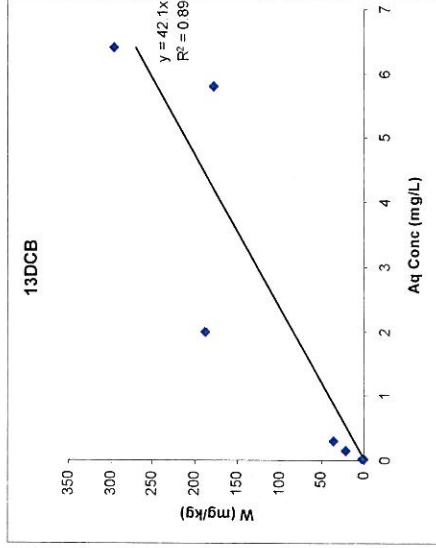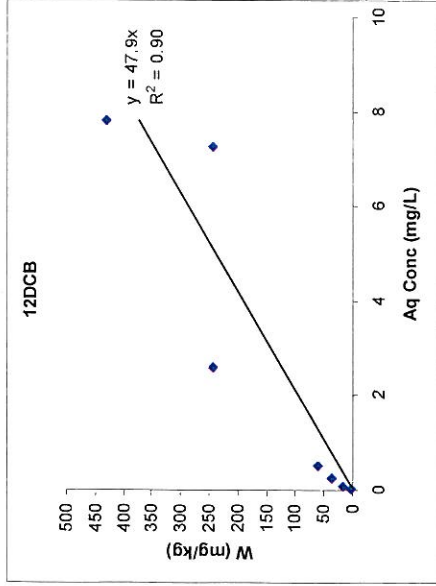| Type	Name	Date	OC	MassOC (mg)	Spike Soln Diln (1/x)	SpikeVol (mL)	Days Tumbled	12DCB C (mg/L)	12DCB w(mg/kg)	13DCB C (mg/L)	13DCB w(mg/kg)	14DCB C (mg/L)	14DCB w(mg/kg)	Bz C (mg/L)	Bz w(mg/kg)	MCB C (mg/L)	MCB w(mg/kg)	EtBz C (mg/L)	EtBz w(mg/kg)	Naph C (mg/L)	Naph w(mg/kg)	Xyl C (mg/L)	Xyl w(mg/kg)	Tol C (mg/L)	Tol w(mg/kg)
Sample	SMU6V19	7/14/08	PM-199	10000	100	0.1	7	0.00156	1.5997	0.00276	1.4112	0.00996	1.6752	0.00188	0.1226	0.0081	2.597	0.00768	1.7116	ND	NA	0.0165	2.15	0.00488	0.6106
Sample	SMU6V20	7/14/08	PM-199	1000	100	0.1	7	0.0162	15.265	0.0307	12.715	0.0832	13.09	0.0138	0.63	0.0807	22.34	0.0768	13.66	ND	NA	0.128	15.925	0.0461	4.045
Sample	SMU6V21	7/14/08	PM-199	1000	100	1	7	0.152	115.9	0.293	90.35	0.777	81.4	0.0992	5.265	0.738	172.35	0.797	122.9	ND	NA	1.44	407.25	0.516	60.95
Sample	SMU6V22	7/14/08	PM-199	100	100	1	7	0.797	836.5	1.27	415	2.14	132.5	0.185	9.75	2.72	732.5	2.51	372.5	0.155	632.5	5.83	1877.5	1.37	182.5
Sample	SMU6Y1	10/24/08	PM-199	100	100	0.1	7	1.94	3320	2.94	1840	5.27	1265	0.143	10.5	4.08	1635	3.43	960	1.63	3155	9.61	3245	1.3	275
Sample	SMU6V23	7/14/08	XB-1	1000	100	0.1	2	0.00996	15.582	0.0205	13.225	0.0544	14.53	0.0169	0.475	0.0922	23.265	0.0735	13.825	ND	NA	0.107	16.975	0.0504	3.63
Sample	SMU6V24	7/14/08	XB-1	1000	100	1	2	0.0908	118.96	0.204	94.8	0.547	92.9	0.108	4.825	0.609	178.8	0.798	122.85	ND	NA	1.91	383.75	0.608	56.35
Sample	SMU6V25	7/14/08	XB-1	1000	100	0.1	4	0.0086	15.645	0.0188	13.31	0.059	14.3	0.0126	0.69	0.0594	23.405	0.0699	14.005	ND	NA	0.148	14.925	0.0398	4.36
Sample	SMU6V26	7/14/08	XB-1	1000	100	1	4	0.0814	119.43	0.196	95.2	0.536	93.45	0.105	4.975	0.588	179.65	0.78	123.75	ND	NA	1.83	387.75	0.582	57.65
Sample	SMU6V27	7/14/08	XB-1	10000	100	0.1	7	ND	NA	0.0022	1.414	0.00215	1.71425	0.0034	0.115	0.0072	2.6015	0.00845	1.70775	ND	NA	0.0195	2.135	0.00815	0.59425
Sample	SMU6V28	7/14/08	XB-1	1000	100	0.1	7	0.00755	15.6975	0.0183	13.335	0.06	14.25	0.012	0.72	0.0578	23.485	0.0693	14.035	ND	0	0.144	15.125	0.039	4.4
Sample	SMU6V29	7/14/08	XB-1	1000	100	1	7	0.077	119.65	0.189	95.55	0.519	94.3	0.102	5.125	0.567	180.9	0.762	124.65	ND	NA	1.77	390.75	0.571	58.2
Sample	SMU6V30	7/14/08	XB-1	100	100	1	7	0.649	910.5	1.24	430	2.09	157.5	0.201	1.75	2.72	732.5	2.72	267.5	0.281	579.5	7.13	1227.5	1.55	92.5
SpikeControl	SMU6V31	7/14/08	none	0	100	0.1	2	0.344	NA	0.307	NA	0.356	NA	0.0218	NA	0.497	NA	0.348	NA	ND	NA	0.457	NA	0.108	NA
SpikeControl	SMU6V32	7/14/08	none	0	100	1	2	2.51	NA	2.14	NA	2.43	NA	0.198	NA	4.08	NA	3.19	NA	1.44	NA	9.42	NA	1.67	NA
SpikeControl	SMU6V33	7/14/08	none	0	100	0.1	7	0.299	NA	0.263	NA	0.334	NA	0.031	NA	0.558	NA	0.352	NA	ND	NA	0.436	NA	0.146	NA
SpikeControl	SMU6V34	7/14/08	none	0	100	1	7	2.43	NA	2.06	NA	2.38	NA	0.211	NA	4.29	NA	3.32	NA	1.4	NA	9.75	NA	1.8	NA
SpikeControl	SMU6V7	10/24/08	None	0	400	0.1	7	0.487	NA	0.397	NA	0.497	NA	0.00692	NA	0.335	NA	0.173	NA	0.0573	NA	0.382	NA	0.0537	NA
SpikeControl	SMU6V8	10/24/08	None	0	3	0.01	7	1.09	NA	0.861	NA	1.01	NA	0.0203	NA	0.837	NA	0.459	NA	0.0177	NA	1.13	NA	0.170	NA
SpikeControl	SMU6V9	10/24/08	None	0	3	0.1	7	8.58	NA	6.62	NA	7.80	NA	0.164	NA	7.35	NA	5.35	NA	7.94	NA	16.1	NA	1.85	NA
Blank(TA)	SMU6V37	6/27/08	none	0	0	0	0	0.009	NA	0.003	NA	0.022	NA	0.013	NA	0.050	NA	0.004	NA	0.120	NA	0.050	NA	0.028	NA
Blank	SMU6V38	7/14/08	none	0	0	0	0	0.00925	NA	0.0029	NA	0.0217	NA	0.015	NA	0.0618	NA	0.0035	NA	0.106	NA	0.0255	NA	0.0053	NA
Blank	SMU6Y10	10/24/08	none	0	0	0	0	0.0114	NA	ND	NA	0.0266	NA	0.00150	NA	0.0666	NA	0.004	NA	0.137	NA	0.0294	NA	0.0053	NA
Blank	SMU6Y11	10/24/08	none	0	0	0	0	0.00956	NA	0.00506	NA	0.0259	NA	0.00154	NA	0.0245	NA	0.00188	NA	0.0603	NA	0.0158	NA	<0.0012	NA
BlankControl	SMU6V35	7/14/08	none	0	0	0	7	0.00322	NA	0.0026	NA	0.0199	NA	ND	NA	ND	NA	ND	NA	ND	NA	0.0026	NA	ND	NA
BlankControl	SMU6V36	7/14/08	none	0	0	0	7	0.0038	NA	0.0029	NA	0.0246	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA

SMU 6/7, Organoclays PM-199 and XB-1
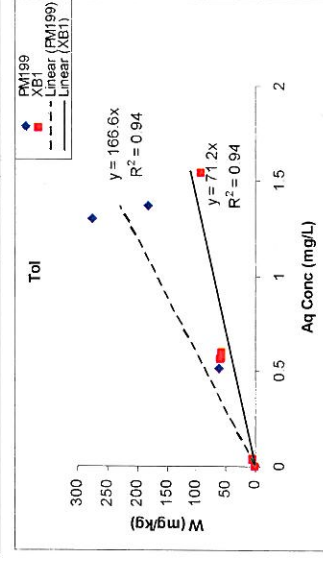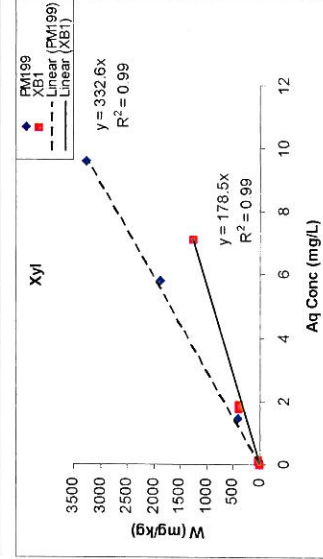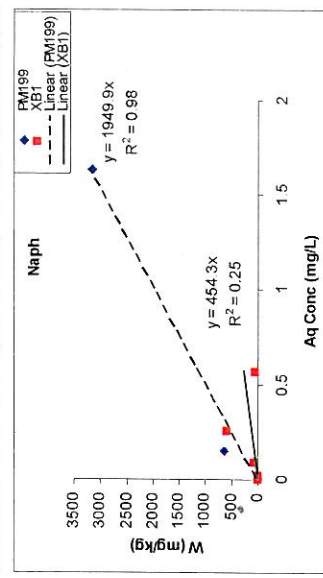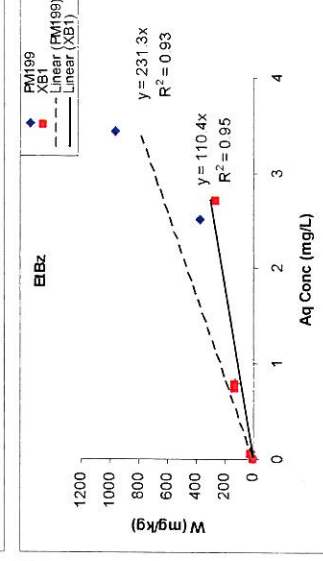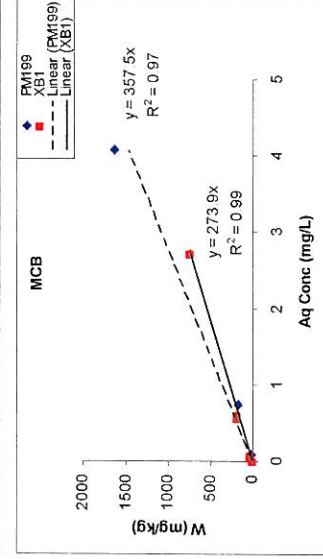
As above, initial concentrations in sample vials were computed from concentrations in spike control vials. For example, the spike control receiving 0.1 mL of a 1/400 diluted spike had 0.71 mg/L of 1,2-DCB, so sample vials receiving 0.1 mL of a 1/400 diluted spike were assumed to have a starting concentration of 0.71 mg/L of 1,2-DCB.

SMU 1, Peat

Concentrations Measured in Control Vials (ug/mL) & Initial Mass using Control Vials (ug)

SampleID	Solid	Stock Nominal DilnFactor	Mass spike (g)	Vol. spike (mL)	Aq Vol (mL)	12DCB	13DCB	14DCB	BZ	CLBZ	ETBZ	NAPH	TOL	XYL	12DCB	13DCB	14DCB	BZ	CLBZ	ETBZ	NAPH	TOL	XYL
SMU1V15	NA	400	0.0817	0.103	50	0.710	0.107	0.671	0.804	1.65	0.148	3.25	0.504	1.38	35.5	5.4	33.6	40.2	82.5	7.4	162.5	25.2	69.0
theoret	NA	400	NA	0.100	50	0.731	0.140	0.713	0.710	1.60	0.161	3.42	0.460	1.36	36.6	7.0	35.6	35.5	79.9	8.1	170.9	23.0	67.8
SMU1V16	NA	400	0.7976	1.007	50	1.73	1.01	1.64	0.818	2.46	0.909	4.46	0.751	3.71	86.5	50.5	82.0	40.9	123.0	45.5	223.0	37.6	185.5
theoret	NA	400	NA	0.010	50	1.58	0.99	1.57	0.74	2.45	1.01	4.27	0.74	3.91	79.1	49.6	78.3	36.9	122.6	50.7	213.4	37.2	195.6
SMU1V17	NA	20	0.8058	1.017	50	12.1	9.37	10.9	1.21	15.0	10.3	16.5	4.80	33.2	605.0	468.5	545.0	60.5	750.0	515.0	825.0	240.0	1660.0
theoret	NA	20	NA	0.100	50	34.95	34.36	35.03	1.85	35.96	34.44	37.62	11.88	104.07	1747.7	1718.1	1751.3	92.7	1797.8	1721.8	1861.1	594.2	5203.7
SMU1V22	NA	3	0.078	0.098	50	8.21	5.83	6.97	0.658	7.81	4.98	12	2.24	15.5	410.5	291.5	348.5	32.9	390.5	249.0	600.0	112.0	775.0
theoret	NA	3	NA	0.100	50	21.29	20.75	21.29	1.19	22.03	20.84	23.43	7.22	63.11	1064.7	1037.3	1064.5	59.6	1101.3	1042.1	1171.5	360.8	3155.3
SMU1V18	NA	NA	0	0	50	0.658	0.0427	0.637	0.714	1.53	0.0678	3.32	0.430	1.09	32.9	2.1	31.9	35.7	76.5	3.4	166.0	21.5	54.5
SMU1V19	NA	NA	0	0	50	0.610		0.594	0.699	1.47	0.0598	6.35	0.425	1.04	30.5	0.0	29.7	35.0	73.5	3.0	317.5	21.3	52.0
SMU1V23	NA	NA	0	0	50	0.755	0.0438	0.702	0.428	1.28	0.0518	3.08	0.264	0.849	37.8	2.2	35.1	21.4	64.0	2.6	154.0	13.2	42.5
theoret	NA	NA	NA	0	50	0.55		0.49	0.5	1.2	0.065	2.7	0.29	0.84	27.5	0.0	24.5	25.0	60.0	3.3	135.0	14.5	42.0

Aqueous Phase Concentrations (ug/mL) & Mass in Aqueous Phase (ug)

SampleID	solid	SolidMass Wet (mg)	DilnFactor	SpikeVol (mL)	Aq Vol (mL)	12DCB	13DCB	14DCB	BZ	CLBZ	ETBZ	NAPH	TOL	XYL	12DCB	13DCB	14DCB	BZ	CLBZ	ETBZ	NAPH	TOL	XYL
SMU1V9	Peat	20000	400	0.1	31.5	0.0242	0.0125	0.0940	0.176	0.112	0.0109	0.0398	0.0555	0.0730	0.7623	0.39375	0	5.544	3.528	0.34335	1.2537	1.74825	2.2995
SMU1V10	Peat	4000	400	0.1	47	0.0861	0.0177	0.524	0.521	0.550	0.0447	0.336	0.237	0.374	4.0467	0.8319	4.418	24.487	25.85	2.1009	15.792	11.139	17.578
SMU1V11	Peat	2000	400	1	50	0.512	0.300	0.524	0.702	1.54	0.512	1.13	0.554	2.05	25.6	15	26.2	35.1	77	25.6	56.5	27.7	102.5
SMU1V12	Peat	4000	400	1	47	0.261	0.158	0.277	0.583	1.00	0.336	0.655	0.416	1.28	12.267	7.426	13.019	27.401	47	15.792	30.785	19.552	60.16
SMU1V13	Peat	1000	20	1	50	7.80	6.41	7.89	1.13	12.7	9.13	9.73	4.35	28.4	390	320.5	394.5	56.5	635	456.5	486.5	217.5	1420
SMU1V20	Peat	4000	3	0.1	47	2.59	1.99	2.42	0.491	4.32	3.05	3.31	1.36	9.15	121.73	93.53	113.74	23.077	203.04	143.35	155.57	63.92	430.05
SMU1V21	Peat	1000	3	0.1	50	7.26	5.81	7.1	0.64	8.09	5.65	9.17	2.15	17.4	363	290.5	355	32	404.5	282.5	458.5	107.5	870

w (mg/kg) = [Mass in control - mass in aq phase of sample] / dry mass of media

SampleID	solid	SolidMass Dry (mg)	DilnFactor	SpikeVol (mL)	Aq Vol (mL)	12DCB	13DCB	14DCB	BZ	CLBZ	ETBZ	NAPH	TOL	XYL
SMU1V9	Peat	10000	400	0.1	31.5	3.47	0.50	14.57	3.47	7.90	0.71	16.12	2.35	6.67
SMU1V10	Peat	2000	400	0.1	50	15.73	2.26	55.80	7.86	28.33	2.65	73.35	7.03	25.71
SMU1V11	Peat	1000	400	1	47	60.90	35.50	34.49	5.80	46.00	19.85	166.50	9.85	83.00
SMU1V12	Peat	2000	400	1	47	37.12	21.54	301.00	6.75	38.00	14.83	96.11	9.00	62.67
SMU1V13	Peat	500	20	1	50	430.00	296.00	215.63	8.00	230.00	117.00	677.00	45.00	480.00
SMU1V20	Peat	2000	3	0.1	50	241.64	187.49	190.00	18.71	273.48	185.83	334.72	88.04	614.98
SMU1V21	Peat	1000	3	0.1	50	242.00	178.00	190.00	28.50	345.50	232.50	366.50	132.50	790.00

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SMU 1, Peat

Nine scatter plots showing W (mg/kg) versus Aq Conc (mg/L) for different compounds:

14DCB: y = 36.1x, R² = 0.87

13DCB: y = 42.1x, R² = 0.89

12DCB: y = 47.9x, R² = 0.90

EtBz: y = 23.7x, R² = 0.68

ClBz: y = 28.2x, R² = 0.79

Bz: y = 16.1x, R² = 0.57

Xyl: y = 27.7x, R² = 0.74

Tol: y = 23.6x, R² = 0.52

Naph: y = 59.2x, R² = 0.90

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SMU 6/7, Peat

Sample setup (spiked/theoretical series)

SampleID	Solid	Stock DilnFactor	Mass spike (g)	Vol. spike (mL)	Aq Vol (mL)
SMU6V7	NA	400	0.0784	0.0979	50
theoret	NA	400	NA	0.0979	50
SMU6V8	NA	3	0.0781	0.0104	50
theoret	NA	3	NA	0.0104	50
SMU6V9	NA	3	0.0775	0.1004	50
theoret	NA	3	NA	0.1004	50
nospike	NA	NA	NA	0	50
nospike	NA	NA	NA	0	50
theoret	NA	NA	NA	0	50

SampleID	12DCB	13DCB	14DCB	BZ	CLBZ	ETBZ	NAPH	TOL	XYL
SMU6V7	0.487	0.397	0.497	0.00692	0.335	0.173	0.0573	0.0537	0.382
theoret	0.2433	0.2376	0.2568	0.0208	0.2851	0.2382	0.3539	0.1281	0.7311
SMU6V8	1.09	0.861	1.01	0.0203	0.837	0.459	0.0177	0.170	1.13
theoret	2.0874	2.0816	2.1058	0.0824	2.1366	2.0851	2.1972	0.7438	6.2660
SMU6V9	8.58	6.62	7.80	0.164	7.35	5.35	7.94	1.85	16.1
theoret	20.7547	20.7490	20.8223	0.7062	20.8787	20.7811	20.8550	6.9755	62.2961
nospike	0.00956	0.00506	0.0259	0.00150	0.0245	0.00188	0.0603	<0.0012	0.0158
nospike	0.00998	0.00484	0.0283	0.00154	0.0252	0.00204	0.0594	<0.0012	0.0176
theoret	0.0091	0.0033	0.0220	0.0130	0.0500	0.0036	0.1200	0.05	0.0280

SampleID	12DCB	13DCB	14DCB	BZ	CLBZ	ETBZ	NAPH	TOL	XYL
SMU6V7	24.35	19.85	24.85	0.346	1675	8.65	2.865	2.685	19.1
theoret	12.17	11.88	12.84	1.04	14.25	11.91	17.70	6.41	36.55
SMU6V8	54.50	43.05	50.50	1.02	41.85	22.95	0.89	8.50	56.50
theoret	104.37	104.08	105.29	4.12	106.83	104.25	109.86	37.19	313.30
SMU6V9	429.00	331.00	390.00	8.20	367.50	267.50	397.00	92.50	805.00
theoret	1037.74	1037.45	1041.12	35.31	1043.93	1039.06	1042.75	348.78	3114.80
nospike	0.48	0.25	1.30	0.08	1.23	0.09	3.02		0.79
nospike	0.50	0.24	1.42	0.08	1.26	0.10	2.97		0.88
theoret	0.46	0.17	1.10	0.65	2.50	0.18	6.00	2.50	1.40

Wet mass series

SampleID	solid	SolidMass Wet (mg)	DilnFactor	SpikeVol (mL)	Aq Vol (mL)
SMU6V2	Peat	20000	400	0.1	31.5
SMU6V3	Peat	2000	400	0.1	50
SMU6V4	Peat	4000	3	0.01	47
SMU6V5	Peat	4000	3	0.1	47
SMU6V6	Peat	1000	3	0.1	50

Aqueous Phase Concentrations (ug/mL)

SampleID	12DCB	13DCB	14DCB	BZ	CLBZ	ETBZ	NAPH	TOL	XYL
SMU6V2	0.0176	0.015	0.0202	0.00335	0.0324	0.0231	0.0298	0.011	0.0388
SMU6V3	0.113	0.0896	0.11	0.00832	0.185	0.123	0.0738	0.0486	0.38
SMU6V4	0.159	0.136	0.168	0.0105	0.292	0.18	0.0472	0.0751	0.436
SMU6V5	2.62	2.13	2.46	0.134	3.36	3.16	1.69	1.24	9.13
SMU6V6	4.96	3.81	4.43	0.141	5.93	4.44	5.04	1.54	13.3

Mass in Aqueous Phase (ug)

SampleID	12DCB	13DCB	14DCB	BZ	CLBZ	ETBZ	NAPH	TOL	XYL
SMU6V2	0.5544	0.4725	0.6363	0.105525	1.0206	0.72765	0.9387	0.3465	1.2222
SMU6V3	5.65	4.48	5.5	0.416	9.25	6.15	3.69	2.43	19
SMU6V4	7.473	6.392	7.896	0.4935	13.724	8.46	2.2184	3.5297	20.492
SMU6V5	123.14	100.11	115.62	6.298	157.92	148.52	79.43	58.28	429.11
SMU6V6	248	190.5	221.5	7.05	296.5	222	252	77	665

Dry mass series

SampleID	solid	SolidMass Dry (mg)	DilnFactor	SpikeVol (mL)	Aq Vol (mL)
SMU6V2	Peat	10000	400	0.1	31.5
SMU6V3	Peat	1000	400	0.1	50
SMU6V4	Peat	2000	3	0.01	47
SMU6V5	Peat	2000	3	0.1	47
SMU6V6	Peat	500	3	0.1	50

w (mg/kg) = [Mass in control - mass in aq phase of sample] / mass dry media

SampleID	12DCB	13DCB	14DCB	BZ	CLBZ	ETBZ	NAPH	TOL	XYL
SMU6V2	2.38	1.94	2.42	0.02	1.57	0.79	0.19	0.23	1.79
SMU6V3	18.70	15.37	19.35	-0.07	7.50	2.50	-0.83	0.26	0.10
SMU6V4	23.51	18.33	21.30	0.26	14.06	7.25	-0.67	2.49	18.00
SMU6V5	152.93	115.45	137.19	0.95	104.79	59.49	158.79	17.11	187.95
SMU6V6	362.00	281.00	337.00	2.30	142.00	91.00	290.00	31.00	280.00

SMU 6/7, Peat

14DCB
y = 71.4x
R² = 0.98

13DCB
y = 69.2x
R² = 0.98

12DCB
y = 69.9x
R² = 0.99

ElBz
y = 20.0x
R² = 0.99

ClBz
y = 25.8x
R² = 0.98

Bz
y = 11.9x
R² = 0.86

Xyl
y = 20.9x
R² = 0.99

Tol
y = 17.7x
R² = 0.97

Naph
y = 61.2x
R² = 0.97
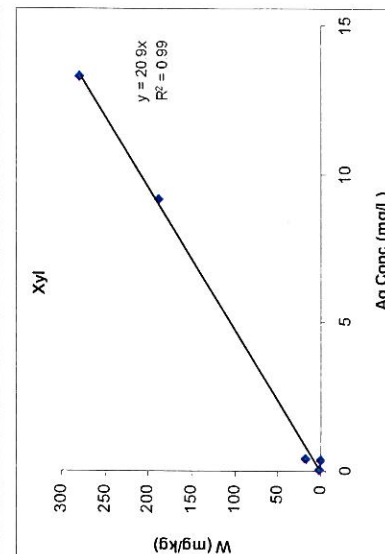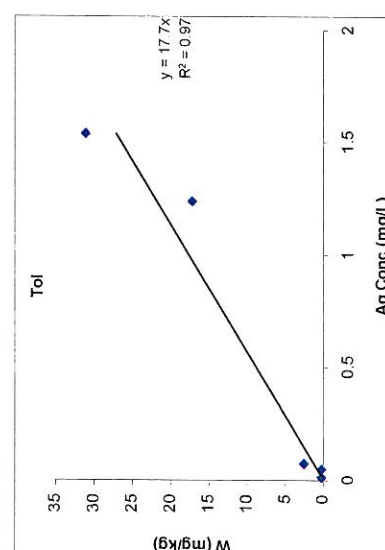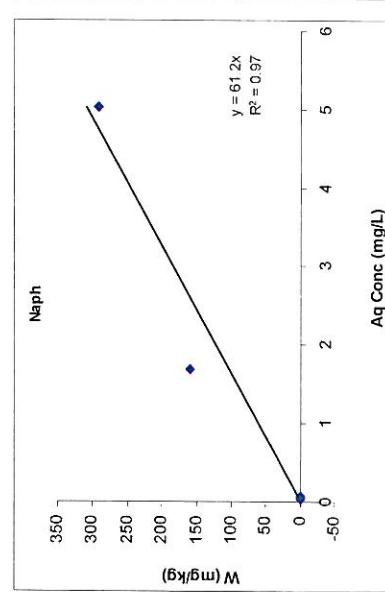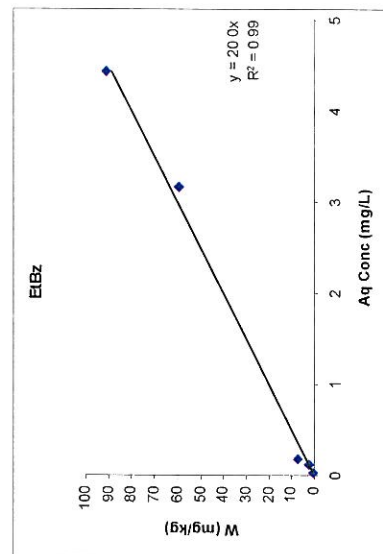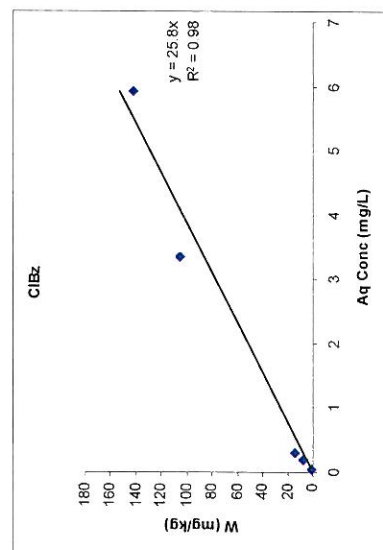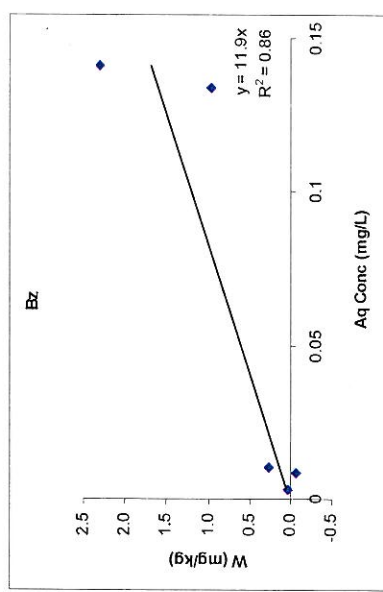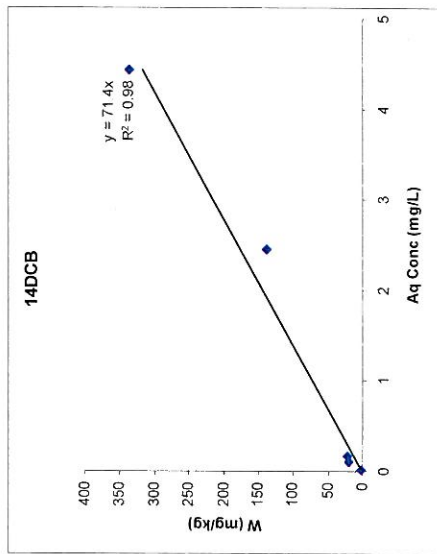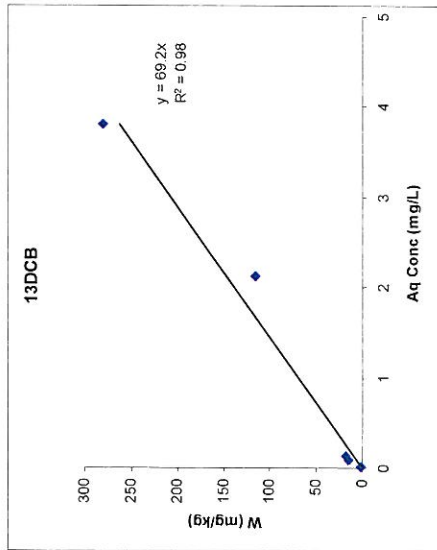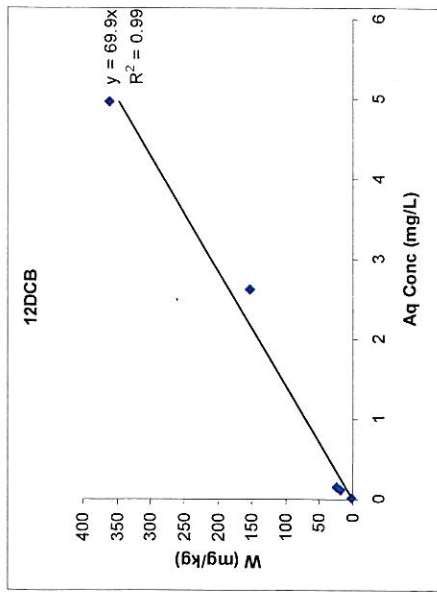
Appendix C: Determination of the Aromaticity of Dissolved Organic Carbon by Specific Ultraviolet Absorbance (SUVA) in Onondaga Lake Porewaters

<u>Purpose</u>

Quantify the aromatic content of dissolved organic carbon in Onondaga Lake porewaters used in experiments measuring partitioning to potential in-situ cap materials.

<u>Procedure</u>

Sediment samples were centrifuged by TestAmerica and porewater was sent to the University of Texas (SMU 1 received 6/6/08, SMU 6/7 received 6/11/08). Porewaters were stored at 4°C until analyzed. By vacuum, a 0.45 μm filter was rinsed with 100 mL of distilled water followed by 25 mL of sample (for saturation of sorption sites on the filter). A 50 mL sample was then filtered and collected. The absorbance of the filtered sample was measured in a quartz cuvette at a wavelength of 275 nm. (Note: EPA method 415.3 describes specific ultraviolet absorbance at 254 nm, but absorbance did not correlate to concentration with this equipment. Traina *et al.* note that percent aromatic content can be obtained from absorbance at 272 nm as well. The wave length 275 nm was selected because the greatest sensitivity to concentration was observed at that wave length.) A calibration curve was created as described in EPA Method 415.3 with potassium hydrogen phthalate (KHP) in phosphate buffer.

Calibration:

Concentration of Organic Carbon (mg/L)	Absorbance (275 nm)
0 (calibration blank)	-7.67×10^{-3}
20	0.054
40	0.18
80	0.39
120	0.66
160	0.84
200	1.02

Standard Method 5910B reports an empirically determined relationship between concentration of KHP and ultraviolet absorbance of

$$\text{KHP-OC conc.} = (UV_{254} - 0.0018) / 0.0144$$

Plots of both calibration curves are shown below. The predicted curve is that represented by the equation above.

$$y = 0.0054x - 0.0374$$
$$R^2 = 0.9954$$
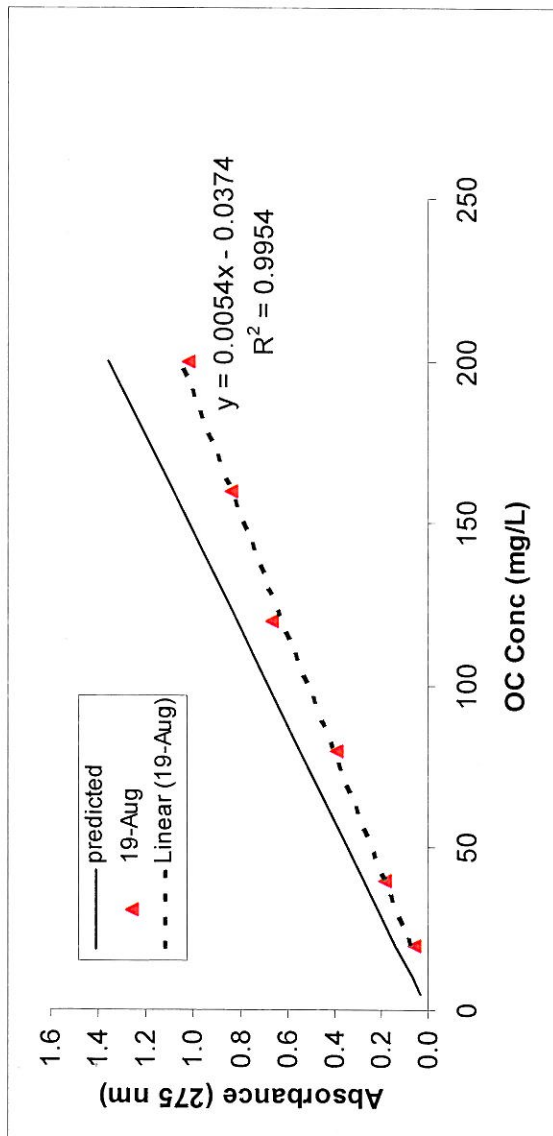
Sample Analysis:

Water samples were sparged, filtered, and analyzed for DOC by TestAmerica prior to shipment to UT. Those results, in conjunction with the absorbance data acquired at UT, were used to compute the specific ultraviolet absorbance. *Note: DOC is reported for a sample at the given dilution.*

Sample	Dilution Factor	Absorbance (275nm)	DOC (mg/L)	SUVA (275 nm)
SMU 1 porewater	10	0.18	79.5	0.23
SMU 6/7 porewater	1	0.84	69	1.22

Method 415.3 prescribes the calculation for SUVA by

$$SUVA\ (L/mg\text{-}m) = UVA(cm^{-1}) / DOC\ (mg/L) * (100\ cm/m)$$

$$UVA = A / d$$

where

UVA $=$ The calculated UV absorbance of the sample in absorbance units

$\qquad$ (cm^{-1})

A $=$ The measured UV absorbance at 254 nm (275 nm in this case) of

$\qquad$ the sample that is filtered through a 0.45-μm filter media

d $=$ The quartz cell path length (1.0 cm)

SUVA was correlated to percent aromaticity by Weishaar et al. according to

$$\% \text{ aromaticity} = 6.52 * SUVA + 3.63 \qquad (R^2 = 0.97)$$

yielding values of 5.1% and 11.6% aromaticity for SMU 1 and SMU 6/7 porewaters, respectively.

Appendix D – Mercury isotherm measurements

Table D1: Hg isotherm data with SMU 1 artificial pore water analyzed at UT by sample oxidation with excess $KMnO_4$ and atomic absorption spectrometry.

SMU1   Excess KMnO4

	#	Hg2+ stock Conc. (mg/L)	Hg2+ stock added (mL)	sorbent mass (mg)	pH	Spiked conc.(ug/L)	measured (ug/L)	dilution	estimated (ug/L)	sorbed Hg2+ (ug/kg)	Kd (L/kg)	logKd	Average
PM199	1	1,000	0.060	102.6	12.36	1200	29.1	10	291.0	442982	1522	3.18	2.99
	2	1,000	0.020	98.3	12.36	400	22.24	5	111.2	146897	1321	3.12	
	3	100	0.080	101.1	12.34	160	45.7	2	91.4	33927	371	2.57	
	4	100	0.030	98.8	12.32	60	17.23	1	17.2	21645	1256	3.10	
MR2	1	1,000	0.060	99.3	12.29	1200	5.47	1	5.5	601475	109959	5.04	4.54
	2	1,000	0.020	100	12.28	400	3.435	1	3.4	198283	57724	4.76	
	3	100	0.080	98.6	12.26	160	3.301	1	3.3	79462	24072	4.38	
	4	100	0.030	101.1	12.22	60	3.041	1	3.0	28170	9263	3.97	
MR4	1	1,000	0.060	99.41	12.38	1200	21.84	10	218.4	493713	2261	3.35	3.72
	2	1,000	0.020	100.87	12.38	400	6.834	5	34.2	181337	5307	3.72	
	3	100	0.080	102.68	12.37	160	8.82	2	17.6	69322	3930	3.59	
	4	100	0.030	100.5	12.34	60	1.818	1	1.8	28946	15922	4.20	
Peat	1	1,000	0.060	100.7	12.3	1200	13.1	10	131.0	530785	4052	3.61	4.09
	2	1,000	0.020	98.5	12.34	400	0.612	5	3.1	201492	65847	4.82	
	3	100	0.080	101.5	12.33	160	1.564	2	3.1	77277	24705	4.39	
	4	100	0.030	101	12.33	60	7.618	1	7.6	25932	3404	3.53	
Sand	1	1,000	0.060	102.08	12.43	1200	31.43	10	314.3	433826	1380	3.14	2.90
	2	1,000	0.020	102.9	12.42	400	23.77	5	118.9	136613	1149	3.06	
	3	100	0.080	103.5	12.45	160	47.79	2	95.6	31121	326	2.51	
	4	100	0.030	104.9	12.41	60	22.88	1	22.9	17693	773	2.89	
Activated Carbon	1	1,000	0.060	50.5	12.4	1200	124.8	1	124.8	1064554	8530	3.93	3.73
	2	1,000	0.020	48.5	12.41	400	47.27	1	47.3	363639	7693	3.89	
	3	100	0.080	50.2	1241	160	57.52	1	57.5	102072	1775	3.25	
	4	100	0.030	50.18	12.39	60	7.301	1	7.3	52510	7192	3.86	

SMU 1

Table D2: Hg isotherm data with SMU 1 artificial pore water analyzed at UT by atomic absorption spectrometry without sample oxidation.

SMU1		No KMnO4											
	#	Hg2+ stock Conc. (mg/L)	Hg2+ stock added (mL)	sorbent mass (mg)	pH	Spiked conc.(ug/L)	measured (ug/L)	dilution	estimated (ug/L)	sorbed Hg2+ (ug/kg)	Kd (L/kg)	logKd	Average
PM199	1	1.000	0.060	102.6	12.36	1200	24.52	10	245.2	465302	1898	3.28	3.18
	2	1.000	0.020	98.3	12.36	400	19.6	5	98.0	153611	1567	3.20	
	3	100	0.080	101.1	12.34	160	30.8	2	61.6	48665	790	2.90	
	4	100	0.030	98.8	12.32	60	11.03	1	11.0	24782	2247	3.35	
MR2	1	1.000	0.060	99.3	12.29	1200	0.172	1	0.2	604143	3512459	6.55	5.36
	2	1.000	0.020	100	12.28	400	0.514	1	0.5	199743	388605	5.59	
	3	100	0.080	98.6	12.26	160	0.836	1	0.8	80712	96545	4.98	
	4	100	0.030	101.1	12.22	60	1.367	1	1.4	28998	21213	4.33	
MR4	1	1.000	0.060	99.41	12.38	1200	19.46	10	194.6	505684	2599	3.41	3.83
	2	1.000	0.020	100.87	12.38	400	6.197	5	31.0	182916	5903	3.77	
	3	100	0.080	102.68	12.37	160	6.59	2	13.2	71494	5424	3.73	
	4	100	0.030	100.5	12.34	60	1.211	1	1.2	29248	24152	4.38	
Peat	1	1.000	0.060	100.7	12.3	1200	11.27	10	112.7	539871	4790	3.68	4.20
	2	1.000	0.020	98.5	12.34	400	0.641	5	3.2	201419	62845	4.80	
	3	100	0.080	101.5	12.33	160	1.108	2	2.2	77726	35075	4.54	
	4	100	0.030	101	12.33	60	4.736	1	4.7	27358	5777	3.76	
Sand	1	1.000	0.060	102.08	12.43	1200	30.3	10	303.0	439361	1450	3.16	3.12
	2	1.000	0.020	102.9	12.42	400	20.18	5	100.9	145335	1440	3.16	
	3	100	0.080	103.5	12.45	160	30.71	2	61.4	47623	775	2.89	
	4	100	0.030	104.9	12.41	60	12.18	1	12.2	22793	1871	3.27	
Activated Carbon	1	1.000	0.060	50.5	12.4	1200	60.95	1	61.0	1127772	18503	4.27	4.07
	2	1.000	0.020	48.5	12.41	400	26.92	1	26.9	384619	14287	4.15	
	3	100	0.080	50.2	1241	160	26.92	1	26.9	132550	4924	3.69	
	4	100	0.030	50.18	12.39	60	3.977	1	4.0	55822	14036	4.15	

SMU 1

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Table D3: Data from Hg isotherm vials with actual site porewater analyzed by TestAmerica, North Canton (not used in isotherm estimation)

SMU1	sorbent	#	Hg2+ stock Conc. (mg/L)	Hg2+ stock added (mL)	sorbent mass (mg)	pH	Spiked conc.(ng/L)	initial Hg2+ conc. (ng/L)	measured (ng/L)	dilution	estimated (ng/L)	sorbed Hg2+ (ng/kg)	Kd (L/kg)	logKd
1	PM199	1	100	0.520	99.57	12.17	1040000	1147000	5.1	2.0E+04	101000	525258612	5201	3.72
		2	100	0.052	99.52	12.18	103169	210169	8.5	2.0E+04	169000	20683821	122	2.09
		3	100	0.026	100.03	12.18	51585	158585	7.3	2.0E+04	145000	6790232	47	1.67
2	MR2	1	100	0.520	100.6	12.16	1040000	1147000	19.1	1.0E+03	19100	560586481	29350	4.47
		2	100	0.052	100.36	12.17	103169	210169	9.0	1.0E+04	90300	59719549	661	2.82
		3	100	0.026	99.51	12.17	51585	158585	23.5	4.0E+03	94100	32401035	344	2.54
		4	1	0.260	101.38	12.18	5200	112200	14.7	4.0E+03	58700	26385875	450	2.65
		5	1	0.026	100.5	12.19	516	107516	17.1	4.0E+03	68500	19410868	283	2.45
3	MR4	1	100	0.520	101.04	12.1	1040000	1147000	12.6	2.0E+04	251000	443388757	1766	3.25
		2	100	0.052	101.05	12.13	103169	210169	9.9	2.0E+04	197000	6516120	33	1.52
		3	100	0.026	99.95	12.14	51585	158585	7.3	2.0E+04	145000	6795667	47	1.67
4	Peat	1	100	0.520	99.07	11.95	1040000	1147000	10.9	1.0E+04	109000	523872010	4806	3.68
		2	100	0.052	98.4	12.01	103169	210169	17.5	1.0E+04	175000	17870467	102	2.01
		3	100	0.026	99.62	12.04	51585	158585	6.4	2.0E+04	128000	15350602	120	2.08
5	Sand	1	100	0.520	101.3	12.16	1040000	1147000	12.4	2.0E+04	248000	443731491	1789	3.25
		2	100	0.052	102.06	12.16	103169	210169	10.2	2.0E+04	204000	3022280	15	1.17
		3	100	0.026	101.13	12.17	51585	158585	7.2	2.0E+04	144000	7210788	50	1.70
		4	1	0.260	100.26	12.19	5200	112200	5.5	2.0E+04	109000	1595851	15	1.17
6	Activated Carbon	1	100	0.520	98.97	12.17	1040000	1147000	7.1	1.0E+01	71.3	579432505	8126683	6.91
		2	100	0.052	100.49	12.19	103169	210169	1.7	1.0E+02	168	104488545	621956	5.79
		3	100	0.026	99.78	12.19	51585	158585	1.9	1.0E+02	185	79374393	429051	5.63
		4	1	0.260	100.78	12.19	5200	112200	6.4	1.0E+02	642	55347291	86211	4.94
		5	1	0.026	100.55	12.19	516	107516	4.2	1.0E+03	4150	51400221	12386	4.09
7	check	1	100	0.000	blank	12.17	0	107000	11.6	1.0E+04	116000			
		2	100	0.052		12.19	103169	210169	0.9	2.0E+04	17900			
		3	100	0.026		12.19	51585	158585	7.1	2.0E+04	141000			
		4	1	0.260		12.19	5200	112200	12.0	1.0E+04	120000			
		5	1	0.000	blank	12.19	0	107000	4.9	2.0E+04	98000			

from TestAmerica

Table D4: Hg isotherm with SMU 6/7 artificial porewater analyzed at UT by atomic absorption spectrometry

			Hg2+ stock Conc. (ppm)	volume added(mL)	sorbent mass (mg)	pH	Spiked conc.(ug/L)	measured Ce (ug/L)	dilution	estimated Ce (ug/L)	sorbed Hg2+ (ug/kg)	Kd (L/kg)	logKd	Average	Stdev
SMU 6/7 Artificial Porewater	MR-2	1	100	1	99.9	7.4	2000	14.77	10	147.7	927077	6277	3.80	4.21	0.6368
		2	100	0.1	104.9	7.24	200	6.182	2	12.364	89436	7234	3.86		
		3	1	0.1	99.62	7.39	2	0.0007005	10	0.0070053	1000	142791	5.15		
		4	1	0.01	102.5	7.42	0	0.0028816	3	0.0086449	93	10798	4.03		
	PM-199	1	100	1	101.05	7.9	2000	13	10	130	925285	7118	3.85	4.01	0.2201
		2	100	0.1	100.65	7.46	200	3.866	2	7.732	95513	12353	4.09		
		3	100	0.01	101.74	7.52	20	1.604	1	1.604	9041	5636	3.75		
		4	1	0.1	101.04	7.52	2	0.0088943	10	0.0889433	946	10633	4.03		
		5	1	0.01	100	7.5	0	0.0015651	3	0.0046952	98	20798	4.32		
	Sand	1	100	1	100.86	7.66	2000	17.99	100	1799	99643	55	1.74	2.66	1.3445
		2	100	0.1	100.47	7.66	200	16.41	10	164.1	17866	109	2.04		
		3	100	0.01	102.08	7.75	20	0.593	1	0.593	9506	16030	4.20		
	Peat	1	100	1	103.78	7.28	2000	47.53	10	475.3	734583	1546	3.19	4.01	0.6853
		2	100	0.1	99.36	7.3	200	7.082	2	14.164	93517	6602	3.82		
		3	1	0.1	100.53	7.2	2	0.0014753	10	0.0147527	987	66929	4.83		
		4	1	0.01	101.22	7.3	0	0.0020447	3	0.0061341	96	15612	4.19		
	Activated Carbon	1	1,000	0.500	50.4	7.79	1000	26.52	10	265.2	728968	2749	3.44	4.69	0.842
		2	1,000	0.200	50.04	8.04	4000	9.043	5	45.2	3951624	87396	4.94		
		3	1,000	0.100	49.2	8.03	2000	16.03	1	16.0	2016230	125779	5.10		
		4	1,000	0.030	49.8	7.91	600	3.25	1	3.3	599147	184353	5.27		

Table D5: Hg isotherm with SMU 6/7 actual porewater analyzed by TestAmerica (not used in isotherm estimation)

	#	Hg2+ stock Conc. (mg/L)	Hg2+ stock added (mL)	sorbent mass (mg)	pH	Spiked conc.(ug/L)	measured (ug/L)	dilution	estimated (ug/L)	sorbed Hg2+ (ug/kg)	Kd (L/kg)	logKd	Average	Stdev
MR2	1	1,000	0.500	100.8	7.84	10000	47.34	100	4734.0	2612103	552	2.74	2.81	0.1059
	2	1,000	0.200	101.2	7.86	4000	34.84	50	1742.0	1115613	640	2.81		
	3	1,000	0.100	101.7	8.02	2000	70.01	10	700.1	639086	913	2.96		
	4	1,000	0.030	100.9	7.93	600	28.78	10	287.8	154708	538	2.73		
PM199	1	1,000	0.500	99.7	7.89	10000	49.48	100	4948.0	2533601	512	2.71	2.79	0.1104
	2	1,000	0.200	100.3	7.97	4000	34.24	50	1712.0	1140578	666	2.82		
	3	1,000	0.100	99.18	7.9	2000	75.02	10	750.2	630067	840	2.92		
	4	1,000	0.030	98	7.95	600	30.78	10	307.8	149082	484	2.69		
Sand	1	100	0.200	100.5	7.49	400	21.73	10	217.3	90896	418	2.62	2.88	0.3246
	2	100	0.100	98.4	7.47	200	20.1	5	100.5	50559	503	2.70		
	3	100	0.050	100.22	7.5	100	20.61	2	41.2	29325	711	2.85		
	4	100	0.010	103	7.54	20	3.594	1	3.6	7964	2216	3.35		
MR4	1	1,000	0.500	100.96	7.84	10000	49.64	100	4964.0	2494057	502	2.70	2.92	0.1671
	2	1,000	0.200	101.25	7.81	4000	29	50	1450.0	1259259	868	2.94		
	3	1,000	0.100	102.2	7.95	2000	55.21	10	552.1	708366	1283	3.11		
	4	1,000	0.030	101.4	7.86	600	22.01	10	220.1	187327	851	2.93		
Activated Carbon	1	1,000	0.500	54.7	7.93	10000	106.2	10	1062.0	8170018	7693	3.89	3.78	0.1089
	2	1,000	0.200	50.4	7.96	4000	94.99	5	475.0	3497073	7363	3.87		
	3	1,000	0.100	49.8	8.04	2000	33.75	10	337.5	1669177	4946	3.69		
	4	1,000	0.030	50.7	7.96	600	101.9	1	101.9	491223	4821	3.68		

(Row group label at far left: SMU 6/7 Actual Porewater)

Note High Concentration range in actual porewater samples. Lower concentrations in artificial porewater more relevant

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References:

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May 28, 2010

To: Caryn Kiehl-Simpson
        Parsons

From: Greg Lowry and Julian Fairey

Re: Phase IV Addendum 2 Report – Preliminary and full isotherm studies with organic
       contaminants of concern and activated carbon

1.0 Executive Summary

Activated Carbon isotherm testing was conducted in compliance with the Phase IV Addendum 2
Work Plan (Work Plan) with changes as described below (Parsons, 2008). Representative
porewater was generated from sediments in SMU 1 and a composite of SMU 6 and 7. The activated
carbon studies were performed at Carnegie Mellon under the direction of Dr. Gregory Lowry.
TestAmerica Pittsburgh conducted the initial generation of porewater and preliminary porewater
analysis. DHL in Austin, Texas performed the analysis on samples generated following the
experiments.

Prior to full isotherm development, preliminary isotherms were collected for four types of activated
carbon (AC) in SMU 1 porewater, to identify the best candidate AC to study in detail. The
preliminary isotherm experiments were designed to obtain the necessary information for executing
the full isotherm experiment. This involved evaluating site-specific Freundlich adsorption isotherm
parameters for each of the nine target compounds (eight individual compounds and total xylenes,
which was the sum of three isomers) on each of the four activated carbons from Calgon Carbon
including TOG, Centaur, and Filtrasorb (F-400), and a regenerated carbon DSR-A. Spec sheets for
each carbon are provided in Appendix B. These experiments were also designed to indicate the
activated carbon most resistant to fouling by natural organic matter through a comparison of
isotherm results in organic free water with those results obtained from SMU 1 porewater. The
preliminary experiments identified F-400 as the best AC to conduct full isotherm studies. This
conclusion was discussed with the New York State Department of Environmental Conservation
(NYSDEC) in a September 2008 meeting and the full scale isotherm experiments were executed in
accordance with the work plan using F-400 as the carbon.

1.1 Preliminary Isotherms

Preliminary isotherm data was collected for four types of activated carbon. The AC used included
TOG, Centaur, F400, and DSR-A which is a regenerated product available from Calgon. Five point
isotherms were collected for these carbons in SMU 1 porewater generated by Test America in
Pittsburgh. The range of initial concentrations of each VOC of concern in the isotherms fell within
the ranges specified in Table 4 of the Work Plan.

The porewater concentrations of the nine VOCs following 15 minutes of sparging were not significantly reduced, and were at levels which would have interfered with the analysis for the isotherms. As such, the porewater was sparged at Carnegie Mellon for an additional six hours using nitrogen to remove all VOCs initially present in the porewater. Nine VOCs of interest were then re-introduced into the porewater to provide the desired range of initial and ultimately equilibrium VOC concentrations.

Five point isotherms for eight VOCs in sparged SMU 1 pore water are shown in Figure 1 and the results are summarized in Table 1. The benzene and toluene data were excluded because the spiked concentrations were too low (<0.10 mg/L) relative to the equilibrium water concentrations, C_e, due to a calculation error in the order for the spike solution from AccuStandard. Freundlich parameters for the eight VOCs and total xylenes were calculated and are provided in Table 1. Based on these data, Centaur was the poorest VOC sorbent; the other three activated carbons performed equally as well. When both performance and cost are considered, DSR-A is the most practical option. However, there could be more performance variability with DSR-A from batch to batch relative to the other activated carbons because it is a regenerated product – it is made using various activated carbons sent back to Calgon Carbon from water treatment plants. Therefore, F400 was chosen as the AC to collect full isotherm parameters in SMU 1 and SMU 6/7. However, DSR-A may be included in future design evaluations as a cost effective carbon option.
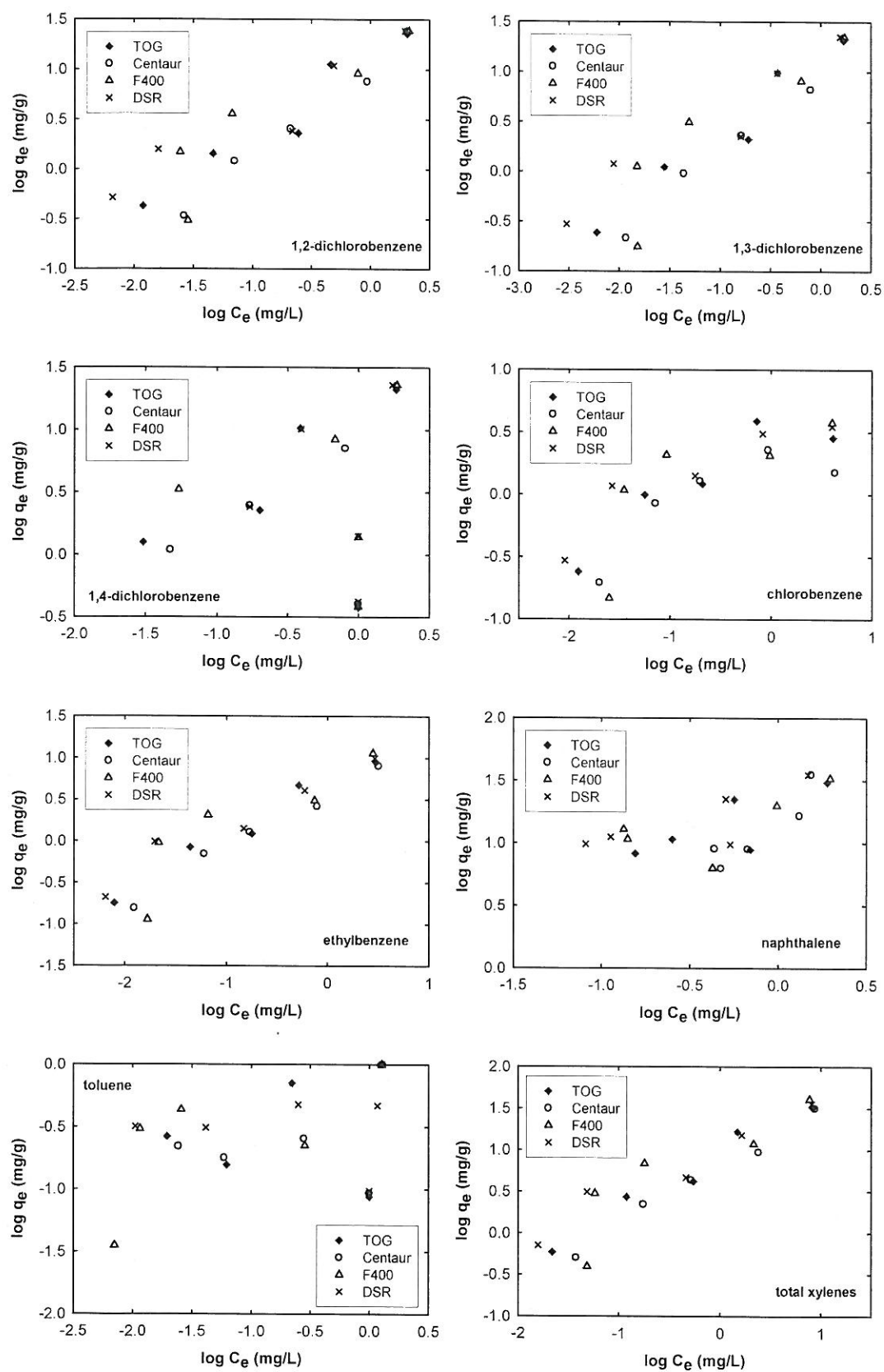
Figure 1. VOC isotherms for sparged SMU 1 porewater on the four activated carbons.

Table 1. Freundlich parameters for the VOCs on the four activated carbons.

| | TOG | | CENTAUR | | F400 | | DSR | |
| | K_F | | K_F | | K_F | | K_F | |
	$(mg/g)(L/mg)^{1/n}$	1/n	$(mg/g)(L/mg)^{1/n}$	1/n	$(mg/g)(L/mg)^{1/n}$	1/n	$(mg/g)(L/mg)^{1/n}$	1/n
1,2-dichlorobenzene	12.96	0.77	10.57	0.91	13.41	0.75	13.10	0.62
1,3-dichlorobenzene	13.81	0.78	11.20	0.86	14.55	0.77	14.31	0.63
1,4-dichlorobenzene	13.27	0.72	10.89	0.79	13.56	0.51	15.95	0.92
Benzene								
Chlorobenzene	2.49	0.44	1.55	0.37	2.42	0.43	2.68	0.37
Ethylbenzene	5.10	0.66	3.67	0.67	5.53	0.66	5.35	0.57
Naphthalene	19.45	0.47	16.26	1.06	19.04	0.36	23.29	0.37
Toluene	0.98	0.42	0.26	0.08	0.48	0.27	0.49	0.10
Total Xylenes	8.83	0.67	6.26	0.72	9.94	0.67	10.40	0.58

1.2 Full Isotherms for F-400

Materials. Based on the results from the scoping study, Filtrasorb 400 (F400) from Calgon Carbon Corporation (Pittsburgh, PA) was selected for developing complete isotherms in SMU 1 and SMU 6/7 porewater. The activated carbon was crushed with a mortar and pestle and dry-sieved to generate the 80×100 mesh fraction. The small particle size helped to ensure rapid equilibration between dissolved and adsorbed contaminants (see results of effect of equilibrium time below). The ground activated carbon was washed repeatedly with distilled-deionized (DDI) water to remove fines and oils. After washing, the activated carbon was dried for 24 hours at 105°C to remove residual water and then stored in a 40 mL amber glass vial sealed with a PTFE-lined screw cap until use in the isotherm experiments.

The nine organic chemicals studied were 1,2-dichlorobenzene (12DCB), 1,3-dichlorobenzene (13DCB), 1,4-dichlorobenzene (14DCB), benzene (B), chlorobenzene (CB), ethylbenzene (EB), naphthalene (N), toluene (T), and total xylenes (TX) which was the sum of o-xylene, p-xylene, and m-xylene. One methanol solution containing all eleven chemicals, each at approximately 50,000 mg/L, was obtained from AccuStandard (New Haven, CT). Spike solutions needed for the isotherm experiments were made by preparing serial dilutions of the stock standard in pesticide-grade methanol.

The three background waters used in the isotherm experiments were organic-free water (OFW), and sediment pore water designated as SMU 1 and SMU 6/7. OFW was made by amending DDI water with 0.01 M $CaCl_2$. SMU 1 and SMU 6/7 pore waters were generated by Test America (Pittsburgh, PA) by centrifuging sediment samples from these locations and decanting the water.

Isotherm Experiments. Isotherm experiments were conducted in 200 mL glass centrifuge bottles with PTFE-lined screw caps. Precisely 200 mL of organic free water or porewater was added to each bottle. Next, spike solution containing the eleven target chemicals was added to a series of the 200 mL glass centrifuge bottles - the target equilibrium aqueous phase concentration range for each chemical was 0.01-10 mg/L to cover the range of contaminant concentrations observed in Onondaga porewater. Lastly, approximately 25 mg of 80×100 mesh F400 activated carbon was added to the sample bottles. The precise weight of AC (to the nearest 0.1 mg) was recorded. All samples contained 25 ± 1 mg. Bottles without activated carbon were prepared to serve as blanks and were used to directly account for losses by assuming mass losses (i.e. to glass wall and cap liner) were proportional to the final (equilibrium) aqueous concentrations. These loses were determined to be negligible in samples containing activated carbon. Samples and blanks were swirled on a rotary shaker at 120 rpm for 7-, 14-, or 28-days at room temperature (22 ± 2°C). After completion of the experiment, the samples were taken off the shaker. The AC in the samples was allowed to settle and then three 40 mL aliquots from each bottle were transferred with a glass

pipette to 40 mL VOA bottles that contained approximately 1 mL of 1+1 HCl. The VOA bottles were sealed with PTFE-lined screw caps, packed in ice, and shipped overnight to DHL Analytical (Round Rock, TX) for analysis.

Data Analysis. Concentrations of the target chemicals obtained from DHL Analytical were analyzed to determine isotherm-fitting parameters. DHL Analytical reported the aqueous phase concentration, C_W, for the nine chemicals (eight individual compounds and total xylenes, which was the sum of three isomers) in each sample and blank. The solid phase concentration, q_e, was determined using equation 1:

$$q_e = \frac{M_{spiked} - C_W\left(K_{aw}V_{headspace} + V_w\right)}{M_{AC}} \tag{1}$$

In equation 1, M_{spiked} was the mass of VOC added, K_{aw} is the air-water partition coefficient (Table 2), $V_{headspace}$ was the headspace volume (if any) in the isotherm bottle, V_W was the aqueous phase volume (200 mL), and M_{AC} was the mass of activated carbon added (approximately 25 mg). For each background water and chemical, a non-linear least-squares regression was conducted on q_e and C_W and a best fit was produced according to the Freundlich isotherm equation:

$$q_e = K_F C_W^{1/n} \tag{2}$$

In equation 2, K_F and $1/n$ are model-fitting parameters that describe the data.

The precision of K_F and $1/n$ was determined by calculating the 95% joint confidence region. It is a *joint* confidence region because it considers the fitting parameters as a pair. If we were to repeat the experiment many times with the same number of observations, 95% of the pairs of the estimated parameter values would be expected to fall within the joint confidence region. Comparison of joint confidence regions permits inferences regarding the relative sorption strength of each contaminant. If a joint confidence interval for Data Set #1 contains the mean of Data Set #2, then their respective values of K_F and $1/n$ are indistinguishable; if the joint confidence regions do not overlap, values of K_F and $1/n$ are dissimilar; if the regions overlap, but not the means, no inference regarding K_F and $1/n$ can be made. Generally, the smaller the confidence region, the better the mean values of K_F and $1/n$ in describing the data.

Isotherm Results. Sorption isotherms and their corresponding 95% joint confidence regions in the three background waters for 12DCB, 13DCB, 14DCB, B, CB, EB, N, T, and TX are shown in Appendix A Figures A1-A18. The fitting parameters for the isotherms, applicable ranges for C_W, and number of observations (i.e., count) are summarized in Table 2.

Table 2. Mean values of the Freundlich parameters (K_F and $1/n$) for the nine target VOCs in three background waters.

Chemical	Water	K_F $(mg/g)(L/mg)^{1/n}$	$1/n$	C_W Range (mg/L)	$-\log K_{aw}$[*]	Count
12DCB	OFW	51.47	0.31	0-11		10
	SMU1	27.80	0.36	0-6	1.04	9
	SMU67	52.09	0.34	0-11		9
13DCB	OFW	57.66	0.33	0-10		10
	SMU1	32.07	0.37	0-5	0.86	9
	SMU67	57.27	0.36	0-10		9
14DCB	OFW	55.57	0.32	0-10		9
	SMU1	30.84	0.36	0-6	1.04	8
	SMU67	55.56	0.35	0-10		7
B	OFW	28.00	0.38	0-15		9
	SMU1	13.96	0.49	0-18	0.65	9
	SMU67	20.41	0.44	0-16		9
CB	OFW	31.90	0.23	0-17		8
	SMU1	13.55	0.37	0-20	0.80	10
	SMU67	28.69	0.28	0-17		8
EB	OFW	40.27	0.27	0-14		10
	SMU1	18.33	0.30	0-9	0.50	9
	SMU67	42.55	0.24	0-15		9
N	OFW	49.24	0.34	0-11		10
	SMU1	24.60	0.65	0-11	1.74	9
	SMU67	91.87	0.24	0-8		6
T	OFW	32.27	0.27	0-15		9
	SMU1	14.36	0.35	0-19	0.60	10
	SMU67	38.81	0.20	0-17		9
TX	OFW	92.93	0.26	0-42		10
	SMU1	43.26	0.30	0-25	0.58	9
	SMU67	117.74	0.26	0-40		9

[*]Source: Schwarzenbach RP, Gschwend PW, and Imboden DM. *Environmental organic chemistry*, 2nd edition, John Wiley & Sons (2003).

All VOCs were strongly adsorbed to F-400. K_F values ranged from a low of approximately 14 for Benzene, Chlorobenzene, and Toluene in SMU 1 to as high as 118 for xylenes in OFW (Table 2). As expected for activated carbon, the mean values of $1/n$ for each sorbate were less than 1. In general, the adsorption parameters measured in OFW and SMU 6/7 were indistinguishable, indicating that SMU 6/7 did not foul the activated carbon and decrease sorption to a significant extent relative to deionized water. Only benzene showed slightly lower adsorption in SMU 6/7 porewater compared to OFW. However, adsorption was always lower in SMU 1 compared to SMU 6/7 and OFW. This is consistent with the findings from the preliminary study and with the high DOC levels in SMU 1 water (~600-1000 mg/L) compared to SMU 67 (~50 mg/L).

Effect of sparging and equilibration time. The solid symbols in the isotherm figures were collected from data using unsparged pore water from anoxic sediment cores. On balance, these data are similar to their corresponding sparged pore water, indicating that sparging or exposure to oxygen did not impact VOC sorption to activated carbon. DOC, pH, alkalinity, cations, anions, TDS did not change significantly with sparging.

Preliminary experiments indicated seven days was sufficient to achieve apparent equilibrium conditions with 80×100 mesh F400 activated carbon. Prior published studies suggest that equilibration times less than three days are sufficient for VOC adsorption equilibrium on activated carbon. The majority of the bottles in this study were sacrificed after Day 7; the remaining bottles were sacrificed after Days 14 and 28 (Table 3). These data (which were not distinguished but were included in the isotherm figures) indicate that a seven day equilibration time was sufficient to achieve adsorption equilibrium.

Table 3. Water Source, Initial VOC Concentration and Equilibration Time of F400 Activated Carbon

Water Source	Initial VOC Concentration for each Parameter(mg/L)	Day Sampled (day)
OFW	125	7
OFW	87.5	7
OFW	50	28
OFW	32.5	7
OFW	12.5	7
OFW	5	14
OFW	3.25	7
OFW	1.25	7
OFW	0.5	7
OFW	0.325	7
OFW	0.125	7
SMU67	125	7
SMU67	87.5	7
SMU67	50	28
SMU67	32.5	7
SMU67	12.5	7
SMU67	5	14
SMU67	3.25	7
SMU67	1.25	7
SMU67	0.5	7
SMU67	0.325	7

SMU67	0.125	7
SMU1	125	7
SMU1	87.5	7
SMU1	50	28
SMU1	32.5	7
SMU1	12.5	7
SMU1	5	14
SMU1	3.25	7
SMU1	1.25	7
SMU1	0.5	7
SMU1	0.325	7
SMU1	0.125	7
SMU67_11E	50	7
SMU67_11E	5	7
SMU1_11E	50	7
SMU1_11E	5	7

2.0 Deviations from work plan.

We were not able to obtain samples of Aquaguard activated carbon for analysis. As such, Calgon F400 was substituted as an affective adsorbent for chlorinated organic contaminants.

Isotherms for mercury were generated independently at the University of Texas.

3.0 Future Work

There is no additional isotherm work recommended at this time.

4.0 Conclusions

All VOCs of interest adsorb strongly to the Calgon Filtrasorb F-400 activated carbon. The presence of high levels of DOC in SMU 1 (600 to 1000 mg/L) decreases the adsorption Freundlich parameter, K_F, for each VOC typically by a factor of 2. Performing the SMU 1 isotherm studies with pore water with DOC concentrations at the high end of the range measured in the ILWD was done to provide conservative results for the ILWD isotherm values. The DOC in SMU 1 did not significantly increase $1/n$ in all cases. Summary statistics for DOC levels in SMU 1 porewater are provided below. The effect of DOC in SMU 6/7 (on the order of 50 mg/L) on VOC adsorption was significantly less than for SMU 1. Adsorption isotherms for SMU 6/7 were similar to those observed in organic free water.

SMU1 DOC STATISTICS

Value	DOC (mg/L)
Maximum	1340
Minimum	1
Average	362
90th Percentile	783
95th Percentile	925

Note: DOC Values in porewater for 0-3 meter sample interval in SMU 1

5.0 References

Parsons, 2008,.Onondaga Lake Pre-Design Investigation: Phase IV Work Plan Addendum 2. Prepared for Honeywell, Morristown, New Jersey. Syracuse, New York.

Reible, D. and Smith, A. 2008. IV Addendum 2 Report –Isotherm Experiments with Organic Contaminants of Concern with Sand, Organoclay and Peat and for Mercury with Sand, Organoclay, Peat and Activated Carbon. University of Texas Austin. Austin, Texas.
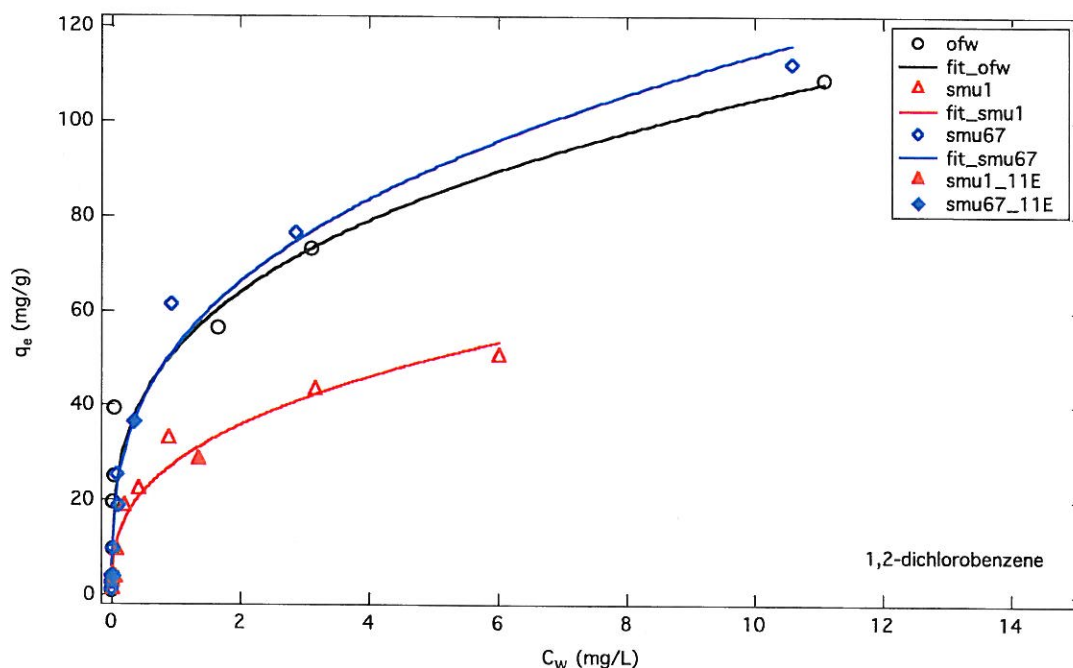
Figure A1. 1,2-dichlorobenzene adsorption isotherms for OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E and the corresponding Freundlich model fits using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.
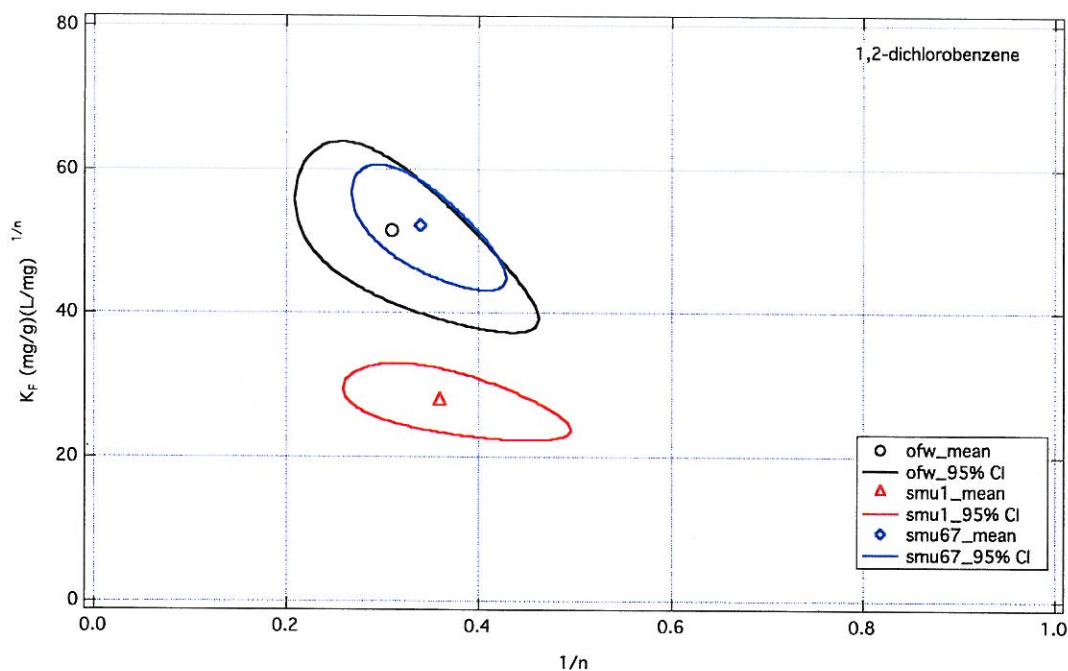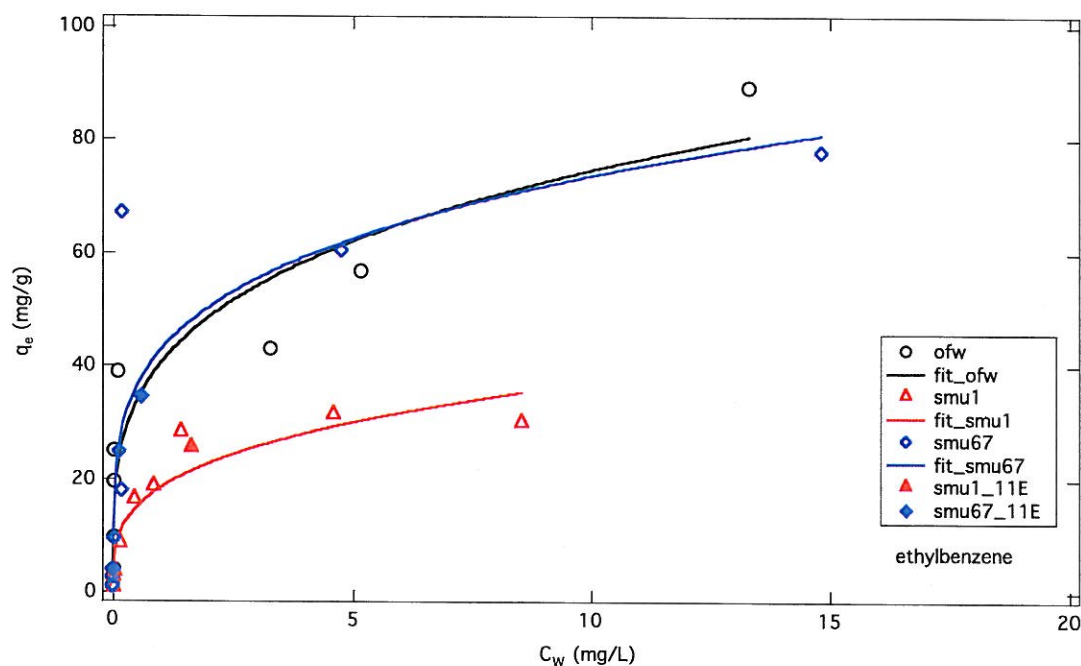

Figure A2. K_F and $1/n$ means and their 95% joint confidence intervals for 1,2-dichlorobenzene with OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.
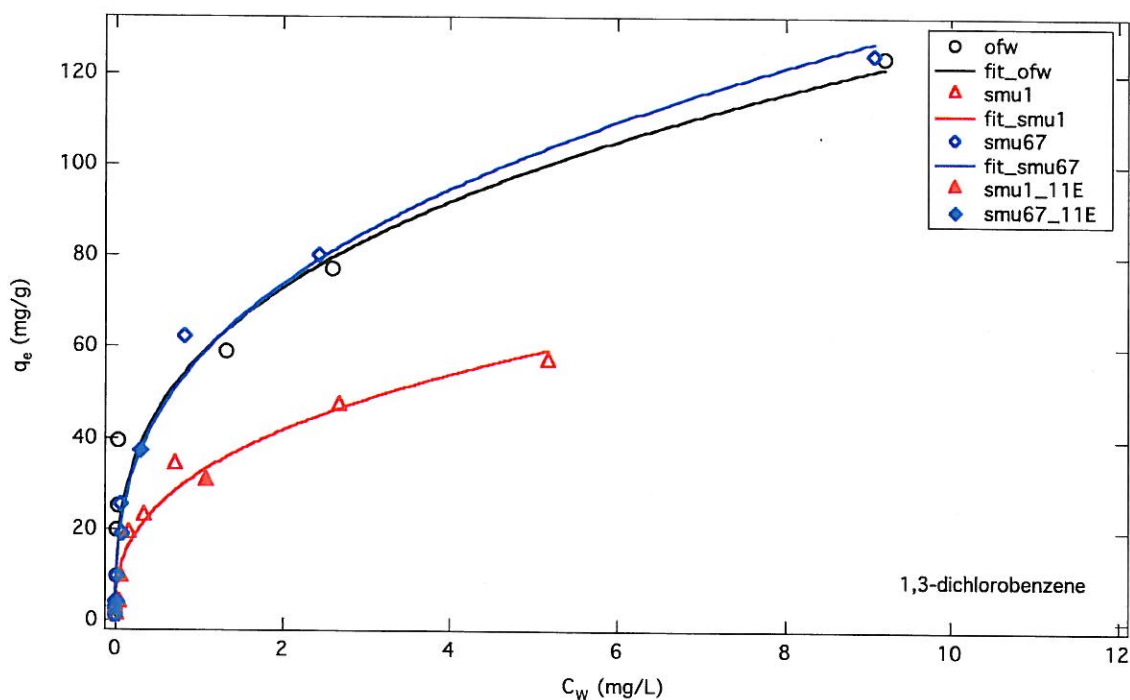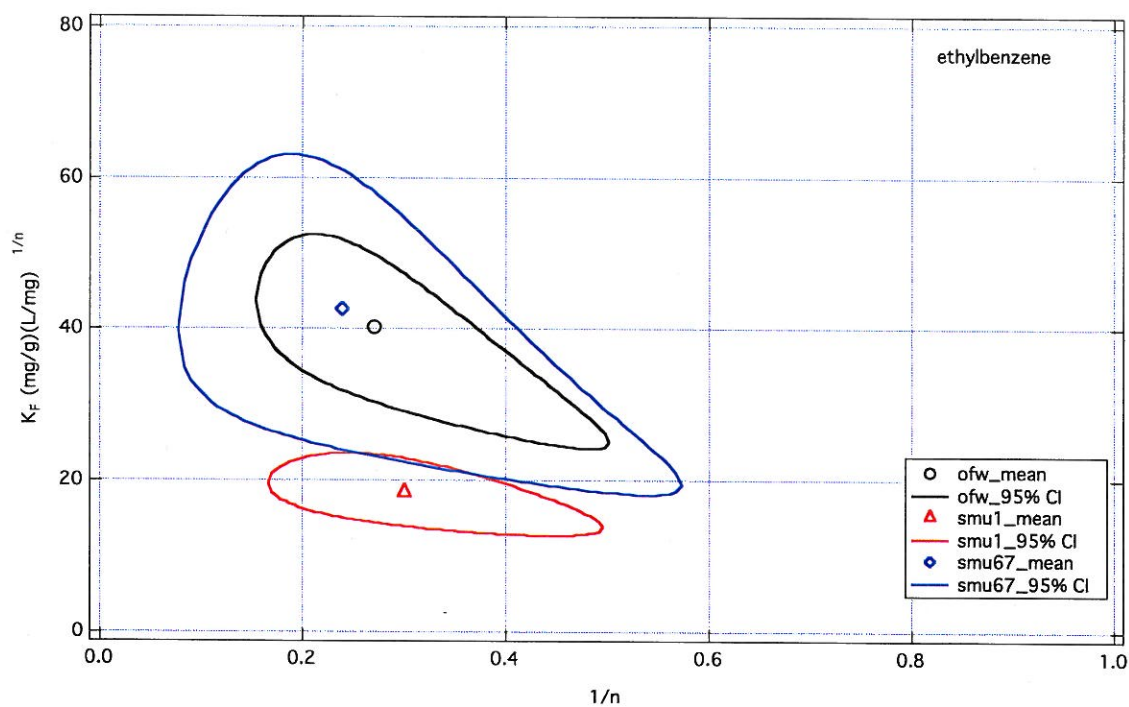
Figure A3. 1,3-dichlorobenzene adsorption isotherms for OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E and the corresponding Freundlich model fits using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.
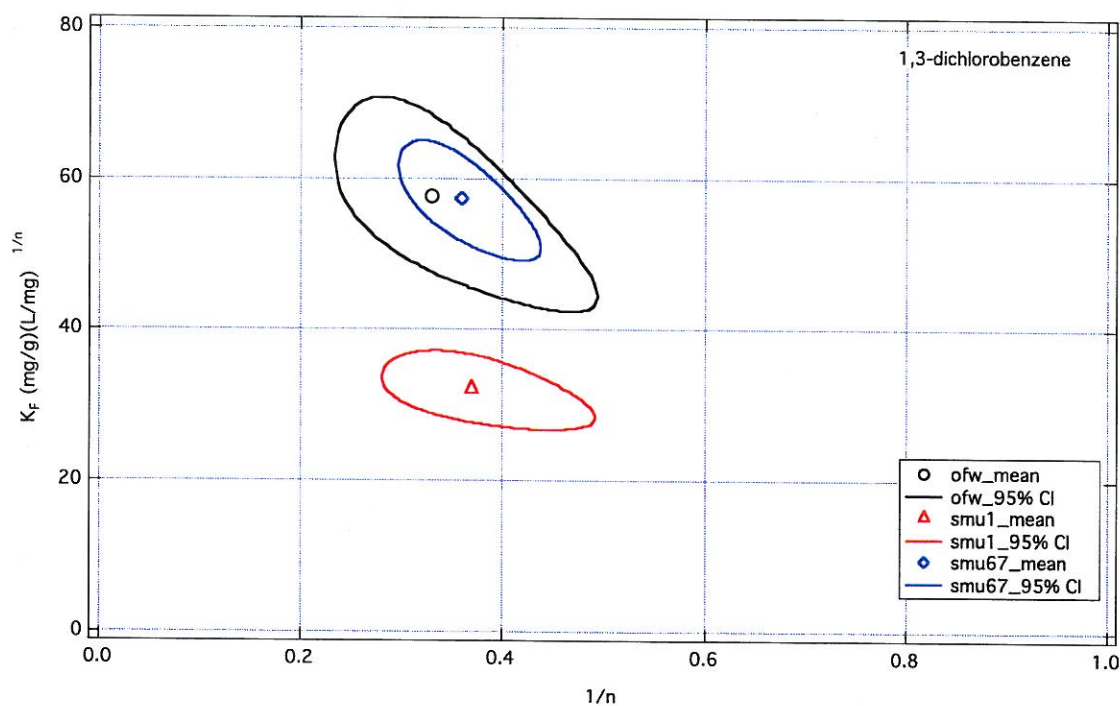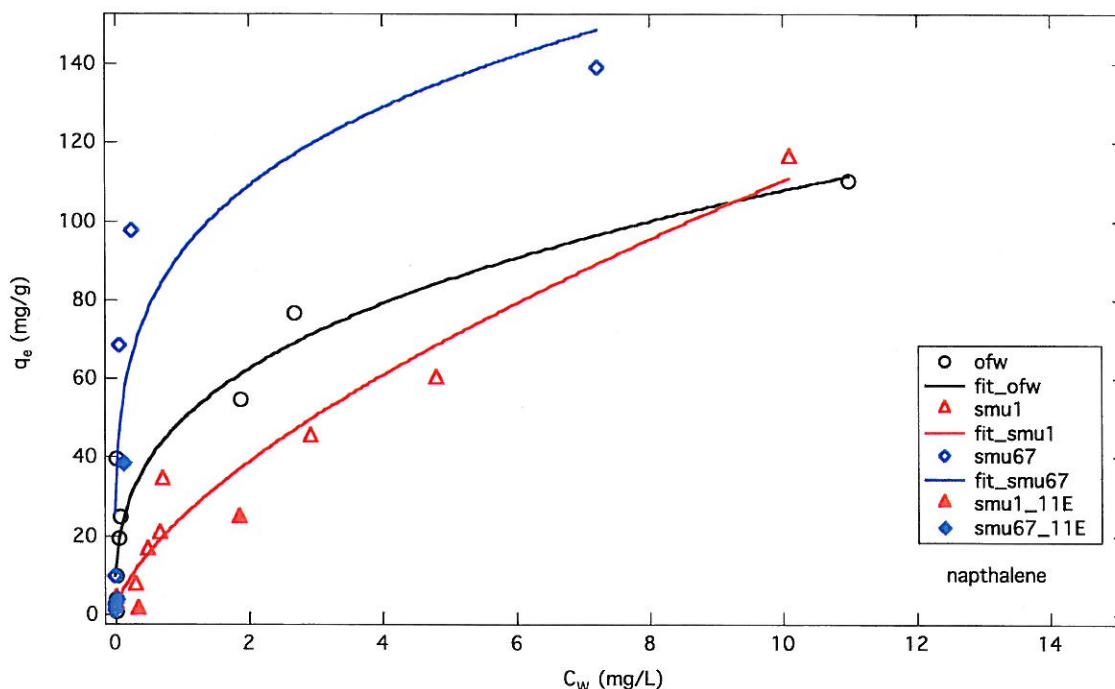

Figure A4. K_F and $1/n$ means and their 95% joint confidence intervals for 1,3-dichlorobenzene with OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.
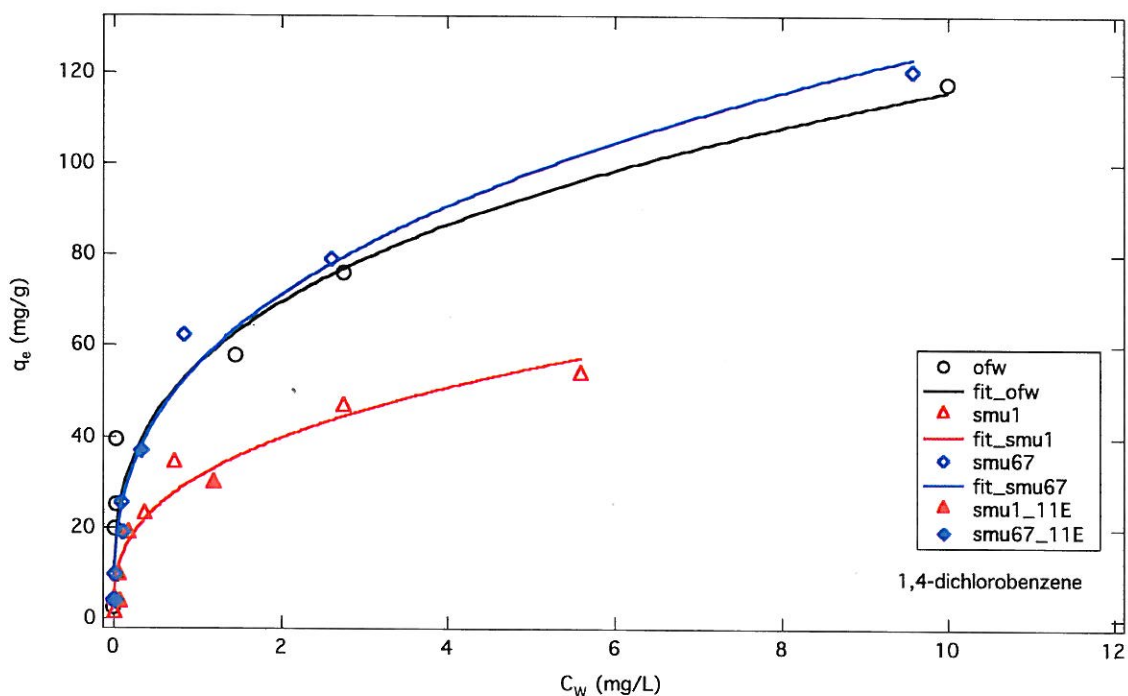
Figure A5. 1,4-dichlorobenzene adsorption isotherms for OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E and the corresponding Freundlich model fits using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.
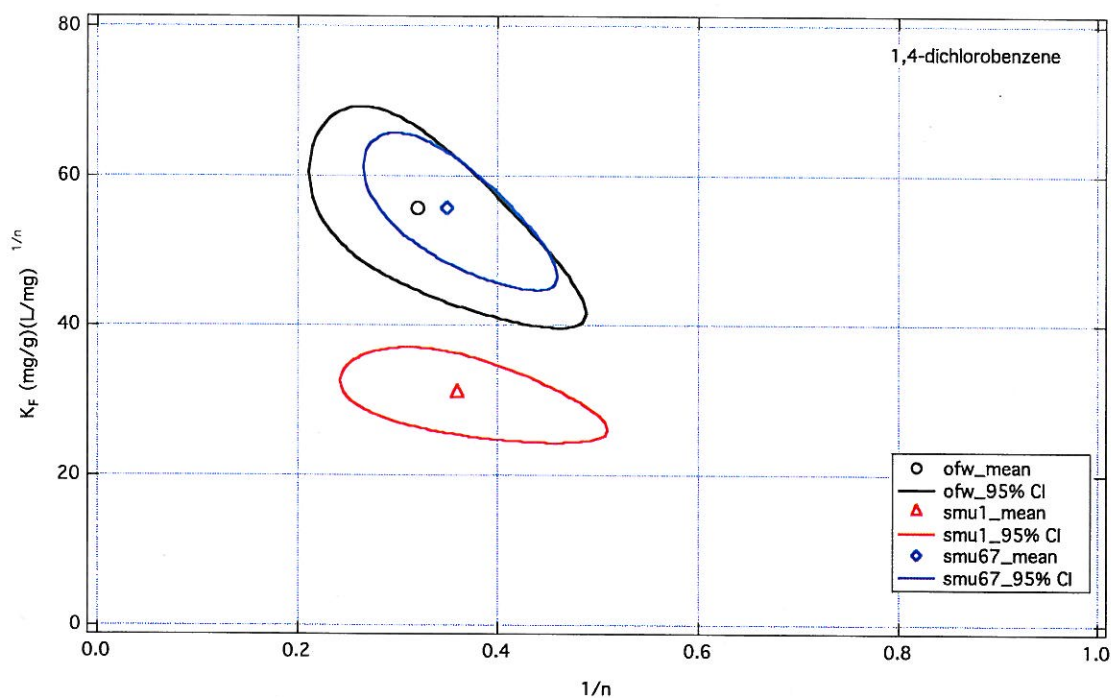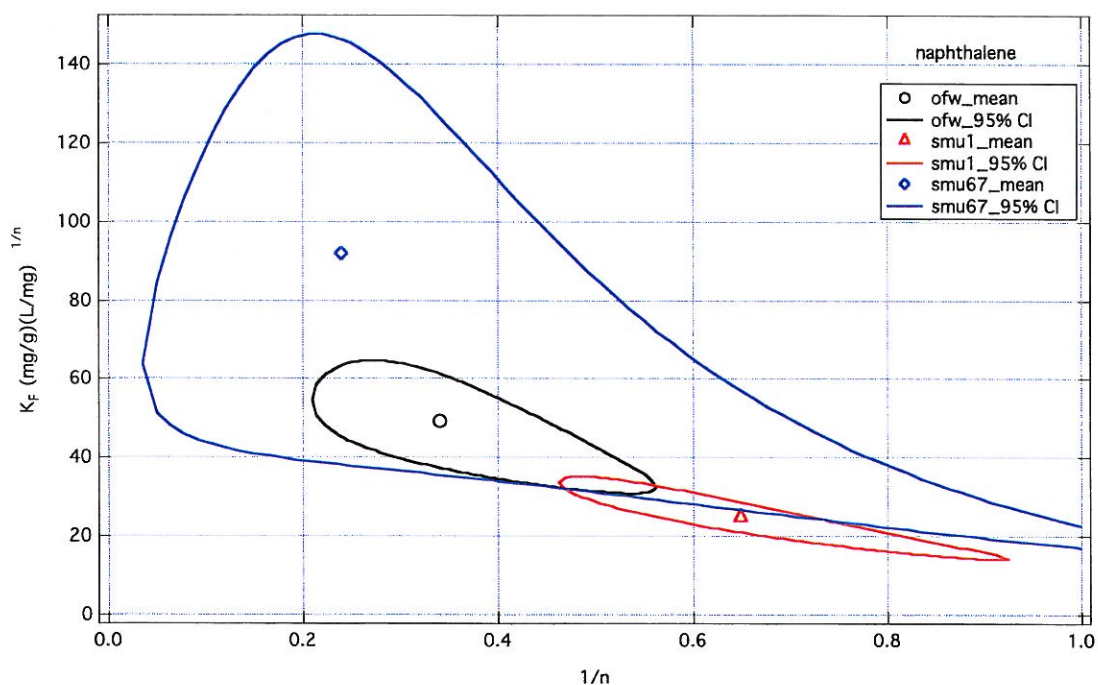

Figure A6. K_F and 1/n means and their 95% joint confidence intervals for 1,4-dichlorobenzene with OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.
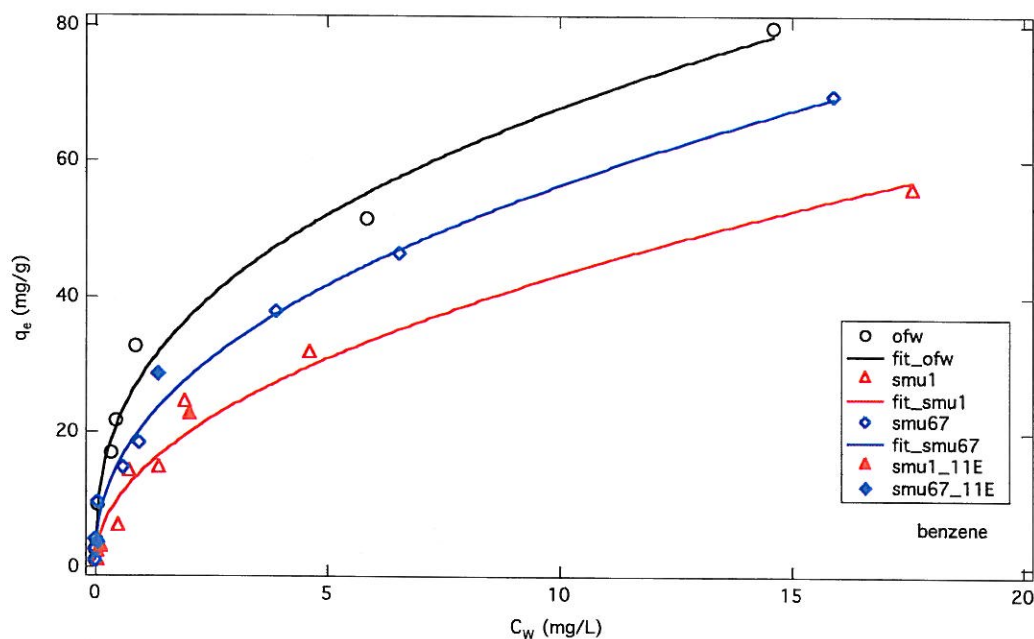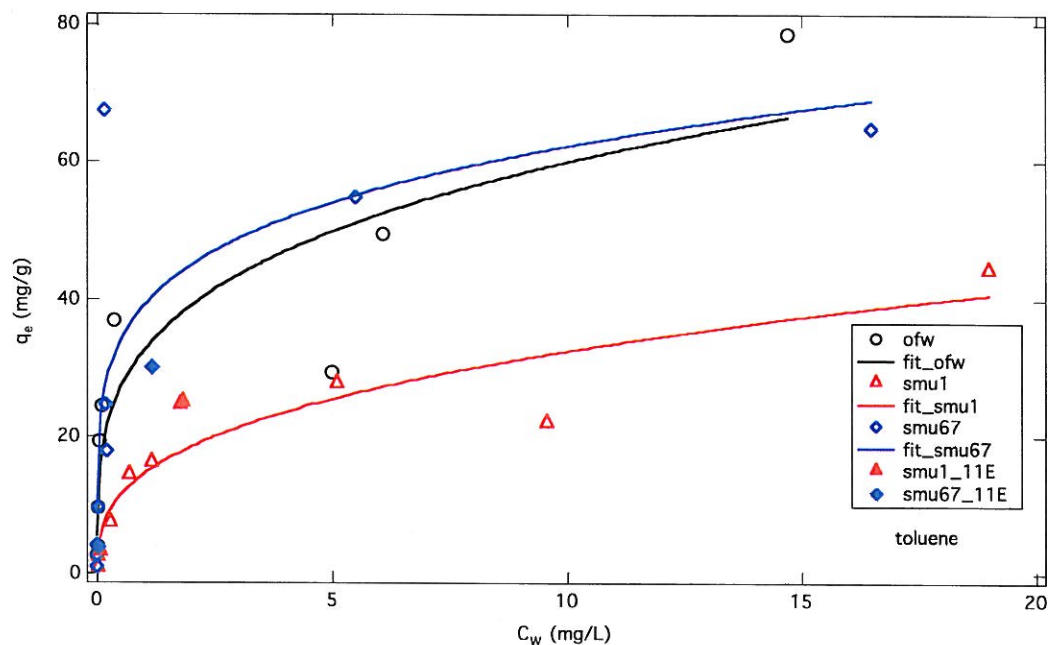
Figure A7. Benzene adsorption isotherms for OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E and the corresponding Freundlich model fits using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.
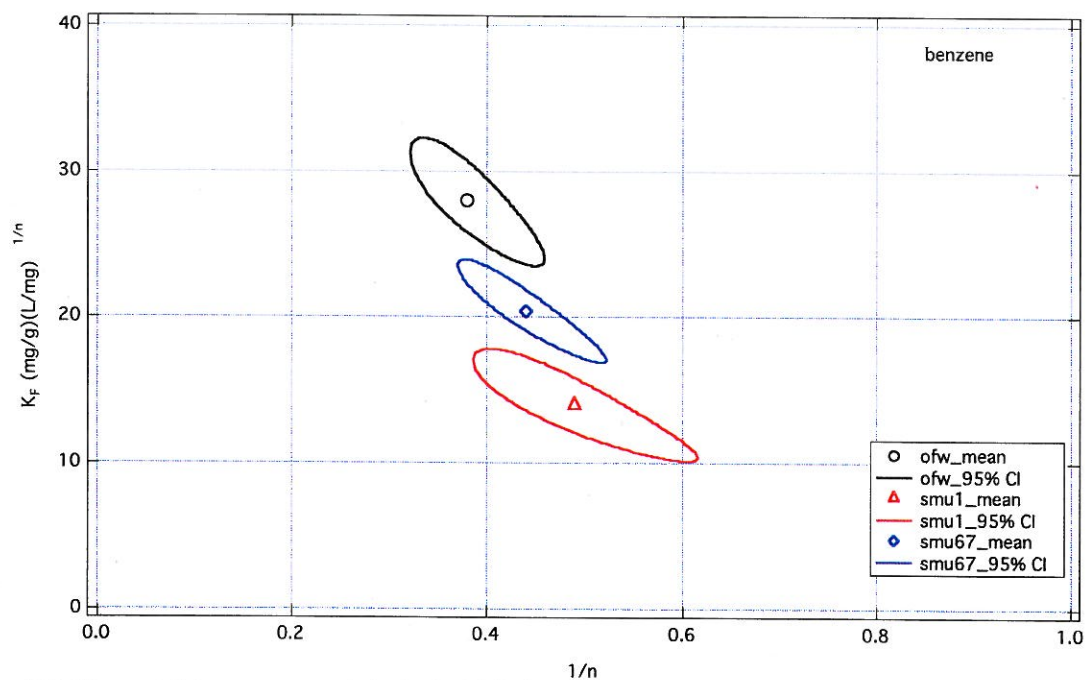
Figure A8. K_F and $1/n$ means and their 95% joint confidence intervals for benzene with OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.
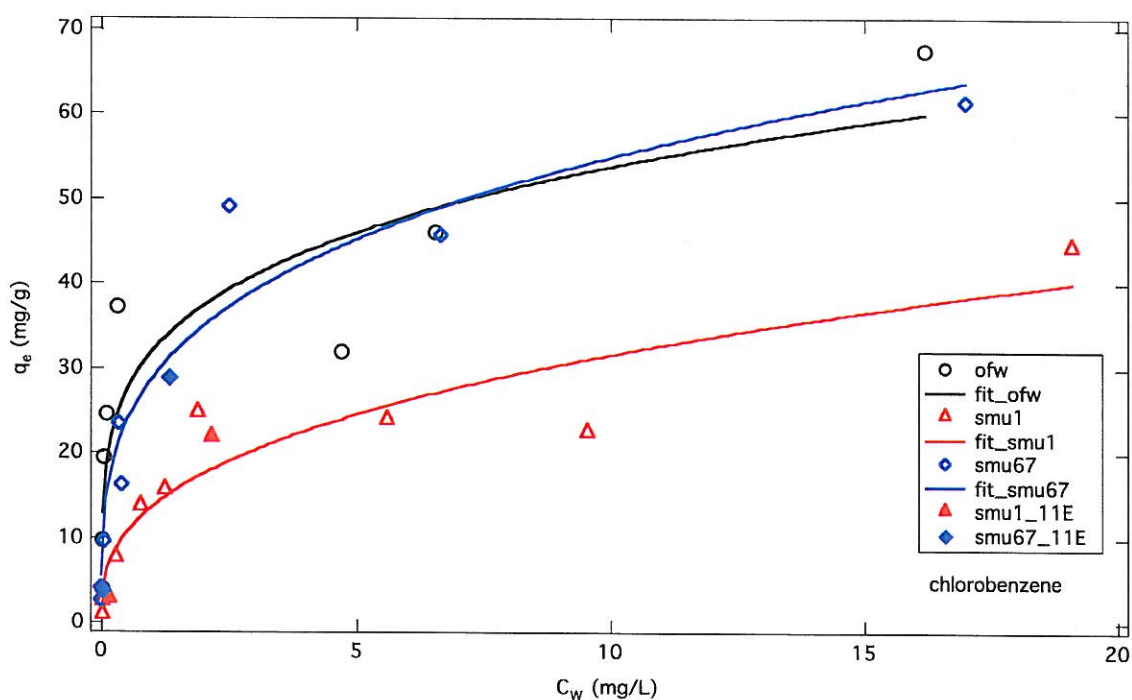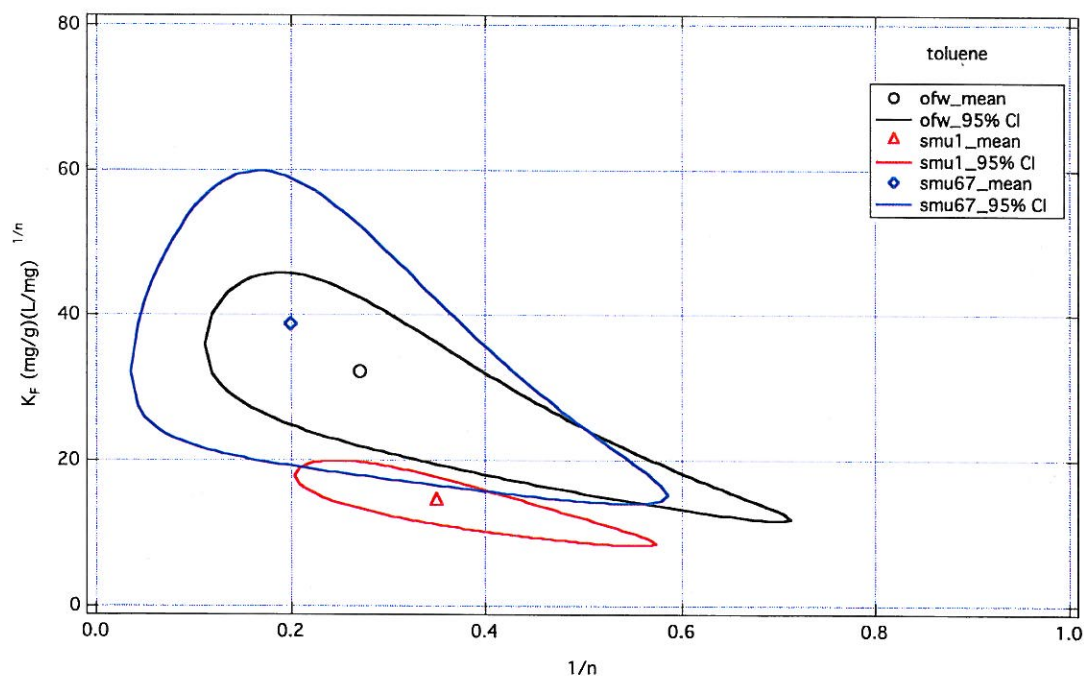
Figure A9. Chlorobenzene adsorption isotherms for OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E and the corresponding Freundlich model fits using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.
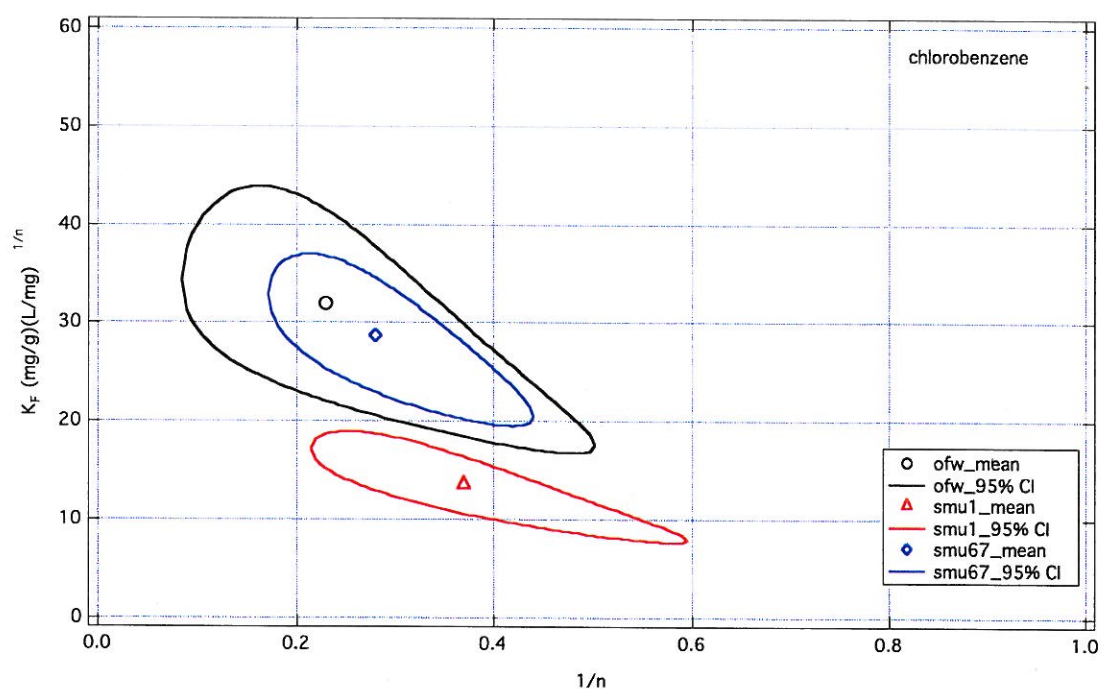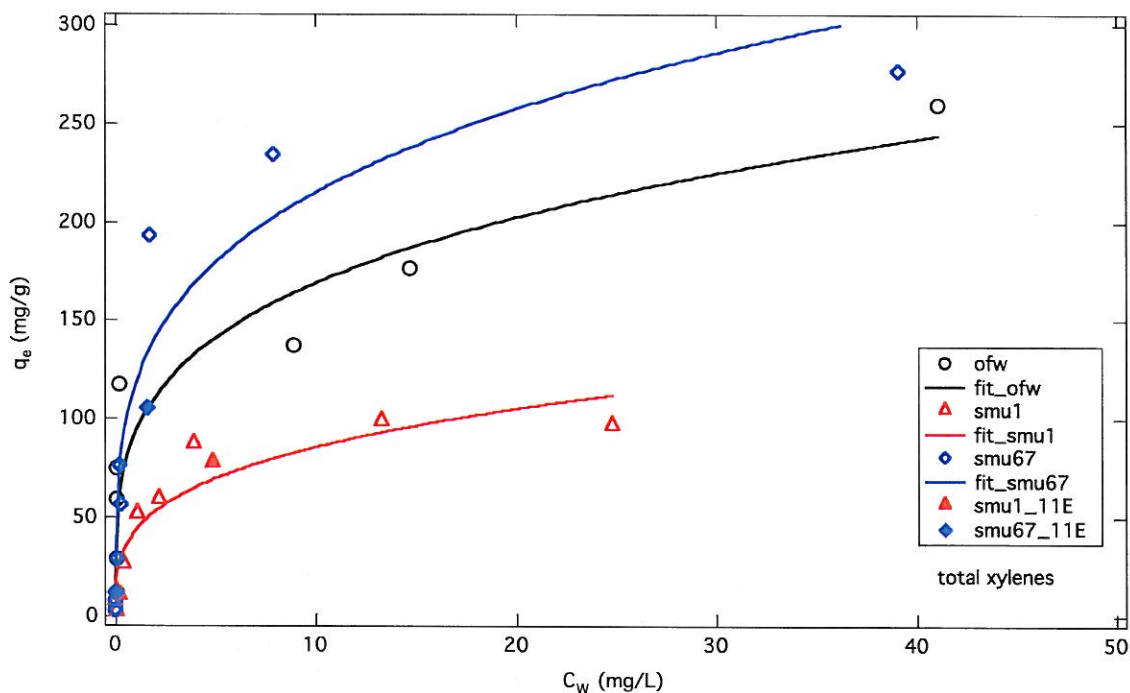

Figure A10. K_F and $1/n$ means and their 95% joint confidence intervals for chlorobenzene with OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.

Figure A11. Ethylbenzene adsorption isotherms for OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E and the corresponding Freundlich model fits using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.
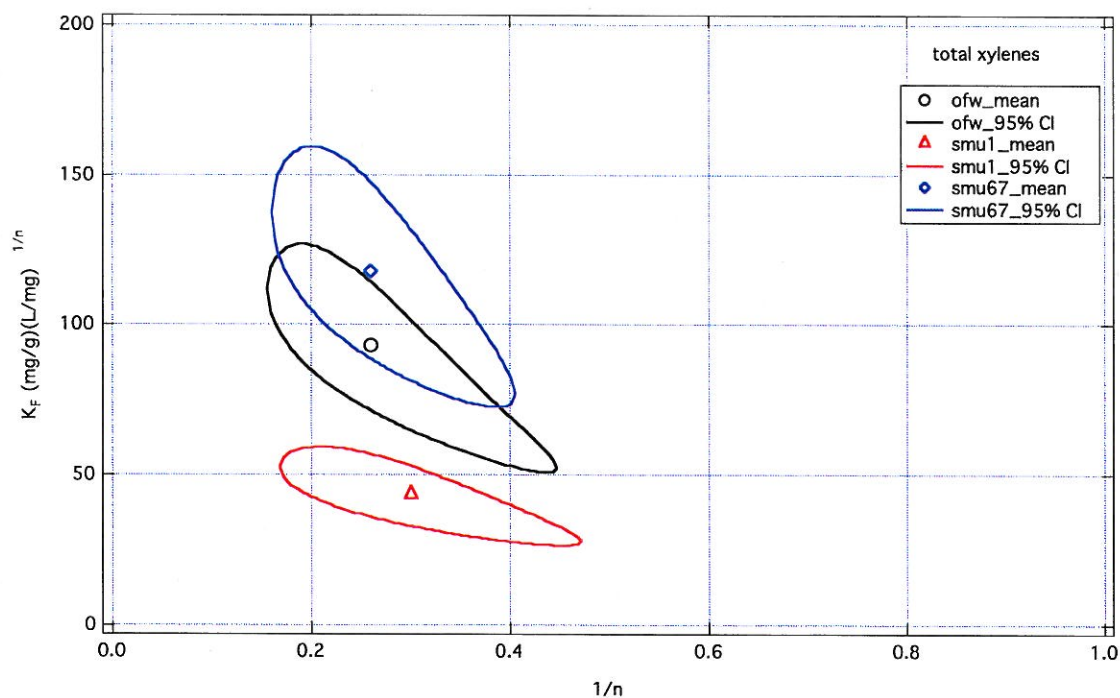

Figure A12. K_F and 1/n means and their 95% joint confidence intervals for ethylbenzene with OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.

Figure A13. Naphthalene adsorption isotherms for OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E and the corresponding Freundlich model fits using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.

Figure A14. K_F and $1/n$ means and their 95% joint confidence intervals for Naphthalene with OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.

Figure A15. Toluene adsorption isotherms for OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E and the corresponding Freundlich model fits using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.

Figure A16. K_F and $1/n$ means and their 95% joint confidence intervals for toluene with OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.

Figure A17. Total xylenes adsorption isotherms for OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E and the corresponding Freundlich model fits using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.

Figure A18. K_F and 1/n means and their 95% joint confidence intervals for total xylenes with OFW, SMU1, SMU1_11E, SMU67, and SMU67_11E using spiked concentrations for the initial aqueous phase concentration, C_0. SMU1_11E and SMU 67_11E are isotherm points determined in samples specially handled to avoid any exposure to air during handling.

Appendix B – Carbon Specifications Sheets

CENTAUR® 12x40

Granular Activated Carbon

Description

CENTAUR® 12x40 is a liquid phase virgin activated carbon that has been manufactured to develop catalytic functionality. The product is unique in that it concentrates reactants via adsorption and then promotes their reaction on the surface of the pores. CENTAUR® 12x40 is produced from bituminous coal using a patented process. Although it is not impregnated with metals or alkalis it displays the catalytic functionality of these materials. In most cases it can be reactivated and does not present the disposal concerns associated with impregnated carbons.

Applications

CENTAUR® 12x40 can be used in liquid phase applications for the promotion of oxidation, reduction, decomposition, substitution, and elimination reactions. Specific applications include chloramine, hydrogen sulfide, bromate reduction, and iron removal from drinking water. This product is particularly suited for use in residential and commercial water filters, for treatment of process water in the bottling and soft drink industries, and for aquarium water treatment. CENTAUR® 12x40 combines a fine pore structure for enhanced adsorption of trace contaminants with high catalytic activity for their elimination. Thermal reactivation is an option for recycle and reuse of this product to minimize operating costs and eliminate disposal concerns.

Design Considerations

CENTAUR® 12x40 is intended primarily for use in liquid phase systems to promote catalytic reactions. Depending on the reactant concentrations the required contact time is usually less than five minutes. The backwashed and drained density of the product is typically 33 lb./ft³. For additional information please contact the Calgon Carbon sales office in your region.

Specifications

Peroxide no., (max)	19
Iodine no., mg/g, (min)	825
Ash, by weight%, (max)	7
Moisture, wt%, as packed, (max)	3
Abrasion no., (min)	75
Apparent Density, g/cc, (min)	0.56
Mean Particle Diameter, mm	0.9 - 1.1
Screen Size, US Sieve Series, (max)	
Percent on 12 mesh	5
Percent through 40 mesh	4

Features

- Catalytic Activity
- Not Impregnated
- Improved Trace Organic Capacity
- High Hardness
- Works at Low Oxidant Levels
- Simple Equipment Design (no pumps or addition of chemicals required)
- Reduced Carbon Requirements
- Enhanced Performance

Benefits

- Smaller system size; lower capital requirements
- No safety concerns with exotherms or toxicity
- More capacity per unit volume; lower use rates
- Reduced fines and handling losses
- Wide applicability; can eliminate chemical addition
- Reduced operating costs
- Achieves greater degree of contaminant removal at reduced costs
- Reliable; handles spikes in concentration; no metering of chemicals

Carbon and Process Media

Visit our website at **www.calgoncarbon.com**, or call 800-422-7266 to learn more about our complete range of products and services, and obtain local contact information.
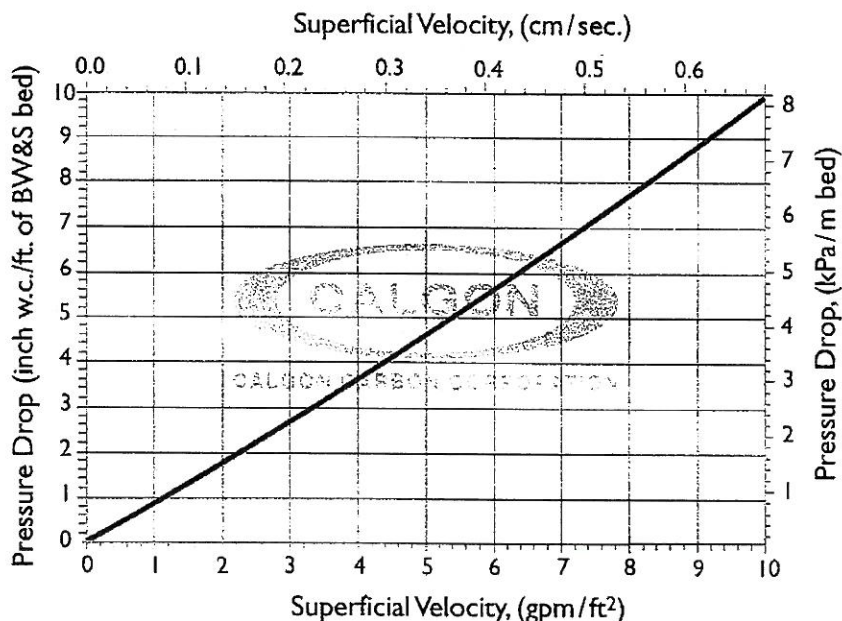
CPM-PB1072-0304

CENTAUR® 12x40

Granular Activated Carbon

Pressure Drop Curve

Nominal Pressure Drop
Liquid Downflow through CENTAUR® 12x40
(Based on Backwashed and Segregated Bed)

Packaging

33 lb. (15.0 kg) Kraft Bag
1,000 lb. Super Sack
225 lb. Fiber Drum
Bulk

Purchase of this product from Calgon Carbon Corporation includes a license under the following U.S. Patents: Numbers 5356849 and 5494869.

Safety Message

Wet activated carbon preferentially removes oxygen from air. In closed or partially closed containers and vessels, oxygen depletion may reach hazardous levels. If workers are to enter a vessel containing carbon, appropriate sampling and work procedures for potentially low oxygen spaces should be followed, including all applicable federal and state requirements.

Limitations of Liability

The Supplier's liability and the Purchaser's exclusive remedy for any cause of action arising out of this transaction, including, but not limited to, breach of warranty, negligence and/or indemnification, is expressly limited to a maximum of the purchase price of spare parts or equipment sold hereunder. All claims of whatsoever nature shall be deemed waived unless made in writing within forty-five (45) days of the occurrence giving rise to the claim. In no event shall the Supplier for any reason or pursuant to any provision of the warranty be liable for incidental or consequential damages, or damages in excess of the purchase price, nor shall the supplier be liable for loss of profits or fines imposed by governmental agencies.

Visit our website at **www.calgoncarbon.com**

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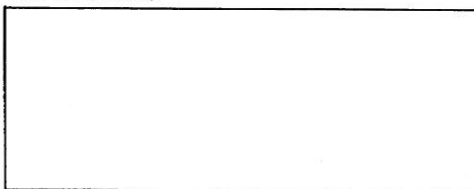
DSR-A 8X40

Granular Activated Carbon

Description

DSR-A is a grade of reactivated carbon designed for the removal of organic contaminants from industrial wastewater. The carbon is manufactured by the reactivation of bituminous coal-based products to produce a high-density, high surface area and durable product capable of withstanding repeated cycles of use and reactivation.

DSR-A is effective in a wide range of applications and fluctuating flows providing reliable removal of dissolved organic compounds. It is also screened prior to packaging to insure consistent performance and low pressure drop.

Applications

- Point source treatment to remove chemicals
- Pre-treatment to biological waste treatment systems
- Product recovery from wastewater
- Recycling wastewater
- Polishing effluent from biological waste treatment systems
- Providing total wastewater treatment

Pressure Drop Curve

Liquid down-flow through DSR-A 8x40 carbon

Design Considerations

The design of an activated carbon adsorption system is dependent on the adsorbate type, influent concentration, temperature, flow rate, performance objective, and other factors. Calgon Carbon has experience designing custom systems and can help evaluate the suitability of DSR-A to satisfy specific needs and assist in the design of an adsorption system. In addition to the supply of activated carbon, Calgon Carbon offers a complete line of standardized, pre-engineered adsorption systems. For additional information on adsorption capacity of organic compounds, please contact the Calgon Carbon Technical Sales Representative in your area.

Specifications

Iodine Number, mg/g (min)	750
Ash, weight % (max)	9
Moisture, weight % (max)	2
Apparent Density, g/cc (max)	0.60
Screen Size, US Sieve Series, weight %	
Smaller than 40 mesh (max)	5

Product Options

In addition to DSR-A, Calgon Carbon offers a variety of products and services to meet your treatment requirements:

Granular Carbon Products

- FILTRASORB® 300 & 400 - virgin liquid phase products
- React pH - for pH sensitive applications
- React AW - for acid purification

Equipment Products

- Standardized, pre-engineered adsorption systems capable of treatment flows from 1 gpm to 1400 gpm
- Custom engineered systems - to meet unique treatment requirements

Service Products

- Technical services including design assistance, calculations of carbon use rates, laboratory and pilot studies, start-up and operations assistance
- On-site exchange services and reactivation service reduce labor requirements and minimize disposal cost

DRS-A is not for use in potable water or food grade applications.

Carbon and Process Media

Visit our website at **www.calgoncarbon.com**, or call 800-422-7266 to learn more about our complete range of products and services, and obtain local contact information.

CPM-LC601-0804

DSR-A 8X40

Granular Activated Carbon

Features

Raw Material:
- Metallurgical grade, bituminous coal based

Miscellaneous:
- Reactivated product

- Recyclable product

- High surface area/pore structure

- Product is screened prior to packaging

Packing

1,000 lb. (453.6kg) Super Sack
Bulk Truck

Safety Message

Wet activated carbon preferentially removes oxygen from air. In closed or partially closed containers and vessels, oxygen depletion may reach hazardous levels. If workers are to enter a vessel containing carbon, appropriate sampling and work procedures for potentially low oxygen spaces should be followed, including all applicable Federal and State requirements.

If at any time our products or services do not meet your requirements or expectations, or if you would like to suggest any ideas for improvement, please call us at 1-800-548-1999. From outside the U.S. please call +1-412-787-6700.

Benefits

- Produces a strongly adsorbing pore structure for a broad range of contaminants and concentrations

- Economical alternative to virgin carbon
- Provides ultimate disposal of pollutants
- Eliminates landfill costs and concerns
- Propagates the cycle of responsible resource utilization
- Efficient in removing a wide range of dissolved organic compounds
- Reliable - accommodates variations in flows or concentrations
- Results in less fines and lower pressure drop
- Minimizes backwashing

Limitations of Liability

The Supplier's liability and the Purchaser's exclusive remedy for any cause of action arising out of this transaction, including, but not limited to, breach of warranty, negligence and/or indemnification, is expressly limited to a maximum of the purchase price of spare parts or equipment sold hereunder. All claims of whatsoever nature shall be deemed waived unless made in writing within forty-five (45) days of the occurrence giving rise to the claim. In no event shall the Supplier, for any reason or pursuant to any provision of the warranty, be liable for incidental or consequential damages or damages in excess of the purchase price, nor shall the Supplier be liable for loss of profits or fines imposed by governmental agencies.

DRS-A is not for use in potable water or food grade applications.

Visit our website at **www.calgoncarbon.com**
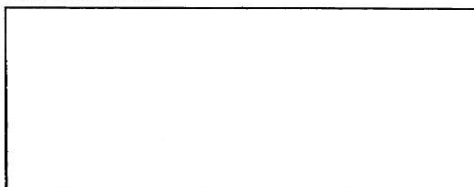
CALGON
CALGON CARBON CORPORATION
Calgon Carbon Corporation
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European Operations of Calgon Carbon Corporation
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Your local office

CPM-LC601-0804

FILTRASORB 400
Granular Activated Carbon

Calgon Carbon

Product Specification

Test	Specification		Calgon Carbon Test Method
	Min	Max	
IODINE NUMBER, mg/g	1000	-	TM-4,ASTM D4607
MOISTURE (AS PACKAGED), wt%	-	2	TM-1,ASTM D2867
ABRASION NUMBER	75	-	TM-9,AWWA B604
EFFECTIVE SIZE, mm	0.55	0.75	TM-47,ASTM D2862
UNIFORMITY COEFFICIENT	-	1.9	TM-47,ASTM D2862
US SIEVE SERIES			ASTM D 2862
12 US MESH [1.70 mm]	-	5	TM-8
wt%			ASTM D2862
< 40 US MESH [0.425 mm] (PAN)	-	4	TM-8
wt%			ASTM D2862

Calgon Carbon Corporation's activated carbon products are continuously being improved and changes may have taken place since this publication went to press. (2030-10/22/2008)

Safety Message

Wet activated carbon preferentially removes oxygen from air. In closed or partially closed containers and vessels, oxygen depletion may reach hazardous levels. If workers are to enter a vessel containing carbon, appropriate sampling and work procedures for potentially low oxygen spaces should be followed, including all applicable Federal and State requirements.

27-267-11/90

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TOG 20x50
Activated Carbon

CALGON
CALGON CARBON CORPORATION
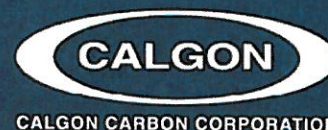
Specification

Test	Min	Max	Calgon Carbon Test Method
IODINE NO., mg/g	850	-	TM-4 or ASTM D 4607
ASH, wt%	-	8	TM-5
MOISTURE, wt%, as packed	-	2	TM-1 or ASTM D 2867
ABRASION NO.	70	-	TM-9
US SIEVE SERIES			ASTM D 2862
+20	-	3	
-50	-	1	

Safety Message

Wet activated carbon preferentially removes oxygen from air. In closed or partially closed containers and vessels, oxygen depletion may reach hazardous levels. If workers are to enter a vessel containing carbon, appropriate sampling and work procedures for potentially low oxygen spaces should be followed, including all applicable Federal and State requirements.

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