ATTACHMENT 2

PARTITIONING COEFFICIENTS AND SEDIMENT TO POREWATER CALCULATION BASIS

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PARTITIONING COEFFICIENT EVALUATION AND SEDIMENT TO POREWATER CALCULATION BASIS

Partitioning coefficients were employed in various aspects of the cap modeling evaluation to describe the equilibrium relationship between contaminant concentrations in the dissolved and sorbed-to-sediment phases within the cap materials as well as in the underlying sediments. This attachment discusses the basis for the selected partitioning coefficients as well as the calculations used to derive porewater concentrations from sediment data or vice versa.

The following sections describe the methods used to estimate partition coefficients for use in the model based on site-specific data or literature studies. Due to differences in data availability, varying methods were used to develop partition coefficients for the different classes of modeled CPOIs (i.e., VOCs, mercury, phenol, PAHs and PCBs). As such, the classes of CPOIs are discussed separately in the sections below.

1.0 PARTITIONING COEFFICIENT EQUATIONS

Partitioning coefficients, by definition, relate equilibrium porewater concentrations to sorbed-to-sediment concentrations. Since the laboratory-reported sediment concentrations for this project account for contaminants in all phases (i.e., sorbed, dissolved, vapor, and NAPL) per dry weight of sediment, the calculation of a partitioning coefficient must relate to this total sediment concentration. The partitioning equation derived from the EPA's Soil Screening Guidance (EPA, 1996) equation 22 of Part 2 (reorganized) for non-NAPL-impacted material is:

$$K_d = \frac{C_{sed}}{C_{pw}} - \frac{\theta}{\rho_b}$$

where

C_{sed} equals the total sediment concentration (dry weight) of the CPOI (µg/kg),
C_{pw} equals the core dissolved porewater concentration (µg/l),
θ is porosity, and
ρ_b is dry bulk density (kg/L).

For hydrophobic organics, the equation is:

$$K_{oc} = \frac{\left[\frac{C_{sed}}{C_{pw}} - \frac{\theta}{\rho_b} \right]}{f_{oc}}$$

where

f_{oc} is the mass fraction of organic carbon of the raw sediment.

The equation, as laid out, assumes there is no NAPL in the sample. The principal reason for doing this is that it is not possible to test for the presence of NAPL using a sample's CPOI

concentrations without first knowing the Koc values. Therefore, the use of this equation would provide an overestimate of mean Koc values since a NAPL-impacted sample would exhibit a higher total sediment concentration than what would be indicated by equilibrium with its porewater phase. This issue affects the assessment of sediments in SMU 1, where NAPL has been observed. However, it is not expected that the presence of NAPL in some of the samples would materially affect the overall estimates, given the large number of usable data pairs in SMU 1 and the lognormal distribution of the data.

As noted above, partition coefficients relate equilibrium porewater concentrations to sorbed-to-sediment concentrations, not to the total sediment concentration as measured in the PDI sampling program. While this distinction, which suggests it is important to account for contaminant mass in the dissolved-phase of a sample, is meaningful for low sorptivity compounds, it is not actually important for highly sorptive compounds. This is due to the fact that for highly sorptive compounds, such as PAHs and PCBs, very little contaminant mass is held in the dissolved-phase of a sediment sample. Therefore in calculating PAH and PCB porewater concentrations from measured sediment concentrations, it is only necessary to also know the f_{oc} of the sediment sample. This procedure actually adds a very small element of conservatism to the estimation of porewater concentration, since complete accounting for the dissolved-phase mass in the sample would lower the estimate of porewater concentration.

For PAHs and PCBs, the equation for calculating the local porewater concentration is:

$$C_{pw} = \frac{C_{sed}}{K_{oc} \bullet f_{oc}}$$

2.0 DEVELOPMENT OF SITE SPECIFIC PARTITIONING COEFFICIENTS FOR VOCs

The analysis of paired sediment and porewater samples, generated via centrifugation procedures in Phases I through VI of the PDI, provided an opportunity to estimate site-specific partitioning coefficients for Onondaga Lake sediments, in the form of an organic carbon-water partitioning coefficient (K_{oc}) for Benzene, Toluene, Ethylbenzene, Xylene, Tri-cholorobenzene, Di-chlorobenzene, chlorobenzene and naphthalene. This section describes the sample processing procedures, and the calculations and analysis methods used to estimate the partitioning coefficients from the sample data (including filtering of the dataset to eliminate unusable results). Results are presented in graphical and tabular formats. The site specific partitioning coefficients generated as described in the following subsections were used in cap modeling to predict partitioning within the sand cap materials used in the chemical isolation and habitat layers, as well as within the underlying sediments for the numerical modeling.

2.1 SAMPLE COLLECTION AND PROCESSING

In Phase I of the PDI, samples of sediment and porewater were collected at 33 locations in SMU 1 and SMU 6. No paired sampling was conducted in Phase II for the purpose of estimating partitioning coefficients. The total number of sample pairs was greatly increased by work

conducted in Phases III through IV. In total over 1,000 samples pairs were collected across the remediation areas over the course of the PDI.

In Phase I, three cores were collected at each location and depth interval to provide material for sediment and porewater analyses. Upon receipt in the lab, the cores were opened and freestanding water decanted and discarded. No homogenization of sediments occurred. One core was used for raw sediment analysis, and the other two were used to fill between four and six centrifuge bottles, which were then centrifuged to generate porewater. All generated porewater was then composited prior to sub-sampling for the various analyses. One of the centrifuged bottles provided material for the dewatered sediment analysis. A sample pair from Phase I, for the purposes of calculating partition coefficients, was comprised of a dewatered sediment sample and an associated porewater sample.

In Phases III through VI, long cores were cut into 2-ft. sections. Upon receipt in the lab the 2-ft. cores were opened, and freestanding water carefully decanted for compositing with porewater subsequently generated by centrifugation of the sediment sample. A portion of the sediment sample from the top of the core was sub-sampled for raw sediment analyses. The balance of the sediment from the 2-ft. core was weighed and placed in centrifugation bottles. The sample bottle was centrifuged and supernatant water was separated and collected. The aqueous sample for volatile organic compounds (VOCs) was then centrifuged again, decanted and placed in volatile organic analyte (VOA) vials for analysis. A sample pair from Phases III through VI, for the purposes of calculating partition coefficients, was comprised of a raw sediment sample and an associated porewater sample.

2.2 AREA-WIDE PARTITION COEFFICIENT ANALYSIS

The partition coefficients estimated from the site data used in the cap modeling effort were developed based on the hypothesis that a single mean partition coefficient could be used to describe the site data within a given area, and that sample-to-sample differences within these areas stem primarily from measurement variability. This is consistent with the fact that partition coefficients are often taken to be chemical-specific properties (after properly normalizing for organic carbon content as appropriate). To estimate the effective partition coefficient for an area containing numerous sediment-porewater sample pairs, the sorbed-to-sediment phase concentration was first calculated for each sample pair. This concentration was calculated by taking the reported total dry weight concentration (Csed in the equations above) and subtracting off the porewater mass (using the measured corrected porewater concentration (see Table A1.2), bulk density, and porosity):

$$C_s = C_{sed} - \left(C_{pw} \frac{\theta}{\rho_b} \right)$$

where Cs is the sorbed-to-sediment phase concentration of a CPOI (µg/kg).

After calculating Cs for all samples within an area, the concentrations were normalized by foc and plotted against their paired porewater concentrations. Plotting these values against

porewater concentration in linear space produces a relationship with a slope that is equivalent to Koc. Thus, a least squares regression analysis can be used to calculate the Koc for a given area (and the confidence interval of the regression line can describe its variability). Preliminary analyses indicated that such regressions could be strongly influenced by the highest concentration data pairs. Given that porewater concentrations within the cap would be expected to be within a lower range, the underlying regression equation (Cs/foc = Koc*Cpw) was log-transformed to remove the effect of a few high concentration samples driving the regression and therefore all measurements were treated as having the same standard error. By doing this, it was equivalent to the model: log (Cs/foc) = log (Koc) + log (Cpw). Least squares regression formulae were derived for this case, which produced a best estimate of log Koc and an associated standard error. The log-transform was judged appropriate since Koc values are typically found to be lognormally distributed (and hence typically reported as log Koc).

For the cap modeling effort, the analysis method described above was used to estimate a Koc value for each modeled VOC. The data from Remediation Areas A and E were pooled together, and data from Remediation Area D were analyzed separately since previous analyses had suggested partitioning within ILWD materials differs from that in sediments from other areas of the lake. Data from Remediation Areas B and C were compared with these two groupings and found to exhibit a relationship between particulate and dissolved phase that more closely resembled that of the ILWD. As such, the data from Remediation Areas B, C, and D were combined for the purposes of calculating Koc values for the VOCs.

2.3 FILTERING OF DATA PAIRS

After compiling the data from Phases I through VI, any data pair (sediment and porewater) which involved a non-detect result was excluded from the analysis, given the uncertainty of the resulting calculation. Additionally, any result which produced a negative value for the sorbed-to-sediment concentration from the above equation was deleted. This would occur when the CPOI mass measured in the porewater phase exceeded the total CPOI mass measured in the bulk sediment (i.e., solids plus porewater). Since such a scenario—where the total contaminant mass (bulk sediment concentration) is insufficient to produce the measured mass in the dissolved-phase (porewater concentration)—is not possible, even though the analytical results support it, the assumption is that there is some error in one or more of the analyses, and therefore the data pair does not allow for calculation of a partitioning coefficient. Such occurrences were rare (≈ 8% of sample pairs), with nearly half involving benzene, the least sorptive of the compounds considered in this analysis.

In an effort to assess the potential effects of surface water on porewater concentrations in the surficial samples, the data set was also sorted and samples collected in the 0-1 ft interval were eliminated.

2.4 RESULTS

Following the filtering step described in Section 2.3, the log-transformed regression analyses described in Section 2.2 were conducted. Figures 1 through 12 present these regressions, the resulting Koc values, and standard errors (derived from the confidence limit on the regression

line). The data and regression lines on Figures 1-12 indicate that while there is scatter in the data (the degree to which varies by CPOI), when taken together, data from Areas A/E and from Areas B/C/D exhibit a relatively consistent relationship between sorbed-to-sediment and porewater concentrations, with standard errors of regression equal to or less than 0.1 log units (for CPOIs with at least 50 sample pairs or more). The presence of such a relationship is consistent with the concept of the area-based approach used in this analysis. The resulting Koc values tend to differ between Areas B/C/D and Areas A/E, with the former group's values being somewhat higher (on average approximately one-third of a log value across CPOIs) – this difference is consistent with results from previous analyses and likely attributable to the effects of elevated pH within the ILWD materials and/or differences related to the solid matrix of waste material versus natural sediment.

For each CPOI, Table 1 presents the number of data pairs, the resulting Koc values and associated standard errors, and includes a comparison to a range of literature values. The differences in resulting Koc values among these CPOIs follow expected trends (e.g., Koc of chlorbenzenes increases with chlorination level from monochlorobenzene to dichlorobenzenes to trichlorobenzenes), and the calculated values are within the range of the literature values.

As such, the values listed in Table 1 for Areas A/E were used to describe the partitioning of VOCs to sand capping materials in all areas of the Lake. These same values were used to simulate partitioning of VOCs within the underlying sediment in the application of the numerical model to Remediation Areas A and E. Likewise, the Koc values estimated from the Remediation Area B/C/D data set were used to describe partitioning within the underlying sediment/waste materials within those areas, for use in the transient numerical modeling. The differences in Koc between ILWD and non-ILWD materials are believed to be due to elevated pH and/or solid matrix differences between ILWD materials and natural sediment as discussed above; however, the Koc values derived from non-ILWD data were used to simulate sorption to sand capping materials within the ILWD and Remediation Areas B and C because the pH amendment to the cap is designed to lower pH in the isolation layer. Thus, the amended cap approach within high pH areas of the lake is expected to eliminate these effects and result in partitioning behavior within the isolation layer that is consistent with that in other capped areas of the lake.

2.5 MERCURY PARTITIONING COEFFICIENTS

Unlike VOCs, the partition coefficients used for simulating mercury were expressed as a Kd value, since organic carbon is not the only significant sorbing phase for mercury. The values used in the cap modeling conducted for mercury were developed as follows:

- Kd values for the underlying sediment (used in the transient numerical modeling) were calculated from the values for paired sediment / porewater data (i.e., using the data sets/filtering methods described above for VOCs), and the average log Kd for each area was used in the model. Separate values for log Kd were calculated for Remediation Areas A, B/C, D, and E, and are presented in Table 2. The variability in estimated Kd values among these Remedial Areas is believed to reflect differences in the nature of the materials, including elevated pH. This simpler method for

calculating the sediment Kd (as compared to the regression-based approach used for VOCs) was used since this parameter only describes the partitioning within the underlying sediment in the numerical model, which has much less influence on predicted concentrations in the cap than the Kd values used to describe partitioning onto capping materials (which are described below).

- Kd values for sorption of mercury onto sand capping material in Remediation Areas A and E were estimated based on the data from isotherm studies conducted using porewater from SMU 6/7 sediments (Parsons, 2008). These data were found to best be described by a Freundlich isotherm equation (Parsons, 2008). As such, the best fit SMU 6/7 isotherm equation was used to calculate a Kd based on the maximum measured porewater concentration in each modeling area. This approach is conservative because at the lower concentrations that would be present in the cap (as compared to the maximum underlying porewater concentration), the SMU 6/7 isotherm relationship produces Kd values that are higher than those calculated for that maximum porewater concentration (thus resulting in even slower transport). The resulting log Kd values for each modeling area within these two Remediation Areas are presented in Table 2.

- Kd values for sorption onto sand capping material in Remediation Areas B, C, and D were also derived from data generated from isotherm studies performed with SMU 1 porewater (Parsons, 2008). These data were found to follow a linear relationship, so a regression-based approach was used, in which the slope of a linear regression line fit through a plot of sorbed-to-sediment phase mercury concentrations versus porewater concentrations was used to estimate the Kd. The resulting log Kd value is presented in Table 2.

In areas where the isolation cap material will consist of sand mixed with activated carbon as a sorptive amendment, the Kd values described above do not account for any increased sorption of mercury that may occur as a result of the amendment.

3.0 PHENOL PARTITIONING COEFFICIENT

Site-specific porewater data for phenol were limited given the large volumes required or analysis. Additionally, sediment-porewater pairs were not available for the direct estimate of a phenol partitioning coefficient. In lieu of a site specific Koc value the NYSDEC Technical Guidance (NYSDEC, 1999) value for phenol was used to describe partitioning of phenol to both the underlying sediment, to supplement existing porewater data, and to simulate partitioning to the cap material. Similar to VOC compounds, phenol partitioning in the cap model is simulated through use of a Koc value. The Technical Guidance document directly provides an octanol/water partition coefficient or Kow. The Technical Guidance suggests that when applying the equilibrium partitioning methodology Koc and Kow values are very similar, for un-chlorinated phenol the Log Kow value is 2.0 (NYSDEC, 1999). This value was used for phenol in all model simulations.

4.0 PCB AND PAH PARTITIONING COEFFICIENTS

Site specific porewater data were not available for PAH and PCB model simulations. Porewater collected during the 2002/2003 groundwater upwelling investigation were mostly non-detect for PAHs and PCBs (Parsons, 2003 and Parsons, 2007). In the absence of site-specific data for PAHs and PCBs a literature review of partitioning of these compounds was conducted. This information was used to calculate initial porewater concentrations in model simulations as well as to describe partitioning to cap materials.

Modeling conducted during the Feasibility Study had used Kow values reported in New York State Department of Environmental Conservation Guidance (NYSDEC, 1999) as estimates of Koc and measured foc values to estimate the concentrations of PAHs and PCBs in sediment porewater beneath the cap. This same approach was taken in the here when modeling fate and transport of PAHs and PCBs within the sand capping material; however, a growing body of literature indicates that the conventional approach of calculating PAH and PCB porewater concentrations in underlying sediments will overestimate actual PAH or PCB porewater concentrations (for discussions see Arp et al., 2009; Hawthorne et al., 2006; and McGroddy et al., 1996). The primary cause of this discrepancy is that natural sediments are composed of different types of organic carbon, with some phases of organic carbon ("hard" carbon) sorbing hydrophobic contaminants stronger but more slowly than other phases ("soft" carbon). For purposes of calculating initial porewater concentrations in the underlying sediment, measured foc values and field-derived effective Koc values measured in natural sediment at other sites that account for strongly-sorbing fractions of sediment, were used. Addendum 1 provides a detailed description of the literature review and partitioning coefficient recommendations.

Recommendations from the evaluation presented in Addendum 1 support the use of corrected PAH and PCB Koc values to most accurately model and predict porewater PAH and PCB concentrations within the underlying Lake sediment in the absence of direct measurements. Based on the data presented in Addendum 1 an increase in effective Koc values of 10X from PAH Kow values is recommended for derivation of PAH porewater concentrations in the non-ILWD impacted sediments (which was taken to consist of Remediation Areas A and E). Likewise, based on the data presented in Addendum 1, an increase in effective Koc values of 5X from PCB Kow values is recommended for derivation of PCB porewater concentrations in the non-ILWD impacted sediments. Effective Koc values are based on the values presented in the NYSDEC Technical Guidance. Partitioning in the underlying sediments of the ILWD and within Remediation Areas B and C is based directly on the Technical Guidance values, as the unusual pH and DOC conditions in those areas create conditions at variance with the natural sediments and so are not addressed by the literature cited above. Partitioning to the cap material is simulated in the model using uncorrected values from the Technical Guidance. Fixed values were used for PAHs and PCBs in all model simulations.

5.0 REFERENCES

NYSDEC, 1999. Technical Guidance for Screening Contaminated Sediments. January 1999.

Parsons, 2003. Groundwater Upwelling Investigation for Onondaga Lake, Syracuse New York. Prepared for Honeywell, Morristown, New Jersey. Syracuse, New York.

Parsons, 2007. Onondaga Lake Pre-Design Investigation, Phase I Data Summary Report. Prepared for Honeywell, Morristown, New Jersey. Syracuse, New York.

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

USEPA, 1996. Soil Screening Guidance: Technical Background Document, Part 2, page 36, EPA/540/R-95/128, May 1996.

TABLES

Table 1. Summary of log K_{OC} values determined by regression analysis, compared to literature-based values.

	Model Areas B,C, and D			Model Areas A & E			Range of log K_{OC} from regression-based formulas in literature[1]		Range of log K_{OC} from published studies (Mackay, et al.)[2]	
	No. of data pairs	log K_{OC}	std error of regression	No. of data pairs	log K_{OC}	std error of regression	Min	Max	Min	Max
Benzene	192	1.78	0.040	131	1.69	0.051	1.63	1.97	1.26	2.01
Toluene	278	2.34	0.030	140	2.18	0.059	2.31	2.64	2.25	2.39
Ethylbenzene	187	2.77	0.041	127	2.59	0.045	2.77	3.10	2.21	
Xylene	306	2.76	0.029	188	2.53	0.046	2.77	3.10	2.22	2.52
Chlorobenzene	197	2.51	0.037	143	2.29	0.056	2.46	2.79	1.92	2.73
1,2-Dichlorobenzene	191	3.00	0.036	77	2.64	0.073	3.00	3.32	2.26	3.51
1,3-Dichlorobenzene	14	2.77	0.20	126	2.72	0.066	3.00	3.32	2.14	4.60
1,4-Dichlorobenzene	200	3.08	0.038	99	2.60	0.068	3.00	3.32	2.78	3.26
1,2,3-Trichlorobenzene	7	3.67	0.15	1	3.21	--	3.87	4.19	2.30	4.70
1,2,4-Trichlorobenzene	39	3.54	0.057	32	2.82	0.141	3.87	4.19	3.09	4.70
1,3,5-Trichlorobenzene	--	--	--	52	3.05	0.100	3.87	4.19	2.85	5.10
Naphthalene	331	2.86	0.032	114	2.47	0.077	2.99	3.31	2.66	5.00

Notes:

1. Range from several representative regression formulas that correlate K_{OW} to K_{OC} (log K_{OW} values presented in Table 1 of NYDEC's *Technical Guidance for Screening Contaminated Sediments* (http://www.dec.ny.gov/docs/wildlife_pdf/seddoc.pdf) were used).

   These formulas were pooled from the following studies:
   - DiToro, D.M., 1985. A Particle Interaction Model of Reversible Organic Chemical Sorption. *Chemosphere 14* :1503-1538.
   - Karickhoff, S.W., 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soil. *Chemosphere 10:* 833-846.
   - Means, J.C., S.G. Wood, J.J. Hassett and W.L. Banwart, 1980. Sorption of polynuclear aromatic hydrocarbons by sediments and soils. *Environmental Science & Technology 14:* 1524-1528.
   - Shimizu, Y., S.Yamazaki and Y. Terashima, 1992. Sorption of anionic pentachlorophenol (PCP) in aquatic environments: The effect of pH. *Water Science & Technology 25:* 41-48.
2. Range of values taken from *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals,* Donald Mackay, Wan Ying Shiu, and Kuo Ching Ma, 1992. Only values from studies utilizing field measurements were included.

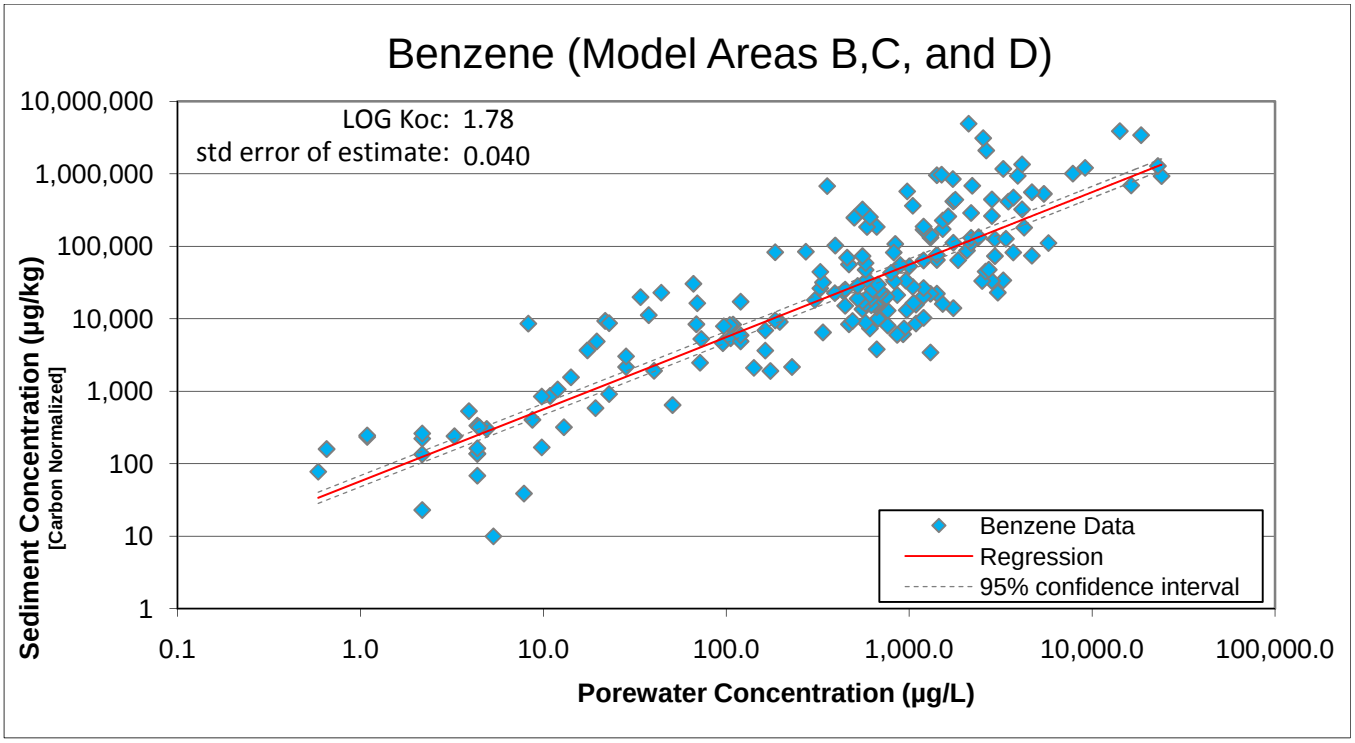
Table 2. Summary of log K_d values for Mercury.

	Mercury log Kd	
	Underlying Sediment	Sand Cap
Remedial Area A-1	4.7	3.3
Remedial Area A-2		2.8
Remedial Areas B & C	2.5	3.1
Remedial Area D	3.1	3.1
Remedial Area E-1	4.2	3.3
Remedial Area E-2		3.8
Remedial Area E-3		3.2

FIGURES

Relationship between porewater concentration and carbon-normalized sediment concentration (with log-transformed regression)

BENZENE – Model Areas B, C, and D



BENZENE – Model Areas A & E

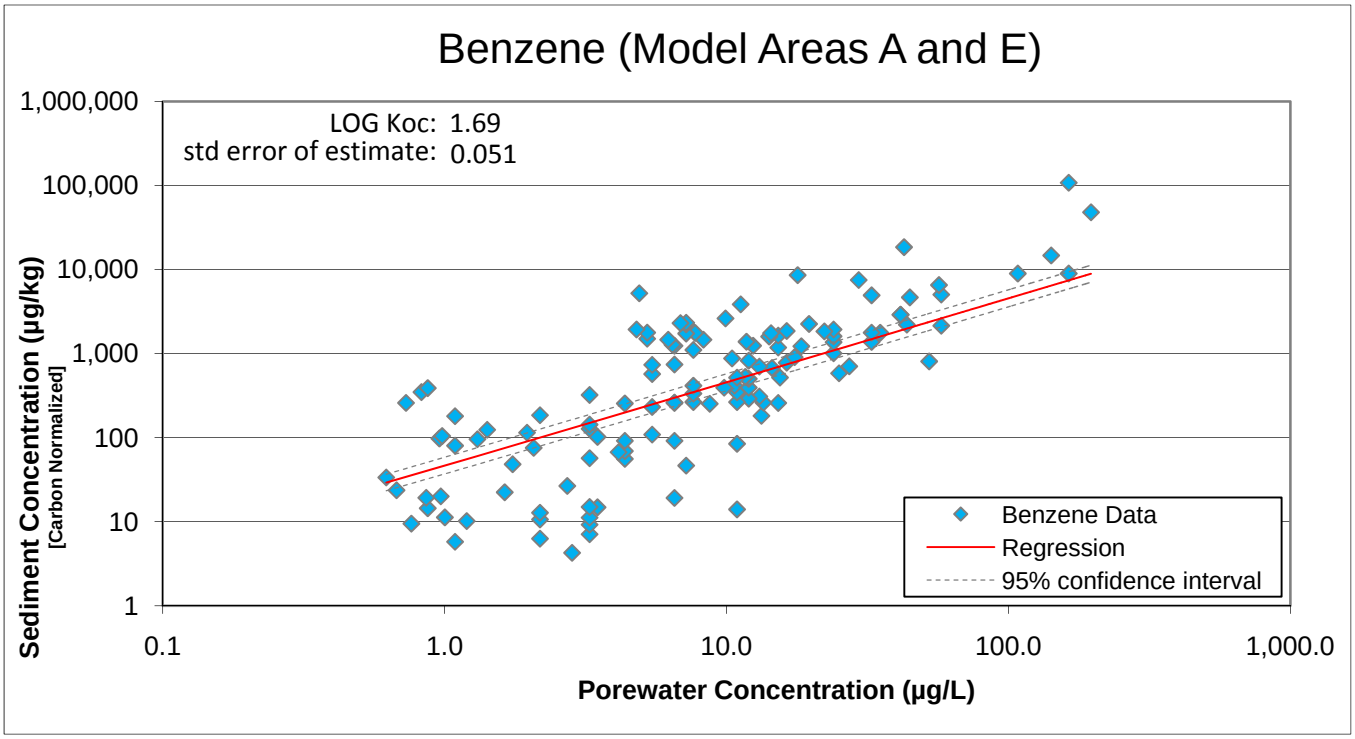
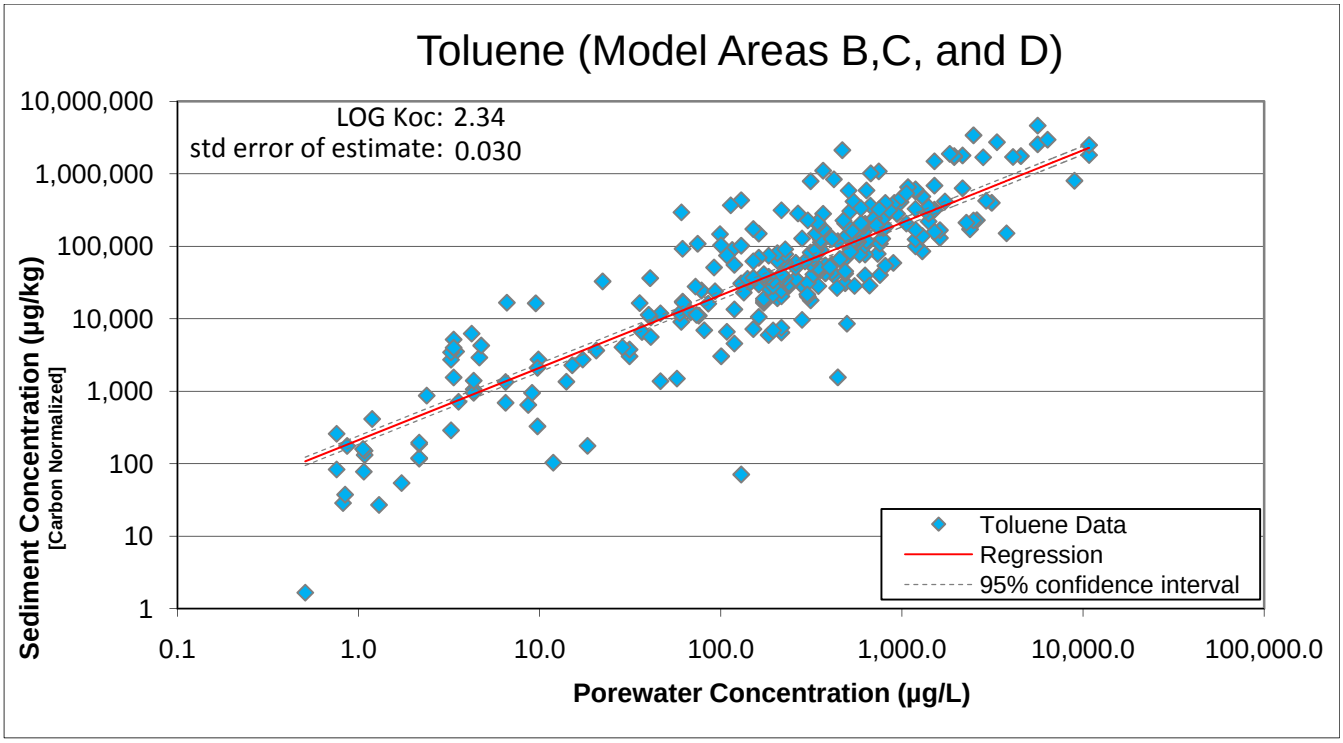


Figure 1. Relationship between *benzene* porewater concentration and carbon-normalized sediment concentration (with log-transformed regression).

TOLUENE – Model Areas B, C, and D



TOLUENE – Model Areas A & E

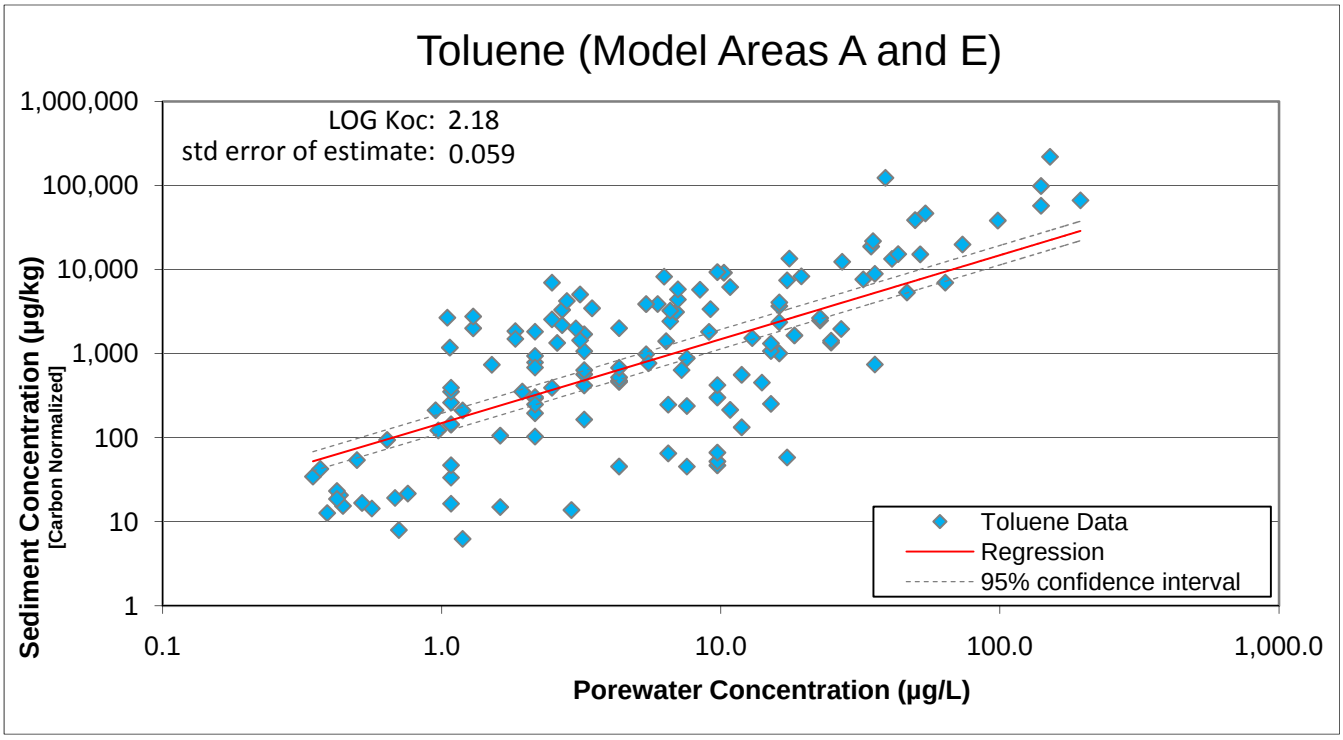
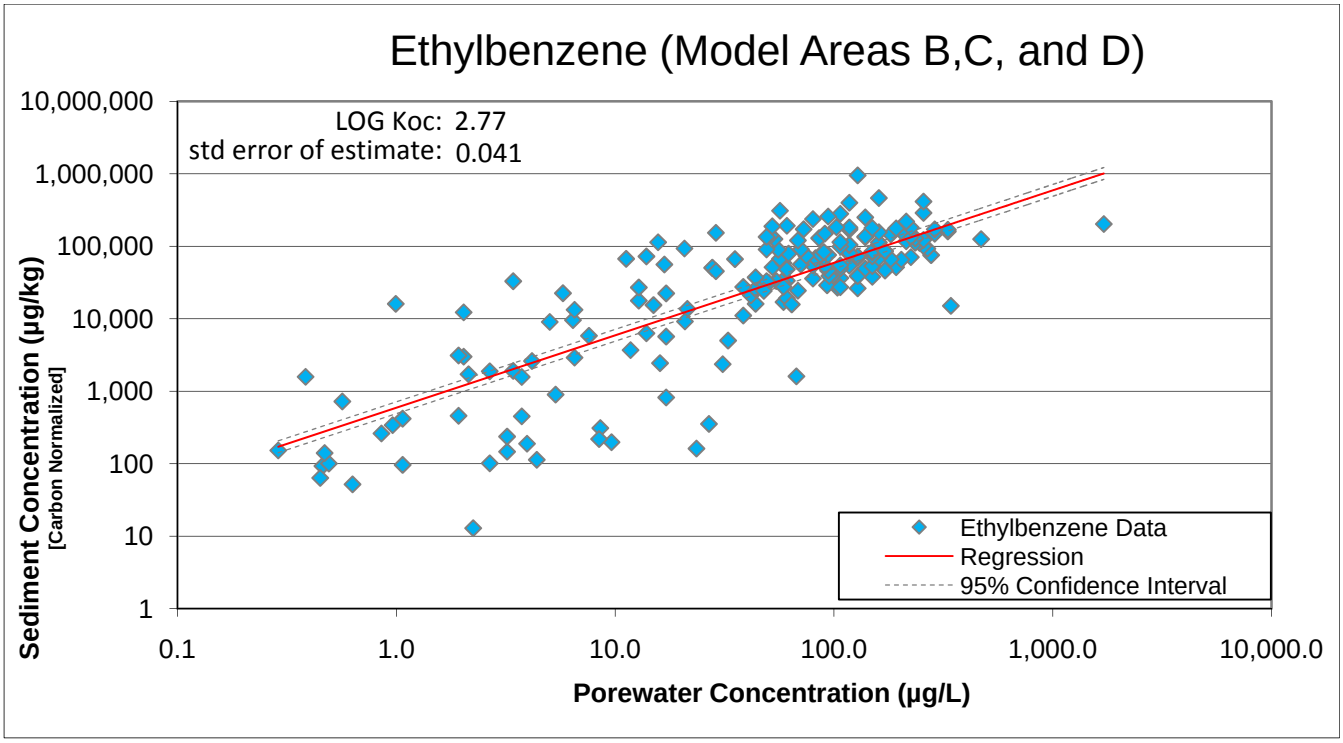


Figure 2. Relationship between *toluene* porewater concentration and carbon-normalized sediment concentration (with log-transformed regression).

ETHYLBENZENE – Model Areas B, C, and D



ETHYLBENZENE – Model Areas A & E

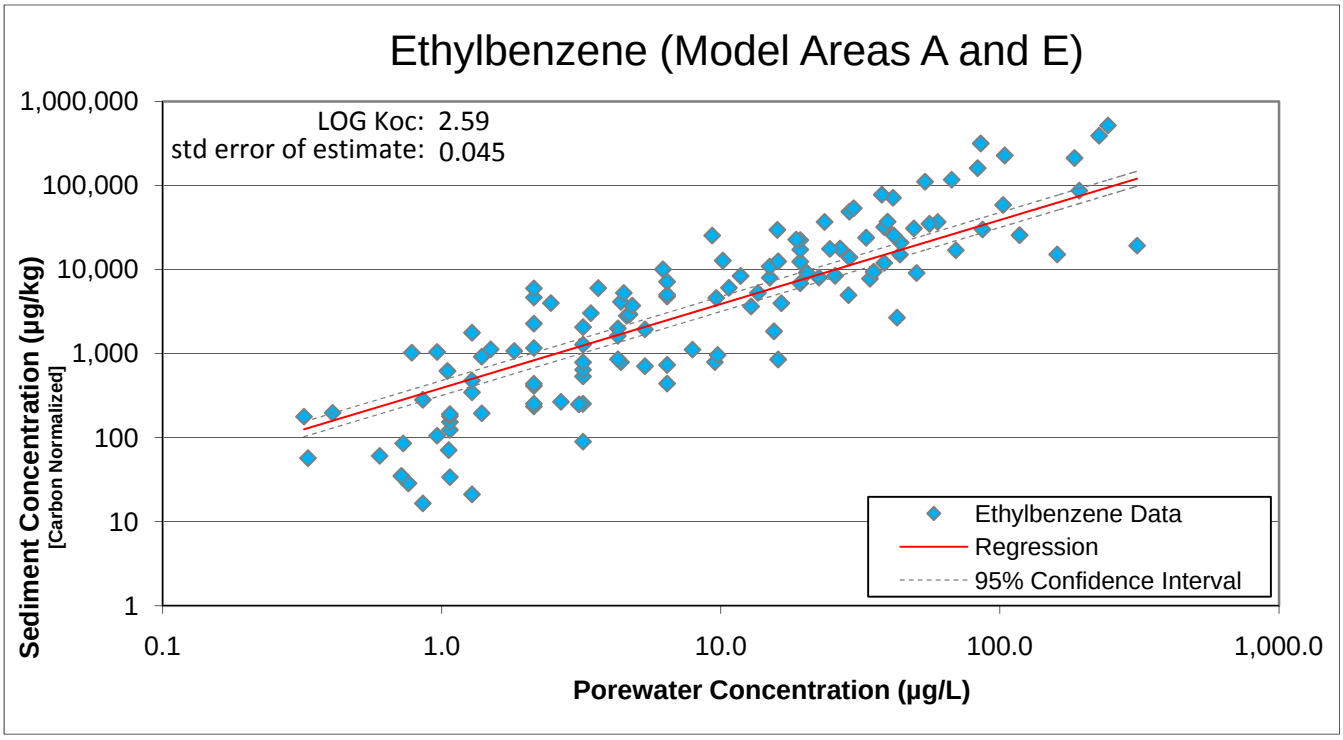
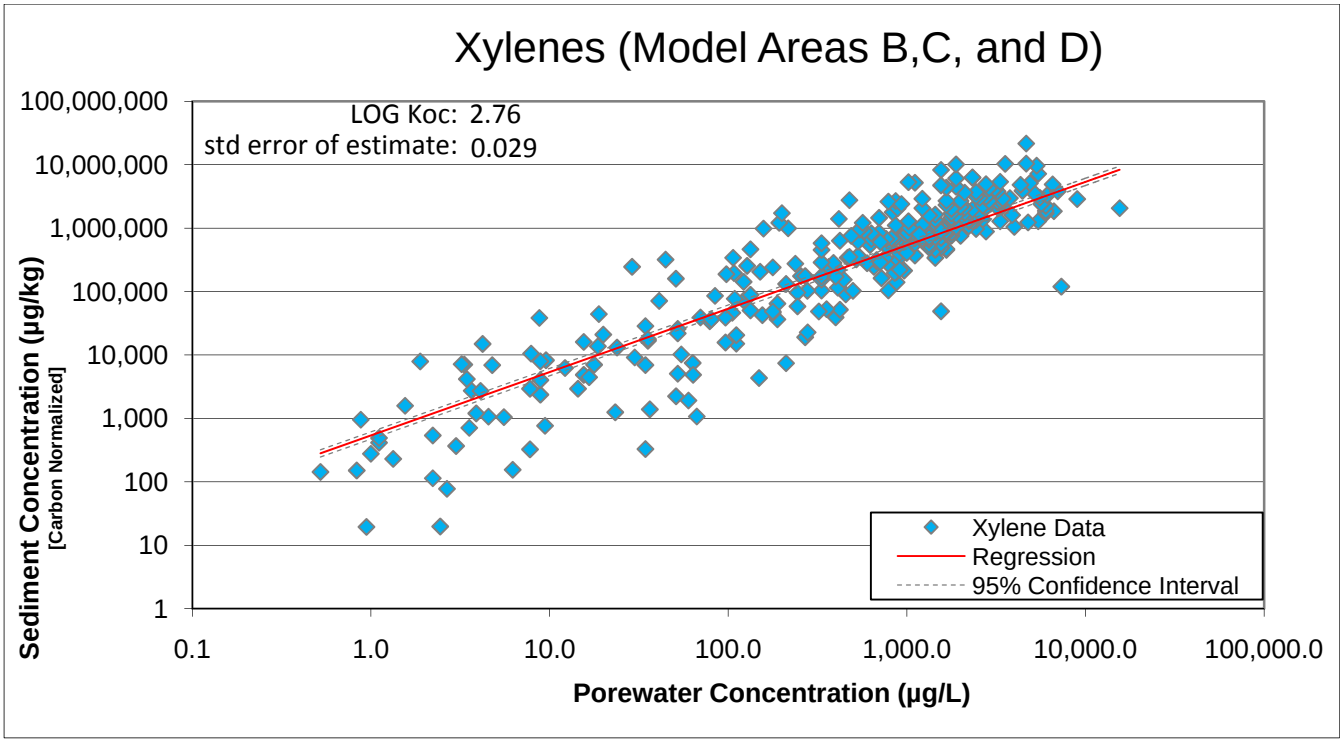


Figure 3. Relationship between *ethylbenzene* porewater concentration and carbon-normalized sediment concentration (with log-transformed regression).

XYLENE – Model Areas B, C, and D



XYLENE – Model Areas A & E

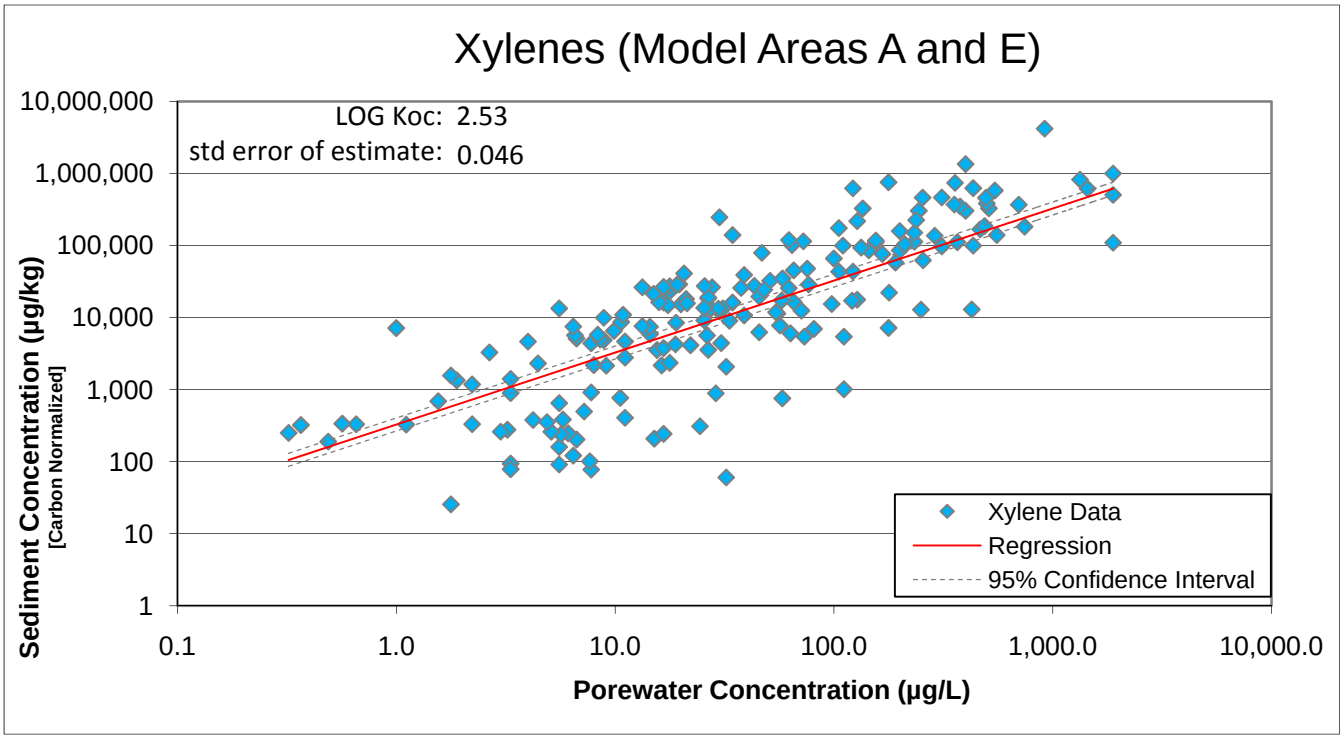
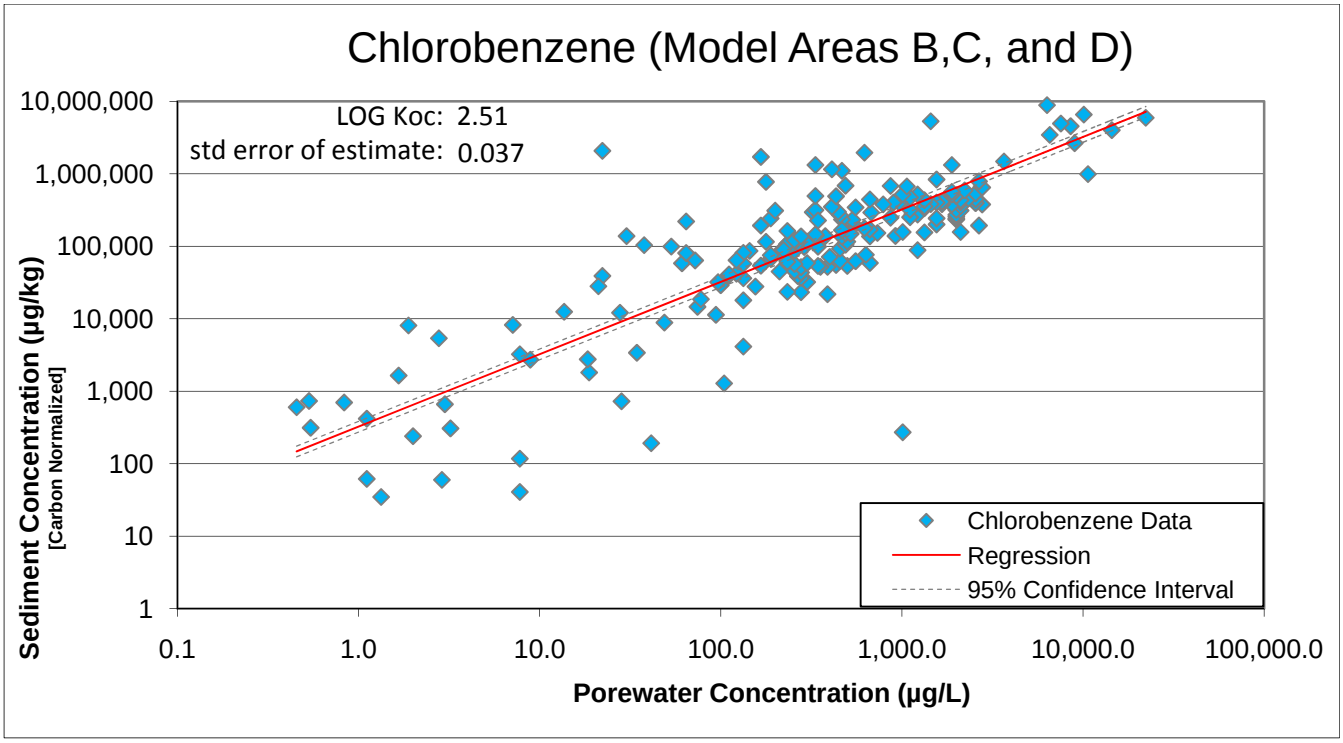


Figure 4. Relationship between *xylene* porewater concentration and carbon-normalized sediment concentration (with log-transformed regression).

CHLOROBENZENE – Model Areas B, C, and D



CHLOROBENZENE – Model Areas A & E

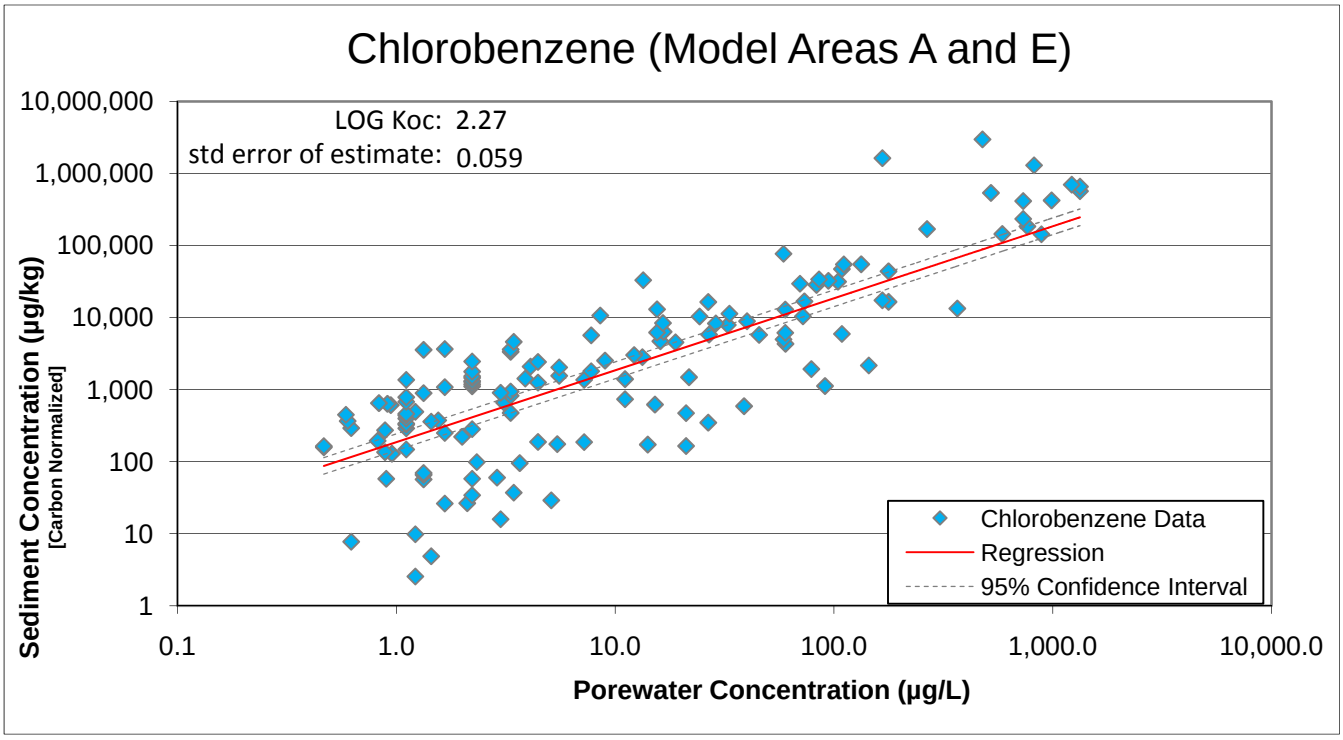
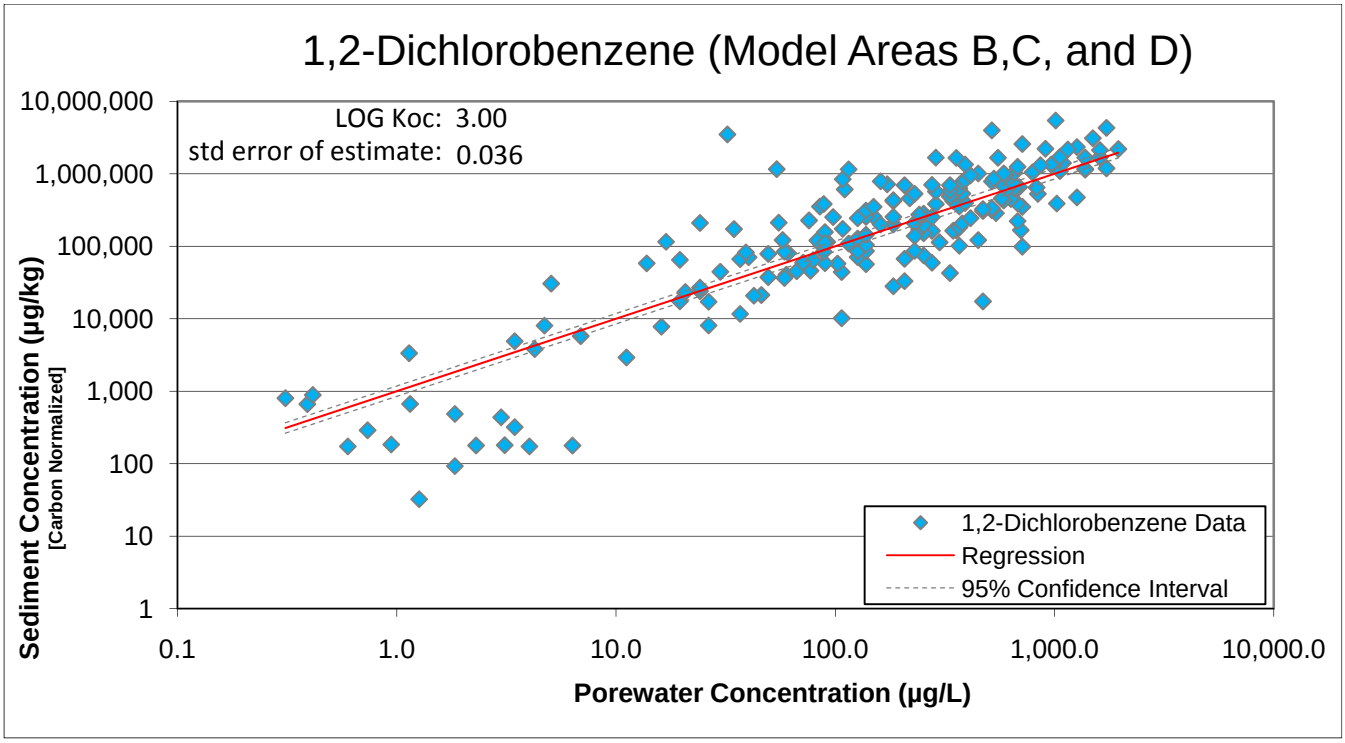


Figure 5. Relationship between *chlorobenzene* porewater concentration and carbon-normalized sediment concentration (with log-transformed regression).

1,2-DICHLOROBENZENE – Model Areas B, C, and D



1,2-DICHLOROBENZENE – Model Areas A & E

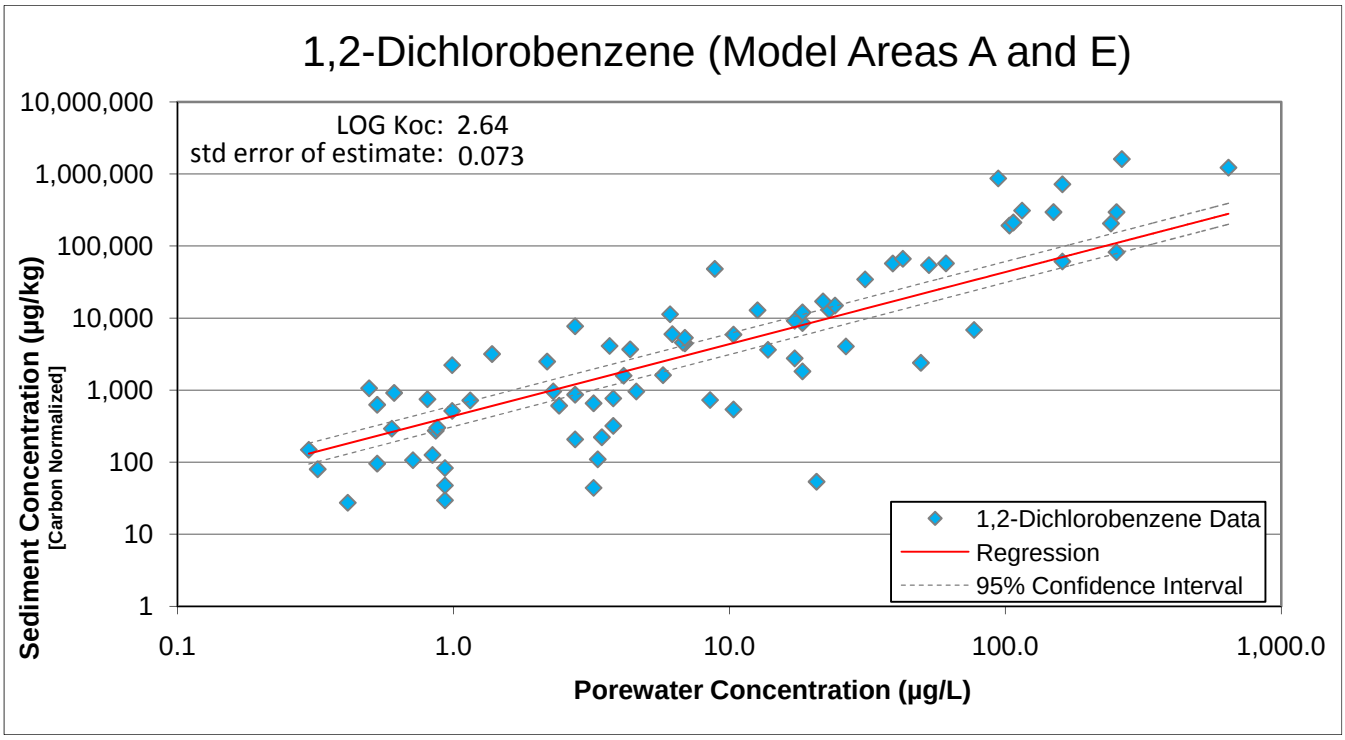
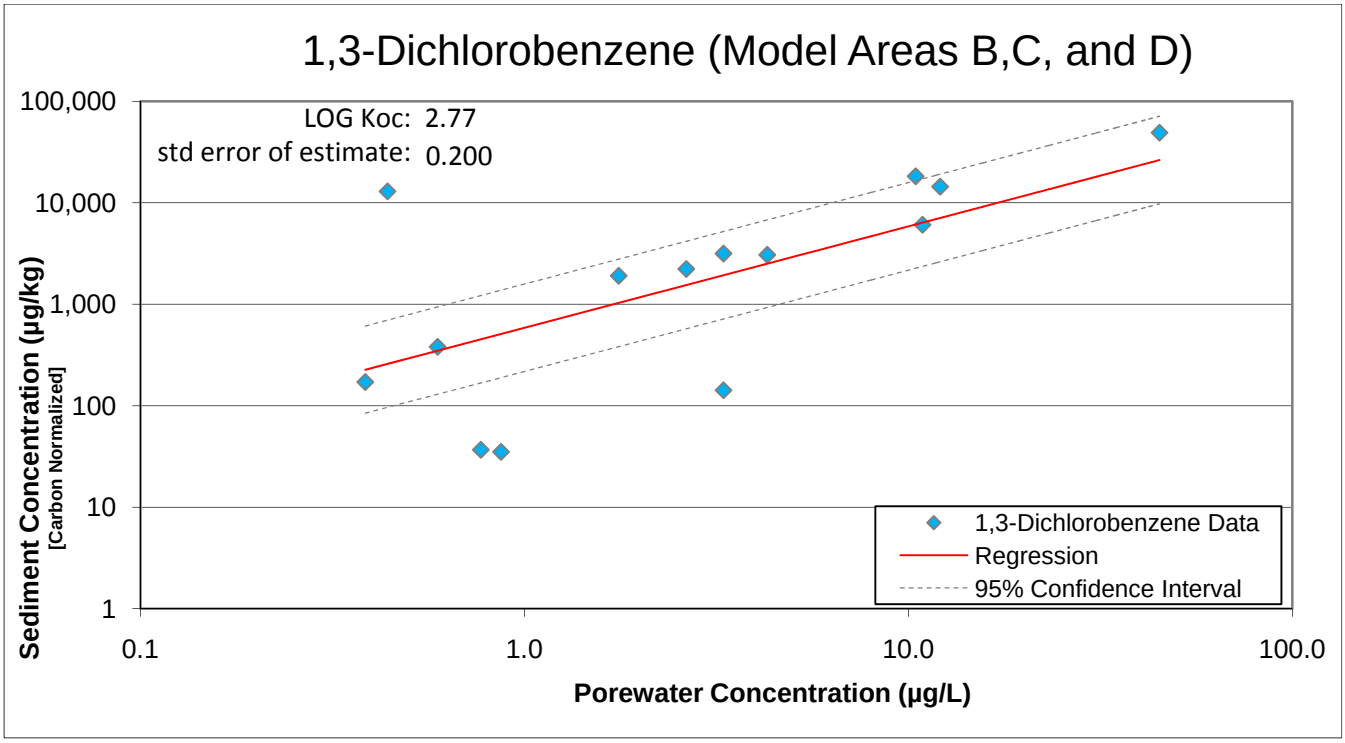


Figure 6. Relationship between *1,2-dichlorobenzene* porewater concentration and carbon-normalized sediment concentration (with log-transformed regression).

1,3-DICHLOROBENZENE – Model Areas B, C, and D



1,3-DICHLOROBENZENE – Model Areas A & E

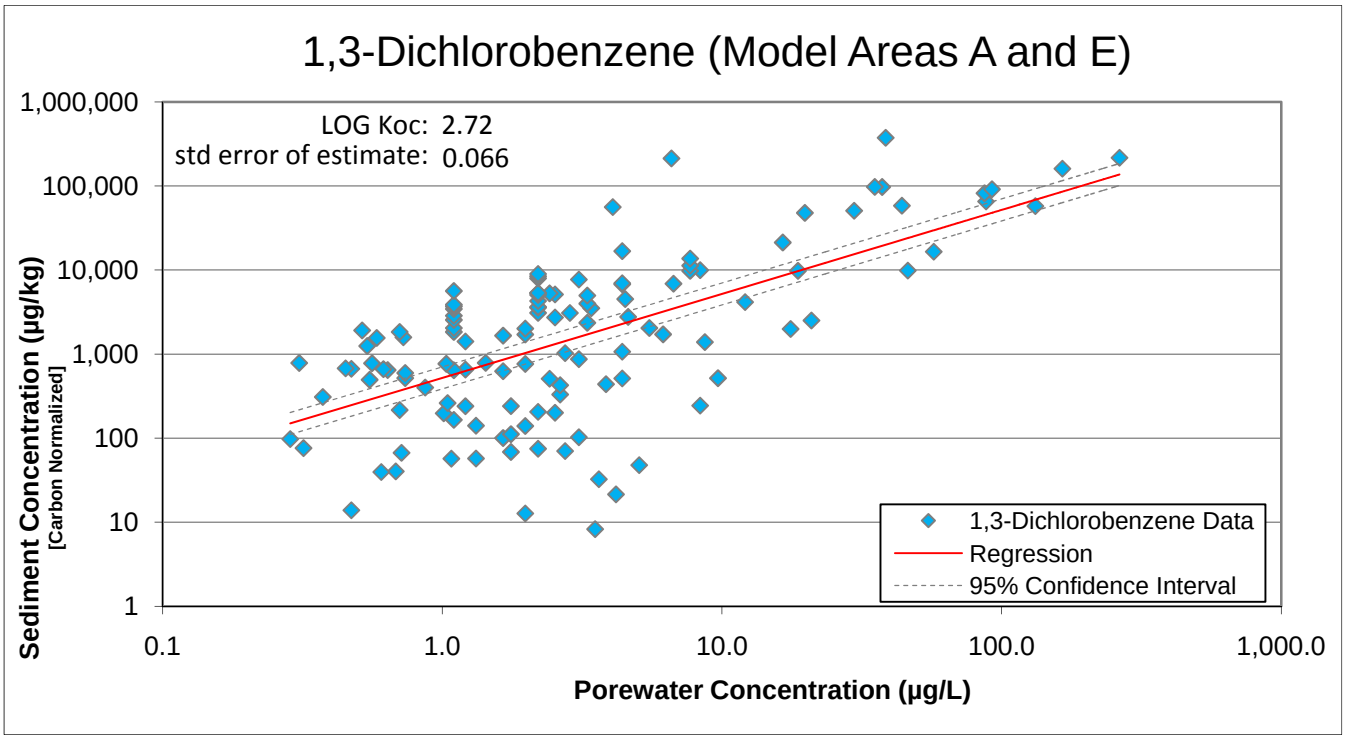
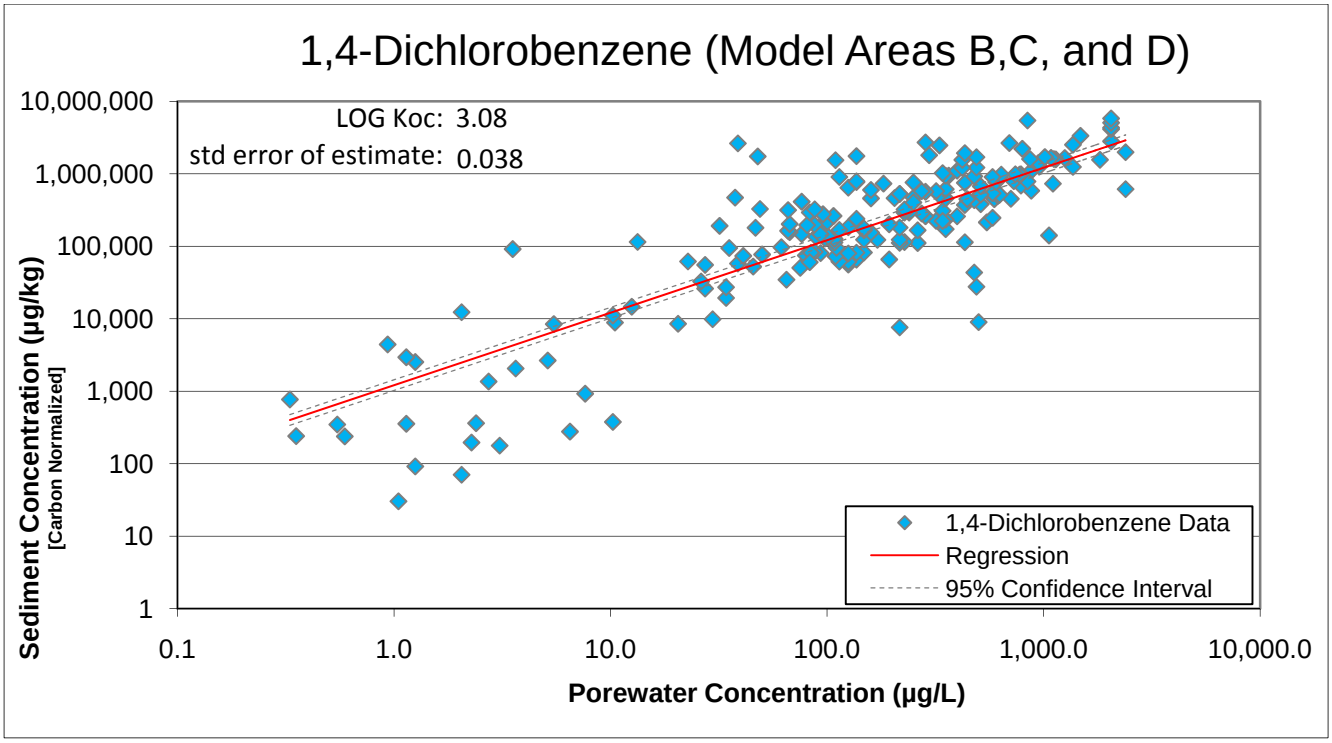


Figure 7. Relationship between *1,3-dichlorobenzene* porewater concentration and carbon-normalized sediment concentration (with log-transformed regression).

1,4-DICHLOROBENZENE – Model Areas B, C, and D



1,4-DICHLOROBENZENE – Model Areas A & E

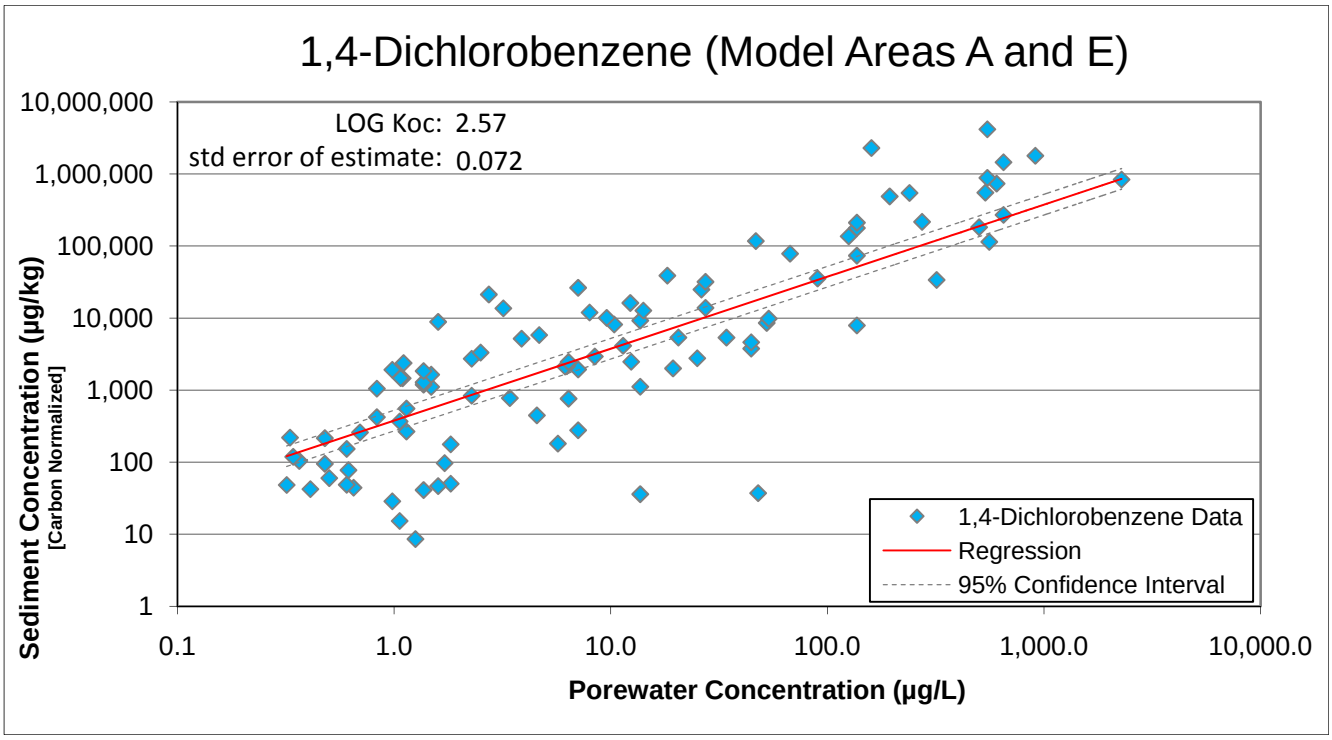
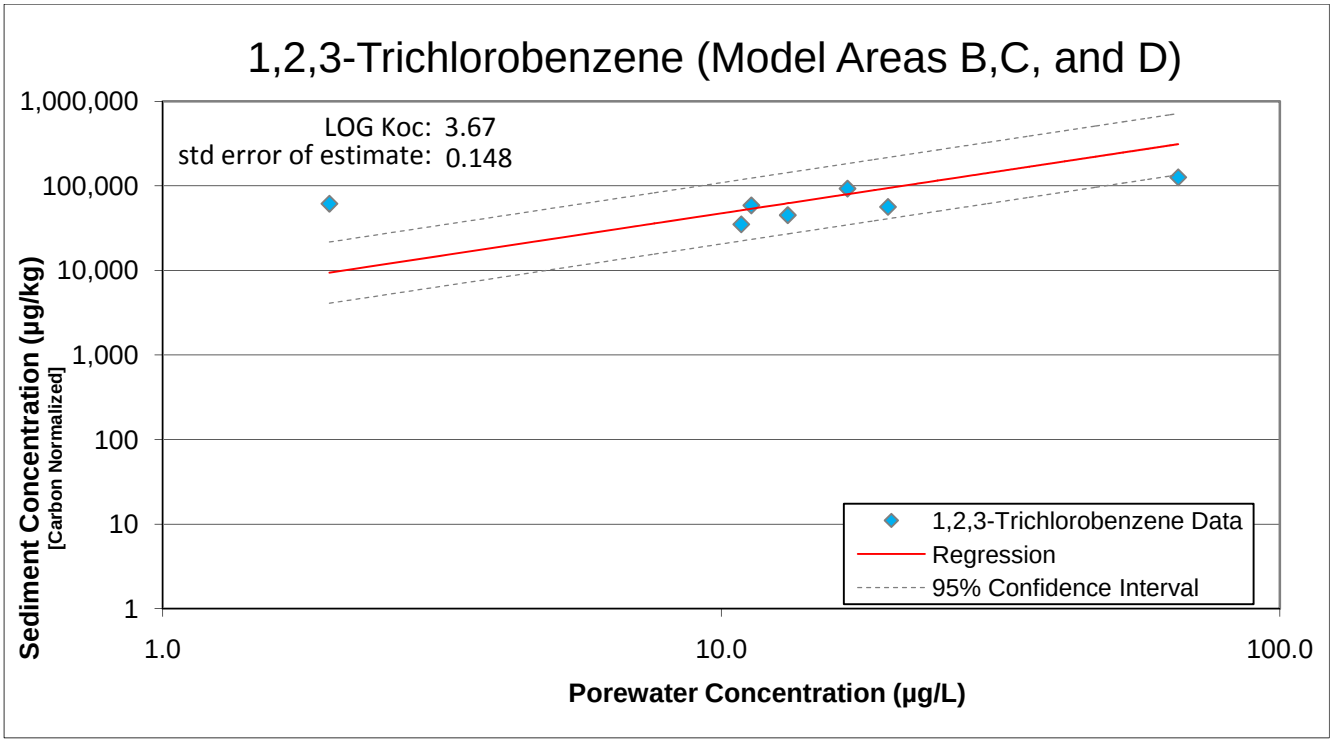


Figure 8. Relationship between *1,4-dichlorobenzene* porewater concentration and carbon-normalized sediment concentration (with log-transformed regression).

1,2,3-TRICHLOROBENZENE – Model Areas B, C, and D

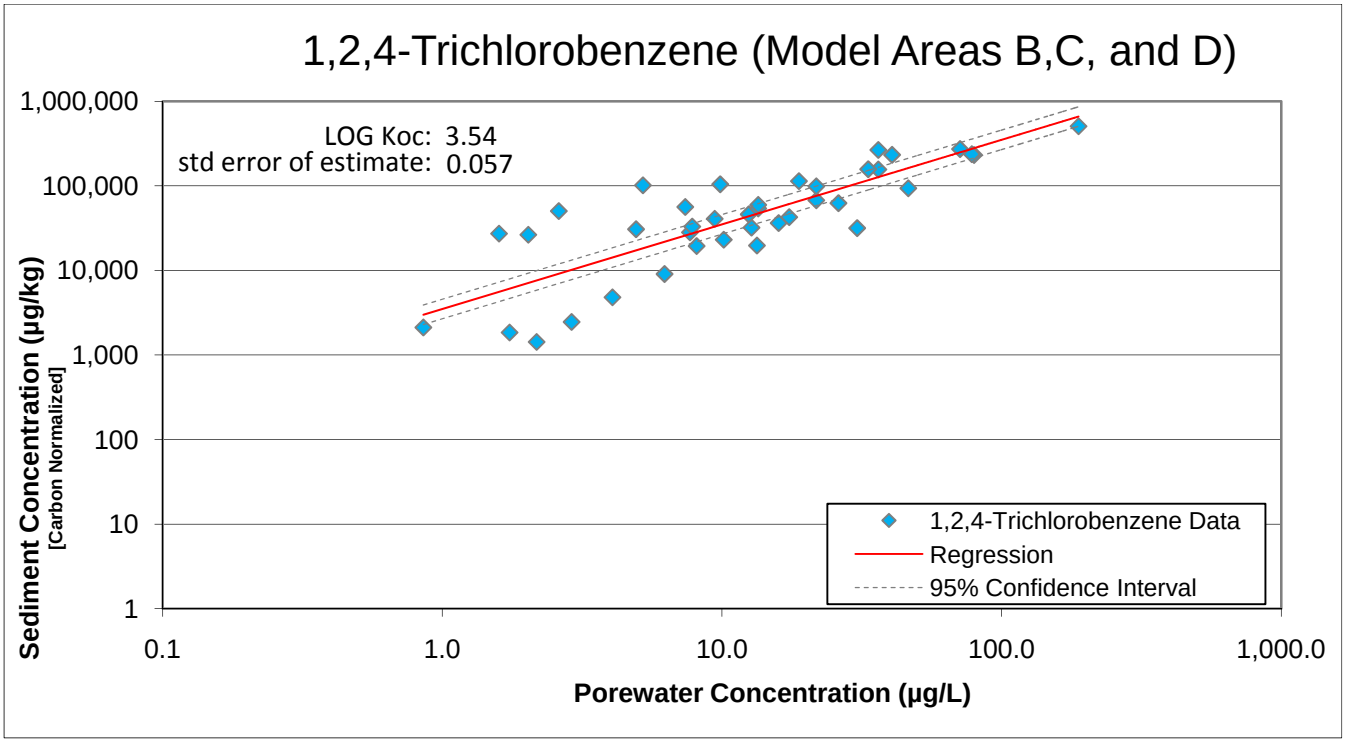


1,2,3-TRICHLOROBENZENE – Model Areas A & E

THERE WAS ONLY A SINGLE USABLE DATA PAIR FOR 1,2,3-TRICHLOROBENZENE IN MODEL AREAS A and E (plot not shown)

Figure 9. Relationship between *1,2,3-trichlorobenzene* porewater concentration and carbon-normalized sediment concentration (with log-transformed regression).

1,2,4-TRICHLOROBENZENE – Model Areas B, C, and D



1,2,4-TRICHLOROBENZENE – Model Areas A & E

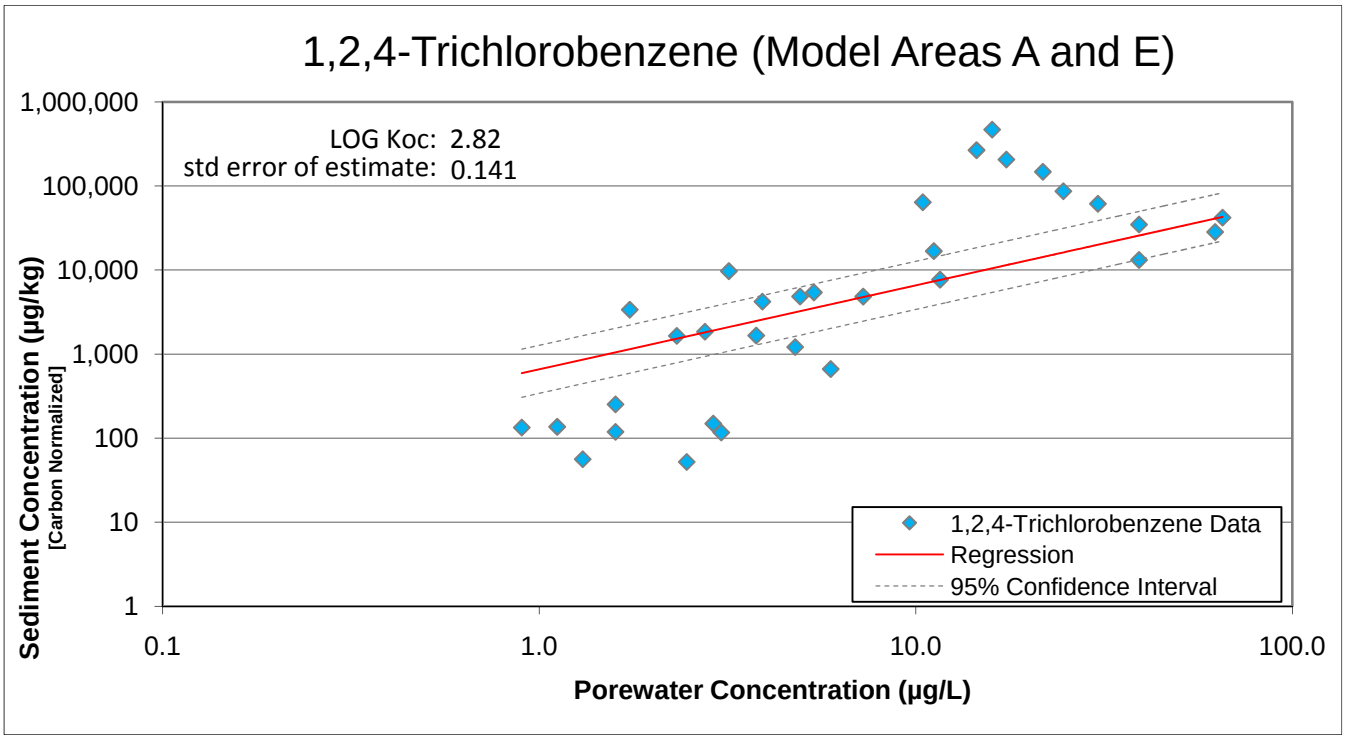


Figure 10. Relationship between *1,2,4-trichlorobenzene* porewater concentration and carbon-normalized sediment concentration (with log-transformed regression).

1,3,5-TRICHLOROBENZENE – Model Areas B, C, and D

THERE WERE NO USABLE DATA PAIRS FOR 1,3,5-TRICHLOROBENZENE IN MODEL AREAS B, C, and D (plot not shown)

1,3,5-TRICHLOROBENZENE – Model Areas A & E

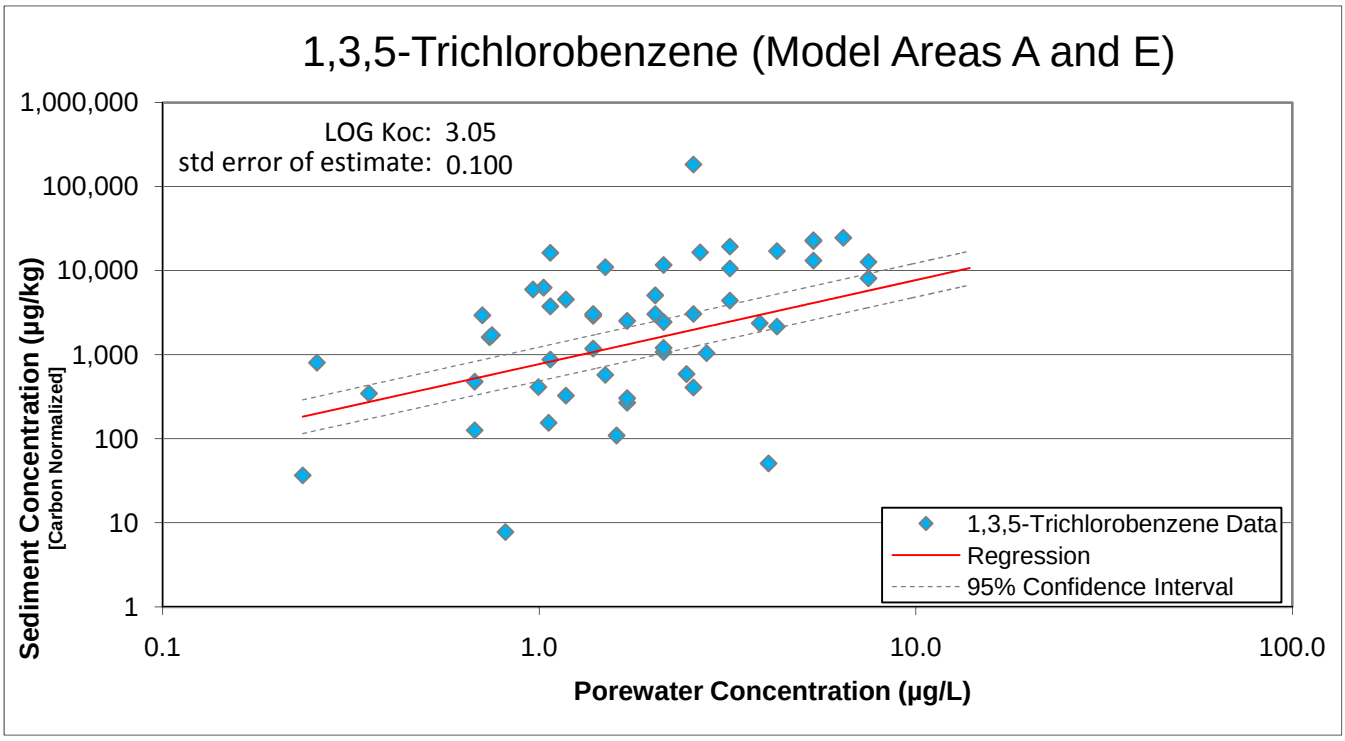
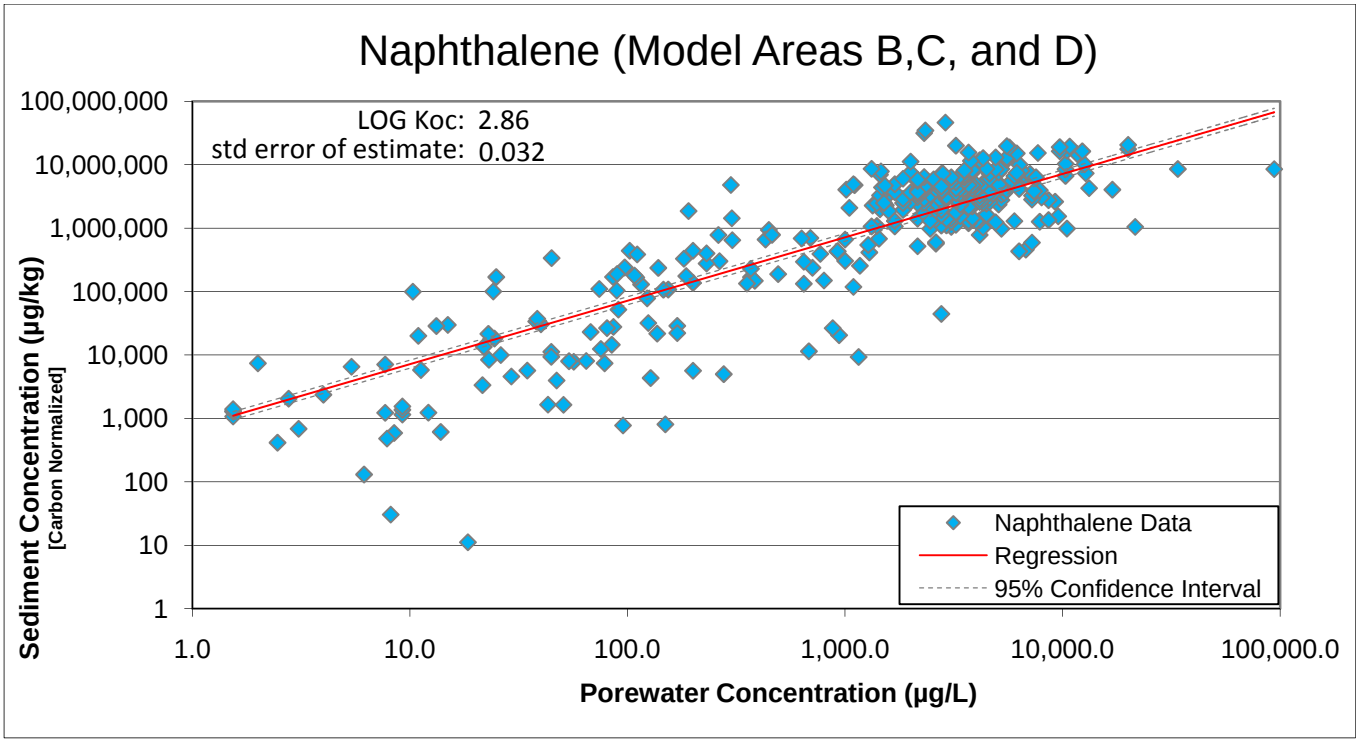


Figure 11. Relationship between *1,3,5-trichlorobenzene* porewater concentration and carbon-normalized sediment concentration (with log-transformed regression).

NAPHTHALENE – Model Areas B, C, and D



NAPHTHALENE – Model Areas A & E

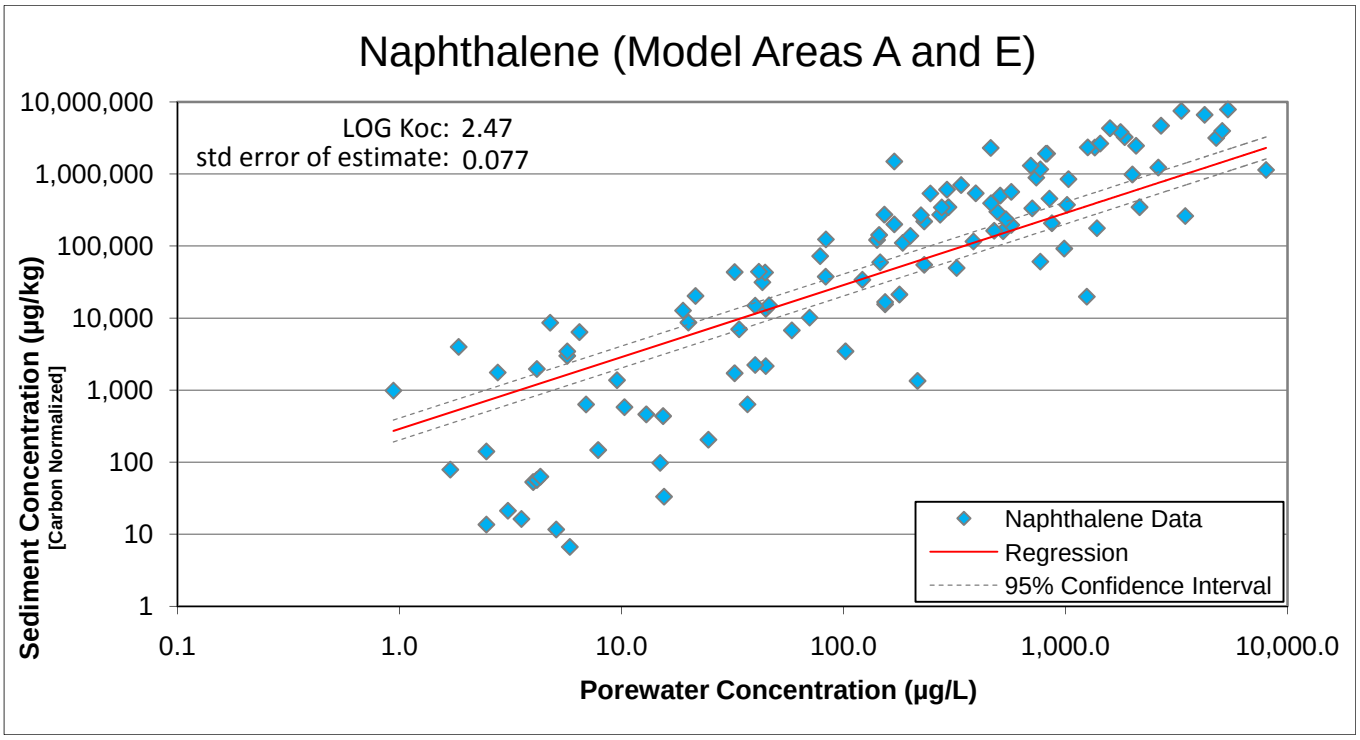


Figure 12. Relationship between *naphthalene* porewater concentration and carbon-normalized sediment concentration (with log-transformed regression).

ADDENDUM 1

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TECHNICAL MEMORANDUM

Date: 09 December 2009

To: Edward Glaza – Parsons

Copies to: Caryn E. Kiehl-Simpson and John Nolan – Parsons

From: Tom Krug and David Himmelheber - Geosyntec Consultants
Danny Reible – University of Texas at Austin

Subject: Establishing Representative PAH Sediment-Porewater Partitioning Coefficients Within Sediments for Input into Transport Modeling, Onondaga Lake, Syracuse, New York

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1. BACKGROUND AND SCOPE

This memorandum has been prepared by Geosyntec Consultants, Inc. (Geosyntec) to provide recommended values for effective sediment-porewater partitioning coefficients (K_{oc}) in lake sediments to be used to calculate sediment porewater concentrations. The values are intended to be incorporated into transport modeling at areas of Onondaga Lake, Syracuse, New York (the "Site") not impacted by in-lake waste deposits (ILWD) that are to be managed with an *in situ* sediment cap. A focused literature review of select datasets was performed to examine the phenomenon of porewater polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) concentrations measured in actual sediment samples being lower than expected based upon conventional estimates derived from octanol-water distribution coefficients (K_{ow}) and bulk sediment concentration. Direct measurement of porewater concentrations of these compounds are unavailable, hence the need to make the best prediction of porewater concentration for the purposes of modeling.

One approach of estimating porewater concentrations of hydrophobic contaminants, such as PAHs and PCBs, in sediments has been to measure bulk sediment concentration (C_s), then assume linear partitioning into the aqueous phase (C_w) based on solid-liquid distribution coefficients (K_d). The distribution coefficient has been generalized as the product of the fraction organic carbon (f_{oc}) in the sediment and K_{oc}:

$$C_w = \frac{C_s}{K_d} = \frac{C_s}{K_{oc} \times f_{oc}} \quad (1)$$

While this approach does not account for mass held in the dissolved-phase associated with the sediment solids, the correction is extremely small for highly sorptive compounds such as PAH

and PCB. Therefore, pore water concentrations can be related to bulk sediment concentrations (which is based on mass in all phases) with negligible adjustment. Measured f_{oc} values are site-specific while K_{oc} values are chemical-specific and can either be determined experimentally or calculated based on chemical structure and/or properties (e.g., octanol-water partitioning coefficient [K_{ow}]). Note that K_{ow} values are physical constants of a particular compound but that values of K_{oc} are partially dependent upon the particular compound and are also influenced by environmental conditions (including factors such as the nature of the f_{oc}) and whether compounds are sorbing or desorbing. Modeling conducted to date has used K_{ow} values reported in New York State Department of Environmental Conservation Guidance (NYSDEC, 1999) as estimates of K_{oc} and measured f_{oc} values to estimate the concentrations of PAHs and PCBs in sediment porewater beneath the cap. A growing body of literature indicates that this conventional approach of calculating PAH and PCB porewater concentrations in sediments will overestimate actual PAH or PCB porewater concentrations (for discussions see Arp et al., 2009; Hawthorne et al., 2006; and McGroddy et al., 1996). The primary cause of this discrepancy is that natural sediments are composed of different types of organic carbon, with some phases of organic carbon ("hard" carbon) sorbing hydrophobic contaminants stronger but more slowly than other phases ("soft" carbon). An illustration of how different forms of carbon present in sediments results in different effective K_{oc} values for phenanthrene was compiled by Ghosh et al. (2003) and reproduced in this document as Figure 1. As a result, when PAHs or PCBs are introduced into sediments, a portion of the contaminant is sorbed strongly to the "hard" carbon component of organic matter and effectively resistant to desorption. This desorption-resistance is not inherently incorporated into the conventional K_{oc} x f_{oc} approach of estimating porewater concentrations since compilations of K_{oc} are often based upon short-term sorption experiments in the laboratory or equivalent correlations with K_{ow}. This discrepancy ultimately leads to lower field measurement of porewater PAH concentrations than are predicted by literature K_{oc} values.

A more realistic approach to modeling PAH and PCB transport within sediments is to use measured f_{oc} values and field-derived effective K_{oc} values measured in natural sediment that account for strongly-sorbing fractions of sediment. A compilation of field-derived effective K_{oc} values from several literature sources has been performed.

2. COMPILATION OF DATASETS COMPARING MEASURED PAH POREWATER CONCENTRATIONS WITH ESTIMATED POREWATER CONCENTRATIONS

Figures 2 and 3 present graphs plotting K_{ow} values for PAHs versus field-derived effective K_{oc} values. PAHs included in the analysis are listed in Table 1. Plotted K_{ow} values were obtained from the NYSDEC Guidance Document (1999) for all but three PAH compounds (acenaphthylene, benzo[ghi]perylene, and dibenz[a,h]anthracene) whose K_{ow} values were obtained from Syracuse Research Corporation's (SRC) KowWIN database. The K_{ow} values utilized in this assessment are the same values being employed for modeling efforts to date. The data utilized for the field-derived observed K_{oc} values were actual porewater sampling and

analysis, providing an accurate measurement of aqueous phase PAH concentrations (Arp et al., 2009). Figure 2 contains the compilation of all sediment site data compiled and Figure 3 contains data from sites with freshwater and brackish conditions (i.e., excluding marine sediments).

The K_{ow} values consistently underestimate observed effective K_{oc} values and thus overestimate PAH porewater concentrations associated with sediment containing a known concentration of PAH compared with the field-derived values. On average, the field-derived PAH K_{oc} values are greater than the K_{ow} values currently utilized in modeling efforts by 1.07 ± 0.14 log units (average ± 95% confidence interval) when examining all the data, and 1.05 ± 0.15 when considering just freshwater and brackish sediment sites. Figures 2 and 3 indicate that adjusting the log K_{ow} values currently employed in modeling efforts by one log unit, or a factor of 10, closely approximates the statistical best-fit lines in both Figures 2 and 3 and falls within the 95% confidence bands of each respective regression line.

3. COMPILATION OF DATASETS COMPARING MEASURED PCB POREWATER CONCENTRATIONS WITH ESTIMATED POREWATER CONCENTRATIONS

Figures 4 and 5 presents graphs of K_{ow} values for PCBs versus field-derived effective K_{oc} values from Arp et al 2009. PCBs included in the analysis are presented in Table 2. Plotted K_{ow} values in Figures 4 and 5 were obtained from the Hawker et al 1988 and Lu et al 2007 respectively.

The K_{ow} values consistently underestimate observed effective K_{oc} values and thus overestimate PCB porewater concentrations associated with sediment containing a known concentration of PCB compared with the field-derived values. On average, the field-derived PCB K_{oc} values are greater than the literature K_{ow} values by a factor of five. Figures 4 and 5 indicate that adjusting the K_{ow} values currently employed in modeling efforts by a factor of five, closely approximates the statistical best-fit lines in both Figures 4 and 5 and falls within the 95% confidence bands of each respective regression line.

4. RECOMMENDATIONS

The literature review described above and relevant experience at other sediment sites supports the use of corrected PAH and PCB K_{oc} values to most accurately model and predict porewater PAH and PCB concentrations within the Onondaga Lake sediment in the absence of direct measurements. Based on the data presented in Figures 2 and 3 an increase in effective K_{oc} values of 10 from PAH K_{ow} values is recommended for derivation of PAH porewater concentrations in the non-ILWD impacted sediments at this time. Based on the data presented in Figures 4 and 5 an increase in effective K_{oc} values of 5 from PCB K_{ow} values is recommended for derivation of PCB porewater concentrations in the non-ILWD impacted sediments.

5. REFERENCES

Arp, H.P.H., Breedveld, G.D., and Cornelissen, G., 2009. Estimating the in situ sediment-porewater distribution of PAHs and chlorinated aromatic hydrocarbons in anthropogenic impacted sediments. *Environ. Sci. Technol.. 43*, 5576–5585.

Cornelissen, G., Gustafsson, O., Bucheli, T. D., Jonker, M. T. O., Koelmans, A. A., and VanNoort, P. C.M., 2005. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. Technol., 39* (18), 6881–6895.

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Hawthorne, S.B., Grabanski, C.B., and Miller, D.J., 2006. Measured partitioning coefficients for parent and alkyl polycyclic aromatic hydrocarbons in 114 historically contaminated sediments: Part 1. K_{oc} values. *Environ. Toxicol. Chem.*, *25* (11), 2901-2911.

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New York State Department of Environmental Conservation (NYSDEC), 1999. Technical Guidance for Screening Contaminated Sediments. Division of Fish, Wildlife and Marine Resources.

Table 1 - Literature Values for Kow and Koc for Polycyclic Aromatic Hydrocarbons

Data Source in Arp et al, 2009	**CAS #**	**Compound**	**Average Log Koc** Arp et al, 2009	**Log Kow** NYSDEC, 1999	**Log Kow** SRC
7	208-96-8	Acenaphthylene	5.11	ns	3.94
9	208-96-8	Acenaphthylene	4.48	ns	3.94
10	208-96-8	Acenaphthylene	4.47	ns	3.94
4	120-12-7	Anthracene	6.24	4.45	
6	120-12-7	Anthracene	6.08	4.45	
7	120-12-7	Anthracene	5.75	4.45	
9	120-12-7	Anthracene	5.41	4.45	
14	120-12-7	Anthracene	6.61	4.45	
15	120-12-7	Anthracene	5.26	4.45	
1	56-55-3	Benz[a]anthracene	7.14	5.61	
4	56-55-3	Benz[a]anthracene	7.38	5.61	
6	56-55-3	Benz[a]anthracene	6.77	5.61	
7	56-55-3	Benz[a]anthracene	6.55	5.61	
8	56-55-3	Benz[a]anthracene	6.95	5.61	
9	56-55-3	Benz[a]anthracene	6.45	5.61	
14	56-55-3	Benz[a]anthracene	7.81	5.61	
6	50-32-8	Benzo(a)pyrene	7.03	6.04	
1	50-32-8	Benzo[a]pyrene	7.77	6.04	
4	50-32-8	Benzo[a]pyrene	8.37	6.04	
7	50-32-8	Benzo[a]pyrene	6.68	6.04	
8	50-32-8	Benzo[a]pyrene	7.96	6.04	
9	50-32-8	Benzo[a]pyrene	6.85	6.04	
11	50-32-8	Benzo[a]pyrene	7.25	6.04	
12	50-32-8	Benzo[a]pyrene	6.79	6.04	
13	50-32-8	Benzo[a]pyrene	6.15	6.04	
14	50-32-8	Benzo[a]pyrene	7.81	6.04	
4	205-99-2	Benzo[b]fluoranthene	7.99	6.04	
6	205-99-2	Benzo[b]fluoranthene	7.06	6.04	
8	205-99-2	Benzo[b]fluoranthene	7.42	6.04	
9	205-99-2	Benzo[b]fluoranthene	6.91	6.04	
15	205-99-2	Benzo[b]fluoranthene	6.59	6.04	
1	191-24-2	Benzo[ghi]perylene	8.25	ns	6.70
4	191-24-2	Benzo[ghi]perylene	9.01	ns	6.70
6	191-24-2	Benzo[ghi]perylene	7.58	ns	6.70
7	191-24-2	Benzo[ghi]perylene	7.13	ns	6.70
8	191-24-2	Benzo[ghi]perylene	7.84	ns	6.70
9	191-24-2	Benzo[ghi]perylene	6.94	ns	6.70
14	191-24-2	Benzo[ghi]perylene	8.91	ns	6.70
15	191-24-2	Benzo[ghi]perylene	6.67	ns	6.70
4	207-08-9	Benzo[k]fluoranthene	8.16	6.04	
6	207-08-9	Benzo[k]fluoranthene	7.25	6.04	
8	207-08-9	Benzo[k]fluoranthene	7.41	6.04	
9	207-08-9	Benzo[k]fluoranthene	6.90	6.04	
12	207-08-9	Benzo[k]fluoranthene	6.74	6.04	
15	207-08-9	Benzo[k]fluoranthene	6.41	6.04	

notes:

ns - not specified

Table 1 - Literature Values for Kow and Koc for Polycyclic Aromatic Hydrocarbons

Data Source in Arp et al, 2009	CAS #	Compound	Average Log Koc Arp et al, 2009	Log Kow NYSDEC, 1999	Log Kow SRC
4	53-70-3	Dibenz[a,h]anthracene	8.06	ns	6.70
6	53-70-3	Dibenz[a,h]anthracene	7.62	ns	6.70
7	53-70-3	Dibenz[a,h]anthracene	6.82	ns	6.70
9	53-70-3	Dibenz[a,h]anthracene	6.88	ns	6.70
6	206-44-0	Fluorantene	6.25	5.19	
1	206-44-0	Fluoranthene	6.26	5.19	
4	206-44-0	Fluoranthene	6.37	5.19	
7	206-44-0	Fluoranthene	5.79	5.19	
8	206-44-0	Fluoranthene	6.04	5.19	
9	206-44-0	Fluoranthene	5.89	5.19	
13	206-44-0	Fluoranthene	6.43	5.19	
14	206-44-0	Fluoranthene	7.41	5.19	
15	206-44-0	Fluoranthene	6.15	5.19	
16	206-44-0	Fluoranthene	6.34	5.19	
7	86-73-7	Fluorene	4.71	4.18	
9	86-73-7	Fluorene	4.65	4.18	
10	86-73-7	Fluorene	4.17	4.18	
15	86-73-7	Fluorene	4.69	4.18	
16	86-73-7	Fluorene	6.49	4.18	
7	91-57-6	2-Methylnaphthalene	4.56	3.86	
16	91-57-6	2-Methylnaphthalene	7.03	3.86	
7	91-20-3	Naphthalene	4.26	3.37	
9	91-20-3	Naphthalene	3.39	3.37	
10	91-20-3	Naphthalene	3.14	3.37	
1	85-01-8	Phenanthrene	5.87	4.45	
4	85-01-8	Phenanthrene	6.15	4.45	
6	85-01-8	Phenanthrene	5.83	4.45	
7	85-01-8	Phenanthrene	5.20	4.45	
8	85-01-8	Phenanthrene	5.70	4.45	
8	85-01-8	Phenanthrene	5.70	4.45	
9	85-01-8	Phenanthrene	5.30	4.45	
10	85-01-8	Phenanthrene	5.03	4.45	
11	85-01-8	Phenanthrene	5.25	4.45	
12	85-01-8	Phenanthrene	4.76	4.45	
13	85-01-8	Phenanthrene	6.50	4.45	
14	85-01-8	Phenanthrene	6.91	4.45	
15	85-01-8	Phenanthrene	4.99	4.45	
16	85-01-8	Phenanthrene	6.59	4.45	
4	129-00-0	Pyrene	6.38	5.32	
6	129-00-0	Pyrene	5.86	5.32	
7	129-00-0	Pyrene	5.82	5.32	
8	129-00-0	Pyrene	6.05	5.32	
9	129-00-0	Pyrene	5.97	5.32	
10	129-00-0	Pyrene	5.08	5.32	
11	129-00-0	Pyrene	5.90	5.32	
12	129-00-0	Pyrene	5.43	5.32	
13	129-00-0	Pyrene	6.06	5.32	
14	129-00-0	Pyrene	6.71	5.32	
15	129-00-0	Pyrene	5.75	5.32	
16	129-00-0	Pyrene	6.80	5.32	

notes:

ns - not specified

Table 2 - Literature Values for Kow and Koc of PCB Congeners

PCB Congener	Log Kow Hawker et al 1988	Log Kow Lu et al 2007	Ave Log Koc Arp et al 2009
PCB-18	5.24	5.33	5.94
PCB-18	5.24	5.33	5.54
PCB-28	5.67	5.71	6.25
PCB-28	5.67	5.71	6.44
PCB-28	5.67	5.71	7.18
PCB-28	5.67	5.71	6.28
PCB-31	5.67	5.68	6.99
PCB-44	5.75	5.73	6.48
PCB-44	5.75	5.73	5.9
PCB-52	5.84	5.79	6.46
PCB-52	5.84	5.79	6.7
PCB-52	5.84	5.79	7.01
PCB-52	5.84	5.79	6.51
PCB-52	5.84	5.79	6.03
PCB-66	6.2	5.98	6.8
PCB-72	6.26	na	6.01
PCB-77	6.36	na	7.32
PCB-77	6.36	na	6.86
PCB-81	6.36	na	7.38
PCB-95	6.13	5.92	6.35
PCB-101	6.38	na	6.56
PCB-101	6.38	na	7.54
PCB-101	6.38	na	7.71
PCB-101	6.38	na	6.95
PCB-101	6.38	na	6.55
PCB-105	6.65	6.79	8.06
PCB-105	6.65	6.79	7.51

PCB Congener	Log Kow Hawker et al 1988	Log Kow Lu et al 2007	Ave Log Koc Arp et al 2009
PCB-118	6.74	6.57	6.83
PCB-118	6.74	6.57	8.02
PCB-118	6.74	6.57	7.58
PCB-118	6.74	6.57	6.85
PCB-118	6.74	6.57	6.86
PCB-126	6.89	na	7.7
PCB-138	6.83	6.73	8.19
PCB-138	6.83	6.73	8.25
PCB-138	6.83	6.73	7.55
PCB-138	6.83	6.73	7.15
PCB-153	6.92	6.8	8.33
PCB-153	6.92	6.8	8.32
PCB-153	6.92	6.8	7.46
PCB-153	6.92	6.8	7.01
PCB-156	7.18	7.44	8.13
PCB-156	7.18	7.44	7.82
PCB-156	7.18	7.44	7.38
PCB-167	7.27	7.29	7.94
PCB-169	7.42	7.55	7.96
PCB-170	7.27	7.08	8
PCB-180	7.36	7.21	7.35
PCB-180	7.36	7.21	8.31
PCB-180	7.36	7.21	8.3
PCB-180	7.36	7.21	7.86
PCB-187	7.17	6.99	7.79
PCB-195	7.56	7.35	7.85
PCB-204	7.3	7.48	8.24

Figure 1 - Phenanthrene K_{oc} values for different types of organic carbon.
Reproduced from Ghosh et al., 2003.

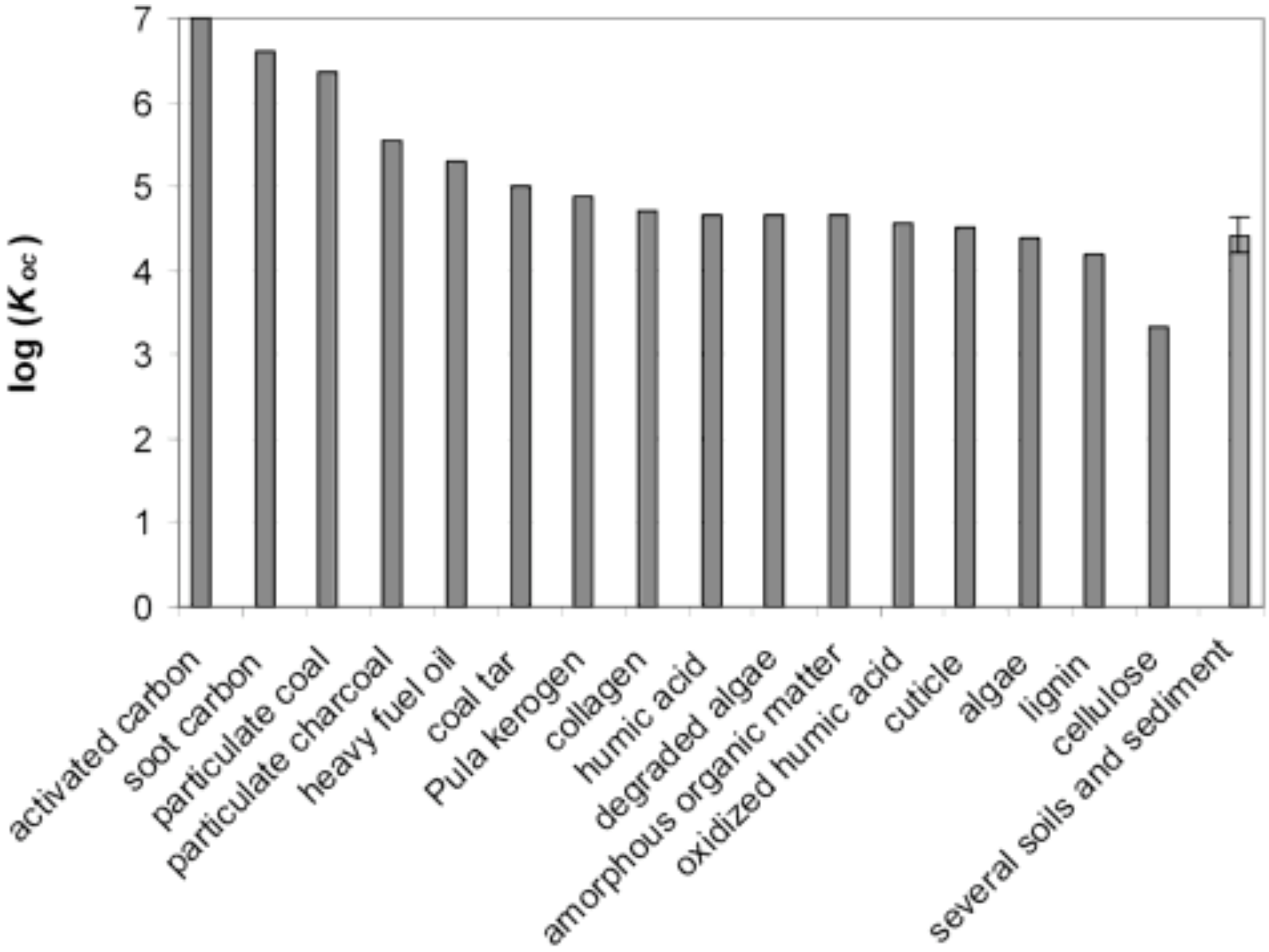


Figure 2 - Log K_{ow} versus Observed K_{oc} All Sediment Site Data

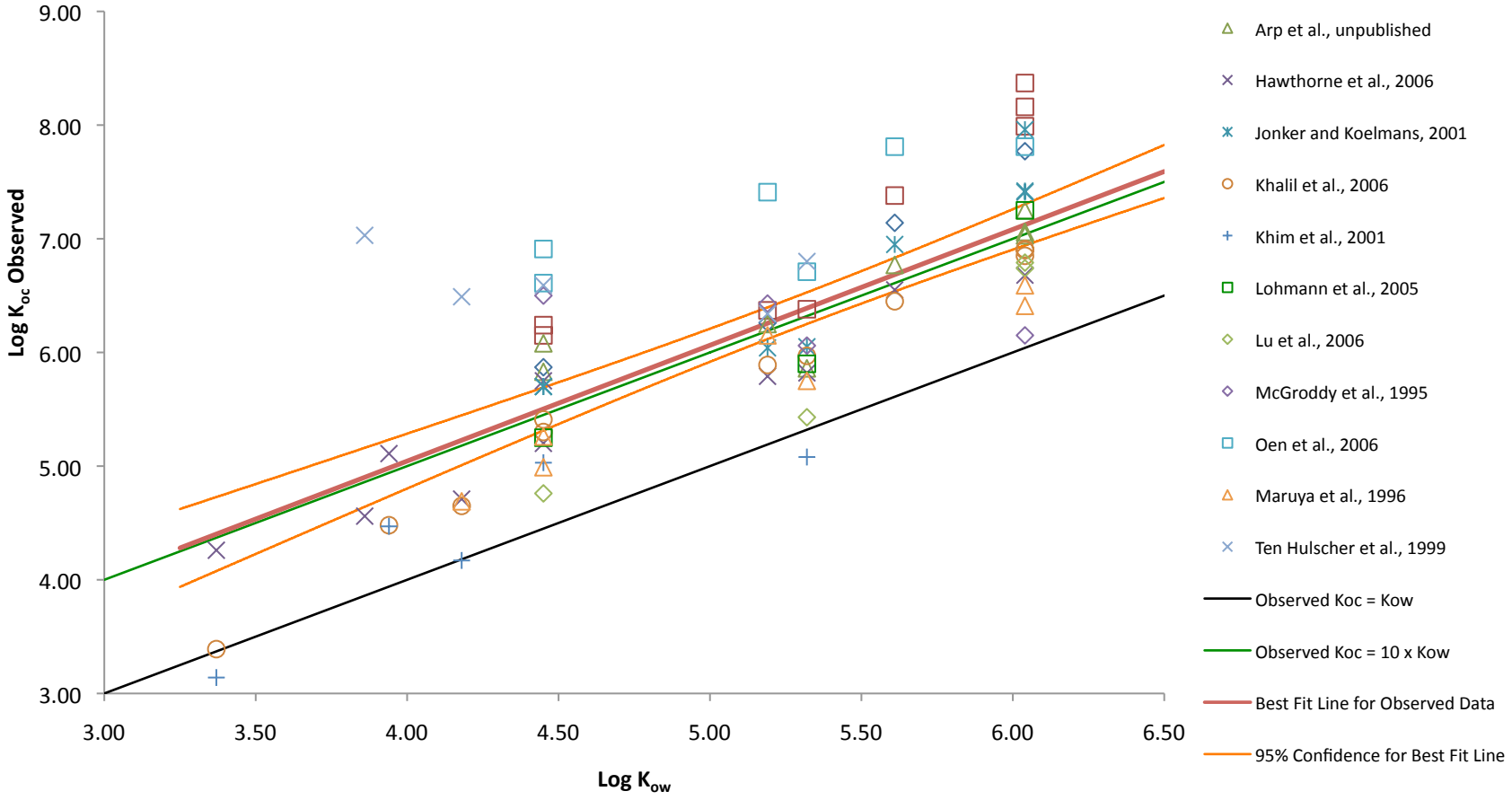


Figure 3 - Log K_{ow} versus Observed K_{oc}
Freshwater to Brackish Sediment Sites

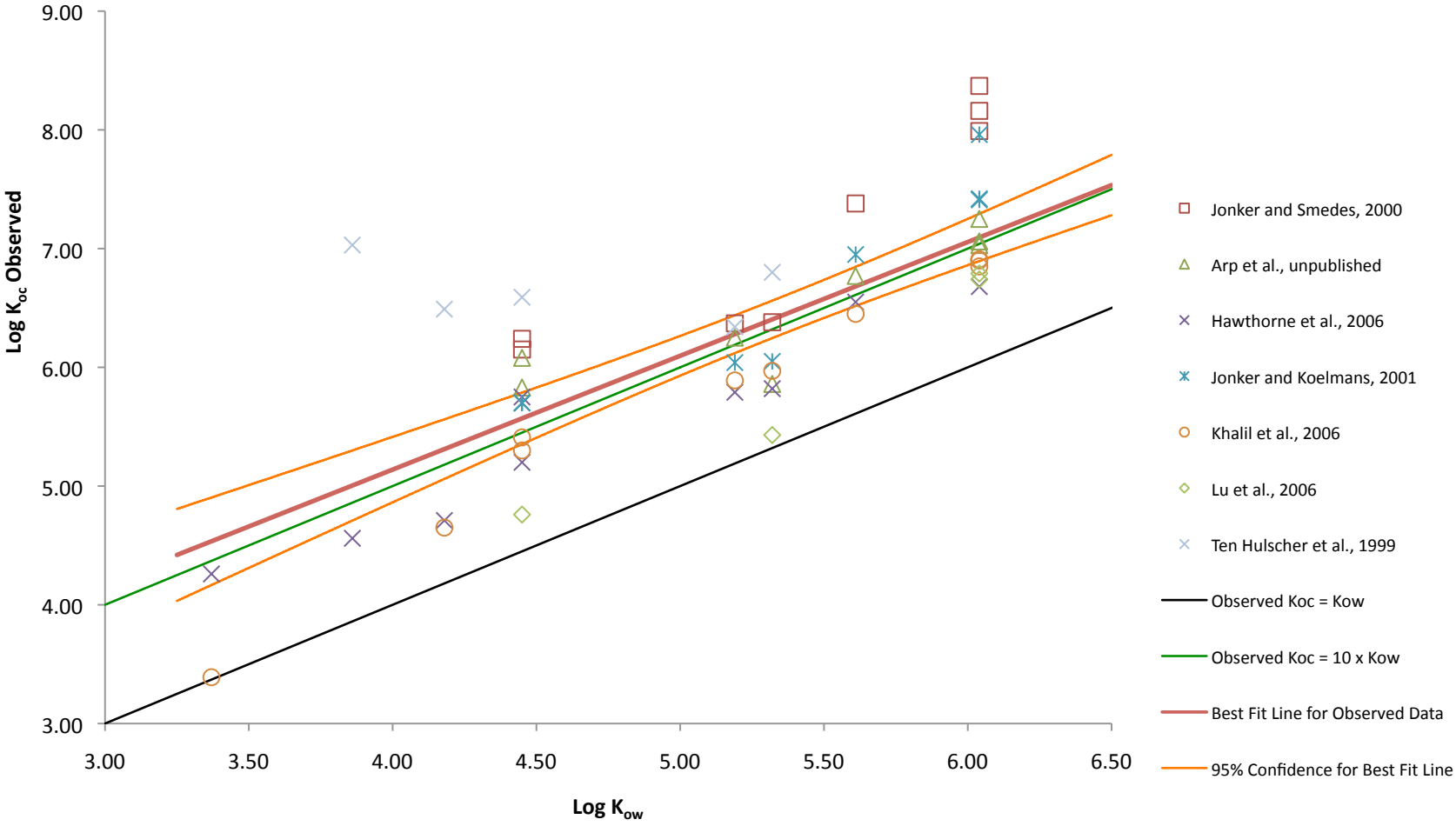
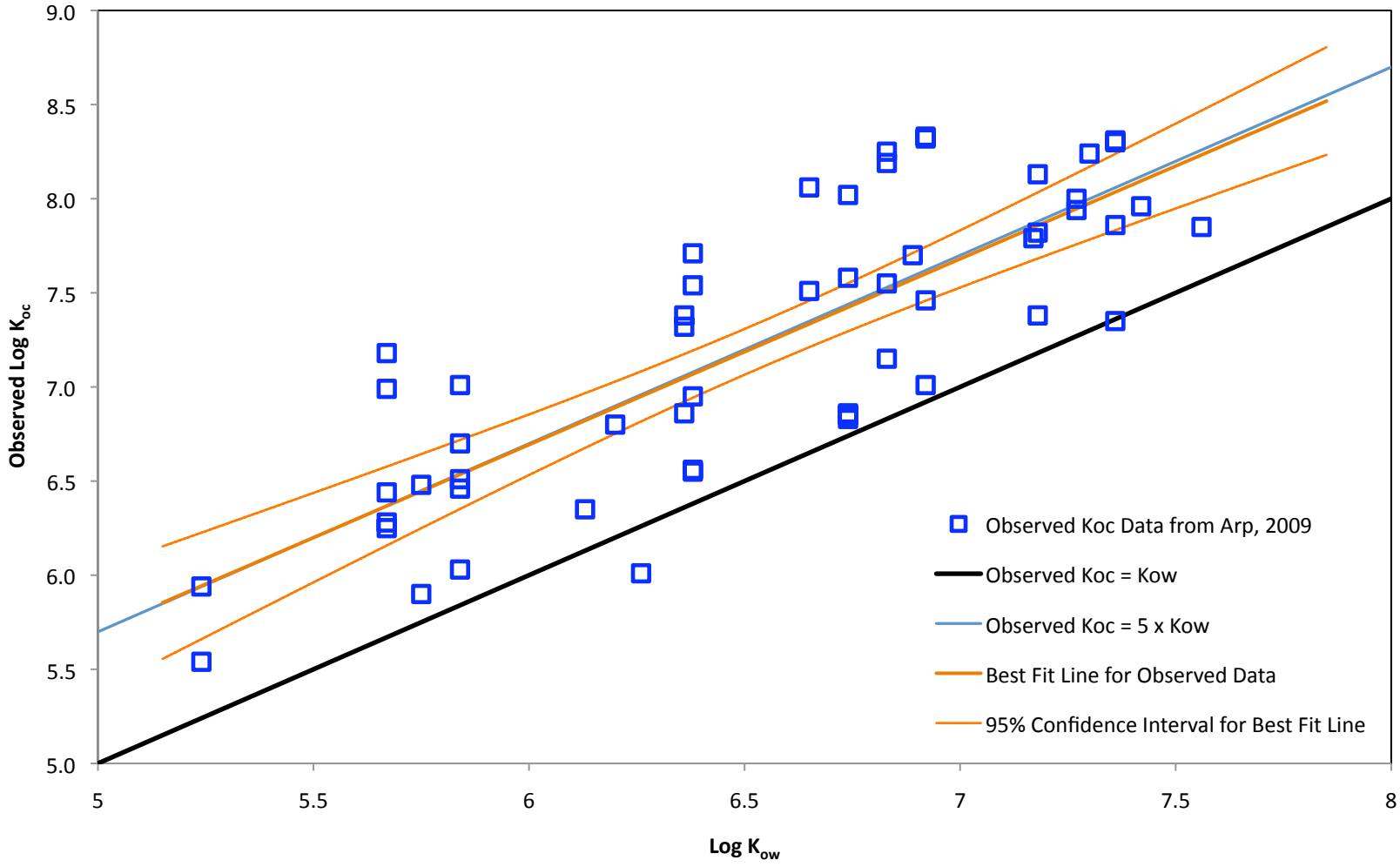
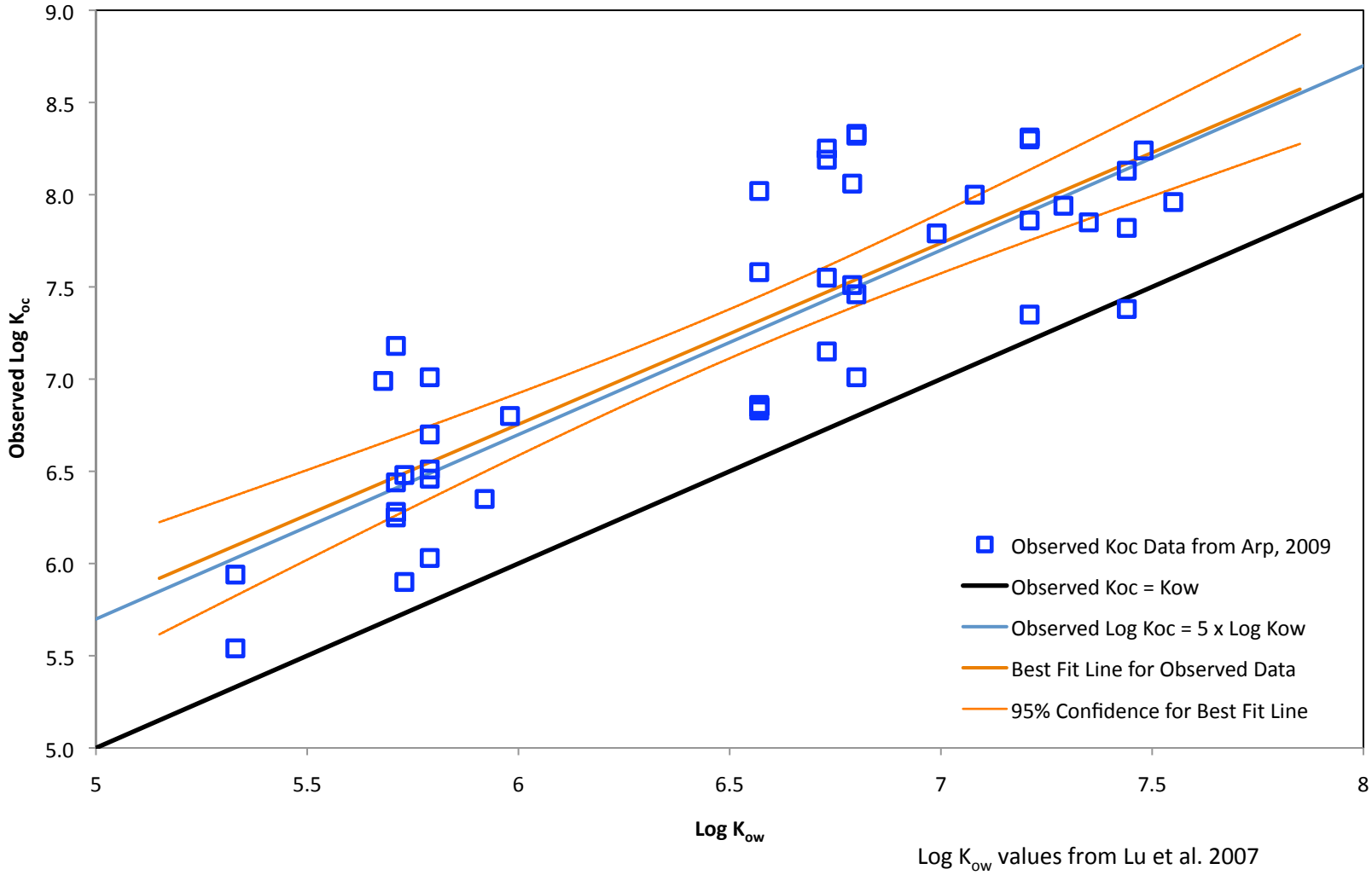


Figure 4 - Log K_{ow} vs Observed Log K_{oc}



Log K_{ow} values from Hawker, 1988

Figure 5 - Log K_{ow} vs Observed Log K_{oc}



Log K_{ow} values from Lu et al. 2007