

USE OF ORGANOCLAY IN MANAGING DISSOLVED ORGANIC CONTAMINANTS

Organoclay has great potential as a permeable adsorptive barrier in treating contaminated groundwater and in-situ capping of contaminated sediments. The attached Technical Memo from the University of Texas at Austin discusses a set of laboratory tests that were conducted to determine sorption coefficient, k_d , values for CETCO PM-199 organoclay relative to several polycyclic aromatic hydrocarbon (PAH) compounds.

During the initial screening tests, organoclay partition coefficients were lower than activated carbon. However, Dr. Reible notes that activated carbon is more susceptible to fouling from free product than organoclay. Also, the adsorption capacity of organoclay is higher than activated carbon. Organoclay adsorption capacity is ~0.5 lb organics/lb organoclay.

In the second set of tests, k_d values were determined for CETCO PM-199 organoclay relative to several PAH compounds. Dr. Reible notes that organoclay partition coefficients will be undercalculated if they are derived using only published organic carbon partition coefficient, k_{OC} , values and the total organic carbon content of the organoclay.

On the last page is a spreadsheet generated by CETCO. The University of Texas data are graphed versus published PAH octanol-water partition coefficient, k_{OW} , values. It shows a high correlation ($r^2 > 0.99$) between PM-199 $\log k_d$ and $\log k_{OW}$ of the PAH compounds. The PM-199 k_d of other PAH compounds can be calculated by using the following equation:

$$\log k_d = 1.20 * \log k_{OW} - 0.467$$

The use of organoclay in managing dissolved contaminants relevant to contaminated sediments

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Summary

Traditionally organo-modified clays have been employed in sediment remediation as a means of absorbing oils or other nonaqueous phase liquid (NAPL) organic contamination in sediment caps serving as permeable absorptive barriers. Activated carbon is normally used to increase the sorption capacity of sediments or cap materials for dissolved contaminants. Although less sorptive than activated carbon, organoclays also adsorb dissolved phase contaminants and have the advantage of retaining significant sorption capacity in a dirty, potentially NAPL contaminated environment. The dissolved contaminant sorption capacity of a pair of commercially available organoclays was measured for the purposes of providing data that could be used in the design of a permeable adsorptive barrier for contaminated sediments. Several polycyclic aromatic hydrocarbons with log K_{oc} values ranging from 3 to 6 were employed as the test compounds both due to their importance as sediment contaminants and as an indicator of the behavior of other hydrophobic contaminants. The most sorbing of the evaluated commercial organoclays, CETCO PM-199, exhibited sorption coefficients that were 2.5 (naphthalene) to 10 times (benzo[a]pyrene) larger than the tabulated value of K_{oc} . The increase in relative sorption of the more hydrophobic compounds was consistent with the hydrophobic nature of the ammonium salt used to prepare this organoclay, bis(hydrogenated tallow alkyl)dimethyl ammonium chloride. The observed sorption of the PAH compounds is approximately 250-1000 times larger than the theoretical sorption expected in a typical sediment containing 1% organic carbon.

Introduction

Although sand can provide an effective containment approach for contaminants in sediments, there are situations where a sediment cap of greater sorption capacity is needed either to minimize the thickness of the cap required to achieve a certain degree of protectiveness or to significantly extend the lifetime of the cap. Previous research at the University of Texas has shown that organoclay, typically bentonite clays that have been treated with organic ammonium salts to replace part or all of the cation exchange capacity of the clay, can be effective at managing NAPL at contaminated sediment sites and this has been demonstrated at the McCormick and Baxter creosote site in Portland OR. The organoclay has a capacity for the creosote that exceeds 1 g dry NAPL per g of organoclay. Cores collected at the McCormick and Baxter site two years after

placement showed that effectively none of the organoclay capacity for NAPL had yet been compromised and that the sorption capacity remains approximately 1 g dry NAPL per g of organoclay.

Although organoclays have demonstrated effectiveness for sorbing separate phase contamination, the ability for organoclay to effectively manage dissolved organic contaminants has not been demonstrated. Permeable adsorptive barriers for contaminated sediments has historically focused on activated carbon, usually placed within a mat to overcome the buoyancy of the carbon, for dissolved phase containment and organoclay has been limited to sites with separate phase contamination.

The purpose of this technical memo is to summarize the sorption characteristics of organoclay for dissolved contaminants of relevance to contaminated sediments. The polycyclic aromatic hydrocarbons (PAHs) are important sediment contaminants and would also indicate the sorption expected of other strongly hydrophobic compounds. Although some tailoring of an organoclay to a specific organic contaminant may provide the best sorption capacity for that contaminant, it is generally expected that a commercial product that effectively sorbs PAHs is likely to be the most effective for other hydrophobic organic compounds in sediments.

The work was conducted in two stages. First, a pair of commercially available organoclays were screened for their ability to sorb PAHs by measurement of an effective linear partition coefficient at a single concentration. The most sorbing of these commercial formulations, CETCO PM-199, was then subjected to further testing to evaluate a complete sorption isotherm for various PAH compounds. In addition to these two sets of measurements, a literature review of physical and chemical sorption characteristics of organoclays was conducted. Although many of the organoclays studied in the open literature are not commercially available, the studies do show that organoclays can be tailored to more effectively sorb specific compounds. The literature shows that the amount and characteristics of the salt used to treat and produce the organo-modified clays controls the sorption characteristics of the clay. The sorption of the hydrophobic organics most relevant to sediments increases with the total organic fraction in the organoclay and the hydrophobicity of the hydrocarbon chain on the salt used to produce the clay. The hydrophobicity of the hydrocarbon chain in the ammonium salt used to produce CETCO PM-199/200, bis(hydrogenated tallow alkyl)dimethyl ammonium chloride, is consistent with the high sorption potential of this organoclay for highly hydrophobic sediment contaminants such as PAHs.

Methods

The objective of this experiment is to screen a pair of commercially available organoclays for the sorption capacity or partition coefficient for hydrophobic organic compounds like PAHs. The materials tested in this study included PM-199 and PM-200 (CETCO, IL). A summary of the materials is shown below

- PM-199, CETCO: proprietary granular adsorption media highly effective in removing oils, greases and other high molecular weight/low solubility organics. PM-199 is treated with the amine bis(hydrogenated tallow alkyl)dimethyl ammonium chloride. The bentonite surface with at least 100%

of its cation exchange capacity (CEC) (70 meq/100 g).

- PM-200, CETCO is identical to PM-199 except that the grain size is slightly coarser.

The water sorbent partitioning coefficient measurement was carried out in 50 mL centrifuge tubes (VWR, PA). A piece of aluminum foil was attached to the inside wall of each cap to minimize sorption loss. 20 mg of each sorbent was weighed and transferred to the tubes. 3-5 replicates were prepared for each sorbent. 50 mL of pre-made contaminated solutions were then added to each tube and the tubes were tumbled in a tumbler for 48 hours. 0.05M sodium azide was added to the electrolyte solution to inhibit bacterial degradation of the PAHs. After the tumbling, the tubes were centrifuged for 30 minutes at 3000 rpm and 1 mL of supernatant was transferred to 2mL HPLC vials. The concentrations of remaining PAHs in the liquid were determined with a High Performance Liquid Chromatograph (Waters, MA) with a Waters 2475 Multi λ Fluorescence Detector and Waters 996 Photodiode Array Detector. Meanwhile, 15 mL of supernatant was transferred to a 15 mL tube where a cm of polydimethylsiloxane (PDMS)-coated fiber was placed shortly before the centrifuge was completed. The vials were then shaken on a shaker table for exactly two hours. The fibers were picked out quickly after the two hour shaking and put into a small insert of the 2mL HPLC vials. 100 μ L of acetonitrile was added to the inserts to desorb contaminants on the fiber. The acetonitrile solution was then analyzed with HPLC and the concentrations were determined through external standards. External standards were prepared by serial dilutions of pre-made stock solution with known concentrations. The standards were treated exactly the same as the samples.

For highly sorptive materials such as CETCO-199, benzo(a)pyrene in the supernatant was lower than the detection limit of direct injection and SPME. In this case, the experiment was repeated as described above except that solvent extraction was utilized in the final stage to analyze contaminants in the supernatant. After centrifugation, 40 mL of liquid was transferred to 100 mL tubes and 10 mL of hexane was used to extract the contaminants. The mixture was allowed to shake on a shaker table for approximately 12 hours. The extraction rate of hexane was determined to be over 95%. Following the extraction, as much as possible hexane was taken out with a pipette and blown down with a RAPIDVAP N2-evaporator (Labcono, MO) to about 0.2 mL. Exact volume of hexane was recorded. Acetonitrile was then added to bring the volume back to 2 mL and re-blown down to approximately 0.1 mL. The concentrations was then determined with the HPLC mentioned above. Due to the effect of dissolved organic carbons (DOCs), the concentrations of PAHs were measurably higher than measured from direct injection or SPME. To remove the effect of DOCs, the dissolved water concentration DOC concentrations in the samples were determined with the following equation:

$$C_w = \frac{C_{WM}}{1 + C_{DOC} K_{DOC}}$$

Where C_{wm} is the water concentration measured via extraction (mg/L), C_w is the free or truly dissolved water concentration (mg/L), C_{DOC} is the DOC content in water and K_{DOC} is the DOC water partition coefficient and was determined from the following correlation provided by Burkhard¹.

$$\log K_{DOC} = \log K_{ow} - 0.58$$

This DOC was then used to correct the partitioning coefficient of benzo(a)pyrene of these materials obtained from solvent extraction. The concentrations of phenanthrene and pyrene obtained by solvent extraction were compared with those obtained by direct injection and SPME, which were similar.

As a result of these initial studies, CETCO PM-199 was selected for further analyses to evaluate a multiconcentration sorption isotherm. Four PAH compounds, Napthalene, phenanthrene, pyrene and benzo[a]pyrene were used as sorbates. The sorption experiments were carried out in 250 ml-amber glass bottles. A piece of aluminum foil was attached to the liner of the cap to minimize sorption loss to the cap. Aqueous solution was prepared by spiking deionized water with PAHs dissolved in acetonitrile. The range of concentration for each compound is listed in Table 1. Due to the very low water solubility of benzo[a]pyrene, very narrow concentration range was employed for this compound. Depending upon the sorption potential of the selected PAHs, 20mg to 100mg of PM199 organoclay was used for each measurement. After adding the organoclay, the bottle was filled with spiked water solution until complete full to minimize the headspace. The bottles were then tumbled for approximately 48 hours. At the end of experiment, the bottles were removed from tumbler and set still for half an hour to let the organoclay settle down. Preliminary test showed that this is enough to get clear water samples. One millimeter of the supernatant was transferred to 2 ml auto-sampling vials and analyzed by HPLC immediately. Three replicates and two blanks were prepared for each concentration. The blank concentration accounts for the loss of the sorbates during the experiment. Loss was within 10% for all compounds during the sorption measurements. The solid concentration (q) is calculated by the following equations:

$$q = \frac{m_{sorbed}}{m_{solid}}$$

$$m_{sorbed} = m_o - m_{loss} - m_{sample} = C_o V - (C_o V - C_{blank} V) - C_{sample} V = C_{blank} V - C_{sample} V$$

¹ Burkhard LP. 2000. Estimating dissolved organic carbon partition coefficients for nonionic organic chemicals. Environmental Science Technology, 34, 4663-4668.

Where m_{sorbed} , m_{solid} , m_0 , m_{loss} , m_{sample} represent mass of sorbates sorbed by the sorbent, mass of the sorbent, mass of sorbates in the original water solution, mass of sorbate loss during sorption, mass of sorbates in the water solution after sorption experiment, respectively.

C_0 , C_{blank} , and C_{sample} represent sorbate concentration in the original water solution, sorbate concentration in blank and sorbate concentration in the samples at the end of sorption experiment, respectively.

V is the volume of the water solution, here 250 ml.

Results

As indicated in Figure 1, equilibrium was reached between 24 to 48 hours for sorption for the sorbent with the highest capacity. Therefore, 48 hours were used as the equilibrium time and all the sorption coefficients were measured at 48 hours. The measured sorption coefficients showed significant differences between materials and the most sorptive material for PAHs was CETCO PM-199. The measured partition coefficients for the CETCO PM-200 were significantly lower than that for CETCO PM-199 despite the fact that they are identical materials but with different particle sizes. This may represent sample heterogeneity (fewer particles of CETCO PM-200 were employed for a given mass of organoclay in the sample vials), or slower uptake dynamics in the large particle sizes of PM-200. The measured sorption coefficients are tabulated in Table 2.

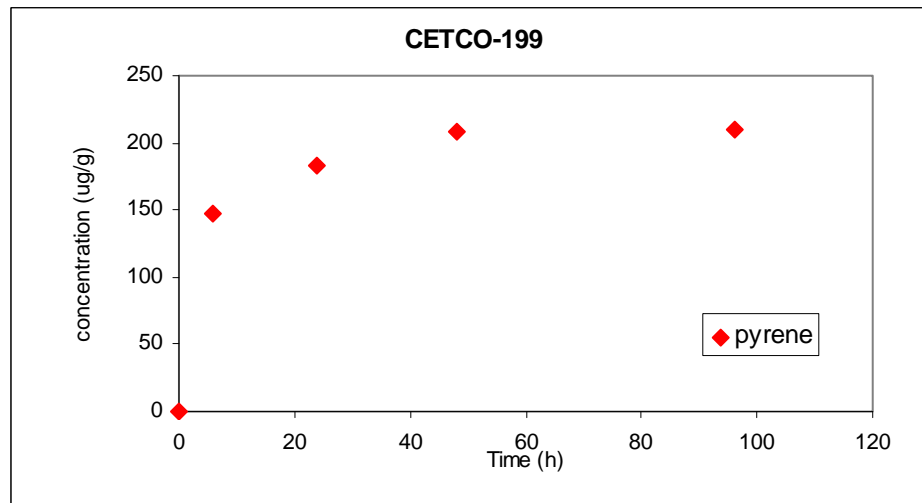
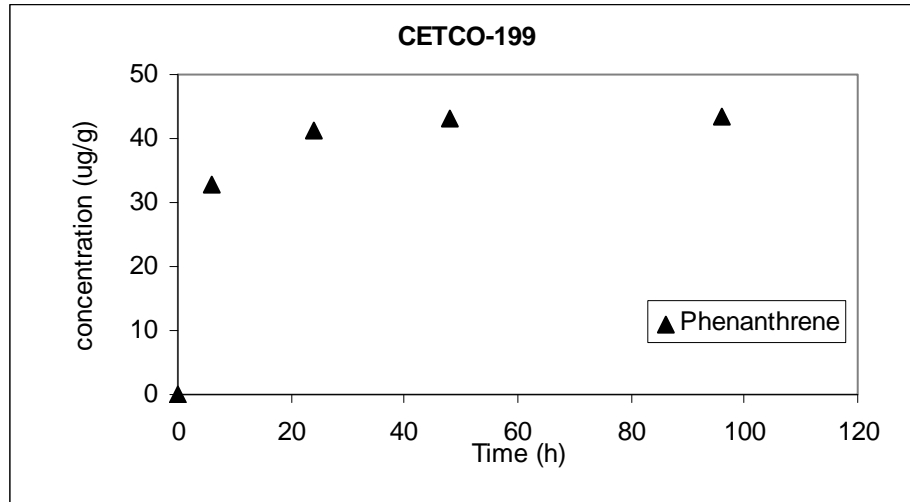


Figure 1 Sorption of phenanthrene and pyrene to CETCO PM-199 with time

Table 1 Results of Sorption Screening Tests (partitioning coefficient in L/Kg) – Standard deviations in parentheses. Values for sediment (Anacostia river), sand and activated carbon were measured for comparison purposes.

	Phenanthrene	Pyrene	Benzo(a)pyrene
CETCO PM-199	68000 (8420)	454000 (104900)	3510000 (442000)
CETCO PM-200	36517* (5790)	98700* (31000)	-
Sediment (~ 5% organic carbon)	711 (119)	2520 (-)	38750 (-)
Sand	1.87 (1.3)	5.34 (2.9)	74.0 (18)
Activated carbon	356000 (-)	2180000 (-)	-

*The lower apparent sorption coefficient in the PM-200 organoclay may indicate slower uptake dynamics in the larger particles compared to the identical organoclay formulation in PM-199. The equilibrium uptake is expected to be equal to PM-199.

A graphical depiction of the relative sorption capacity of the various sorbents is shown in Figure 2.

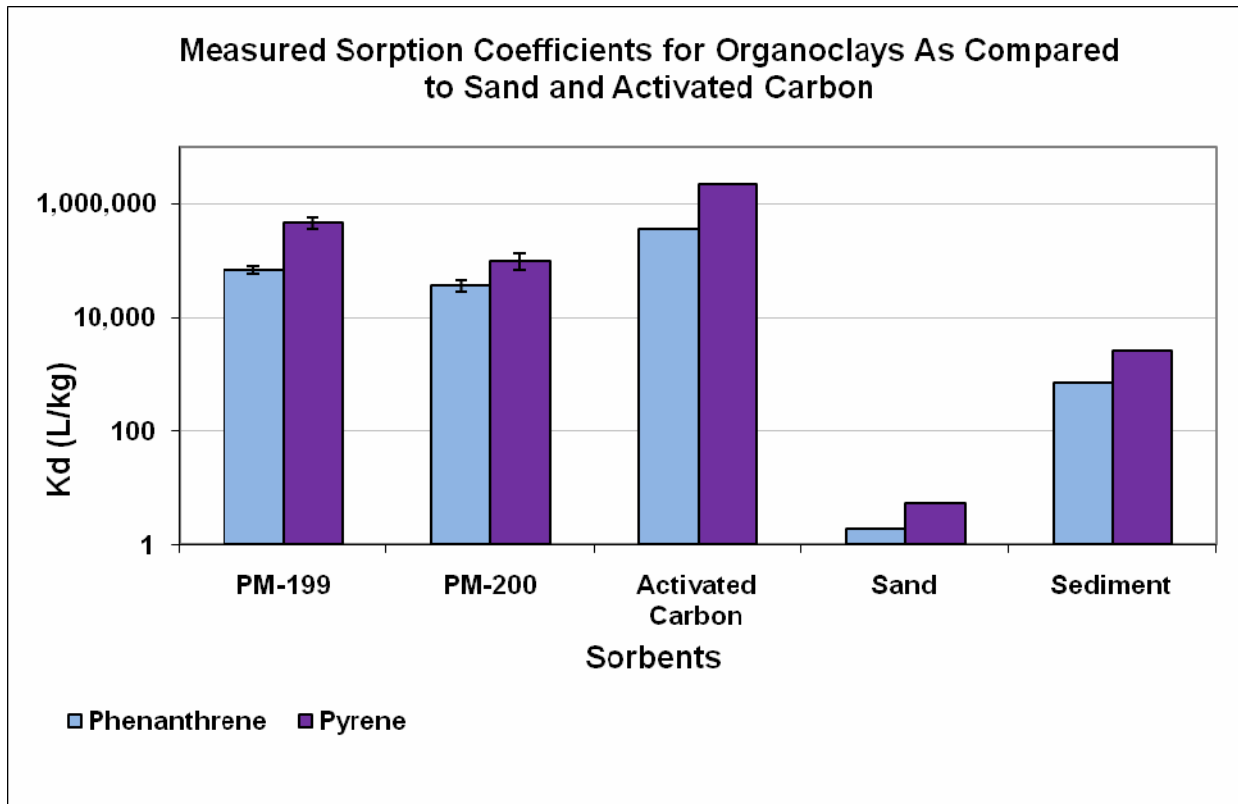


Figure 2 Relative Sorption of Tested Sorbents

On the basis of the screening measurements, PM-199 was selected for further sorption measurements to examine sorption as a function of concentration.

Sorption isotherms are plotted with solid concentrations versus the aqueous concentrations as shown in Figure 3. Organoclay-water partition coefficients (K_d) are calculated as the slope of the regression line. Partition coefficients and correlation coefficients are listed in Table 2. The sorption isotherms exhibited high linear pattern ($r^2 > 0.95$) except benzo[a]pyrene, which showed poor linear isotherm ($r^2 = 0.5$). This is due to the instability of benzo[a]pyrene in the aqueous solution and low analytical confidence due to its very low aqueous concentration especially after sorption by organoclay.

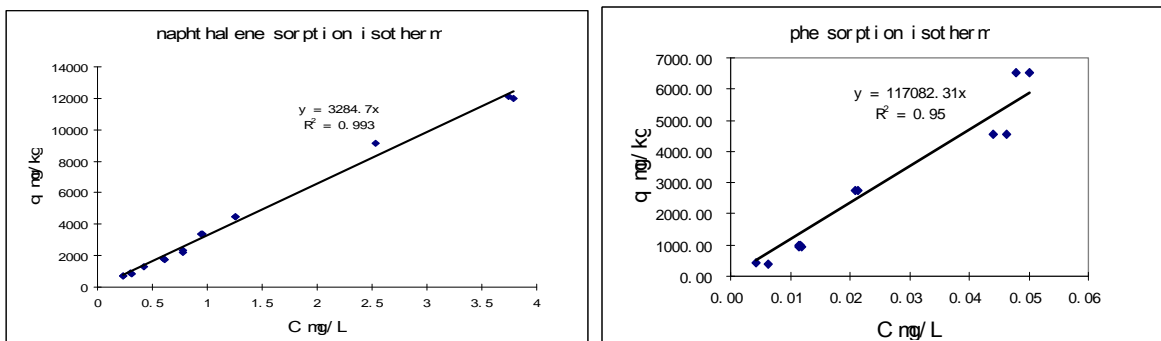
The organic carbon based partition coefficient and the ratio of the measured partition coefficient to the organic carbon based partition coefficient is also shown in the table. On average the measured partition coefficient was approximately 5 times the organic carbon based partition coefficient. Thus although the organoclay contained only about 30% organic carbon it behaved as a sorbent containing the equivalent of 500% organic carbon. Alternatively, if compared to a sediment containing 1% organic carbon, the organoclay is approximately 500 times more sorbing and compared to a sediment containing 5% organic carbon, the

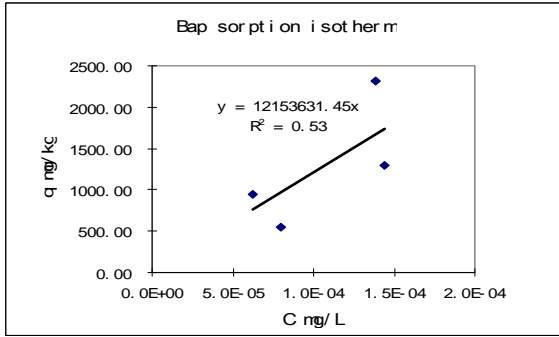
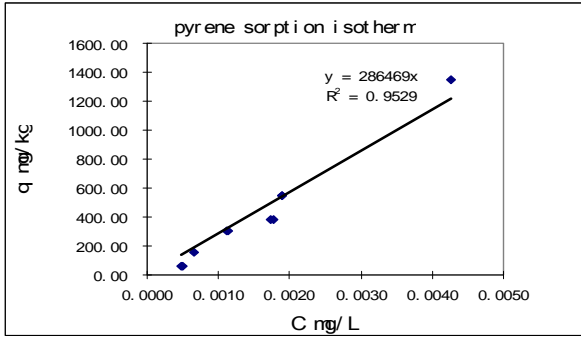
organoclays is approximately 100 times more sorbing. Although significantly less sorbing than fresh activated carbon, the organoclay has significant sorbing capacity and has the advantage of also being able to sorb separate phase NAPL and is likely less subject to fouling than the microporous structure of the activated carbon.

Table 2. CETCO PM-199 Organoclay-water partition coefficients of PAHs

compounds	K_d	Concentration range	R^2	Log K_{oc}	K_d/K_{oc}
naphthalene	3280	0.381-8.507mg/L	0.99	3.1	2.6
phenanthrene	117000	0.090-0.866mg/L	0.95	4.4	4.7
pyrene	286000	0.0018-0.1376mg/L	0.95	4.9	3.6
Benzo[a]pyrene	1E+07	0.000953-0.001277mg/L	0.53	6.0	10

Figure 3 Sorption isotherms of various PAHs on CETCO PM-199



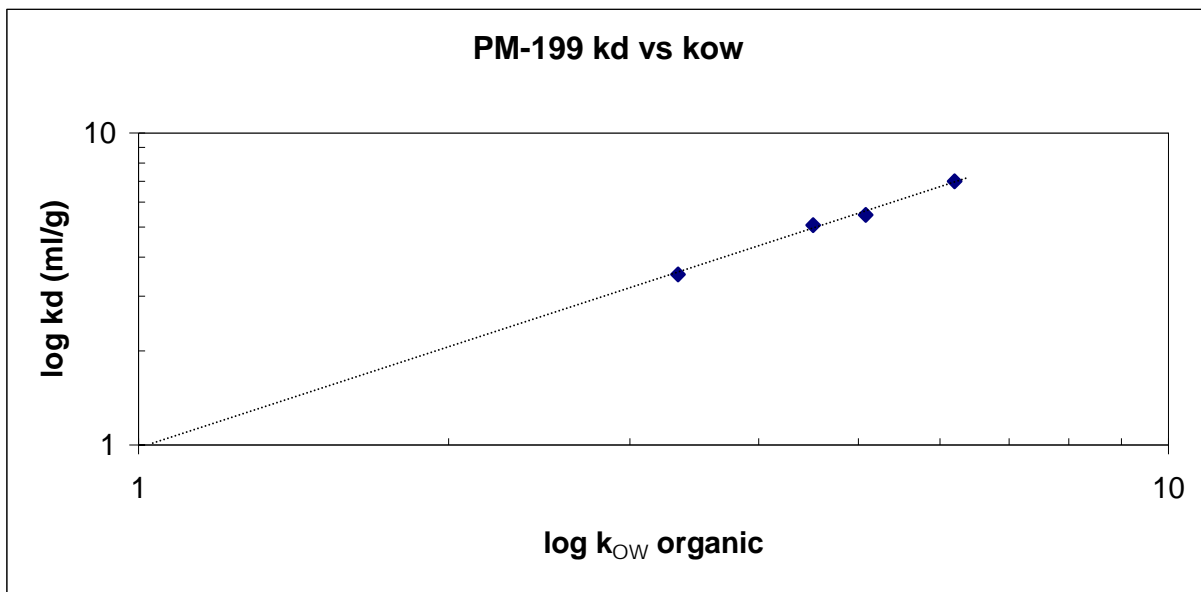


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	log k_{OW} *	log k_d (ml/g)
naphthalene	3.34	3.52
phenanthrene	4.52	5.07
pyrene	5.08	5.46
benzo(a)pyrene	6.20	7

* k_{OW} data @ 25°C from CRC Press Handbook of Chemistry & Physics, 88th ed., 2007-2008

slope	1.20	log k_d = (1.20* log k_{ow}) - 0.467
intercept	-0.467	
correl	0.997	



CETCO Excel Spreadsheet