

## A PES Study of Factors Influencing Metal Partitioning in Aquatic Systems “Design of Experiment As, Cd, Co, Cr, Cu, Pb, Ni, and Zn”

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### Abstract

*Mobility and bioavailability of heavy metals are related to their partitioning amongst suspended sediment and water. A Particle Entrainment Simulator (PES) is used to simulate sediment resuspension in natural surface water systems. The simulations were carried out under various conditions of water/suspended solids conditions. Five factors, each at various levels, are tested collectively: the pH of water at two levels (4 and 8), shear stress on bottom sediment at three levels (0.1, 0.3, and 0.5 N/m<sup>2</sup>) salinity of water at two levels (0.01 and 14.0 ppt), organic matter in sediment at three levels (0.50, 1.93, and 3.80%) and temperature at three levels 6, 15, and 30°C). The 3<sup>3</sup> x 2<sup>2</sup> factorial experiment was generated using Mini Tab 16<sup>®</sup> software. The metals evaluated in this study are the top eight metals commonly found in New England sediments. Each metal concentration was simulated at a level slightly higher than its Effective Range Median (ERM), above which, detrimental effects are frequently observed when exceeded. For the eight metals tested in this study, multiple regression equations are generated to predict the partition coefficient  $K_d$  of each metal under the various conditions of the five factors studied. The most significant factors influencing partitioning of each metal and the interactions between the factors were evaluated and validated.*

### Introduction

The mobility, fate and bioavailability of metals in surface water are directly related to their partitioning between suspended solids and water as well as the state of the metal within the water environment. Periods of high discharge in rivers or large tidal currents in estuaries can increase bottom shear stress leading to a higher presence of metals in suspension. Processes in which metals are bound to suspended materials ‘solid matrices are referred to as *sorption reactions*, therefore, metals that are bound to solids are considered to be *sorbed*. The metal partition coefficient  $K_d$  (L/kg) is the ratio of sorbed metal concentration on the solid phase  $m$  (mg/kg) to the dissolved metal concentration at equilibrium  $C$  (mg/L).

$$K_d = m \text{ (mg/kg)} / C \text{ (mg/L)} \quad (1)$$

The partitioning of metals can be influenced by many factors in varying degrees. Such factors include pH, organic matter content (OM) in sediment, salinity, degree of bottom sediment resuspension and temperature. Additional complexity is imparted by the mineralogy of the sediment and its particle-size distribution. The difficulty in describing the impacts of these factors and their relationships is that these processes are interconnected with no dominant associations among them.

The partitioning behavior of metals ( $K_d$ ) has been previously evaluated by many researchers and their values were determined based on experimental and field measurements. Log  $K_d$  values for metal partitioning in literature ranges between 2.1 to 6.9 for various metals in surface water (Alkhatib and Berna 2008; Alkhatib et. al. 2016; Allison D. et.al. 2005), where higher Log  $K_d$  values indicate more metals are adsorbed on sediment. Much of the work relating to metal partitioning has involved *in situ* measurements. Other work involved the use of well-defined models such as clay and iron, manganese and aluminum oxides (Dong et. al. 2000; Forstner 1989; Eggleton and Thomas 2004). Many of these studies investigated the partitioning under one or two conditions of pH and OM content but rarely at the same time. To our knowledge, no attempts have been made to correlate these factors or assess their impact on metal partitioning collectively. Herein, we attempt to gain better understanding of the partitioning of 8 common metals (As, Cd, Co, Cr, Cu, Pb, Ni and Zn) under different conditions of pH, salinity, temperature, OM and degree of sediment suspension, collectively at the same time. The sediment resuspension will be simulated by using a particle entrainment simulator (PES) in a recreated water column. During this process the metals in the sediment may desorb from the particles and enter the water column. A series of factorial design experiments are evaluated in which all these variables, each under different levels, were investigated collectively. The design of the experiments was generated by the statistical software MiniTab16<sup>®</sup>. We maintain that this work will help to shed some light on the processes affecting metal mobility in rivers and estuarine systems.

## **Background**

### **Factors Affecting Metal Partitioning Behavior**

The pH in stream water can vary considerably across the water column both horizontally and vertically (Eggleton and Thomas 2004). However, pH levels are often dependent on dissolved organic carbon content. Solubility of metals increase under more acidic conditions (pH of 5 to pH of 3.3) (Chauanet al. 1996), with a low pH resulting in a higher solubility of metals, which may create competition between metals and hydronium ions for attachment sites on suspended sediment. An increase in pH of the medium generally results in a higher  $K_d$  value, whereas an increase in ionic strength resulted in a lower  $K_d$  value (Hassan et al.1996).

Among sediment and suspended solids properties, OM content, whether as particulate organic matter (POM) or dissolved organic matter (DOM), plays an important role in metal speciation. Sources and distribution of OM varies considerably in surface waters and sediments with the OM content of sediments in a river dominated estuary range between 0.07% in silty sand sediments to 5.6% in muddy sediments (Alkhatib et al. 2016, Alkhatib and Berna 2008; Goni et al. 2003). These investigators also found that DOM concentrations significantly exceeded POM in the surface water samples. Structural determination of OM can indicate the presence of chemical units including: phenolic, aliphatic-OH, carbonyl and carboxyl groups all of which may play a role in metal speciation (Van Loon and Duffy 2011; Eggleton and Thomas 2004). Aside from acting as a proton acceptor, DOM can react with metals in solution through the formation of ionic or covalent bonds. The strength of this interaction depend on a variety of factors such as the number and nature of binding sites on the OM, the property of metal, other environmental factors such as pH and the presence of competing ligands. OM can be found in water in its free form or completed with metal ions/other species; it also can be found in association with other solids such as clay. It is well known that OM form coatings on such mineral surfaces (Van Loon and Duffy 2011). Metal complexes in water can take various forms depending on the availability of legends, pH, the pE of the water and the increase of the ionic index of the metal (represented as  $Z^2/r$ , formal charge squared/radius). Metal-aqua complexes can exist where no other ligands other than water are available. In natural water, few inorganic species can act as legends and form complexes with metals. These inorganic species may include carbonates, bicarbonates, chlorides or sulfates.

The ability of metals to react with OM is inversely related to ionic strength (Van Loon and Duffy 2011). This can be attributed to competition for ligand sites from alkaline earth cations in saline water and the ability of anions to react with metals, thus inhibiting metal-humate reactions. Reactive particulate phases present in the water column include DOM, aluminosilicates (clays), sulfides and hydroxides of Fe, Al and Mn (Warren and Haack 2001). OM, including DOM, has been found to be the primary transport agent of metals in water. However, DOM and POM also serve as an energy source for microorganisms; this interaction can increase the mobility of metals by releasing adsorbed metals into the dissolved phase (Goonetilleke et al. 2005).

Sediment grain size is important primarily due to the effect that surface area has on the potential binding sites for metals—finer sediments have greater surface area. In some instances, however, sediment grain size was observed to have little effect on Cu and Pb sediment concentration, but did show some influence on Zn concentration (Feng et al. 2004).

In addition, grain size affects how sediments interact with the overlying surface water by either diffusive flow or by advection (Ren and Packman 2004). Metals are particle-reactive due to the fact that they become closely associated with sediments that collect in the stream bottom and are representative of surface water metal concentrations at the time of deposition (Olsen et al. 1982; Chalmers et al. 2007). Succeeding deposition buries the deposited particle with the sorbed metals unless resuspension mobilizes or further alters the metal or particle (DiToro 2001). During wet weather periods, rain increases the discharge (and hence velocity) of the river flow thus resuspending particles that were previously settled on the river bottom. The amount of resuspension is dependent upon river currents and the amount of shear stress exerted by the flow on bottom sediments. Total suspended solids (TSS) in the water column can reach values up to 8,000 mg/L at river-bed flows with a shear stress of 0.6 N/m<sup>2</sup> (Alkhatib and Castor, 2000). Meanwhile, these same processes occur in coastal areas, where deposited sediments can be disturbed by greater wave action during storms or from the passage of ships (e.g. Rapaglia et al. 2011).

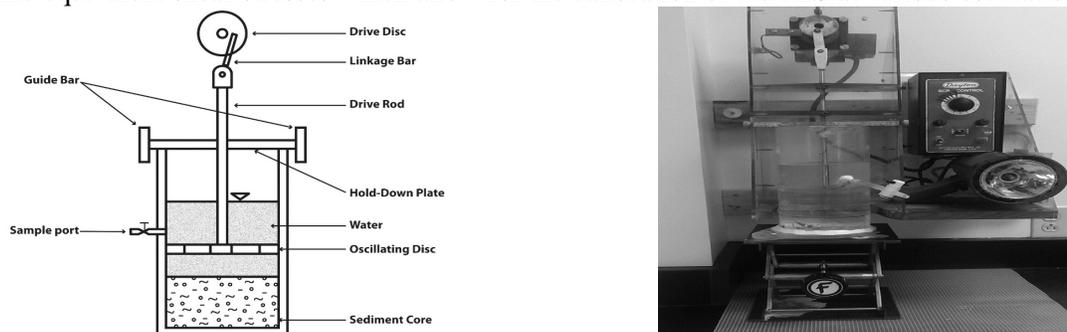
### ***Metal Toxicity***

The toxicity of metals in sediments is well-known; however, regulatory agencies have not established a sediment standard for toxicity because toxicity has been found to be unrelated to concentration. The majority of metal concentrations within New England, U.S.A. fall under Tier 2 of the National Assessment of Sediment Conditions which states that impacts from sediment contaminants are likely to occur but are expected infrequently (U.S. EPA 1997). Data were collected and compared to existing toxicity test results to create an equilibrium partitioning method called the Effective Range Medium (ERM). ERM values are concentrations above which adverse effects are frequently observed (Ingersoll and Haveland 1996). Toxicity studies show that the concentrations of metals released during resuspension are not acutely toxic, although some chronic effects have been observed (Eggleton and Thomas 2004). ERM values of As, Cd, Co, Cr, Cu, Pb, Ni and Zn (metals analyzed in this study) are reported to be 70, 9.6, 230.0, 370.0, 270.0, 219.0, 51.6, and 410 mg/kg of dry weight sediment, respectively (Long et al. 1995, Chalmers et al. 2007).

### ***Methodology***

#### **Particle Entrainment Simulator (PES)**

The PES, Fig. 1, is the device used to simulate the resuspension of sediments in this study. The PES uses an oscillating grid to generate turbulence above sediment that simulates erosive shear stress found in a shear flow. The PES used in this study was constructed using EPA PES specifications. The resuspension generated in this device is comparable to that generated in annular flumes. Annular flumes are chambers in which water is allowed to flow over a bed of sediment and they have been used to simulate shear stress, but were often time consuming, less versatile, and difficult to use. By direct comparison of flume and PES suspension data it has been possible to find equivalent shear stresses which allow for the calibration of the PES at various oscillation speeds.



***Figure 1: Particle Entrainment Simulator (PES)***

### Design of Experiment

In this study, a factorial experiment was conducted in order to collectively evaluate the impact of multiple factors and levels on partitioning of metals in surface water systems. For the metals investigated a  $3^3 \times 2^2$  factorial design of experiment was applied. The response variable of interest in this study is the partitioning coefficient of the metal  $K_d$ , calculated collectively under the five factors and their levels. The selection of these factors and levels are substantiated by the background discussion presented in this paper.

Table 1. Presents the selected factors and their levels. A total of 108 PES runs were conducted in the randomized order and conditions dictated by Minitab<sup>16®</sup> software. Example of the first 10 randomized run orders and criteria for each run is presented in Table 2.

**Table 1 – Factors and levels**

Factor	Factor Value, (level)		
	Shear stress, N/m <sup>2</sup>	0.1,	0.3, (2)
Temperature, °C	6.0, (1)	15.0, (2)	30.0, (3)
Salinity, ppt	0.0, (1)	14.0, (2)	-----
Organic matter in sediment, (%)	0.5, (1)	1.93, (2)	3.8, (3)
pH	4.0, (1)	8.0, (2)	-----

**Table 2\* – Design of experiment as generated by MiniTab16®**

Run Order	Organic matter in sediment	pH	Salinity	Shear Stress	Temp.
1	3.80	4	14.0	0.1	6
2	3.80	8	0.01	0.3	6
3	0.50	4	14.0	0.5	30
4	3.80	8	14.0	0.5	6
5	3.80	4	14.0	0.5	30
6	1.93	8	14.0	0.3	30
7	0.5	4	14.0	0.3	6
8	0.5	4	14.0	0.1	30
9	0.50	8	14.0	0.3	15
10	1.93	4	0.01	0.1	15

\* The table only presents the first 10 of 108 runs with various combinations of factors and levels performed in this study.

### Sediment Collection and Preparation

Sediments were collected from the top 5-8 centimeters of the Housatonic River bed in Southern Connecticut, U.S.A. About 70,000 cm<sup>3</sup> of sediment was collected, enough to make about 150 PES simulation runs. The sediments were transported back to the lab and placed in a pre-weighed large plastic container. River water was added to just cover the sediments in the container then mixed and homogenized thoroughly. The sediment was spiked with saturated solutions of the soluble salts of the 8 metals. The amount of each metal solution spiked was calculated to achieve concentration in the sediment around its ERM.

The metal salts used to spike the sediments are: As<sub>2</sub>O<sub>3</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, Cr(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, and Zn(NO<sub>3</sub>)<sub>2</sub>.6(H<sub>2</sub>O). The sediments were mixed thoroughly and split into three equal portions. A subsample from each bulk portion of sediment was ashed in a muffle furnace at 550°C in order to determine the OM% in each portion in accordance with procedures described in standard methods (APHA, AWWA, and WEF, 2005). The resulting OM% measured in each bulk portion of sediments then adjusted by adding clean sediments with higher or lower OM content to achieve the three levels of OM contents in the three batches of the sediments. The final OM% in the three batches of sediments were 0.32, 1.93 and 3.8%. Each dried sub-sample was then sieved to separate grain sizes from 14 to 230 meshes (using U.S. standard sieves). Grain size distribution graphs were also plotted and uniformity coefficients (C<sub>u</sub>) were calculated for the three batches of sediments.

### PES Runs

We allowed three weeks for the samples to reach equilibrium before any PES runs were conducted. We believe that the three weeks' time period was enough time to achieve equilibrium between the metals and sediment.

After the equilibration period, 450 cm<sup>3</sup> portion of the contaminated sediment was transferred to the sample holder in the PES in order to leave an even 4.0 cm thick layer of contaminated sediment. This amount was considered sufficient to work with since in prior work (Alkhatib and Weigand 2002 and Alkhatib and Berna 2008) breakthrough did not occur during suspension to the underlying layer. A tamping device is used to compact the layer of sediment and provide uniform coverage of the sediment surface to 4 cm thick. Each PES run was prepared to specification of the factors and the levels at each of the run orders presented in Table 2. The following procedure was followed in order to simulate sediments resuspension under these conditions of factors and levels. One source of water common to all runs was collected from Housatonic River in southern Connecticut. The river water was brought into the lab and stored in a refrigerator until needed. The amount of water needed for each run was then obtained and adjusted to satisfy the factors of salinity, pH and temperature needed for that run. The pH was adjusted by the addition of small amounts of HNO<sub>3</sub> or NaOH, as necessary, to attain the desired pH. The temperature of the water was chilled or heated to achieve the desired temperature level. To adjust for salinity, "Instant Ocean" sea salt was used to prepare the needed level of salinity in each run. The required sediment with the corresponding organic matter content was collected from the specific batch of sediment previously prepared. Sediment with the required OM% was added to the PES and leveled to a 4 cm thick layer as described before. The conditioned river water was then added to the PES to provide a 15.2 cm layer of overlaying water above the sediment. The height was adjusted so that the oscillating grid reached 5.1 cm above the surface of the surface of the sediment at its lowest point in oscillation. In order to prevent disturbance of the sediment when water is added, the tamping device was kept in place above the sediment until the needed amount of water poured into the PES. The level of shear stress was generated by running the PES at oscillation speed determined to create each shear stress (121, 345, and 567) oscillations per minutes which translate to shear stresses of 0.1, 0.3 and 0.5 N/m<sup>2</sup> respectively. The exact number of oscillations per minutes was verified with a digital strobe light. At each oscillation rate the PES was kept under stress for 10 minutes to achieve sediment suspension equilibrium during the run.

### ***Sampling and metal analysis***

Two 100 mL duplicate samples per run were drawn from the sample port while the PES was being agitated. A total of 230 samples were collected for all simulation runs including QA/QC samples. All samples bottles were previously cleaned following proper procedures for trace metal analysis and soaked in 1% nitric acid until time of analysis. Sample analysis was performed in accordance with EPA method 200.7 for trace element analysis, 2001. The two collected samples of each run were treated as follow: For the total recoverable metals (samples containing more than 1% undisclosed solids) 100 mL sample was placed in a 250 mL Griffin beaker and acidified with 2.0 mL of (1+1) trace metals quality HNO<sub>3</sub> and 1 mL of (1+1) trace metals quality HCl. The beaker was placed on a hot plate for reflux extraction of the metals. The hot plate was located in a fume hood and a temperature regulator thermostat was inserted in the solution and connected to the hot plate to control constant reflux temperature of 85°C. The volume of the sample aliquot was reduced to about 20 mL by gentle heating at 85°C without boiling. Then the lip of the beaker was covered with a watch glass to reduce additional evaporation and gently refluxed for 30 minutes and cooled. The sample solution was quantitatively transferred to a 50-mL volumetric flask and made up to the mark with type-1 purified water and allowed to cool. The sample then filtered using 0.45 µm syringe filter.

The filtrate then stored in a clean plastic bottle labeled "total recoverable metals" and placed in a refrigerator until ready for analysis. The second duplicate 100 mL sample was also immediately filtered using Nalgene filter holder with 250 mL filtration flask. A pre-dried pre-weighed 0.45 µm fiberglass filter was placed in the filter holder. The fiberglass filter was previously placed in the muffle furnace at 550 °C for 20 minutes. The filtrate in the filtration flask was collected in a clean plastic bottle. An appropriate volume of (1+1) nitric acid was added to adjust the acid concentration to 1% (v/v) nitric acid. The filtrate bottle was labeled "dissolved metals" and stored in a refrigerator until ready for analysis. The filter papers were then dried for one hour at 103°C and re-weighed to determine the concentration of total suspended solids (TSS) in the sample. The difference between dissolved metals concentration and total metals concentrations is used to calculate the metals concentration on the suspended particles. The fiberglass filter was placed again in a muffle furnace at 550°C for 20 minutes, desiccated and reweighed to determine the volatile suspended solids (VSS) organic matter in the suspended solids. All metal analysis was performed using a Shimadzu ICP-AES 9000.

The eight metals  $K_d$ (L/kg) values for each run were then calculated using equation 1 and logged as  $K_d$ /TSS and  $K_d$ /VSS for each metal. QA/QC samples were taken through the entire analytical protocol.

## Results and Discussion

### Sediment Characteristics

Sediment characteristic, grain size, and cumulative frequency curves were run for the three batches of sediment. The arithmetic mean of particle size ranged between 0.13 mm to 0.46 mm particle diameter. Size-fractionating the sample also allowed for the calculation of the uniformity coefficient ( $C_u$ ), which is calculated by dividing the 60<sup>th</sup> percentile grain size by the 10<sup>th</sup> percentile.

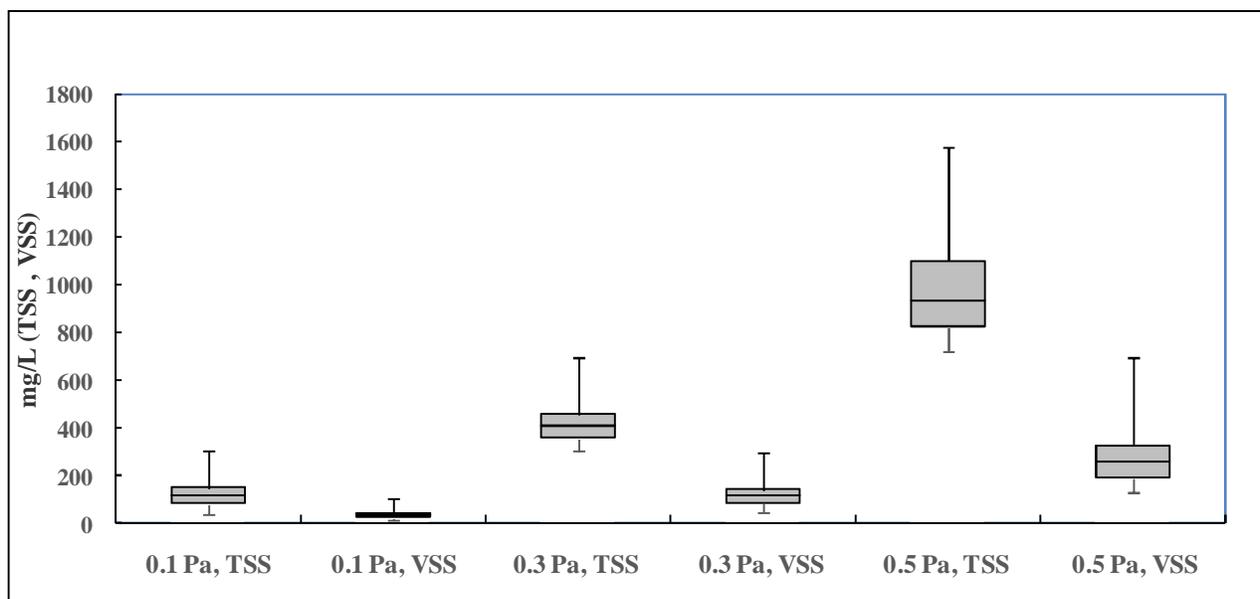


Figure 2: TSS/VSS bar chart at various shear stresses values

This is described as a measure of how well or how poorly sediment is sorted. The calculated  $C_u$  values of the three batches of sediment ranged from 3.15 to 3.36 and showed no substantial variation in uniformity coefficients among the three batches. Therefore, we believe that the physical characteristics of the sediment were consistent among the three batches used in the study and could not have substantially influenced the  $K_d$  values of metals under the factors and levels tested in the study. Figure 2 shows the results of TSS and VSS measured from all the PES runs. Clearly, there is a trend of both TSS and VSS concentrations increasing alongside the increase in the level of shear stress applied during the PES runs. Sediment concentrations in the water column ranged from 24 to 1735 mg/L for TSS and from 11 to 649 mg/L for VSS, at the simulated shear stresses 0.1, 0.3, and 0.5 N/m<sup>2</sup>. For the three batches of sediment used in this study, we found that  $d_{50}$  = 494.9 microns and  $d_{10}$  = 256.1 microns. These numbers are representative of river beds in general, and may be finer than what one may expect to find in the sediment at the bottom of estuaries.

### Partitioning Coefficients ( $K_d$ )

The partitioning coefficients  $K_d$ /TSS and  $K_d$ /VSS were calculated based on the sampling and metal analysis discussed in the methodology section and equation 1. Table 3 presents a summary of  $K_d$  values of all 108 PES runs for the eight metals. The fairly large standard deviation observed is a reflection of the change in  $K_d$  values under different factors and levels. The wide variation in both  $K_d$ /TSS and  $K_d$ /VSS values between metals is also attributed to the impact of the varied factors. It can be seen that the  $K_d$ /VSS values of all metals are higher than  $K_d$ /TSS. The VSS concentration in the PES water column represents higher levels of organic matter, finer grain-size distribution, larger surface area, and higher metal binding sites compared to that of TSS. Among the metals tested, Cd, Pb, and Zn (3197.7, 2422.2, and 2273.2 L/kg respectively) have the highest  $K_d$ /TSS values and Cr, Cd, and Zn (5279.1, 3597.6, and 2683.5 L/kg respectively) have the highest  $K_d$ /VSS values. The behavior of metals in natural surface water is complex and their partition can be impacted by many factors.

As such, it is difficult to describe the impact and relationships of these processes since they are interconnected with no dominant association amongst them. In this research article we attempted to include the most influential factors in multiple regression models without regard into how each factor individually may impact the  $K_d$  values of each metal. We believe that this approach is more practical and more similar to the behavior of metals in natural conditions; also, this method is more amenable to use in mathematical transport models. Most transport models in water systems investigate the behavior of a liquid under the action of a shearing force using computer simulated molecular dynamics. Values for the partitioning of metals can be incorporated into these models to allow for evaluating the impact of partitioning of metals between suspended solids and water.

**Table 3: Partitioning coefficients  $K_d$  for the 8 metals calculated based on TSS and VSS**

Metal	Number of Runs	Avg. $K_d$ , L/kg		S.D. $K_d$ , L/kg		Max. $K_d$ , L/kg		Min. $K_d$ , L/kg	
		TSS	VSS	TSS	VSS	TSS	VSS	TSS	VSS
As	108	542.2	743.1	130.1	801.0	810.8	6854.0	302.4	345.4
Cd	108	3197.7	3597.6	837.9	965.4	4900.7	5565.4	1852.0	435.6
Co	108	1167.8	1918.8	566.6	1752.6	2367.0	7622.7	347.0	153.0
Cr	108	1771.7	5279.1	771.2	2686.2	3563.0	9456.4	567.0	188.9
Cu	108	1455.2	3115.3	624.5	2686.2	2894.0	9958.5	567.0	37.2
Ni	108	1351.2	2010.6	607.8	1989.6	2673.0	8838.7	530.0	65.9
Pb	108	2422.2	2585.0	1851.5	1975.9	5609.4	6341.0	120.5	132.2
Zn	108	2273.2	2683.5	902.5	1103.2	3757.4	7371.8	1018.3	1176.0

### Analysis of Results

Factorial experiments are useful in assessing the statistical significance of multiple design factors. This provides information about what happens when the factor is changed and about the potential interactions between the factors. An interaction occurs when the effect of one main factor depends on the levels of another factor (or factors).

The evaluation of experiments' results was done by means of the Analysis of Variance (ANOVA) and multiple regression analysis. The use of ANOVA ensures that the real effect can be distinguished from those arising from the random error. The ANOVA procedure consists of decomposing the total sum of squares into components for each source of variability in the experiment. In our experiment, there are 5 sources of variability pH, salinity, shear stress, temperature and OM; each with multiples levels. The interactions can be between any numbers of factors. The procedure leads to a set of F-statistics and P-statistics to test the hypotheses that each factor, including interactions, is non-significant. The analysis of the eight metals were all conducted in the same manner, however, taking into consideration the length of the paper, we are only presenting the results of Pb  $K_d$ /TSS, seen in Table 4. From the ANOVA analysis of Pb presented in Table 4, it can be seen that the total sum of square (Seq SS) reflects the variance in the entire sample. The subtraction of all the sums of squares of the individual factors from total sum of squares yields the residual mean square (error). Each sum of square is calculated as a comparison between two sets of results (averages for high and low level) for the two levels factors, with one degree of freedom (DF). For the three levels factor, however, it has 2 DF.

**Table 4: Analysis of Variance (ANOVA) for Pb (based on TSS)**

Source	DF	Seq SS	Adj SS	Adj MS	F	P
pH	1	229524270	224834103	224834103	629.23	0.000
Sal	1	12810403	12252112	12252112	34.29	0.000
Shear S.	2	910507	1070514	535257	1.50	0.230
OM	2	4414486	4021762	2010881	5.63	0.005
Temp.	2	5363179	4930223	2465111	6.90	0.002
pH* Sal	1	307050	373998	373998	1.05	0.310
pH* Shear S.	2	163331	99682	49841	0.14	0.870
pH* OM	2	1008110	1133624	566812	1.59	0.212
pH* Temp	2	3857780	4074045	2037023	5.70	0.005
Sal*Shear S.	2	681259	689934	344967	0.97	0.386
Sal*OM	2	1378303	1376782	688391	1.93	0.153
Sal*Temp.	2	2737484	2697320	1348660	3.77	0.027
Shear S.*OM	4	207634	214904	53726	0.15	0.962
Shear S.*Temp.	4	4085967	4101012	1025253	2.87	0.029
OM*Temp.	4	2786703	2786703	696676	1.95	0.111
Error	74	26441374	26441374	357316	-	-
Total SS	107	296677840	-	-	-	-

The F-criterion must be compared with critical values which are normally tabulated in statistical tables at various confidence limits. For the five factors investigated for the Pb  $K_d$ /TSS, all factors were significant ( $0.00 < p < 0.05$ ) and ( $5.63 < F < 629.23$ ) except for the shear stress which has a P value of 0.23 and F value 1.5 which is only marginally significant within 75% confidence level. For the interaction between two factors, there is evidence of interactions between pH and temperature, salinity and temperature, and shear stress and temperature for which all their P values were less than 0.05. The results of R-squared value of 0.852, about 85% indicates that the variability in  $K_d$  of the metal Pb can be explained by pH, temperature, salinity, OM, pH\*temperature, salinity\*temperature and shear stress\*temperature interaction. In this study, we excluded the possibility of the three-way interactions amongst the factors. This would have required running the PES study in replication runs which would have increased the number of PES runs substantially. Table 5 presents a summary of the ANOVA results of all 8 metals. The table only presents the P and F-statistics for all the metals'  $K_d$ 's/TSS. From the data in the table, one can identify which factors and factor interactions are significant for all the metals studied.

**Table 5: Summary ANOVA results of all metals ( $K_d$  based on TSS)**

Source	As		Cd		Co		Cr		Cu		Ni		Pb		Zn	
	F	P	F	P	F	P	F	P	F	P	F	P	F	P	F	P
pH	605.4	0.00	924.6	0.00	471.4	0.00	419.6	0.00	469.1	0.00	435.0	0.00	629.2	0.00	3360	0.00
Sal	63.4	0.00	90.8	0.00	493.2	0.00	510.7	0.00	340.9	0.00	191.7	0.00	34.3	0.00	241.9	0.00
Shear S.	4.7	0.01	0.12	0.88	0.44	0.64	2.14	0.13	0.84	0.43	0.16	0.85	1.54	0.23	0.77	0.47
OM	4.5	0.02	12.9	0.00	32.2	0.00	132.4	0.00	167.3	0.00	120.0	0.00	5.62	0.01	40.7	0.00
Temp.	2.8	0.07	0.67	0.51	0.82	0.45	1.12	0.33	2.72	0.07	5.37	0.01	6.93	0.00	1.22	0.30
pH* Sal	4.1	0.05	2.68	0.11	92.5	0.00	27.5	0.00	48.6	0.00	35.4	0.00	1.11	0.31	32.8	0.00
pH* Shear S.	0.6	0.53	1.28	0.28	0.21	0.81	0.78	0.46	2.63	0.08	0.86	0.43	0.14	0.87	0.23	0.79
pH* OM	2.1	0.13	0.63	0.54	1.37	0.26	7.5	0.00	8.24	0.00	2.44	0.11	1.62	0.21	3.48	0.04
pH* Temp.	0.6	0.55	0.16	0.85	0.51	0.60	0.63	0.53	.92	0.43	0.13	0.88	5.72	0.01	3.62	0.03
Sal.*Shear S.	0.7	0.52	0.57	0.57	0.84	0.44	0.65	0.55	0.58	0.56	1.85	0.17	0.97	0.39	0.97	0.38
Sal*OM	4.21	0.02	0.87	0.42	1.34	0.27	0.87	0.42	2.02	0.14	1.63	0.21	1.93	0.15	1.11	0.33
Sal*Temp	0.3	0.72	0.48	0.62	1.83	0.17	0.11	0.89	0.19	0.83	0.94	0.37	3.77	0.03	1.42	0.25
Shear S.*OM	0.8	0.56	1.53	0.22	0.84	0.47	0.35	0.84	0.85	0.54	1.12	0.35	0.15	0.96	0.39	0.82
Sheer S.*Temp	0.61	0.66	0.42	0.79	0.74	0.57	0.11	0.98	1.61	0.18	1.32	0.27	2.87	0.03	0.25	0.91
OM*Temp	1.93	0.11	3.28	0.02	0.93	0.45	0.74	0.57	4.1	0.0	1.32	0.27	1.95	0.11	1.31	0.28

Figure 3 shows the validation indicator plots of the model for Pb  $K_d$ /TSS. These plots are created by plotting the differences between the empirical and the predicted values (residuals) against the empirical. Residuals of a well fitted model are randomly distributed around zero. The histogram and the normality probability plots in Figure 3 indicate that the residual and the fitted plots also indicate a random distribution of values with no noticeable shape or trend across all the 108 PES runs conducted. The four plots in Figure 3 appear satisfactory, so we have no reason to suspect problems with the validity of our conclusions. No appreciable differences were noticed for the rest of the seven metals tested for both  $K_d$ /TSS and  $K_d$ /VSS.

**Fitting Multiple Linear Regression Equations**

The other approach of evaluating the factors effects is to apply regression equations to fit the partitioning coefficients  $K_d$  for each metal. The response variable is the partitioning coefficient  $K_d$  and the predictor variables are the factors. The difference between the observed and fitted values from the model aids in checking model adequacy. In this study, we used the multiple linear regression model to predict  $K_d$  of each metal in terms of the five factors and any significant interactions between factors that may have been observed. The general model equation is:

$$K_d = \beta_0 + \sum_{i=1}^5 \beta_i x_i + \sum_{i=1}^5 \sum_{j>i}^5 \beta_{ij} x_i x_j \tag{2}$$

Where  $\beta_{0-5}$  are the regression coefficients,  $x_i$  ( $i = 1-5$ ) represent the five independent factors and  $\beta_{ij}$  represents the coefficient for significant interactions between the factors  $x_i x_j$  if any. The significance of the coefficients is determined according to t-student distribution. The results of the multiple regression coefficients for the 8 metals studied are presented in Table 6. In order to verify the quality of the model, it is possible to predict the responses using equation 2 and compare them with the actual results. For example, the fitting of the regression equation for the metal Cd as generated from the information presented Table 6 (only using the significant factors and interactions with  $P < 0.05$ . would be:

$$K_{d,Cd} = -1692 + 693.3 x_{pH} - 42.8 x_{Temp} + 9.8 x_{OM} x_{Temp} \tag{3}$$

Similar equations can be generated for all the metals studied. We only showed the Cd  $K_d$ /TSS equation just to limit the length of this article.

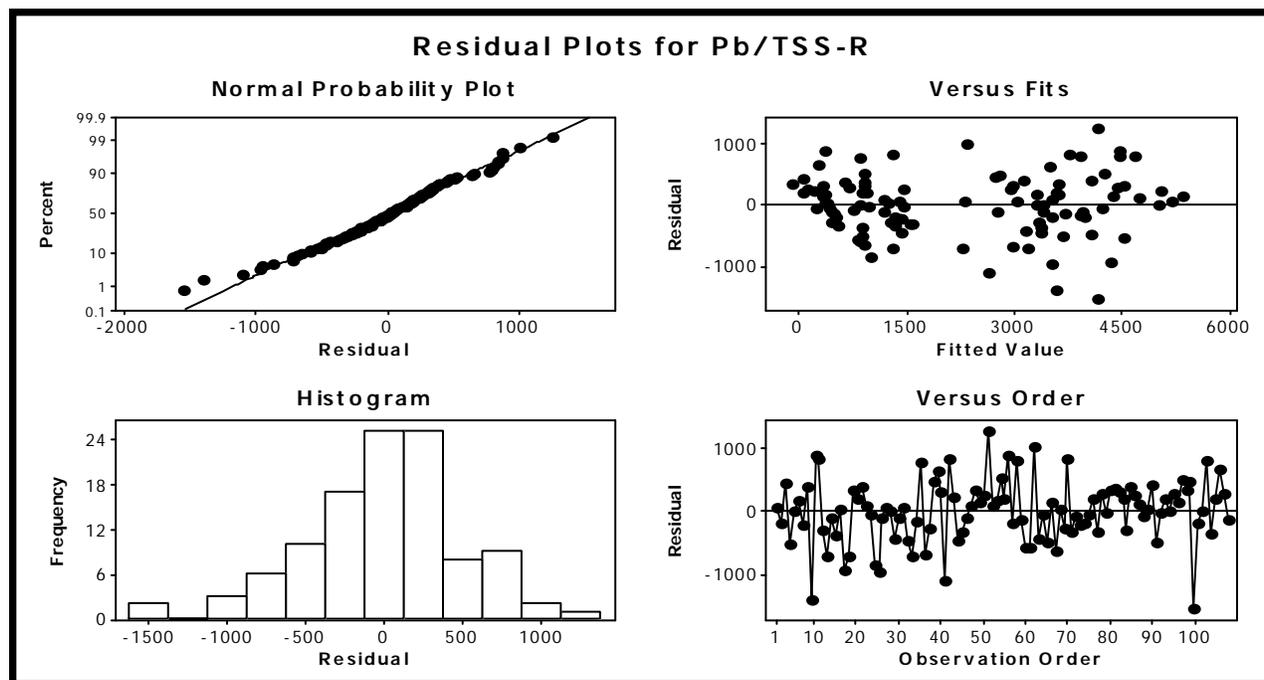


Figure 3: Example residual plots of Pb with  $K_d$  values calculated based on TSS

Table 6:  $K_d$  Prediction regression equations based on 108 runs of each metal.

Metal	$\beta$		$X_1$		$X_2$		$X_3$		$X_4$		$X_5$		$X_2X_4$		$X_3X_5$		$X_1X_2$		$X_1X_4$		$R^2$	
	$\beta_0$	P	$\beta_1$	P	$\beta_2$	P	$\beta_3$	P	$\beta_4$	P	$\beta_5$	P	$\beta_{12}$	P	$\beta_{15}$	P	$\beta_{21}$	P	$\beta_{14}$	P		
As	209.0	0.00	56.6	0.00	-2.9	0.01	32.2	0.28	16.9	0.01	-1.0	0.04	-1.1	0.02	---	---	---	---	---	---	---	87.2
Cd	968.3	0.00	374.9	0.00	-33.7	0.00	-65.3	0.67	127.2	0.01	2.0	0.66	---	---	-2.2	0.24	---	---	---	---	---	89.6
Co	57.6	0.49	102.2	0.00	-6.5	0.32	-109.1	0.27	100.1	0.00	-2.4	0.13	---	---	---	---	9.6	0.0	---	---	---	90.7
Cr	-115.6	0.00	157.8	0.00	67.0	0.00	-249.1	0.07	93.0	0.08	0.88	0.69	---	---	---	---	---	---	26.3	0.02	90.2	
Cu	147.7	0.26	86.8	0.00	1.9	0.80	-153.7	0.18	107.6	0.02	1.9	0.29	---	---	---	---	7.2	0.0	20.5	0.01	89.3	
Ni	-274.8	0.00	140.6	0.00	-6.4	0.42	-66.4	0.57	218.8	0.00	3.4	0.08	---	---	---	---	7.4	0.0	---	---	---	88.2
Pb	-1692.0	0.00	693.3	0.00	27.4	0.28	-574.0	0.13	-15.9	0.86	-42.8	0.00	---	---	9.8	0.04	3.7	0.36	---	---	---	85.2
Zn	-25.0	0.8	393.2	0.0	-32.5	0.0	-28.5	0.78	11.3	0.78	-2.1	0.22	---	---	---	---	---	---	13.7	0.03	95.1	

$X_1$  = pH,  $X_2$  = Salinity,  $X_3$  = Shear Stress,  $X_4$  = OM,  $X_5$  = Temp.

Conclusion

- The survey of chemical literature proves that the principles of factorial experiments are rarely applied to real research and that the traditional “one factor at a time” method is still prevalent.
- The applied Factorial Design of Experiments approach used in this study offers many advantages over conventional experiments by allowing researchers the ability to determine interactions between factors, more efficient utilization of data and statistical optimization of results.
- For the eight metals studied, multiple regression equations are generated to predict the partition coefficients  $K_d$  of each metal under various conditions of the five factors tested. The most significant factors and interactions influencing partitioning of each metal were evaluated and validated.
- Future work should focus on further verifications and tuning of the multiple regression equations generated using more sediment samples collected from several locations in Long Island Sound and Connecticut rivers. These data will help us better understand the distribution and mobility of toxic metals in aquatic and estuary systems, specifically under varying levels of shear stress. Having a verified model would be useful in coastal zone and watershed management, possibly reducing costs associated with metal contamination.

Acknowledgements

The authors would like to acknowledge Raghda Maseeri and Eman Althagafi for setting up the PES runs and preparation for analysis. This work was funded through an exploratory grant from the Connecticut Sea Grant.

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