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Multi-Regression Prediction of Metal Partition Coefficients under Various Physical/Chemical Conditions “Design of Experiments As, Cr, Cu, Ni and Zn”

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Abstract

The behavior of metals in surface water is complex and their partition coefficients can be impacted by many factors. Organic matter (OM) content in sediments, pH and salinity, are factors that may influence speciation and partitioning of metals. The difficulty in describing the impacts and relationships are that these processes are interconnected with no dominant associations among all. In this study, the partitioning of five metals (As, Cr, Cu, Ni and Zn) under different levels of salinity, pH, and OM content were investigated. A series of factorial design experiments are evaluated in which three levels of OM are tested each time against five levels each of salinity and pH; the design of experiments was generated by the statistical software program MiniTab16[®]. All metals tested showed a trend of increasing K_d with the increase of OM 0.36% to 4.32%. Higher K_d were the result of the increase in pH from 3-10.5 and lower K_d values resulted after an increase in salinity 0-3%. However, within that lower range of salinity, a positive linear correlation between K_d and salinity was observed which is attributed to potential formation of insoluble metal species with the increase of salinity. Multiple regression equations with the variables pH, OM and salinity were generated to predict K_d of each metal. The study showed no interaction between salinity/OM and pH/OM for all five metals.

Keywords: Metal pollution; Stream water; Ligands

Introduction

Metal pollution continues to be a complex problem, which plagues many of the world's river systems, estuaries, and coastal embayments. The mobility, fate and bioavailability of metals in surface water systems are directly related to their partitioning between suspended solids and water as well as the form of the metal itself and the other compounds within the environment. Roughly one percent of metal pollutants remain suspended within the water column; the residual metals settle on and are stored within the sediments, thus creating a sink [1]. High bottom shear stress often seen in fast flowing rivers or estuaries with large tidal currents can lead to a higher presence of metals in suspension. Metals present in sediments and on suspended solids is result of precipitation and/or adsorption to active sites on sediment particles. Processes in which metals are bound to 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).

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

The partition coefficients of metals can be influenced by many factors in varying degrees. Such factors include pH, organic matter content (OM) and salinity, degree of bottom sediment mixing and temperature variations. Additional complexity is imparted by the presence of solutes and particles in water as well as at the water/air and water/sediment interfaces. The difficulty in describing the impacts of

these factors and their relationships are that these processes are interconnected with no dominant associations among all. 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 ranges between 2.1 to 6.9 for various metals in surface water [2,3], 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 [4-6]. Many of these studies investigated the partitioning under one or two conditions of pH and OM content but never at the same time. To our knowledge, no attempts have been made to correlate these factors or assess their impact on metal partitioning. Herein, we attempt to gain better understanding of the partitioning of five common metals (As, Cr, Cu, Ni and Zn) under different conditions of pH, salinity and OM. We maintain that this work will help to shed some light on the processes affecting metal mobility in aquatic and marine systems. Consequent results can be used in formulating pollutant transport models.

Factors affecting metal partitioning behavior

The pH in stream water can vary considerably across the water column within river channels [6]. However, pH levels are often dependent on dissolved organic carbon content. A low pH results in a higher solubility of metals thus creating competition between metals and hydronium ions for attachment sites on the functional groups. 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 [7]. Solubility of metals increase under more acidic conditions (pH of 5 to pH of 3.3) [8].

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. The OM content of sediments in a river dominated estuary range between 0.07% in silty sand sediments to 5.6% in muddy sediments [2,9]. They also showed 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 [6,10]. 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 the metal, other environmental factors such as pH and the presence of competing ligands.

OM can be found in water in its free form or complexed 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 [10]. Metal complexes in water can take various forms depending on the availability of ligands, 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-aquo complexes can exist where no other ligands other than water are available. In natural water, few inorganic species can act as ligands 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 [10]. 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 [11]. 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 [12].

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 majorities of metal concentrations within New England 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 [13]. 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 [14].

Toxicity studies show that the concentrations of metals released during resuspension are not acutely toxic, although some chronic effects have been observed [6]. ERM values of As, Cr, Cu, Ni, Zn (the

metals analyzed in this study) were 70, 370, 270, 51.6 and 410 mg/kg of dry weight, respectively. When conducting *in-situ* testing of bed sediments in New England, concentrations were measured up to 440, 407, 83, and 2015 mg/kg for Cr, Cu, Ni, Pb and Zn, respectively [15]. These concentrations are above the ERM values for Cr, Cu and Zn.

Methodology

Design of experiments

In a traditional experiment, each investigated factor is individually varied while all of the other factors are held constant. This method ignores possible synergistic effects (interactions) involving two or more factors; each experiment serves only one purpose, that is, to evaluate the impact of that given factor. Therefore, a factorial experiment was conducted in order to evaluate multiple factors at the same time. The experiment was designed in MiniTab16[®] software determine if any significant interactions occurred between factors. For each As, Cr, Cu, Ni, and Zn, two factorial designs of experiments were generated by MiniTab16[®]: pH/OM and Salinity/OM (Table 1). A total of 102 isotherm runs were conducted in the randomized order as dictated by MiniTab16[®] software (Table 2).

Factor	Factor value (Level)				
pH	3.0(1)	5.0(2)	7.20(3)	9.0(4)	10.5(5)
Salinity (%)	0.00(1)	0.5(2)	1.0(3)	2.0(4)	3.0(5)
Organic Matter Content (%)	0.36(1)	2.12(2)	4.32(3)	-	-

Table 1: Factors and levels for experimental design.

Random Order	Run Order	Salinity (%)	OM (%)
12	1	2	4.32
1	2	0	0.36
11	3	2	2.12
5	4	0.5	2.12
14	5	3	2.12
3	6	0	4.32
13	7	3	0.36
7	8	1	0.36
6	9	0.5	4.32
4	10	0.5	0.36

Table 2: Example design of experiment salinity/OM.

Sediment collection and preparation

Sediments were collected from the top 5-8 centimeters of the Housatonic River bed in Southern Connecticut. The sediments were mixed thoroughly and split into three equal portions. Each dried subsample was then sieved to separate grain sizes from 14 to 230 units' meshes (using US standard sieves). For the three portions of sediments used in this study we found that $d_{50}=494.9$ microns and $d_{10}=256.1$ microns. 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 [16]. The resulting OM% measured in each bulk portion of sediments were 0.36%, 2.12% and 4.32%, respectively. These known amounts were then added to each sample in order to simulate the three levels of OM factor in the sediments. Cumulative frequency distribution curves were plotted as a function of grain size, which were used to determine the d50 and d10 values of the sediment used in this study.

Sediment isotherm studies

Isotherm samples were analyzed in the order generated by the Minitab16[®] software (Table 2). All samples bottles were previously cleaned and soaked in 1% nitric acid until start of analysis. "Instant Ocean" was used to prepare the needed salinity concentration in each bottle. For all isotherm runs, the types of water were categorized based on salinity as fresh (0%), brackish (0.5-2%) or sea water (3%). For the salinity/OM runs, the pH in all bottles was kept constant at pH 7.2. An exact amount of 0.2500 gram retrieved from the sediments with the proper amount of OM was then added to each bottle. For the pH/OM runs, the runs were divided into three categories of water: acidic (pH 3 and 5), neutral (pH 7.2) and basic (pH 10.5). These pH values coincide with the metal precipitating pH as calculated from their solubility products (K_{sp}). Using these data, the mass was calculated of the metal in mg/kg within the sediment (Table 3).

Two mg/L stock solutions of metal nitrates for Cr, Cu, Ni and Zn and As₂O₃ were then prepared. The selection of the 2 mg/L metal concentration is based on the average EMR values of 200 mg/kg for the metals tested in this study [15]. Fifteen runs were prepared in duplicate to measure total recoverable metals and dissolved metal concentrations for each of the factor/metal analyses in order to use for K_d calculations. The final volume of solution was maintained at 100 ml volume. Each

sample was stirred for 48 hours to achieve a state of equilibrium and full partitioning of metals [2,17]. The same procedure salinity/OM was followed for the pH/OM runs. Trace metal quality 0.1 M HNO₃ and 0.1 M NaOH were used to adjust for the needed pH of solution in each bottle. The change in pH after the addition of sediment was in the range between 0.1-0.25 pH units which we considered acceptable and within the scope of this study. Two blank samples were also prepared for each set of duplicates in order to maintain quality assurance.

Metal analysis

Sediment samples were digested in order to obtain the metal concentrations in accordance with USEPA method for trace metal analysis [18]. All samples were subsequently stored in a refrigerator until analysis could be completed. A total of six standards were created to formulate the calibration curves at the following concentrations: 0, 0.5, 2, 4, 8 and 16 mg/L. Metal analyses were performed using Shimadzu ICP-AES 9000 and standard QA/QC procedures were followed (triplicate runs, continuing calibration verification, blanks etc.). All isotherms were run under constant room temperature, constant degree of mixing and oxic conditions.

Partition coefficient calculations (K_d)

The metal concentration in the "total recoverable metal" sample represents the total metal extracted from the 0.2500 grams of sediment whereas the "dissolved metal" samples only extracted the dissolved fraction of the metal within the sample. Adjusting for volume and subtracting the two gives the metal concentration extracted from the 0.2500 grams sediment. Using these data, we can calculate the mass (m) of metal in mg/kg within the sediment. K_d values were created using Eq from the introduction.

Metal	Solubility Product of M. hydroxide K _{sp}	Precipitating pH as hydroxide	Metal First Hydrolysis pK _h	Ionic index Z ^{2/r}	Covalent index X ^{2/r}
As(III)	-	-	-	14.8	2.7
Cr	6.8 × 10 ⁻²⁹	7.16	4.0, Cr ³⁺	4.8	2.3
Cu	1.1 × 10 ⁻¹⁵	9.12	7.5	5.2	2.9
Ni	4.48 × 10 ⁻¹⁶	8.98	9.4	5.7	2.6
Zn	3.0 × 10 ⁻¹⁷	8.59	9.6	5.3	2.2

Table 3: Ionic/covalent indices, pK_h, and K_{sp}, values of studied metals.

Statistical analysis

Multivariable regression analyses were complete in MiniTab16[®] for all factors. The characteristic of the design of the experiment method is the ability to test the combination of main effects (factors) at different levels. This application shows how the factors (pH, salinity and OM) affect the partition coefficient K_d and how these factors may relate. Minitab16[®] implemented the method of least squares to estimate the regression coefficients. In addition, analysis of variance (ANOVA) were completed to determine if any interactions occurred between salinity and OM or pH and OM. The assumptions of normality and variance were verified and found normally distributed allowing for the use of ANOVA without transformation.

Results

Impact of pH and OM on partition coefficient K_d

At the end of each pH run, K_d values generally increased when OM % increased. K_d values progressively increase from acidic to basic conditions. Arsenic showed no change of K_d values beyond pH of 9 (Figure 1). However, a sudden increase in K_d was observed Cr after pH of 8 (Figure 2) and in Cu, Ni, Zn after a pH of 9 (Figures 3-5). Metals' adsorbent affinity to suspended solids follows the order: Ni>Cr>Zn>As>Cu. For As, K_d increased from 272 to 521 L/kg, for Cr from 84 to 301 L/kg, for Cu from 32 to 2688 L/kg, for Ni from 85 to 149 and for Zn from 127 to 973 L/kg (Table 4). ANOVA results in Table 6 determined that the pH/ OM models showed significant

differences in K_d values (for all metals, $p < 0.05$, $df=101$, f -values vary). For the OM factor, the p and F values showed significant impact of OM on K_d for As, Cr and Cu. However, OM was not significant on the K_d values of Ni and Zn (Ni: $p=0.159$, $df=101$, $F=2.34$; Zn: $p=0.105$, $df=101$, $F=3.03$). Within the multiple regressions, R^2 values for the pH/OM model for the five metals ranged between 92.1% and 99.4% (Table 6).

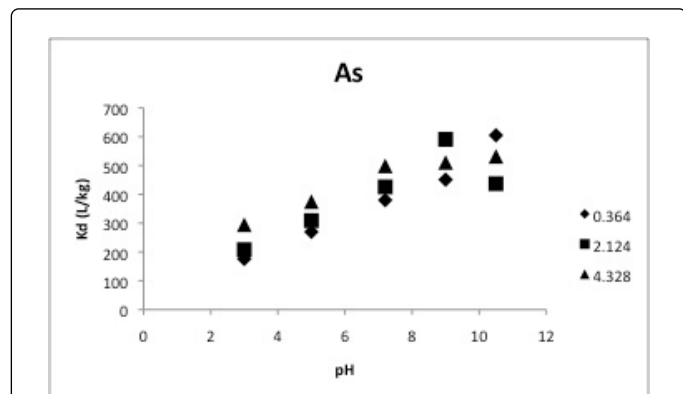


Figure 1: Partition Coefficient of As at various levels of pH.

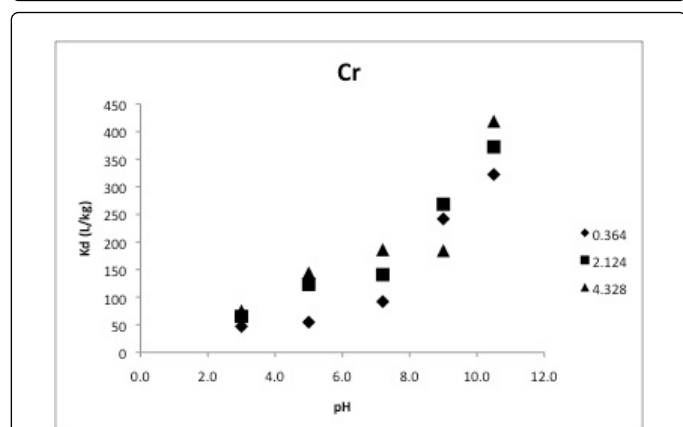


Figure 2: Partition Coefficient of Cr at various levels of pH.

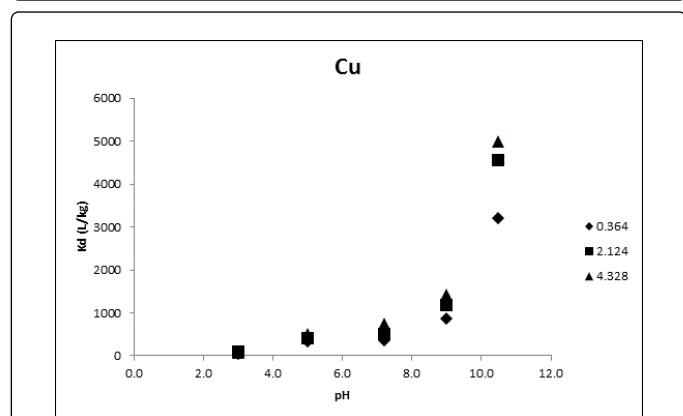


Figure 3: Partition Coefficient of Cu at various levels of pH.

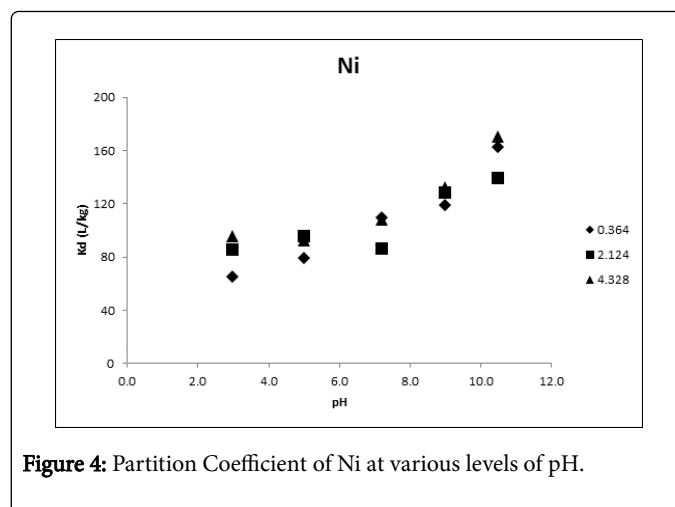


Figure 4: Partition Coefficient of Ni at various levels of pH.

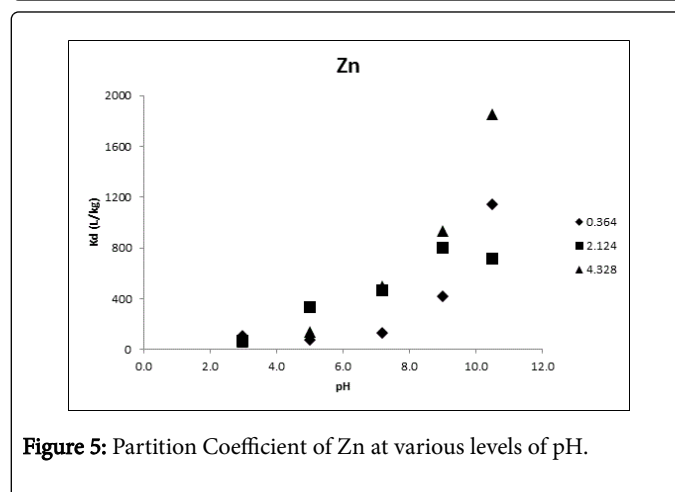


Figure 5: Partition Coefficient of Zn at various levels of pH.

Parameter	Type of Water	As	Cr	Cu	Ni	Zn
pH	3	272.2	84.9	232.1	85.3	127.4
	Acidic					
	5	435	139.7	530	100.9	361.3
	Neutral					
	7.2					
pH	9	521.2	301.5	2688.8	149.7	973.9
	Basic					
	10.5					
Salinity	0	46.3	49.4	86.9	369.1	157.2
	0.5	76.1	111.8	188.3	479.9	236.4
	1					
	2					
	3	149.3	210.5	365.6	561.6	430.3

Table 4: Average K_d (L/kg) values of As, Cr, Cu, Ni and Zn under various conditions.

Factor	Level	Type of Water	As	Cr	Cu	Ni	Zn
OM%	0.36%	Fresh	26	30	56.9	296.9	91.4
		Brackish	55.3	99.1	135.4	433.7	219.9
		Sea	175	193.4	278.8	544.5	338.8
		Acidic	223	50.8	182.4	71.9	88.3
		Neutral	380	92	359.7	109.1	128.2
		Basic	528	282.2	2019	140.4	775.7
	2.12%	Fresh	53	48.7	94	377.3	217.1
		Brackish	75.3	103.9	184.3	480.3	247.6
		Sea	120	211.7	365.9	628.1	396.6
		Acidic	258.5	94.3	238.9	90.2	198.6

4.32%	Neutral	426	140.8	485.1	85.7	460.8
	Basic	514	320.4	2851	133.7	755.6
	Fresh	60	69.5	109.9	433.1	162.9
	Brackish	97.7	132.3	245.3	520	271.8
	Sea	153	226.4	452.1	512.1	555.6
	Acidic	335	109.8	274.9	93.8	95.2
	Neutral	499	186.3	745.3	107.8	494.8
	Basic	521.5	301.8	3196.4	151.06	1390.4

Table 5: Average K_d (L/kg) values of As, Cr, Cu, Ni and Zn under various OM% and salinity/ pH values.

Metal	pH		% OM		R^2	Regression Equation	R^2 Prediction
	F-value	P-value	F-value	P-value			
As	50.6	0	14.6	0.002	96.6	$K_d = -86.7+95.6 \text{ pH}-4.4 \text{ pH}^2+24.5 \text{ OM}$	91.6
Cr	44.9	0	4.14	0.058	96.4	$K_d = 97.2-36.5 \text{ pH}+5.5 \text{ pH}^2+14.5 \text{ OM}^2$	91.2
Cu	275.1	0	4.61	0.047	99.4	$K_d = 3110.4-1424.0 \text{ pH}+141.5 \text{ pH}^2+14.2 \text{ OM}$	91.3
Ni	20.3	0	2.34	0.159	92.3	$K_d = 91.0-10.1 \text{ pH}+1.5 \text{ pH}^2+4.0 \text{ OM}^2$	84.6
Zn	18.2	0	3.03	0.105	92.1	$K_d = 426.1-150.1 \text{ pH}+16.1 \text{ pH}^2-88.2 \text{ OM}^2 + 23.1 \text{ pH} \times \text{OM}$	92.8

Table 6: pH/OM regression equations and ANOVA values for the partitioning coefficient (K_d) values of the five metals.

Metal	Salinity		% OM		R^2	Regression Equation	R^2 Prediction
	F-value	P-value	F-value	P-value			
As	40.8	0	20.38	0.001	96.2	$K_d = 22.9+28.4 \text{ Sal}\% +9.6 \text{ OM}\%$	91.5
Cr	86.93	0	10.56	0.006	97.8	$K_d = 28.6+54.3 \text{ Sal}\% +8.8 \text{ OM}\%$	96.5
Cu	34.86	0	16.03	0.002	95.5	$K_d = 27.6+86.5 \text{ Sal}\%+27.9 \text{ OM}\%$	88.4
Ni	24.26	0	12.35	0.004	93.8	$K_d = 344.4+65.0 \text{ Sal}\%+21.5 \text{ OM}\%$	79.3
Zn	11.36	0.002	5.07	0.036	87.4	$K_d = 88.9+84.7 \text{ Sal}\% +26.6 \text{ OM}\%$	69.2

Table 7: Salinity/OM regression equations and Analysis of Variance (ANOVA) for the K_d values of five metals.

Impact of salinity and OM on partition coefficients K_d

The lowest values of K_d were all recorded in fresh water (40 L/kg) and the highest in seawater (560 L/kg) (Table 5). ANOVA results determined that the salinity/ OM models showed significant differences in K_d values for all metals analyzed ($p < 0.05$, $df = 101$, F-values vary). Within the salinity/OM model, the R^2 values ranged between 87.4% and 97.8% for the five metals tested (Table 7). The ANOVA table and the estimated effects coefficients generated by MiniTab 16[®] did not indicate any significant two way interactions between salinity/OM nor pH/OM (p values > 0.4 , $df = 101$, F-values vary).

Discussion

pH/OM

The majority of metal partitioning generally occurs on clay minerals, Fe and Mn oxides/hydroxides, carbonates and humic acids. Due to the composition of the added sediment being the same for all runs, the sudden shift of K_d values exhibited in the experiment at the various pHs can be partially attributed to precipitation of metals. It is assumed that the precipitation of metals observed during K_d shifts were due to the concentration added to each sample (2 mg/L). When comparing the experimental results of the tested metals with those

previously obtained, the general trend is that the metal uptake increases with an increase in pH [7,19,20].

Other researchers [19,21] showed that adsorbent affinity follows the metal's first hydrolysis constant (K_h). For the metals tested in this study, Cr was found to have a $pK_h=4$ and Cu was found to have a $pK_h=8$ which supported the previous finding yet Zn and Ni deviated from them. When Comparing the ionic and the covalent indices Z^2/r and X^2r with the order of K_d values of the studied metals, .

Large changes (<6.5->8.2) in pH can occur in estuaries, as high pH seawater mixes with low pH riverine water. Given the fact that K_d values substantially increase at higher levels of pH it is likely that estuarine mixing acts as a sink for such metals before it is able to reach the open coastal area [22]. Meanwhile, recent evidence has shown that pH values in sandy aquifers may reach values of around 10 in the mixing zone between fresh groundwater and seawater [23]. If this were the case, this mixing zone may lead to the precipitation of Cr, Cu, Ni and Zn effectively removing them from solution and storing them in sandy coastal sediments.

Salinity/OM

In general, the calculated K_d values for the five metals (at pH 7.2) were considerably lower than that determined in the pH/OM runs at the same pH. Such a decrease in K_d values due to an increase in ionic strength (salinity) would indicate competition from ions for the adsorption sites on sediments. The sea salt used in the study would have positively charged sodium ions that could compete with the studied metals for these sites.

These values are considerably lower than the pH/OM model predicted, which indicate that salinity suppresses the adsorption of metals onto sediments leading to these lower K_d values. However, within this lower range, a positive linear correlation between K_d and salinity is still observed (Figures 6-10). Under this controlled isotherm study (oxic, pH 7.2, similar types of sediment except for OM %), the studied metal species will be mostly chlorides, sulfates and other potential insoluble metal species which can, in effect, increase K_d values. Salinity, may acts as an "iron curtain" for these metals before entering the open coastal zone and may play an influential role in reducing the toxic effects of high metal concentration in coastal and open ocean waters. As the suspension of OM increases, the K_d of each metal will increase as well. Organic matter is often in higher concentrations in estuarine areas, due to inputs from rivers, decomposition, and human influences.

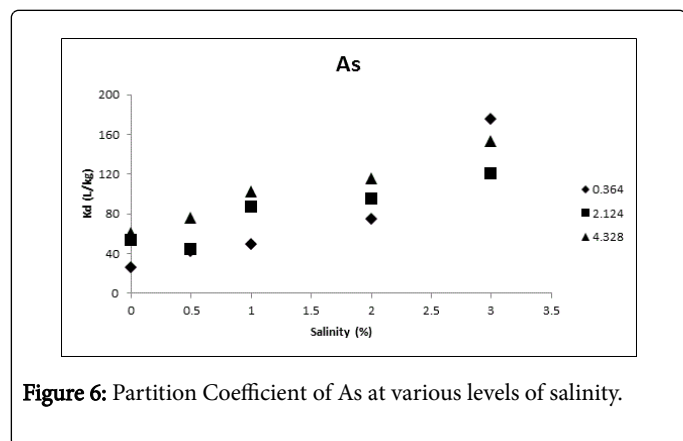


Figure 6: Partition Coefficient of As at various levels of salinity.

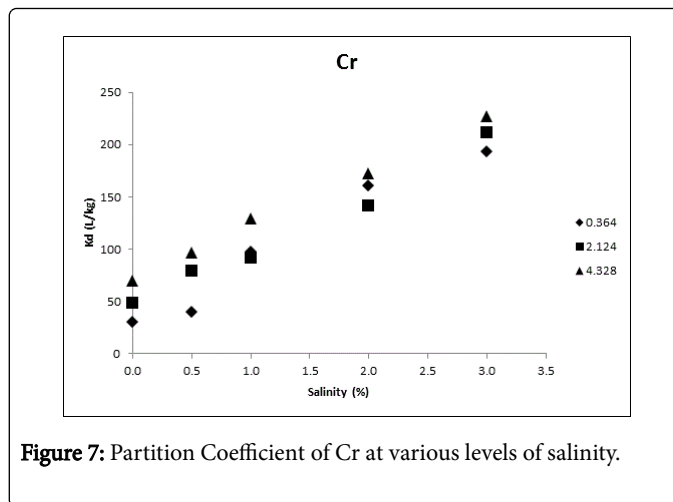


Figure 7: Partition Coefficient of Cr at various levels of salinity.

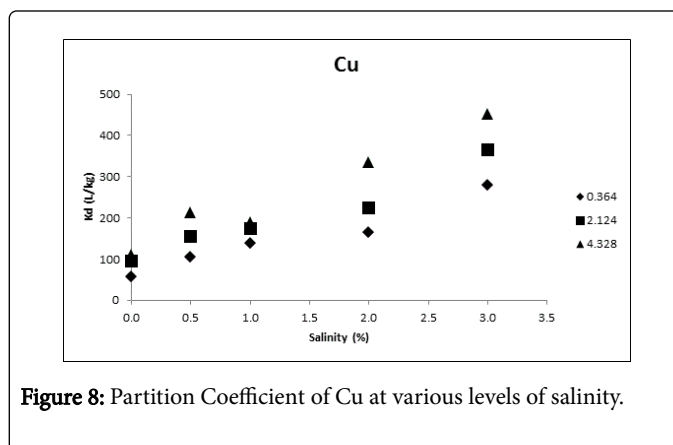


Figure 8: Partition Coefficient of Cu at various levels of salinity.

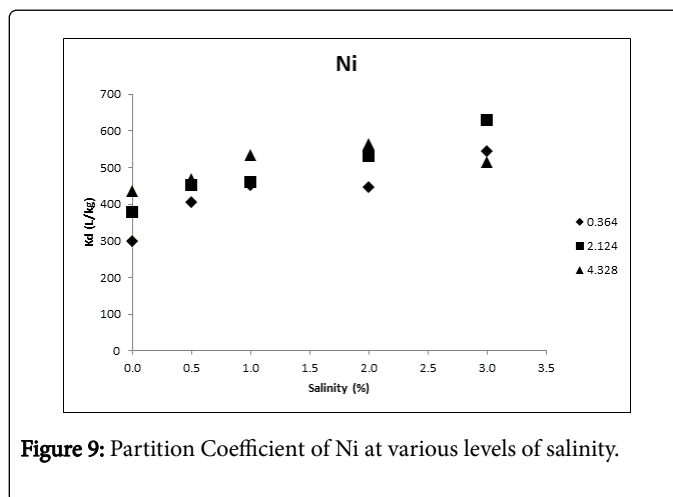


Figure 9: Partition Coefficient of Ni at various levels of salinity.

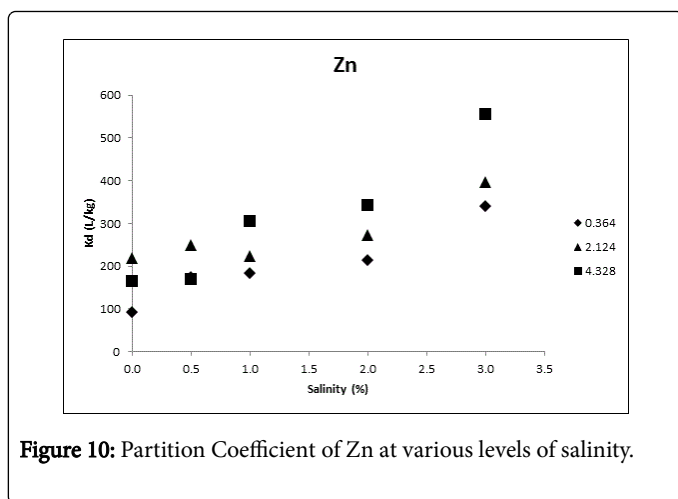


Figure 10: Partition Coefficient of Zn at various levels of salinity.

Significant changes may occur at the discharge point of rivers in seawater, otherwise known as estuaries. Subsurface and surface estuaries exhibit gradual to steep gradients in salinity, both horizontally and vertically, making it very difficult to pinpoint spatial and temporal processes for metal cycling. This research is critical in determining how multiple factors can affect metal availability within an estuarine zone by shedding light on the role of salinity, pH and OM on K_d processes. Future work should examine factorial design of experiments as such with additional factors at different levels such as water oxidation potential, temperature and degree of agitation as well as the field verifications of the generated multiple regression equations already completed.

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