



Prediction of Metal Remobilization from Sediments under Various Physical/Chemical Conditions “Design of Experiments Cd, Co and Pb”

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Abstract

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. 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. In this study, the partitioning coefficient of three metals (Cd, Co and Pb) under different levels of salinity, pH, and OM content were examined. A series of factorial experiments were 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 an increase of OM from 0.36% to 4.36%. Salinity experiments showed that the lower values of K_d were all recorded in freshwater and the highest K_d values were recorded in saltwater. The metal Pb showed the highest K_d values. The average K_d values under acidic conditions for Cd, Co and Pb are 234, 83 and 5,618 L/kg respectively. The relatively higher value of K_d for Pb compared to that of Cd and Co can be attributed to its lower precipitating pH. Multiple regression equations were generated to predict K_d of each metal when comparing multiple factors at the same time (salinity/OM and pH/OM). The study showed no significant interactions between salinity/OM and pH/OM for all three metals. This supports that tested factors are all affected K_d but act independently.

Keywords

Metal partitioning; Metal remobilization; Sediments resuspension

Introduction

Metal pollution from previous commercial and industrial use continues to plague many of the world's water systems. Within surface waters, the mobility and bioavailability of heavy metals are directly related to their partitioning amongst suspended solids and water which is dependent on the state of the metal and other compounds that the metals may interact with. In general, one percent of metal pollutants remain suspended in the water column; the remaining

99% of metals are stored within the sediments, which create a sink for heavy metals [1]. The precipitation or adsorption of metals onto active sites of sediment particles are the result of this sink. These metals that are bound to solids within the sediment are considered to be *sorbed*. The metal partition coefficient K_d (L/kg) is the relationship between the sorbed state to the dissolved state of these metals as indicated in the following equation.

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

The K_d of metals can be influenced by many abiotic factors including shifts in redox states, pH, organic matter content (OM), degree of sediment mixing, salinity and temperature. This complex interaction is compounded by the interactions between the water/air as well as the water/sediment interfaces. However, it is unclear how these factors are interconnected as no dominant relationships are displayed among all. Metal partitioning has been a topic of research for many years. Log K_d values for metal partitioning ranges between 2.1 to 6.9 for various metals in surface water [2,3]. Although K_d values of metals have been useful in determining how metals attach onto sediments, no *in situ* experiments have been conducted on multiple parameters at once.

Much of the previous work has used 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. In attempt to gain better understanding of the partitioning of three common metals (Cd, Co, and Pb), each metal was analyzed under compound conditions of various pH, salinity and OM levels. This work will help expand the current knowledge of how abiotic parameters affect metal mobility in aquatic and marine systems.

Factors affecting metal partitioning behavior

pH: Within all water bodies, especially streams and flowing water, pH values can vary drastically [6]. Hydronium ions and metals often compete for attachment sites on functional groups within sediments. This competition is often the result of a low pH in conjunction with a higher solubility of metals. As the pH increases, a higher partitioning coefficient of metals is also observed [7]. Metals are sparingly soluble under alkaline conditions (pH=8.0) yet the solubility increases under slightly acidic conditions (pH=5.0) and increases drastically when pH is very acidic (pH=3.3) [8].

Organic matter

Among sediment and suspended solids properties, OM content, in all of its various forms, plays an important role in metal speciation. The origins of OM can vary greatly in both surface waters and sediments. Previous research has shown that the percent OM within estuarine river sediments range from 0.07% in silty sand sediments to 5.6% in muddy sediments [2,9].

Apart from size, the physical shape of the OM can also indicate the presence of various chemicals such as: carbonyl groups, carboxyl groups, phenolics and aliphatic-OH which may play a part in metal speciation [6,10]. Aside from acting as a proton acceptor, dissolved OM can create ionic or covalent bonds with metals. This interaction is dependent on various factors like the state of the metal, abiotic factors

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Received: January 09, 2016 Accepted: May 26, 2016 Published: June 03, 2016

like pH, the presence of ligands competing for attachment sites as well as the number of binding sites on the OM. In natural water bodies, few inorganic species can act as ligands and form complexes with metals. Thus, OM can be found in water by itself or complexed with other species such as clay [10]. The resulting metal complexes depend on the availability of ligands, pH and pE of the water and the increase of the ionic index of the metal (represented as Z^2/r , formal charge squared/radius).

Metals ability to react with OM is related inversely to ionic strength which can be attributed to the competition for ligands binding sites from alkaline cations and the ability for anions to react with metals which can inhibit metal-humate reactions [10]. Reactive particulate phases present in the water column include hydroxides of Fe, Al, and Mn, aluminosilicates, sulfides and dissolved OM [11]. Therefore, OM is often a primary metal transporter in water. This correlation has biological impacts as OM is often a food source for microorganisms, when ingested, the mobility of the metals may increase by releasing the adsorbed metals back into a dissolved phase [12].

Metal toxicity

Metal toxicity has been well studied; however no regulatory agency has thus created a standard for sediment toxicity due to its lack of relation to concentration. Within USA/New England, most metal concentrations fall under Tier 2 of the National Assessment of Sediment Conditions meaning that impacts from sediment contaminants are likely to occur at some point in time, but are infrequent at most [13]. Previous data collected were compared to existing toxicity test results in order to create the Effective Range Medium (ERM) which standardized the equilibrium partitioning of metals. ERM values of metals are concentrations at which detrimental effects are frequently observed when exceeded [14]. Previous studies have shown that concentrations of metals released during re-suspension such as in the wake of a large barge or in a storm surge, are not acutely toxic, although some lasting, habitual effects have been noted [6].

Methodology

Design of experiments

In a traditional experiment, each investigated factor is changed individually, while other factors are held constant. This method neglects the possibility of analyzing synergistic effects (interactions) involving multiple factors. In this study we used factorial design method. Factorial experiment allows us to evaluate multiple factors, at varying levels, simultaneously. This experiment was designed in the MiniTab16 software determines if any significant interactions occurred between factors. For each Cd, Co and Pb, two factorial designs of experiments were generated by MiniTab16: pH/OM (Table 1) and Salinity/OM (Table 2). One hundred and two (102) isotherm runs were conducted in a randomized order dictated by MiniTab16.

Sediment collection and preparation

Sediments were collected from the top 5-8 centimeters of the Housatonic River bed in Southern Connecticut, USA. Each sample was then sieved to separate grain sizes from 14 to 230 mm. A subsample from each bulk portion of sediment was ashed in a muffle furnace at 550° in order to determine the OM% [15]. The resulting OM% measured in each bulk portion of sediments was 0.36%, 2.12%

and 4.32%. These known amounts were then added to each sample bottle in the isotherm runs in order to simulate the three levels of OM factor in the sediments.

Sediment Isotherm Studies

Isotherm samples were analyzed in the order generated by the MiniTab16 software (Tables 1 and 2). All samples bottles were previously cleaned and soaked in 1% nitric acid until start of analysis. "Instant Ocean Salt" was used to prepare the needed salinity concentrations, types of water were categorized as: fresh (0%), brackish (0.5-2%) and seawater (3%). pH in all bottles was kept constant at 7.2 during all salinity/OM runs. An exact amount of 0.2500 gram retrieved from the sediments with the fixed OM% was then added to each bottle. pH/OM were divided into three categories: acidic (pH 3 and 5), neutral (pH 7.2) and basic (pH 9 and 10.5). These pH values match the metal precipitating pH as calculated from their solubility products (K_{sp}) (Table 3).

Two mg/L stock solutions of metal nitrates for Cd, Co and Pb were then prepared. The selection of the 2 mg/L metal concentration is based on the average ERM values for 200 mg/kg for the metals [16]. Fifteen runs were prepared with duplicates to measure total recoverable metals and dissolved metal concentrations for each factor/metal analyses in order to calculate K_d . The final volume of solution was kept at 100 ml volume. Each sample was stirred for 48 hours to achieve a state of equilibrium and complete partitioning of metals [2,17]. Trace metal quality 0.1 M HNO₃ and 0.1 M NaOH were used to adjust pH of solution if needed. Two blank samples were also prepared for each set of duplicates in order to maintain quality assurance.

Metal Analysis

Table 1: Factors and levels.

Factor	Factor value, (level)				
pH	3.0 (1)	5.0 (2)	7.2 (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 2: Example Design of Experiment Salinity/OM.

Random Order	Run Order	Salinity %	Organic Matter %
12	1	2.0	4.32
1	2	0.0	0.36
11	3	2.0	2.12
5	4	0.5	2.12
14	5	3.0	2.12
3	6	0.0	4.32
13	7	3.0	0.36
7	8	1.0	0.36
6	9	0.5	4.32
4	10	0.5	0.36

The table shows the first 10 of 15 runs with various combinations of the factor Salinity and organic matter

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

Metal	K_{sp} Solubility Product of M. hydroxide	Precipitating pH as hydroxide	pK_h Metal First Hydrolysis	Ionic index Z^2/r	Covalent index X^2r
Cd	$7.2 \cdot 10^{-15}$	9.39	10.1	4.0	2.8
Co	$5.92 \cdot 10^{-15}$	9.36	9.8	5.1	2.6
Pb	$1.43 \cdot 10^{-20}$	7.48	7.7	4.1	3.4

Sediment samples were digested at 85 degree Celsius in order to obtain the metal concentrations in accordance with USEPA method 200.7 for trace metal analysis. Calibration curves were created at the following concentrations: 0, 0.5, 2, 4, 8 and 16 mg/L. Metal analyses were performed using Shimadzu ICP-AES 9000.

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. Calculating the mass (m) of metal in mg/kg within the sediment. K_d values were created using Eq. 1 from the introduction.

Statistical Analysis

Multivariable regression analyses were complete in MiniTab16. This application shows how factors (pH, salinity and OM) affect the partition coefficient K_d and if these factors are affected by each other. Analysis of variance (ANOVA) was completed within the program to determine if any interactions occurred between salinity and OM or pH and OM. The assumptions of normality and variance were verified and found to be normally distributed allowing for the use of ANOVA without transformation.

Results

Impact of pH and OM on partition coefficient K_d

pH is a significant factor affecting K_d values for Cd, Co and Pb (Figures 1-3). A sudden and substantial increase in K_d was observed around a pH of 9.5 for Cd and Co, meanwhile the increase was steepest after a pH of 7.5 (Figures 1 and 2). K_d values peaked at a pH of 7 for Pb and quickly dropped off after that (Figure 3). These pH values coincide with the metal precipitating pH as calculated from their solubility products K_{sp} (Table 3). The resulting K_d values were averaged for each pH of water and demonstrated that metals' adsorbent affinity (for all pH's of water) to suspended solids follows the order $Pb > Cd > Co$ (Table 4). Additionally, K_d values progressively increase from acidic to basic conditions with values increasing from 83 to 1140 L/kg for Co; 234 to 2353 L/kg for Cd and 5618 to 16434 L/kg for Pb. The affinity of metals to solids also increased with the increase of pH (Pb, Cd and Co had $pK_{pb} = 7.7$; $pK_{Cd} = 10$; $pK_{Co} = 9.8$) (Table 3).

Of the metals tested, Pb and Cd had the highest adsorbent affinity with an index Z^2/r of 4.1 compared to the adsorbent affinity of Co with an index value of 5.1 Z^2/r . At each of the tested pHs, K_d values were higher for all metals at the higher OM% (Figures 1-3). Additionally, a trend of increased K_d values was observed with an increase of OM in basic and acidic conditions for all three metals (Table 5). However, the p and F values only showed significant impact of OM on K_d for Cd and Pb ($p < 0.05$ for both) and did not have a significant impact on Co ($p = 0.12$, $df = 101$, $F = 2.69$). Effects and interactions between pH/ OM were significant for all metals tested however, the ANOVA table and the estimated effects coefficients table generated by MiniTab16 did not indicate any significant two way interactions between pH/OM (P values > 0.3) (Table 6). Resulting R^2 values from the MiniTab16 analysis for the three metals ranged between 83.7% and 98% indicating a good fit between K_d and pH/OM.

Impact of salinity and OM on partition coefficients K_d

An increase in K_d was observed as the salinity increased with Pb having the largest K_d value of the three metals. The average K_d values for Cd, Co and Pb (L/kg) in fresh water measured 53, 58 and 234; brackish water measured 152, 100 and 575; seawater measured 256, 176 and 1341 (Figure 4). The regression equations for each metal regarding salinity/OM model showed a good fit between K_d and salinity/OM with R^2 values ranging between 83.7% to 98.4 % and with $p < 0.05$ for all metals. The regression equations for pH/OM model also showed good fit between K_d with values R^2 ranging between 89.1% to 98.1 %. A "p" values of less than 0.05 were calculated for all three metals except for Co which was 0.123. The analysis of variance generated by MiniTab16 did not indicate any significant two way interactions between salinity/OM for the three metals tested (P values > 0.3).

Discussion

pH/OM

The majority of metal partitioning is generally onto clay minerals, Fe and Mn oxides/hydroxides, carbonates and humic

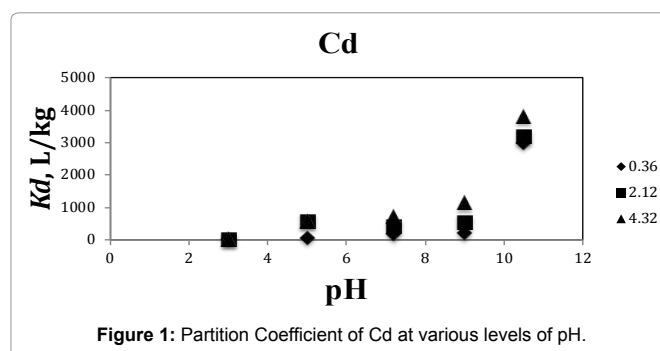


Figure 1: Partition Coefficient of Cd at various levels of pH.

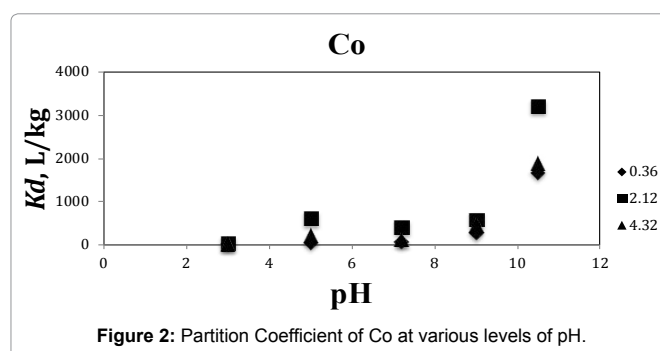


Figure 2: Partition Coefficient of Co at various levels of pH.

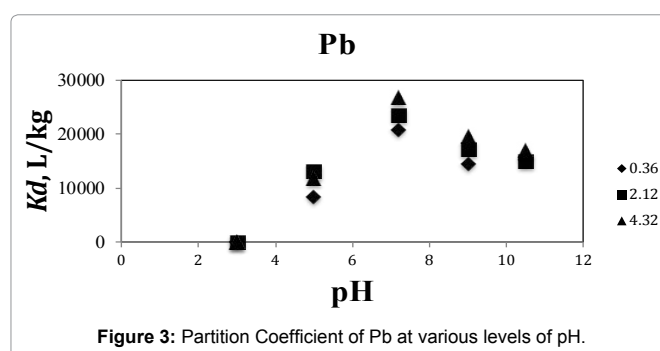


Figure 3: Partition Coefficient of Pb at various levels of pH.

Table 4: Average K_d (L/kg) values of Cd, Co and Pb under various conditions.

Factor/level	Type of Water	Cd	Co	Pb
pH	3	234	83	5618
	5			
	7.2	440	125	23821
	9	2353	1140	16534
10.5				
Salinity%	0	53	58	234
	0.5	152	100	575
	1			
	2			
3	256	176	1341	

* All salinity levels were run at pH 7.2

Table 5: Variation of K_d values under various OM content, type of water and acidic condition.

Factor	Level	Type of water	Co L/kg	Cd L/kg	Pb L/kg
OM%	0.36%	Fresh	40	30	25
		Brackish	132	84	274
		Sea	244	151	893
		Acidic	64	38	4214
		Basic	1103	616	14934
	2.12%	Fresh	60	72	226
		Brackish	167	96	513
		Sea	284	164	1480
		Acidic	321	86	6619
		Basic	1896	1165	16228
	4.32%	Fresh	60	72	451
		Brackish	159	119	674
Sea		141	213	1650	
Acidic		317	126	6020	
Basic		2988	1638	18442	

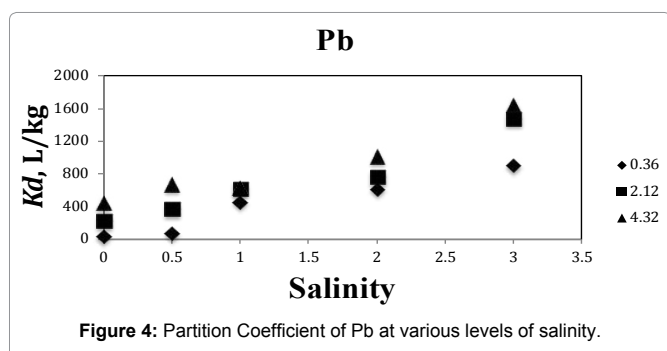


Figure 4: Partition Coefficient of Pb at various levels of salinity.

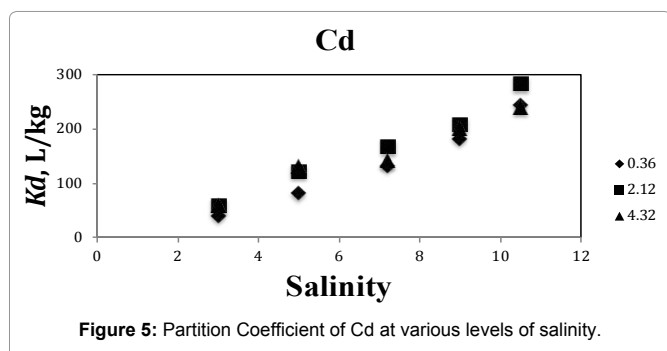


Figure 5: Partition Coefficient of Cd at various levels of salinity.

acids. Considering that the composition of the added sediment was the same for all runs, the sudden shift of K_d values at these pHs may be attributed to both adsorption and precipitation of metals. Thus, the concentration of metals added was 2 mg/L was high enough to induce the observed sudden shift of K_d values due to precipitation. Additionally, 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 for all metals tested substantially increases at a pH of around 7.5, it is likely that estuarine mixing acts as a sink for Pb and other metals before it is able to reach the open coastal area. 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 [18]. If this were the case, this mixing zone may lead to the precipitation of Cd and Co effectively removing them from solution and storing them in sandy coastal sediments. The presence of OM within the sediment also increases the affinity of metals. Whether it is dissolved in water or present as part of the solid phase, suspended/dissolved OM has functional groups that are capable of acting as ligands in forming complexes with metals thus increasing K_d values of these metals.

Salinity/OM

Salinity causes an increase in ionic strength; this results in a decrease of K_d values indicating competition from ions for the adsorption sites on sediments. These values are considerably lower than pH/OM K_d values that indicate that salinity suppresses the adsorption of metals onto sediments. Cd and Co both have a strong linear relationship with salinity/OM (Figures 5 and 6). In natural environment metal species are primarily chlorides, carbonates and other potential insoluble metal species that increases K_d values. For example, under our experimental conditions Cd can be mostly Cd, Cl⁻, Co can be CoCO₃, and Pb can be PbSO₄ [6,7]. Salinity, therefore, seems to act as an "iron curtain" for Cd, Co, and Pb, before entering the open coastal and may play an influential role in reducing the toxic effects of high metal concentration in coastal and open ocean waters.

Conclusions

- Organic matter, pH and salinity are significant factors in influencing metal mobility and distribution.
- An increase in pH generally resulted in a higher K_d , whereas an increase in salinity generally resulted in a lower K_d value. However in this study we observed a positive correlation between K_d and salinity. We believe that this is mainly attributed to formation of insoluble metal species, which led to higher K_d values with the increase of salinity.
- The analysis of variance and the estimated effects coefficients generated by MiniTab16 did not indicate any significant interactions between salinity/OM and pH/OM. This supports that tested factors are all affected K_d but act independently.
- Factorial Design of Experiments offer 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.
- Future work should examine factorial design of experiments with additional factors; different levels such as water redox potential (ORP), temperature and degree of agitation.

Table 6: Regression Equations and Analysis of Variance for K_d values of Cd, Co and Pb.

Factor Metal	Cd		Co		Pb		
	F-Value	P	F-Value	P	F-Value	P	
Sal.	Salinity %	116.8 (significant)	0.00	55.8 (significant)	0.00	36.6 (significant)	0.00
	OM%	8.9 (significant)	0.01	16.1 (significant)	0.002	23.1 (significant)	0.00
	Regression	$K_d = 60.7 + 63.8 \text{ Sal} + 4.4 \text{ OM}$		$K_d = 29.5 + 41.2 \text{ Sal} + 10.5 \text{ OM}$		$K_d = -92.1 + 322.5 \text{ Sal} + 128.4 \text{ OM}$	
	R ²	98.4%		96.9%		83.7%	
pH	pH	86.7 (significant)	0.00	172.6 (significant)	0.00	120.8 (significant)	0.00
	OM%	6.8 (significant)	0.02	2.69 (not significant)	0.123	8.06 (significant)	0.012
	Regression	$K_d = 2032.4 - 993.0 \text{ pH} + 165.4 \text{ OM} + 98.2 \text{ pH}^2$		$K_d = 1326.4 - 597.5 \text{ pH} + 42.6 \text{ OM} + 57.9 \text{ pH}^2$		$K_d = -37318.8 + 14040.7 \text{ pH} + 933.2 \text{ OM} - 904.5 \text{ pH}^2$	
	R ²	98.1%		89.1%		91.0%	

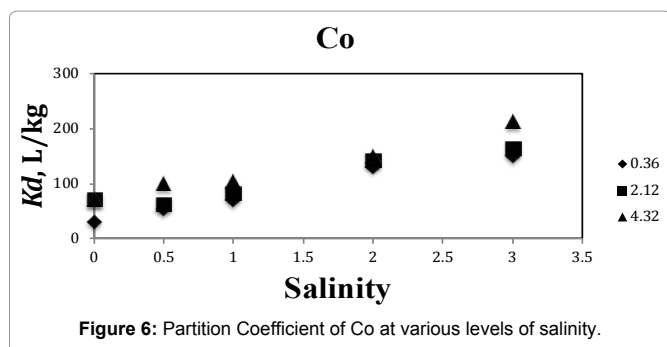


Figure 6: Partition Coefficient of Co at various levels of salinity.

Acknowledgements

The authors would like to acknowledge Abdullah Akhdhar and Fawziah Altirad for setting up the isotherm studies and preparation for analysis and Dr. John Rapaglia for his assistance editing the paper. This work was funded through an exploratory grant from the Connecticut Sea Grant.

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