Trace Metal Adsorption Capacity of Clays under Riverine, Marine, and Estuarine Environmental Conditions

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Introduction

As phyllosilicate minerals, clays play a important role in the geochemical cycling of elementals. The fine grain size leads to high surface reactivities, making them ideal materials for trace metal adsorption in aqueous environments. However, how trace metal adsorption capacity of clays change as a function of varying aqueous conditions (pH and ionic strength) remains unknown. This leads to the questions of whether clays act as a source of or sink for trace metals in estuaries as they are transported by rivers to the ocean. Our experiments investigate the adsorption capacity of three clay minerals for Cd under two environmental conditions: river water (pH=6, ionic strength=0.01M) and seawater (pH=8, ionic strength=0.56), in an effort to assess changes in the Cd adsorption capacity.

Figure 2: (EGU, 2015; Wilkins, 2016) Clay structural units: tetrahedra and octahedra.

Factors affecting Metal Binding Capacity

Ionic strength (proportional to NaCl concentration)
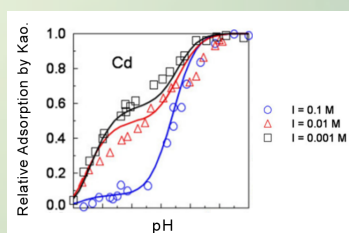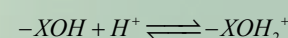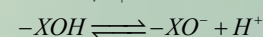**pH** (increased pH, negative surface charge)

Figure 1: (Xueyuan, J. Evans, 2007) Kaolinite adsorption at different ionic strengths as a function of pH

Surface Complexation Reactions

1) Protonation/deprotonation reactions

$$-XOH \rightleftharpoons -XO^- + H^+$$

$$-XOH + H^+ \rightleftharpoons -XOH_2^+$$

2) Cadmium adsorption reactions

$$-XOH + Cd^{2+} \rightleftharpoons -XOCd^+ + H^+$$

Characteristics of Clays

Fine-grained, high surface areas
High concentrations of binding sites
Phyllo-aluminosilicate structure
- Silicon tetrahedron, Aluminum octahedron
Isomorphic substitution

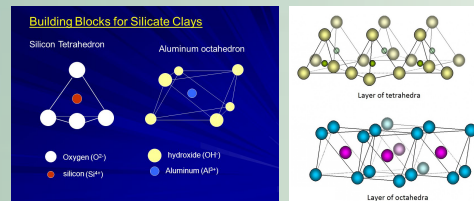Figure 3: (University of Alberta, 2017) Clay Mineral Groups

	Formula	Layer	Information
Kaolinite	Al₂Si₂O₅(OH)₄	TO (2)	- No expansion in contact with water - Pure: little variation in Composition
Illite	K,Al₄(Si₆,Al₂)O₂₀ (OH)₄	TOT (3)	- Most common - K, Ca, or Mg interlayer cations prevent H₂O entrance into structure: *Non-Expanding*
Montmorillonites (½Ca,Na) (Al,Mg,Fe)₄ (Si,Al)₈O₂₀(OH)₄.nH2O		TOT (3)	- Weak linkage by cations - Permanent layer charge - Interlayer is expansible: *Swelling clay*

Methods

Table 1: Replicated Environmental Conditions

River	Ocean
pH 6	pH 8
0.01 M NaCl	0.56 M NaCl

Table 2: Sample Breakdown (84 total)

	0.01 M NaCl		0.56 M NaCl	
Kaolinite	1-80ppm Cd initial	1-80ppm Cd final	1-80 ppm Cd Initial	1-80ppm Cd final
Illite	1-80 ppm Cd initial	1-80ppm Cd final	1-80 ppm Cd initial	1-80ppm Cd final
Montmorillonite	1-80 ppm Cd initial	1-80ppm Cd final	1-80 ppm Cd initial	1-80ppm Cd final

Figure 6: ICP-MS machine (left) and pH probe (right)

Solution Preparation

A set of seven 50 mL solutions with varied Cd concentrations (1, 5, 10, 20, 40, 60, 80 ppm) were prepared for each clay mineral and each environmental condition

1) Batches of 0.01M and 0.56 M salt water solutions were made by weighing NaCl and filling volumetric flasks with ultrapure water.
2) A 1000 ppm Cd stock solution was diluted with the prepared salt water solution to reach the desired concentrations.
3) 5 mL of each solution was extracted and stored for initial analysis of Cd concentration.
4) 50 mg of clay was weighed and added into each sample so that each clay had sets of 7 samples for both environmental conditions.
5) Using a pH probe and 0.1 M solutions of NaOH and HNO₃, the pH of each sample was adjusted to the desired condition.
6) Once the pH was stable, each sample was filtered through a 0.2 μm nylon filter using a 5 mL syringe for final analysis of Cd concentration.

ICP-MS Analysis

Cd concentrations for all 84 samples were measured on an inductively coupled plasma mass spectrometer. A set of standard samples with known Cd concentrations were used to determine a calibration curve and find the linear relationship between the counts per second and Cd concentration.
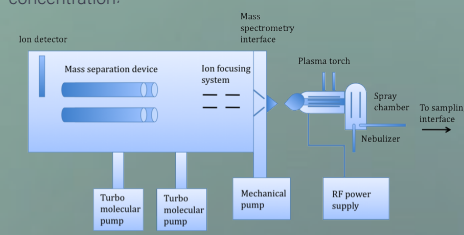

Figure 4: (R. Thomas, 2008) Scheme depicting components of an ICP-MS system.
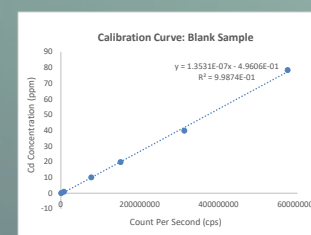

Figure 5: Count per second vs. Cd Concentration

Molar Ionic Strength Quantification

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$$

c_i - molar concentration of ion i (M, mol/L)
z_i - charge number of ion

Table 2.3: Saltwater Condition Ionic Strength Calculations

0.01M NaCl	$I_{0.01M\,NaCl} = \frac{1}{2}[0.01(1^+)^2 + 0.01(1^-)^2] = 0.01$
0.56M NaCl	$I_{0.56M\,NaCl} = \frac{1}{2}[0.56(1^+)^2 + 0.56(1^-)^2] = 0.56$

Results & Data Analysis

Adsorption Capacity

The amount of Cd adsorbed per unit mass of clay minerals was calculated using the equation below. Since the volume of each solution was 50 mL and the mass of each clay was 50 mg, the expression can be simplified as:

$$q_e = \frac{V}{W}(C_o - C_e) = C_o - C_e$$

q_e - adsorption capacity, amount of solute sorbed per unit weight of sorbent (mg/g)
C_o and C_e - Cd concentration in the initial and equilibrium solution (mg/L)
V - volume of the aqueous solution (L)
W - mass of clay (g).

Langmuir Model

- The Langmuir isotherm models the interaction between adsorbate molecules (Cd ions) and an adsorbent (clay surface) as a function of adsorbate concentration
- Explains binding capacity as a competition between ions for adsorption onto limited surface sites.
- Basic assumption: formation of monolayer takes place at the surface of the adsorbent, where the adsorbent surface is homogeneous and has identical adsorption sites.
- The Langmuir constant can be derived from the slope and intercept of a graph comparing C_e to q_e.

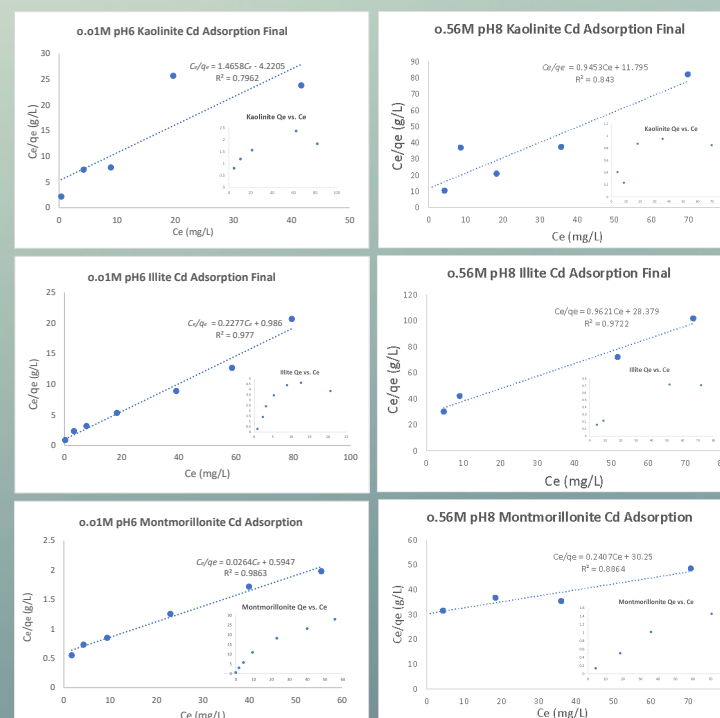$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

C_e - equilibrium concentration (mg/L)
q_e - adsorption capacity, (mg/g)
K_L - energy of adsorption
q_m - Langmuir constant or the saturated monolayer sorption capacity (mg/g)

Figure 7: Graphs for Ce vs Qe (curve) and Ce vs Ce/qe (linear) for 0.01 M and 0.56 M Salt Concentrations

Conclusions

- After determining the values for the Langmuir constant across all experimental conditions, a comparison can be made for q_m for each clay mineral between riverine and seawater conditions.
- While studies have been done isolating the effects of pH and ionic strength conditions on Cd adsorption independently, little is known about how the combination of these factors impacts metal adsorption under real world conditions, where both factors may vary simultaneously.
- An increase in q_m from riverine to seawater conditions indicates a greater effect of pH level on trace metal adsorption, while a decrease indicates a proportionally greater effect of ionic strength on adsorption.
- Results indicate a trend of decreasing Langmuir constant values from river to seawater, indicating that clays often act as sinks rather than sources in estuary. Ionic strength has a greater impact on adsorption capacity than pH.
- Montmorillonite has the greatest adsorption capacity (perhaps because it is a swelling clay), while Kaolinite has the lowest. Data for Kaolinite models consistently had poor r2 values, perhaps indicating a special property making the clay especially unstable.

Table 3: Determined Langmuir Constants (q_m, mg/g)

	river	seawater
Kaolinite	2.197802	1.057865
Illite	4.391744	1.039393
Montmorillonite	37.87879	4.154549

Sources of Potential Errors

- NaCl precipitation on the bottles may have led to decreased ionic strength
- Minor analytical uncertainties in Cd concentrations or pH measurements

Future Directions

Findings from these experiments can be used to expand the limited database of numerical values for trace metal adsorption within transitioning water systems. This has significant implications for whether clay particles transported into estuaries by rivers, will act as a source or sink of trace metals in marginal marine environments.

Acknowledgements

References

Scheme depicting the basic components of an ICP-MS system. Adapted from R. Thomas, Practical Guide to ICP-MS: A Tutorial for Beginners, CRC Press, Boca Raton, 2nd edn. (2008).

Hao, Weiduo & Flynn, Shannon & Alessi, Daniel & Konhauser, Kurt. (2018). Change of the point of zero net proton charge (pH PZNPC) of clay minerals with ionic strength. Chemical Geology. 10.1016/j.chemgeo.2018.06.023.

Altın, Orhan, H.Önder Özbelge, and Timur Doğu. "Use of General Purpose Adsorption Isotherms for Heavy Metal–Clay Mineral Interactions." Journal of Colloid and Interface Science 198.1 (1998): 130–140. Crossref. Web.

Gu, Xueyuan & Evans, Les. (2008). Surface complexation modelling of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) adsorption onto kaolinite. Geochimica et Cosmochimica Acta. 72. 267-276. 10.1016/j.gca.2007.09.032.