

# Using Geological Facies to Estimate Chromate Sorption to Soils

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Quantifying the extent to which contaminant metals bind to subsurface soils is important for risk assessment, the tendency for a contaminant to migrate, and developing environmental remediation strategies. Unfortunately, subsurface soils vary widely in their composition, which in turn affect their tendency to bind metals. The hypothesis of this study was predicated on how a better understanding of geological facies would reduce uncertainty associated with predicting contaminant metal sorption. Facies are layers of sediment deposited in the subsurface due to similar depositional conditions, including energy of an overlying waterway. As such, facies are expected to have similar assemblages of minerals, particle size distributions, origins of organic matter, and similar microbial population structures. These are all important factors affecting contaminant metal sorption. The approach of this study was to collect 42 composite soil samples from a 5 m by 1.5 m grid outcrop in Graniteville, South Carolina and five end-member facies samples. The fraction of each of the five facies comprising the 42 composite soil samples were estimated. Particle size distribution (gravel, sand, silt, and clay fractions), pH, organic matter (OM), iron coating content, and microbial colony forming units were determined for each composite soil and the five end-member facies soils. Because hexavalent chromium (Cr) is the most common contaminant metal in the U.S. to exceed drinking water limits, this highly toxic and soluble metal was used as a model contaminant to provide a measure of contaminant sorption. Chromium distribution coefficients ( $K_d = Cr_{\text{soil}}/Cr_{\text{water}}$ ) were measured. Significant correlations were identified between several soil chemical and microbial properties. A significant correlation ( $r = 0.423$ ;  $p \leq 0.05$ , d.f. = 47) was also determined between measured  $K_d$  values and  $K_d$  values calculated based on knowledge of facies  $K_d$  values. Importantly, the calculated values were characterized by large amount of inherent error. Additional work is needed to determine the applicability of this approach for remediation of contaminated sites and how best to identify appropriate facies for this novel application.

## Introduction

Changes in physical and biogeochemical factors affect microbial community composition and can lead to shifts in microbial composition that drives ecosystem processes (Coleman et al., 2017). Controlling factors such as permeability of sediment, water chemistry, and organic matter play key role in regulating microbial structure and activity in riverine environments (Coleman et al., 2017; Shade et al., 2012).

Because sediment grain size distribution dictates permeability, it affects hydraulic linkage between surface porosity and the supply of energy source. For example, grain size has been reported to affect organic matter accumulation, microbial abundance and activity, and pore-water dissolved oxygen (Gupta and Lawson 1979). Increase in fine particle content in the anaerobic environment tends to promote higher microbial abundances in anoxic sediments due to higher surface area available for colonization. In contrast, increases in metabolic activity and limited recharge rates due to low permeability result in sub-oxic or anaerobic conditions. Thus, it appears that sediment characteristic and structure dictate the dynamic feedback between localized geochemistry and microbial community structure and function.

Facies are basic classification elements used in sedimentology to simplify and group complex geologic materials into a manageable set of classes (Nichols 2009). Once facies classes are delineated based on known properties (e.g., grain size distribution) and adequate spatial resolution then the well-defined facies can be used to characterize larger domain of interest. Furthermore, if the facies are well correlated to some quantitative properties of interest then it is possible to obtain estimates of the quantitative properties without performing direct costly measurement. This is routinely done by hydrologist to predict the hydraulic conductivity (the potential for water to move through pore spaces or fractures) of the facies. By studying spatial distribution and properties of facies, pertinent information needed to model and describe the geochemical and microbial transformation in the sediment environment can be obtained.

With the availability of sediment information either obtained from direct measurements or inferred from verifiable source, sediment-based facies (Millot, 2013) for characterizing depositional sediment and delineating biogeochemical and microbial properties across a given landscape of interest can be obtained to develop robust remedial solution for heavy metals such as the toxic, hexavalent chromium (Thompson et al., 1982).

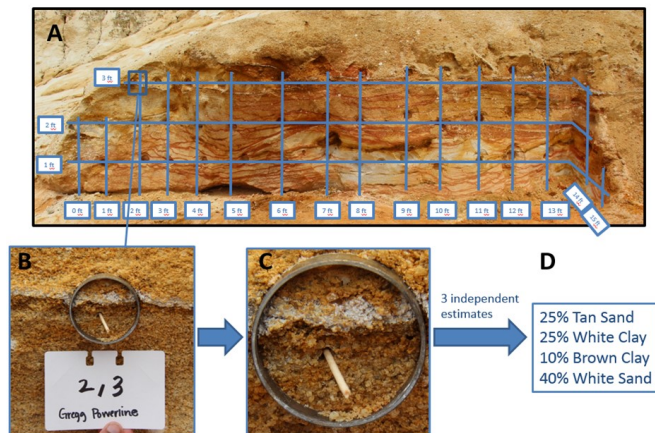
The hypothesis for this study is that contaminant metal sorption to soils can be estimated based on the sorption of the metal to end member facies comprising the soil sample. It is anticipated that because facies are formed under similar depositional conditions and originate from largely the same mineral sources, that the particle size distribution, mineral assemblages, and organic matter (OM) origin would also be similar within a facies class. These soil properties are well known to strongly influence microbial populations (Bulluck et al. 2002; Hamarshid et al. 2010). Together, these abiotic and biotic components of soil are known to strongly influence the tendency of contaminant metals to bind to soils. It was anticipated that a component additive-type model could be used to estimate sorption to a composite soil sample. More precisely, the amount of a contaminant metal that binds to a soil is the sum of the sorption to the individual facies that make up the composite soil sample.

To investigate the relationships between facies and attenuation capacity for contaminant metal, grain size distribution (proxy for bed permeability), chemical and microbiological properties were determined in 42-core samples taken along 3-grind transect along an exposed sediment deposit at an abandoned kaolin mine near Graniteville, South Carolina. Additionally, five end-member facies samples were collected that comprised of single facies used to define the properties of the facies. The results of this research will provide quantitative relationships between microbiology and geochemistry of chromium that can be leveraged in assessing biogeochemical distributions and reactive transport processes on a watershed scale. Furthermore, these relationships will facilitate better understanding of mechanisms driving geological control on chromium biogeochemical processes, for example, the influence of surface area, pore accessibility, and oxygen availability on redox chemistry of chromium.

## Materials and Methods

**Site Description.** The study area was located just north of Gregg Highway in Graniteville, South Carolina: 33° 34' 13''N, 81° 47' 15'' W. The sampling face was oriented 10° south/southwest and was 4.2 m long (Figure 1). Additional samples were collected along a perpendicular surface for an additional 0.4 m length that had a 0° west orientation (Figure 1; grid columns identified as 14 ft and 15 ft). The site geology is the upper Cretaceous formation, comprising predominantly of the fluvial or marine deposits. These sediments are characterized by micaceous, kaolinitic sands interbedded with lenses of clay of variable thickness. The fine- to coarse-grained sands are predominantly poorly-sorted.

**Samples Collection.** Forty-four soil samples were collected along an X, Y grid arrangement (Figure 1A and 1B). Five additional end-member facies samples were also collected adjacent to the sample grid. These five samples represent the facies existing at the study site. End-member facies samples were: White Clay, White Sand, Red Sand, Brown Clay, and Tan Sand. They were characterized to provide biogeochemical information about “end-member facies.” About 200 g of each grid sample and 2000 g of each end-member facies sample were collected using a 5-cm diameter auger. All sediment samples were air-dried for 48 hours and then stored at room temperature in labeled plastic bags.



**Figure 1.** (A) Sampling grid at study site. (B) example of a sample location (sample # 2,3 = 2 ft from left edge and 3 ft from the bottom). (C) Closeup of the sample location showing the 4 facies. (D) Three independent estimates were then used to establish the percentage of each end member making up the sample. After these estimates were made, sample was collected with a soil auger for a 10-cm depth.

**Microbial Colony Forming Units.** Colony forming units were counted using standard methods (Weaver et al. 1994). Approximately 1g of soil was taken from each end-member facies and added to 9 mL of nutrient broth in a test tube (Peptone, tryptone, yeast, glucose (PTYP) nutrient broth (pH 6.7), as described in Wilson et al. (2006). The test tube was shaken on a vortex for ~3 min and then 1 mL of soil solution was added to a new tube of nutrient broth. This step was repeated until a dilution of  $10^5$ . Spread plates were made for each dilution using 0.1mL of solution. These spread plates were left to incubate for at least 48 hours until there were enough colonies of microbes to count. The plates within a dilution series with about 300 colony forming units were used.

**Microbial Carbon Source Utilization Patterns.** A smear was done over the bacteria colonies and onto a microscope slide. The smear was heat fixed and flooded with crystal violet for 30 seconds. The slide was then washed off with water. The smear was then covered for iodine for 1 minute then washed off with ethanol and followed by water. Lastly the slide was covered with safranin for 1 minute, rinsed with water and set to air dry. After drying the slides were put underneath a microscope. If the bacteria were pink the organisms were gram negative meaning they have an outer membrane. If the bacteria were purple then they were gram positive meaning they do not have an outer membrane. A suspension of isolated bacteria and liquid medium was mixed until an absorbance reading of 0.14 – 0.15 was reached on the spectrophotometer with a wavelength of 490 nm. The solution was then put in Biolog® GN and GP microplates (Biolog, Inc., Hayward, CA) that were either gram negative/positive based on the type of organism. These well plates were incubated for 24 hours. The well plates were placed in a Biolog® plate reader and the bacteria were identified based on the carbon sources used in each plate.

**Particle Size Distribution.** Particle size distribution was determined through standard methods using a combination of appropriate sieves to quantify the gravel, sand, and silt fractions and settling in water and Stokes’ Law to quantify the clay fraction (Sparks, 1996). Approximately

30 g of each sediment sample were used in this analysis. Gravel was defined as those particles that were retained on a 2-mm sieve; sand as <2 mm and >53 μm, silt as <53 μm and >2 μm, and clay as <2 μm particles. To quantify the clay fraction, ~10 g of sediment was added to 34 mL of dispersant solution (sodium hexametaphosphate and sodium hydroxide) in a centrifuge tube. The sample was shaken for 15 minutes and then left to settle for 110 minutes. According to Stokes’ Law, larger particles will settle to the bottom of a container while smaller particles will remain in suspension. 2.5mL of the solution were slowly removed from a depth of 2.5 cm. The 2.5mL solution was added to a weighing boat and placed in an oven to dry. A control was created with only 2.5mL of dispersant solution and was also placed in the oven. The weight of the dried dispersant fluid was subtracted from the weight of the dried sample to account for the weight of the salts in the dispersion solution. The resulting weight was labeled as clay weight.

**Soil pH.** pH was measured using standard methods (Sparks 1996). A 1:2 soil:water suspension was stirred and allowed to equilibrate for 30 minutes. Using a calibrated pH meter, the pH of each sample was recorded after 2 minutes of equilibration with an electrode. After 10 pH measurements, the pH meter was recalibrated with standards meeting a ±0.05 pH unit requirement.

**Soil Sorption of Cr.** Chromate ( $\text{CrO}_4^{2-}$ ) sorption to soils was determined using standard batch methods (ASTM 2010). Briefly, 0.5 g soil was equilibrated with 20 mL of a simulated Graniteville SC groundwater. A 5-mL solution of a 121 mg/L Cr (from  $\text{K}_2\text{Cr}_2\text{O}_7$ ) stock solution was added to each tube. This concentration was selected primarily because it exceeds the EPA Cr drinking water limit (0.1 mg/L), and also because it is within the range of commonly reported contaminant plume concentrations (0.1 to 300 mg/L; (Richard and Bourg, 1991)). A no-soil control sample was included to provide information about whether the added Cr sorbed to the glassware walls during the experiment. The samples were equilibrated for 2 days on a platform shaker and then the phases were separated using Whatman #42 filter paper. The pH of the equilibrated aqueous phase was measured. The amount of Cr in the aqueous phase was measured using the S-diphenylcarbazide (DPC) spectrophotometric methods (wavelength set to 540 nm) (Sparks 1996). Sorption was quantified using the distribution coefficient,  $K_d$  value:

$$K_d = \frac{(C_{r_i} - C_{r_{eq}}) \times m_{\text{soil}}}{C_{r_{eq}} \times V_{\text{liq}}} \quad (1)$$

Where  $C_{r_i}$  and  $C_{r_{eq}}$  are the Cr concentrations initially at the start of the equilibration, and after the equilibration period, respectively,  $m_{\text{soil}}$  is soil mass, and  $V_{\text{liq}}$  is the volume of the liquid phase.

**Soil Total Organic Matter Lost on Ignition.** Three grams of soil were added to a tared crucible and heated at 105 °C for 24 hours to remove all water from the sample. The crucible and oven-dried soil was cooled and weighed to 0.0001 g accuracy. The controls were empty crucibles (no sediment). The samples were then placed in a muffle furnace at 400 °C for approximately 16 hours. The beakers were then cooled and weighed to 0.0001g accuracy. Weight loss resulting from heating in the muffle furnace was assumed to be organic matter.

**Soil Fe-oxides.** Soil Fe-oxide content was determined using the dithionite-citrate buffer method (Sparks 1996). This method does not measure the total iron in the soil, instead it measures the readily reducible fractions, which can be thought of as the crystalline Fe-oxide coatings on soil particles. This Fe fraction is useful for studying soil sorption processes as this Fe is in direct contact with aqueous contaminants, as opposed to the Fe found within the mineral structure. Briefly, 5.0 g soil, 20 mL of a 0.3 M  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ , and 2.5 mL of 1 M  $\text{NaHCO}_3$  were combined in a 50-mL centrifuge tube. The tubes were placed in an 80°C water bath and stirred intermittently for 20 min. Then 0.5 g  $\text{Na}_2\text{S}_2\text{O}_4$  powder was added and stirred in a water bath for an additional 10 min. A second aliquot of 0.5 g of  $\text{Na}_2\text{S}_2\text{O}_4$  was added and stirred for 10 min until the soil appeared white. The tubes were then removed from the hot bath and 5 mL of saturated NaCl was added to

facilitate soil settling. Solution Fe concentrations were determined using the 1,10-phenanthroline method (Sparks 1996).

## Results and Discussion

### Soil Abiotic Properties and Their Relationship to Cr $K_d$ Values.

Forty-four soil samples were collected within the two-dimensional grid in the outcrop (Figure 1) and an additional five end-member facies were collected and characterized. The statistics associated with the chemical analyses of these samples are presented in Table 1. Particle size distribution, pH, Fe concentrations and organic matter concentrations reported at the study site were typical of coastal plain soils in South Carolina. The pH of these 49 soils were acidic and had a remarkably narrow range; the average pH was 4.74 with a range of 4.17 to 5.25. The particles size distribution was dominated by sand, which on average accounted for 96% of soil. The gravel fraction, not included in the Cr  $K_d$ , OM or Fe analyses, generally accounted for the second largest fraction in these soils, on average  $9\% \pm 10\%$ . Cr  $K_d$  values were generally quite large, averaging  $68.2 \pm 102$  mL/g. This value is rather high for an anion and can likely be attributed to the mineralogy and low pH of these sediments. Anions tend to bind more strongly to low pH soils, where the surfaces are more protonated than at higher pH levels (Tabatabai and Sparks 2005). The range of Cr  $K_d$  values was highly variable, ranging from -30.4 to 520.0 mL/g. The negative  $K_d$  value is likely due to closure problem (i.e. grain size fractions must sum up to one, resulting in false correlations among grain size classes) and analytical error. Not surprisingly, the OM concentrations are extremely low, averaging only 0.061% OM. Iron concentrations also varied widely. This is not surprising given the vastly different soil colors; the yellow color was attributed to the predominance of goethite (FeO(OH)) coating on the soil, while the darker brick color represents the presence of both hematite (Fe<sub>2</sub>O<sub>3</sub>) and goethite.

The properties of the five facies are presented in Table 2. The pH, percent sand, percent silt, and percent clay values did not differ significantly among these samples, whereas the Cr  $K_d$ , OM, and Fe concentration had a very wide range of values. It is noteworthy that the Brown Clay facies had a Cr  $K_d$  that was more than an order of magnitude greater than that of the White Sand facies.

Statistical analysis was performed on eight soil properties measured in all 44 grid samples and 5 endmember facies soils (Table 3). There was no significant correlation with Cr  $K_d$  values and thus no insight into the soil properties that may contribute to Cr sorption to these soils. The lack of significant correlations with pH is likely the result of the unusually narrow range of pH values at the study site. Similarly, there was only a very narrow range of clay contents in these soils. There were six significant correlation among other soil properties, however they are related to particle size distribution. As noted in the Materials and Methods section, these parameters are concomitant insofar that they are numerically related through the calculation of the percentages. Additionally, principal component analysis (PCA, a dimensionality reduction method that capture the essence of the original data without loss of accuracy) analysis showed clear separation along the first and second principal component accounting for 49.2% of the variance between key controlling variables of Red Sand facies samples and that of Tan Sand, White Sands and Brown Clay facies samples. The PCA results are depicted in Fig. 3. In general, analysis by separation along the first four principal components (represents 77 % of the variability in the data set) reveal significant differences in biogeochemical properties among samples. The results indicate that physical properties such as sand and clay are negatively correlated, while chemical attributes such as pH is negatively correlated with organic matter (OM) and positively correlated with Cr  $K_d$ . Concentration of iron and clay are positively correlated. The PCA shows that silt and sand are almost orthogonal to

Table 1. Statistical description of the soil abiotic properties.

Statistic	pH	% sand <sup>a</sup>	% silt <sup>a</sup>	% clay <sup>a</sup>	% gravel <sup>a</sup>	Cr $K_d$ (mL/g)	OM (%)	Fe (mg/kg)
Mean	4.74	96	3	1	9	68.2	0.061	197.5
Standard Deviation	0.25	3	3	0	10	102.4	0.092	188.4
Minimum	4.17	84	0	0	0	-30.4	0.000	0.2
Maximum	5.25	100	15	2	42	520.0	0.494	671.0
Count	49	48	48	48	48	49	49	48

<sup>a</sup> The %sand + %silt + %clay = 100%; % gravel is the percentage of the entire sample, i.e., (gravel/(gravel+sand+silt+clay)) x 100.

Table 2. End-member facies characterization.

Facies	pH	% sand <sup>a</sup>	% silt <sup>a</sup>	% clay <sup>a</sup>	% gravel <sup>a</sup>	Cr $K_d$ (mL/g)	OM (%)	Fe (mg/kg)
Red Sand	5.03	97.9	3.1	1.0	5.4	72.2	0.210	52.9
Tan Sand	4.54	98.6	1.3	0.2	9.4	44.8	0.003	201.0
Brown Clay	4.89	97.1	2.6	0.3	7.8	380.9	0.277	92.2
White Clay	4.5					36.9	0.147	13.6
White Sand	4.69	99.4	0.0	0.3	0.0	31.3	0.016	0.2

<sup>a</sup> The %sand + %silt + %clay = 100%; % gravel is the percentage of the entire sample, i.e., (gravel/(gravel+sand+silt+clay)) x 100.



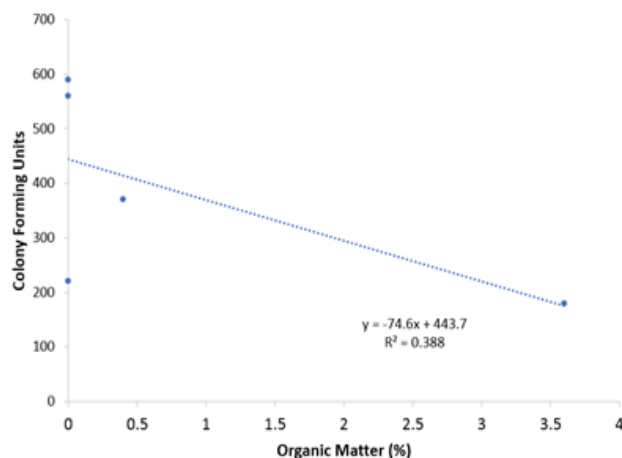


**Table 4.** Microbial colonies identified in the end-member facies soils.

Soil (colony size)	Colony
Red Sand	<i>Staphylococcus kloosii</i>
Tan Sand (large)	<i>Brevibacterium mcbrellneri</i>
White Clay	<i>Sphingobacterium multivorum</i>
Brown Clay	<i>Achromobacter cholinophagum</i>
White Sand (large)	<i>Serratia ficaria</i>
White Sand (small)	<i>Burkholderia phenazinium</i>

gram negative or gram positive. The similarity between all the species is their common habitation of water, soil or the digestive tract of humans, animals and insects.

Correlation coefficients were calculated between colony forming units and the eight soil properties of the end-member facies samples (Table 2). The only significant correlation was between OM ( $r = -0.623$ ,  $p \leq 0.05$ , d.f. = 4). This inverse relationship is unexpected as OM is a common organic carbon source and energy source that promotes microbial growth. Clearly additional samples are required.



**Figure 4.** Colony forming units versus organic matter content in the five end-member facies sediments (described in Table 2).

## Conclusion

It was hypothesized that by understanding the sorption of contaminant metals to end-member facies, it would be possible to predict sorption in composite samples consisting of multiple facies. The logic was that facies are formed under similar depositional conditions and originate from largely the same mineral sources, such that the particle size distribution, mineral assemblages, and natural organic matter origin are largely uniform. These soil properties are well known to greatly influence microbial populations. Together, these abiotic and biotic components of soil are known to influence the tendency of contaminant metals to bind to soils. While Figure 2 shows that there is a significant correlation between the estimated and actual  $K_d$  values, it is clear that additional testing and perhaps better identification of facies of interest are needed. The fact that pH and clay content was not significantly correlated with Cr  $K_d$  values was likely the result of the limited range of the study site. This indicates that the facies hypothesis may only be appropriate for locations where significant differences in the facies exists, such as clay layers separated sand-textured deposits, or where the clay facies are of a significantly different origin than the sand facies. Finally, the experimental design could be improved with more replicates for each soil parameter and fewer samples in the grid. Additional testing

is necessary to confirm the usefulness of the facies hypothesis for predicting the binding and migration of contaminants (heavy metals, radionuclides) and nutrient elements (organic and inorganic) through soils.

## Acknowledgements

Funding for this work was provided by the U.S. Department of Energy Office of Environmental Management's Minority Serving Institutions Partnership Program (MSIPP). This support was provided through the Savannah River National Laboratory (SRNL) under contracts SCB00032 and SCB00038 to the South Carolina Universities Research and Education Foundation (SCUREF) under a program that supports environmental science summer studies for students from minority serving institutions. The program was administered by the University of South Carolina Aiken (USCA). The authors are grateful to USCA and to the SRNL for their support and are especially grateful to their scientists who participated in the program. The views and conclusions contained in this article are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the U.S. Department of Energy.

## Notes and References

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