Chemical Extractions to Determine Metal Partitioning to Sediments and Soils

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Undergraduate Senior Thesis
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Honors Thesis

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Preface:

For my senior thesis project I have performed single extractions of a highly characterized sediment. Single extractions involve the addition of a chemical reagent to a sediment and analyzing the metals, solubilized by the extraction treatment. This work is important for understanding contaminant partitioning to various geochemical phases of sediment. If contaminant partitioning is understood then remediation strategies can be devised. Remediation may be important for sites that have mobile contaminants to reduce potential health risks.

This project has enabled me to gain laboratory experience. I have learned many valuable skills and techniques, which have helped to prepare me for graduate school. I have also had the opportunity to attend the American Chemical Society Nuclear Summer School at Brookhaven National Laboratory, where I learned the fundamentals of nuclear science and had the opportunity to work with other students from all over the country. I was fortunate enough to present my work this April at the American Chemical Society National Meeting in San Diego. This was a very valuable experience, which helped to prepare me for future talks and an opportunity to be part of a great learning experience. This work has helped me receive an internship this summer at Argonne National Laboratory West, where again I will acquire knowledge and experience to better prepare me for a career in chemistry. I have also had the opportunity to work with many talented individuals and learn from them.

Abstract:
Previously, we have reported on methods for sequential extractions to determine the partitioning of contaminants and stable elements within soils and sediments. Recently, we have explored single step extractions to obtain similar information. Using a well-characterized pond sediment, we have applied single step extractions to remove stable metals partitioned as exchangeable metals, those metals associated with iron oxides, and those metals associated with natural organic matter. The results obtained using single extractions will be compared to observations made when a sequential extraction method is employed with the same sediment.

Introduction:

Background

Research and development of nuclear weapons and power plants began during World War II. Since this time radiological contamination of sediments, soils, and water has occurred. In the United States, the DOE has documented over 4000 radiologically contaminated sites. This represents over 250,000 km$^2$ of impacted soils, sediments, and waters [1] in 28 states. Plutonium contamination has resulted from above ground nuclear tests and operation of defense and civilian nuclear facilities. Remediation of these sites is likely necessary. If it is not feasible to remediate all of these sites, remediation decisions must be based on risk. Risk is correlated to contaminant or environmental availability.

Analytical methods are needed to help define the contaminant availability. The fraction of contaminant that is mobile (i.e. contaminant available) represents the risk, as compared to the total contaminant concentration. Contaminant cycling in lakes or ponds
can occur by chemical processes at the sediment-water interface. Therefore, knowledge of contaminant partitioning to sediments and soils are important for understanding the mobilization of contaminants. The specific sediment being studied was collected from Pond B of the Savannah River Site (SRS), located in Barnwell County, South Carolina. Pond B was used as a secondary cooling reservoir for two nuclear production reactors until 1964, and was contaminated with actinides due to a leaky cooling system. The sediment is typical of southeastern coastal sediment in that it is sandy and highly weathered.

The environmental availability of a contaminant is related to its geochemical association or partitioning to a sediment. Partitioning therefore refers to the distribution of contaminants among various solid phases in a heterogeneous mixture. This is contrasted to speciation, which refers to molecular level information and indicates chemical form. Speciation and partitioning are not equivalent, although they are related.

**Sequential and Single Extractions**

Methods for determining contaminant availability include sequential extractions [2]. Sequential extractions are useful but they have limitations. Some of these limitations are they are time consuming and the results are operationally defined. An operational definition means that the results are dependent upon the method used. Another method for determining contaminant availability is single extractions. This method can provide additional useful information about a sediment matrix.

Interpretation of both single and sequential extraction results can be bolstered by additional information about the sediment. The Pond B sediment was characterized for pH, total organic carbon, particle size, cation exchange capacity, and percent carbon,
nitrogen and hydrogen. Extracts from both single and sequential extractions can be analyzed for both contaminant and stable metals. Solubilization of the stable metals into certain sequential or single extracts may be indicators of dissolution of specific soil or sediment phases.

Methods

Sequential and Single Extractions

In a sequential extraction procedure treatments are applied to a single sample sequentially. The contaminants removed by each treatment are determined. Each successive extract used is chemically more aggressive than the previous treatment. This is contrasted to a single extraction in which a single treatment is applied to a given sample, and the samples and extractions are independent of each other.

The method used was designed by Stacey Loyland Asbury and is specific for actinide contaminants [2]. Both the sequential and single extraction procedures used similar methods. The sequential extraction is a four-step sequential extraction method intending to target exchangeable, reducible, oxidizable, and residual pools of metal cations. The single extraction procedure takes each of the treatments of the sequential extraction and applies them independently. The exchangeable fraction targets metals associated with changes in water ionic composition, the reducible fraction targets metals associated with iron and manganese oxides and the oxidizable fraction targets metals associated with organic matter. The residual fraction should only contain primary and secondary mineral phases.
The sequential extractions were performed on 6 g and 9 g samples in 250 mL polyethylene centrifuge tubes with sealing caps. After each extraction step shown in table 1, the samples were filtered using a 0.45μm Metricel membrane filter (Gelman Sciences, Ann Arbor, MI), and collected in a preweighed beaker. The remaining solids were rinsed twice with 18 MΩ water prior to subsequent SE steps. The slurry was separated by centrifugation, and the rinsate was discarded after filtration to collect any remaining sediment. The filter was added to the remaining sediment [3]. Each extraction step was analyzed for six stable metals.

The single extractions were performed on 3 g samples in 250 mL polyethylene centrifuge tubes with sealing caps with 45 mL of specified reagent. After the extraction procedure shown in table 2 the samples were centrifuged at 4400 rpm (IEC Centra MP4R) for 30 minutes. The supernatant was filtered through either a 0.45μm Metricel membrane filter or a 0.10μm Metricel membrane filter (Gelman Sciences, Ann Arbor, MI), and collected in a pre-weighed beaker. The remaining solids were rinsed twice with 18 MΩ water and collected in a pre-weighed crystallizing dish and dried down at 60-70°C along with the filter. The supernatant was dried down and reconstituted in 2.0M nitric acid and analyzed by ICP-AES for six stable metals.

The stable metal cations analyzed include calcium, potassium, iron, aluminum, scandium, and zirconium. The stable metals were analyzed using a Jobin Yvon JY24 ICP-AES, equipped with a pneumatic nebulizer [4].

**Amorphous and Organically Bound Iron**

The results from the single extractions were compared to other single extraction type procedures published by the Soil Science Society of America [5]. These methods
are considered standard methods for the determination of amorphous and organically bound iron. The methods are shown in table 3. The amorphous iron procedure initially called for a carbonate removal step. This step was eliminated as Pond B sediment has no carbonates present as indicated by the soil pH values. The reagent was added and the sample agitated for the time shown, it was then centrifuged and filtered through a 0.45 μm Metricel filter. The supernatant was dried and reconstituted in 2.0M nitric acid and analyzed by ICP-AES. The organically bound iron used no filter pore size. The supernatant was decanted directly into a preweighed beaker, dried, and reconstituted in 2.0M nitric acid and analyzed by ICP-AES.

Results and Discussion

The extraction of the stable metals is shown in figures 1,2,3. The elements are grouped according to expected geochemical behavior. The single extraction results for Ca and K (figure 1) show large percentages being extracted in the reducible and oxidizable fractions whereas the sequential extractions do not. This is because the single extractions are independent of each other whereas the sequential extractions are not. This trend is shown again for the Fe and Al (figure 2), although only in the oxidizable fraction since very little Fe or Al is extracted in the exchangeable since it is refractory. The Zr and Sc (figure 3) show little differences between the single and sequential extraction steps. The Zr and Sc are also refractory.

The single extractions were performed with two different filter pore sizes 0.10 μm and 0.45 μm. Two filter pore sizes were used to determine if colloids effected the
partitioning of the trace metals. Colloids are defined approximately as being from 0.10 μm to 1.0 μm in size. The 0.10 μm filter pore size would allow fewer colloids and other suspended particles to be filtered into the supernatant. The filter pore size shows no significant effect on the percent extraction of Ca and K or Fe and Al. The filter pore size shows more of a difference when the metals are refractory as in Zr and Sc. This affects the later steps of the sequential extraction, which are the more aggressive treatments. This would make a difference for the actinides and uranium, which come out in the later steps of the sequential extractions.

The results for the amorphous and organically bound iron as defined by the Soil Science Society of America methods are shown in figure 4. The amorphous iron is not associated with any specific mineral phase and is the most reactive iron in the sediment. The results from the single extraction 0.45 μm pore size and the "oxidizable iron" which is the difference between the oxidizable and reducible iron in the single extraction are shown in figure 4 as well. There are differences in the results of the amorphous iron and the reducible iron in part because the amorphous treatment targets the most reactive iron in the sediment and the reducible treatment targets just the iron that can be reduced. This operational definition helps to explain differences between the organically bound and the oxidizable iron. The differences are not highly significant between the different approaches. The reducible and oxidizable single extractions quantify the amount of Fe$^{3+}$ and Fe$^{2+}$ present in the sediment.

Conclusions
The single extraction results in this study are consistent with the sequential extraction results published by Loyland et al. In the Ca and K results the percent extracted in the reducible and oxidizable fractions of the single extraction are significantly higher than that of the sequential extraction. This is shown also in the Fe and Al in the oxidizable fraction. The differences arise from the single extraction phases being independent of each other unlike the sequential extractions. Therefore when comparing results of a single extraction to a "mid-procedure" sequential extraction step, one must remember to include fractions of contaminant extracted by previous steps in sequential results. The results, however, are consistent between sequential and single extractions. The single extractions are faster, which is less expensive and gives results quicker. Single extractions do not provide as much information as the sequential extractions, because each step is independent and the more aggressive treatments may include non-targeted metals. This occurs mainly in the reducible and oxidizable steps, where the more aggressive hydrogen peroxide treatments may dissolve metals that would normally be reduced. This can lead to overestimation of the contaminant availability. In the future, single extractions of actinide contaminants and uranium will be performed. Uranium and the actinides are the contaminants of interest since they pose the greatest health hazards. Identifying the geochemical phase(s) to which these contaminants are associated will be helpful when designing soil remediation strategies.
Acknowledgements:

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References:


### Table 1

**Sequential Extractions**

<table>
<thead>
<tr>
<th>Desired Geochemical Phase</th>
<th>Extraction Reagent</th>
<th>Reagent/Sample Ratio</th>
<th>Temp °C</th>
<th>Time (hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>H₂O/0.4 M MgCl₂, pH 4.5</td>
<td>15:1</td>
<td>room</td>
<td>1</td>
</tr>
<tr>
<td>Reducible</td>
<td>0.4 M NH₂OH·HCl in 25% HAc, pH 2 (HNO₃)</td>
<td>15:1</td>
<td>room</td>
<td>5</td>
</tr>
<tr>
<td>Oxidizable</td>
<td>30% H₂O₂, 0.02 M HNO₃</td>
<td>15:1</td>
<td>room</td>
<td>5</td>
</tr>
<tr>
<td>Residual</td>
<td>Pyrosulfate Fusion or Lithium Metaborate Fusion</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Loyland, S.M., LaMont, S.P., S.E. Herbison and S.B. Clark Radiochimica Acta 88 93-98 2000

### Table 2

**Single Extractions Scheme**

<table>
<thead>
<tr>
<th>Desired Geochemical Phase</th>
<th>Extraction Scheme</th>
<th>Reagent: Sample Ratio</th>
<th>Temp °C</th>
<th>Time (hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>0.4 M MgCl₂, pH 4.5</td>
<td>3:1</td>
<td>Room</td>
<td>1</td>
</tr>
<tr>
<td>Reducible</td>
<td>0.4 M NH₂OH·HCl</td>
<td>3:1</td>
<td>Room</td>
<td>5</td>
</tr>
<tr>
<td>Oxidizable</td>
<td>30% H₂O₂, In 0.02 M HNO₃</td>
<td>3:1</td>
<td>Room</td>
<td>5</td>
</tr>
</tbody>
</table>
### Table 3

**Published Methods from Soil Science Society of America**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Extraction method</th>
<th>Reagent: Sample ratio</th>
<th>Time (hrs)</th>
<th>Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous iron</td>
<td>NH4-oxalate-oxalic acid pH 3 in dark</td>
<td>60:1</td>
<td>2</td>
<td>room</td>
</tr>
<tr>
<td>Organically bound iron</td>
<td>Pyrophosphate pH 10</td>
<td>100:1</td>
<td>16</td>
<td>room</td>
</tr>
</tbody>
</table>

Sparks, D.L. Methods of Soil Analysis Part 3 Chemical Methods, 2nd ed., Soil Science Society of America, 1996 pg 648-651
Figure 1

Extraction of Ca and K

Single Extraction

Sequential Extraction

Exch Reducible Oxidized

Exch Reducible Oxidizable
Figure 2

Extraction of Fe and Al

Single Extraction

Sequential Extraction
Extraction of Zr and Sc

Single Extraction

Sequential Extraction

[Sc]_{total} = 5.08 \pm 0.30 \mu g/g

[Zr]_{total} = 497 \pm 38 \mu g/g

Exch -- Reducible -- Oxidized

[Sc]_{total} = 5.08 \pm 0.30 \mu g/g

[Zr]_{total} = 497 \pm 38 \mu g/g

Exch -- Reducible -- Oxidized
Figure 4

Amorphous and Organically Bound Iron Content