Background Concentrations of Metals in Wetland Soils On and Near the Savannah River Site\textsuperscript{(U)}
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Background Concentrations of Metals in Wetland Soils On and Near the Savannah River Site

K. L. Dixon

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BACKGROUND CONCENTRATIONS OF METALS IN WETLAND SOILS ON AND NEAR THE SAVANNAH RIVER SITE

K. L. Dixon

ABSTRACT

A study was conducted to determine the naturally occurring concentrations of metals in unimpacted wetland soils at the Savannah River Site located near Aiken, SC. Soil samples were collected from three broad categories of wetlands: 1) large stream floodplain wetlands, 2) small stream floodplain wetlands, and 3) upland bays and depressions. Samples were collected from 75 locations to a depth of 3.1 m. All samples were analyzed for selected metals using EPA protocol and standard methods. Additionally, the pH, exchange capacity, and total organic carbon content of each sample was determined. Standard summary statistics were calculated and results are presented for each constituent. Box plots were also created relating metals concentrations to grain size distribution. Metals concentrations were found to increase with increasing silt and clay content. This increase in concentration was attributed to increasing cation exchange capacity and increasing organic matter content.

INTRODUCTION

The Savannah River Site (SRS), located in Aiken, Allendale, and Barnwell Counties, South Carolina, is a nuclear materials production facility operated for the U.S. Department of Energy (DOE) by Westinghouse Savannah River Company (WSRC). As a result of the end of the cold war, emphasis has shifted from nuclear materials production to environmental clean-up.

Currently, there is a gap in the literature concerning background concentrations of many common contaminants in wetland soils. Characterization of wetland soils has been identified as a major research need in the area of wetland science (Reddy and Gale, 1994). Most data available are for upland soils and sedimentary material (Frink, 1996; Kabata-Pendias and Pendias, 1992; Swaine, 1955) with limited data available for wetland soils (Gambrell, 1994). Further, these studies have primarily focused on the total elemental concentrations of contaminants present in the soil; however, standard Environmental Protection Agency (EPA) analytical methods used for waste site characterizations result in partial dissolution of the soil sample yielding only the leachable quantity of a particular analyte. As a result, comparisons between total concentrations and leachable concentrations may be inappropriate.

Recent studies of wetland soils near various waste units at SRS show that some wetlands have been impacted by SRS operations. Waste waters originating from the operations facilities historically have been discharged into seepage basins located in upland soils or to surface streams; direct discharge of waste water to wetland areas has been minimal. This suggests that impacted wetland areas have been affected indirectly as a result of transport mechanisms such as surface runoff, groundwater seeps, fluvial or sediment transport, and leaching.

Looney et al. (1990) conducted a study to characterize the geochemical and physical properties of upland soils and shallow sediments on the SRS. A primary objective of the upland study was to collect the data...
The objectives of this paper are to
needed to assess the qualitative and
quantitative impacts of SRS operations on the
environment. By comparing the upland soils
data to data collected from waste units
located in similar soils, SRS impacts could be
assessed. The data were also intended to aid
in selection of remediation alternatives.
Because waste units at SRS have historically
been located in upland areas, wetland soils
were not sampled. However, there are
fundamental differences between the
physical, biological, chemical, and geological
processes occurring in the upland soils
sampled by Looney et al. (1990) and wetland
soils. Thus, data from the upland soils study
cannot be used to assess potential wetland
contamination.

To address the lack of background data, a
database of geochemical and physical
properties of wetland soils has been
developed. The wetland soils study was
designed to characterize the naturally
occurring background concentrations of a
wide range of constituents in unimpacted
wetland soils on and near the SRS (Dixon et
al., 1996). Standard EPA methods were used
to analyze each constituent in the background
database to facilitate comparisons to data
from future human health and ecological risk
assessments, treatability studies, remedial
investigations, and feasibility studies for
wetland areas. Samples were analyzed for
selected metals, organics, inorganics,
agricultural and physical properties.

The resulting data are used to characterize
wetland soils at SRS. This baseline
characterization may be used to assess the
impact from SRS waste units on wetland
areas. The characterization may also aid in
selecting remedial activities to minimize
contaminant propagation and ecological
damage within and downstream of the
wetland areas.

METHODS

This study was designed to collect soil
samples that are representative of unimpacted
wetland soils at the SRS. Soil cores were
collected using vibracoring technology from
75 locations. Samples were collected from
both onsite wetlands and wetlands located
offsite at state parks across South Carolina.
Eight duplicate cores were collected yielding
a total of 83 cores. Each core was subdivided
into 5 depth increments producing 415 soil
subsamples submitted for chemical and
physical analyses.

Soil Groupings

The wetlands on the SRS consist of nine
different soil types that vary greatly in their
geological and hydrogeological
characteristics. There are about 40,000 acres
classified as wetland soils at SRS. These soils
have formed in three general topographic
positions: along low-lying areas of the
floodplain near streams, at the toe slope of
upland soils, and in isolated upland
depressions. These soils vary in age,
thickness of profile, texture, organic content,
and horizon development. To limit the
number of soil types considered, the soils
were combined into five groupings with
similar geochemical and physical
characteristics. The five soil groupings are
listed in Table 2.

Three broad categories of soils were
considered when grouping the soil types:
soils occurring in upland bays and
depressions, including Carolina bays; soils
occurring in small stream floodplains; and
Soils occurring in the Savannah River floodplain. Soils were assigned to each of the five soil groupings based on known chemical and physical differences (Rogers, 1990). Factors considered in assigning a particular soil to a group included the type of watershed the soil developed within, the topographic position of the soil in the watershed, the parent material from which the soil weathered, the age of the soil, and the amount of organic matter present in the soil.

**Sampling Locations**

All sampling locations were carefully selected in an effort to avoid areas within close proximity or down-gradient of any facility with operations that might result in soil contamination. Areas near power line right-of-ways were avoided, because these locations are routinely treated with herbicides. An area was considered potentially impacted if it was located downstream from an SRS operations area or waste unit, if any portion of its source was groundwater from a waste unit or operations area, or if previous investigations suggest it may have been impacted.

Each location was selected to be (1) in a wetland formed prior to development of the SRS, (2) in a watershed with no history of impacts from SRS operations, and (3) in areas representing each of the soil types typical of wetlands at SRS. To fully represent SRS wetland soils, sampling locations were selected from as many areas of the site as possible, while avoiding areas with potential impacts from operations.

**Sample Collection**

Seventy-five 3.1 m (10 ft) long soil cores were collected from 50 locations on SRS and 25 locations of the SRS property in July, August, and September 1992, and in September 1993. Cores were collected with minimum disturbance to the wetland areas. Vehicles were not used in the wetlands; all equipment, materials, and cores were hand carried to and from the study sites.

Cores were collected by two methods: vibracore and hand auger. The study design was to collect samples to 3.1 m (10 ft) below land surface. If the vibracore equipment could not penetrate to the study design depth, a bucket hand auger was used to retrieve samples.

**Vibracore Sampling Methodology**

Vibracoring technology was chosen because it enables the collection of continuous soil cores, to depths exceeding the design depth (3.1 m) in most cases, with minimal impact to the wetlands being sampled. Vibracoring equipment is also light-weight and portable. This facilitated carrying the equipment long distances to areas that are inaccessible by vehicle.

The vibracore sampling methodology involved vibrating a 7.6 cm (3 in) diameter aluminum tube down to the maximum sampling depth. The cutting edge of the tube was beveled and sharpened to facilitate penetration into the soil profile. Sandy and gravelly soils tended to fall from the end of the tube upon withdrawal; therefore, when possible, the sample tube was vibrated to a depth of 3.4 to 3.7 m to help ensure recovery of the full 3.1 m interval. After the aluminum tube was vibrated down to the desired depth, the headspace in the core barrel was filled with deionized water and capped with a plumber's test plug. The plug inhibited loss of the core from the sample tube during withdrawal. The aluminum tube was then extracted using a jack, tripod, and tackle arrangement. Core penetration and core compaction were recorded prior to core extraction. The hole created by removal of the core was backfilled with soil obtained
adjacent to the sampling area. All cores were maintained at 4°C for transport from the field to the laboratory for core sampling.

Because a large volume of sample was needed to perform the laboratory analyses, it was necessary to collect two cores at most sampling sites. If any core was compacted more than five percent during collection, an additional core was collected at that station.

**Hand Auger Sampling Methodology**

When vibracore sampling was not possible, typically due to clayey or gravelly soil layers, a 8.3 cm (3.25 in) stainless steel bucket auger was used for sample collection. The soil was divided by sampling interval and placed in plastic bags, sealed, labeled according to sampling location and depth and, maintained at 4°C for transport to the core sampling laboratory. Both augered depth and vibracoring depth were noted in the field log. While sampling with the auger, the field crew wore rubber gloves, which they replaced between soil intervals to prevent cross-contamination.

When flowing sands were encountered during the sampling, the bucket auger technique was replaced with the vibracore in order to obtain the sample. This was accomplished either by vibrating or pushing the tube through the material. The tube was then filled with deionized water, capped with the plumber's test plug, and extracted from the hole. After extraction, the deionized water was drained from the tube. At some locations it was necessary to extract the soil from the tube in the field. When this was done, the soil was divided by horizon and placed in plastic bags. The bags were then sealed, labeled by sampling location and depth, and maintained at 4°C during transport to the core sampling laboratory.

**Core Opening and Subsampling**

At the core sampling laboratory, each core was cut longitudinally using a radial saw with a decontaminated carbide-tipped saw blade. The core was cut to minimize disturbance to the core sample (by cutting the aluminum tube only).

Each core was divided into five subsamples based on general soil horizon changes (Dixon et al., 1996). All intervals were corrected for compaction, which was averaged over the entire length of the core sample. The A and B sample intervals for soil groupings 3, 4, and 5 were determined only after visual inspection of a given core, with their sum total not to exceed 40 inches. For these three soil groupings, the A and B sampling intervals were determined by soil horizon, with intervals in the A sample coming from the A horizon, and the B sample coming from the horizon below.

After opening the core, each interval was then removed from the core barrel, placed into a decontaminated stainless steel mixing bowl, and thoroughly agitated with a decontaminated stainless steel spoon to maximize sample homogenization. Samples were divided into quadrants in the bowl for filling the sample jars. Each jar was filled with soil taken from one quadrant. After four jars were filled, the remaining soil was homogenized and divided again. This procedure was repeated until all sample jars were filled. All sample jars were sealed, labeled, stored at 4°C, and packaged for shipment to the analytical laboratory. Samples were packed one core per cooler for shipment to the analytical laboratory.

**Sampling Equipment Decontamination**

All sampling equipment that came in contact with the cores, including sample tubes, sample trays, sample spoons, and saw blades,
was decontaminated using a detergent wash followed by a water-alcohol-water rinse. This equipment was steam cleaned as well. All aluminum coring tubes were steam cleaned prior to sample collection and wrapped in polyethylene for transport to the field. To monitor the quality of equipment decontamination, three rinsate samples were collected from the final rinse water used in decontamination.

RESULTS AND DISCUSSION

Chemical and physical analyses performed on soil samples collected for the wetland soils study included selected metals, organics, inorganics and agricultural and physical properties (Dixon et al., 1996). The parameters selected were intended to characterize the levels of naturally-occurring trace elements and to determine physical and chemical parameters. Standard EPA analytical methods were used in this study. These methods are the same as those used in waste unit characterizations under RCRA and/or CERCLA programs.

For this paper, only selected metals results and physical properties are presented. Summary statistics were computed for all samples without distinguishing between depth interval or soil grouping. The maximum, minimum, median, arithmetic mean, geometric mean, standard deviation, total number of samples, and percent of samples above detection were determined for each analyte and are presented in Table 3. Dixon et al. (1996) provides the same summary statistics for each analyte by depth interval and soil grouping.

Processing of Analytical Results

In environmental samples, such as those collected for this study, the number of samples that exceed the analyte detection limits may range from the entire set of samples to none of the samples. If no samples exceeded the limit of detection (LOD) for a given analyte, then the analyte was dropped from further consideration.

Analytical results determined to be below the LOD are said to be left censored. To compensate for this censoring effect, results below the LOD were included in subsequent statistical analyses as one-half the limit of detection (LOD/2). Use of the LOD/2 is intended to provide a “best estimate” of the actual concentration, and provides a means by which to include the below LOD data in the statistical analyses. Statistical analyses were performed only when fifty percent or more of the data for a given analyte were reported as above the LOD. In cases where all samples exceeded the LOD, then the summary statistics were determined without any modifications to the database.

The value of results reported below the LOD is a function of the method detection limit, the dilution factor, and the percent solids in the sample (i.e. moisture content). Thus, the LOD is sample dependent and the variation of the LOD among a group of samples for the same analyte can be large. In the database for his study, there were instances where results reported as below the LOD were larger than some of the results reported as above the LOD for a given analyte. To remove the influence of large below LOD results, any result reported as below the LOD that exceeded the median detection limit was replaced. The replacement value was the median LOD result for the analyte for all samples. For a given sample and analyte, results above detection were not replaced, nor were results reported as below the LOD if the result was smaller than the calculated median detection limit.
Computation of Summary Statistics

All laboratory replicate and field duplicate measurements were averaged to obtain one value representing each analyte for each sample. The arithmetic and geometric averages and standard deviation were computed only when more than fifty percent of the results were reported as above the LOD for a given analyte. The arithmetic and geometric averages and standard deviation estimates were considered biased when more than fifty percent of the results for an analyte were reported as below the LOD. The geometric mean was computed by finding the average of the log transformed results for a given summary group for each analyte and site group and converting the average back to the original units.

The maximum, minimum, and median result was determined for each analyte. If all results in a group were reported above the LOD, then the maximum, median, and minimum values were computed and reported without any qualifiers. If all results in a group were reported as below the LOD, the maximum, median, and minimum values were computed and reported with a "<" symbol. In cases where results were reported above and below the LOD, the maximum and minimum values were determined using all of the data for the group without considering the result qualifier. The median value was reported as above the LOD if 50 percent or more of the results were reported as above the LOD. Otherwise, the median value was reported with a "<" symbol.

Summary statistics for each analyte are presented in Table 3. Aluminum results are presented in Table 3, but should be interpreted with caution. Aluminum core barrel was used for sample collection. Subsampling activities may have resulted in some sample contamination with aluminum fragments even though extreme care was taken to minimize this occurrence. Further, aluminum is an important structural component of the soil and the EPA methods are not designed to reproducibly extract such elements for analysis.

Data Analysis

Constituent concentrations measured in this study are generally comparable to those reported by Looney et al. (1990) for upland soils at the SRS. This observed correlation is not unexpected because both the upland and wetland soils were derived from generally the same parent material. Differences in specific concentrations are likely due to the differences in the soil forming processes for upland and wetland soils.

To further characterize the analytical data, box plots were created relating analyte concentration to grain size. Each sample was grouped into one of six categories based upon the percent of the sample finer than a particle size of 0.075 mm (#200 sieve). Grain sizes smaller than 0.075 mm fall mostly within the range of silt and clay and exhibit colloidal behavior that can greatly influence geochemical properties.

Plots were created for each analyte. Figures 1 through 8 are box plots for example analytes: lead, arsenic, calcium, sodium, iron, cation exchange capacity (CEC), and total organic carbon (TOC). Each box represents the 25th and 75th percentiles for a category and the whiskers represent the 10th and 90th percentiles. The line in the middle of each box gives the median concentration for the category. Outliers are plotted as individual data points.

In each plot, a trend of increasing median concentration with increasing silt and clay content can be seen. This is particularly true for silt and clay contents in excess of 30 percent. This behavior can be partially
explained by increasing CEC. Figure 6 shows that median CEC concentrations increase with increasing silt and clay content, but not as distinctly as the metals concentrations. Soils at the SRS have developed in a moderately aggressive weathering environment which has resulted in the leaching of minerals and fines from the surface layers of the soil profile. This has resulted in eluviated sandy surficial soils that have limited ion retaining properties. Further, this aggressive weathering environment has resulted in clay minerals in the most stable crystalline arrangements. The clay fraction of soils from the SRS have been shown to be primarily kaolinitic (Rogers, 1990; Looney, et al., 1990). Kaolinitic clays have characteristically low CEC concentrations which range from 5 to 15 cmol/kg. Exchange capacities presented in Figure 6 generally fall within this range. As a result, soils composed of predominantly kaolinitic clays can obtain much of their exchange capacity from organic matter. This is particularly true in wetland soils where an abundance of organic matter is typically available. This suggests that organic matter may be an additional contributor to the increased metals concentrations with increasing fines. As expected, Figure 7 shows that median TOC concentrations also increase with increasing silt and clay content.

Also observed in Figures 1 through 8, is increasing variation of the sample means with increasing silt and clay content. Increased variation with increasing fines may be reflective of the wide range of wetland soil types grouped together for the analysis (ranging from organic mucks to stratified sands). The analytical methods chosen for this study may also contribute to the observed variation. Standard Environmental Protection Agency (EPA) analytical methods were used for this study to ensure that the results would be comparable to existing or future site characterizations of wetland soils. Standard EPA extraction methods result in partial dissolution of the soil minerals rather than complete dissolution. Ions that are tightly bound to the soil particles are only partially extracted. This partial dissolution may result in more variable major, minor, and trace element concentrations than if the sample were completely dissolved. This can be particularly true for elements found in the crystalline structure of some soil minerals (i.e. aluminum, calcium, magnesium, etc.).

At silt and clay contents of less than 30%, variation among the sample means is small. This may be indicative of the many results reported as below the LOD for these categories. This is expected since sandier soils do not have the capability to adsorb elements to the soil matrix.

Arsenic is a metal of particular environmental significance as it is used in various industrial and agricultural processes (Kroschwitz and Howe-Grant, 1992). Arsenic concentrations were reported below the LOD for slightly more than half of the sample population. Thus, the arithmetic and geometric means and standard deviation are not presented in Table 3. However, from Figure 2, it is observed that arsenic exhibits the trend of increasing concentration with increasing fines. Closer examination of the arsenic data revealed that 41% of the results reported as above the LOD came from soil grouping 5 (Savannah River floodplain). This grouping is typified by soils with high clay content influenced primarily by offsite activities. Arsenic is used in the timber industry as a wood preservative and in agricultural activities in various pesticides. The most likely source for the observed arsenic concentrations is upstream agricultural activities.
SUMMARY

The wetland soils study was conducted to determine the naturally occurring background concentrations of a wide range of constituents in unimpacted wetland soils on the SRS (Dixon, et al. 1996). Soil cores were collected using vibracoring technology from 50 locations. Five duplicate cores were collected yielding a total of 55 cores. Each core was subdivided into 5 depth increments producing 275 soil subsamples submitted for chemical and physical analyses.

Metals concentrations were observed to increase with increasing silt and clay content. This increase in concentration was attributed to increases in exchange capacity and organic matter content with increasing silt and clay content. Increased variation was observed in analyte means with increasing silt and clay content. The metal concentration variability was attributed to the wide range of wetland soil types sampled and to the analytical methods chosen for the study.

Results from this study help fill the gap in the current literature concerning background metals concentrations in wetland soils. These results will be used as background concentration values for future human health and ecological risk assessments, treatability studies, remedial investigations, and feasibility studies for wetland areas at SRS.

REFERENCES


<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Reference</th>
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<td>Arsenic</td>
<td>EPA 7060</td>
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Table 2. Wetland Soil Groupings

<table>
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<tr>
<th>Soil Group and Dominant Series</th>
<th>Broad Category</th>
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<tr>
<td>Group One - Dorovan, Other Histosols</td>
<td>Small Stream Floodplain - Organic Soils</td>
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<td>Group Two - Pickney, Johnston</td>
<td>Small Stream Floodplain - Intergrade Mineral-Organic Soils</td>
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<td>Group Three - Fluvaquents</td>
<td>Small Stream Floodplain - Mineral Soils</td>
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<td>Group Four - Rembert, Ogeechee, Williman</td>
<td>Upland Bays and Depressional Soils</td>
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<td>Group Five - Chastain, Tawcaw</td>
<td>Large Stream Floodplain Soils</td>
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Table 3. Summary statistics for all constituents for the wetland soils study.

<table>
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<th>Percent Above Detect</th>
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<th>Median</th>
<th>Minimum</th>
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¹Aluminum core barrel was used during for sampling. This should be considered when interpreting aluminum results.
Figure 1. Lead as a function of percent silt and clay. Boxes represent 25th and 75th percentiles with median line in between. Whiskers give 10th and 90th percentiles.

Figure 2. Arsenic as a function of percent silt and clay. Boxes represent 25th and 75th percentiles with median line in between. Whiskers give 10th and 90th percentiles.

Figure 3. Calcium as a function of percent silt and clay. Boxes represent 25th and 75th percentiles with median line in between. Whiskers give 10th and 90th percentiles.

Figure 4. Sodium as a function of percent silt and clay. Boxes represent 25th and 75th percentiles with median line in between. Whiskers give 10th and 90th percentiles.
Figure 5. Iron as a function of percent silt and clay. Boxes represent 25th and 75th percentiles with median line in between. Whiskers give 10th and 90th percentiles.

Figure 7. Total Organic Carbon as a function of percent silt and clay. Boxes represent 25th and 75th percentiles with median line in between. Whiskers give 10th and 90th percentiles.

Figure 6. Cation Exchange Capacity as a function of percent silt and clay. Boxes represent 25th and 75th percentiles with median line in between. Whiskers give 10th and 90th percentiles.