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**SEDIMENT QUALITY ASSESSMENT OF
HERRINGTON LAKE,
GARRETT COUNTY, MARYLAND**

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Contents

| | |
|--|----|
| Executive Summary | 7 |
| Introduction | 8 |
| Study Area | 8 |
| Study Objectives | 8 |
| Methods | 8 |
| Field Methods | 8 |
| Laboratory Methods | 10 |
| Grain Size | 10 |
| Elemental Analysis | 12 |
| Carbon, Nitrogen and Sulfur Analysis | 13 |
| Results and Discussion | 13 |
| Physical Analysis | 13 |
| Carbon, Nitrogen, Sulfur and Phosphorus Analysis | 16 |
| Elemental Analysis | 21 |
| Enrichment Factors | 28 |
| Summary and Conclusions | 30 |
| References | 31 |
| Appendix A | 34 |
| Appendix B | 44 |
| Textural Analyses | 45 |
| Carbon, Nitrogen and Sulfur Analyses | 45 |
| Appendix C | 46 |

List of Figures

| | |
|---|----|
| Figure 1. Map of grab sample locations. | 10 |
| Figure 2. Shepard (1954) classification of sediment types. Sediment type classification is based on relative percentages of each size component (sand, silt, and clay). | 12 |
| Figure 3. Pejrup's Diagram (1988) classification of sediment type. | 13 |
| Figure 4. Distribution of sediment types based on Shepard (1954) classification. | 16 |
| Figure 5. Concentration profile plots of several major elements by Herrington Lake station number, shown with clay content. Concentrations are in percent for clay, and in milli-moles per kilogram for the elements shown. | 26 |
| Figure 6. Concentration profile plots of several trace elements by Herrington Lake station number. Concentrations are in milli-moles per kilogram for the elements shown. | 27 |

List of Tables

| | |
|---|----|
| Table 1. Sediment grain size definitions used in this study are based on the Wentworth (1922) scale. The term Mud is used to describe all particles smaller than sand (less than 0.0625 millimeters). The term Gravel is used to describe all rock fragment particles that are 2 millimeters or larger. | 13 |
| Table 2. Summary table of physical properties result for Herrington Lake. ¹ Approximate depths were measured with rope while the sample was retrieved. | 17 |
| Table 3. Nitrogen, Carbon, Phosphorus and Sulfur results for Herrington Lake. ¹ Sample 9 was taken in a slightly peaty and very organic matter-rich location within Herrington Lake, which is why nitrogen and carbon values are higher than that of other samples within the Lake. | 18 |
| Table 4. Comparison of total N, C, P and S in surficial sediment in Maryland freshwater reservoirs/lakes. Values given are percent dry sediment weight. ¹ Sample 9 was omitted from all averages and ranges. | 19 |
| Table 5. Comparison of mass ratios of C, N and P observed in different sample sources. ¹ Herrington sample 9 was omitted and not used to calculate the ratios. | 20 |
| Table 6. Correlation matrix for textural, nutrient and target metal data based on all of the sediment samples collected at Herrington Lake. The correlations were determined using a Pearson product-moment technique (Johnson and Wichern, 1982). Values listed in the table are Pearson correlation coefficients (r). Shaded values are statistically significant at the 95% confidence level ($p < 0.05$). | 22 |
| Table 7. Summary statistics of select metal concentration measured in Herrington Lake | |

sediments. All values are ppm unless otherwise indicated. For comparison, benchmark levels for freshwater sediments are included along with the number of lake samples exceeding the respective limit values. These benchmarks for freshwater sediments are based upon chronic, long-term impacts of contamination to benthic organisms (Buchman, 2008). The Lowest Effect Level (LEL) is a level of sediment contamination that can be tolerated by the majority of benthic organisms. The Severe Effect Level (SEL) is that at which pronounced disturbance of the sediment-dwelling community can be expected. This is the concentration that would be detrimental to the majority of the benthic community. 23

Table 8. Comparisons of average enrichment factors in several Maryland freshwater reservoirs/lakes. Enrichment factors are relative to the average earth's crust (Taylor, 1964.) 29

Table A-1. Sample descriptions and coordinates, with approximate water depth. 35

Table B-1. Results of nitrogen, carbon and sulfur analyses of the standard reference materials (SRMs) compared to the certified or known values. MGS values were obtained by averaging the results of all SRM analyses run during this study. 45

Table C-1. Elements (analytes) reported in this study include 50 elements analyzed by ActLabs. Methods abbreviations: High Temp. Combustion-GC: High Temperature combustion, followed by Gas chromatography; TD-ICP: Total Digestion followed by Inductively Coupled Plasma Spectrometry; INAA: Instrumental Neutron Activation Analysis. 47

Table C-2. Herrington Lake sediment elemental data. All values are ppm (mg/kg) unless indicated otherwise. 48

Table C-3. Results of analyses of Standard Reference Material (NIST SRM #8704 - Buffalo River Sediment) submitted as blind unknowns with the Herrington Lake surficial samples. Also given are the method detection limits for each element reported by Act Labs, Inc. Shaded values, if any, differ from the certified or known value by >25%. 49

Table C-4. Results of analyses of Standard Reference Material (NIST SRM #1646a- Estuarine Sediment) submitted as blind unknowns with the Herrington Lake surficial samples. Also given are the method detection limits for each element reported by Act Labs, Inc. Shaded values, if any, differ from the certified or known value by >25%. 51

Table C-5. Results of analyses of Standard Reference Material (NIST SRM #2702- Inorganics in marine sediment) submitted as blind unknowns with the Herrington Lake surficial samples. Also given are the method detection limits for each element reported by Act Labs, Inc. Shaded values, if any, differ from the certified or known value by >25%. 53

Table C-6. Results of Act Labs analyses of Reference material for the TD-ICP method. Act Labs' measure values compared to the certified values. Reference materials include USGS geochemical exploration references. 55

Acronyms and Abbreviations used in this report

| <i>Abbreviation</i> | <i>Description</i> |
|-----------------------------------|--|
| Act Labs | Activation Laboratories, Inc. |
| Al, Ca, Fe, K, Na and Mg | major rock forming elements aluminum, calcium, iron, potassium, sodium and magnesium |
| As, Cd, Cr, Cu, Mn, Ni, Pb and Zn | trace elements arsenic, cadmium, chromium, copper, manganese, nickel, lead and zinc. |
| °C | Degrees Celsius |
| C, N, S and P | carbon, nitrogen, sulfur and phosphorus |
| CNS | carbon, nitrogen, and sulfur (gas chromatography analysis) |
| cm | Centimeters |
| CRC | Canadian Research Council |
| DNR | Maryland Department of Natural Resources |
| EF | Enrichment Factor |
| EPA | Environmental Protection Agency |
| GIS | Geographical Information System |
| INAA | Instrumental Neutron Activation Analysis |
| HCl | Hydrochloric Acid |
| LEL | Lowest Effect Level |
| MGS | Maryland Geological Survey |
| mg/kg | Milligrams per kilogram |
| ml | Milliliter |
| mmol/kg | Milli-mole per kilogram |
| NAD83 | North America [Horizontal] Datum of 1983 |
| NIST | National Institute of Standards and Technology |
| NOAA | National Oceanic and Atmospheric Administration |
| ppm | part per million |
| RAS | Resource Assessment Service (DNR) |
| RTK GPS | Real-Time Kinematic Global Positioning System |
| SAV | Submerged Aquatic Vegetation |
| SEL | Severe Effect Level |
| SRM | Standard Reference Material |
| TD-ICP | “near total” Digestion Inductively Coupled Plasma Spectrophotometer |
| TEA | Tidewater Ecosystem Assessment (DNR) |
| ug/g | Microgram per gram (parts per million) |
| US SCS | U.S. Soil Conservation Service (in 1994, name changed to NRCS) |
| UTM | Universal Transverse Mercator (coordinate system) |

Executive Summary

Maryland Geological Survey, in conjunction with other Maryland Department of Natural Resources programs, including Tidewater Ecosystem Assessment (TEA) and Fishing and Boating Services, was asked to perform sediment quality assessments of state-owned lakes in Maryland. The goal is to provide surficial sediment data for each lake to determine general sediment physical and chemical characteristics as a pre-assessment for potential future lake sediment dredging. Physical and chemical analysis of the sediments from each lake will pose as a baseline for the lake's sediment data. The sediment data will be incorporated into other study aspects, including fish populations, water quality, and submerged aquatic vegetation (SAV) abundance and distribution in order to generate overall lake health and status.

This report focuses on Herrington Lake in Garrett County, Maryland. The lake is 53 acres and is located within Herrington Manor State Park. Fifteen surficial sediment samples were collected throughout the lake and coordinates were stored using Real-Time Kinematic Global Positioning System (RTK GPS). Sediment at each site was described and sampled for analysis. Analysis includes physical properties, including bulk density and grain size, and elemental analysis.

The majority of the samples collected are fine-grained sediments, with an average textural content of 10% sand, 42% silt and 45% clay. Seven samples classify as silty-clay, five samples classify as clayey-silt and three samples classify as sand-silt-clay.

The shallow sediments collected from Herrington Lake were found to have fairly high averages of total carbon (C) content (5.1% by dry weight), nitrogen (N) content of 0.5%, phosphorus (P) content of 0.7% and a sulfur (S) content of 0.1%. C, N and S concentrations were highly inter-correlated at Herrington Lake, which we suspect may be due to the abundant fresh organic material in the sediments.

The elemental concentrations of 15 surficial sediments followed similar spatial patterns to each other when plotted by station, to correlate generally with clay content. This was true for Al, Fe, K, Na, Mg, although Ca was slightly different. Many trace elements also had profiles that were generally similar to each other. These include Zn, Cr and Ni, Cu and Pb in a muted way, and As and Cr in an amplified way. When compared relative to two eco-toxicological screening levels for freshwater sediments, all metals of concern were above the more conservative lowest effect level (LEL) and Fe and Mn were above the higher severe effect level (SEL) in some samples. Since these concentrations represent more than that which is environmentally available, eco-toxicological harm is not anticipated. When compared to relative crustal abundance via the use of Fe-normalized enrichment factors, the elements Cd, Hf, Pb, Sb and Zn were elevated. However, these elements are often encountered in high concentrations in clay-rich sedimentary rocks and the sediments derived from them.

The 15 collected samples throughout Herrington Lake were similar to sediments of other lakes nearby, including Deep Creek Lake. No abnormalities were found in regard to the physical or chemical properties of the bottom sediments of Herrington Lake.

Introduction

Study Area

Herrington Lake is a man-made lake at the headwaters of Herrington Run in Garrett County, Maryland. The lake is 53 acres in area and is located within Herrington Manor State Park and owned by the State of Maryland.

The Herrington Lake watershed is located within the Appalachian Plateau Physiographic Province of Maryland. The bedrock of this region contains gently folded sedimentary rock composed of shales, sandstones and limestone bedrock. Regional formations are mapped as the Conemaugh Group, including two halves: the upper Casselman and lower Glenshaw Formations. The Pennsylvanian-age Conemaugh Group is comprised of: interbedded, light gray, micaceous sandstone, gray silty shale and thin, dark gray, marine shales in the lower half of the group and greenish-gray and reddish brown to variegated mudstone, shale, claystone, and nodular non-marine limestone in its upper part (Brezinski and Conkwright, 2013). Some coal beds have also been reported within the lower Glenshaw Formation.

Study Objectives

The objectives of this study are to:

1. Document sediment through the collection of grab samples from Herrington Lake.
2. Analyze the samples for physical properties, including bulk density and grain size.
3. Process each sample for carbon, nitrogen and sulfur (CNS) and elemental analysis.

Methods

Field Methods

On September 9, 2019, MGS staff collected 15 sediment grab samples in Herrington Lake (Figure 1). A 16-foot aluminum jon boat with an electric motor was used to collect the samples around the lake. Prior to sampling, using ESRI ArcMap 10.3, 15 proposed sample locations were placed throughout the lake to ensure full lake coverage. During sample collection, a TopCon Real-Time Kinematic Global Positioning System (RTK GPS) antenna and Carlson SurvPC software were used to locate each of the proposed locations and record the actual grab sample coordinates for each sample. Location coordinates were documented in UTM NAD83 Zone 17 State Plane, meters (Appendix A). Pictures were captured for each sample, displaying sediment properties and any present submerged aquatic vegetation (SAV). Pictures can also be found in Appendix A. The SAV was later provisionally identified visually as *Sagittaria* species present in most grab samples and as *Potamogeton* species present at locations 11 and 14 (DNR Resource Biology staff, including J. Bortz and M. Lewandowski, personal correspondence).

Sediment samples were collected with a hand-operated LaMotte stainless-steel dredge that sampled a bottom surface area of 19 centimeters (cm) x 14 cm and a mean sediment depth of 10 cm. Upon collection, samples were photographed, described, placed in Whirl-Pak™ bags and kept cool until delivery to the MGS laboratory. Samples were refrigerated at 4° Celsius (C) until analysis. Sample descriptions and coordinates can be found in Appendix A.

**Sediment Samples from Herrington Lake
September 9, 2019**



Figure 1. Map of grab sample locations.

Laboratory Methods

Grain Size

Sediment grab samples were analyzed for water content, bulk density and grain size (sand, silt and clay contents, as well as gravel, when present). Two homogeneous splits of each sample were processed, one for bulk property analysis and the other for grain size characterization. Analyses were performed within one week of sample collection and all samples were stored at 4° C prior to analysis.

Water content was determined by weighing 20-30 grams (g) of sediment. The sediment was then dried at 65° C and then re-weighed. Water content was calculated as the percentage of water weight to the weight of the wet sediment using Equation 1.

$$\%Water = \frac{W_w}{W_t} * 100 \quad \text{Equation 1}$$

where: W_w is the weight of water; and
 W_t is the weight of wet sediment.

Wet Bulk Density (ρ_B) is calculated from water content utilizing Equation 2 by assuming an average grain density (ρ_s) of 2.72 g/cm³ and saturation of voids with water of density $\rho_w = 1.0$ g/cm³. This method was adopted from the work of Bennett and Lambert (1971):

$$\rho_B = \frac{W_t}{W_d / 2.72 + W_w} \quad \text{Equation 2}$$

where: W_d is the weight of dry sediment.

Gravel, sand, silt and clay contents were determined using the textural analysis detailed in Kerhin and others (1988). Grain size, in this report (Table 1), is given in phi units, a scale devised by Krumbein (1936) where phi is defined as the negative log (to the base 2) of the particle diameter (millimeters (mm)). For example, 4 phi corresponds to a particle with a diameter of $1/2^4$ mm (=1/16 mm, or 0.0625 mm or 62.5 microns).

Grain size analysis consisted of cleaning the sediment samples in solutions of 10 percent hydrochloric acid (HCl) and 6 or 15 percent hydrogen peroxide (determined by water content) with subsequent rinsing with deionized water. This process removed soluble salts, carbonates and organic matter that could interfere with the dis-aggregation of the individual grains. The samples were then treated with a 0.26 percent solution of the dispersant sodium hexametaphosphate ((NaPO₃)₆) to ensure that individual grains did not re-aggregate (floculate) during pipette analysis.

The separation of sand and silt-clay (mud) portions of the sample was accomplished by

wet-sieving through a 4-phi mesh sieve (0.0625 mm, U.S. Standard Sieve #230). The gravel-sand fraction (*i.e.* that portion of the sample not passing through the sieve) was dried and weighed, and saved for further analysis. The finer silt and clay-sized particles (*i.e.*, passing through the sieve) were suspended in a 1000 milliliter (ml) cylinder in a solution of 0.26 percent sodium hexametaphosphate. The suspension was agitated and, at specified times thereafter; 20 ml pipette withdrawals were made (Carver, 1971; Folk, 1974). The rationale behind this process is that larger particles settle faster than smaller ones (Stoke's law). By calculating the settling velocities for different sized particles, times for withdrawal can be determined at which all particles of a specified size will have settled past the point of withdrawal. Sampling times were calculated to permit the determination of the amount of particles corresponding to 4 phi (silt class) and 8 phi (clay class) particles in the suspension. Withdrawn samples were dried at 65°C and weighed. From these data, the percentages by dry weight of sand, silt and clay were calculated for each sample and classified according to Shepard (1954) and Pejrup (1988) nomenclatures (Figures 2 and 3). Sample weight loss due to cleaning was determined; the weight loss approximates the amount of non-clastic components in the sediment.

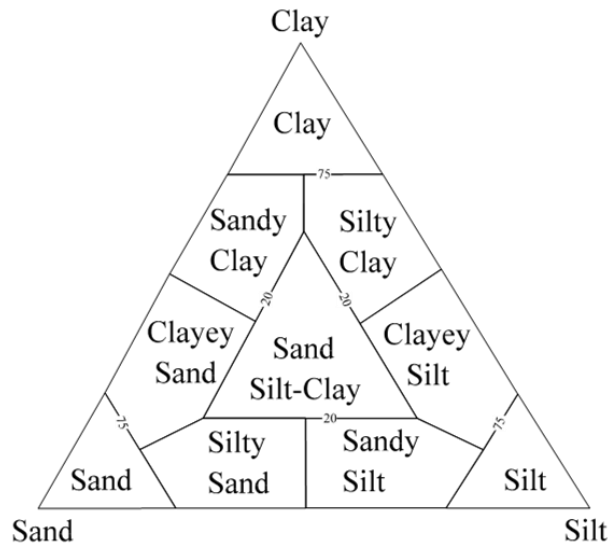


Figure 2. Shepard (1954) classification of sediment types. Sediment type classification is based on relative percentages of each size component (sand, silt, and clay).

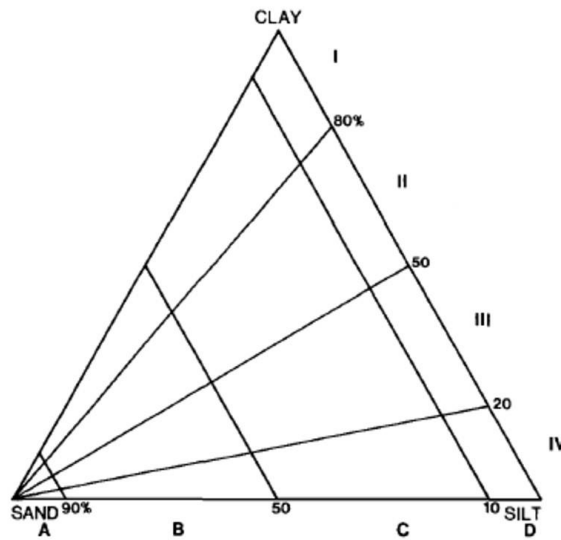


Figure 3. Pejrup's Diagram (1988) classification of sediment type.

Table 1. Sediment grain size definitions used in this study are based on the Wentworth (1922) scale. The term Mud is used to describe all particles smaller than sand (less than 0.0625 millimeters). The term Gravel is used to describe all rock fragment particles that are 2 millimeters or larger.

| Descriptor | Grain Size (millimeters) | Class Sizes (phi) |
|-------------------------|--------------------------|-------------------|
| Mud | < 0.0625 | > 4 |
| Clay | < 0.004 | > 8 |
| Silt | 0.004 to 0.0625 | > 4 to 8 |
| Sand | 0.0625 to 2 | 4 to -1 |
| Very Fine Sand | 0.0625 to 0.125 | 4 to 3 |
| Fine Sand | 0.125 to 0.25 | 3 to 2 |
| Medium Sand | 0.25 to 0.5 | 2 to 1 |
| Coarse Sand | 0.5 to 1 | 1 to 0 |
| Very Coarse Sand | 1 to 2 | 0 to -1 |
| Gravel | 2 to 4,096 | -1 to -12 |
| Granule | 2 to 4 | -1 to -2 |
| Pebble | 4 to 64 | -1 to -6 |
| Cobble | 64 to 256 | -6 to -8 |
| Boulder | 256 to 4,096 | -8 to -12 |

Elemental Analysis

Samples were ground in-house to the point until 95 percent of the sample could pass through a 200-mesh sieve (0.074 mm screen opening). Each sample was divided, with a three to five gram portion of the sample submitted to Activation Laboratories Inc. (Act Labs), while the remainder of the sample was retained for in-house analysis of total carbon, nitrogen and sulfur (CNS).

The quality assurance and quality control of Act Labs has proved to meet MGS standards and requirements. Fifty elements (Ag, Al, As, Au, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Eu, Fe, Hf, Hg, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Rb, S, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Th, Ti, U, V, W, Y, Yb and Zn; refer to Appendix C for symbol key) were analyzed at Act Labs. Samples were prepared and ground in-house and sent to Act Labs for analyses using both Instrumental Neutron Activation Analysis (INAA) and a four acid “near total” digestion technique followed by analysis on an Inductively Coupled Plasma Spectrophotometer (TD-ICP). In addition to the standards and blanks used by Act Labs, National Institute for Standards and Technology (NIST) Standard Reference Materials (SRMs) were inserted every eighth sample to run as blind, known sample analyses. Replicates of the Herrington samples were also placed throughout the batch and were blindly run every eighth sample.

Carbon, Nitrogen and Sulfur Analysis

Sediments were analyzed by MGS for total carbon, nitrogen and sulfur (CNS) contents using a Carlo Erba NA1500 analyzer. This analyzer uses complete combustion of the sample followed by separation and analysis of the resulting gases by gas chromatographic techniques employing a thermal conductivity detector. The NA1500 Analyzer was configured for CNS analysis using the manufacturer's recommended settings. As a primary standard, sulfanilamide was used and was run after every eight unknown sediment samples. As a secondary standard, one of several NIST SRMs was run after every eight sediment samples. Blanks (tin capsules containing only vanadium pentoxide) were run at the beginning and end of the analyses each day. Replicates of every seventh sample were also run.

Results and Discussion

Physical Analysis

Based on the textural analyses of the 15 surficial sediment samples (representing the top 10 cm of the sediment column), the majority of the samples collected are fine-grained sediments, with an average textural content of 10% sand, 42% silt and 45% clay. Seven samples classify as silt-clay, five samples classify as clayey-silt and three samples classify as sand-silt-clay (Table 2). Clay represents a major component of the collected sediments, which is not unexpected given the abundance of shale in the underlying formations within the watershed. Sand and gravel are relatively minor components in most samples. Three samples, numbers 4, 10 and 13, were composed of 3%, 22% and 16% gravel, respectively, but all three were still classified as a sand-silt-clay. Sample 13 was collected approximately 10 feet from the sandy beach area used for swimming. Complete sample field descriptions, including coordinates and pictures for each sample can be found in Appendix A.

The physical and chemical behavior of sediment is influenced by its texture. Particle diameter reflects the energy environment in which the sediment was deposited. Generally, coarse grained sediments (i.e., sand and gravel) are found in higher energy environments, such as areas subjected to wave activity or high water currents, which tend to winnow out any fine grained sediment. Fine-grained sediments, which are transported further from the source and take a long time to settle, are usually found in areas that are not subjected to high waves or winds, or below the depth of wave motion, such as deeper areas in the central area of the lake, or coves that are

sheltered from high waves and winds. Herrington Lake is a rather shallow lake, with an average sample depth of approximately 4 feet (ranging from 1 foot to 8 feet deep). Grain size is often inversely proportional with depth, but may not sort completely in such a shallow body of water. The sediment distribution at Herrington Lake loosely follows this pattern (Figure 4). The finest-grained sediments (i.e., sediment with highest clay content) are in the deepest part of the lake, whereas sandier sediments are found in shallower depths and in the up-stream areas, which would be the sandy samples 4 and 10 (excluding sample 13, which is believed to have received additional gravel and sand from the swimming area). Textural QA/QC analyses can be found in Appendix B.

Size also reflects the mineral composition of the sediments, which, in turn, is a product of the parent rock. Herrington Lake is located in the Appalachian Plateau physiographic province in Maryland. This area in western Maryland, where the Herrington Lake watershed lies, consists of sedimentary rock, namely shales and sandstones. Clay minerals are abundant in the lake since shale is a common parent rock. Shales are lithified mud deposits, composed of silt sized particles (mainly quartz) and clay minerals. Clay minerals are the remaining particles after complete weathering of the shale. Clay particles are small, plate-like particles, with a diameter of less than two microns and have a relatively large surface area. Depending on the crystalline lattice, clays have an enormous capacity to incorporate both organic and metal cations onto the lattice surface, and water and organic compounds within lattice layers. These bound substances, in turn, contribute to the cohesiveness of the clays. Organic rich clays, in turn, support active benthic bacteria and plankton communities.

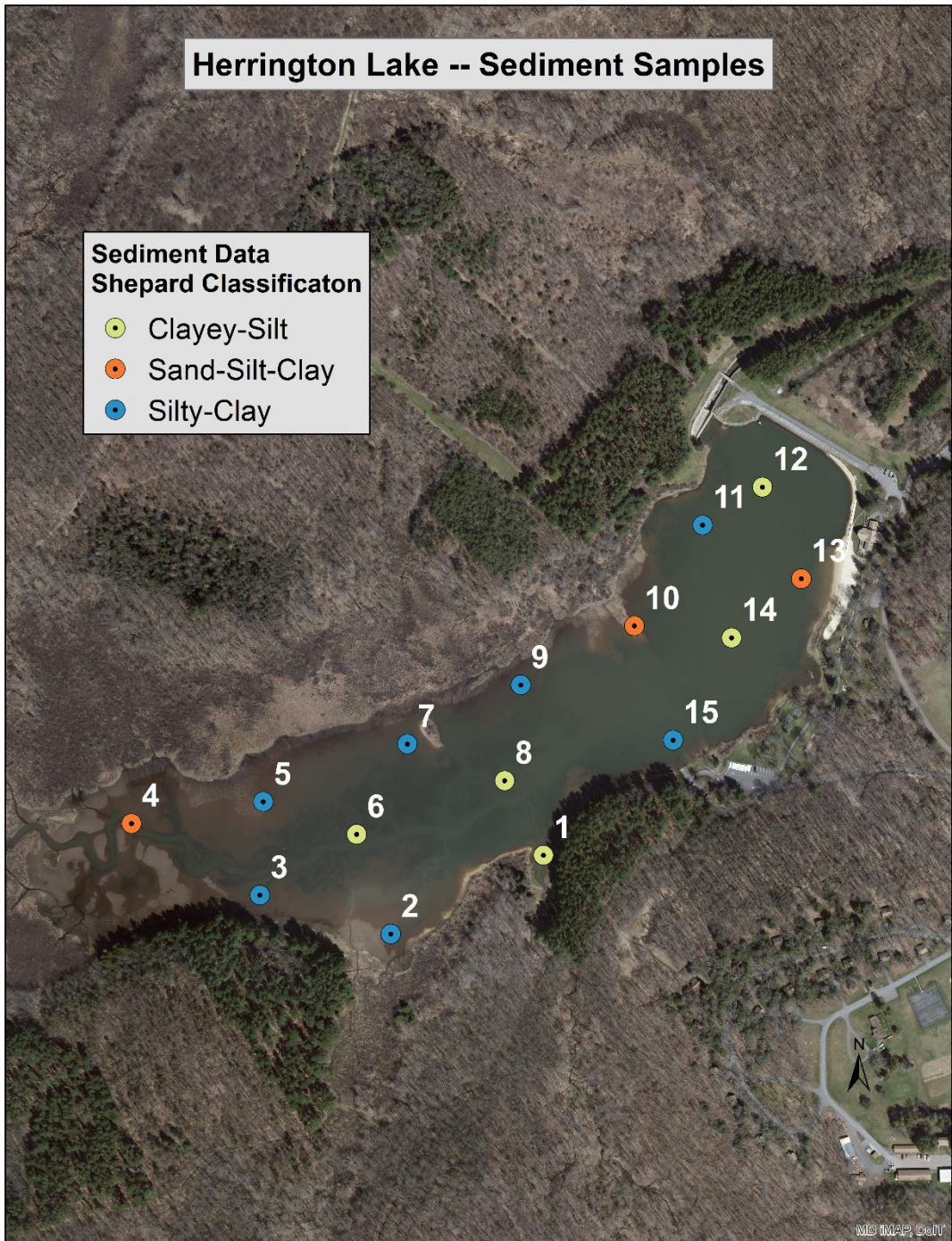


Figure 4. Distribution of sediment types based on Shepard (1954) classification.

Table 2. Summary table of physical properties result for Herrington Lake.
¹Approximate depths were measured with rope while the sample was retrieved.

| Sample ID | % H ₂ O | Bulk Density | % Gravel | % Sand | % Silt | % Clay | Shepard Class | Pejrup Class | Clay:Mud | Approx. Depth ¹ (feet) |
|-----------|--------------------|--------------|----------|--------|--------|--------|----------------|--------------|----------|-----------------------------------|
| 1 | 73.67 | 1.20 | 0.00 | 5.13 | 52.89 | 41.98 | Clayey-Silt | D,III | 0.44 | 1 |
| 2 | 56.13 | 1.38 | 0.00 | 0.79 | 44.18 | 55.03 | Silty-Clay | D,II | 0.55 | 1 |
| 3 | 73.71 | 1.20 | 0.00 | 0.22 | 39.46 | 60.33 | Silty-Clay | D,II | 0.60 | 2 |
| 4 | 65.28 | 1.28 | 2.70 | 27.74 | 39.61 | 29.96 | Sand-Silt-Clay | C,III | 0.43 | 3 |
| 5 | 68.64 | 1.25 | 0.00 | 6.96 | 40.31 | 52.72 | Silty-Clay | D,II | 0.57 | 1 |
| 6 | 59.90 | 1.34 | 0.00 | 10.18 | 49.40 | 40.42 | Clayey-Silt | C,III | 0.45 | 3.5 |
| 7 | 67.56 | 1.26 | 0.00 | 5.32 | 41.15 | 53.53 | Silty-Clay | D,II | 0.57 | 2.5 |
| 8 | 59.98 | 1.34 | 0.00 | 10.84 | 53.65 | 35.52 | Clayey-Silt | C,III | 0.40 | 4 |
| 9 | 83.28 | 1.12 | 0.00 | 4.83 | 46.38 | 48.79 | Silty-Clay | D,II | 0.51 | Not recorded |
| 10 | 34.71 | 1.70 | 22.48 | 26.24 | 26.05 | 25.23 | Sand-Silt-Clay | C,III | 0.49 | 1 |
| 11 | 57.16 | 1.37 | 0.00 | 8.87 | 34.77 | 56.36 | Silty-Clay | D,II | 0.62 | 6.5 |
| 12 | 53.50 | 1.42 | 0.00 | 14.88 | 43.02 | 42.10 | Clayey-Silt | C,III | 0.49 | 8 |
| 13 | 53.62 | 1.42 | 16.41 | 21.07 | 32.65 | 29.87 | Sand-Silt-Clay | C,III | 0.48 | 5.5 |
| 14 | 63.59 | 1.30 | 0.00 | 1.25 | 50.84 | 47.91 | Clayey-Silt | D,III | 0.49 | 5.5 |
| 15 | 56.93 | 1.37 | 0.00 | 5.68 | 44.04 | 50.28 | Silty-Clay | D,II | 0.53 | 3.5 |

Carbon, Nitrogen, Sulfur and Phosphorus Analysis

Results of nitrogen (N), carbon (C), phosphorus (P) and sulfur (S) analysis of each sample are shown in Table 3. In overview, these were organic-rich sediments. It is important to note sample 9 was collected from a slightly peaty and highly organic matter-rich location of the Lake, which has caused this sample to have a higher nitrogen and carbon content than other samples throughout the lake that were not as highly organic. Sample 9 was analyzed a second time for confirmation of the high concentrations, and both results returned similar concentrations of carbon, nitrogen and sulfur, ruling out analytical error as the cause of the high concentration.

Table 3. Nitrogen, Carbon, Phosphorus and Sulfur results for Herrington Lake.

¹Sample 9 was taken in a slightly peaty and very organic matter-rich location within Herrington Lake, which is why nitrogen and carbon values are higher than that of other samples within the Lake.

| Sample ID | % Nitrogen | % Carbon | % Phosphorus | % Sulfur |
|----------------|------------|----------|--------------|----------|
| 1 | 0.438 | 6.387 | 0.078 | 0.118 |
| 2 | 0.339 | 4.207 | 0.075 | 0.082 |
| 3 | 0.562 | 6.612 | 0.110 | 0.108 |
| 4 | 0.398 | 6.160 | 0.055 | 0.114 |
| 5 | 0.460 | 5.751 | 0.091 | 0.096 |
| 6 | 0.405 | 5.782 | 0.061 | 0.105 |
| 7 | 0.485 | 6.007 | 0.102 | 0.094 |
| 8 | 0.400 | 6.381 | 0.070 | 0.114 |
| 9 ¹ | 2.065 | 30.286 | 0.070 | 0.362 |
| 10 | 0.125 | 1.335 | 0.050 | 0.034 |
| 11 | 0.387 | 5.569 | 0.092 | 0.101 |
| 12 | 0.281 | 4.007 | 0.061 | 0.089 |
| 13 | 0.272 | 3.956 | 0.048 | 0.112 |
| 14 | 0.390 | 5.517 | 0.082 | 0.155 |
| 15 | 0.305 | 4.034 | 0.065 | 0.075 |

Total C contents measured in Herrington Lake sediments range from 1.3% to 30.3% (dry weight), with a mean of 6.8%. However, it must be noted that sample 9, collected from a peaty and highly organic matter-rich location within the Lake, was found to have anomalously high C content of 30.3%. Excluding sample 9, the average total C measured in Herrington Lake is 5.1% with a range of 1.3% to 6.6%. These values are similar to that of the average C reported for New Germany Lake and Deep Creek Lake (Table 4).

Total C in the sediments is the sum of organic and inorganic carbon. Organic carbon is present in SAV, algal, bacterial, and detrital terrigenous plant biomass, whereas inorganic carbon is present in detrital limestone. As carbon is deposited with the sediments, most of it is remineralized to carbon dioxide by decomposing bacteria. These bacteria utilize a sequence of electron acceptors to decompose organic matter, starting with dissolved oxygen, followed by dissolved nitrate, amorphous Fe and Mn oxyhydroxides, and dissolved sulfate. Pore-water dissolved oxygen is often consumed within the top 2 cm of the interface in clayey sediments, although plant roots can release oxygen deeper into micro-environments in the sediments, often observed as precipitation of iron solids along a root fiber (Appendix A).

Table 4. Comparison of total N, C, P and S in surficial sediment in Maryland freshwater reservoirs/lakes. Values given are percent dry sediment weight.

¹Sample 9 was omitted from all averages and ranges.

| Reservoir/Lake | Physiographic Province | % N | | % C | | % P | | %S | |
|--|----------------------------|-------------|------------------|-------------|------------------|-------------|------------------|-------------|------------------|
| | | Avg. | Range | Avg. | Range | Avg. | Range | Avg. | Range |
| Loch Raven (Ortt <i>et al.</i> , 1999) | Piedmont | 0.32 | 0.24 - 0.40 | 3.17 | 2.53-3.94 | 0.16 | 0.12-0.19 | 0.057 | 0.0-0.15 |
| Triadelphia Reservoir (Wells <i>et al.</i> , 2007) | Piedmont | 0.26 | 0.11-0.48 | 2.77 | 1.48-4.12 | 0.10 | 0.04-0.17 | 0.074 | 0.027-0.28 |
| Rocky Gorge Reservoir (Wells <i>et al.</i> , 2007) | Piedmont | 0.22 | 0.05-0.41 | 2.67 | 0.83-4.17 | 0.09 | 0.03-0.16 | 0.08 | 0.02-0.17 |
| Little Seneca Lake (Ortt <i>et al.</i> , 2011) | Piedmont | 0.29 | 0.18-0.34 | 3.25 | 2.07-5.06 | 0.08 | 0.06-0.14 | 0.11 | 0.04-0.15 |
| New Germany Lake (Ortt and Wells, 2009) | Appalachian Plateau | 0.51 | 0.09-0.81 | 6.20 | 2.02-7.54 | 0.06 | 0.01-0.10 | 0.08 | 0.01-0.21 |
| Deep Creek Lake (Wells and Ortt, 2011) | Appalachian Plateau | 0.33 | 0.12-0.62 | 4.11 | 1.55-9.60 | 0.06 | 0.01-0.13 | 0.26 | 0- 0.98 |
| Blairs Valley Lake (Sylvia <i>et al.</i> , 2020) | Ridge and Valley | 0.27 | 0.19-0.40 | 3.06 | 2.06-6.20 | 0.05 | 0.04-0.08 | 0.08 | 0.05-0.11 |
| Herrington Lake (this study)¹ | Appalachian Plateau | 0.38 | 0.12-0.56 | 5.12 | 1.33-6.61 | 0.07 | 0.05-0.11 | 0.10 | 0.03-0.15 |
| St. Mary's Lake (Sylvia <i>et al.</i> , 2020) | Coastal Plain | 0.15 | 0.04-0.32 | 2.55 | 0.62-5.13 | 0.02 | 0.00-0.05 | 0.07 | 0.02-0.16 |

Total N measured in Herrington Lake sediments averages 0.5%, with values ranging from 0.1% to 2.1%. With removing the outlier of sample 9, the average is 0.4% with a range of 0.1% to 0.6%. These modified values are within the same range as New Germany Lake and Deep Creek Lake, analogous lakes found in the Appalachian Plateau physiographic province.

Sources of N to the lake include atmospheric input, septic flow and fertilizers. Nitrogen is buried as organic nitrogen in biomass and as inorganic nitrate in pore-water. It is then utilized by decomposers and may be reduced to N₂ gas which will diffuse upwards and out of a sedimentary system or to dissolved ammonium (NH₄⁺). As organic matter is “cycled through the natural system”, relative proportions of P and, to a lesser degree, N increase as C decreases. Table 5 lists the Redfield ratios (Redfield *et al.*, 1963) for N, C and P for different sources and in sediment from several Maryland fresh and marine environments. The ratios of C to N, C to P, and N to P in Herrington Lake sediments are calculated using total C. Redfield ratios are the stoichiometric proportions of C, N and P in organic matter; they were first recognized in seawater receiving only plankton biomass, but have since been expanded to describe biomass produced in terrestrial, riverine, lacustrine or estuarine sources.

Table 5. Comparison of mass ratios of C, N and P observed in different sample sources.

¹Herrington sample 9 was omitted and not used to calculate the ratios.

| | C:N | C:P | N:P |
|--|-------------|-------------|------------|
| Global forest litter (McGroddy <i>et al.</i> , 2004) | 57.3 | 1166.1 | 20.4 |
| Global forest foliage (McGroddy <i>et al.</i> , 2004) | 37.1 | 470.0 | 12.7 |
| Dried marsh plant (Wells <i>et al.</i> , 2002) | 32.3 | 711.2 | 21.7 |
| Marsh sediments (Wells <i>et al.</i> , 2002) | 18.1 | 243.6 | 13 |
| St. Mary's Lake (Sylvia <i>et al.</i> , 2020) | 16.7 | 158.4 | 9.5 |
| Herrington Lake (this study)¹ | 13.7 | 68.9 | 5.0 |
| New Germany (Ortt <i>et al.</i> , 2009) | 13.5 | 109.2 | 8.1 |
| Dried algae (Wetzel, 1983) | 13.3 | 40.0 | 3.0 |
| Deep Creek Lake sediments (Wells and Ortt, 2011) | 12.9 | 87.5 | 6.5 |
| Rocky Gorge Reservoir (Wells <i>et al.</i> , 2007) | 12.5 | 31.2 | 2.5 |
| Blairs Valley Lake (Sylvia <i>et al.</i> , 2020) | 11.1 | 66.2 | 5.8 |
| Triadelphia Reservoir (Wells <i>et al.</i> , 2007) | 11.1 | 29.2 | 2.6 |
| Loch Raven (Ortt <i>et al.</i> , 1999) | 10.1 | 19.9 | 2.0 |
| Coastal Bays bottom sediments (Wells <i>et al.</i> , 1994) | 7.0 | 65.1 | 9.3 |
| Plankton (Redfield <i>et al.</i> , 1963) | 5.7 | 41 | 7.2 |

Total P measured in the sediments average 0.07%, with values ranging from 0.05% to 0.11%. Removing sample 9 from the average had no effect on these values. These values are similar to those found in New Germany Lake and Deep Creek Lake (Table 5). Total P was found to be associated with the sediment clay content, and also with As, Cu, and Zn (Table 6). When comparing the relative amounts of C, N and P in the Herrington Lake sediments to those of dried algae, P appears to be the limiting nutrient, common for freshwater ecosystems; thus, C:P and N:P ratios are greater than those of dried algae.

Regarding phosphorus, although total P does not directly undergo reduction-oxidation processes in sediments, its cycling within the lake is controlled, in part, by the redox state of certain metals, particularly S and Fe, and by the concentration of organic material (C). Sources of P include weathering of natural soils and rocks, runoff from agricultural land and seepage from septic systems. Phosphate (PO_4^{3-}) from fertilizers binds to soils, which erode during storm events adding suspended phosphate to streams that drain into the lake. Septic seepage may contribute phosphate in the form of orthophosphate and organic phosphorus. Unlike N and C, P has no gaseous form. Therefore, P does not cycle out of the system like N by way of denitrification or C by respiration. Thus P tends to accumulate in the sediments. Once in the sediments, P is slowly released into the interstitial water as organic material is oxidized. Free phosphate is rapidly bound to ferric oxyhydroxides and oxidized manganese which are found in the upper, oxidized layer of the sediments (i.e., oxidized flocculant layer on sediment surface). Deeper in the sediment column where anoxic conditions prevail and metals oxides have been reduced, P is released into the interstitial water and, if sulfide is low or absent, reacts with reduced forms of metals, particularly Fe, forming hydrous phosphates. However, if present, free sulfide will bind more readily to the reduced Fe and the phosphate remains free to diffuse upward to the oxidized layer where it is “captured” by excess ferric oxyhydroxides (FeOOH) and manganese oxides

found in the upper sediment layer. If the overlying water column becomes anoxic, the “captured” P may be released in the overlying water column where it can contribute to increased algae/plankton production. The portion of total P active in this cycle includes the loosely sorbed phosphate, fresh, leachable, organic P and iron-bound phosphate. These available forms of P make up 40% to 50% of the total P in the upper one centimeter of sediments and are largely depleted below three centimeters in the sediment column (Jorgensen, 1996). Any P below this depth usually consists of the more stable forms, bound to clay minerals, or associated with apatite or calcium carbonate minerals, and become permanently buried in the sediments.

Sulfur measured in the sediments, averaging 0.12% with a range of 0.03% to 0.36%. With sample 9 still being an outlier, if removed from the calculations, the data shows an average of 0.10% and a range of 0.03% to 0.15%. S concentrations in Herrington Lake are similar to that found in New Germany Lake sediments, but lower than the sediments found in Deep Creek Lake.

Reduced S and dissolved sulfate (SO_4^{2-}) concentration is an important variable controlling P release from sediments (Caraco *et al.* 1989; Wetzel, 1983). The increased P release from sediments at higher sulfate concentrations may help explain why primary production in freshwater systems (with relatively low S concentrations) tends to be P limited, whereas in many saline systems (with high sulfate concentrations) production is often P sufficient. Sulfur also plays an important role in arsenic cycling (Fisher *et al.*, 2008). At Herrington Lake, S was found to be very strongly associated with carbon and nitrogen at statistical significance, as well as with calcium (Table 6). Interestingly, S was found to be anti-correlated with Fe and several trace metals, suggesting that the S present in the sediments was more likely to be present in fresh organic material and not yet in biogenic sulfide (pyrite) minerals present in mature sediments.

In summary, the shallow sediments collected from Herrington Lake were found to have fairly high total C content (5.1% by dry weight), N content of 0.5%, P content of 0.7% and S content of 0.1%. The shallow sediments collected from Herrington Lake were similar to sediments collected from other freshwater lakes like St. Mary’s Lake and New Germany Lake. In many cases, very strong associations were found between these components; between C and N (correlation coefficient [r^2] of 1.0), between C and S (r^2 of 0.97) and between N and S (r^2 of 0.96, [Table 6]). The correlations between any of these components and clay were actually non-significant, with the exception of P (which was itself not correlated with C, N or S). One way of interpreting these findings would be to assume that most C, N and S are still present in organic matter which has been minimally decomposed and reworked. Minimal decomposition has liberated P from the organic material (P usually being the limiting nutrient in freshwater lakes) but not completely decomposed the remaining organic material. Relatedly, plant roots are efficient at extracting dissolved phosphorus from sediment pore-waters.

It should also be noted that in most of the sediment grab samples, abundant living SAV was observed, as well as abundant root fibers and partially decomposed organic matter. Although intact plant material was excluded from the sediment sample, we presume that root fibers and peaty material have been included which have been partially decomposed.

Quality assurance and quality control (QA/QC) of C, N, S and P analysis can be found in

Appendix B. Briefly, four sediment SRMs were analyzed for C, N, S and P content, and the majority of the results were within $\pm 5\%$ of the true value, indicating high accuracy of measurements.

Table 6. Correlation matrix for textural, nutrient and target metal data based on all of the sediment samples collected at Herrington Lake. The correlations were determined using a Pearson product-moment technique (Johnson and Wichern, 1982). Values listed in the table are Pearson correlation coefficients (r). Shaded values are statistically significant at the 95% confidence level ($p < 0.05$).

| | % H ₂ O | GRAVEL | SAND | % SILT | CLAY | %N | %C | %S | %P | As | Cd | Cr | Cu | Mn | Ni | Pb | Zn | %Al | %Ca | %Fe | %K | %Mg | %Na |
|-------------------|--------------------|--------|-------|--------|-------|-------------|-------------|-------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------------|-------|-------|-------------|-------------|-------------|
| %H ₂ O | | -0.67 | -0.56 | 0.54 | 0.50 | 0.69 | 0.68 | 0.69 | 0.53 | 0.20 | 0.69 | -0.38 | -0.08 | 0.18 | -0.03 | 0.15 | 0.18 | -0.45 | 0.70 | -0.27 | -0.51 | -0.57 | -0.26 |
| %GRAVEL | -0.67 | | 0.70 | -0.73 | -0.69 | -0.28 | -0.27 | -0.28 | -0.57 | -0.13 | -0.57 | -0.05 | 0.08 | 0.13 | -0.19 | -0.20 | -0.32 | -0.05 | -0.26 | 0.27 | 0.08 | 0.26 | -0.25 |
| %SAND | -0.56 | 0.70 | | -0.86 | -0.87 | -0.30 | -0.25 | -0.27 | -0.73 | -0.52 | -0.61 | -0.11 | -0.33 | -0.16 | -0.47 | -0.43 | -0.46 | -0.16 | -0.18 | -0.16 | -0.10 | -0.02 | -0.22 |
| %SILT | 0.54 | -0.73 | -0.56 | | 0.22 | 0.24 | 0.26 | 0.34 | 0.16 | -0.14 | 0.65 | 0.00 | -0.24 | -0.27 | 0.13 | -0.19 | 0.10 | -0.16 | 0.03 | -0.34 | -0.18 | -0.39 | 0.25 |
| %CLAY | 0.50 | -0.69 | -0.87 | 0.22 | | 0.25 | 0.19 | 0.16 | 0.85 | 0.61 | 0.40 | 0.12 | 0.39 | 0.23 | 0.42 | 0.61 | 0.50 | 0.27 | 0.29 | 0.20 | 0.16 | 0.13 | 0.16 |
| %N | 0.69 | -0.28 | -0.30 | 0.24 | 0.25 | | 1.00 | 0.96 | 0.13 | 0.04 | 0.40 | -0.80 | -0.37 | 0.04 | -0.59 | 0.04 | -0.34 | -0.85 | 0.79 | -0.48 | -0.85 | -0.76 | -0.75 |
| %C | 0.68 | -0.27 | -0.25 | 0.26 | 0.19 | 1.00 | | 0.97 | 0.07 | -0.04 | 0.39 | -0.81 | -0.43 | -0.02 | -0.63 | -0.02 | -0.39 | -0.88 | 0.78 | -0.54 | -0.87 | -0.79 | -0.75 |
| %S | 0.69 | -0.28 | -0.27 | 0.34 | 0.16 | 0.96 | 0.97 | | 0.04 | -0.12 | 0.51 | -0.80 | -0.46 | -0.16 | -0.61 | -0.06 | -0.35 | -0.87 | 0.71 | -0.59 | -0.87 | -0.83 | -0.66 |
| %P | 0.53 | -0.57 | -0.73 | 0.16 | 0.85 | 0.13 | 0.07 | 0.04 | | 0.68 | 0.41 | 0.25 | 0.52 | 0.49 | 0.50 | 0.50 | 0.63 | 0.34 | 0.28 | 0.39 | 0.20 | 0.21 | 0.14 |
| As | 0.20 | -0.13 | -0.52 | -0.14 | 0.61 | 0.04 | -0.04 | -0.12 | 0.68 | | 0.25 | 0.13 | 0.56 | 0.73 | 0.45 | 0.73 | 0.65 | 0.31 | 0.12 | 0.72 | 0.20 | 0.32 | -0.09 |
| Cd | 0.69 | -0.57 | -0.61 | 0.65 | 0.40 | 0.40 | 0.39 | 0.51 | 0.41 | 0.25 | | -0.18 | -0.01 | -0.10 | 0.07 | 0.22 | 0.51 | -0.22 | 0.31 | -0.12 | -0.37 | -0.51 | -0.06 |
| Cr | -0.38 | -0.05 | -0.11 | 0.00 | 0.12 | -0.80 | -0.81 | -0.80 | 0.25 | 0.13 | -0.18 | | 0.71 | 0.09 | 0.74 | -0.14 | 0.45 | 0.87 | -0.44 | 0.61 | 0.87 | 0.79 | 0.74 |
| Cu | -0.08 | 0.08 | -0.33 | -0.24 | 0.39 | -0.37 | -0.43 | -0.46 | 0.52 | 0.56 | -0.01 | 0.71 | | 0.48 | 0.68 | 0.17 | 0.55 | 0.60 | 0.01 | 0.82 | 0.59 | 0.66 | 0.29 |
| Mn | 0.18 | 0.13 | -0.16 | -0.27 | 0.23 | 0.04 | -0.02 | -0.16 | 0.49 | 0.73 | -0.10 | 0.09 | 0.48 | | 0.36 | 0.36 | 0.35 | 0.14 | 0.19 | 0.70 | 0.14 | 0.31 | -0.27 |
| Ni | -0.03 | -0.19 | -0.47 | 0.13 | 0.42 | -0.59 | -0.63 | -0.61 | 0.50 | 0.45 | 0.07 | 0.74 | 0.68 | 0.36 | | 0.28 | 0.64 | 0.80 | -0.41 | 0.65 | 0.82 | 0.71 | 0.75 |
| Pb | 0.15 | -0.20 | -0.43 | -0.19 | 0.61 | 0.04 | -0.02 | -0.06 | 0.50 | 0.73 | 0.22 | -0.14 | 0.17 | 0.36 | 0.28 | | 0.61 | 0.25 | -0.11 | 0.30 | 0.09 | 0.11 | 0.01 |
| Zn | 0.18 | -0.32 | -0.46 | 0.10 | 0.50 | -0.34 | -0.39 | -0.35 | 0.63 | 0.65 | 0.51 | 0.45 | 0.55 | 0.35 | 0.64 | 0.61 | | 0.57 | -0.20 | 0.58 | 0.38 | 0.28 | 0.35 |
| %Al | -0.45 | -0.05 | -0.16 | -0.16 | 0.27 | -0.85 | -0.88 | -0.87 | 0.34 | 0.31 | -0.22 | 0.87 | 0.60 | 0.14 | 0.80 | 0.25 | 0.57 | | -0.61 | 0.64 | 0.95 | 0.87 | 0.80 |
| %Ca | 0.70 | -0.26 | -0.18 | 0.03 | 0.29 | 0.79 | 0.78 | 0.71 | 0.28 | 0.12 | 0.31 | -0.44 | 0.01 | 0.19 | -0.41 | -0.11 | -0.20 | -0.61 | | -0.21 | -0.63 | -0.50 | -0.66 |
| %Fe | -0.27 | 0.27 | -0.16 | -0.34 | 0.20 | -0.48 | -0.54 | -0.59 | 0.39 | 0.72 | -0.12 | 0.61 | 0.82 | 0.70 | 0.65 | 0.30 | 0.58 | 0.64 | -0.21 | | 0.61 | 0.73 | 0.20 |
| %K | -0.51 | 0.08 | -0.10 | -0.18 | 0.16 | -0.85 | -0.87 | -0.87 | 0.20 | 0.20 | -0.37 | 0.87 | 0.59 | 0.14 | 0.82 | 0.09 | 0.38 | 0.95 | -0.63 | 0.61 | | 0.94 | 0.81 |
| %Mg | -0.57 | 0.26 | -0.02 | -0.39 | 0.13 | -0.76 | -0.79 | -0.83 | 0.21 | 0.32 | -0.51 | 0.79 | 0.66 | 0.31 | 0.71 | 0.11 | 0.28 | 0.87 | -0.50 | 0.73 | 0.94 | | 0.59 |
| %Na | -0.26 | -0.25 | -0.22 | 0.25 | 0.16 | -0.75 | -0.75 | -0.66 | 0.14 | -0.09 | -0.06 | 0.74 | 0.29 | -0.27 | 0.75 | 0.01 | 0.35 | 0.80 | -0.66 | 0.20 | 0.81 | 0.59 | |

Elemental Analysis

Laboratory results are located in Appendix C.

Table 7 lists summary statistics for those metals having specified threshold limits listed in National Oceanic and Atmospheric Administration (NOAA) Screening Quick Reference Tables (SQiRTs) (Buchman, 2008). Most elements listed in Table 7 are above background levels for freshwater sediments; including all 15 samples for As, Cd, Cr, Fe, most for Mn, Ni, Pb and Zn, and only one for Cu. Because the Herrington Lake samples were analyzed using a near total decomposition method (four-acid digestion), caution is warranted when comparing the resulting concentration values for some metals to the screening limits given in the NOAA tables. The values listed in the NOAA tables are based on Environmental Protection Agency (EPA) sample digestion methods which utilize partial decomposition of sediment samples and thus reflect that portion of any element that may become biologically available/mobile under environmental conditions. For example, the NOAA tables list background levels in soil/sediments for Al as 0.26% which reflects the average Al which is biologically available. However, Act Labs' results for Al range from 2.8% to 7.28% (6.36 to 7.28% when omitting sample 9, which had lower Al concentration than the other 14 samples), reflecting total recovery of the element by the stronger digestion method used. Al is a major component of most minerals found in native rock and soils. The Al in most minerals is not liberated by conventional digestion but is liberated when using the more vigorous digestion. Likewise, average concentrations of Fe and Mn are greater than NOAA background levels for the same reasons given for Al. Caution is therefore warranted in making direct comparisons.

Table 7. Summary statistics of select metal concentration measured in Herrington Lake sediments. All values are ppm unless otherwise indicated. For comparison, benchmark levels for freshwater sediments are included along with the number of lake samples exceeding the respective limit values. These benchmarks for freshwater sediments are based upon chronic, long-term impacts of contamination to benthic organisms (Buchman, 2008). The Lowest Effect Level (LEL) is a level of sediment contamination that can be tolerated by the majority of benthic organisms. The Severe Effect Level (SEL) is that at which pronounced disturbance of the sediment-dwelling community can be expected. This is the concentration that would be detrimental to the majority of the benthic community.

| | As | Cd | Cr | Cu | Fe (%) | Mn | Ni | Pb | Zn |
|---|------|-----|-----|-----|--------|------|-----|-----|-----|
| Average | 13.2 | 1.9 | 82 | 22 | 4.76 | 730 | 52 | 35 | 262 |
| Std. Dev. | 3.7 | 0.6 | 17 | 5 | 1.07 | 388 | 12 | 5 | 63 |
| min | 8.8 | 0.5 | 30 | 13 | 2.76 | 314 | 23 | 28 | 149 |
| max | 21.0 | 2.8 | 106 | 38 | 6.84 | 1390 | 68 | 46 | 373 |
| Background ¹ | | | | | | | | | |
| Background ¹ | 1.1 | 0.3 | 13 | 25 | 1.8 | 400 | 9.9 | 17 | 35 |
| LEL | 6 | 0.6 | 26 | 16 | 2 | 460 | 16 | 31 | 120 |
| SEL | 33 | 10 | 110 | 110 | 4 | 1100 | 75 | 250 | 820 |
| #>Background | | | | | | | | | |
| #>Background | 15 | 15 | 15 | 1 | 15 | 11 | 15 | 15 | 15 |
| #>LEL | | | | | | | | | |
| #>LEL | 15 | 14 | 15 | 13 | 15 | 10 | 15 | 11 | 15 |
| #>SEL | | | | | | | | | |
| #>SEL | 0 | 0 | 0 | 0 | 11 | 4 | 0 | 0 | 0 |
| ¹ Background as provided in NOAA SQuiRTs for freshwater sediments (Buchman, 2008). | | | | | | | | | |

The two screening levels considered here were the freshwater sediment Lowest Effect Level (LEL) and Severe Effect Level (SEL). The freshwater sediment LEL is a level of sediment concentration that can be tolerated by the majority of benthic organisms. The SEL is the concentration that would be detrimental to the majority of the benthic community. Derivations of these screening limits are explained in the reference, but briefly: a survey of at least 20 aquatic species presence is performed, and the LEL corresponds to 5th percentile concentrations and the SEL corresponds to the 95% percentile of concentrations where a benthic community is observed to exist.

While most metals of concern (As, Cd, Cr, Cu, Ni, Pb and Zn) are above more conservative LEL in most sediments (Table 7), only Fe and Mn exceed the higher SEL value. The average Fe content of the Herrington sediments was 4.76%, and 11 of the sediment samples were above the SEL of 4%. The average Mn content of the Herrington sediments was 730 ppm, and four of the sediment samples were above the SEL of 1100 ppm. However, as stated above, these elemental concentrations were generated with a more vigorous total digestion than were the screening concentrations in the SQuiRTs tables, and represent a concentration greater than that which would be environmentally available through mineral decomposition in natural settings. Therefore, no ecotoxicological harm is anticipated.

As was shown in Table 6, some of the “major” rock-forming elements show very strong correlations with each other (e.g. K and Al with a r^2 of 0.95, K and Mg with a r^2 of 0.94), and Fe and Na were also well correlated to Al. Many of the “trace” metals are also well correlated to the major elements. To examine some of the associations more closely, plots of the elemental concentrations by station number are provided as Figures 5 and 6. Concentrations are shown in milli-moles per kilogram (mmol/kg, where a milli-mole is Avogadro’s number divided by 1000).

The profiles of major rock forming elements Al, Fe, K, Na, Mg and Ca are shown in Figure 5, as well as percent clay in the middle plot. Al was the most abundant major element, followed in descending order by Fe, K, Mg, Na and lastly Ca. The first five (Fe, K, Mg and Na) of these elements show similar profiles by station number, with relatively higher concentrations found at stations #2, 3, 5, 7, 10, 11 and 15. The similarity in profile implies either a common source (from shale weathering) or a common process which redistributes and deposits these elements together. These stations with relatively higher concentrations of major elements frequently corresponded to stations where the clay content approached or exceeded 50% (middle plot of Figure 5) or rather, where the sediment was classified as a silty-clay (Figure 4). In exception to the trend of clay association, the five major elements all show a marked decrease at station #9, despite a clay content of 48% at this station. As has been previously discussed, the sediment collected at this station was anomalously high in C, N and S due to the abundance of organic and peaty material. Also in exception was the major element Ca, which showed a slight spatial correlation with clay content, but had a disproportionately high concentration at station #9. Ca is an essential, secondary plant nutrient, present in cell walls.

Several of the trace metals showed a generally similar profile to the major elements (Figure 6). The most abundant trace metal was Mn, followed in decreasing order by Zn, Cr, Ni, Cu, Pb and As. Zn, Cr and Ni followed the clay association trend of having high concentrations at stations #3, 5, 7, 10, 14 and 15 where there was also comparatively higher clay content (at or above 50%, most being silty-clays). Cu and Pb showed general similarity as well, but with more muted profiles. In exception were Mn and As, which followed the clay influence trend of having high concentrations at stations #3, 5, 7, 10 and 15 but with amplified profiles where the increase in metals was disproportionate with an increase in clay content. For example, the change in clay content between stations #4 and #5 was an increase from 30% to 53%: a 76% increase. For Zn, the change in concentrations between stations #4 and 5 was an increase from 0.68 mmol/kg to 1.04 mmol/kg: a 52% increase. But the change in Mn content between stations #4 and 5 was an increase from 10 mmol/kg to 23.5 mmol/kg: a 135% increase. A proportionate, or slightly less than proportionate increase between clay and metal is intuitive, but a greater than proportionate increase is less so. It may be that trace metals such as Mn and As have a greater affinity for the sorptive surface of the clay minerals found in the Herrington sediments.

From these observations, some preliminary interpretations are offered. It is hypothesized that the major rock forming elements (here Al, Fe, K, Mg and Na) share a common source, and that source is likely to be weathered shales, mudstones, coal and to a lesser extent sandstones and limestones encountered in the local country rock. Several of the trace metals (here Cr, Cu, Ni, Pb and Zn) also followed a similar pattern. Local country rock has been mapped and described as the Conemaugh group, with two halves; the Casselman and Glenshaw formations. The Conemaugh group is comprised of: interbedded, light gray, micaceous sandstone, gray silty shale and thin, dark gray, marine shales in the lower half of the group and greenish-gray and reddish brown to variegated mudstone, shale, claystone, and nodular non-marine limestone in its upper part (Brezinski and Conkwright, 2013). Some coal beds have also been reported within the lower Glenshaw Formation. The clay mineralogy of these sedimentary units is variable since the units themselves contain cycles of sedimentary rocks. There are numerous flint clay deposits (i.e. high kaolinite) as well as fire clay deposits (high Al refractory kaolinite and illite) in the Conemaugh (Brezinski and Kollar 2011, Cecil et al 1985). There is also presumed illite, chlorite and smectite

in the shale units, as well as muscovite in the sandstones. The lower portion of the Conemaugh group contains marine shales where it is presumed some Na-rich clays exist. The mineralogical composition of kaolinite is $\text{Al}_2\text{Si}_2\text{O}_5$, illite is $(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$, muscovite is $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$, chlorite is $(\text{Mg},\text{Fe})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$ and smectite is variable in composition, but montmorillonite is provided as example smectite: $(\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2(n\text{H}_2\text{O})$.

These shale and mudstone minerals would therefore be reasonably inferred sources of Al, Fe, K, Mg and Na. The trace metals Cr, Cu, Pb and Zn may be absorbed to these mica and clay minerals, and Ni may be either absorbed or incorporated in chlorite. The trace metals Cu, Ni, Pb and Zn are likely to exist as positively charged ions at circum-neutral pH and transitional redox (declining dissolved oxygen) environment, and to adhere to negatively charged clay particle surfaces. Lastly, the by-station profiles for As and Mn were similar to each other and both differed slightly from the other trace metals in the amplified response. As is often found associated with S in sediments, however it was not in this case, and was instead more associated with Fe, clay and other trace metals. As is often found associated with Fe in soils. In circum-neutral and transitional to reducing sedimentary environments, dissolved As^{3+} may exist as an oxyanion with negative charge (H_2AsO_3^-) or as an uncharged species. In a neutral and transitional to reducing sedimentary environment, Mn is expected to be predominantly found as a divalent cation (Mn^{2+}) as are most of the trace metals. It may be that the distribution of As and Mn is slightly different from other metals if they have a different sorptive affinity for clays.

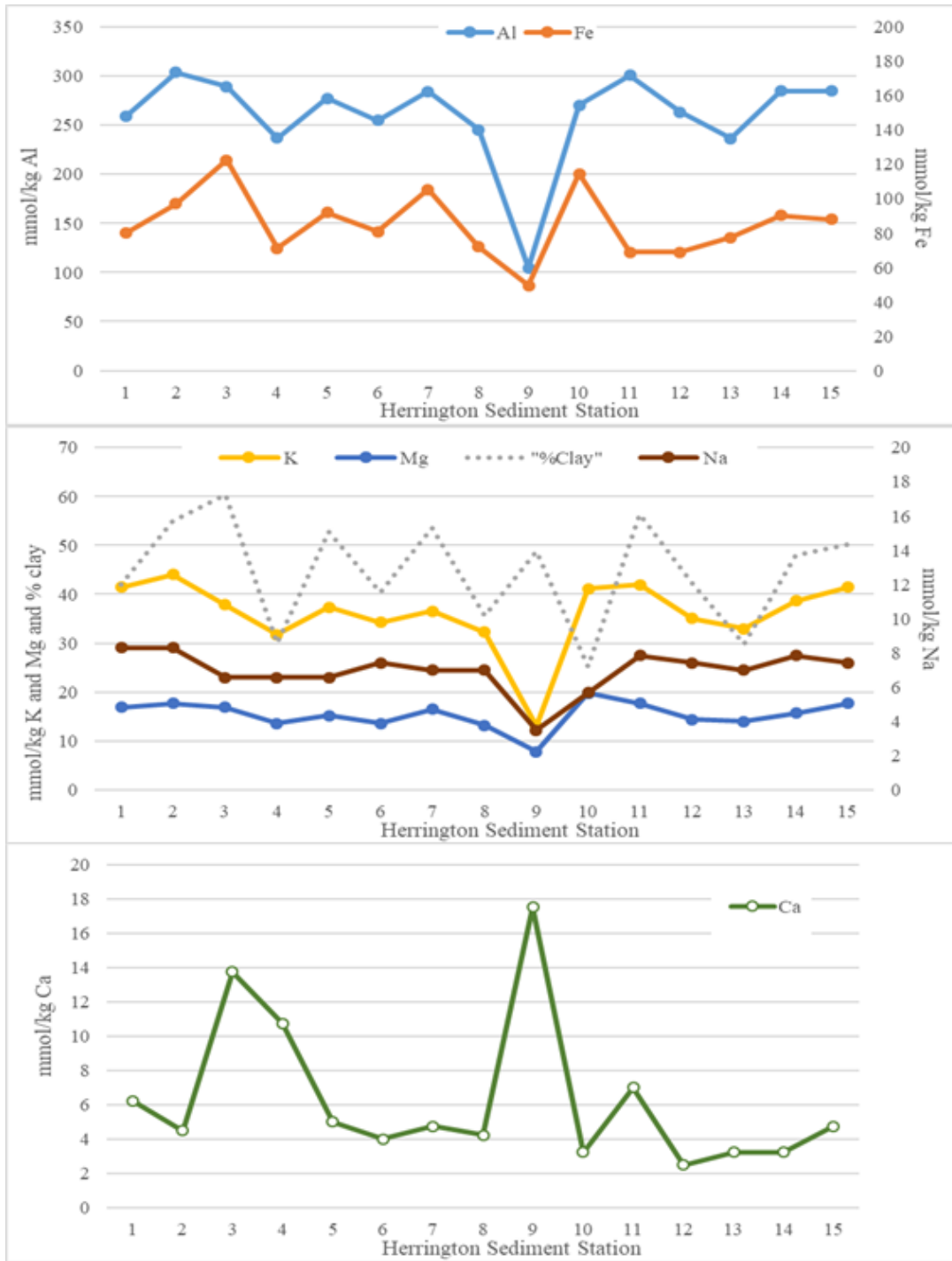
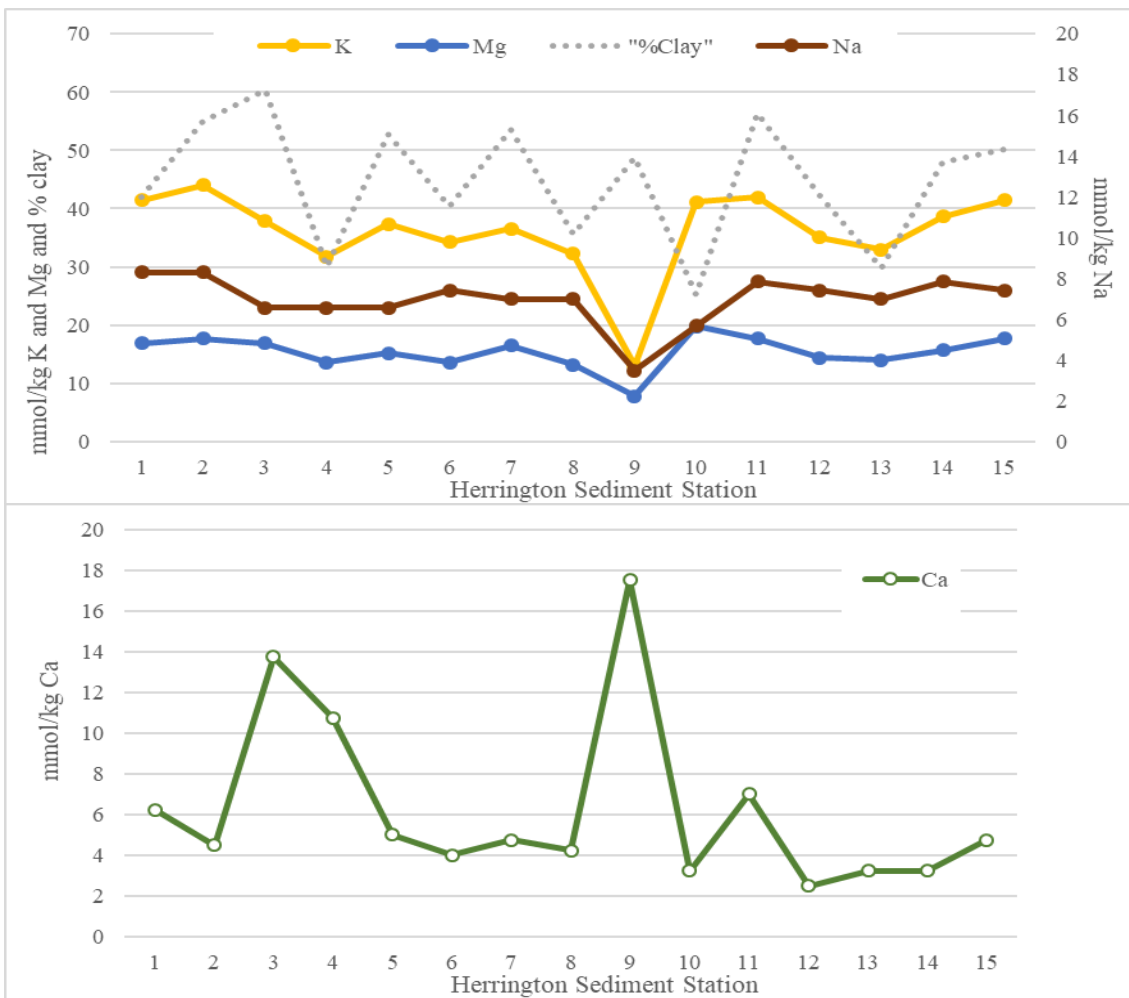


Figure 5. Concentration profile plots of several major elements by Herrington Lake station number, shown with clay content.

Concentrations are in percent for clay, and in milli-moles per kilogram for the elements shown.



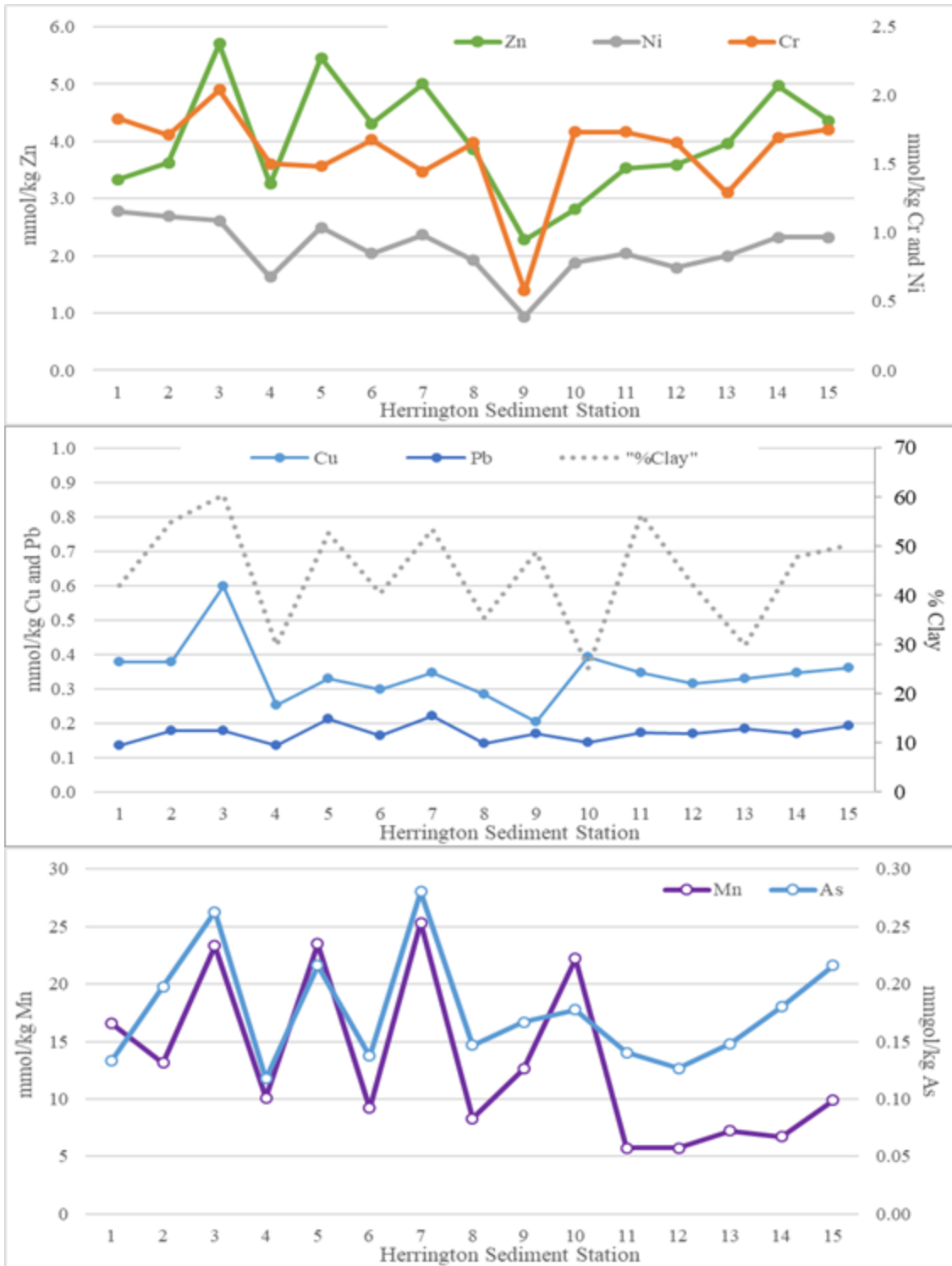


Figure 6. Concentration profile plots of several trace elements by Herrington Lake station number. Concentrations are in millimoles per kilogram for the elements shown.

Enrichment Factors

Because of the wide range of sediment types analyzed, comparisons of absolute metal concentrations between the surficial sediments are difficult. Therefore, metal concentrations are discussed in terms of enrichment factors (EF). The enrichment factor approach normalizes a concentration of an element, or a ratio of concentrations of elements in the sediment, to those found in a standardized material like average crustal rock. The use of enrichment factors also allows for comparisons of sediments from different environments and the comparisons of sediments whose trace metal contents were obtained by different analytical techniques (Cantillo, 1982; Hill *et al.*, 1990; Sinex and Helz, 1981). However, the use of enrichment factors to assess metal data does not entirely eliminate the influence of textural variation.

Enrichment factor is defined as:

$$EF_{(x)} = X/Fe_{(sample)} / X/Fe_{(reference)}$$

Equation 3

where: $EF_{(x)}$ is the enrichment factor for the metal X;

$X/Fe_{(reference)}$ is the ratio of the concentrations of metal X to Fe in a reference material, such as an average continental crust rock.

Fe is chosen as the element for normalizing because anthropogenic sources for Fe are small compared to natural sources (Helz, 1976). Taylor's (1964) average continental crust is used as the reference material. Average crustal abundance data may not be representative of Herrington Lake sediments because there is a higher proportion of clay and silt in the sediments compared to the average crustal rock. However, abundance data is useful as a relative indicator when comparing the data with other studies.

The average EF values for most metals are within the range of values obtained for other freshwater lakes and reservoirs in Maryland (Table 8). The sediments in Herrington Lake are significantly enriched (*i.e.*, $EF > 3$) in As, Cd, hafnium (Hf), Pb, antimony (Sb) and Zn with respect to average continental crust rock. Herrington Lake falls within the Appalachian Plateau Physiographic Province of Maryland where bedrock is gently folded and faulted sedimentary rock and comprised of shale, limestone and sandstone bedrock. The regional formations around Herrington Lake are mapped as the Conemaugh Group, which is comprised of; interbedded, light gray, micaceous sandstone, gray silty shale and thin, dark gray, marine shales in the lower half of the group and greenish-gray and reddish brown to variegated mudstone, shale, claystone, and nodular non-marine limestone in its upper half. The enrichment factors at Herrington Lake may be most comparable to those at Deep Creek Lake and because both of these lakes lie within the Appalachian Plateau and their environments are similar. The EF values are similar to those reported for Deep Creek Lake, and since they are in similar sedimentary bedrocks, it can be expected that these lakes will be similar in geochemistry. The enrichment factor values for As, Cd, Hf, Pb, Sb and Zn are all near or above and EF of 3 for the both lakes. The highest EF values for As, Cd and Pb were located at station #9, which did not have particularly high raw concentrations (mg/kg) of these elements, but when expressed as a ratio over Fe were more marked. But local maxima for the other high EF elements Hf, Sb and Zn were each distributed differently throughout the lake, without a general pattern. This may be due to several factors. There may be more than one source of the elements. The elements may have different

geochemical behaviors during and after deposition in the lake.

These elements are enriched relative to crustal abundance, but when compared relative to the ranges for argillaceous (clay-rich) sedimentary rocks (Kabata-Pendias, 2011), the average concentrations of As, Pb and Sb were within range. The average concentration of Hf was just above range, although higher concentrations were reported in sandstones rich in zircon. The average concentration of Cd was approximately 10 times higher than the high concentration of the range. The average concentration of Zn was approximately 3 times higher than the high concentration of the range.

In summary, the sediments at Herrington Lake contained concentrations of As, Cd, Hf, Pb, Sb and Zn with enrichment values above 3, when compared to crustal abundance. However, these EFs were similar to Deep Creek Lake and other western Maryland Lakes, and the un-normalized concentrations were mostly typical of the ranges encountered in shales and other clay-rich rocks.

Table 8. Comparisons of average enrichment factors in several Maryland freshwater reservoirs/lakes. Enrichment factors are relative to the average earth's crust (Taylor, 1964.)

| Element | Loch Raven | Triadelphia Reservoir | Rocky Gorge Reservoir | New Germany Lake | Deep Creek Lake | Blairs Valley Lake | St. Mary's Lake | Herrington Lake |
|---------|-----------------------------|----------------------------|------------------------------|-----------------------------|------------------------------|--------------------------------|--------------------------------|-----------------|
| | (Ortt <i>et al.</i> , 1999) | (Wells <i>et al.</i> 2007) | (Wells <i>et al.</i> , 2007) | (Ortt <i>et al.</i> , 2009) | (Wells <i>et al.</i> , 2011) | (Sylvia, <i>et al.</i> , 2020) | (Sylvia, <i>et al.</i> , 2020) | (this study) |
| Cd | 0.28 | 4.93 | 1.89 | 0.9 | 8.9 | 2.47 | | 11.81 |
| Cr | 1.62 | | 0.93 | 1.05 | 1.19 | 0.96 | 1.61 | 0.99 |
| Cu | 0.85 | 0.83 | 0.95 | 0.52 | 0.62 | 0.93 | 0.61 | 0.47 |
| Mn | 1.25 | 1.09 | 1.45 | 0.5 | 0.94 | 0.72 | 0.7 | 0.89 |
| Ni | 0.86 | 0.8 | 0.77 | 0.69 | 0.91 | 0.8 | 0.65 | 0.83 |
| Pb | 4.35 | 4.26 | 3.83 | 3.46 | 5.24 | 4 | 5.94 | 3.49 |
| Zn | 2.87 | 1.98 | 1.92 | 2.62 | 4.09 | 2.49 | 2.51 | 4.49 |
| Al | | 0.78 | 1.27 | 1.24 | 0.94 | 1.07 | 1.52 | 1.02 |
| As | | | 3.61 | 9.13 | 15.61 | 10.2 | 8.98 | 8.79 |
| Ce | | | 2.41 | 1.88 | 2.21 | 2.19 | 0 | 1.77 |
| Co | | 1.74 | 1.17 | 0.87 | 2.13 | 1.44 | 1.31 | 1.88 |
| Cs | | | 1.87 | 2.99 | 3.54 | 3.14 | 3.96 | 2.44 |
| Eu | | | 2.56 | 1.83 | 2.16 | 1.62 | 3.23 | 1.21 |
| Hf | | | 3.79 | 6.77 | 7.48 | 4.26 | | 3.65 |
| Sb | | | 3.19 | 10.64 | 24.41 | 5.65 | 11.27 | 5.26 |
| Th | | 0.08 | 1.64 | 1.91 | 1.78 | 1.68 | 3.22 | 1.37 |
| Ti | | | 1.21 | 0.94 | 1.05 | 0.69 | 1.44 | 0.81 |
| U | | | 1.64 | 3.1 | 2.32 | 2.46 | 4.01 | 1.76 |
| V | | 1.09 | 1 | 0.78 | 0.85 | 0.71 | 0.67 | 0.71 |
| Y | | 2.25 | 2.29 | 1.48 | 1.39 | 1.42 | 3.36 | 1.14 |

Summary and Conclusions

In September 2019, 15 surficial sediment samples were collected from Herrington Lake and based on the textural analyses of the samples, the majority of the samples collected are fine-grained sediments, with an average textural content of 10% sand, 42% silt and 45% clay. This area in western Maryland, where the Herrington Lake watershed lies, consists of sedimentary rock, namely shales, siltstones and sandstones. Clay minerals are abundant in the lake since shale is a common parent rock. Shales are lithified mud deposits, composed of silt sized particles (mainly quartz) and clay minerals which are the end product of weathering of other minerals.

Ignoring an outlier, total C contents measured in Herrington Lake sediments ranged from 1.3% to 6.1% (dry weight), with a mean of 5.1%, total N measured in the Lake's sediment averaged 0.38%, with values ranging from 0.1% to 0.6%, total S measured in the sediments averaged 0.10% and ranged from 0.03% to 0.15% and total P measured in the sediments average 0.07%, with values ranging from 0.05% to 0.11%. C, N and S concentrations were highly inter-correlated at Herrington Lake, which is hypothesized to be due to the abundant fresh organic material in the sediments. Concentrations of C, N, S and P were similar to that found in comparable nearby lakes, including Deep Creek Lake and New Germany Lake.

The elemental concentrations of 15 surficial sediments followed similar spatial patterns to each other when plotted by station, to correlate generally with clay content. This was true for Al, Fe, K, Na, Mg, although Ca was slightly different. Many trace elements also had profiles which were generally similar to each other. These include Zn, Cr and Ni, Cu and Pb in a muted way, and As and Cr in an amplified way. When compared relative to two eco-toxicological screening levels for freshwater sediments, all metals of concern were above the more conservative LEL and Fe and Mn were above the higher SEL in some samples. Since these concentrations represent more than that which is environmentally available, eco-toxicological harm is not anticipated. When compared to relative crustal abundance via the use of Fe-normalized enrichment factors, the elements Cd, Hf, Pb, Sb and Zn were elevated. However, these elements are often encountered in high concentration in clay-rich sedimentary rocks and the sediments derived from them.

The 15 samples collected throughout Herrington Lake were similar to sediments of other lakes nearby, including Deep Creek Lake. No abnormalities were found in regard to physical or chemical properties of the bottom sediments of Herrington Lake.

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Appendix A

Field Descriptions, Sample Coordinates and Pictures

| Table A-1. Sample descriptions and coordinates, with approximate water depth. *Approx. depths were collected as a reference and were not recorded at all stations due to collection limitations. | | | | |
|--|-----------------------------------|---|--|---|
| Sample Number | Approx. Water Depth (ft.)* | Northing (NAD83 State Plane, meters) | Easting (NAD83 State Plane, meters) | Description |
| 1 | 1 | 188649 | 201269 | 5Y 4/1 soft smooth silty mud, oxidized roots, SAV ~6-8 inches |
| 2 | 1 | 188494 | 201189 | Mottled 10YR 5/4 and 5Y 4/1 firm silty mud, firmer with depth, SAV ~3-4 inches with extensive roots (sample taken in patch of water lilies), oxidized roots |
| 3 | 2 | 188361 | 201229 | 5Y 4/4 very soft smooth silty mud, similar to sample #1, SAV ~5-6 inches, extensive roots |
| 4 | 3 | 188231 | 201301 | Soft soupy watery mud over firmer gritty watery sand, some SAV, fine gassy and short ~2-3 inches |
| 5 | 1 | 188365 | 201323 | 5Y 4/1, soft smooth not gritty silty mud, firmer with depth, 10Y 5/4 oxidized roots, extensive roots, SAV ~2 inches |
| 6 | 3.5 | 188459 | 201290 | Mottled 5Y 4/1 with 10Y 5/4 oxidized roots, soft smooth not gritty slightly lumpy, firmer and drier with depth, SAV ~6 inches, plentiful roots |
| 7 | 2.5 | 188511 | 201382 | 5Y 4/1 with 10YR 5/4 oxidized roots, soft soupy watery silty mud, firmer with depth but deeper than samples 5 and 6, also deeper roots than samples 5 and 6; two types of SAV, one is shorter and bladed, and the other is longer |
| 8 | 4 | 188610 | 201345 | Smooth not gritty mottled, oxidized roots, slightly lumpy, not soupy like other samples, lots of roots, same Munsell for sediment/oxidized, SAV ~6-7 inches |
| 9 | Not recorded | 188626 | 201442 | 5Y 4/1 at surface, grades to 5Y 2/1 at depth, smooth not gritty slightly peaty and very organic at depth, lots of fine roots, little mottling/oxidation, SAV ~4-5 inches |
| 10 | 1 | 188741 | 201502 | 5Y 4/1, soft watery soupy mud (2-3 cm) over firm gritty sandy gravel mud below root material, some fine roots, less dense than previous samples, SAV 1-2 inches, bladed and fine grass |
| 11 | 6.5 | 188810 | 201604 | 5Y 4/1 very smooth fine slightly lumpy clayey mud, very few very fine roots, SAV, very fine grass |
| 12 | 8 | 188871 | 201642 | 5Y 4/1 lumpy, drier, silty mud, firmer with depth, no SAV, no roots |
| 13 | 5.5 | 188910 | 201549 | 5Y 4/1 thin medium sand over very soft soupy smooth silty mud, SAV – bladed grass 4-5 inches, some roots, not as much as previous samples |
| 14 | 5.5 | 188840 | 201490 | 5Y 4/1 soft smooth slightly lumpy not gritty silty mud, very few very fine roots, no mottling/oxidization, lots of fine dill-like SAV |
| 15 | 3.5 | 188781 | 201386 | 5Y 5/2 with 10YR 5/4 mottling, fine roots, slightly grayer than other samples, oxidized root casts, slightly firm not gritty silty mud, firmer with depth, slightly lumpy, SAV – bladed ~4 inch, roots at surface, fewer at depth |

Sample 1



Sample 2



Sample 3



Sample 4



Sample 5



Sample 6



Sample 7



Sample 8



Sample 9



Sample 10



Sample 11



Sample 12



Sample 13



Sample 14



Sample 15



Appendix B

QA/QC

Textural Analyses

Although the techniques used to determine grain size are based on traditional analytical methods developed for the sedimentology laboratory, some analytical error is inherent to the techniques. For example, results can be affected by level of technician skill and/or changes in laboratory conditions (such as sudden temperature changes). Furthermore, there is no standard reference material available that includes the broad range of particle sizes and shapes contained in natural sediment. To maximize consistency of textural analysis, several “checks” are used to monitor results. The calculated sand, silt, clay and gravel (when present) percentages are checked against 1) sample field descriptions; 2) calculated water contents; and 3) calculated weight loss of sample during processing. These comparisons are made to determine if the size components match the visual description of the sample and/or fall within an expected classification with respect to water content and weight loss. Any discrepancy is “flagged” and the results are reviewed further to determine if re-analysis is warranted.

Carbon, Nitrogen and Sulfur Analyses

Table B-1. Results of nitrogen, carbon and sulfur analyses of the standard reference materials (SRMs) compared to the certified or known values. MGS values were obtained by averaging the results of all SRM analyses run during this study.

| Element | NIST SRM 8704 | | | NIST SRM 1646a | | | NIST SRM 2702 | | | Canadian SRM MESS 4 | | |
|-------------------------------|--------------------------|-----------------|------------|--------------------------|-----------------|------------|-------------------------------|-----------------|------------|--------------------------|--------------|------------|
| | Buffalo River Sediment | | | Estuarine Sediment | | | Inorganics in Marine Sediment | | | Marine Sediment | | |
| | NIST Values ¹ | MGS Results | % Recovery | NIST Values ² | MGS Results | % Recovery | NIST Values ³ | MGS Results | % Recovery | NIST Values ⁴ | MGS Results | % Recovery |
| Total Nitrogen (% dry weight) | 0.188 | 0.179 ±0.006 | 95.3 | 0.058 | 0.056 ±0.004 | 96.4 | 0.25 | 0.253 ±0.007 | 101.1 | 0.142 | 0.138 ±0.010 | 96.8 |
| Carbon (% dry weight) | 3.351 ±0.017 | 3.235 ±0.054 | 96.6 | 0.583 | 0.563 ±0.017 | 95.9 | 3.36 | 3.167 ±0.091 | 94.2 | 1.79 | 1.780 ±0.103 | 99.5 |
| Sulfur (% dry weight) | 0.261 | 0.206 ±0.060 | 78.91 | 0.352 ±0.004 | 0.347 ±0.017 | 98.6 | 1.5 | 1.577 ±0.069 | 105.12 | 0.158 ±0.020 | 0.169 ±0.019 | 106.2 |

¹ For NIST 8704, the value for carbon is certified by NIST. The value of nitrogen and sulfur was obtained from repeated analyses in-house and by other laboratories (Haake Buchler Labs and U.S. Dept. of Agriculture).

² For NIST SRMs 1646a, the value for sulfur are certified values reported by NIST; nitrogen and carbon values were obtained from repeated analyses in-house and by Act Labs.

³ For NIST SRM 2702, the value for sulfur are information values reported by NIST; nitrogen and carbon values were obtained from repeated analyses in-house and by Act Labs.

⁴ For Canadian SRM, the value for sulfur is certified from the National Research Council Canada (NRCC). The value for carbon is an information value reported by the NRCC. The value for nitrogen was obtained from repeated analyses in-house.

Appendix C

Elemental Analysis Results and QA/QC

Table C-1. Elements (analytes) reported in this study include 50 elements analyzed by Act Labs. Methods abbreviations: High Temp. Combustion-GC: High Temperature combustion, following by Gas Chromatography; TD-ICP: Total Digestion followed by Inductively Coupled Plasma Spectrometry; INAA: Instrumental Neutron Activation Analysis.

| Element | Symbol | Reporting Unit | Detection Limit | Analysis Method | Element | Symbol | Reporting Unit | Detection Limit | Analysis Method |
|-----------|--------|----------------|-----------------|-----------------|------------|--------|----------------|-----------------|-----------------|
| Aluminum | Al | % | 0.01 | TD-ICP | Mercury | Hg | ppm | 1 | INAA |
| Antimony | Sb | ppm | 0.1 | INAA | Molybdenum | Mo | ppm | 1 | TD-ICP |
| Arsenic | As | ppm | 0.5 | INAA | Neodymium | Nd | ppm | 5 | INAA |
| Barium | Ba | ppm | 50 | INAA | Nickel | Ni | ppm | 1 | INAA / TD-ICP |
| Beryllium | Be | ppm | 1 | TD-ICP | Phosphorus | P | % | 0.001 | TD-ICP |
| Bismuth | Bi | ppm | 2 | TD-ICP | Potassium | K | % | 0.01 | TD-ICP |
| Bromine | Br | ppm | 0.5 | INAA | Rubidium | Rb | ppm | 15 | INAA |
| Cadmium | Cd | ppm | 0.3 | TD-ICP | Samarium | Sm | ppm | 0.1 | INAA |
| Calcium | Ca | % | 0.01 | TD-ICP | Scandium | Sc | ppm | 0.1 | INAA |
| Cerium | Ce | ppm | 3 | INAA | Selenium | Se | ppm | 3 | INAA |
| Cesium | Cs | ppm | 1 | INAA | Silver | Ag | ppm | 0.3 | INAA / TD-ICP |
| Chromium | Cr | ppm | 2 | INAA | Sodium | Na | % | 0.01 | INAA |
| Cobalt | Co | ppm | 1 | INAA | Strontium | Sr | ppm | 1 | TD-ICP |
| Copper | Cu | ppm | 1 | TD-ICP | Sulfur | S | % | 0.01 | TD-ICP |
| Europium | Eu | ppm | 0.2 | INAA | Tantalum | Ta | ppm | 0.5 | INAA |
| Gold | Au | ppb | 2 | INAA | Terbium | Tb | ppm | 0.5 | INAA |
| Hafnium | Hf | ppm | 1 | INAA | Thorium | Th | ppm | 0.2 | INAA |
| Iridium | Ir | ppb | 5 | INAA | Tin | Sn | % | 0.01 | INAA |
| Iron | Fe | % | 0.01 | INAA | Titanium | Ti | % | 0.01 | TD-ICP |
| Lanthanum | La | ppm | 0.5 | INAA | Tungsten | W | ppm | 1 | INAA |
| Lead | Pb | ppm | 3 | TD-ICP | Uranium | U | ppm | 0.5 | INAA |
| Lithium | Li | ppm | 1 | TD-ICP | Vanadium | V | ppm | 2 | TD-ICP |
| Lutetium | Lu | ppm | 0.05 | INAA | Ytterbium | Yb | ppm | 0.2 | INAA |
| Magnesium | Mg | % | 0.01 | TD-ICP | Yttrium | Y | ppm | 1 | TD-ICP |
| Manganese | Mn | ppm | 1 | TD-ICP | Zinc | Zn | ppm | 1 | INAA / TD-ICP |

Table C-2. Herrington Lake sediment elemental data. All values are ppm (mg/kg) unless indicated otherwise.

| Station | Ag | Al% | As | Au | Ba | Be | Bi | Br | Ca% | Cd | Ce | Co | Cr | Cs | Cu | Eu | Fe% |
|---------|------|------|------|----|-----|----|----|------|------|-----|-----|----|-----|----|----|-----|------|
| 1 | 0.4 | 6.96 | 10 | <2 | 570 | 4 | 3 | 15.6 | 0.25 | 1.7 | 99 | 29 | 95 | 6 | 24 | 1.5 | 4.47 |
| 2 | 0.3 | 8.18 | 14.8 | <2 | 520 | 5 | <2 | 9.2 | 0.18 | 1.6 | 106 | 32 | 89 | 8 | 24 | 1.5 | 5.43 |
| 3 | 0.3 | 7.79 | 19.7 | <2 | 630 | 5 | <2 | 22.3 | 0.55 | 2.5 | 94 | 64 | 106 | 8 | 38 | 1.3 | 6.84 |
| 4 | <0.3 | 6.37 | 8.8 | 3 | 510 | 3 | 2 | 14.9 | 0.43 | 1.6 | 87 | 37 | 78 | 4 | 16 | 1.3 | 3.97 |
| 5 | 0.3 | 7.47 | 16.2 | 3 | 330 | 5 | <2 | 15.7 | 0.2 | 2.1 | 88 | 63 | 77 | 4 | 21 | 1.4 | 5.13 |
| 6 | <0.3 | 6.86 | 10.3 | <2 | 570 | 4 | <2 | 12.2 | 0.16 | 2.2 | 93 | 43 | 87 | 6 | 19 | 1.3 | 4.52 |
| 7 | <0.3 | 7.65 | 21 | <2 | 580 | 4 | <2 | 19 | 0.19 | 1.9 | 92 | 56 | 75 | 7 | 22 | 1.3 | 5.89 |
| 8 | 0.5 | 6.6 | 11 | <2 | 540 | 4 | 3 | 11.1 | 0.17 | 2.4 | 96 | 37 | 86 | 7 | 18 | 1.4 | 4.02 |
| 9 | <0.3 | 2.81 | 12.5 | <2 | 450 | 2 | <2 | 25.6 | 0.7 | 2.4 | 35 | 18 | 30 | 3 | 13 | 0.6 | 2.76 |
| 10 | 0.3 | 7.27 | 13.3 | <2 | 290 | 3 | <2 | 7.8 | 0.13 | 0.5 | 88 | 34 | 90 | 4 | 25 | 1 | 6.4 |
| 11 | 0.6 | 8.1 | 10.5 | 9 | 610 | 4 | 3 | 11.3 | 0.28 | 1.4 | 91 | 31 | 90 | 7 | 22 | 1 | 3.85 |
| 12 | <0.3 | 7.09 | 9.5 | <2 | 600 | 4 | <2 | 8.8 | 0.1 | 1.3 | 88 | 34 | 86 | 6 | 20 | 0.7 | 3.85 |
| 13 | <0.3 | 6.36 | 11.1 | <2 | 410 | 4 | <2 | 9.2 | 0.13 | 1.9 | 79 | 37 | 67 | 5 | 21 | 1.1 | 4.32 |
| 14 | 0.4 | 7.66 | 13.5 | <2 | 240 | 5 | <2 | 14.1 | 0.13 | 2.8 | 98 | 44 | 88 | 7 | 22 | 1.4 | 5.04 |
| 15 | <0.3 | 7.67 | 16.2 | <2 | 520 | 4 | <2 | 11 | 0.19 | 1.9 | 89 | 39 | 91 | 9 | 23 | 1.3 | 4.91 |

Table C-2 (cont.) Herrington Lake sediment elemental data. All values are ppm (mg/kg) unless indicated otherwise.

| Station | Hf | Hg | Ir | %K | La | Li | Lu | Mg% | Mn | Mo | Nb% | Nd | Ni | Pb | Rb | Sb% |
|---------|----|----|----|------|------|----|------|------|------|----|------|----|----|----|-----|------|
| 1 | 11 | <1 | <5 | 1.62 | 45.6 | 55 | 0.47 | 0.41 | 909 | <1 | 0.19 | 34 | 68 | 28 | 127 | 0.09 |
| 2 | 7 | <1 | <5 | 1.72 | 48.7 | 70 | 0.48 | 0.43 | 721 | <1 | 0.19 | 51 | 66 | 37 | 123 | 0.06 |
| 3 | 6 | <1 | <5 | 1.48 | 45.4 | 65 | 0.4 | 0.41 | 1280 | <1 | 0.15 | 40 | 64 | 37 | 115 | 0.1 |
| 4 | 12 | <1 | <5 | 1.24 | 42 | 49 | 0.52 | 0.33 | 554 | <1 | 0.15 | 28 | 40 | 28 | 131 | 0.1 |
| 5 | 9 | <1 | <5 | 1.45 | 44.8 | 60 | 0.42 | 0.37 | 1290 | <1 | 0.15 | 45 | 61 | 44 | 109 | 0.08 |
| 6 | 11 | <1 | <5 | 1.34 | 45.1 | 54 | 0.53 | 0.33 | 505 | <1 | 0.17 | 42 | 50 | 34 | 138 | 0.09 |
| 7 | 7 | <1 | <5 | 1.43 | 42.2 | 60 | 0.44 | 0.4 | 1390 | <1 | 0.16 | 29 | 58 | 46 | 100 | 0.08 |
| 8 | 12 | <1 | <5 | 1.26 | 43.1 | 51 | 0.53 | 0.32 | 455 | <1 | 0.16 | 40 | 47 | 29 | 74 | 0.1 |
| 9 | 4 | <1 | <5 | 0.51 | 16.1 | 20 | 0.2 | 0.19 | 694 | <1 | 0.08 | 27 | 23 | 35 | <15 | 0.41 |
| 10 | 8 | <1 | <5 | 1.61 | 40.9 | 51 | 0.47 | 0.48 | 1220 | <1 | 0.13 | 45 | 45 | 30 | 162 | 0.02 |
| 11 | 8 | <1 | <5 | 1.64 | 41.2 | 70 | 0.46 | 0.43 | 314 | <1 | 0.18 | 34 | 50 | 35 | 148 | 0.09 |
| 12 | 11 | <1 | <5 | 1.37 | 41.2 | 55 | 0.51 | 0.35 | 314 | <1 | 0.17 | 40 | 44 | 35 | 105 | 0.08 |
| 13 | 9 | <1 | <5 | 1.29 | 37.2 | 49 | 0.41 | 0.34 | 395 | <1 | 0.16 | 32 | 49 | 38 | 87 | 0.1 |
| 14 | 9 | <1 | <5 | 1.51 | 44.4 | 60 | 0.46 | 0.38 | 368 | <1 | 0.18 | 36 | 57 | 35 | 125 | 0.15 |
| 15 | 8 | <1 | <5 | 1.62 | 41.8 | 61 | 0.45 | 0.43 | 542 | <1 | 0.17 | 38 | 57 | 40 | 124 | 0.06 |

Table C-2 (cont.) Herrington Lake sediment elemental data. All values are ppm (mg/kg) unless indicated otherwise.

| Station | Sb | Sc | Se | Sm | Sr% | Ta | Tb | Th | Ti% | U | V | W | Y | Yb | Zn |
|---------|-----|------|----|-----|-------|-----|------|------|------|------|-----|-----|----|----|-----|
| 1 | 0.9 | 14.6 | <3 | 8.9 | <0.02 | 120 | <0.5 | 0.7 | 12.3 | 0.43 | 5 | 84 | <1 | 34 | 218 |
| 2 | 0.7 | 16.1 | <3 | 9.3 | <0.02 | 133 | <0.5 | 1.3 | 13.1 | 0.42 | 5.7 | 95 | <1 | 34 | 237 |
| 3 | 1 | 13.9 | <3 | 8.1 | <0.02 | 116 | <0.5 | 0.6 | 12.6 | 0.44 | 2.3 | 98 | <1 | 32 | 373 |
| 4 | 0.5 | 11.6 | <3 | 7.7 | <0.02 | 108 | <0.5 | 0.5 | 10.7 | 0.37 | 4.4 | 58 | <1 | 34 | 213 |
| 5 | 1.3 | 13.1 | <3 | 7.8 | <0.02 | 115 | <0.5 | <0.5 | 11.6 | 0.39 | 2.7 | 92 | <1 | 33 | 357 |
| 6 | 0.9 | 12.8 | <3 | 8.3 | <0.02 | 111 | <0.5 | <0.5 | 12.4 | 0.38 | 4.8 | 81 | <1 | 32 | 282 |
| 7 | 1 | 13.1 | <3 | 7.1 | <0.02 | 111 | <0.5 | <0.5 | 11.1 | 0.27 | 4.2 | 75 | <1 | 30 | 327 |
| 8 | 1 | 12.1 | <3 | 7.9 | <0.02 | 109 | 1 | 1 | 10.3 | 0.49 | 4.7 | 83 | <1 | 33 | 252 |
| 9 | 0.5 | 5.4 | <3 | 3.3 | <0.02 | 54 | <0.5 | <0.5 | 3.3 | 0.21 | 1.6 | 44 | <1 | 17 | 149 |
| 10 | 0.9 | 14.2 | 6 | 7.1 | <0.02 | 77 | <0.5 | <0.5 | 11.7 | 0.26 | 2.9 | 74 | <1 | 27 | 184 |
| 11 | 1 | 15 | <3 | 7.7 | <0.02 | 108 | <0.5 | 0.5 | 10.9 | 0.52 | 4.9 | 115 | <1 | 30 | 231 |
| 12 | 0.7 | 12.6 | <3 | 7.5 | <0.02 | 111 | <0.5 | <0.5 | 11.3 | 0.37 | 5 | 77 | <1 | 29 | 235 |
| 13 | 0.8 | 11.4 | 4 | 6.9 | <0.02 | 95 | <0.5 | <0.5 | 10.6 | 0.25 | 3 | 41 | <1 | 31 | 259 |
| 14 | 0.9 | 13.9 | <3 | 8.4 | <0.02 | 118 | <0.5 | 1.3 | 11.5 | 0.43 | 2.3 | 88 | <1 | 34 | 325 |
| 15 | 1 | 13.6 | <3 | 7.7 | <0.02 | 119 | <0.5 | <0.5 | 12.1 | 0.37 | 3.9 | 87 | <1 | 31 | 285 |

Table C-3. Results of analyses of Standard Reference Material (NIST SRM #8704 - Buffalo River Sediment) submitted as blind unknowns with the Herrington Lake surficial samples. Also given are the method detection limits for each element reported by Act Labs, Inc. Shaded values, if any, differ from the certified or known value by >25%.

| Analyte | Symbol | Unit | Detection Limit | Certified value | Std dev | Act Labs Results | | |
|------------|--------|------|-----------------|-----------------|---------|------------------|---------|------------|
| | | | | | | Average | Std dev | % Recovery |
| Silver | Ag | ppm | 0.3 | | | 0.5 | 0.1 | |
| Gold | Au | ppb | 2 | | | 6 | 6 | |
| Aluminum | Al | % | 0.01 | 6.1 | 0.18 | 5.68 | 0.07 | 93.1 |
| Arsenic | As | ppm | 0.5 | 17 | | 19.9 | 1.8 | 117.3 |
| Barium | Ba | ppm | 50 | 413 | 13 | 577 | 93 | 139.6 |
| Beryllium | Be | ppm | 1 | | | 2 | 0 | |
| Bismuth | Bi | ppm | 2 | | | < 2 | | |
| Bromide | Br | ppm | 0.5 | | | 8.8 | 0.9 | |
| Calcium | Ca | % | 0.01 | 2.641 | 0.083 | 2.71 | 0.01 | 102.7 |
| Cadmium | Cd | ppm | 0.3 | 2.94 | 0.29 | 3.1 | 0.0 | 105.4 |
| Cerium | Ce | ppm | 3 | 66.5 | 2 | 64 | 8 | 96.2 |
| Cobalt | Co | ppm | 1 | 13.57 | 0.43 | 14 | 3 | 103.2 |
| Chromium | Cr | ppm | 2 | 121.9 | 3.8 | 128 | 13 | 104.7 |
| Cesium | Cs | ppm | 1 | 5.83 | 0.12 | 8 | 1 | 131.5 |
| Copper | Cu | ppm | 1 | | | 91 | 2 | |
| Europium | Eu | ppm | 0.2 | 1.31 | 0.038 | 1.2 | 0.1 | 89.1 |
| Iron | Fe | % | 0.01 | 3.97 | 0.1 | 4.28 | 0.15 | 107.8 |
| Hafnium | Hf | ppm | 1 | 8.4 | 1.5 | 8 | 1 | 99.2 |
| Mercury | Hg | ppm | 1 | | | 1 | 1 | |
| Iridium | Ir | ppb | 5 | | | < 5 | | |
| Potassium | K | % | 0.01 | 2.001 | 0.041 | 1.92 | 0.04 | 96.1 |
| Lanthanum | La | ppm | 0.5 | | | 30.6 | 2.6 | |
| Lithium | Li | ppm | 1 | | | 47 | 0 | |
| Lutetium | Lu | ppm | 0.05 | | | 0.42 | 0.05 | |
| Magnesium | Mg | % | 0.01 | 1.2 | 0.018 | 1.15 | 0.01 | 95.6 |
| Manganese | Mn | ppm | 1 | 544 | 21 | 554 | 11 | 101.8 |
| Molybdenum | Mo | ppm | 1 | | | 2 | 1 | |
| Sodium | Na | % | 0.01 | 0.553 | 0.015 | 0.66 | 0.06 | 118.7 |
| Neodymium | Nd | ppm | 5 | | | 26 | 8 | |
| Nickel | Ni | ppm | 1 | 42.9 | 3.7 | 44 | 1 | 103.3 |
| Phosphorus | P | % | 0.001 | | | 0.081 | 0.005 | |
| Lead | Pb | ppm | 3 | 150 | 17 | 155 | 5 | 103.1 |
| Rubidium | Rb | ppm | 15 | | | 117 | 36 | |
| Sulfur | S | % | 0.01 | | | 0.35 | 0.01 | |
| Antimony | Sb | ppm | 0.1 | 3.07 | 0.32 | 2.9 | 0.2 | 94.5 |
| Scandium | Sc | ppm | 0.1 | 11.26 | 0.19 | 11.7 | 0.4 | 104.2 |
| Selenium | Se | ppm | 0.1 | | | < 3 | | |
| Samarium | Sm | ppm | 0.1 | | | 6.1 | 0.3 | |
| Tin | Sn | % | 0.01 | | | 0.02 | 0.03 | |
| Strontium | Sr | ppm | 1 | | | 132 | 1 | |

Table C-3 con't. Results of analyses of Standard Reference Material (NIST SRM #8704 - Buffalo

River Sediment) submitted as blind unknowns with the Herrington Lake surficial samples. Also given are the method detection limits for each element reported by Act Labs, Inc. Shaded values, if any, differ from the certified or known value by >25%.

| Analyte | Symbol | Unit | Detection Limit | Certified value | Std dev | Act Labs Results | | |
|-----------|--------|------|-----------------|-----------------|---------|------------------|---------|------------|
| | | | | | | Average | Std dev | % Recovery |
| Tantalum | Ta | ppm | 0.5 | | | < 0.5 | | |
| Terbium | Tb | ppm | 0.5 | | | < 0.5 | | |
| Thorium | Th | ppm | 0.2 | 9.07 | 0.16 | 9.7 | 0.6 | 106.6 |
| Titanium | Ti | % | 0.01 | 0.457 | 0.02 | 0.40 | 0.01 | 88.3 |
| Uranium | U | ppm | 0.5 | 3.09 | 0.13 | 3.2 | 0.2 | 104.6 |
| Vanadium | V | ppm | 2 | 94.6 | 4 | 83 | 4 | 88.1 |
| Tungsten | W | ppm | 1 | | | < 1 | | |
| Yttrium | Y | ppm | 1 | | | 23 | 1 | |
| Ytterbium | Yb | ppm | 0.2 | | | 3.1 | 0.2 | |
| Zinc | Zn | ppm | 1 | 408 | 15 | 403 | 13 | 98.8 |

Table C-4. Results of analyses of Standard Reference Material (NIST SRM #1646a- Estuarine Sediment) submitted as blind unknowns with the Herrington Lake surficial samples. Also given are the method detection limits for each element reported by Act Labs, Inc. Shaded values, if any, differ from the certified or known value by >25%.

| Analyte | Symbol | Unit | Detection Limit | Certified value | Std dev | Act Labs Results | | |
|------------|--------|------|-----------------|-----------------|---------|------------------|---------|------------|
| | | | | | | Average | Std dev | % Recovery |
| Silver | Ag | ppm | 0.3 | | | 0.2 | 0.2 | |
| Gold | Au | ppb | 2 | | | 4 | 4 | |
| Aluminum | Al | % | 0.01 | 2.297 | 0.018 | 2.22 | 0.03 | 96.8 |
| Arsenic | As | ppm | 0.5 | 6.23 | 0.21 | 10.0 | 2.5 | 160.0 |
| Barium | Ba | ppm | 50 | | | 223 | 188 | |
| Beryllium | Be | ppm | 1 | | | < 1 | | |
| Bismuth | Bi | ppm | 2 | | | < 2 | | |
| Bromide | Br | ppm | 0.5 | | | 58.9 | 1.8 | |
| Calcium | Ca | % | 0.01 | 0.519 | 0.02 | 0.59 | 0.01 | 114.3 |
| Cadmium | Cd | ppm | 0.3 | 0.148 | 0.007 | < 0.3 | | |
| Cerium | Ce | ppm | 3 | | | 36 | 2 | |
| Cobalt | Co | ppm | 1 | | | 7 | 1 | |
| Chromium | Cr | ppm | 2 | 40.9 | 1.9 | 42 | 6 | 101.9 |
| Cesium | Cs | ppm | 1 | | | < 1 | | |
| Copper | Cu | ppm | 1 | 10.01 | 0.34 | 10 | 0 | 99.9 |
| Europium | Eu | ppm | 0.2 | | | 0.6 | 0.2 | |
| Iron | Fe | % | 0.01 | 2.008 | 0.039 | 2.21 | 0.08 | 109.9 |
| Hafnium | Hf | ppm | 1 | | | 12 | 1 | |
| Mercury | Hg | ppm | 1 | | | < 1 | | |
| Iridium | Ir | ppb | 5 | | | < 5 | | |
| Potassium | K | % | 0.01 | 0.864 | 0.016 | 0.87 | 0.01 | 100.7 |
| Lanthanum | La | ppm | 0.5 | | | 19.7 | 4.5 | |
| Lithium | Li | ppm | 1 | | | 19 | 1 | |
| Lutetium | Lu | ppm | 0.05 | | | 0.17 | 0.06 | |
| Magnesium | Mg | % | 0.01 | 0.388 | 0.009 | 0.39 | 0.01 | 101.4 |
| Manganese | Mn | ppm | 1 | 234.5 | 2.8 | 237 | 6 | 101.2 |
| Molybdenum | Mo | ppm | 1 | | | < 1 | | |
| Sodium | Na | % | 0.01 | 0.741 | 0.017 | 0.78 | 0.06 | 105.3 |
| Neodymium | Nd | ppm | 5 | | | 15 | 8 | |
| Nickel | Ni | ppm | 1 | | | 25 | 1 | |
| Phosphorus | P | % | 0.001 | 0.027 | 0.001 | 0.027 | 0.000 | 100.0 |
| Lead | Pb | ppm | 3 | 11.7 | 1.2 | 10 | 1 | 88.3 |
| Rubidium | Rb | ppm | 15 | | | 8 | 14 | |
| Sulfur | S | % | 0.01 | 0.352 | 0.004 | 0.35 | 0.01 | 99.4 |
| Antimony | Sb | ppm | 0.1 | | | 0.2 | 0.1 | |
| Scandium | Sc | ppm | 0.1 | | | 4.9 | 0.1 | |
| Selenium | Se | ppm | 0.1 | 0.193 | 0.028 | < 3 | | |
| Samarium | Sm | ppm | 0.1 | | | 3.3 | 0.1 | |
| Tin | Sn | % | 0.01 | | | < 2 | | |
| Strontium | Sr | ppm | 1 | | | 73 | 1 | |

Table C-4 con't. Results of analyses of Standard Reference Material (NIST SRM #1646a- Estuarine Sediment) submitted as blind unknowns with the Herrington Lake surficial samples. Also given are the

method detection limits for each element reported by Act Labs, Inc. Shaded values, if any, differ from the certified or known value by >25%.

| Analyte | Symbol | Unit | Detection Limit | Certified value | Std dev | Act Labs Results | | |
|-----------|--------|------|-----------------|-----------------|---------|------------------|---------|------------|
| | | | | | | Average | Std dev | % recovery |
| Tantalum | Ta | ppm | 0.5 | | | < 0.5 | | |
| Terbium | Tb | ppm | 0.5 | | | < 0.5 | | |
| Thorium | Th | ppm | 0.2 | | | 5.5 | 0.3 | |
| Titanium | Ti | % | 0.01 | 0.456 | 0.021 | 0.43 | 0.06 | 95.0 |
| Uranium | U | ppm | 0.5 | | | 2.1 | 0.7 | |
| Vanadium | V | ppm | 2 | 44.84 | 0.76 | 34 | 14 | 76.6 |
| Tungsten | W | ppm | 1 | | | < 1 | | |
| Yttrium | Y | ppm | 1 | | | 10 | 0 | |
| Ytterbium | Yb | ppm | 0.2 | | | 1.4 | 0.2 | |
| Zinc | Zn | ppm | 1 | 48.9 | 1.6 | 50 | 1 | 101.6 |

Table C-5. Results of analyses of Standard Reference Material (NIST SRM #2702- Inorganics in marine sediment) submitted as blind unknowns with the Herrington Lake surficial samples. Also given are the method detection limits for each element reported by Act Labs, Inc. Shaded values, if any, differ from the certified or known value by >25%.

| Analyte | Symbol | Unit | Detection Limit | Certified value | Std dev | Act Labs Results | | |
|------------|--------|------|-----------------|-----------------|---------|------------------|---------|------------|
| | | | | | | Average | Std dev | % recovery |
| Silver | Ag | ppm | 0.3 | 0.622 | 0.078 | 1.2 | 0.1 | 192.9 |
| Gold | Au | ppb | 2 | | | 17 | 20 | |
| Aluminum | Al | % | 0.01 | 8.41 | 0.22 | 7.63 | 0.26 | 90.7 |
| Arsenic | As | ppm | 0.5 | 45.3 | 1.8 | 49.8 | 2.6 | 110.0 |
| Barium | Ba | ppm | 50 | 397.4 | 3.2 | 170 | 151 | 42.8 |
| Beryllium | Be | ppm | 1 | | | 3 | 0 | |
| Bismuth | Bi | ppm | 2 | | | 6 | 2 | |
| Bromide | Br | ppm | 0.5 | | | 65.8 | 3.4 | |
| Calcium | Ca | % | 0.01 | 0.343 | 0.024 | 0.35 | 0.01 | 103.0 |
| Cadmium | Cd | ppm | 0.3 | 0.817 | 0.011 | 0.9 | 0.1 | 106.1 |
| Cerium | Ce | ppm | 3 | 123.4 | 5.8 | 117 | 8 | 94.8 |
| Cobalt | Co | ppm | 1 | 27.76 | 0.58 | 30 | 6 | 109.3 |
| Chromium | Cr | ppm | 2 | | | 324 | 28 | |
| Cesium | Cs | ppm | 1 | | | 6 | 2 | |
| Copper | Cu | ppm | 1 | 117.7 | 5.6 | 115 | 5 | 97.4 |
| Europium | Eu | ppm | 0.2 | | | 2.0 | 0.3 | |
| Iron | Fe | % | 0.01 | | | 7.78 | 0.24 | |
| Hafnium | Hf | ppm | 1 | | | 10 | 2 | |
| Mercury | Hg | ppm | 1 | 0.4474 | 0.0069 | < 1 | | |
| Iridium | Ir | ppb | 5 | | | < 5 | | |
| Potassium | K | % | 0.01 | 2.054 | 0.072 | 1.91 | 0.15 | 93.2 |
| Lanthanum | La | ppm | 0.5 | 73.5 | 4.2 | 64.5 | 5.4 | 87.8 |
| Lithium | Li | ppm | 1 | | | 77 | 2 | |
| Lutetium | Lu | ppm | 0.05 | | | 0.55 | 0.15 | |
| Magnesium | Mg | % | 0.01 | 0.990 | 0.074 | 0.92 | 0.02 | 93.3 |
| Manganese | Mn | ppm | 1 | 1757 | 58 | 1653 | 35 | 94.1 |
| Molybdenum | Mo | ppm | 1 | 10.8 | 1.6 | 9 | 1 | 83.3 |
| Sodium | Na | % | 0.01 | 0.681 | 0.020 | 0.75 | 0.05 | 109.6 |
| Neodymium | Nd | ppm | 5 | | | 63 | 14 | |
| Nickel | Ni | ppm | 1 | 75.4 | 1.5 | 77 | 2 | 102.1 |
| Phosphorus | P | % | 0.001 | 0.1552 | 0.0066 | 0.133 | 0.012 | 85.9 |
| Lead | Pb | ppm | 3 | 132.8 | 1.1 | 126 | 4 | 94.6 |
| Rubidium | Rb | ppm | 15 | 127.7 | 8.8 | 89 | 78 | 69.4 |
| Sulfur | S | % | 0.01 | | | 1.50 | 0.09 | |
| Antimony | Sb | ppm | 0.1 | 5.6 | 0.24 | 4.9 | 0.7 | 86.9 |
| Scandium | Sc | ppm | 0.1 | 25.9 | 1.1 | 24.1 | 1.1 | 93.2 |
| Selenium | Se | ppm | 0.1 | 4.95 | 0.46 | < 3 | | |
| Samarium | Sm | ppm | 0.1 | | | 10.6 | 0.7 | |
| Tin | Sn | % | 0.01 | 31.6 | 2.4 | < 0.02 | | |
| Strontium | Sr | ppm | 1 | 119.7 | 3.0 | 118 | 4 | 98.9 |

Table C-5 con't. Results of analyses of Standard Reference Material (NIST SRM #2702- Inorganics in marine sediment) submitted as blind unknowns with the Herrington Lake surficial samples. Also given are the method detection limits for each element reported by Act Labs, Inc. Shaded values, if any, differ from the certified or known value by >25%.

| Analyte | Symbol | Unit | Detection Limit | Certified value | Std dev | Act Labs Results | | |
|-----------|--------|------|-----------------|-----------------|---------|------------------|---------|------------|
| | | | | | | Average | Std dev | % recovery |
| Tantalum | Ta | ppm | 0.5 | | | 3.4 | 3.4 | |
| Terbium | Tb | ppm | 0.5 | | | < 0.5 | | |
| Thorium | Th | ppm | 0.2 | 20.51 | 0.96 | 19.5 | 0.1 | 95.1 |
| Titanium | Ti | % | 0.01 | 0.884 | 0.082 | 0.81 | 0.05 | 91.3 |
| Uranium | U | ppm | 0.5 | | | 9.0 | 1.4 | |
| Vanadium | V | ppm | 2 | 357.6 | 9.2 | 327 | 12 | 91.5 |
| Tungsten | W | ppm | 1 | | | 1 | 2 | |
| Yttrium | Y | ppm | 1 | | | 34 | 1 | |
| Ytterbium | Yb | ppm | 0.2 | | | 3.9 | 0.3 | |
| Zinc | Zn | ppm | 1 | 485.3 | 4.2 | 473 | 10 | 97.4 |

Table C-6. Results of Act Labs analyses of Reference material for the TD-ICP method. Act Labs' measure values compared to the certified values. Reference materials include USGS geochemical exploration references.

| Analyte Symbol | Unit Symbol | Detection Limit | USGS DNC-1a | | USGS DNC-1a | | USGS SBC-1 | | Method Blank |
|----------------|-------------|-----------------|----------------|-----------------|----------------|-----------------|----------------|-----------------|--------------|
| | | | Dolerite | | Dolerite | | Shale | | |
| | | | Measured value | Certified value | Measured value | Certified value | Measured value | Certified value | |
| Ag | ppm | 0.3 | | | | | | | < 0.3 |
| Cu | ppm | 1 | 97 | 100 | 97 | 100 | 32 | 31 | < 1 |
| Cd | ppm | 0.3 | | | | | 0.4 | 0.4 | < 0.3 |
| Mo | ppm | 1 | | | | | < 1 | 2 | < 1 |
| Pb | ppm | 3 | < 3 | 6.3 | < 3 | 6.3 | 30 | 35 | < 3 |
| Ni | ppm | 1 | 248 | 247 | 248 | 247 | 87 | 83 | < 1 |
| Zn | ppm | 1 | 59 | 70 | 60 | 70 | 187 | 186 | < 1 |
| S | % | 0.01 | | | | | | | < 0.01 |
| Al | % | 0.01 | | | | | | | < 0.01 |
| Be | ppm | 1 | | | | | 3 | 3.2 | < 1 |
| Bi | ppm | 2 | | | | | < 2 | 0.7 | < 2 |
| Ca | % | 0.01 | 7.63 | 8.21 | 7.76 | 8.21 | | | < 0.01 |
| K | % | 0.01 | | | | | | | < 0.01 |
| Li | ppm | 1 | 5 | 5.2 | 6 | 5.2 | 181 | 163 | < 1 |
| Mg | % | 0.01 | | | | | | | < 0.01 |
| Mn | ppm | 1 | | | | | | | 2 |
| P | % | 0.001 | | | | | | | < 0.001 |
| Sr | ppm | 1 | 136 | 144 | 138 | 144 | 185 | 178 | < 1 |
| Ti | % | 0.01 | 0.27 | 0.29 | 0.28 | 0.29 | 0.5 | 0.51 | < 0.01 |
| V | ppm | 2 | 133 | 148 | 135 | 148 | 207 | 220 | < 2 |
| Y | ppm | 1 | 16 | 18 | 16 | 18 | 34 | 36.5 | < 1 |