

Geochemical Fingerprinting of Natural Waters in Middle Tennessee

Bryant Davis^(a,b), Dr. Andrew Callender^(a)

(a) Department of Chemistry
(b) School of Environmental Studies



Abstract

Geochemical fingerprinting is the use of chemical species to determine the source and alteration of natural waters that comprise various bodies of water. These chemical fingerprints are defined by specific patterns of chemical species unique to each body of water. Different ratios of chemical species can then be determined so that a comparative analysis can occur between each body of water. These analytes are quantified by ICP-MS and ICP-OES.

Introduction

Geochemical fingerprinting is the use of "chemical fingerprints" to examine the source and alteration of natural waters. A chemical fingerprint is defined as "a unique pattern that indicates the presence of a particular combination of chemical elements or molecules." (Kamber) Fingerprinting can be applied to numerous branches of science including geology, botany, petroleum science, and agricultural science^[1].

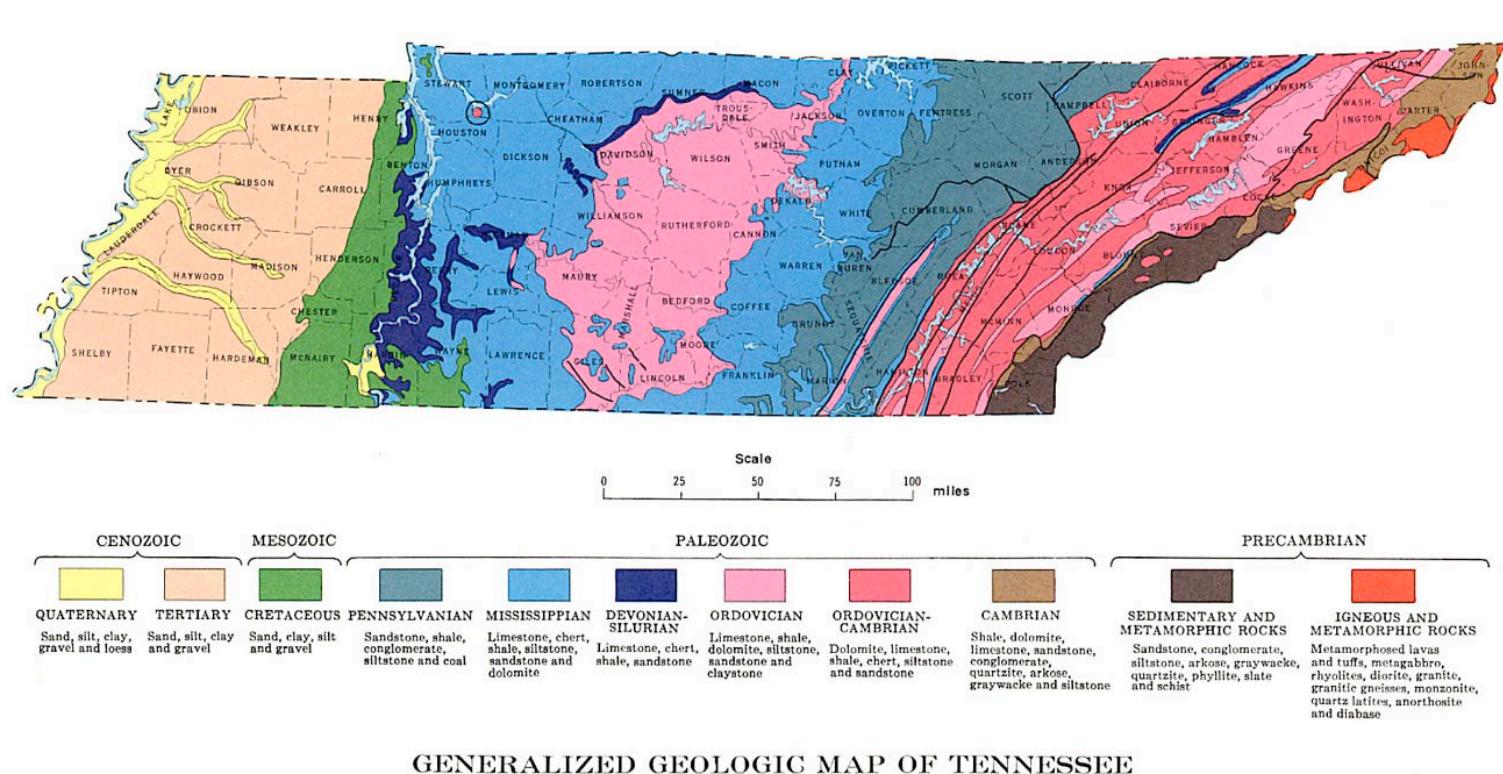


Figure 1. Geologic Map of Tennessee^[2].

Our analysis focused on water samples from two distinct physiographic regions of Tennessee: the Highland Rim and the Cumberland Plateau. These locations were chosen due to the differences in local geology, and their proximity to our lab. An agricultural lake, that is part of Coley Creek, was chosen for the location on the Cumberland Plateau, while Falling Water River was selected for the location on the Highland Rim.

These water bodies were chosen due to their similarities in land use, as land use has the potential to drastically alter the fingerprint of a given location, as well as their accessibility.

Water samples were taken from these locations at various times throughout the year in an attempt to determine any seasonal variation at each location. Water temperature, dissolved oxygen, conductivity, and pH were analyzed with a Extech DO700 portable meter prior to sample collection.

Sample Collection & Analysis

Samples were collected in a 250 mL polypropylene bottle certified clean for trace metal analysis, and acidified with 2.50 mL (1% v/v) of trace metal grade nitric acid, to preserve the samples for analysis.

A known amount of indium solution was added to each sample as an internal standard, and the sample was syringe filtered (0.22 µm nylon filters) into a clean polypropylene centrifuge tube.

Calibration standards were prepared by serial dilution of commercially available standards (Inorganic Ventures). Calibration was based on 6 standards plus a blank, spanning a range of 2.5 ug/L to 100 ug/L (ICP-MS) and 100 ug/L to 5000 ug/L (ICP-OES).

Each run of samples began with a calibration, and separate aliquots of the same calibration standards were used as QC standards during the run and at the end. This allowed confirmation that the instrument's response was consistent, and documentation of the accuracy and precision of the method.

All water samples were randomly assigned to runs.

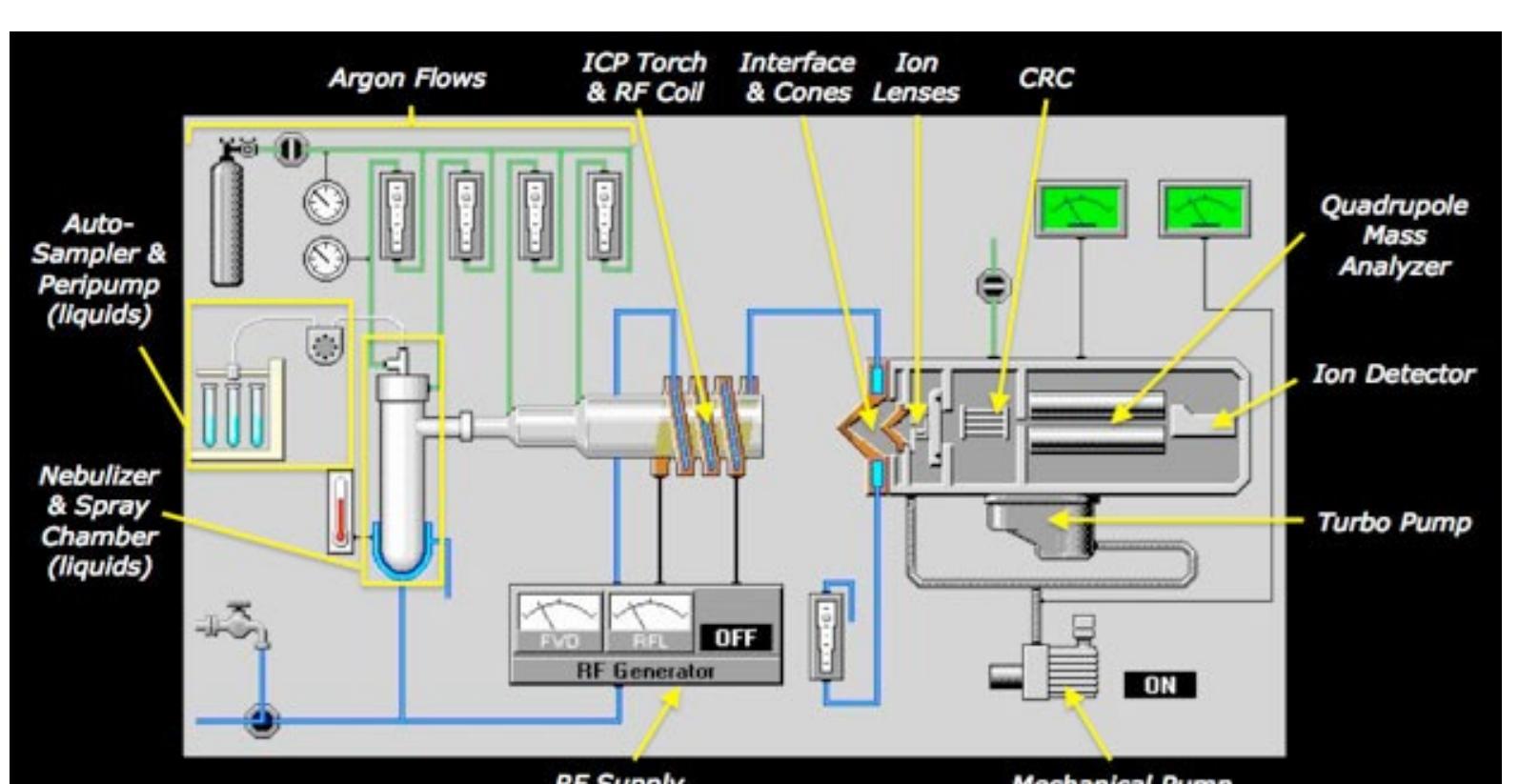
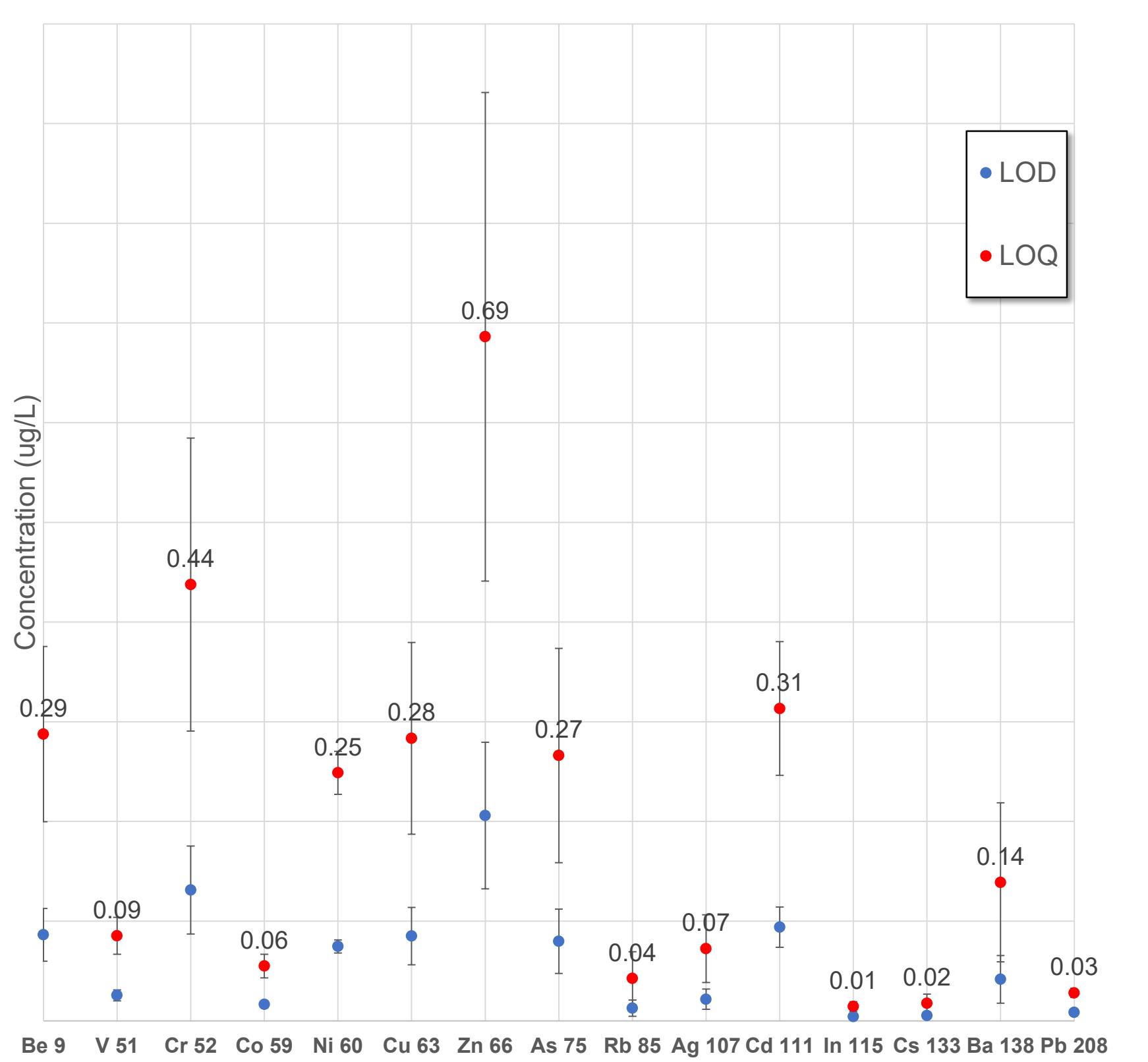


Figure 2. Schematic of an ICP-MS^[3].

Sensitivity



Water Composition

A total of 13 different analytes were selected for comparative analysis. These analytes were selected due to their ability to produce reliable, reproducible results during analysis via ICP-MS. Although several analytes were routinely quantified below both the limit of detection and limit of quantification, other analytes displayed interesting variability. Of the 13 analytes, Barium-138 showed the highest variance, despite the origin of the water sample. Waters obtained on the Cumberland Plateau displayed the highest variability for this analyte. Additionally, waters from this region exhibited higher concentrations of this analyte, testing as high as 167.9 ug/L.

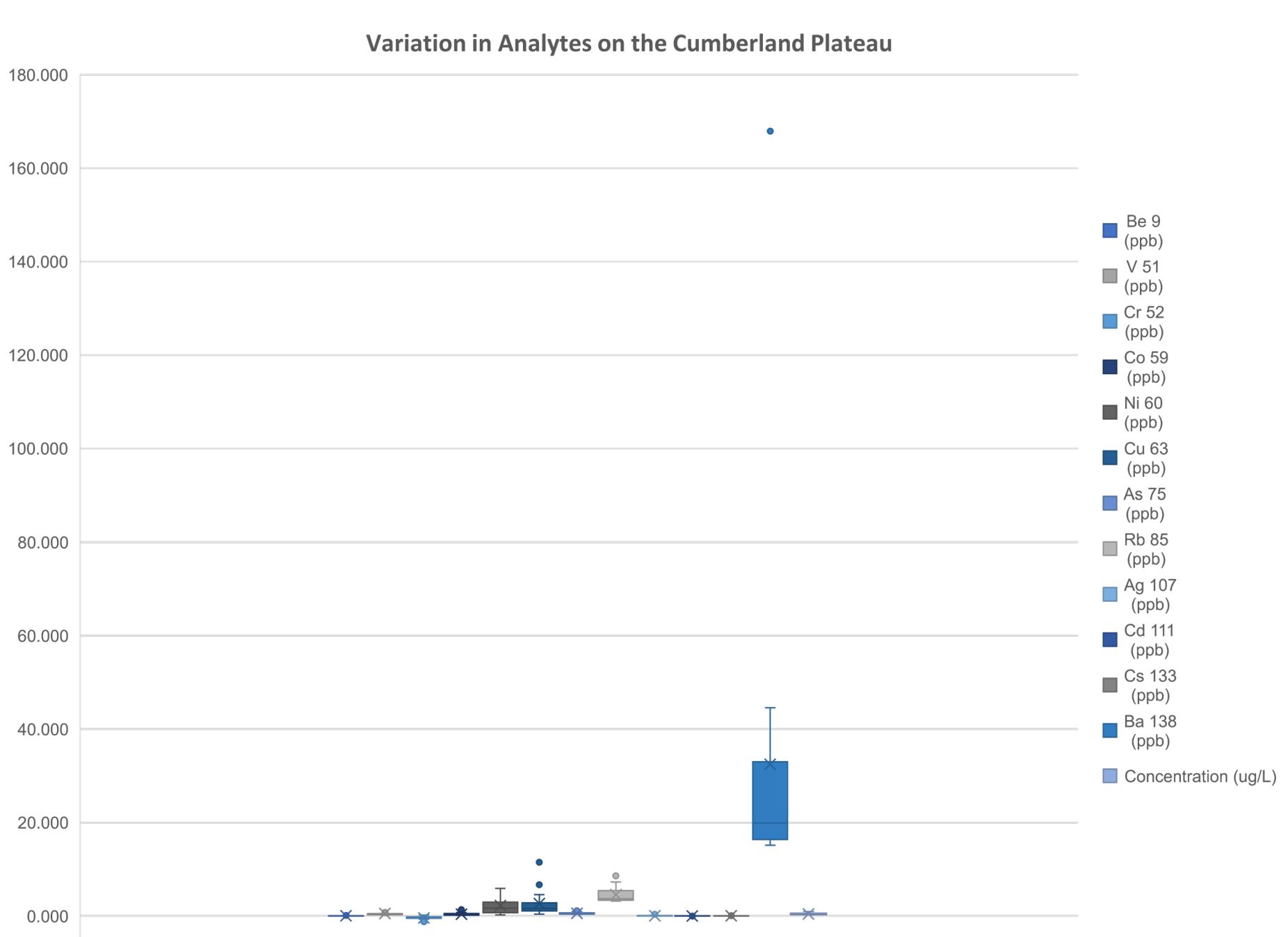


Figure 4. Box and whisker plot showing variation of analytes for samples originating on the Cumberland Plateau.

Waters obtained on the Highland Rim routinely contained a lower concentration of all analytes included in this analysis. Again, Barium-138 was the most concentrated species for these water samples, testing as high as 28.9 ug/L. Of these analytes, Nickel-60 also exhibited interesting variation, testing as high as 13.7 ug/L at the Cookeville Boat Dock.

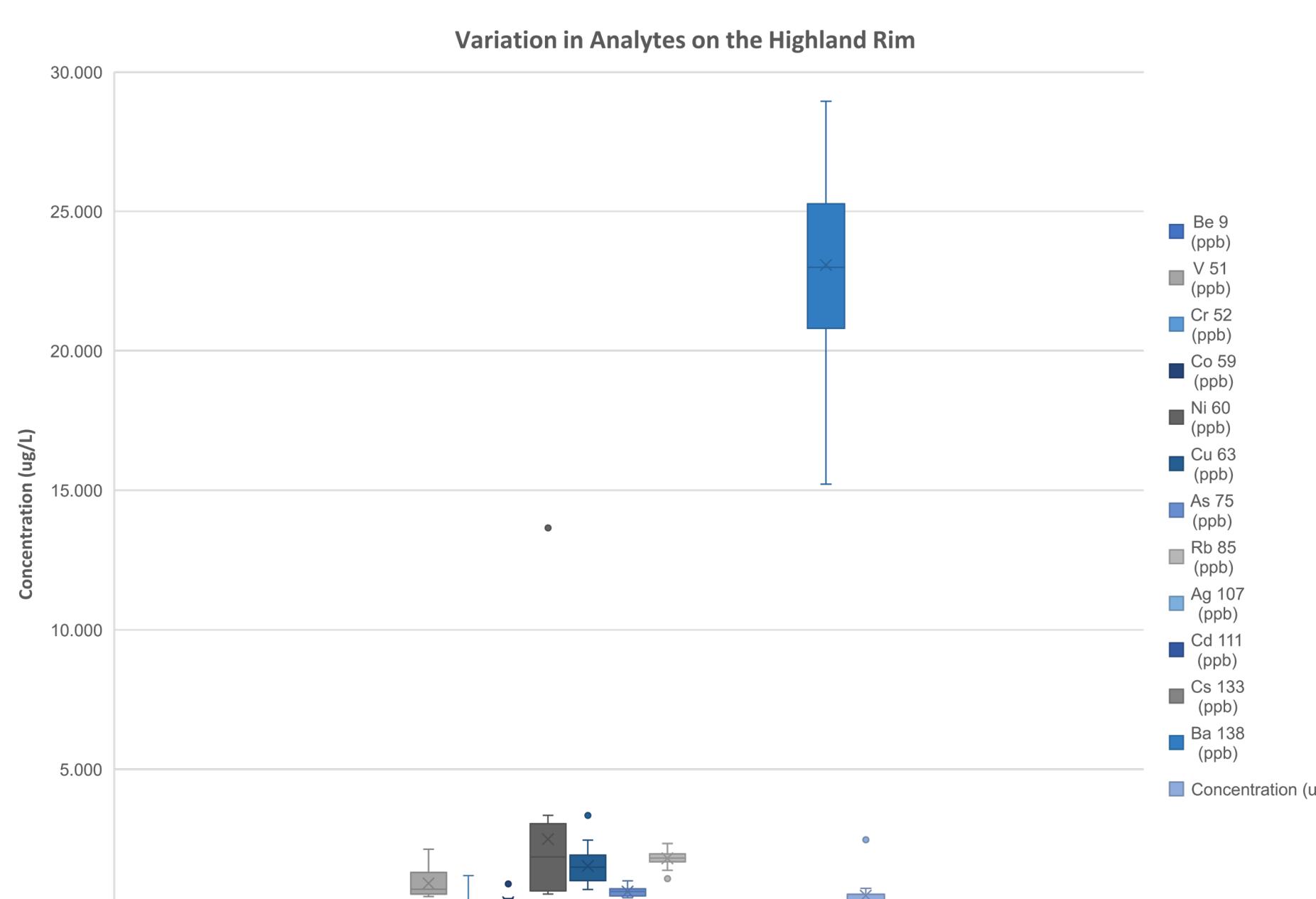


Figure 5. Box and whisker plot showing variation of analytes for samples originating on the Highland Rim.

Conclusion

In conclusion, the water samples included in our data set show that analytes do seem to vary from location to location. In particular, waters originating from a dammed section of Coley Creek will routinely contain higher concentrations of the 13 chemical species included in our analysis. This is likely due to the stagnation of water in this particular water body. Longer periods of contact are likely contributing to the leaching of these analytes into the system.

Data obtained on the ICP-OES showed some interesting variation as well, however, the analysis of quality control standards revealed several inconsistencies in the instrument's performance. More work needs to be done to determine the instruments exact limits of detection and limits of quantification. For these reasons, this data was omitted from this poster.

Additionally, future work should include multivariate analysis of variance (MANOVA) to determine ratios of these analytes to one another. These ratios can then be utilized to further distinguish between waters based upon their origin. Furthermore, these ratios can help us determine how waters change as they flow throughout these complex systems. The presence of certain analytes could even serve as markers that are indicative of pollution.

Acknowledgements

TTU Department of Chemistry Student Research Grant

The College of Environmental Sciences

Chemistry: Mr. Gene Mullins, Tammie Hanchey, Lisa Norsworthy, Julie Hudson, Robert Oliver

SOES: Dr. Hayden Mattingly, Dr. Steve Sharp, Irene Mauk

References

1. Kamber, B. S. (2009). Geochemical fingerprinting: 40 years of analytical development and real world applications. *Applied Geochemistry*, 24(6), 1074-1086.
2. Tennessee State Government – TN.gov (2019). List of Maps and Publications. Retrieved from www.tn.gov/environment/programareas/tennessee-geological-survey/geology-redirect/mapspublication/list-of-maps-publications.html.
3. Jackson School of Geosciences - University of Texas at Austin (2020). ICP-MS?. Retrieved from www.jsg.utexas.edu/icp-ms/icp-ms/