Development and Application of a Method for Determination of Metals in Environmental Sediments

by

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ABSTRACT

Metals are considered contaminants in the Safe Drinking Water Act. At a certain level, some metals become toxic and result in organ impairment of fish and other aquatic species. Sediment is one of the reservoirs of metals and has direct contact with water. Metals in the sediment should be monitored to prevent pollution of drinking water sources and can be monitored by Inductively Coupled Plasma—Mass Spectrometry (ICP-MS) according to US EPA 200.8 and 6020B.

This work was part of a larger study of the Yellow Creek that was performed in collaboration with Prof. Johnston's group (from Biology). Several different water quality parameters were studied, including the different metals and their concentrations in the sediments. As part of the studies, it was important to develop an ICP-MS method and show that it would provide useful measurement results for the metals.

Water and sediment samples were collected at three sites along Yellow Creek which have different characteristics in order to evaluate the possible effects of the woods, the traffic and a storm drain on the observed concentrations of metals.

An ICP-MS method was fully developed in this study to measure metal concentrations in sediment samples. The method was evaluated in terms of instrument detection limit and interferences and validated based on the recoveries of reference material Buffalo River sediment NIST® RM 8704. The procedure was then applied to measure metal concentrations in the sediment samples collected during a water quality study of the Yellow Creek in Poland, Ohio conducted over three consecutive seasons.

Metal concentrations of all samples were generally evaluated based on Freshwater Sediment Screening Benchmarks and Probable effect concentration referenced from US EPA internet database. The trend of metal concentrations over time and in three sampling days were studied. Metal concentrations of the sediments in the Yellow Creek overall appear to be low.

Finally, concentrations of metals measured by ICP-MS were compared to those measured by XRF (X-ray Fluorescence Spectrometry). The two methods were compared regarding the level of metals and the trend of changing in concentration over time. XRF is a complimentary method for ICP which can be used to measure some elements that are difficult to be extracted from the sediment, such as Cr and Al. Major elements such as Ca, Fe, Mn, Mg can be measured by XRF which is a direct method, while ICP-MS requires several digestion and dilution steps. Trace elements like Pb, Cd, Co, Ni are better measured by ICP-MS due to their low concentrations in the sediments.

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I. INTRODUCTION

1.1. Trace elements in the environment

Metals can be released in the waste of industrial and agricultural activities and cause environmental contamination of soil, water, and sediments. Some metals are essential for plants and animals such as Chromium (Cr), Cobalt (Co), Cooper (Cu), Manganese (Mn), Nickel (Ni), Zinc (Zn)[1]. Plants and animals that are exposed can take up and release the metals resulting in cycling of the elements in the environment. Other metals such as Cadmium (Cd) and Lead (Pb) are released into the environment but can affect living organisms.

Once absorbed into human body, metals can react with oxygen to produce reactive oxygen species, leading to oxidative stress and damage to major organs such as the brain, liver, and kidneys[2]. Cadmium binds to cysteine, glutamate, histidine in the liver and accumulates in kidneys, causing the deficiency of the organs. Chromium presents at different oxidation levels, its intramolecular reduction producing reactive oxidative species whose damaging effects are intensive. Aluminum has neurotoxicity, like neuronal atrophy, and may result in Alzheimers disease.[3] Consequently, there is an increasing need for determination of metals when human health is considered.

Accurate and precise concentrations of metals are necessary to evaluate health risks from environmental contamination. For example, it may be important to measure metal concentrations in an agricultural area to determine whether it is safe for planting crops or whether a food source meets the requirement of food safety. Heavy metals are also measured to evaluate their mobility in soil-plant systems. The presence of metals in sediments in different forms, complexing acid-volatile sulfides, organic matter, texture, which can affect their bioavailability. If metals combine with organic matter, their probability of being reabsorbed by plants is higher. [4]

Metals can be quantified by various methods where each has both advantages and disadvantages. The methods used are selected based on the sample characteristics, required sensitivity and possible interferences. Electrochemical techniques such as potentiometry and voltammetry methods can suffer from competing ions in samples. X-ray fluorescence (XRF) is a method of high specificity but relatively low sensitivity. Nuclear techniques are not ideal due to low sample throughput and relatively high cost. Flame atomic absorption spectrometry and Graphite Furnace Atomic Absorption Spectrometry are relatively sensitive and cost-effective methods. For some applications, the flame or graphite furnace atomizer may have low atomization efficiency for some refractory metals resulting in low sensitivity. However, this may be overcome by the use of the Inductively coupled plasma (ICP) atomizer in ICP-OES (Atomic emission spectrometry) and ICP-MS (Mass spectrometry) methods.

If the object of the analytical method is to measure the total amounts of the elements, the atomic spectroscopy methods are well suited due to their low instrument detection limits. Their advanced configuration can also minimize many measurement interferences. While each element can emit many characteristic spectral lines in ICP-OES, these emissions can result in spectral overlaps and interferences. By comparison, ICP MS measures each element as a unique atomic ion or isotope ion and the lower number of isotopes for each element greatly reduces the chance of spectral overlaps and higher selectivity results.[5]

1.2. Yellow Creek Watershed

Yellow Creek watershed referred by EPA as identification number 18-007 starts from northeast Columbiana County to north into eastern Mahoning County. The creek goes through several townships and municipalities such as Columbiana County and Mahoning County. The Creek goes through residential and forested areas, including Mahoning County. Agricultural activities and livestock production have been developed in the region. From 18-20th century, there were sawmills, gristmills, and steel mills. The Iron and steel industry was developed along the watershed to have easy access to water. The mining activities left behind big holes, from which water was drain, polluting Yellow Creek watershed with heavy metals. These big holes were not filled with soil or plants, resulting in consistent erosion, washing out heavy metals to the creek. The consequences have been lasted your years even the mining activity had been terminated. [6]

1.3. Inductively coupled plasma - Mass spectrometry (ICP -MS)

1.3.1. Principles

The main components of an ICP-MS include the inductively coupled plasma (ICP), the interface, the extraction lenses, the reaction cell, and a quadruple mass separator and ion detector.

The liquid sample solution is pumped into a nebulizer where it is mixed with argon gas at high velocity and high pressure to form a sample ***aerosol***. Larger aerosol droplets are removed from the spray chamber while finer aerosols are carried into the central channel of the ICP.

The Plasma torch is a combination of concentric quartz tubes that contain separate channels for individual argon gas flows.

As shown in Figure 1.1, near the exit of the torch, a radiofrequency electric field produced by a copper coil electrode produces an intense magnetic field. The magnetic field induces motion of electrons in the argon gas flows. Collisions of electrons and ions causes gas atoms to become positively ionized and form a stable high temperature plasma discharge composed of argon ions and electrons with high kinetic energy. As the sample aerosol travels through the high temperature plasma, aerosol droplets undergo desolvation, evaporation, dissociation and finally ionization. This produces a source of ***positively charged sample ions***. Some electrons of analytes in excited states do not escape from the atomic orbitals but return back to bound states and release photons resulting in intense emissions. These photons can cause measurement errors and are prevented from reaching the detector. Analyte ions and photons are separated in the ICP MS by reflecting the ions away from the photons that are allowed to follow a straight path.

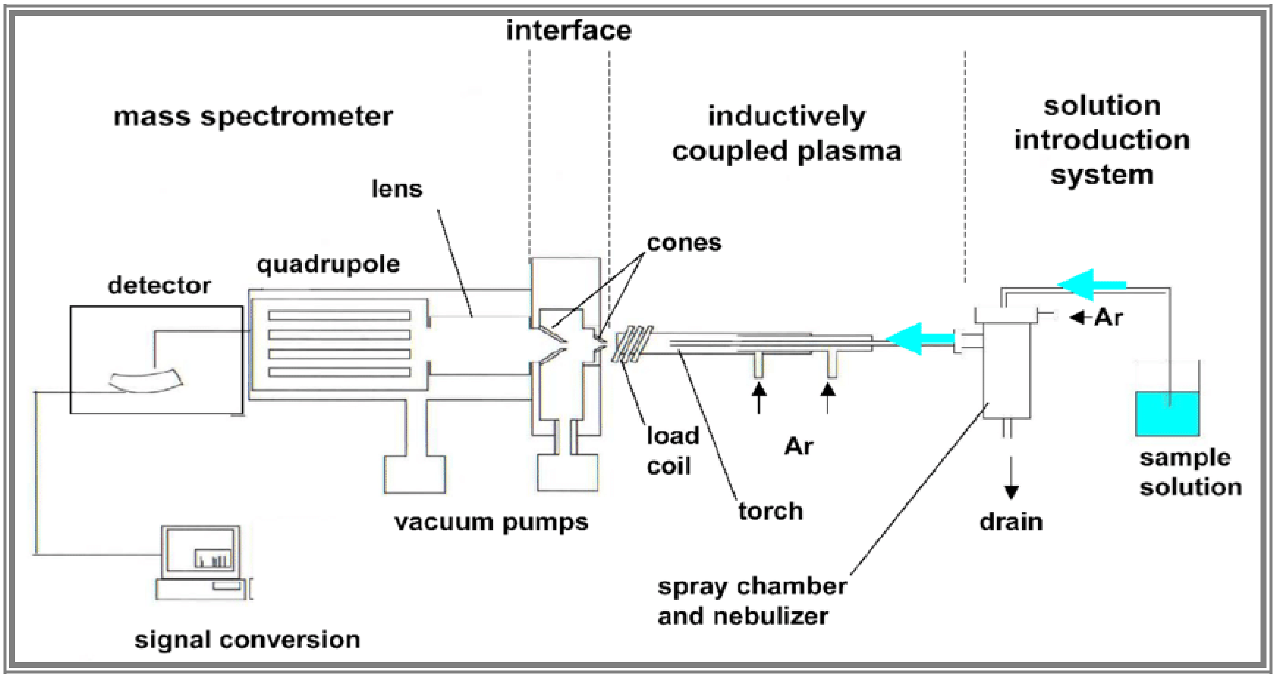


Figure 1.1: Schematic of an Inductively Coupled Plasma Mass Spectrometer ICP[7]

The flow of cations is directed towards the ***interface*** which is made of 2 metallic cones (0.6-1.2 mm diameter orifice) known as the sampler cone and the skimmer cone. This space is water cooled and maintained at low vacuum. The interface region is a transition space between high pressure, high temperature plasma and high vacuum and low temperature environment of the mass spectrometer.

Ion optics are used to guide the analyte ions toward the mass analyzer.

Mass spectral interferences, especially polyatomic ions, are reduced or eliminated in *the collision cell*, which uses a non-reactive gas to attenuate polyatomic interferences. The probability that the larger diameter polyatomic particles collide with the gas (for example Helium) is higher than the probability that of smaller diameter monoatomic analyte ions of the same mass. This leads to a larger loss of kinetic energy of the polyatomic interference and makes it possible to reject them using a bias voltage.[8]

Following the collision cell, the ion beam is delivered to a ***quadrupole mass separator*** that is held at high vacuum. The mass separator consists of 4 electrodes divided into 2 perpendicularly aligned pairs. Each electrode pair has time dependent, and time independent potentials applied to it. The *time dependent potential* focuses and defocuses the beam of positive ions onto the center axis of the electrode pairs by rapid switching from positive to negative potentials. Whether a particular ion is affected by the potential depends on its mass and the magnitude of the potential. One pair of electrodes causes lower mass ions to collide with an electrode and be discharged while allowing heavier mass ions to pass. As a result, the combination of the electrode geometry and the applied potential acts as a high pass mass filter. The other electrode pair also has time dependent potentials applied but out of phase compared to that of the first pair and is used as a low pass mass filter. The final range of masses that is transmitted by the mass separator is determined by the range of masses that are transmitted simultaneously by both pairs of electrodes.

Table 1.1: Quadrupole mass separator – out of phase applied voltage

	Pair 1		Pair 2		Accelerated ions	Eliminated ions
	Time dependent potential	*Time independent potential*	*Time dependent potential*	*Time independent potential*		
Out of phase	(-)	(+)			**High mass**	Low mass
			(+)	(-)	**Low mass**	High mass
Time dependent potential affect low mass ions, but high mass ions are only filtered by time independent potential.						

Ions that are transmitted from the quadrupole are converted to electrical signal using an ion detector that also amplifies the electron pulses using a chain of dynodes. The amplified pulses are usually recorded as counts per measurement period before being processed by the data handling system.[9]

1.3.2 Strengths and weaknesses of the ICP MS

Advantages

- The atomization and ionization efficiencies in ICP MS are both high due to the combination of a solution nebulizer and the high temperature of the ICP atomizer and ionization source.
- The ICP-MS mass spectra are relatively simple, which allows elements as well as their isotopes to be easily identified. This also provides elemental isotopic ratio information.
- Multi-element and multi-isotope analysis the entire periodic table can be measured in a single scan.
- Interferences can usually be suppress by a collision/reaction cell.
- Measurements are extremely sensitive, ranging from the sub-part per trillion to part per million range with good linearity.
- ICP MS has a large dynamic working range.
- ICP-MS can be coupled effectively with HPLC and GC for high sensitivity separation methods.

Disadvantages

- Initial and maintenance costs are high due to the ICP plasma, which uses large amounts of high purity argon gas, and regular replacement of instrument components.

- Highest performance for ICP MS requires the use of ultraclean reagents, which is costly.

- Sample variations and complex sample matrices cause instability in the ICP.

- Measurement errors due to interferences can be significant due to isobars and polyatomic interferences.[10]

1.3.3 Special precautions for handling samples in ICP-MS

Sample containers are critically important in such a sensitive method. According to instructions in the FDA Elemental Analysis Manual for food and related products, labware must be sufficiently clean. Labware used for elemental analysis should be cleaned by detergent, rinsed with water, soaked in 10% HNO_3 and finally rinsed with DI water.

No glass or metal spatulas should be used because of the possibility of releasing contaminants. Virgin (non-recycled) Teflon® FEP (Fluorinated ethylene propylene), PFA (Perfluoro alkoxy alkanes), PP (polypropylene), LDPE (Low-density polyethylene) or HDPE (High Density Polyethylene) are recommended materials.

Sample containers should be washed with 1% nitric acid which is then tested for contaminants.[11]

1.3.4 ICP MS interferences-types and principles and instrumentation for corrections

1.3.4.1 ICP-MS interferences

Based on the principles of the instrument, there are spectral and nonspectral interferences. The latter is nonspectral since it does not relate to mass of elements.

- ***Non spectral interferences*** are from sample matrix such as soluble salts. They probably induce or suppress the readout signals. Non spectral interferences could be solved by using aerosol dilution, internal standards, standard addition methods, isotope dilution, and matrix separations.

- ***Spectral interferences*** are ions and molecules whose masses are equal to those of elements of interest. They are isobarics, doubly charged ions and poly atomic ions, which cause severe systematic errors. Our elements of interest are Cr, Fe, Ni, Co, Cd. These elements are exposed to severe interferences from argon gas, chloride in aqua- regia, Ca in sample matrix, especially Mo which are at high concentrations in samples.

To have appropriate methods to deal with interferences, the interference effects should be studied in advance. For instance, if an element has multiple isotopes, if their recoveries are way different, some of the isotopes are probably interfered. This includes which elements are interfered by which interference, the severity of the effect. Depending on the instrument being used, there are some components designed to remove the interferences. If the problem cannot be solved by available equipment, mathematical equations can be employed.

1.3.4.2 Instrumental solutions

Vendors make their product competitive by inventing additional components which can solve the problem of interferences.

High resolution sector field ICP-MS, Tandem mass spectrometry (ICP MS-MS) can differentiate polyatomic interferences or increasing resolution of the instrument.

The desolvating nebulizer system removes water from samples, preventing the oxidation of analytes.

DRC (Dynamic reaction cell) uses reactive gases such as ammonia and oxygen which react with interference. This changes their relative mass and finally discriminates against unwanted species. This is based on different chemical activities of analytes. However, the reactive gases could result in new interferences. Reactive gases are analyte specific. DRC is selected when sample matrix is known.

Different from DRC, KED (Kinetic energy discrimination) is called passive filtration, and unspecific to any analytes and no prior knowledge of sample matrix is required. There is no chemical reaction. The method discriminates between interferences and analytes by making their kinetic energy different. Collision gas is an inert gas, He. The probability of collision between He with polyatomic interference is higher than that of analytes due to the larger diameter of the interferences. Although the gas does not react with analyte, it still causes the analyte to lose their energy and reduce method sensitivity.

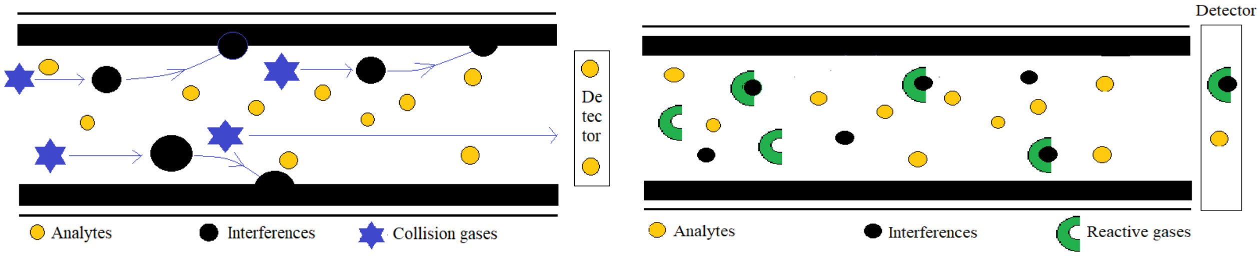


Figure 1.2. Working principle of KED and DRC mode

1.3.4.3 Mathematical interferences corrections

Instrumental methods can not completely depress interferences, mathematical methods are combined to correct intensities of atoms of interest. It is suitable for all spectral interferences. Equations are established using intensities of interference and analytes. Take Cobalt as an example. Its isotope is 59 and interfered by Molybdenum. The samples could be spiked with the standards of Mo with increasing concentrations. If the intensity of Co goes up corresponding to those in Mo. This means a certain amount of Mo is understood by the instrument as Co. The correlation coefficient of the equation drawn based on Mo concentrations and Co intensities is the factor to establish correction equations for Co. The equation is then entered into the instrument set up. The instrument will correct Co signals automatically. This method is challenging when one analyte is affected by multiple interferences.

In general, correction methods work well at low level of interferences or at high concentration of analytes. Otherwise, interferences need to be removed from sample matrix by other separation methods like ion exchange chromatography.

1.3.4.4 Internal standards

Internal standards possess a similar mass/charge ratio and are free of interferences. Their behavior in sample matrix is like analytes. If signals at specific mass/charge ratio are suppressed by sample matrix or suffer from positive bias, signals of the standards respectively decrease or increase. The instrument now is designed to correct signal and concentrations of elements according to recoveries of internal standards.

1.4 Acid extractions [12]

Sample preparations for atomic spectrometry analysis depend on the methods used. In general, Atomic Absorption Spectrometry, Atomic Emission Spectrometry and Atomic Mass spectrometry methods require solution phase samples. Therefore, samples subjected to these methods should be digested prior to measurement. The reliability of results varies according to the effectiveness of the digestion procedure.

Acid extractions can use different acids such as HF, HNO_3, $HClO_4$ or mixture of acids such as aqua regia (3:1) HCl-HNO_3, (v/v). The acids used are selected based on the range of organic material or the amounts of metal in the samples. Other digestion conditions also affect the efficiencies such as the ratio of acid to soil, acid concentrations, digestion times and temperatures, and whether the digestions are assisted by reflux or microwave heating and whether the digestion is performed in an open or closed system. The recovery yield of various acid leaching methods is measured with respect to total metal contents.

Sample solutions prepared by acid digestion generally have several steps including pre-digestion, digestion, dilution and filtration.

1.4.1 Microwave total digestion

Total sample digestion schemes often include strong acids such as hydrofluoric acid (HF), which allows analyte elements to be efficiently extracted from aluminosilicate phases. However, HF is hazardous and difficult to use and is generally not recommended for routine analysis.

Total digestion methods can be based on solutions or mixtures of the following reagents: 70% HNO_3, 40% HF, 70% $HClO_4$ and 30% H_2O_2. Samples having high organic or carbonate content that can cause foaming after acid addition are recommended to be digested according to procedure B shown below instead of procedure A.

While acid digestions using standard (non-microwave) heating sources may underestimate the levels of some elements, total digestion using microwave heating sources can increase the extraction efficiency and provide enhanced efficiencies for the determination of some elements.

Nitric acid may be a good alternative to microwave digestion for samples whose organic content is high. The quantitative results of both digestion methods are close for Cd, Cu and Pb, but Zn was underestimated.

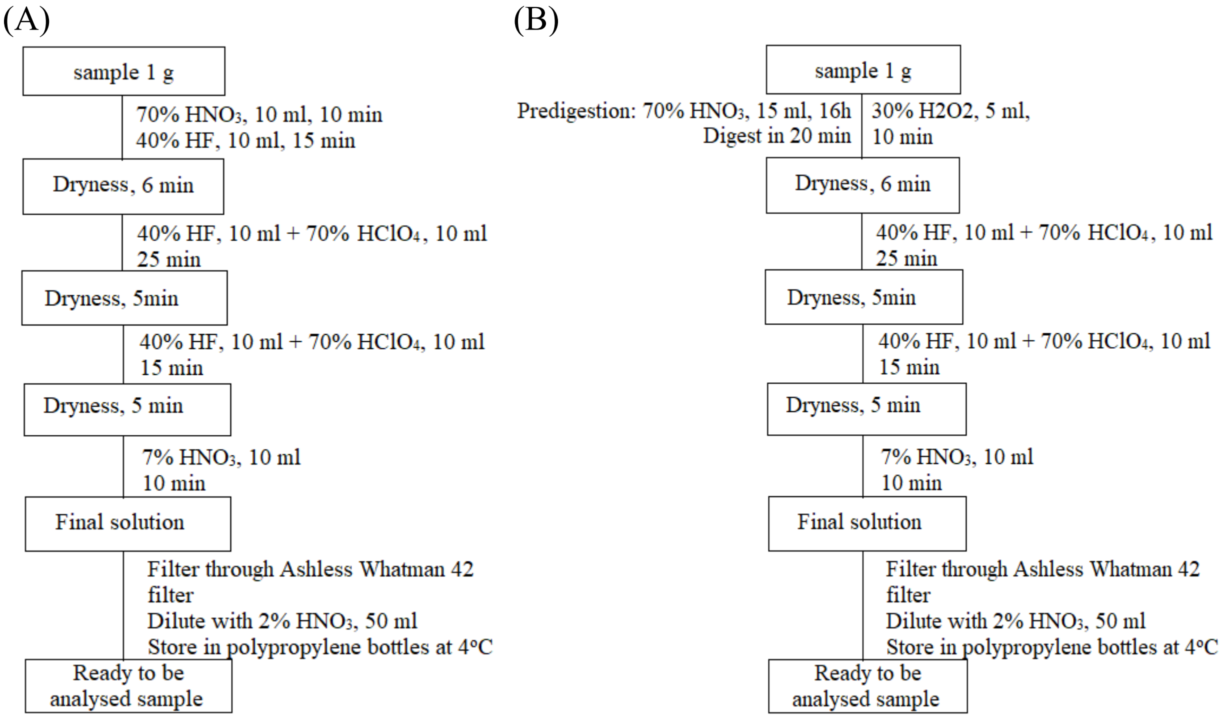


Figure 1.3. US EPA method[13]

1.4.2 Aqua regia extraction

Aqua regia is a solution mixture of HNO_3 and HCl acids that is used to release a variety of metals from their complexes due to reactions with nitrosyl chloride (NO-Cl) and molecular chlorine (Cl_2) which are formed by reaction of the two acids. These two molecular products are strong oxidizing agents that react aggressively with organic material and are able to release metals from samples containing high amounts of organic matter.

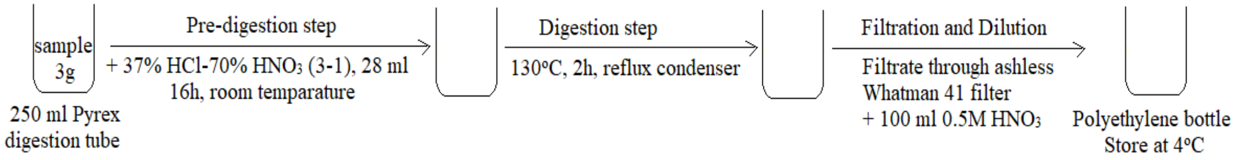


Figure 1.4. Aqua regia extraction

However, digestion aqua regia is not effective for all sample types, especially silicates, and does not necessarily provide a good indication of the extractable amount that can be potentially released to the water under natural conditions. Many samples can be digested at the same time with an aluminum block heater. For many sample types, this approach can result in similar extractable metal amounts compared to microwave total digestion. [14]

Cd, Zn, Cu, and Pb have similar recovery when comparing the microwave and aqua regia protocols for Cd, Zn, Cu, and Pb in environmental samples. Aqua regia appears to be a better choice since it is cheaper and faster[15, 16] . However, aqua regia is not aggressive enough to extract Co, Cd, Cr and Ni from sediments. The determination of these elements may be underestimated by up to 50%. Hence, the method is not always appropriate for heavy metals in complicated environmental matrices.[17]

1.4.3 Nitric acid extraction

For samples with high organic content, especially carbonates, total digestion causes foaming when adding acid. This can cause sample losses and increases the hazard of the procedure. Nitric acid extraction is more appropriate for these circumstances.

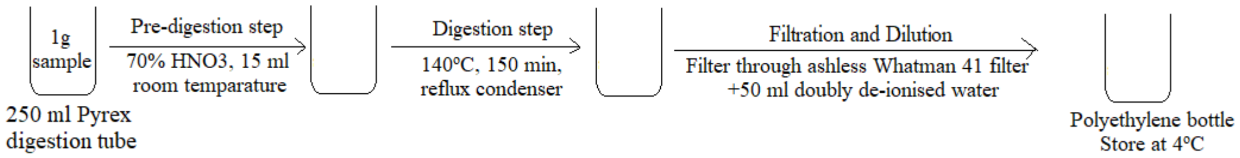


Figure 1.5. Nitric acid extraction

Nitric acid metal extraction is recommended by Environmental Protection Agency (EPA) and assisted by microwave. The leaching method is commonly applied to soils, sludges and forest floor samples. Concentrated nitric acid is powerful enough to dissolve metals like total digestion.

Nitric acid could also extract metals from high organic matter content samples.[18]

Table 1.2. Comparison of two digestion reagents (HNO_3 and Aqua regia)[19]

HNO_3	**Aqua regia**
High organic matter content (≤38%)	Higher chance of foaming when high organic content sample is digested. (In aluminum block): low carbonate or organic matter content.
Suitable to extract Cr, Cu, Pb	Higher extraction efficiency for Co, Ni, Pb, Zn**
Recoveries depend on specific conditions of leaching procedure	Maximize solubility of metals with recoveries from 89-110%.

1.4.5. Three step sequential extractions

It is important to measure the concentration of metals under different chemical conditions. Sequential extractions characterize the release of metals into the environment under different chemical conditions.

Sequential extraction brings about data closely relating to environmental impacts of metals. For example, exchangable ions is an indication of nutrient retention capacity of soil. These ions are themselves important to plant's lives or they can be exchanged with more important elements with similar charge. Instead of being extracted by one digestant, samples are sequentially processed with different reagents such as with CH_3COOH, $NH_2OH.HCl$, H_2O_2 + CH_3COONH_4, Aqua regia, etc to fractionate metals.

Table 1.3. Results from three step sequential extraction[20]

Three steps sequential extractions Target metals (Cd, Cr, Cu, Ni, Pb and Zn)			
Fractions		Reagents	Metals
1	Soil solutions, carbonates, exchangeable metals	0.11 M CH_3COOH	Cd 31-53%
2	Fe–Mn oxides	0.5 M $NH_2OH.HCl$	Cd 38-61%, Cu 7-19% Ni 7-13%, Pb 52-77% Zn 7-15%
3	Organic matter and sulfides	8.8 M H_2O_2 then 1 M CH_3COONH_4, pH 2	Cd 9-14%, Cu 2-5% Ni 6-8%
4	Remaining, non-silicate bound metals	Aqua regia ($HCl-HNO_3$, 3:1 (v/v))	Cr 29-46%, Cu 66-85% Ni 40-56%, Pb 9-36% Zn 65-74%
5	Residuals		Cr 47-65%, Pb 8-21% Zn 7-15%

In this study, BCR sequential extraction was employed. The procedure was summarized in figure 1.6.

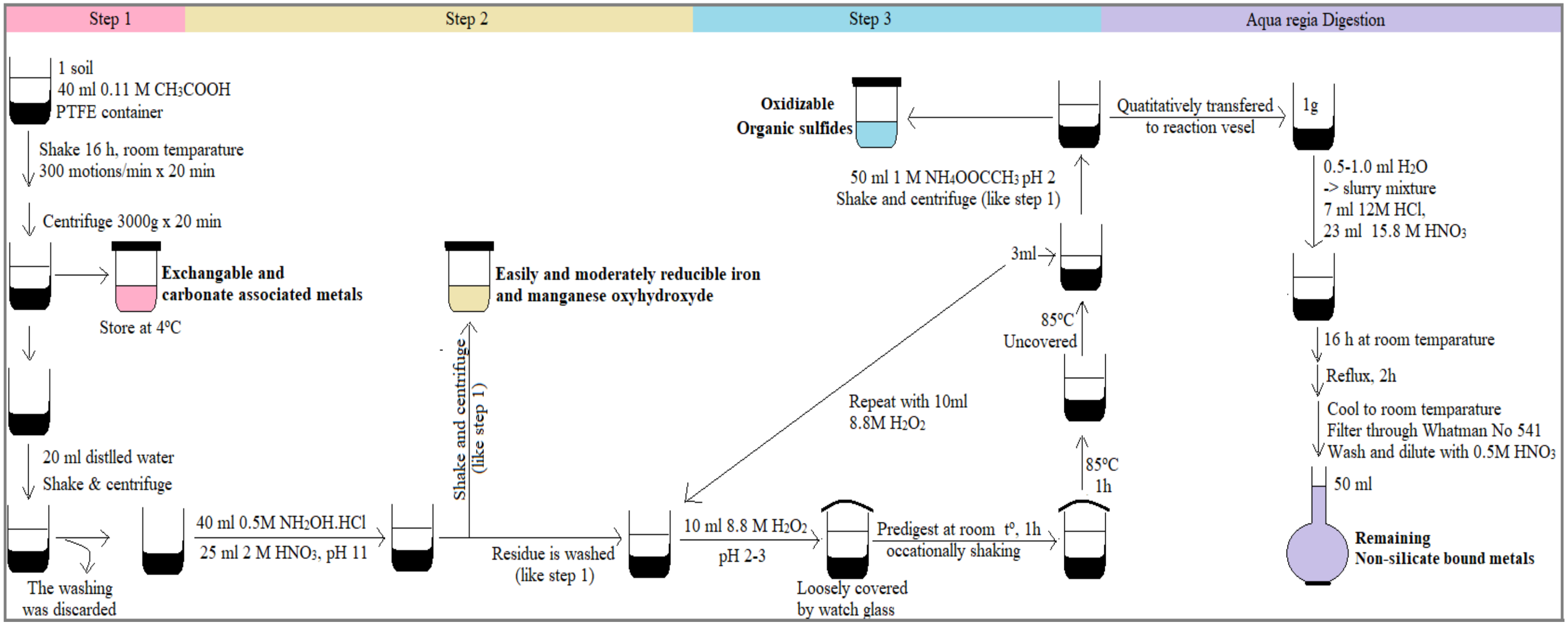


Figure 1.6. Reference for modified BCR three-step procedure[21]

II. EXPERIMENTAL

2.1. Instrumentation and glasswares

The instrument used was a Thermo Scientific™ iCAP™ RQ ICP-MS. This is a single quadrupole ICP-MS and ideal for trace analysis. Besides basic components of an ICP-MS, the instrument has Kinetic Energy Discrimination (He KED) technology to use for polyatomic mass interference removal. He KED is further combined with QCell collision/reaction cell. The combination is able to reduce or minimze interferences. Software for data accessing is Intuitive Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS). The ICP-MS operating conditions are described in Appendix 1.

Digestion tubes are made of borosilicate. Volumetric flasks are of 50 mL, 250 mL. All glasswares were (1) wash with tape water, (2) rinsed with milliQ water, (3) soaked in 10% HNO_3 overnight, (4) rinse with milliQ water and (5) left until dry.

The heating bath and filter presses were from Environmental Express. Heating bath was a Environmental Express HotBlock® 200 SC2015-96V240 Heating Block, 96-position, 15mL; 240 VAC. The heating block was ramped 3^{o}C/min from room temparature to reach 130 ^{o}C. After two hours, it was cooled down at the same rate to room temparature. Total ramping time was 3 hours. Uniformity between unit was ±2 ^{o}C. Filter presses were FilterMate SC0409 Digestion Cup Filter, Certified PVDF/ PTFE/ 0.45 µm/ 50 mL. Vials of the filter presses were of UltimateCupTM 50 mL with green caps.

2.2. Reagents and standards

Hydrochloric and Nitric acids were used to prepare aqua regia. Nitric acid was diluted to (1) 0.5N HNO_3 to dilute samples after they are digested, (2) to 2% HNO_3 to rinse the instrument, and (3) 10% HNO_3 to acid wash glassware. They are diluted by MilliQ water which was filtered through a system name (Millipore, USA). Multielement standards were diluted to 0.0025-5.0 ppm by 0.5N HNO_3 prior to each run. The experiment used the following reagents and standards listed on Appendix 2.

2.3. Sampling and sample treatment

Samples were collected from downstream to upstream, Poland Riverside Cemetery Memorials, Poland Library and Poland Municipal Forest, respectively. Each site was divided into 4 sub-sites which are about one meter away. Yellow Creek flowing through these three sites has gravel bed. Sediment accumulates behind the stable body such as rocks. The layer of sediment was not thick, and the sediment was scooped repeatedly to fill the 50mL vials.

- Cemetery, located between a road and cemetery which had the potential for nutrient run off, had the widest stream channel and the highest current, and the riparian zone was well covered with vegetation.

- Library, located behind The Municipal Poland Library in Poland. This site is susceptible to pollutants since it is adjacent to a large parking lot and under a road bridge (Route 224) which is busy all the time. Since it is in a crowded municipal region, there is a storm drain with dirty water, lots of matters with color dumped directly into the creek. This site had the lowest flow.

- Woods, located within the Poland Municipal Forest. People and animals are not allowed to get into the creek. This site has abundant vegetation, a very shallow stream with a normal current.

Samplings were carried in three seasons, 4- 5 times per season (Fall 2021, Spring 2022, Summer 2022). At each position, an amount of 100 g of sediment was taken in the middle and at the bottom of the creek. Sample containers are polyethylene vials which are specialized for ICP-MS. Sediments were dried at 105°C for 24 hours and then sieved through a non-metal membrane (size 1mm) to get rid of gravel. They were stored at room temperature until analysis.

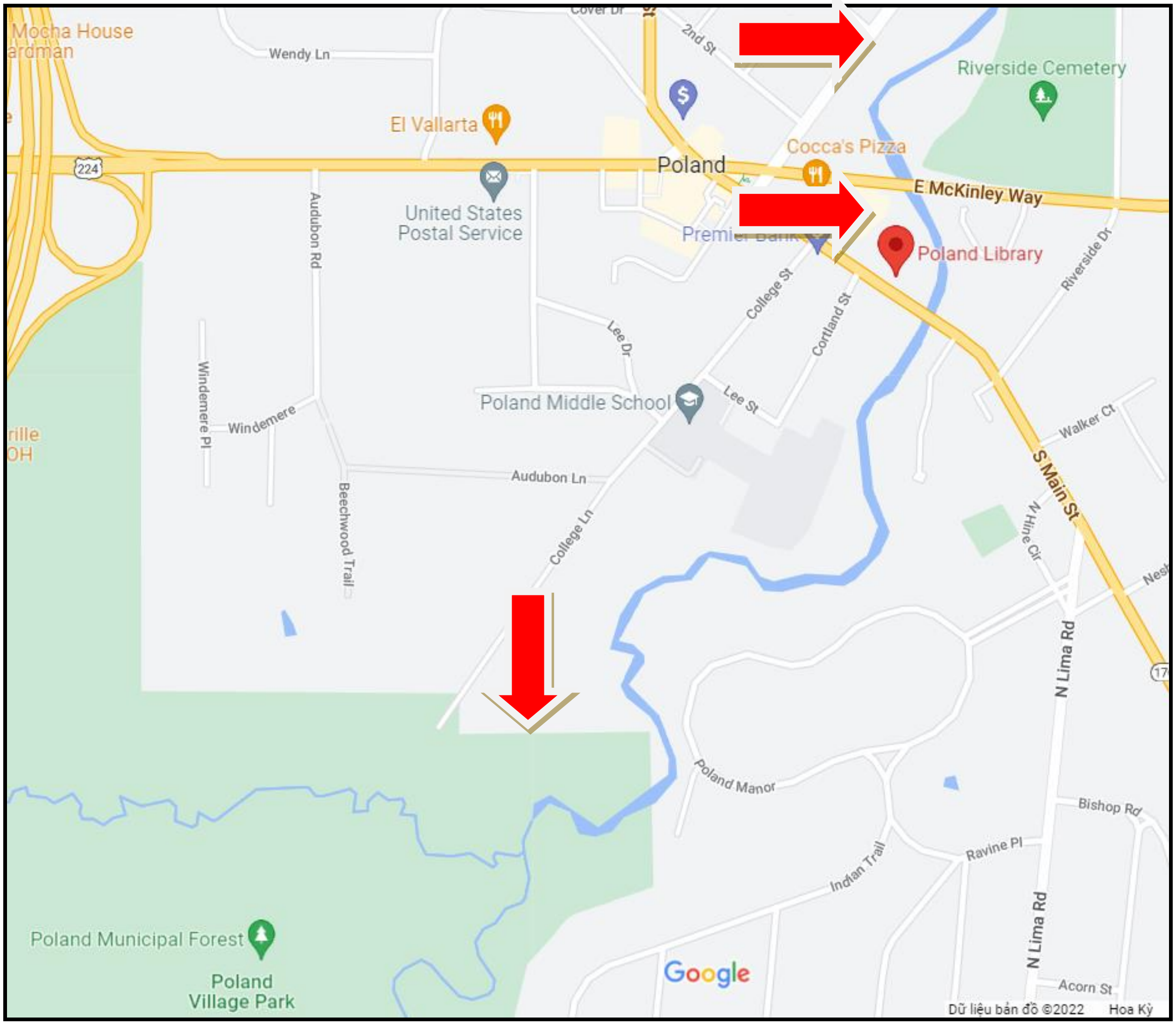


Figure 2.1 The three sampling sites (Poland Riverside Cemetery Memorials, Poland Library and Poland Municipal Forest)

2.4. Sample digestion

To determine metal content in sediment samples, firstly metals need to be extracted from sample matrix. This process uses concentrated acid or acid mixtures at high temperature so is called digestion. In general, the first object of this thesis is to establish a digestion procedure which is relatively efficient. Secondly, interference effects and internal standards are studied to control data quality in the ICP-MS, which is then applied to validate the digestion method. Finally, the validated digestion procedure and data control methods are applied to measure real samples collected along Yellow Creek, Poland, Ohio in three consecutive seasons. The procedure employs aqua regia which is a mixture of HCl -HNO_3 (18 mL – 6 mL). The digestion procedure took at least three days.

Samples were dried at 105^{o}C for 2 hours. 0.5000 g of each sample were first predigested with aqua regia overnight under hood at room temperature in 24 hours. Then, they were heated at 130_{o}C for 2 hours in a heating block until temperature of the heating block reached room temperature. The sample solutions were quantitatively transferred to filter press vials and residues in the tubes' wall were completely rinsed. These solutions were let to settle down overnight. After being filtered, these solutions were diluted to 250 mL for trace elements (Cr, Co, Ni, Zn, Cd, Pb). The solutions in 250 mL volumetric flasks were further diluted 50 times for major elements (Mg, Mn, Fe, Cu). This step directly relates to extraction efficiency.

The procedural blanks and standards solutions were treated in the same way as trial samples except for sediments. The later were added multielement standard 100 mg/L with various amount to obtain concentrations ranging from 0.0025-5.0 ppm.

2.5. Internal standards Y, Yb, Eu (2021/10/15), KED only

In order to better account for drift in the ICP MS response during measurements, a mixture of internal standards was added to each sample solution (and also the standard and blank solutions).

The measurements of the Buffalo River Sediment and the Tomato Leaves reference materials using the aqua regia extraction/ICP MS procedure were performed using internal standards.

Spike recoveries, calibration curves, limits of detection, and blank concentrations were determined, and the results were compared with and without internal standards. Internal standards was selected based on spike recoveries and the recovery of Buffalo river sediment.

2.5.1. Intermediate internal standard solution

The internal standard solution was prepared as follows: (1) Pipet 5.00 mL each of the Yb and Eu 1000 ppm standards and 1.25 mL of the Y standard into a 100 mL volumetric flask. (2) Dilute the mixture to 100 mL, mix thoroughly and then transfer the final solution to an acid washed plastic bottle for storage. This intermediate internal standard solution contains 50 ppm of Yb and Eu and 12.5 ppm of Y. (3) Pipette 1.00 mL of this intermediate solution to a sample digest, the final concentrations in the 250 mL sample solutions will be 200 ppb of Yb and Eu and 50 ppb of Y. (4) The internal standards are also added to all of the standards and blanks (to account for changes in the instrument response). The volumetric amount of the internal standard "spike" should be adjusted proportionally for standard and blank solution volumes that are different from 250 mL.

2.5.2. Proposed internal standard procedure

Following is a proposed procedure for using internal standards in the sediment samples. (1) After each sediment sample has been digested/extracted with aqua regia, transfer the sample solution to a filter vial and filter all the undissolved materials out of the solution. (2) Next transfer the filtered solution to a 250 mL volumetric flask. Be sure to rinse the filter vial with small amounts of 0.5N nitric acid to recover and transfer as much of the sample digest/extract solution as possible. (3) After the sample solution has been transferred to the 250 mL volumetric flask, add 1.00 mL of the intermediate internal standard solution mixture containing Yb, Eu and Y. (4) Finally dilute and mix the sample and internal standard solutions and bring the volume of the final solution mixture to 250 mL.

2.5.3. Instrument setup and calculations

Set up the ICP MS lab book and identify Y and Yb as internal standards in the analytes list. In the standards section, create list each element (Y, Yb) individually with its own concentration, i.e. "Internal Standard Y" "Internal Standard Yb". In the quantification section, select/activate the internal standard mode. By doing this, After the measurements have been performed, the observed results (concentrations) appeared in an excel file with percent recoveries of both Y and Yb nut had not been corrected yet. Corrected concentrations of elements in response of Y and Yb recoveries by multiplying the observed concentrations with 100 and then being divided by %Y (or Yb).

2.6. Statistical comparisons

2.6.1. Comparison with certified values

Comparison of experimental result to determine if experimental result does not agree with (is statistically different from) the certified value:

Experimental result = xexp + /- $s/N^{1/2}$

Certified result = $x_{cert} \pm ku_x$

Calculate tcalc for the difference of the two results:

$t_{calc} = [x_{exp} - x_{cert}] / [(s/N^{1/2})^2 + (ku_x/2)^2]^{½}$

To test the difference of tcalc to ttable, use 95% probability and n degrees of freedom for t_{table}

$\nu = [(s/N^{1/2})^2 + (ku_x/2)^2]^2 / [((s/N^{1/2})^4)/(N-1) + ((ku_x/2)^4)/60.4]$

2.6.2. Comparison of two means

Mean 1: $\bar{y}_1$, s_1; Mean 2: $\bar{y}_2$, s_2

$s_{pooled} = \sqrt{((N_1 - 1) \times s_1^2 + (N_2 - 1) \times s_2^2)/(N_1 + N_2 - 2)}$

$t_{calc} = [| \bar{y}_1 - \bar{y}_2| / s_{pooled}] \times \sqrt{((N_1 \times N_2)/(N_1 + N_2))}$

If $t_{calc} > t_{table}$ for 95% at $(N_1 + N_2 - 2)$ degree of freedom, then they are different.

2.7. Acetic acid extraction

2 samples of Buffalo River sediment and four samples of sediments from Poland Wood.

This study is to determine the appropriate dilution for each sample. Each sample was measured (1) directly, (2) after being diluted 5 times, (3) after being added aqua regia and diluted 5 times. Residues after being extracted with acetic acid were digested with aqua regia and measured (AcOH_Buff_Residue and AcOH_Poland_Residue).

Both sets of the samples were digested with aqua regia to get total concentrations of all elements.

Procedural blanks were also prepared together with all these samples. Yb was added to each sample to have concentration of 200 ppb.

The sum of elements' concentration from acetic extract and from the residues will be compared to the results from total extraction by aqua regia.

Acetic extraction is the first step of BCR three-step sequential extraction procedure [Figure 1.6]. 20 mL of 0.11mol/L AcOH was added to 0.5g of sediments in centrifuge tubes with caps. The sediments were shaken shake overnight at room temperature.

III. RESULTS

Table of results:

3.1 Sum of Pb versus individual Pb isotopes (206, 207, 208)

The determination of lead (Pb) by ICP MS is based on measurements of one or more stable isotopes. In these studies, Pb measurements are based on the sum of three Pb isotope intensities. This is done to account for effects of any variations in the abundance of 206, 207, and 208 isotopes on the overall results. The intensities of all Pb isotopes in each sample (procedural blanks, standards, and calibration curves) were summed.

$$\text{Total intensity Pb (corrected)} = [\text{intensity } (^{206}\text{Pb}) + \text{intensity } (^{207}\text{Pb}) + \text{intensity } (^{208}\text{Pb})]$$

The sum of intensities from all standard solutions were then used to build calibration curves and calibration equations. The sum of intensities of other samples were then used to determine the Pb concentrations based on the calibration equations.

From these results, it is observed that Pb amounts determined by summation of the responses for the 3 isotopes are roughly equal to the amount measured based on ^{208}Pb, however there appears to be sample to sample variations for the SRM 8704 results, indicating the measurements may need to be repeated or improved. Detailed results of Pb isotope study are mentioned on Appendix 3.

3.2 Detection limit

3.2.1. Calibration curves and Instrument detection limit, HNO_3 blank

The limits of detection are important for determining the amounts of each element that can be quantified in a given sample. The instrumental limits of detection have been determined by measuring 0.5 N HNO_3 blanks (16 samples) in both STD and KED modes.

When comparing calibration curves measured by the two modes, KED method provides y intercepts that are smaller than STD method, which suggests lower uncertainty in measuring signals of standards and blanks. The KED mode reduces the effects of possible polyatomic interferences, resulting in improving confidence of the measurement. As a result, KED is expected to provide more accurate intensities and concentrations in the samples and blanks. Furthermore, Y intercepts also show fewer negative values, suggesting there could be fewer interferences in the KED mode.

The slopes (m) by KED are lower than by STD as expected, as the measurements are more selective. KED has lower sensitivity since a portion of the analytes lose their energy after colliding with Helium and do not reach the detector. On the other hand, STD mode has larger signal and higher slopes, but this is not necessarily better.

In brief, KED mode brings about higher accuracy but lower sensitivity, STD has higher uncertainty but is more sensitive. To decide which mode is working properly, the two criteria are combined in a ratio called Limit of detection. The limits of detection (LODs) by KED are roughly 1x-10x lower than by STD as expected. Calibration data of all elements of interest is in Appendix 4.

In the calibration curve in figure 3.1, the slope is the sensitivity, the signal is the intensity of a given concentration. It is important to note that the signal is about magnitude but not stability of signal or signal of noise.

When concentration values of the blanks are determined, they are reported in units of ppm. Limit of detection (LOD) is the lowest concentrations of analytes that give signals statistically different from the background. LOD can then be calculated by using the standard deviation (s) of the blank values and multiplying it by 3, i.e. LOD = 3*s in units of ppm. LOD is inversely related to signal to noise ratio.

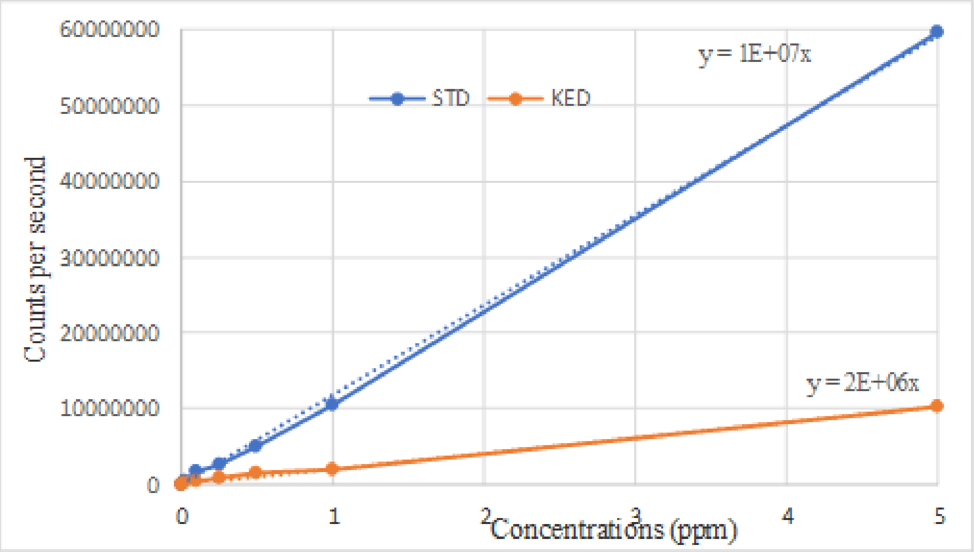


Figure 3.1: Calibration curves of ^{52}Cr measured by STD and KED modes

Even though KED has lower sensitivity, it has much lower background signal and as a result KED mode is overall better. Thanks to collision gas, KED is much more selective, and greatly reduces many interferences.

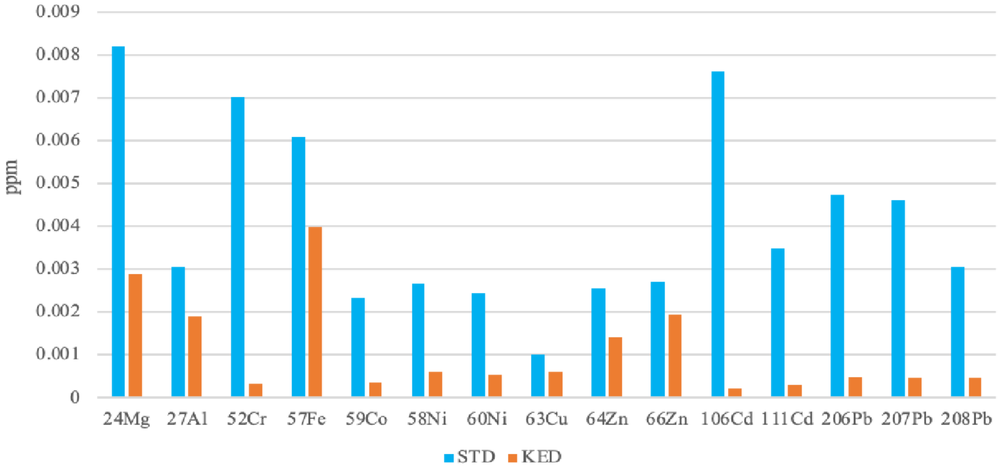


Figure 3.2. LODs of STD and KED modes (LOD of ^{57}Fe, $^{114\text{Cd}}$ not included)

As shown in the table below, the LODs are mostly in the range of 0.1 - 1 ppb for these elements, which is a reasonable value for the digested sediment samples that are targeted for measurement.

*Table 3.1. Instrument detection limit of both STD and KED modes compared to LOD provided by Thermo Scientific(**KED, HNO_3)***[22]

	STD (ppm)	**KED (ppm)**	**Appr. ratio**	**Thermo Scientific (ppb)**		**STD (ppm)**	**KED (ppm)**	**Appr. Ratio**	**Thermo Scientific (ppb)**
^{24}Mg	0.008	0.003	2.7	0.2	**^{63}Cu**	0.001	0.0006	1.7	0.001
^{27}Al	0.003	0.002	1.5	0.1	**^{64}Zn**	0.003	0.0010	3	0.003
^{55}Mn	0.08	0.0003	266.7	0.0005	**^{66}Zn**	0.003	0.0020	1.5	
^{57}Fe	0.006	0.004	1.5	0.02	**^{106}Cd**	0.008	0.0002	40	0.0003
^{52}Cr	0.007	0.0003	23.3	0.0005	**^{111}Cd**	0.003	0.0003	9.1	
^{59}Co	0.002	0.0004	5	0.0005	**^{114}Cd**	0.03	0.2000	0.2	
^{58}Ni	0.003	0.0006	5	0.001	**^{206}Pb**	0.005	0.0005	10	0.0005
^{60}Ni	0.002	0.0005	4		**^{207}Pb**	0.005	0.0005	10	
					^{208}Pb	0.003	0.0005	6	

As expected, the KED measurement provides better signal to noise and overall lower limits of detection than the STD mode. The ratios of the STD/KED LODs show that KED is typically 1-10 times more sensitive than STD. The KED mode is designed to reduce interferences which are plasma based or matrix based and the lower LODs suggest that the ICP MS measurements have higher accuracy (lower interferences) when KED mode was enabled.

3.2.2. Method detection limit (KED only)

Instrument detection limits were improved when measured with KED mode. From there, all measurements were conducted with this mode.

MDL was determined by measuring 16 samples of procedural blanks. 24 mL of aqua regia were digested and diluted to 250 mL. These blanks were run with calibration solutions. Internal standards (Y, Yb) were added to each solution. The internal standards were used in method detection limit in cooperation with spike recoveries and recoveries of Buffalo River sediment to decide which internal standard is the most appropriate.

MDL can then be calculated by using the standard deviation (s) of the procedural blank values and multiplying it by 3, i.e. LOD = 3*s in units of ppm.

Measurements of the background/blank levels of the elements in each of the different solution media (procedural blanks) with and without the use of internal standards to determine (LODs) with and without the use of internal standards were performed; to compare results when using individual internal standards or no internal standards. The limit of detections in Aqua regia were compared to those of blank nitric.

Table 3.2. Limit of detection with Aqua regia blanks and Nitric blanks

LOD-KED	**2022/02/13 Aqua-regia**	**2021/06/26 HNO_3**	**Elements**	**2022/02/13 Aqua-regia**	**2021/06/26 HNO_3**
^{24}Mg	0.001	0.003	**^{63}Cu**	0.0003	0.0006
^{27}Al	0.003	0.002	**^{64}Zn**	0.0008	0.001
^{55}Mn	0.0001	0.0003	**^{66}Zn**	0.0008	0.002
^{57}Fe	0.008	0.004	**^{106}Cd**	0.0003	0.0002
^{52}Cr	0.002	0.0003	**^{111}Cd**	0.00003	0.0003
^{59}Co	0.00002	0.0004	**^{114}Cd**	0.00002	0.0004
^{58}Ni	0.0006	0.0006	**^{206}Pb**	0.0002	0.0005
^{60}Ni	0.0007	0.0005	**^{207}Pb**	0.0002	0.0005
			^{208}Pb	0.0002	0.0005

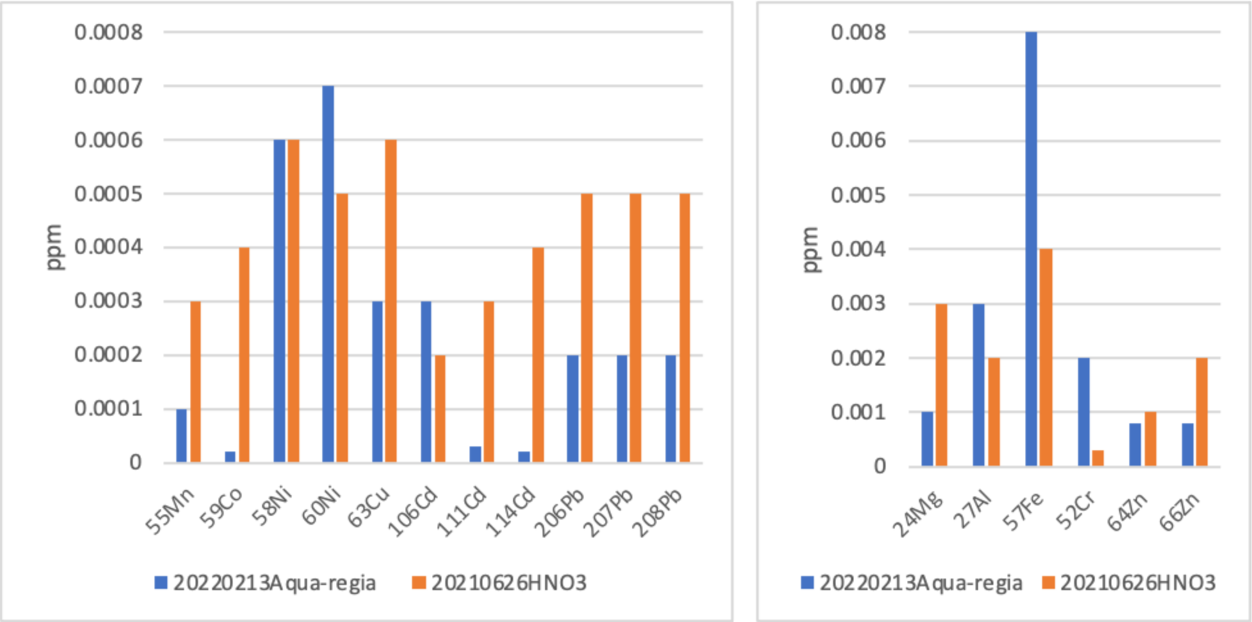


Figure 3.3. Limit of detections with Aqua regia blanks and Nitric blanks

Table 3.3. Limit of detection in this study and other literatures

	KED (ppm)	a[23]	b[24]	c[25]	d[25]		KED (ppm)	a	b	c	d
^{24}Mg	0.001					**^{60}Ni**	0.0007	0.04	0.18	0.51	7.75
^{27}Al	0.003					**^{63}Cu**	0.0003	0.03	0.15	0.57	2.58
^{55}Mn	0.0001	0.02	0.64	0.04	0.88	**^{66}Zn**	0.0008	2.3	2.8	8.24	14.2
^{57}Fe	0.008					**^{111}Cd**	0.00003	0.01	0.01	0.16	0.02
^{52}Cr	0.002	0.04	0.58	0.86	1.96	**^{206}Pb**	0.0002	0.01	0.58	0.27	0.56
^{59}Co	0.00002	0.01	0.01	0.03	0.03						

Limit of detections without internal standards and with Yttrium and Ytterbium were compared in Table 3.4.

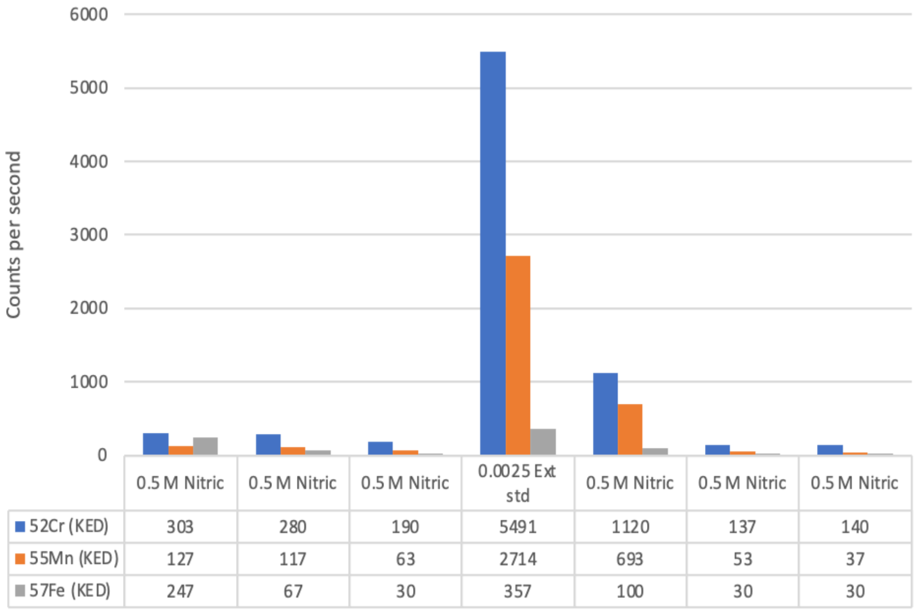
Table 3.4. Instrument limit of detection with and without internal standards

LOD-KED	No int_std	Y	Yb	LOD-KED	No int_std	Y	Yb
^{24}Mg	0.001	0.002	0.002	**^{63}Cu**	0.0003	0.0005	0.0004
^{27}Al	0.003	0.004	0.004	**^{64}Zn**	0.0008	0.001	0.001
^{55}Mn	0.0001	0.0002	0.0002	**^{66}Zn**	0.0008	0.001	0.001
^{57}Fe	0.008	0.01	0.01	**^{106}Cd**	0.0003	0.0005	0.0005
^{52}Cr	0.002	0.003	0.002	**^{111}Cd**	0.00003	0.00004	0.00004
^{59}Co	0.00002	0.00003	0.00003	**^{114}Cd**	0.00002	0.00003	0.00002
^{58}Ni	0.0006	0.001	0.0009	**^{206}Pb**	0.0002	0.0003	0.0003
^{60}Ni	0.0007	0.001	0.001	**^{207}Pb**	0.0002	0.0003	0.0002
				^{208}Pb	0.0002	0.0003	0.0002

3.3. Memory effect

Memory effect is a problem that can occur when using tubing system. Some metals whose solubility is not good tend to accumulate to the tube wall and cause inaccurate measurements.

In theory, intensities from 0.5N HNO_3 blank should be equal and close to background signals. This was not observed to happen as expected even rinse times and uptake times were 3 minutes and 2 minutes, respectively. When three blank samples were placed between unknown samples, the intensities of elements in the blank right after the unknown was higher than the following ones, causing positive bias if the tubing system were not rinsed carefully. Therefore, sufficient rinse time and blank solutions between unknown are the two solutions. All the runs in this thesis were inserted three blank nitric at the beginning, between different sets of unknown.



	0.5 M Nitric	0.5 M Nitric	0.5 M Nitric	0.0025 Ext std	0.5 M Nitric	0.5 M Nitric	0.5 M Nitric
■ 52Cr (KED)	303	280	190	5491	1120	137	140
■ 55Mn (KED)	127	117	63	2714	693	53	37
■ 57Fe (KED)	247	67	30	357	100	30	30

Figure 3.4. Memory effect of Chromium, Manganese and Iron

3.4 Investigation of background levels and isotope distribution

To demonstrate that the analytical procedure is free of background contamination, measurements were performed using different blank solutions including Milli Q water, 0.5 M Nitric acid, and procedural blanks. Intensities were plotted versus isotope values. The intensities (y values) are currently shown on logarithmic scales (not linear). For the milli q water samples, the first four (4) values are averaged, and that value was used for the milli q. For the 0.5 M HNO_3 and the procedural blanks, all the values of the same type are averaged, i.e. all of the 0.5 M HNO_3 values were averaged together and all of the procedural blanks were averaged together.

Overall, the KED method provides a somewhat better background compared to the STD as expected. This proves that KED remove interferences. The background levels of the elements generally increase going from the milli q water to the nitric acid solution to the procedural blanks (where the amounts of reagents increase). The low intensities of elements in the procedural blanks indicate that the analytical procedure is good, and that the lab environment is under control (glassware, surfaces, air, reagents, and procedure steps). Procedural blanks are generally only about 10x higher than water levels and are probably limited by the purity of the reagents.

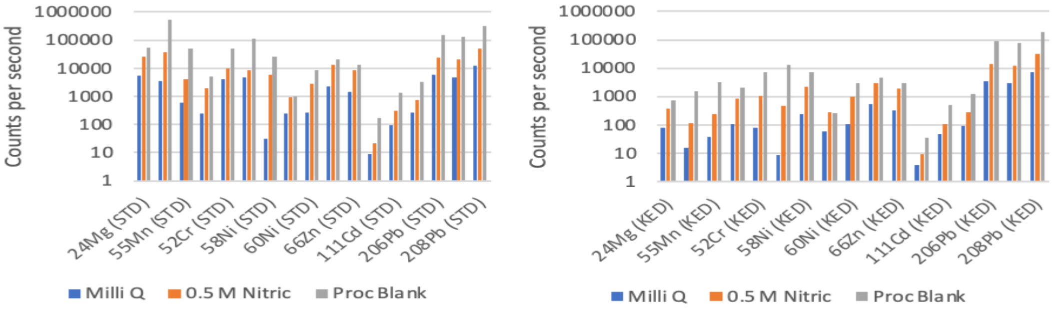


Figure 3.5. Charts of the background intensities measured for the milli q water (blue), 0.5 M HNO_3 (orange) and procedural blanks (gray) when measured by STD (Left) and KED (Right) modes.

3.5. Interference study

The method was calibrated with multielement standards as usual. Three samples of 0.5N nitric were run in between each type of interference solution. All multielement standards and interference standards were prepared diluted with 0.5N nitric.

Interference standards: Zr, Ti, Mo, Ca. Stock solution 1000 µg/mL. Dilute 250 µL, 500 µL, 2500 µL, 5000 µL, 15000 µL of each solution successively to 50 mL in volumetric flasks with 0.5N nitric, obtaining solutions with concentration ranging is 0.5-30 ppm. Interference standard solutions were measured as unknown in terms of intensities and concentrations for all elements of interest. Regression lines are correlations between intensities of interference and interfered elements.

Ca concentrations are very high in milli q water even when Ca standard was not added. 3-4 ppm; standard solutions: expected ConC+0.7 ppm.

Slope (sensitivity) of the regression line drawn by STD and KED mode: y-intercept (uncertainty) was reduced from 10 times to 600 times (Ca/Fe) by collision gas. KED removed interference for several elements. Correlation between intensities of inference and element of interest pronounce in STD mode but not KED mode. These are ^{59}Co and ^{66}Zn.

However, KED cannot completely remove interferences. Correction equations are still needed. The equations were formulated using the slope of the regression lines. All measurement of real samples were carried out in KED mode, only equations of KED mode are necessary. The equations were entered into the instrument setup to correct for real samples even after the measurement was completed. ^{59}Co and ^{66}Zn are not affected by interference in KED mode.

Table 3.5. Correction equations for elements of interest in KED mode

^{24}Mg	- 0.00001 * ^{90}Zr - 0.0003 * ^{48}Ti – 0.00008 * ^{40}Ca
^{52}Cr	– 0.00004 * ^{90}Zr – 0.000004 * ^{98}Mo - 0.00003 * ^{40}Ca
^{55}Mn	- 0.000008 * ^{90}Zr
^{57}Fe	- 0.00001 * ^{90}Zr – 0.00008 * ^{40}Ca
^{58}Ni	– 0.00001 * ^{90}Zr
^{60}Ni	– 0.000005 * ^{90}Zr
^{59}Co	– 0.0000006 * ^{90}Zr
^{63}Cu	– 0.000005 * ^{90}Zr – 0.00004 * ^{48}Ti – 0.000001 * ^{98}Mo
^{64}Zn	- 0.0002 * ^{48}Ti
^{106}Cd	- 0.0026 * ^{90}Zr
^{111}Cd	– 0.00006 * ^{90}Zr – 0.00006 * ^{98}Mo
^{114}Cd	– 0.0000006 * ^{90}Zr - 0.0001 * ^{98}Mo

Correction equations would be applied Buffalo samples and Poland samples. Details of Regression correlations between intensities of interference and their possible forms of interference and interfered elements are on Appendix 5.

Two isotopes of Ni (58, 60) did not have any change after their correction equation applied. ^{58}Ni is interfered by elements such as ^{57}Fe^{1}H, ^{41}K^{16}O^{1}H which were not studied. Correction effects pronounce more obviously in Poland sample but Buffalo River sediment. It is that their matrix is different. Nonetheless, those effects are relatively low compared to the original concentrations of elements in solvents (10^{-4}).

When comparing an isotope after being corrected with another isotope of the same element such as Cd (106, 111, 114). After ^{106}Cd concentrations were corrected. Its concentrations in Buffalo River sediment were close to those of ^{111}Cd, ^{114}Cd in the same samples. In Poland samples, ^{106}Cd concentrations corrected by the equations are still much higher than concentrations of the other two isotopes.

Details of metals concentrations were corrected and were not corrected by mathematical equations are on Appendix 6. In general, the applications of mathematical equations do not have effect on the mass ratios of metals in samples. These above equations would be applied in the measurement of Poland samples.

3.6. Spike recovery with internal standard

A known amount of elements were spiked into sample with its matrix. Spike recovery is the ratio between an observed amount compared to added amounts, no matter the original content of the same element in the samples.

3.6.1. Sample preparation

Samples are divided into two groups: spiked and unspiked samples. Spike recovery measurements have been performed where a second set of Buffalo River Sediment samples have been "spiked" with a known amount of the multielement standard solution used to prepare the calibration standards. The spike is added to the Buffalo River Sediment solutions after they have been digested/extracted but before they are diluted to in the volumetric flasks. Trace elements are Cu, Cr, Co, Zn, Ni, Cd, Pb and major elements are Mg, Al, Fe, Mn.

Internal standards were added to calibration solutions, blanks, procedural blanks, and all Buffalo sample solutions so that the final concentrations of Y and Yb are 200 ppm and 50 ppm, respectively.

From the concentration of unspiked samples, calculate average observed mass fractions.

Observed mass fraction (m.f.) = Corrected Concentration*250/ mass

Mass fractions of spiked samples were predicted based on the mass fraction above and the spike amount (0.5 mL * 100 μg/mL = 50 μg).

Predicted mass fraction of spiked samples = [(Sediment mass of trial * average m.f.) + 50]/ Sediment mass of trial. Observed mass fraction of spiked samples were calculated in the same way of unspiked samples. Spike recoveries of trace elements = (Observed m.f of spiked samples – Observed m.f of unspiked samples) *100/ (Predicted m.f - Observed m.f of unspiked samples)

Spike recoveries of major elements (in 50 mL volumetric flask) were calculated based on samples (B) which was spiked with 50 μg of multielement standard when diluted to 50 mL. Spike recoveries of major elements = (Observed concentration of spiked samples - Observed concentration of unspiked samples) *100.

Table 3.6. Preparation steps of spiked samples

Step 1: Trace elements	**Spiked samples (A)**	**Unspiked samples (B)**	
Mass (in triplicate)	≈ 0.5000g	≈ 0.5000g	
Multielement standards	500 μL	0 μL	
Dilute to	250 mL	250 mL	
Step 2: Major elements		**Spiked samples**	**Unspiked samples**
Further dilution		1mL of (B)	1mL of (B)
Multielement standards		500 μL	0 μL
Dilute to		50 mL	50 mL

3.6.2. Spike recovery

The range of spike recoveries is generally 80-120%. Elements whose recoveries were in this range include ^{24}Mg, ^{27}Al, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{66}Zn, all isotopes of Cd and Pb, while some having recoveries above the range are ^{52}Cr, ^{55}Mn, ^{58}Ni, ^{63}Cu, and ^{64}Zn. Recoveries of two isotopes of the same element such as Ni and Zn give some suggestions about interferences when the ratios differ from their natural abundances. Based on these results, ^{58}Ni and ^{64}Zn appear to be more severely interfered by other polyatomic interferences as compared to ^{60}Ni, ^{66}Zn. Among the three isotopes of Cd, ^{106}Cd appears to be the least affected by interference. The instrument gives reliable results for ^{24}Mg, ^{27}Al, ^{57}Fe, ^{66}Zn, ^{106}Cd, all isotopes Pb and their isotopes do not appear to be affected by the sample matrix for these samples.

Table 3.7. Spike recoveries obtained with and without internal standards

	WO itnstd	**Y**	**Yb**		**WO itnstd**	**Y**	**Yb**		**WO itnstd**	**Y**	**Yb**
^{24}Mg	101.8	97.7	103.3	**^{59}Co**	119.3	93.1	132.5	**^{106}Cd**	88.9	69.7	99.2
^{27}Al	101.0	95.4	101.8	**^{58}Ni**	129.1	94.1	134.7	**^{111}Cd**	113.8	89.2	127.0
^{52}Cr	127.2	96.1	137.2	**^{60}Ni**	119.0	91.7	130.6	**^{114}Cd**	114.4	89.7	127.6
^{55}Mn	132.6	130.1	135.8	**^{63}Cu**	124.2	97.7	133.8	**^{206}Pb**	97.3	70.8	101.4
^{57}Fe	101.2	91.2	100.1	**^{64}Zn**	149.3	102.2	147.0	**^{207}Pb**	100.0	73.3	105.0
				^{66}Zn	110.7	74.7	107.6	**^{208}Pb**	100.3	73.5	105.2

As shown in figure 3.6, Y and Yb as internal standards brought about different results. Compared to the original recoveries without using internal standards, Y reduced while Yb generally improved the spike recoveries of elements of interest. Based on the results of these studies, Yb appears to be more appropriate for the measurement of Buffalo River sediment.

Spike recovery indicated the effect of the sample matrix on the measurements of elements. If the spike recoveries are high and recoveries of the same element in Buffalo River sediment are low, the low recoveries are due to low extraction efficiency (^{24}Mg, ^{52}Cr, ^{57}Fe, ^{66}Zn, all isotopes of Pb). High recoveries of an element in both spike samples and Buffalo River samples are likely due to interferences (^{58}Ni). Spike recoveries also contribute to internal standard selection.

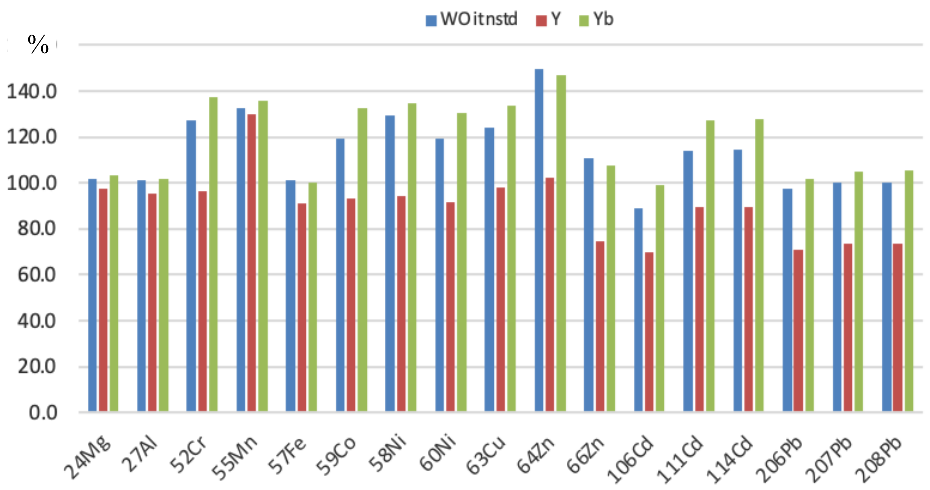


Figure 3.6. Spike recoveries obtained with Y (red bars), Yb (green bars) and without internal standards (blue bars)

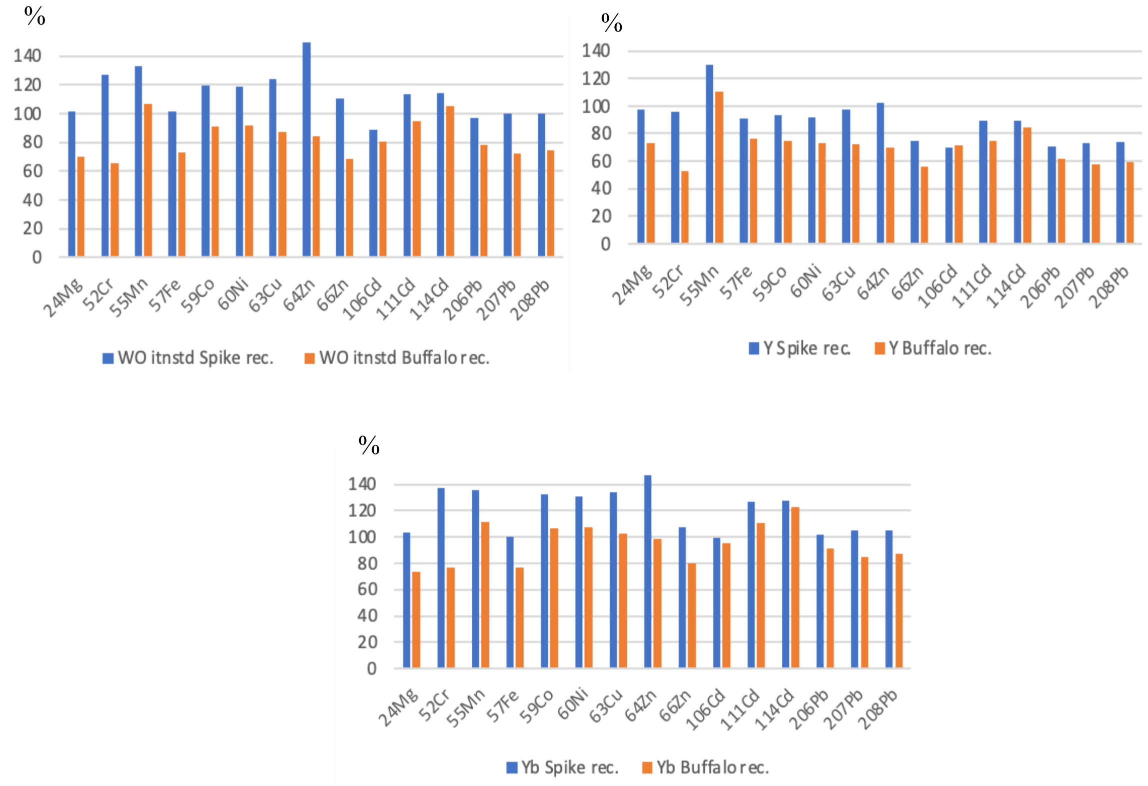


Figure 3.7. Spike recovery (blue bars) and Buffalo River sediment recovery (orange bars) obtained with and without internal standards. Details are on Appendix 7

3.7. Buffalo river sediment recovery and internal standard

The method developed in these studies was used to measure metals in real sediment samples. It should be evaluated by comparing to a reference material with similar sample matrix. Mass fractions of elements in the reference material are all certified by using different instrumental methods. To evaluate the metal extraction efficiency, the measured amounts using the proposed method were compared to the certified values and reported in terms of recoveries.

In addition, the recoveries found in this study were compared to those reported previously (EPA methods), which all were measuring the same Buffalo River Sediment reference material (Table 3.9). Aqua regia extraction provides higher recoveries compared to HNO_3, HNO_3-HCl (3:1) but is lower than those digested by HF. Results of the last column is from samples digests by aqua regia also. Recoveries in this study are equal or higher than that one.

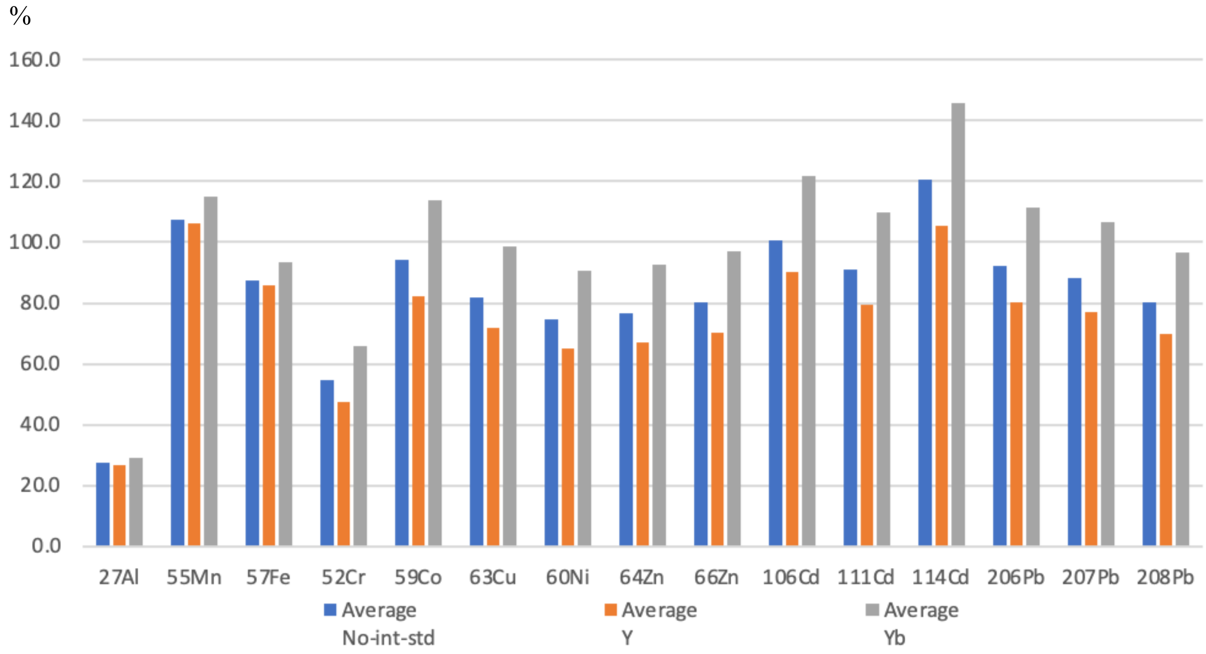


Figure 3.8. Average recoveries of Buffalo River Sediment in four experiments

Table 3.8. Average recoveries of Buffalo River sediment in four experiments

	WO itnstd (%)		Y		Yb	
	Average	s	Average	s	Average	s
^{27}Al	27.4	1.5	26.8	3.6	29.3	1.8
^{52}Cr	54.5	4.6	47.5	5.1	65.9	5.9
^{55}Mn	107.5	17.3	106.4	26.9	114.9	20.5
^{57}Fe	87.4	4.8	85.6	10.0	93.3	5.2
^{59}Co	94.1	3.0	82.3	5.9	113.9	5.2
^{60}Ni	74.7	5.9	65.2	7.5	90.4	7.5
^{63}Cu	82.0	15.2	71.7	14.8	98.7	16.1
^{64}Zn	76.8	5.6	67.0	5.9	92.7	4.3
^{66}Zn	80.4	7.9	70.2	8.2	97.1	7.8
^{106}Cd	100.7	9.4	90.1	8.6	121.6	10.2
^{111}Cd	90.9	8.3	79.5	8.4	109.8	9.3
^{114}Cd	120.7	12.1	105.4	12.5	145.7	13.2
^{206}Pb	92.0	6.8	80.2	5.1	111.2	7.3
^{207}Pb	88.1	3.5	76.9	4.1	106.5	1.9
^{208}Pb	80.1	4.5	69.8	4.3	96.7	3.4

As shown in table 3.8, the recoveries of elements are generally higher than 70%. Those of Co, Ni, Cd are even higher than 100% and are identified as having positive bias. Bias can be introduced during sampling, analysis, and data evaluation. In this study, the positive bias can be due to some following reasons. Buffalo River sediment samples may not have been shaken sufficiently before being weighed. Sample solutions also may not have been shaken sufficiently before being diluted. In the ICP-MS, metals can accumulate in the tubing system and increase the concentrations of these metals the following samples. Interferences can also make recovery higher than the real amount of the metal in the samples.

This appears to be due to polyatomic interferences from argon gas, chlorides from Aqua-regia (NaCl interferes with Ni), Ca (CaO interferes with Ni), and Mo (MoO interferes with Cd) in the matrix. Another reason relates to the trace level of these elements in the samples, where a small error due to a polyatomic interference can cause a relatively large error in the apparent recoveries. Future studies will focus on methods for reducing or correcting these interferences. The aqua regia extraction and ICP MS measurement procedure will continue to be developed and validated using reference materials and then applied to measurements of metals in environmental soil and sediment samples.

The average recoveries calculated using internal standards (Y and Yb) are all higher than recoveries obtained with using internal standards. A statistical test can be used to evaluate whether the higher recoveries calculated using internal standards are statistically different from those obtained without internal standards. These tests are comparisons between recoveries without internal standard and Ytterbium, and between recoveries without internal standard and Yttrium.

Statistical tests make it easier to differentiate effects of internal standards on the observed recoveries. The two standards correspond for two groups of elements. Yttrium can make up for the instrument drift of elements at lower mass which are ^{27}Al, ^{55}Mn, and ^{57}Fe while Ytterbium works well for ^{52}Cr, ^{59}Co,^{58}Ni, ^{60}Ni, ^{63}Cu, ^{64}Zn, ^{66}Zn, all isotopes of Cd, and all isotopes of Pb. The tests of all elements are at confidence level 95% except for ^{27}Al and ^{64}Zn which are both at 90%. As the results in Table 3.11 indicate, the internal standards did improve recoveries of all the elements. Detailed data of Statistical comparisons of recoveries when using internal standards are on Appendix 8.

A further comparison was performed to test the differences between the mean mass fraction of four runs (20220416, 20220426, 20220426, 20220426) with respective internal standards for two group of elements and certified value in Buffalo River sediment certificate. Appendix 9.

As the results in table 3.12 show, in comparison to the certified values, the observed recoveries of elements corrected using internal standards are statistically:

- Higher than the certified value for **^{55}Mn**
- Lower than certified value for **^{27}Al**, **^{52}Cr, ^{57}Fe, ^{64}Zn, ^{106}Cd, ^{114}Cd.**

- Not different from the certified value for **^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{111}Cd, ^{206}Pb, ^{207}Pb, ^{208}Pb.**

According to EPA for evaluations of ICP-MS data, if the recovery of an analyte is > 120% or < 20%, the sample results are non-detects, and the data should not be qualified.[26] As shown in Table 3.19, the recovery of elements of interest in this study are good.

Table 3.9. Recoveries (%) of elements compared to other literatures [27]

	This study (Int std Yb)	HNO$_3$	HNO$_3$–HCl (3:1, v/v)	HNO$_3$-HF (9:4, v/v)	**Aqua-regia**	**Aqua-regia** (J. Sastre et al)	**70% HNO3, 40% HF, 70%, HClO4 and 30% H2O2** (J. Sastre et al)
^{27}Al	29.3						
^{52}Cr	65.9	62.7	57.1	98.4	**65.93**		
^{55}Mn	114.9						
^{57}Fe	93.3						
^{59}Co	113.9						
^{60}Ni	90.4	103.2	95.7	98.9	**99.77**		
^{63}Cu	98.7					**95.45**	**91.3**
^{64}Zn	92.7			100.9	**97.48**	**97.58**	**105.63**
^{66}Zn	97.1						
^{106}Cd	121.6	98.6	104.9	101.5		**95.74**	**111.32**
^{111}Cd	109.8						
^{114}Cd	145.7						
^{206}Pb	111.2	101.2	100	96.3	**90.68**	**103.33**	**107.14**
^{207}Pb	106.5						
^{208}Pb	96.7						

Except for elements that have only one main isotope (Al, Cr, Mn, Fe, Co, Cu), isotopes of other elements (Ni, Zn, Cd, Pb) were selected based on method's figures of merit and interference study. All isotopes were measured throughout the study. They were then compared in terms of limit of detection, probability of being interfered by other elements in the interference study, spike recovery and Poland sediment recovery. The isotope selection in this study is similar to those selected by Luis Arroyo et al (2010)[28]. The study selected ^{27}Al, ^{52}Cr, ^{55}Mn, ^{57}Fe, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{111}Cd, $^{206, 207, 208}$Pb.

Table 3.10: Comparisons of isotopes

	Limit of detection (µg/g)	Interference study (Intensity)	Spike recovery (%)	Buffalo river sediment recovery (%)	Isotope selected
^{58}Ni	0.0006	$0.0001*^{90}$Zr	134.7	400-500	^{60}Ni seems to suffer less from interference and has good recovery.
^{60}Ni	0.0005	$0.000005*^{90}$Zr	130.6	90.4	
^{64}Zn	0.001	$0.0002*^{48}$Ti	147.0	92.7	^{66}Zn is not affected by interference and has good recoveries.
^{66}Zn	0.002	None	107.6	97.1	
^{106}Cd	0.0002	$0.0026*^{90}$Zr	99.2	121.6	^{111}Cd has better detection limit, appears to be not affected by interference, has good recoveries
^{111}Cd	0.0003	$0.00006*^{90}$Zr+ $0.00006*^{98}$Mo	127.0	109.8	
^{114}Cd	0.2	$0.0000006*^{90}$Zr+$0.0001*^{98}$Mo	127.6	145.7	
^{206}Pb	0.0005	None	101.4	111.2	^{208}Pb appears to have sample variations for the SRM 8704 results
^{207}Pb	0.0005	None	105.0	106.5	
^{208}Pb	0.0005	None	105.2	96.7	

3.8. Poland samples

Sediment samples collected in Fall 2021, Winter 2022 and Spring 2022 were measured. The elements and corresponding isotopes measured are ^{27}Al, ^{55}Mn, ^{57}Fe, ^{52}Cr, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{111}Cd, ^{206}Pb. Measured concentrations were corrected using ^{174}Yb added to each sample as an internal standard. Samples were digested and measured along with Buffalo River Sediment SRM 8704.

Four samples were collected at subsites at each location (Wood, Cemetery and Library). Mass ratios of elements at the four subsites were averaged and relative standard deviations were calculated. Results are presented in appendix 10-19 below, in which W is wood, C is cemetery and L is library.

Table 3.11. References for metal levels in sediments

	Freshwater Sediment Screening Benchmarks (µg/g)[29]	Probable effect concentration (µg/g)[30]
Cd	0.99	4.98
Cr	43.4	111
Co	50	
Cu	31.6	149
Fe	20000	
Pb	35.8	128
Mn	460	
Ni	22.7	48.6
Zn	121	459

Metals were evaluated individually and changes in concentrations over time (5 sampling days) of 5 elements (Mn, Fe, Cr, Cu, Zn) in samples from the wood were compared using ICP-MS and XRF results. Metal concentrations measured by ICP-MS are converted from ppm to % to make it easier to compare between the two set of data. Detailed comparisons are in Appendix 20.

3.8.1. Aluminum

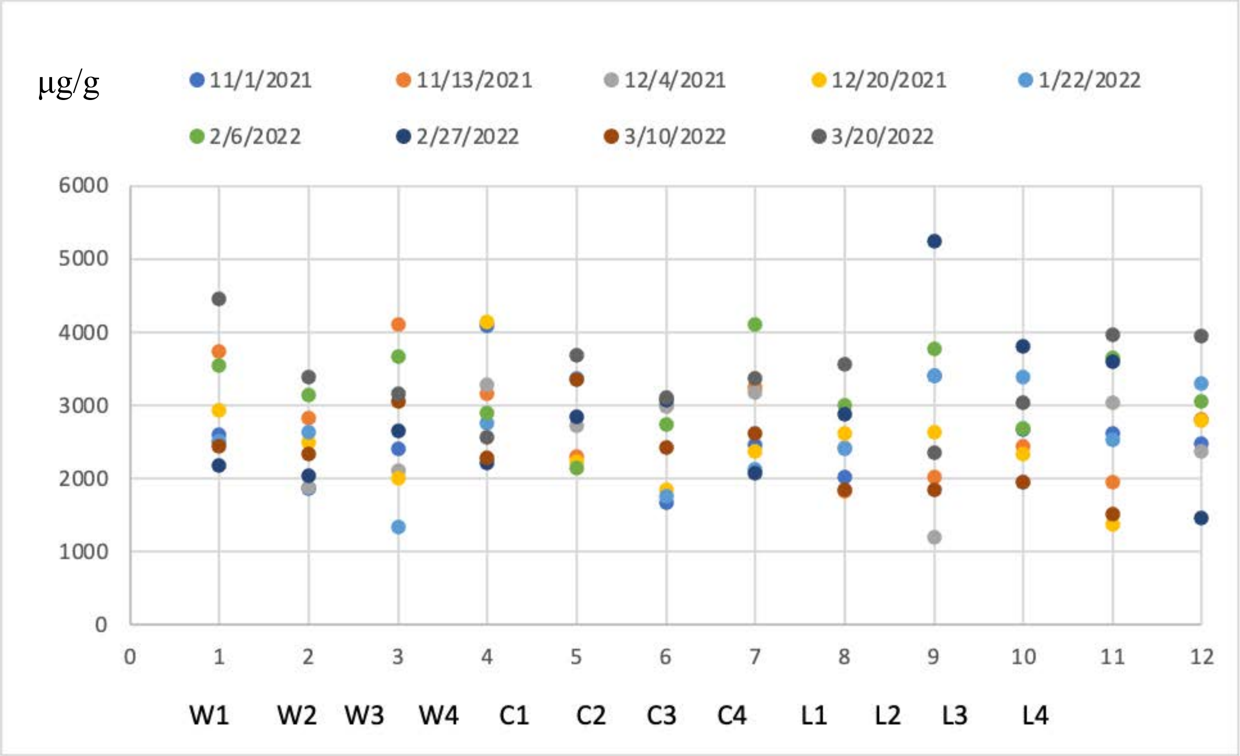


Figure 3.9: Mass ratios (µg/g) of Al measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

Aluminum is expected to be released in acidic conditions such as acid rain or acidic industrial waste. High concentrations of aluminum in the water are toxic to fish at concentrations between 500 µg/L[31].

As shown in Figure 3.9 and Appendix 10, Al mass ratios in Yellow Creek sediment are in the range of 1000-5000 µg/g. Even though ICP-MS can measure Al, its recovery in reference material is about 29.3 ± 1.8 % by the current method due to the extraction process. Al has a high affinity for oxygen and its oxide is a very stable compound[32]. To have better evaluation on Al concentrations, it should be measured by direct methods such as XRF.

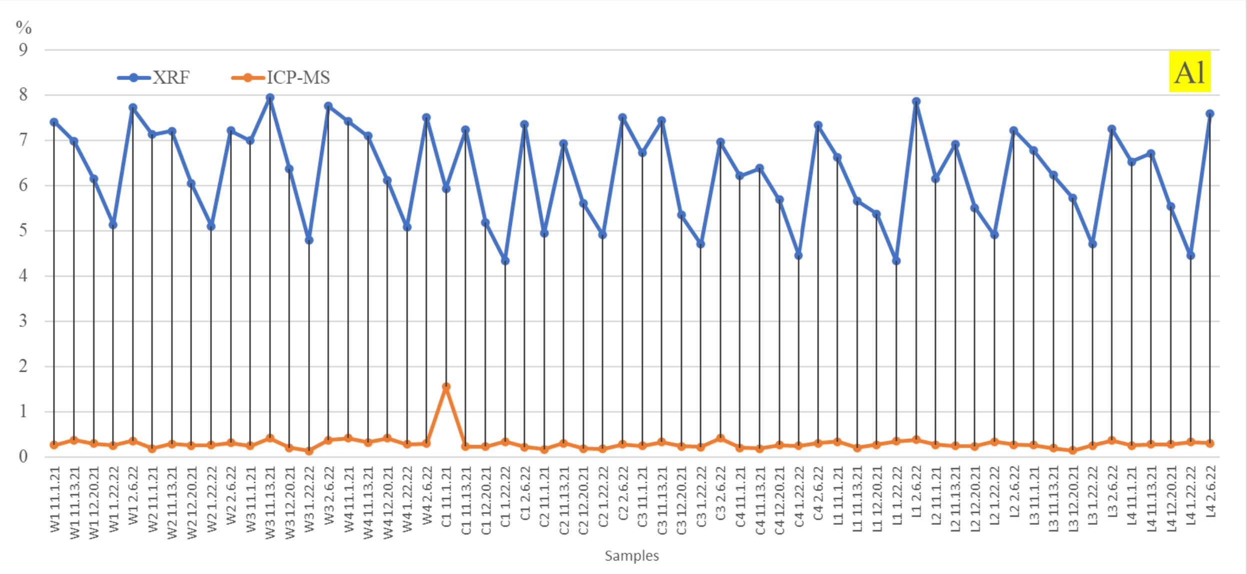


Figure 3.10. Mass ratios (%) of Al measured by XRF and ICP-MS

As shown in Figure 3.10 and Appendix 20, Al mass ratios are in range of 4-7% (40000-70000 µg/g), which is more than x40 times higher than results measured by ICP-MS. Al can be leached from the sediment under very critical conditions (aqua-regia). The releasing of Al in the aquatic system is affected by sediment mineralogy, pH and the presence of other ions. Therefore, to better evaluate the effect of Al on aquatic species, Al concentrations in water should be measured.

As shown in Figure 3.11, there are fluctuations of Al concentrations in different sampling days and at different sampling sites. Al determined by ICP-MS from the four subsites of the wood have similar trend. When comparing Al concentrations in samples collected in three different sites, higher concentrations of Al were observed more often in the site of Library, in 3/9 sampling days.

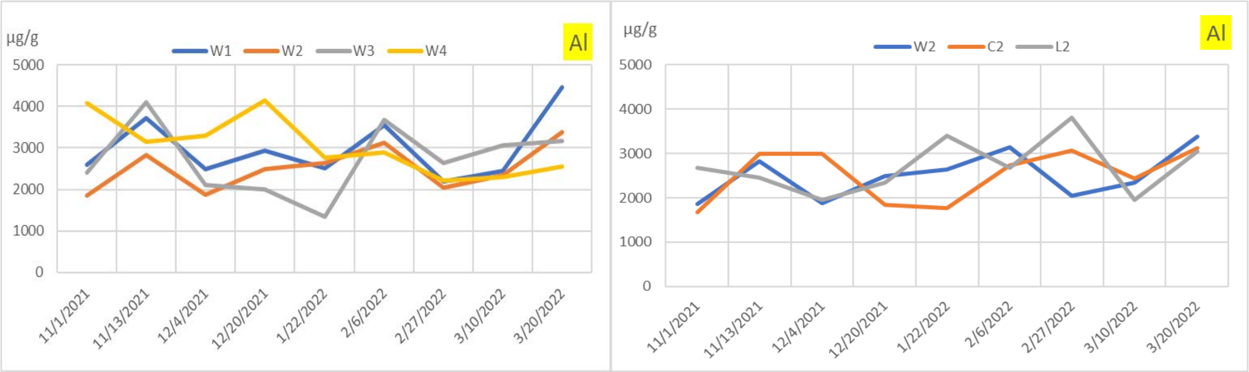


Figure 3.11. Spatial and seasonal variations of Al in Yellow Creek sediments. (Left: samples from 4 subsites from the wood (W1, W2, W3, W4), Right: samples from the Wood-W, Cemetery-C and Library-L)

3.8.2. Manganese

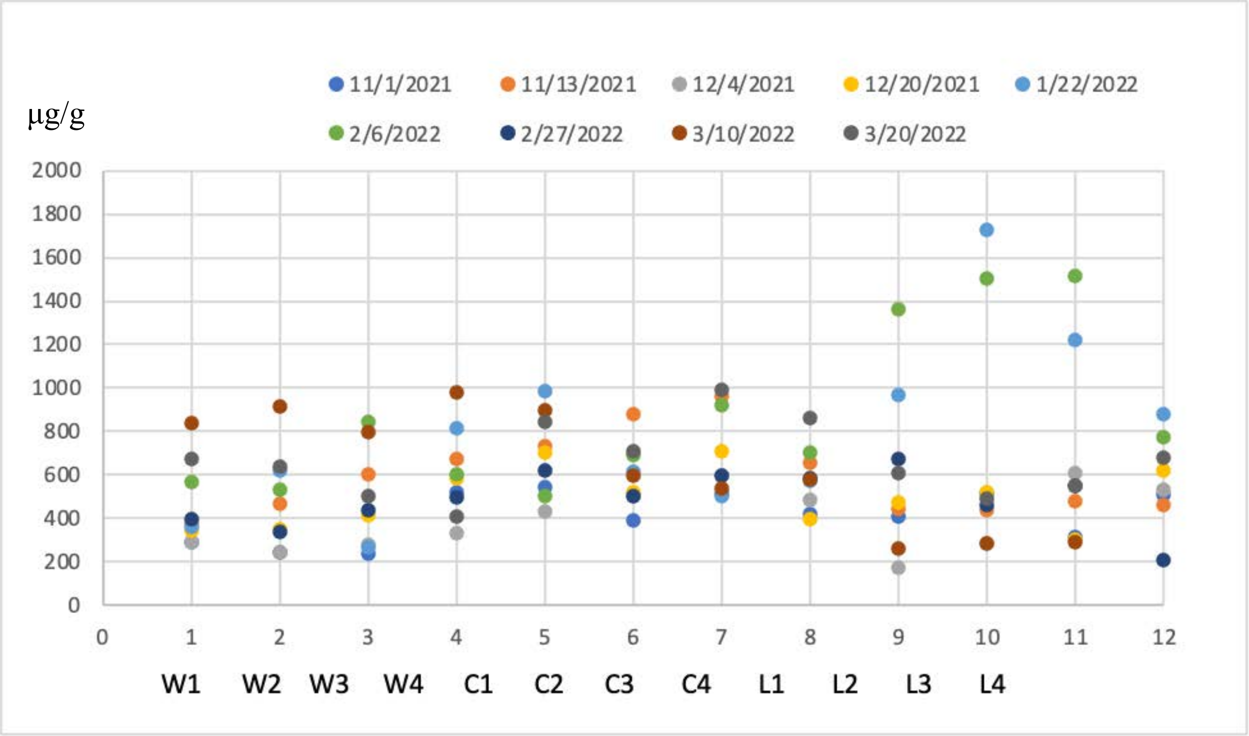


Figure 3.12. Mass ratios (μg/g) Mn measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

Manganese is an essential element for fish but becomes toxic at high concentrations. Suspended sediments can absorb Mn and act as a means of Mn transport[33]. Mn is dissolved from the reduction of Fe and Mn oxides. This can be related to the the degradation of organic matter or other reductants[34].

As shown on Figure 3.12 and Appendix 20, Mn concentration in the Yellow Creek sediment is in the range of 200-1800 µg/g. According to EPA Freshwater Sediment Screening Benchmarks in Table 3.11, the level of Mn in many sediment samples are higher than the benchmark (460 µg/g). Mn solubility/accumulation is affected by the presence of oxygen. The water body of Yellow Creek is shallow and has high flow and high turbulence suggesting dissolved oxygen levels can be high. This probably leads to the formation of Mn oxide which is insoluble[35]. This can be one of the reasons Mn concentrations in the sediments are high.

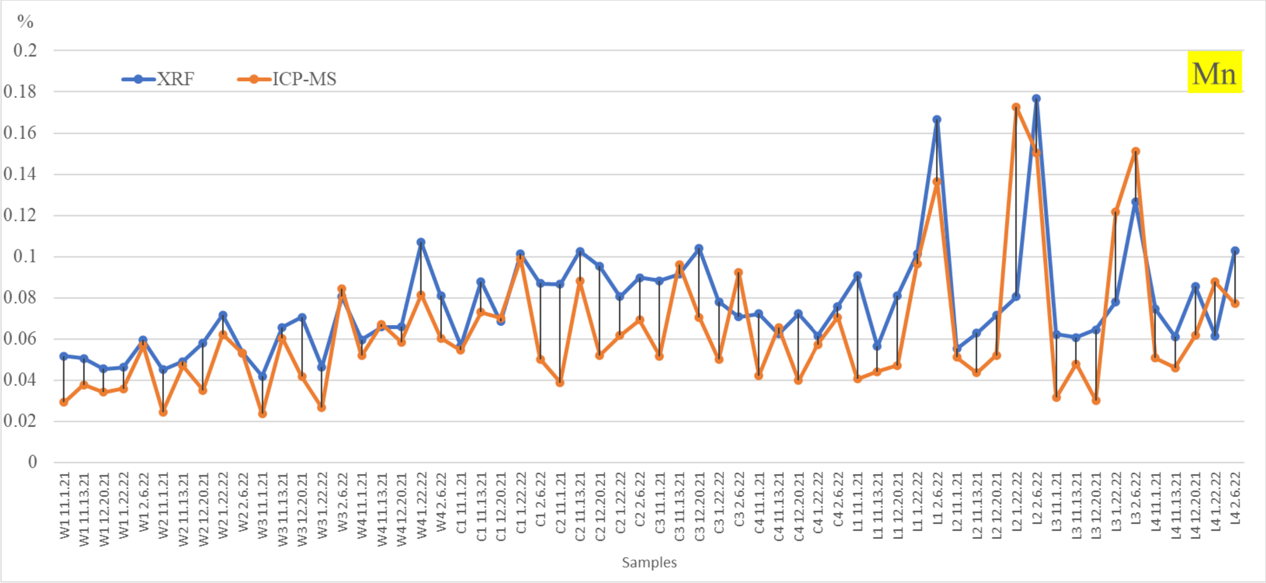


Figure 3.13. Mass ratios (%) of Mn measured by XRF and ICP-MS

As shown in Figure 3.13 and Appendix 20, mass ratios of Mn measured by XRF and ICP-MS are in good agreement. The concentrations measured by the two methods are close. One of the reasons is that Mn has good recovery in Buffalo River sediment 114.9 ± 20.5 %, suggesting that Mn is efficiently extracted by this method. Both sets of results follow the same trend and suggest both methods provide reliable results for Mn.

Samples L1 2.6.22, L2 2.6.22, L3 2.6.22 show high concentration of Mn. These samples are collected on the same day. The high concentrations are not because of interferences in either method. The elevated concentration may be due to factors at the sampling sites such as storm waste. Among all the elements measured by both methods in this study, Mn showed the best agreement.

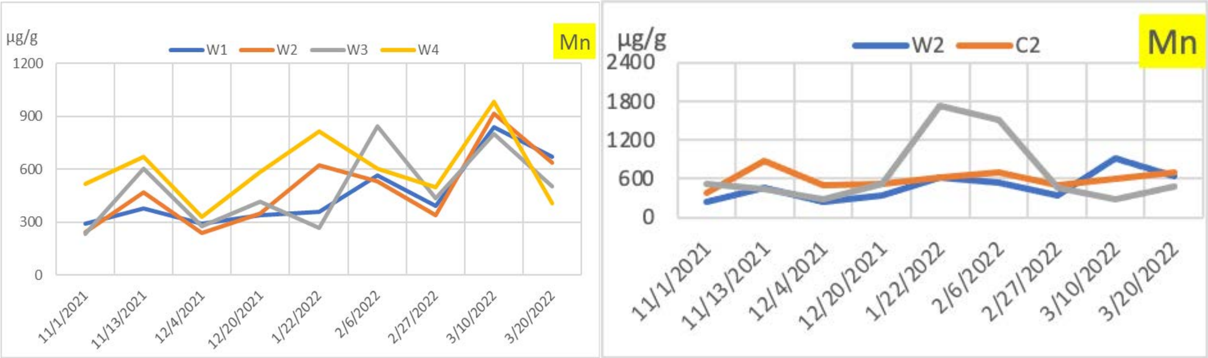


Figure 3.14. Spatial and seasonal variations of Mn in Yellow Creek sediments (Left: samples from 4 subsites from the wood (W1, W2, W3, W4), Right: samples from the Wood-W, Cemetery-C and Library-L)

The sediments from four subsites of the woods are in good agreement for Mn concentration and are all relatively close. At the woods, there is less chance of metals or dust getting into the creek from human activity.

Samples collected from the library on January 22 and February 06, 2002, have high concentrations of Mn. According to the weather report, there was almost no precipitation or melted ice on those two days (0.00-0.01 Inch) so it may be that Mn was released from the storm waste drain located nearby.

3.8.3. Iron

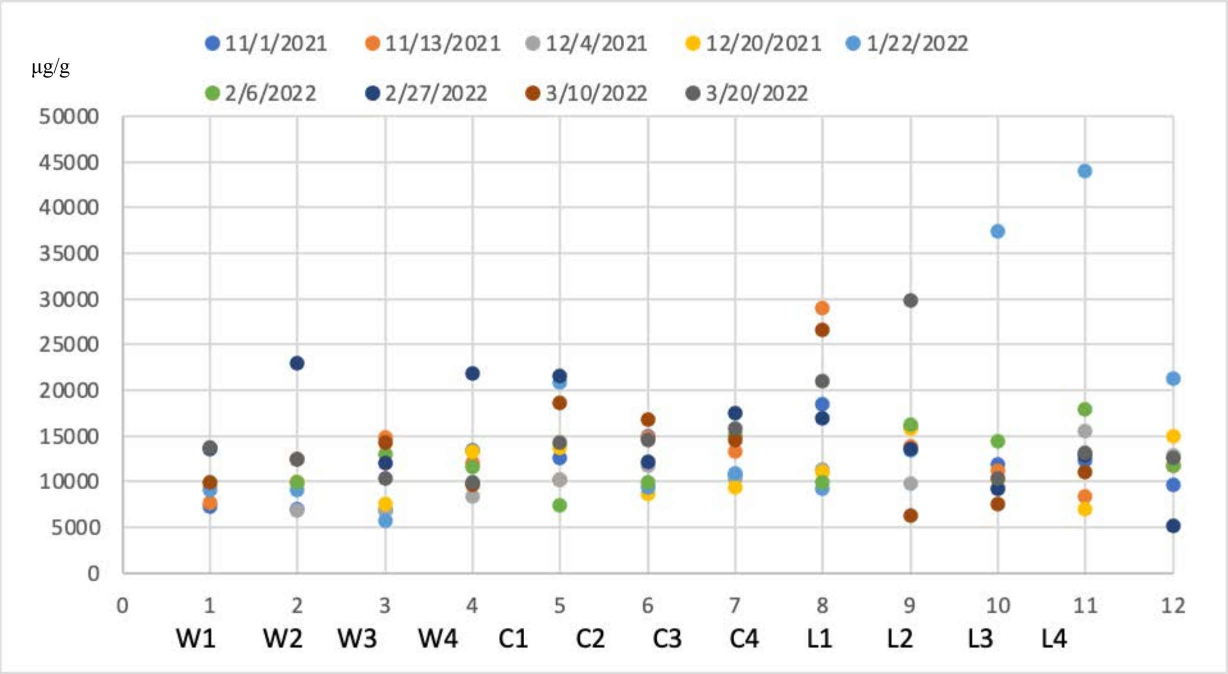


Figure 3.15. Mass ratios (µg/g) Fe measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

Iron is an abundant element in water, seas, and ground water. Fe (II) and Fe (III) are the main species of concern in the aquatic environment. Fe (II) is oxidized to Fe (III) in the presence of dissolved oxygen and Fe (III), iron hydroxide and iron oxide, precipitates to the bottom sediments, and have bad effects on aquatic life such as bottom-dwelling invertebrates, plants or incubating fish eggs. The Fe concentration limit in water needed to protect aquatic life is 1000 µg/L (total recoverable)[36].

According to EPA Freshwater Sediment Screening Benchmarks in Table 3.11, several samples have Fe concentrations higher than 20000 µg/g. As shown in Figure 3.15 and

Appendix 12, Fe concentrations measured by ICP-MS are in range of 5000-45000 µg/g. Sample C1 and C4 at the cemetery site have elevated concentrations, which may be due to the steel bridge and metal fragments collected with the sediment. Several samples collected from the library (L2 1.22.22, L3 1.22.22) site have relatively high concentrations of Fe. This needs to be double-checked with the results of XRF.

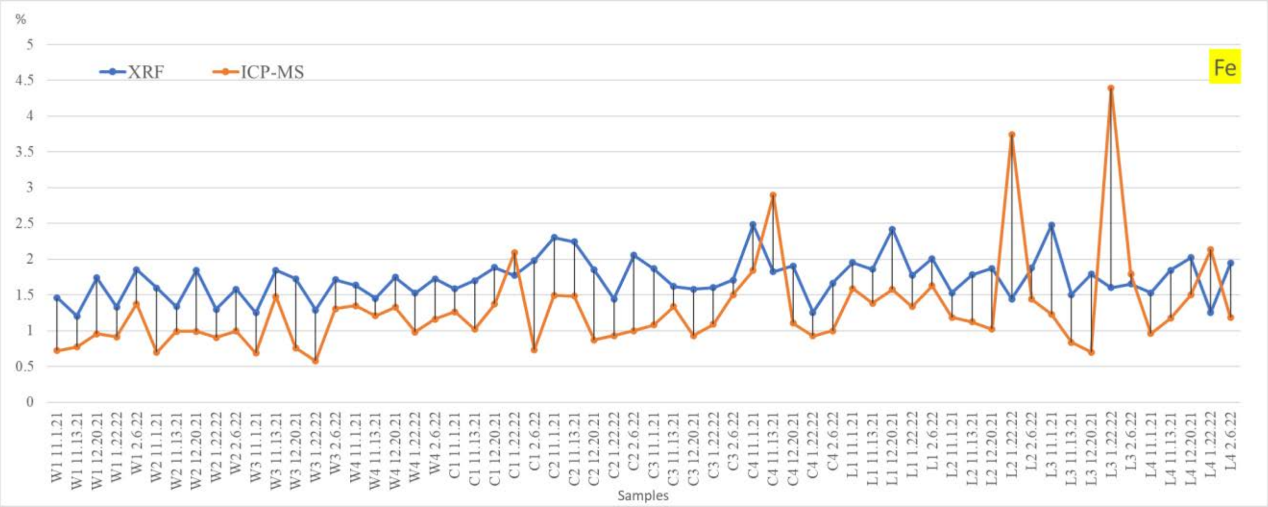


Figure 3.16. Mass ratios (%) of Fe measured by XRF and ICP-MS

As shown in figure 3.16 and Appendix 20, Fe was measured in 60 sediment samples by both ICP-MS and XRF. The two sets of results are in good agreement, having close concentrations (in %) and having the same trend through 60 samples. Iron recovery in Buffalo River sediment is 93.3.4 ± 5.2 %.

However, L2 1.22.22, L3 1.22.22 have high concentration when measured by ICP-MS but lower when measured by XRF. The problem is not caused the the sediments themselves. This may be due to sample contamination in the digestion process. Vials were covered by the reflux caps which could mean that dust from the hood is able to get into the samples and possibly contaminate the samples with Fe. It is also possible that some samples had locally high concentrations of Fe containing sediment.

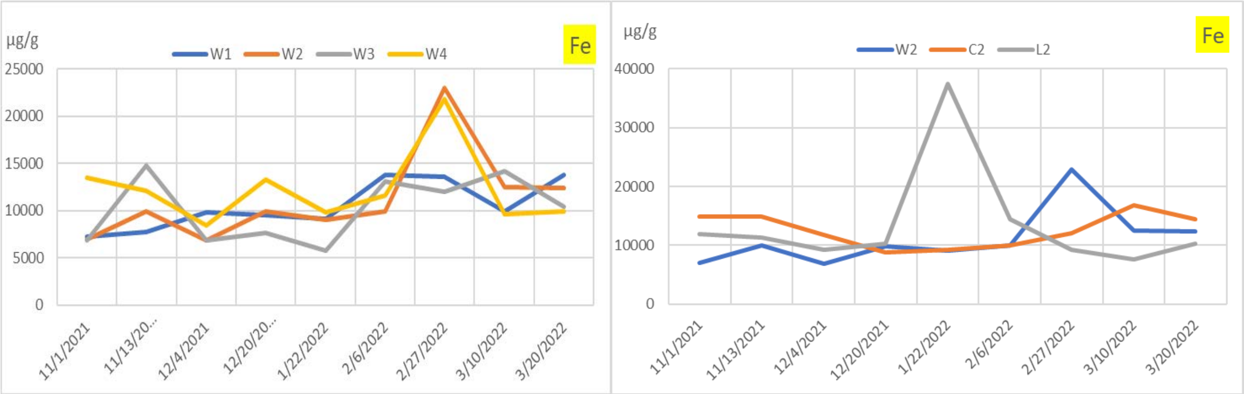


Figure 3.17. Spatial and seasonal variations of Fe in Yellow Creek sediments (Left: samples from 4 subsites from the woods (W1, W2, W3, W4), Right: samples from the Wood-W, Cemetery-C and Library-L)

As shown in Figure 3.17 and Appendix 12, the correlation of Fe concentrations in sediments collected from the four subsites is relatively good. There are variations between W1, W3 and W2, W4 in samples collected on 2/27/2022. Regarding spatial variations, Fe concentrations in samples from three different sites also have good agreement except for L 2 2.6.22 which was explained above.

In order to make evaluations of the correlation of Fe and Mn concentration easier to visualize, Fe concentrations were divided by 10. As shown in figure 3.18, Fe and Mn show a similar trend when measuring 60 samples. The two metals are likely to occur in the sediment in form of Fe-Mn oxide and may both accumulate in the sediment. When the redox and acidity of the aquatic environment change, they may respond in a similar way. This trend may also affect the accumulation of elements that coprecipitate with Fe-Mn oxides, such as Co, Ni, Cu and Zn.

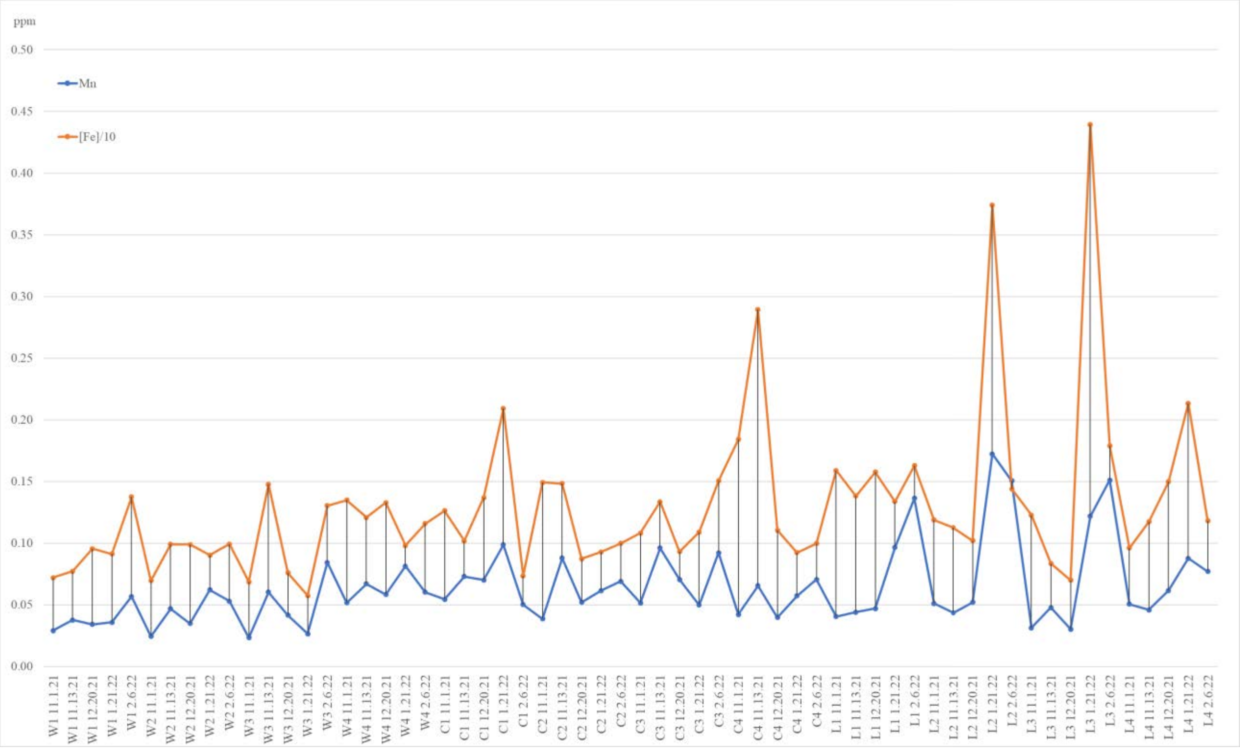


Figure 3.18. The correlation of Fe and Mn concentration on 60 samples of sediment

3.8.4. Chromium

Chromium is release into the environment when burning coal and oil or from the industry[37]. Cr has two oxidation states in environmental water conditions, Cr (III) and Cr (VI). Cr (III) can coprecipitate with iron and Mn oxides. Therefore, Cr (III) is relatively insoluble and nontoxic. By comparison, Cr (VI) is more soluble and also toxic[38].

As shown in Figure 3.19 and Appendix 13, the Cr concentration range in the sediment is in the range of 3-70 µg/g but there are very few samples having more than 43 µg/g of Cr which is the EPA Freshwater Sediment Screening Benchmarks. The high concentration may be due to metal fragments collected with the sediment.

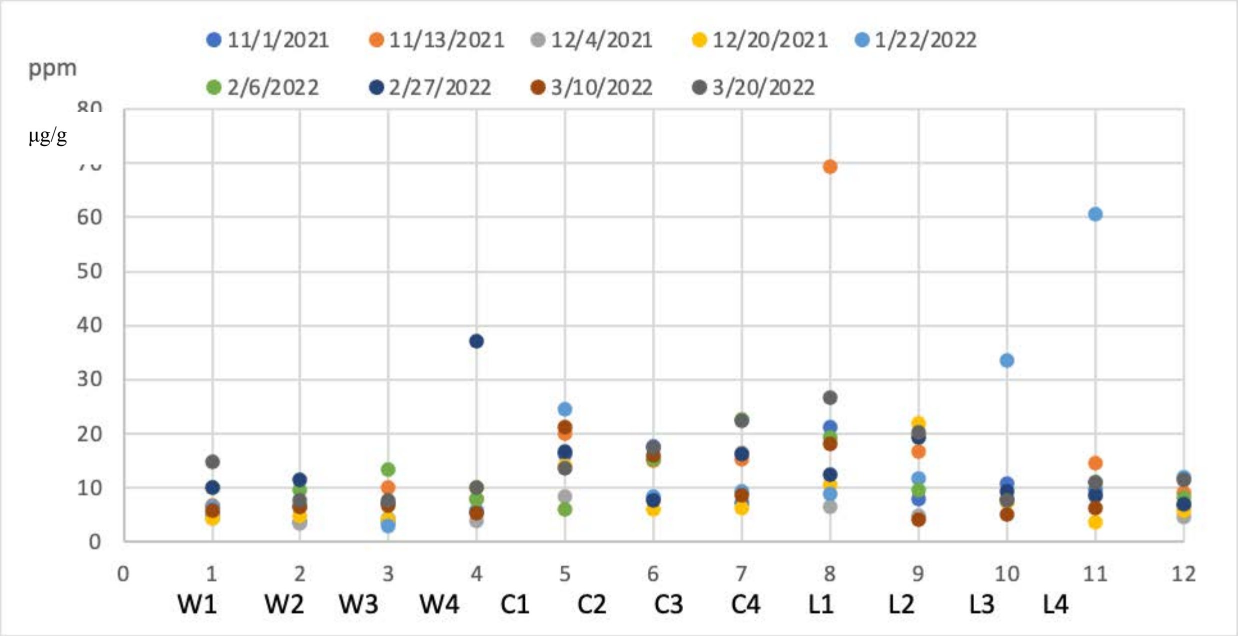


Figure 3.19. Mass ratios (µg/g) Cr measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

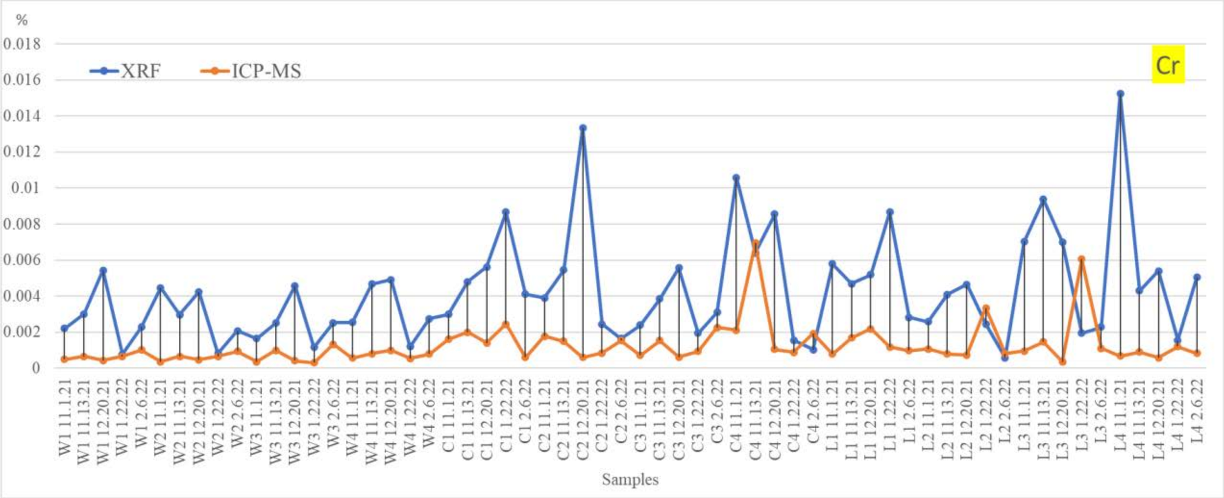


Figure 3.20. Mass ratios (%) of Cr measured by XRF and ICP-MS

As shown in Figure 3.20 and Appendix 20, Cr concentrations measured by ICP-MS and XRF are in good agreement, both increasing and decreasing when measuring various samples. At some points, they give the same results, such as W1 1.22.22, W2 1.22.22, W4 1.22.22, C2 2.6.22, C4 11.13.21, L2 1.22.22, L2 2.6.22, L4 1.22.11. The recovery of Cr in Buffalo River sediment is 65.9 ± 5.9 % and its spike recovery is 137.2 %. The lower recovery may be due to the extraction methods. Aqua regia cannot completely release Cr from Fe-Mn oxides. On the other hand, Cr in sediments is a trace element whose concentrations in many samples are lower than the limit of quantitation of XRF (0.03%). As a result, Cr concentrations measured by ICP-MS are more reliable.

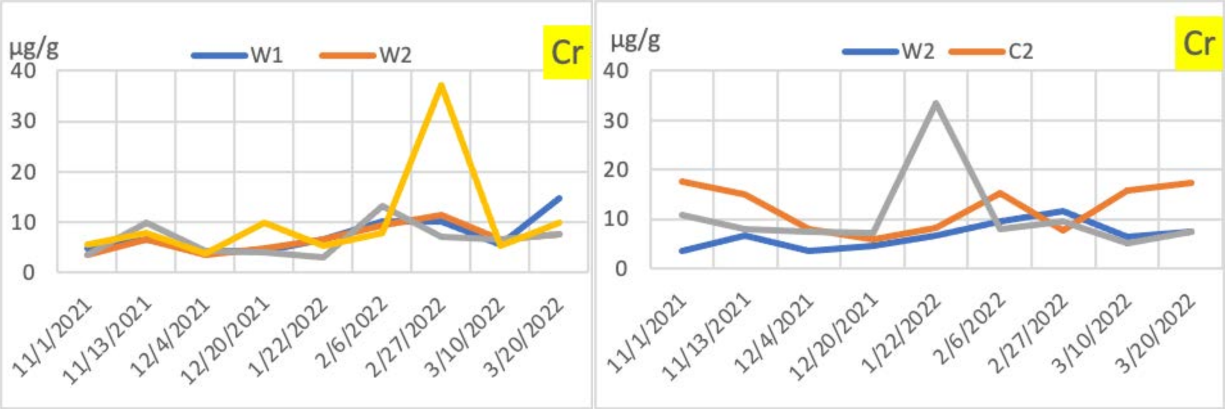


Figure 3.21. Spatial and seasonal variations of Cr in Yellow Creek sediments (Left: samples from 4 subsites from the woods (W1, W2, W3, W4), Right: samples from the Wood-W, Cemetery-C and Library-L)

Similar to other elements, as shown in figure 3.21, Cr concentration samples collected from the same site have good agreement over three seasons. The Cr concentration in sediments collected from the cemetery is mostly equal or higher compared to those collected from the sites of Library and the Wood. The Cr concentration in L 2.6.22 is high and is equal to result measured by XRF.

3.8.5. Cobalt

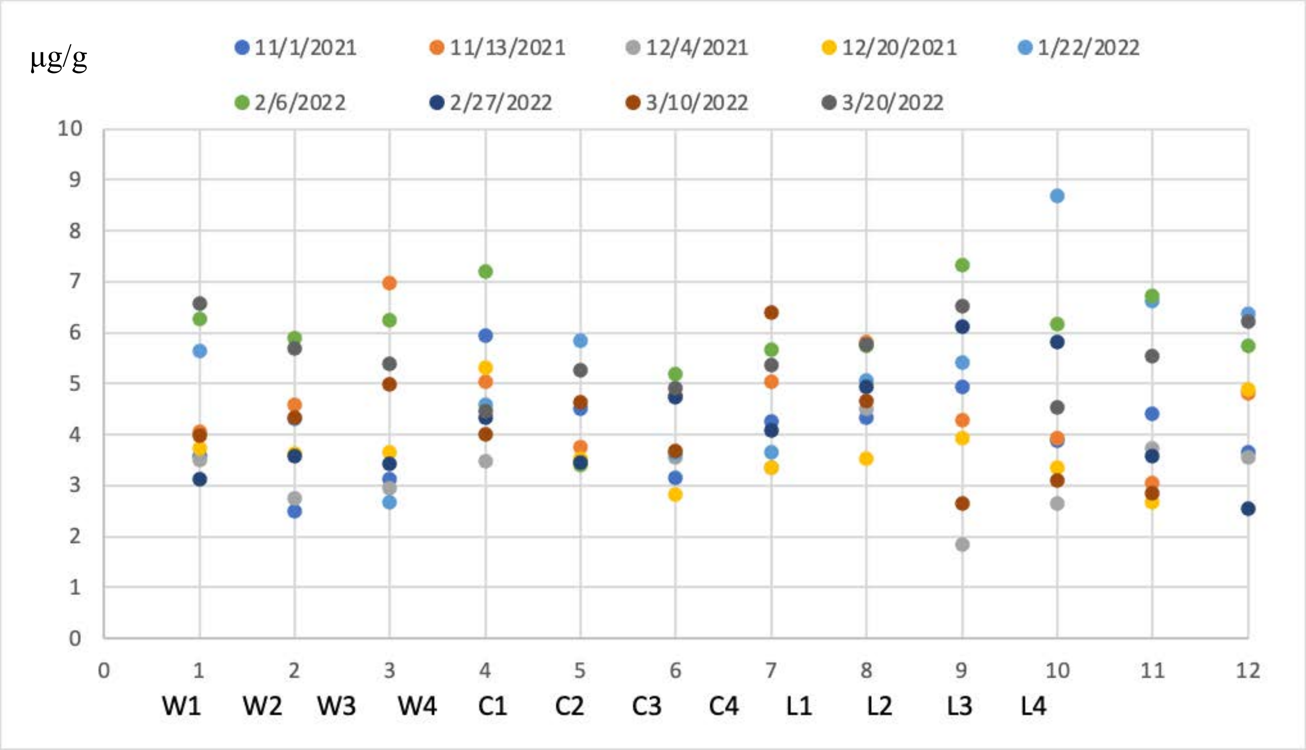


Figure 3.22. Mass ratios (µg/g) Co measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

The useful form of Co in living organisms is cobalamin. Co in the environment is not always beneficial for species living in aquatic environments[39]. According to EPA Freshwater Sediment Screening Benchmarks in Table 3.11, sediments having Co higher than 50 µg/g are above the benchmark.

As shown on Figure 3.22 and Appendix 15, the Co concentrations in Yellow Creek sediments are lower than 9 µg/g. This shows that the sediment has low concentration of Co. Moreover, Co has a good recovery on Buffalo River sediment of 113.9 ± 5.2 %. Results measured by ICP-MS appear to be reliable. In this study, XRF cannot measure

Co in the sediment since we did not have enough reference material to build the calibration curve.

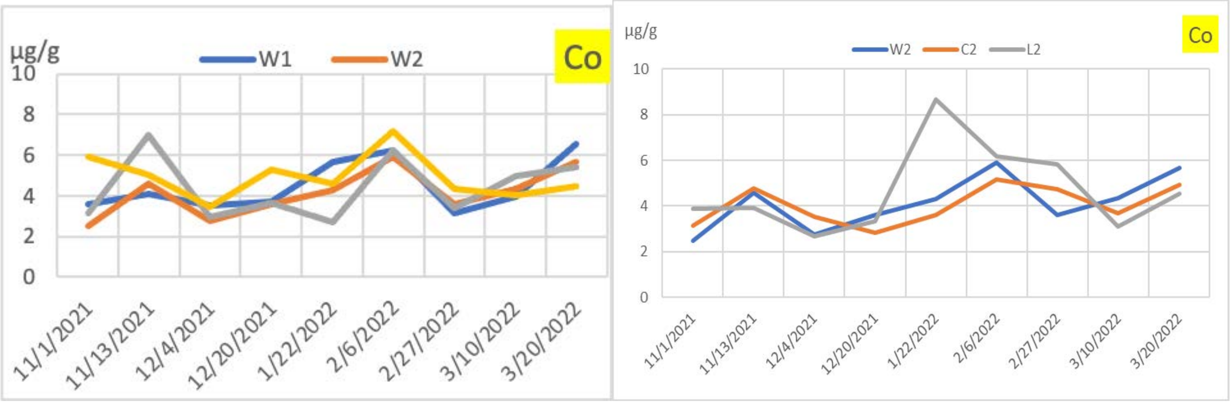


Figure 3.23. Spatial and seasonal variations of Co in Yellow Creek sediments (Left: samples from 4 subsites from the woods (W1, W2, W3, W4), Right: samples from the Wood-W, Cemetery-C and Library-L)

As shown in Figure 3.23 and Appendix 14, there is good agreement in Co concentrations when measuring samples in 9 sampling days. Samples from the woods have similar Co concentrations. Little variations in Co level is observed in samples from three different sites. Co from the library site L 1.22.22, L 2.27.22 are higher than the other sites.

3.8.6. Nickel

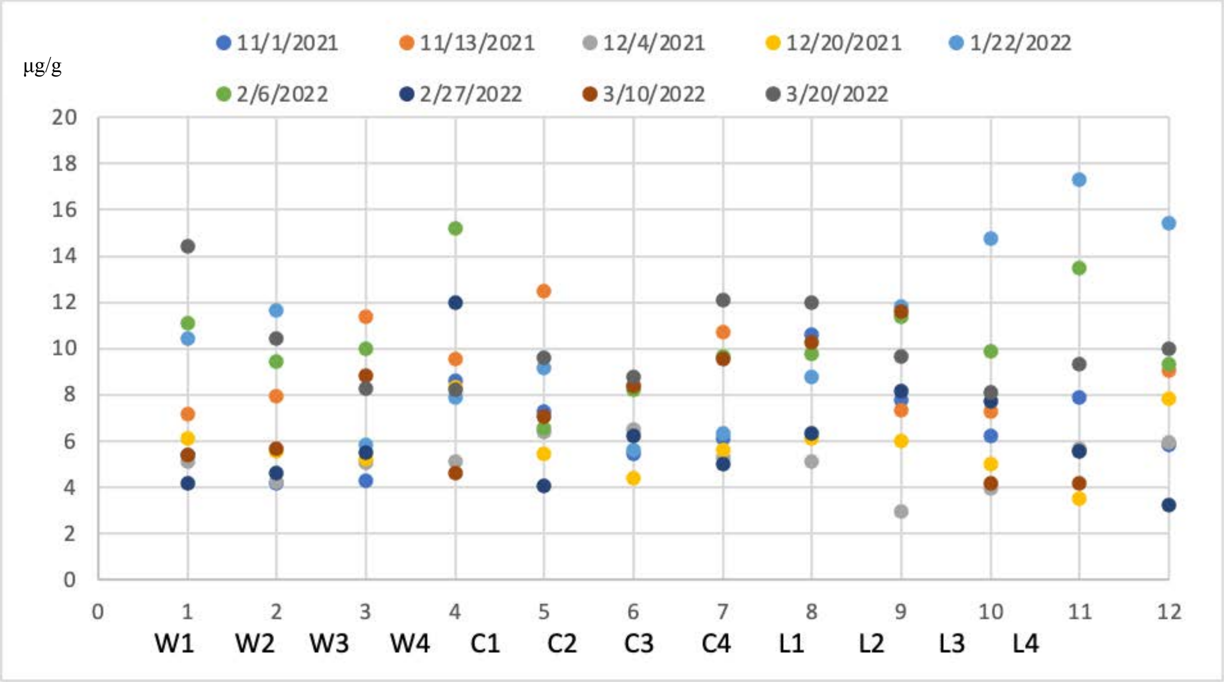


Figure 3.24. Mass ratios (µg/g) Ni measured in samples collected in Fall 2021, Winter

The toxicity of Nikle depends on its speciation. In a water environment, Ni is in the oxidized form Ni (II). This metal precipitates in Fe-Mn complex or when forming insoluble complexes with sulfides under anaerobic conditions[40]. According to table 3.11, the Probable Effect Concentration of Ni is 48.6 µg/g. Sediments having Ni higher than 27 µg/g is above the benchmark.

As shown in Figure 3.24 and Appendix 15, Ni concentrations are lower than 18 µg/g. The recovery of Ni in Buffalo sediment is good at 90.4 ± 7.5 %. Therefore, the results of Ni measured by ICP-Ms are expected to be reliable. Overall, the level of Ni in the sediment collected from the Yellow Creek is low. In this study, XRF cannot measure Ni in the sediment since we did not have enough reference material to build the calibration curve.

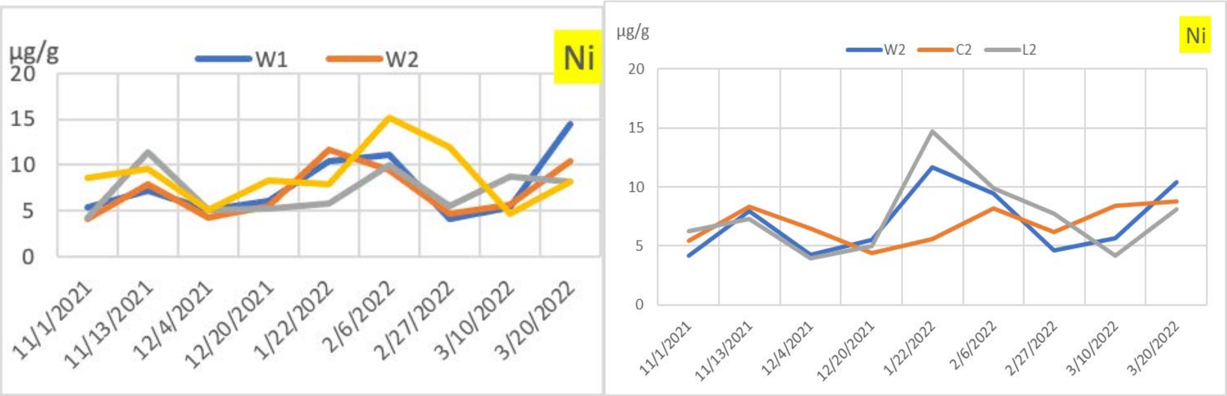


Figure 3.25. Spatial and seasonal variations of Ni in Yellow Creek sediments (Left: samples from 4 subsites from the woods (W1, W2, W3, W4), Right: samples from the Wood-W, Cemetery-C and Library-L)

As shown in figure 3.25 and Appendix 20, Ni variations between samples of the same site and from different sites are in good agreement. Its concentrations in samples collected on the same day are relatively close.

As shown in Figure 3.26, there is a good correlation in concentrations of Co and Ni when measuring samples collected in 9 sampling days. Both Co and Ni can coprecipitate with Fe-Mn oxide, their accumulation in the sediment are similar. For example, if the chemical conditions of the Yellow Creek become acidic, Fe and Mn are dissolved, both Co and Ni will be released, and their concentration become lower in the sediment. Otherwise, if dissolved oxygen in the water is higher, more Fe and Mn is oxidized and precipitate. The coprecipitation of Co and Ni with Fe-Mn oxide increases their concentrations in the sediments.

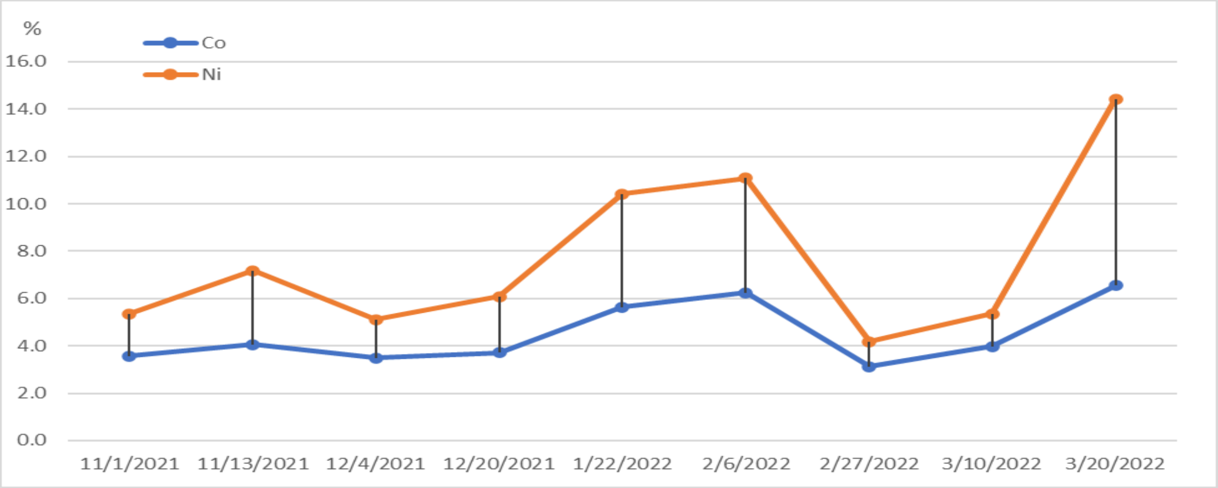


Figure 3.26: Concentrations of Co, Ni measured in measured in sample W1 collected in Fall 2021, Winter 2022 and Spring 2022

3.8.7. Copper

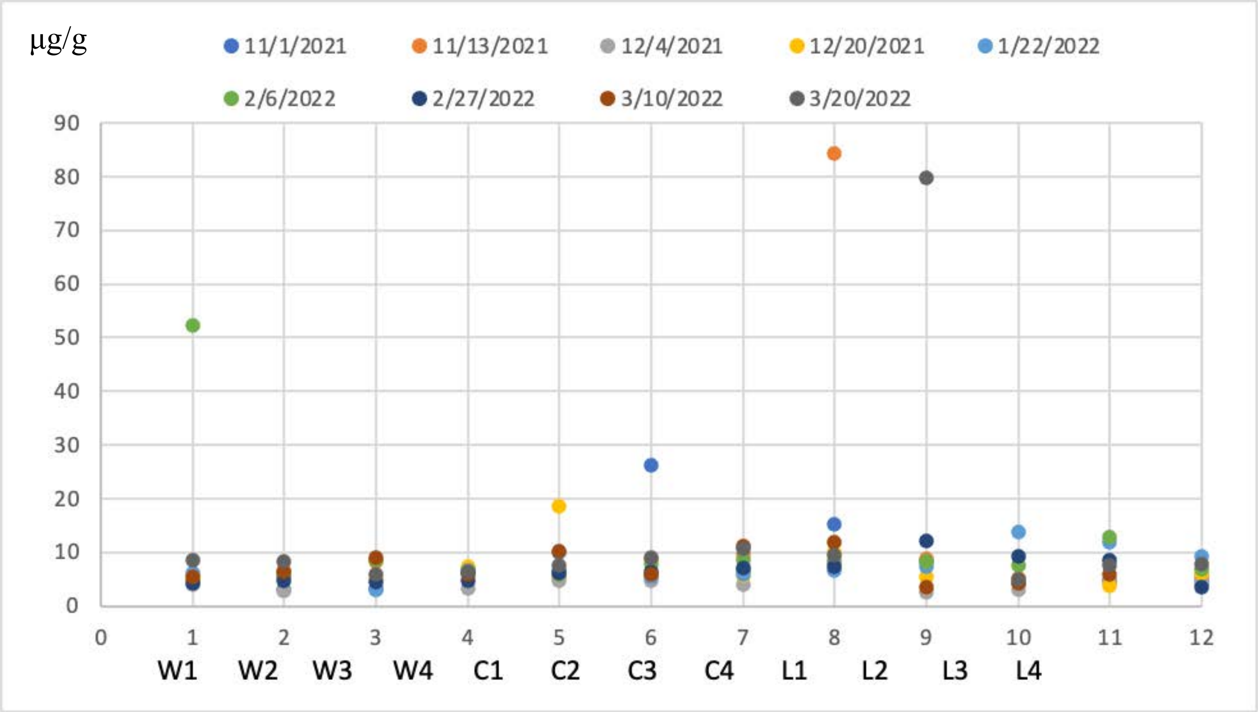


Figure 3.27. Mass ratios (μg/g) Cu measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

Dissolved Cu is more bioavailable than sediment-binding form[41]. The structure and function of the sediment microbial community can be affected when exposed to Cu in the environment[42]. In the water column, Cu combines with functional groups and settles in the sediment. This process is irreversible and results in the permanent capture of copper[43]. According to table 3.11, the Probable Effect Concentration of Cu is 149 µg/g µg/g. Sediments having Cu higher than 31.6 µg/g are above the benchmark.

As shown in Figure 3.27 and Appendix 16, overall concentrations of Cu in most samples are lower than 20 µg/g, except for four samples collected on different sampling days (W1 2.6.22, C2 11.1.21, C4 11.13.21, L1 3.20.22). Otherwise, as shown in Figure 3.15 and available XRF data in appendix 20, Cu mass ratio (%) in W1 2.6.22, C2 11.1.21, C4 11.13.21 are 0.0030%, 0.0024%, 0.0031%, respectively. The high concentration observed by ICP-MS may be because of contamination during the digestion process.

Results of Cu measured by ICP-MS and XRF have the same trend as seen in Figure 3.28. Cu concentrations measured by ICP-MS are generally lower than by XRF by about 0.002%. The recovery of Cu in Buffalo sediment is very good 98.7 ± 16.1 %. The XRF limit of quantitation of Cu (0.04%) is very close to or higher than Cu concentration in the sediment. Therefore, the results of Cu measured by ICP-MS are expected to be more reliable.

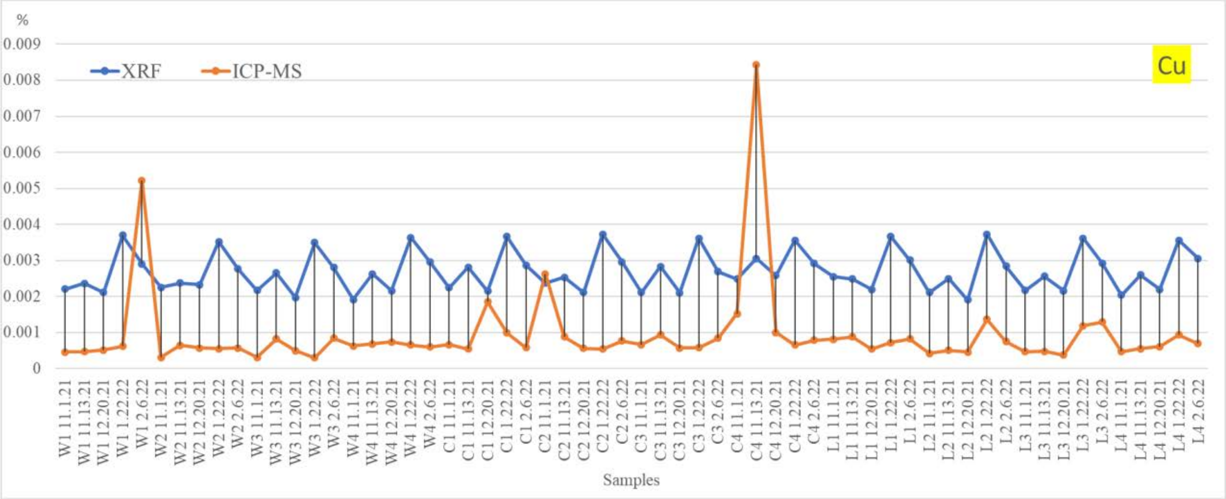


Figure 3.28. Mass ratios (%) of Cu measured by XRF and ICP-MS

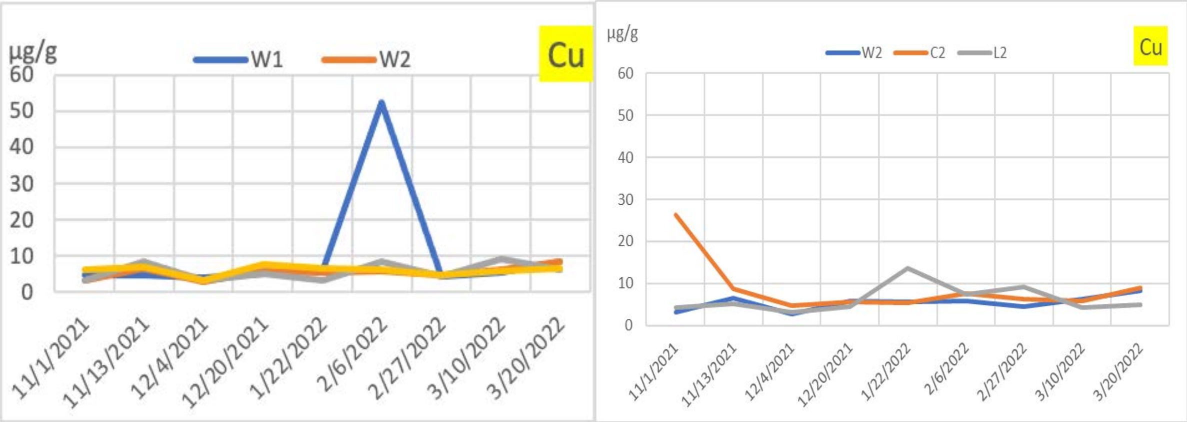


Figure 3.29. Spatial and seasonal variations of Cu in Yellow Creek sediments (Left: samples from 4 subsites from the woods (W1, W2, W3, W4), Right: samples from the Wood-W, Cemetery-C and Library-L)

As shown in Figure 3.29 and Appendix 16, Cu concentrations in sediments collected in 9 sampling days are generally close. As discussed above, the high concentration on W 2.6.22 and C2 11.1.21 are possibly due to sample contamination. There is good agreement between the four subsites of the woods and between the three sites.

3.8.8. Zinc

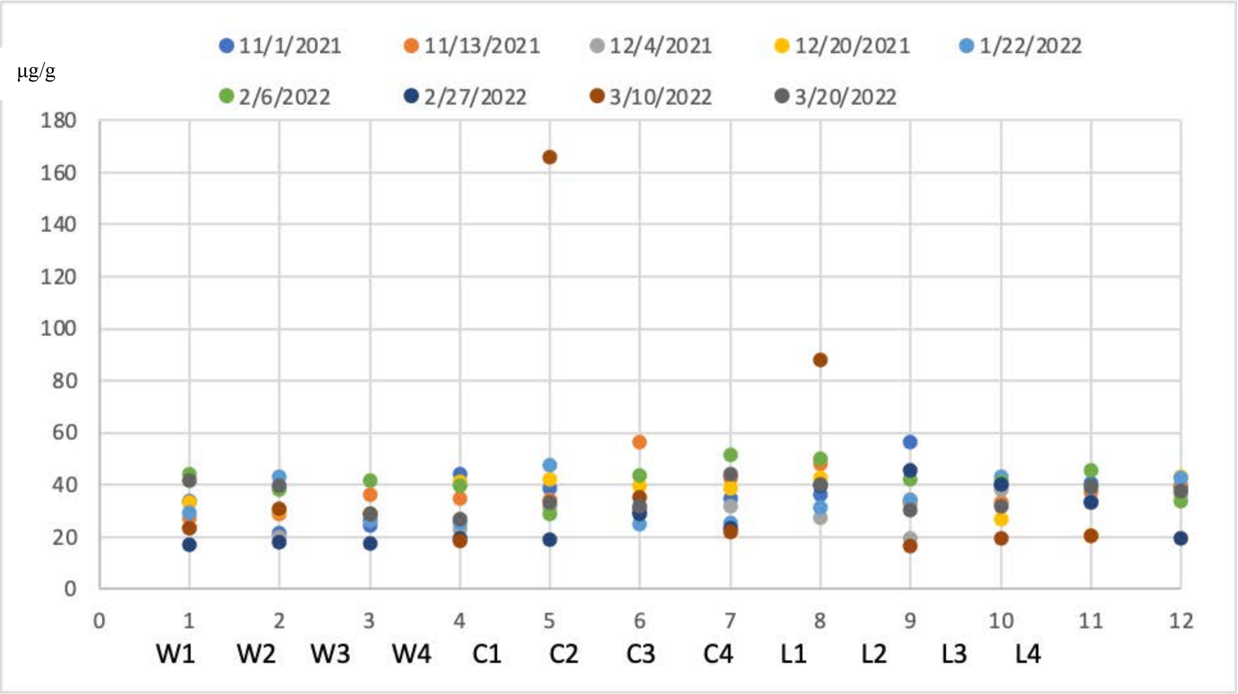


Figure 3.30. Mass ratios (µg/g) Zn measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

Zn is one of the most commonly found metals in wastewater[44]. Once released into the environment, Zn can be adsorbed by particulates in the aquatic environment or coprecipitate with Fe-Mn oxides, and other minerals[45]. According to table 3.11, the Probable Effect Concentration of Zn is 459 µg/g. Sediments having Zn higher than 121 µg/g are above the benchmark.

As shown in Figure 3.30 and Appendix 17, Zn concentrations are lower than 60 µg/g and the overall concentration of Zn is low. The recovery of Zn in Buffalo sediment is relatively good 97.1 ± 7.8 %, and the results of Zn measured by ICP-MS are expected to be reliable.

There are two samples collected on 3/10/22 at the cemetery that have very high concentrations of Zn, this cannot be double checked by results from XRF because XRF does not have data available on this sampling day. The two samples, C1 and C4, have unusually high concentrations of Zn compared to other samples from the same site and samples from other sites which may be due to metal fragments or sample contamination.

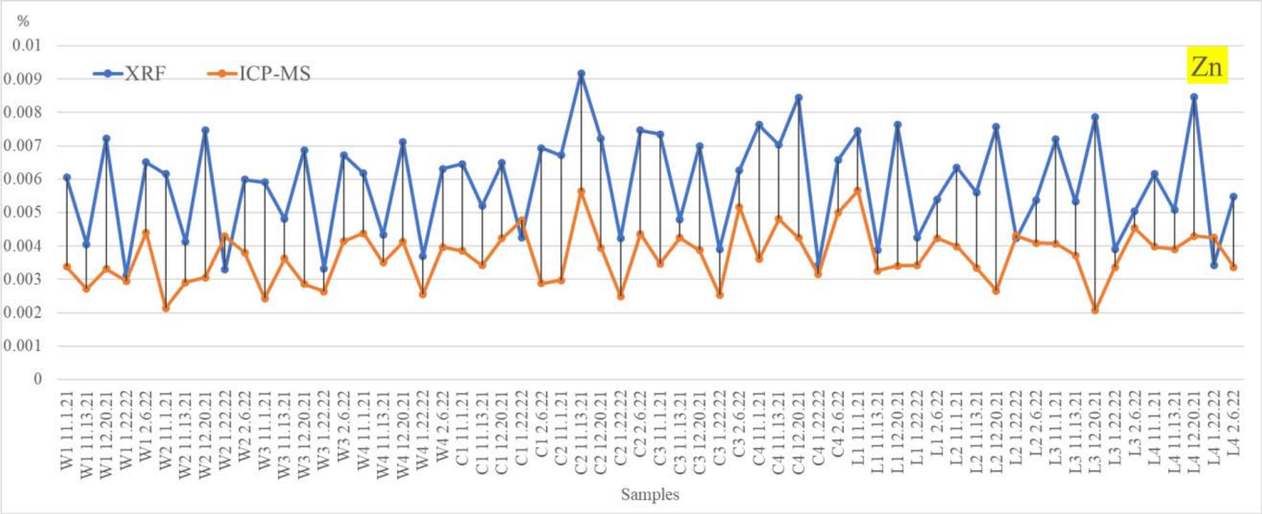


Figure 3.31. Mass ratios (%) of Cu measured by XRF and ICP-MS

As shown in figure 3.31 and Appendix 20, the concentration of Zn measured by XRF and ICP-MS are in good agreement. XRF provides a higher concentration of Zn. However, they give very close results at many points in the graph of concentration of Zn in 60 samples measured.

As shown in Figure 3.32 and Appendix 17, the fluctuations of Zn concentration between samples collected at the same sampling site are close and in good agreement. There are differences in trend for samples collected from the woods, cemetery and library. According to the graph on the right, Zn concentrations in the library sediments are not increasing or decreasing together with the other two sites. The Zn concentration at the library is often high and fluctuates differently compared to samples from the woods and the cemetery and may be due to a municipal storm drain located near the library.

Figure 3.32. Spatial and seasonal variations of Zn in Yellow Creek sediments (Left: samples from 4 subsites from the woods (W1, W2, W3, W4), Right: samples from the Wood-W, Cemetery-C and Library-L)

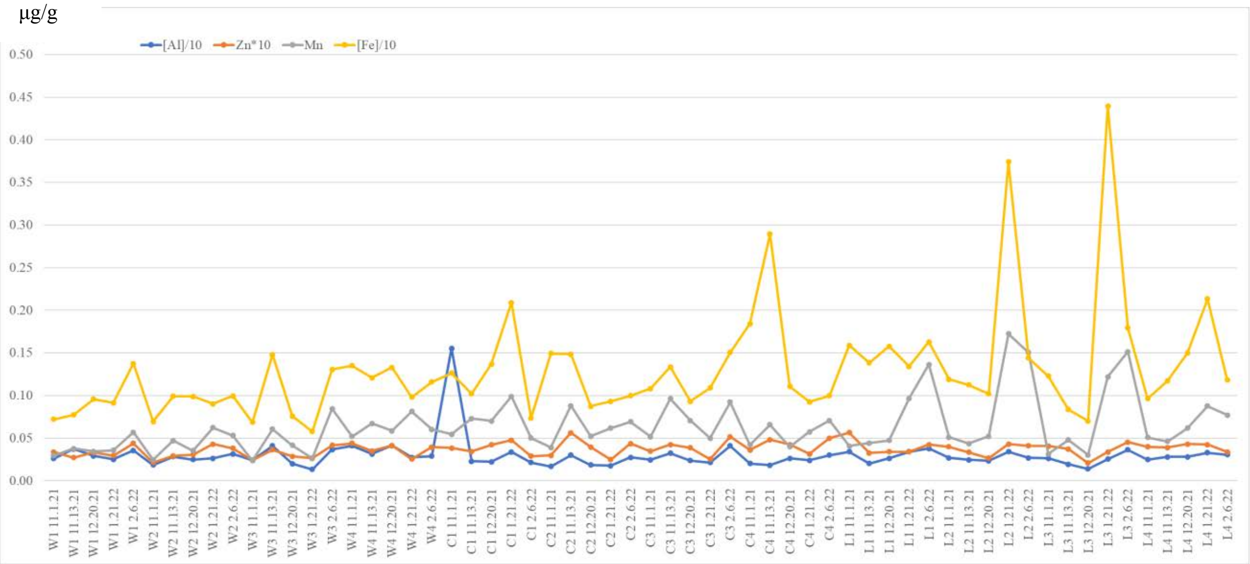


Figure 3.33. The correlation of Al, Zn, Mn and Fe concentrations on 60 samples of sediment

Al, Zn, Mn, and Fe have concentrations that differ by many orders of magnitudes. In Figure 3.33, Al and Fe concentrations were divided by 10 and Zn concentrations were multiplied by 10. As shown in the figure, the trends in concentration of the four metals are similar and may be due to their coprecipitation in the sediment.

3.8.9. Cadmium

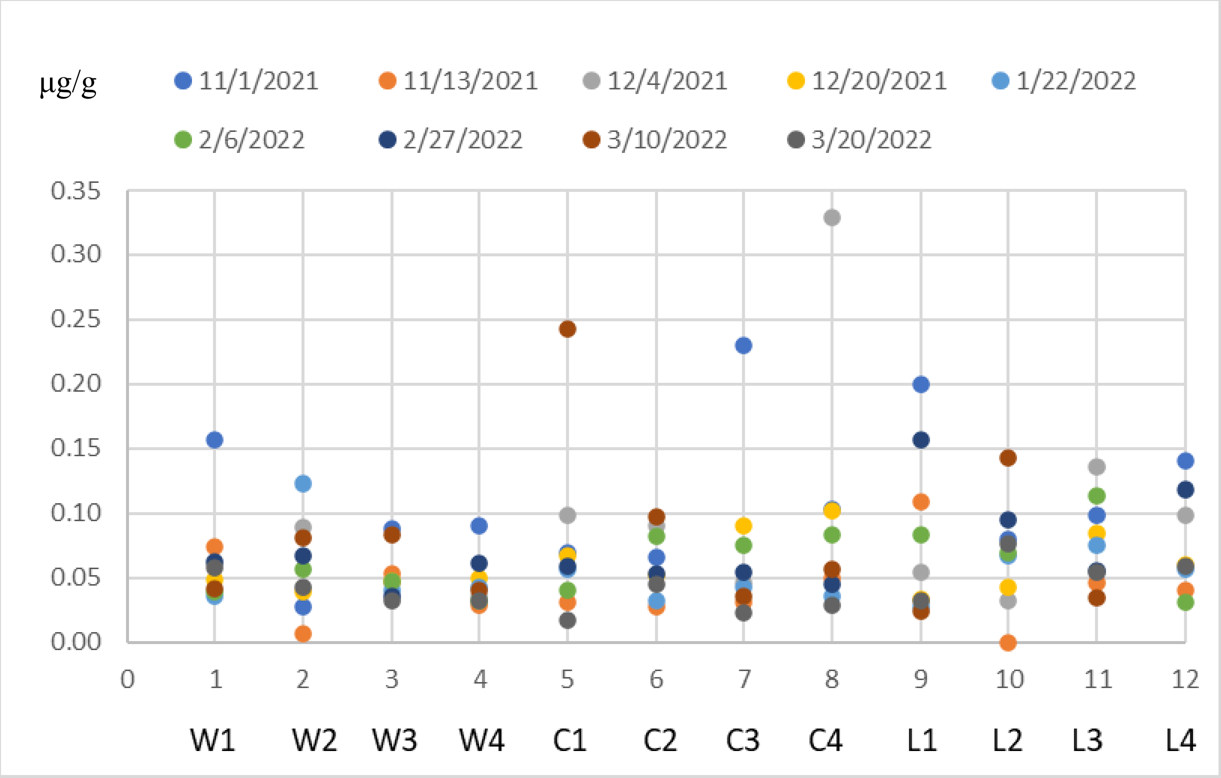


Figure 3.34. Mass ratios (µg/g) Cd measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

Cd is not essential to living organisms in aquatic systems. The toxicity of this trace metal to organisms is high [46]. The mobilization of Cd depends on total and easily exchangeable amount, pH of the environment and suspended particles[47]. According to table 3.11, the Probable Effect Concentration of Cd is 4.98 µg/g. Cd at concentrations higher than 0.99 µg/g is above the benchmark.

As shown in Figure 3.34 and Appendix 18, none of the samples from Yellow Creek has Cd concentrations higher than 0.5 µg/g. Cd levels in the sediments are low. The extraction method in this study has 109.8 ± 9.3 % of Cd recovered. In this study, there are three procedural blanks whose concentration of elements were subtracted from the measured amounts of samples to eliminate the effects of contamination due to reagents. Therefore, results of trace elements are expected to be relatively reliable. The available reference materials are not enough to calibrate and measure Cd by XRF.

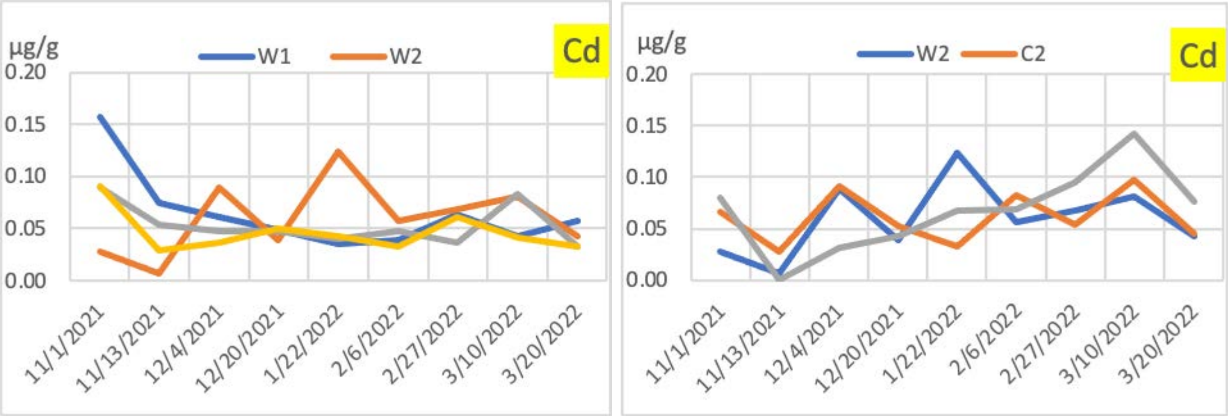


Figure 3.35. Spatial and seasonal variations of Cd in Yellow Creek sediments (Left: samples from 4 subsites from the woods (W1, W2, W3, W4), Right: samples from the Wood-W, Cemetery-C and Library-L)

As shown in Figure 3.35 and Appendix 18, Cd concentrations at different subsites of the woods behave differently. The measured concentrations on many sampling days are close. The agreement of Cd concentration in the sediments collected from the three sites is good. It is also observed that the average concentration of Cd is increasing during the sampling period.

3.8.10.Lead

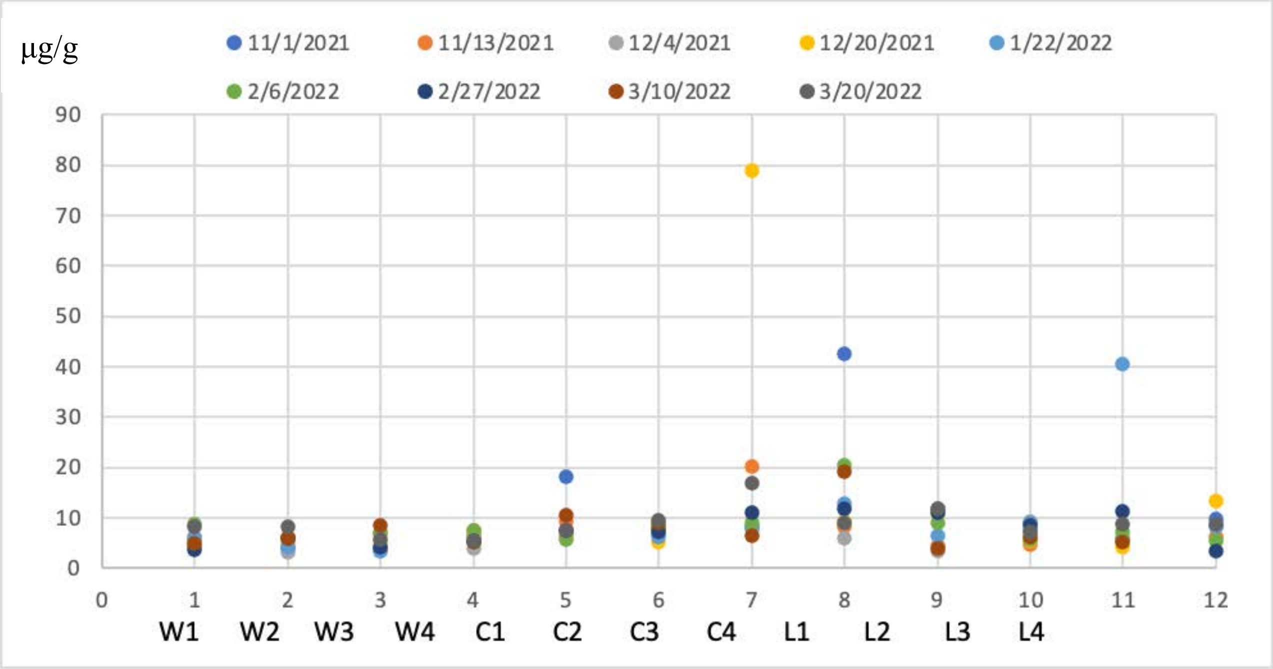


Figure 3.36. Mass ratios (μg/g) Pb measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

Like Cd, Pb can cause serious effects on aquatic living organisms because of its bioaccumulation[48]. According to table 3.11, the Probable Effect Concentration of Pb is 128 μg/g. Pb at concentrations higher than 35.8 μg/g is above the benchmark.

As shown in Figure 3.36 and Appendix 19, only three of 60 samples from Yellow Creek have Pb concentrations higher than 40 μg/g. Overall, the Pb concentrations in these samples are low. The extractable amount of Pb in this study is 111.2 ± 7.3 % so it is expected that the measured values closely reflect the real amount of Pb in the sediment. There are three samples collected from the library and cemetery on 12/20/21 and 1/22/22 have more than 40 μg/g of Pb, which is x2 to x4 times higher than the average mass ratio of Pb. This may be due to sample contamination. There is no XRF data of Pb available to compare with as the Pb concentration in the sediments are too low to be measured by XRF.

Figure 3.37. Spatial and seasonal variations of Pb in Yellow Creek sediments (Left: samples from 4 subsites from the woods (W1, W2, W3, W4), Right: samples from the Wood-W, Cemetery-C and Library-L)

Plots in figure 3.37 were used to analyze the change in mass ratio of elements over time and the trend in changing concentrations between sites in the three seasons. Samples from the four subsites of the woods were compared. Also, samples of one subsite at each site were plotted in the same graph. Samples of the same sampling day were measured in the same run. Pb concentrations measured in sediments of the four subsites of the woods are close and in good agreement. When comparing Pb level at the three sites, Pb concentration at the library site have a different trend from the cemetery and the woods and may be explained by the storm drain released directly into the creek.

3.9. Acetic acid extraction

3.9.1. Total extraction and the recovery of metals in Bufflalo river sediments

Sampling days of samples measured by ICP-MS and XRF are 03-20-2022 (ICP-MS/Woods) and 6-24-22 (XRF/Woods).

Table 3.12. Total extraction of Buffalo River sediments extracted by aqua regia

Element	**Recovery (%)**	**Ave. (µg/g)**	**STD%**	**Element**	**Recovery (%)**	**Ave. (µg/g)**	**STD%**
^{27}Al	29.0	17692.2	11.7	**^{60}Ni**	**101.5**	43.5	0.6
^{55}Mn	123.1	669.5	9.16	**^{63}Cu**	**94.0**	92.7	5.2
^{57}Fe	92.1	36563.0	1.79	**^{66}Zn**	**63.3**	258.4	12.3
^{52}Cr	**74.9**	91.3	8.2	**^{111}Cd**	**75.1**	2.2	6.8
^{59}Co	**101.8**	13.8	11.6	**^{206}Pb**	**86.3**	129.4	8.4

As shown in table 3.12, the total extraction procedure has good recoveries for most elements except for ^{27}Al. This indicates that the procedure can be applied to samples from the Woods. Total extractions were also carried out for residues after the acetic acid extraction.

The sum of metal amount extracted by acetic acid (AcOH) and by aqua regia can be compared to total amount of metals extracted by aqua regia at the beginning.

Table 3.13. Total extraction of samples from 4 subsites of the Woods (Poland)

µg/g	^{27}Al	^{55}Mn	^{57}Fe	^{52}Cr	^{59}Co	^{60}Ni	^{63}Cu	^{66}Zn	^{111}Cd	^{206}Pb
W1	2217.6	384.4	9105.1	5.8	4.4	7.5	6.7	21.3	0.04	5.8
W2	2434.7	478.2	9332.6	7.4	4.9	8.0	8.2	24.7	0.03	6.7
W3	2497.8	451.5	9649.2	7.1	4.0	6.9	5.7	19.7	0.01	5.6
W4	1829.1	447.6	7582.1	16.9	3.7	7.9	6.2	21.1	0.01	5.5
Average	**2244.8**	**440.4**	**8917.3**	**9.3**	**4.2**	**7.6**	**6.7**	**21.7**	**0.02**	**5.9**

3.9.2. Determination of dilution factors for acetic extract

The study of acetic acid extraction was performed to determine if the extract should be measured directly or diluted further.

As the results in Figure 3.38 show,

- Buffalo River sediment: all elements that have mass ratio (µg/g) calculated from diluted samples are higher than or equal to those in direct measurements. The concentrations of the metals in the acetic extract from these samples is high. If samples were not diluted, their concentrations would be higher or out of the linear range of their calibrations.

- Samples from the Poland woods: mass ratios of Al, Mn, Fe are higher when calculated from diluted samples. This means the mass ratio of these elements is high in the extracts and should be diluted to be in the linear range.

As a result, when doing acetic acid extraction for sediments from the woods or from Poland, the extracts should be measured directly for trace elements and diluted 5 times measurements of major elements (Al, Mn, Fe)

Table 3.14. Concentrations calculated from measuring samples directly and after diluting samples 5 times. msm is measurement.

	µg/g	**^{27}Al**	**^{55}Mn**	**^{57}Fe**	**^{52}Cr**	**^{59}Co**	**^{60}Ni**	**^{63}Cu**	**^{66}Zn**	**^{111}Cd**	**^{206}Pb**
Buff AcOH	Direct msm	149.3	206.6	827.6	3.5	2.1	5.2	15.4	139.4	2.1	13.3
	Diluted	**167.2**	**311.9**	**958.3**	**3.8**	**2.2**	**5.2**	**18.9**	**171.0**	**2.6**	**18.8**
Wood AcOH	Direct msm	82.2	226.5	39.6	0.1	0.8	0.9	0.8	5.7	0.05	0.6
	diluted	**78.3**	**292.8**	64.7	0.1	**0.8**	**0.5**	**0.6**	**2.0**	**0.02**	**0.2**

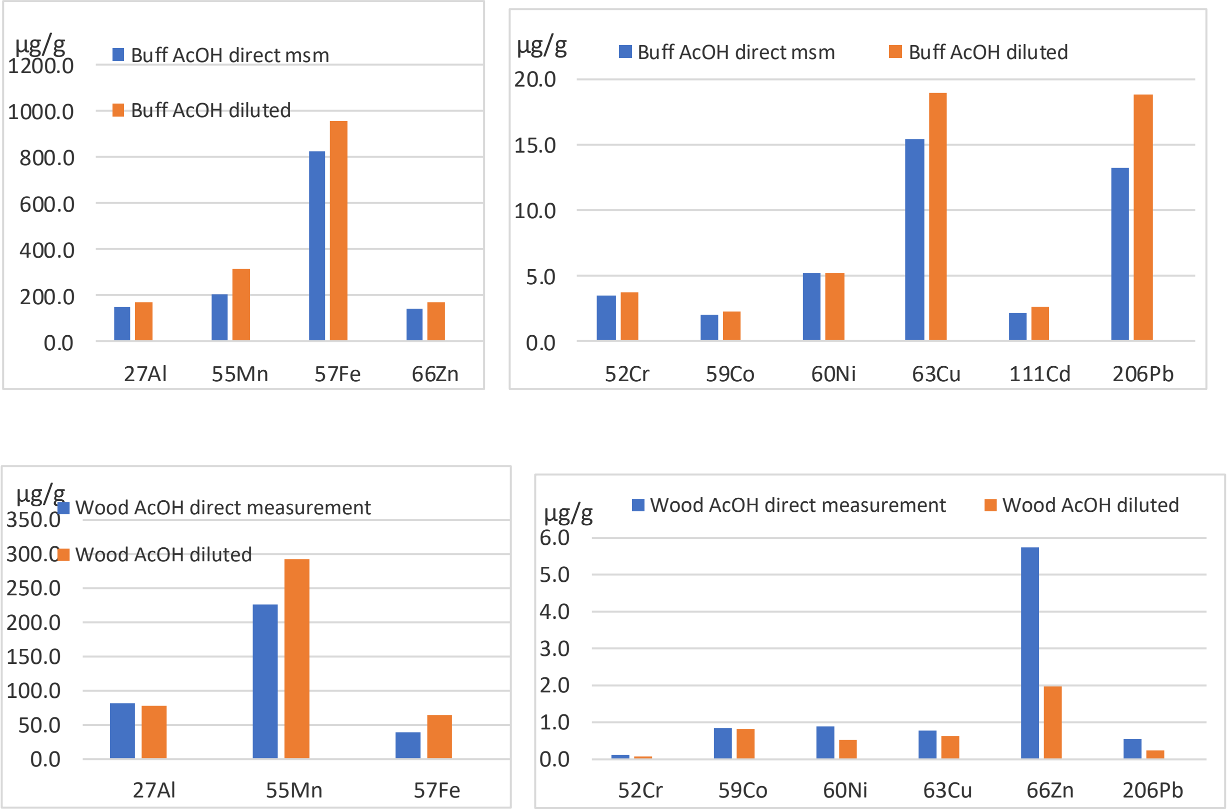


Figure 3.38. Mass ratios of all elements calculated from samples measured directly and from those were diluted 5 times.

3.9.3. Metals extracted by acetic acid compared to total extractions by aqua regia

The percentage of metals extracted by acetic acid were calculated. The percentage is equal to mass ratio from the acetic extract*100/mass ratio of elements from the total extraction.

As shown in figure 3.16, for both sets of samples, percentages of elements extracted by acetic acid are different between the two sets of samples. This can be due to their difference in sample matrix. More Mn can be extracted from the wood sediments and more Zn can be extracted from the Buffalo River sediment. A significant amount of Mn and Zn can be extracted by acetic acid in both types of samples. Many other elements (Co, Ni, Cu, Pb) were extracted >10% by the acid. Cd is a special case. 100% of Cd was extracted by acetic acid from Buffalo River sediment. The percentage of Cd extracted from the wood sediments are higher than 100% and appears to be because their original concentrations in the wood samples are very low and have high level uncertainty.

%	Buffalo	Wood
^{27}Al	0.9	3.5
^{55}Mn	46.6	66.5
^{57}Fe	2.6	0.7
^{52}Cr	4.1	1.3
^{59}Co	16.1	20.0
^{60}Ni	11.9	11.8
^{63}Cu	20.4	11.6
^{66}Zn	66.2	26.5
^{111}Cd	117.1	232.1
^{206}Pb	14.6	9.3

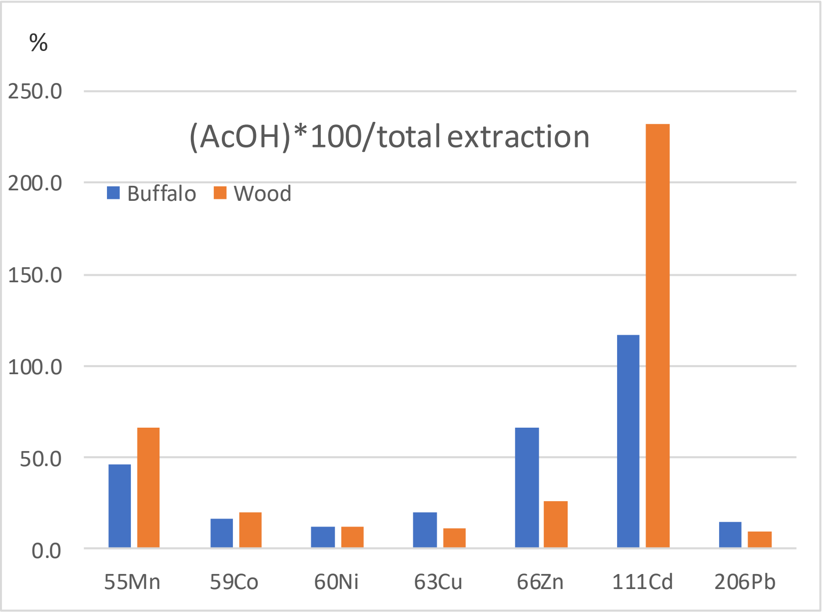


Figure 39.. Percentage of metals extracted by acetic acid compared to total extraction

3.9.4. Total amount of metals extracted by acetic acid and from the residue compared to total extractions by aqua regia

The sediments after being extracted by acetic acid are called residues. Any metals remaining in the residues are then extracted by aqua regia as the total extraction procedure. The sums of metal concentrations in the acetic acid extract and the residue were calculated and then compared with metal concentrations in total extraction in part 3.9.1.

As shown in figure 3.39 for the Buffalo River sediment (blue bars), the percentage of the amount extracted by AcOH followed by aqua regia compared to total extraction are relatively high, around 100% while these ratios for Poland wood samples are lower. This can be because there was no significant loss of samples during the acetic extraction process.

Table 3.15. The recovery of elements in Buffalo River sediment and in sediment from the woods by acetic and aqua regia extraction

	Buffalo 8704 (%)	Wood (%)	Full SEQ[20] (%), by ET-AAS
^{27}Al	93.3	39.1	
^{55}Mn	102.4	103.9	
^{57}Fe	97.8	97.2	
^{52}Cr	100.9	53.7	94-95
^{59}Co	106.5	81.4	
^{60}Ni	101.3	81.1	90-92
^{63}Cu	109.8	62.6	100-101
^{66}Zn	122.8	79.7	98-101
^{111}Cd	148.6	199.3	96-104
^{206}Pb	117.7	77.3	97-101

Moreover, in the wood sediments (orange bars), the recoveries of Mn and Fe are almost 100%. Co, Ni, Pb have good recoveries which are about 80%. The recoveries of other elements (Al, Cr, Cu) are low. This can be because some sediments were lost while being decanted. Only 0.5g of the sediment was analyzed and the metal mass ratios of these elements in the samples are low. To lower uncertainties or errors, the amount of sediment should be increased to 1g in AcOH extraction, and internal standards should be added from the beginning of the process.

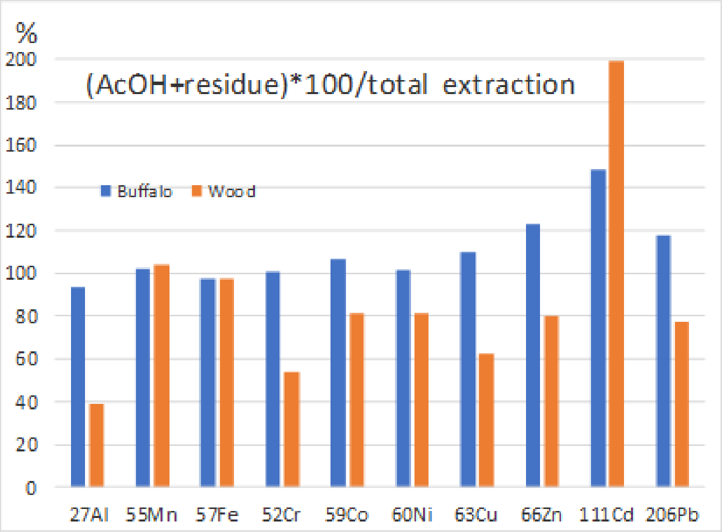


Figure 3.40. Total amount of metals extracted by acetic acid and from the residue compared to total extractions by aqua regia

3.9.5. Acetic acid extraction by ICP-MS versus XRF

ICP-MS and XRF are able to quantify different elements. The table below only lists metals that both methods can measure. Samples measured by ICP-MS were always digested and measured with a Buffalo River Sediment samples RSM 8704.

In ICP-MS method: % of metal extracted = mass ratio in AcOH extract *100/mass ratio in total extraction.

In XRF method: % of metal extracted = (% of metal in the sediment prior to extraction - % of metal in the residue after AcOH extraction) *100 / % of metal in the sediment prior to extraction.

%	ICP-MS	XRF	Buff recovery by ICP-MS
Al	3.5	30.7	29
Mn	66.5	66.9	123.1
Fe	0.7	NA	92.1
Cr	1.3	7.9	74.9
Cu	11.6	12	94
Zn	26.5	9	63.3
Pb	9.4	9.3	86.3

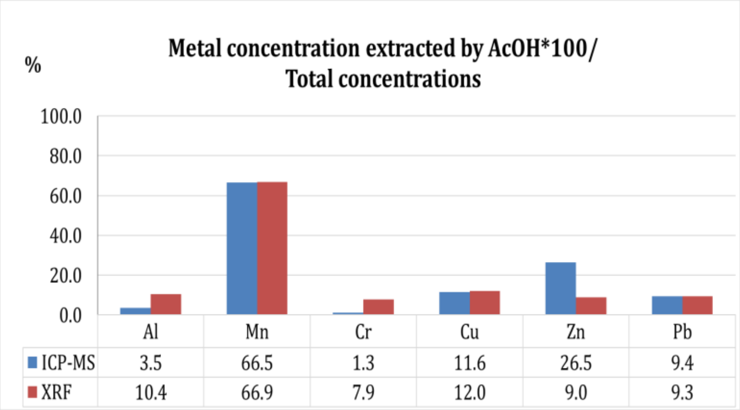


Figure 3.41. Relative percentage (%) of metals extracted by acetic acid measured by ICP-MS versus XRF

As shown in figure 3.41, many elements in good agreement between the two methods are Mn, Cu, Pb. Percentages of Al, Cr, Zn measured by ICP-MS are lower than those measured by XRF. The recovery of those elements in ICP-MS methods is low. Hence, the result of these elements should not be compared.

These preliminary results are promising and suggest that the sequential extraction procedure can be carried out both by ICP-MS in parallel with XRF.

IV. Conclusions

This study demonstrated the successful development of an ICP-MS method for the quantitative determination of metals in environmental sediments. The method was studied from different aspects.

The ICP-MS can be operated in STD or KED modes. It was demonstrated in this study that compared to STD mode, KED mode is more selective, and reduces interferences. This improvement was observed in the limit of detection and interference study. KED mode is typically 1-10 times more sensitive than STD. The LODs measured by KED mode are at part per billion levels for many elements (Al, Cr, Co, Ni, Cu, Zn, Pb), which are below the level of metals in the digested sediment samples. KED mode effectively reduces the effect of interference on the elements of interest. The correlation equation of intensities between elements of interest and the interference measured by KED has lower slope than when they were measured by STD mode. It is recommended that KED mode be used to measure samples that have complicated matrix.

Ytterbium (Yb) was used as an internal standard in this method to account for possible drift in the ICP MS response during measurements, which usually takes from 2 to 12 hours. When being corrected by the Yb signal, the spike recovery and Buffalo River sediment recovery are highest compared to results corrected using Yttrium signals or not corrected by internal standards. The range of spike recoveries is generally 80-120%, which shows that after being corrected, the instrument has high accuracy. Moreover, Buffalo River sediment has the highest recovery when data are corrected by Yb as the internal standard. Except for elements which are difficult to extract like Al and Cr, the recovery of other elements is in the range of 80-120%. The measured concentrations of metals were compared with the certified values and are generally statistically equal to or sometimes higher than the certified value, and higher than the recovery of Buffalo River sediment reported in other comparable studies.

The ICP-MS method was applied to measure metal concentrations in sediments collected from Yellow Creek in Poland, Ohio. The ICP MS results were compared with those measured by XRF. Elements that have good agreement between the two methods are Mn, Fe and Zn. Calibration curves of Ni, Cd, Pb cannot be obtained in this study by using XRF. Therefore, ICP-MS gave more reliable results for these elements and many other trace elements such as Co and Cu. XRF can provide reliable results for elements that have low extraction efficiency, such as Al and Cr. In general, metal concentrations in the Yellow Creek sediments are low. Sediments collected from the Poland Library often have higher concentrations of metals and may be due to the presence of a storm drain located nearby. Also, there are no obvious seasonal fluctuations in the metals concentration when samples collected in three seasons were measured. To have better evaluation about spatial and temporal trends, future studies should include measurements of samples collected at more sites and on more sampling days.

APPENDIX

Appendix 1. ICP-MS operating conditions

RF power (W)	1500 W	Acquisition parameters	
Scanner cone Skimmer cone	- Solid Ni, 1.1 mm diameter orifice - Ni, 0.5 mm diameter orifice	Rinse time	180s
Argon flow rates		Uptake time	120s
Purity	> 99.996 %	Integration time	0.2s
Cool gas	13.8 L/min	Survey runs	
Auxillary	0.79 L/min	Mass range	4.6-245u
Nebulizer	1.0 L/min	Number of sweeps	2
Collision gas and flow	Helium	Dwell time	0.001s
Internal standards	89Y, 174Yb	Main runs	
Isotopes	24Mg, 27Al, 52Cr, 55Mn, 57Fe, 59Co, 58Ni, 60Ni, 63Cu, 64Zn, 66Zn, 106Cd, 111Cd, 114Cd, 206Pb, 207Pb, 208Pb	Number of sweeps	3
		Dwell time	0.02 s
		Scan speed	> 3700 amu/s

Appendix 2. Reagent and standards

	Brand name	Formula Concentrations
Reagent		
Hydrochloric acid Trace metal grade	Fischer Chemical	HCl, 37%
Nitric acid ICP-OES for trace metal analysis	Thermo Scientific	HNO_3 70%
Multielement standard		
Multielement standard solution VIII	Sigma-Aldrich ®	100 mg/L: Al, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr, Te, Tl, Zn
Internal standards		
Ytterbium for AAS	Sigma-Aldrich ®	Yb, 1000 mg/L
Yttrium for AAS	Sigma-Aldrich ®	Y, 1000 ± 5 mg/L
Standard of interferences		
Calcium standard for AAS	Sigma-Aldrich ®	Ca^{+2}, 1000 g/L
Molybdenum standard for AAS	Sigma-Aldrich ®	Mo, 999 ± 4 mg/L
Titanium standard for AAS	Sigma-Aldrich ®	Ti, 1000 ± 4 mg/L
Zirconium standard for ICP	Sigma-Aldrich ®	Zr, 998 ± 3 mg/L

Appendix 3. Pb concentrations determined by single isotopes and average of all isotopes

Samples	**Single isotope**			**All isotopes**
	Buff_2704_8704			
	206Pb	**207Pb**	**208Pb**	**Pb**
Buff_2704	169.15±36.21	147.04±28.41	156.86±32.59	157.75 ± 13.09
Buff_8704	181.47±74.65	155.70±62	166.11±64.89	157.59 ± 26.81
First set of desert crusts				
Buff 8704	136 ± 10.41	117.5 ± 8.72	124.5 ± 9.16	126.08 ± 9.33
S1LA	50.04 ± 16.01	43.82 ± 14.65	37.38 ± 32.00	42.04 ± 24.45
S1RB	131.92 ± 14.4	115.67 ± 13.35	121.85 ± 17.49	123.05 ± 15.79
S2RB	54.06 ±21.17	46.91 ± 17.78	34.95 ± 13.40	42.34 ± 16.20
C2a	186.88 ± 9.25	161.20 ± 12.11	170.79 ± 8.57	172.67 ± 9.45
C3a	101.32 ± 4.97	88.94 ± 3.66	94.07 ± 1.52	94.84 ± 2.63
Second set of desert crusts				
Buff 8704	158.39 ± 16.65	137.16 ± 15.5	146.79 ± 15.63	147.99 ± 15.86
S1LB	77.65 ± 13.82	68.78 ± 11.49	67.72 ± 28.65	70.82 ± 21.14
S1RA	41.07 ± 3.0	35.87 ± 2.70	30.67 ± 2.91	34.76 ± 2.88
Base 1	71.00 ± 6.99	65.75 ± 12.73	56.33 ± 9.64	62.45 ± 7.64
S1LC	161.80 ± 28.01	140.52 ± 24.80	151.19 ± 25.85	151.92 ± 21.17
S2RA	60.17 ± 35.57	60.67 ± 47.76	52.51 ± 42.46	56.69 ± 42.13

Appendix 4. Calibrations curve results by STD and KED modes

	Modes	**Slopes**	**Y-intercepts**	**R^2**		**Modes**	**Slopes**	**Y-intercepts**	**R^2**
^{24}Mg	**STD**	5828489	88522	0.999	**^{63}Cu**	**STD**	6910354	117373	0.999
	KED	114837	-1470	1.00		**KED**	2509088	197704	0.999
^{27}Al	**STD**	7891915	-134337	1.00	**^{64}Zn**	**STD**	3467327	195468	1.00
	KED	33872	-442	1.00		**KED**	673824	103906	0.99
^{55}Mn	**STD**	20142932	-548412	1.00	**^{66}Zn**	**STD**	2056273	308913	1.00
	KED	1119433	147925	0.996		**KED**	504414	47875	1.00
^{57}Fe	**STD**	419386	58380	0.997	**^{106}Cd**	**STD**	573767	-13227	1.00
	KED	79407	-1369	1.00		**KED**	161044	-2479	1.00
^{52}Cr	**STD**	11940495	-334951	1.00	**^{111}Cd**	**STD**	4144575	236895	1.00
	KED	2031208	106957	1.00		**KED**	1351965	177124	1.00
^{57}Fe	**STD**	419386	58381	0.997	**^{114}Cd**	**STD**	10032075	111990	1.00
	KED	7940	-1369	1.00		**KED**	3456906	202860	1.00
^{59}Co	**STD**	15480240	-377210	1.00	**^{206}Pb**	**STD**	27677755	-16294	1.00
	KED	3775543	199413	1.00		**KED**	16172900	52226	1.00
^{58}Ni	**STD**	6919893	108811	1.00	**^{207}Pb**	**STD**	27010286	-38025	1.00
	KED	2054205	157838	1.00		**KED**	15870213	1024.4	1.00
^{60}Ni	**STD**	3003599	180749	1.00	**^{208}Pb**	**STD**	62595679	-706181	1.00
	KED	941460	140469	0.99		**KED**	36523250	57440	1.00

Appendix 5. Regression correlations between intensities of interference and their possible forms of interference and interfered elements

	^{90}Zr	^{48}Ti	^{98}Mo	^{40}Ca
^{24}Mg		**Ti^{2+}**		**Ca^{2+}**
KED	$y = 10^{-5}x + 24.217$	$y = 0.0003x - 112.78$		$y = 8.10^{-5}x - 229.23$
STD	$y = 0.0003x - 1887.9$	$y = 8.10^{-5}x + 22681$		$y = 4.10^{-5}x - 29415$
^{52}Cr	**ZrC^{+}, ZrN^{+}**		**MoC^{2+}**	**CaC^{+}**
KED	$y = 4.10^{-5}x + 817.09$		$y = 4.10^{-6}x + 207.76$	$y = 3.10^{-5}x + 75.755$
STD	$y = 8.10^{-5}x + 13908$		$y = 3.10^{-5}x + 9045.3$	$y = 10^{-5}x - 7996.8$
^{55}Mn	**ZrO^{2+}**			
KED	$y = 8.10^{-6}x + 191.78$			
STD	$y = 5.10^{-5}x + 10025$			
^{57}Fe	**$ZrOH^{2+}$**			**CaO^{+}, CaN^{+}, $CaOH^{+}$**
KED	$y = 10^{-5}x + 79.533$			$y = 8.10^{-5}x - 267.49$
STD	$y = 2.10^{-5}x + 11974$			$y = 0.0002x - 174314$
^{58}Ni	**(FeH)**	**TiC^{+}**		CaO^{+}, $CaOH^{+}$, **CaN^{+}**
KED	$y = 10^{-5}x + 475.28$			
STD	$y = 10^{-5}x + 10829$			
^{60}Ni				
KED	$y = 5.10^{-6}x + 249.17$			
STD	$y = 4.10^{-6}x + 2869.3$			
^{59}Co		**TiC^{+}**	**MoO^{2+}**	**CaO^{+}**
KED	$y = 6.10^{-7}x + 13.068$		No	No
STD	$y = 6.10^{-7}x + 647.11$		$y = 3.10^{-7}x + 432.44$	$y = 2.10^{-6}x - 1845.2$

	^{90}Zr	^{48}Ti	^{98}Mo	^{40}Ca
^{63}Cu				
KED	$y = 5.10^{-6}x + 102.73$	$y = 4.10^{-5}x + 70.031$	$y = 10^{-6}x + 62.535$	
STD	$y = 4.10^{-6}x + 977.97$	$y = 0.0001x + 6979.4$	$y = 2.10^{-6}x + 873.7$	
^{64}Zn		**TiC^+, TiN^+, TiO^+, $TiOH^+$**		
KED		$y = 0.0002x + 1618.1$		
STD		$y = 0.0011x + 189905$		
^{66}Zn		**TiO^+, $TiOH^+$**		
KED		No		
STD		$y = 0.0001x + 28222$		
^{106}Cd	**ZrO^+, ZrC^+, ZrN^+**			
KED	$y = 0.0026x + 46069$			
STD	$y = 0.0065x + 88432$			
^{111}Cd	**ZrO^+, $ZrOH^+$, ZrN^+**		**Mo^+, $MoOH^+$, MoC^+, MoN^+, MoO^+**	
KED	$y = 6.10^{-5}x + 283.26$		$y = 6.10^{-5}x + 490.42$	
STD	$y = 0.0001x - 2964.1$		$y = 0.0002x + 18886$	
^{114}Cd	**$ZrOH^+$**		**Mo^+, $MoOH^+$, MoN^+**	
KED	$y = 6.10^{-7}x + 47.441$		$y = 0.0001x + 817.64$	
STD	$y = 10^{-6}x + 164.39$		$y = 0.0004x + 32601$	
	Interferences were interfered			
^{48}Ti	$y = 0.00002x - 36.065$			$y = 0.0084x - 28133$
^{98}Mo	$y=0.000002x + 249.56$	$y = 0.00007x + 227.56$		

Appendix 6: Concentrations of elements corrected by interference correction equations

	24Mg (KED)		**52Cr (KED)**		**55Mn (KED)**		**57Fe (KED)**		**58Ni (KED)**		**59Co (KED)**	
	Y (ppm)	Corr.	Y (ppm)	Corr.	Y (ppm)	Corr.	Y (ppm)	Corr.	Y (ppm)	Corr.	Y (ppm)	Corr.
Buff 0.5031	20.5453	20.5397	0.2459	0.2457	1.5421	1.5421	**58.2710**	**58.2738**	0.4887	0.4887	0.0368	0.0368
Buff 0.5035	18.4839	18.4782	0.2300	0.2298	1.4836	1.4836	**54.5372**	**54.5393**	0.4565	0.4565	0.0355	0.0355
Buff 0.5502	17.8458	17.8407	0.2233	0.2232	1.4184	1.4184	**52.8502**	**52.8530**	0.4447	0.4447	0.0329	0.0329
Buff spike 0.5022	18.8408	18.8344	0.8471	0.8469	2.0992	2.0992	**56.0013**	**56.0027**	1.0963	1.0963	0.6344	0.6344
Buff spike 0.5056	19.0936	19.0876	0.8824	0.8823	2.1659	2.1659	**57.0495**	**57.0515**	1.1148	1.1148	0.6499	0.6499
Buff spike 0.5011	19.4926	19.4868	0.8817	0.8816	2.1431	2.1431	**56.7381**	**56.7402**	1.1163	1.1163	0.6576	0.6576
L1 0.4985	**1.9126**	**1.9080**	0.0226	0.0226	0.9108	0.9108	**15.2068**	**15.2045**	0.1037	0.1037	0.0069	0.0069
L1 0.5079	**2.2505**	**2.2470**	0.0321	0.0321	1.1590	1.1590	**17.4445**	**17.4439**	0.1034	0.1034	0.0082	0.0082
L1 0.5046	**1.7060**	**1.7022**	**0.0220**	**0.0219**	0.9317	0.9317	**12.9616**	**12.9598**	0.0765	0.0765	0.0058	0.0058
L2 0.5015	**1.4006**	**1.3956**	**0.0410**	**0.0409**	0.8601	0.8601	**19.8738**	**19.8727**	0.1189	0.1189	0.0063	0.0063
L2 0.4950	**4.2296**	**4.2264**	0.0441	0.0441	1.1008	1.1008	**22.8199**	**22.8211**	0.1352	0.1352	0.0086	0.0086
L2 0.5054	**1.8645**	**1.8600**	**0.0589**	**0.0588**	1.7341	1.7341	**42.9799**	**42.9850**	0.2241	0.2241	0.0083	0.0083
L3 0.4995	**1.3059**	**1.3041**	0.0231	0.0231	1.1374	1.1374	**19.9434**	**19.9462**	0.1062	0.1062	0.0052	0.0052
L3 0.5086	**1.8700**	**1.8675**	0.0144	0.0144	0.7651	0.7651	**21.7916**	**21.7939**	0.1262	0.1262	0.0053	0.0053
L3 0.4945	**1.6315**	**1.6290**	0.0204	0.0204	0.7935	0.7935	**20.6911**	**20.6932**	0.1124	0.1124	0.0053	0.0053
L4 0.4909	**2.3004**	**2.2977**	**0.0187**	**0.0186**	0.9975	0.9975	**26.1414**	**26.1441**	0.1391	0.1391	0.0075	0.0075
L4 0.5030	**2.4911**	**2.4892**	0.0263	0.0263	1.0148	1.0148	**30.9241**	**30.9292**	0.1577	0.1577	0.0099	0.0099
L4 0.5001	**1.4454**	**1.4434**	0.0142	0.0142	1.0007	1.0007	17.6090	17.6107	0.1030	0.1030	0.0059	0.0059

Appendix 6: Continued

	60Ni (KED)		**63Cu (KED)**		**64Zn (KED)**		**106Cd (KED)**		**111Cd (KED)**		**114Cd (KED)**	
	Y (ppm)	Corr.	Y (ppm)	Corr.	Y (ppm)	Corr.	Y (ppm)	Corr.	Y (ppm)	Corr.	Y (ppm)	Corr.
Buff 0.5031	0.1216	0.1216	0.2735	0.2735	**1.2617**	**1.2616**	**0.0113**	**0.0105**	0.0104	0.0104	0.0108	0.0108
Buff 0.5035	0.1214	0.1214	0.2510	0.2510	**1.1536**	**1.1535**	**0.0094**	**0.0086**	0.0100	0.0100	0.0108	0.0108
Buff 0.5502	0.1188	0.1188	0.2519	0.2519	**1.1042**	**1.1041**	**0.0097**	**0.0090**	0.0093	0.0093	0.0101	0.0101
Buff spike 0.5022	0.7431	0.7431	0.8628	0.8628	1.8559	1.8559	**0.5366**	**0.5360**	0.6760	0.6760	0.6901	0.6901
Buff spike 0.5056	0.7488	0.7488	0.9072	0.9072	1.8632	1.8632	**0.5520**	**0.5513**	0.6717	0.6717	0.7088	0.7088
Buff spike 0.5011	0.7531	0.7531	0.9242	0.9242	1.9404	1.9404	**0.5702**	**0.5695**	0.6964	0.6964	0.7087	0.7087
L1 0.4985	0.0334	0.0334	0.0139	0.0139	**0.0918**	**0.0918**	**0.0024**	**0.0019**	0.0004	0.0004	0.0005	0.0005
L1 0.5079	0.0210	0.0210	0.0123	0.0123	0.1177	0.1177	**0.0019**	**0.0014**	0.0002	0.0002	0.0002	0.0002
L1 0.5046	0.0154	0.0154	0.0086	0.0086	**0.0776**	**0.0775**	**0.0018**	**0.0014**	0.0001	0.0001	0.0002	0.0002
L2 0.5015	0.0234	0.0234	0.0101	0.0101	**0.2727**	**0.2726**	**0.0017**	**0.0014**	0.0001	0.0001	0.0001	0.0001
L2 0.4950	0.0264	0.0264	0.0125	0.0125	**0.1270**	**0.1270**	**0.0021**	**0.0015**	0.0002	0.0002	0.0002	0.0002
L2 0.5054	0.0205	0.0205	0.0111	0.0111	**0.1205**	**0.1204**	**0.0023**	**0.0018**	0.0003	0.0003	0.0003	0.0003
L3 0.4995	0.0129	0.0129	0.0084	0.0084	**0.0584**	**0.0583**	**0.0018**	**0.0015**	0.0002	0.0002	0.0002	0.0002
L3 0.5086	0.0211	0.0211	0.0137	0.0137	0.0658	0.0658	**0.0017**	**0.0014**	0.0002	0.0002	0.0013	0.0013
L3 0.4945	0.0165	0.0165	0.0102	0.0102	**0.0734**	**0.0733**	**0.0015**	**0.0012**	0.0002	0.0002	0.0002	0.0002
L4 0.4909	0.0181	0.0181	0.0169	0.0169	**0.0827**	**0.0827**	**0.0017**	**0.0013**	0.0003	0.0003	0.0003	0.0003
L4 0.5030	0.0195	0.0195	0.0092	0.0092	**0.0864**	**0.0863**	**0.0017**	**0.0012**	0.0003	0.0003	0.0003	0.0003
L4 0.5001	0.0202	0.0202	0.0097	0.0097	**3.5539**	**3.5538**	**0.0400**	**0.0397**	0.0476	0.0476	0.0485	0.0485

Appendix 7: Spike recoveries compared to Buffalo River recoveries

	WO itnstd (%)		**Y**		**Yb**	
	Spike rec.	**Buffalo rec.**	**Spike rec.**	**Buffalo rec.**	**Spike rec.**	**Buffalo rec.**
^{24}Mg	101.8	69.9	97.7	73.3	**^{24}Mg**	103.3
^{27}Al	101.0	22.3	95.4	23.4	**^{27}Al**	101.8
^{52}Cr	127.2	65.7	96.1	52.4	**^{52}Cr**	137.2
^{55}Mn	132.6	106.8	130.1	110.8	**^{55}Mn**	135.8
^{57}Fe	101.2	72.9	91.2	76.1	**^{57}Fe**	100.1
^{59}Co	119.3	91.2	93.1	74.7	**^{59}Co**	132.5
^{58}Ni	129.1	377.9	94.1	310.5	**^{58}Ni**	134.7
^{60}Ni	119.0	92.0	91.7	73.4	**^{60}Ni**	130.6
^{63}Cu	124.2	87.5	97.7	72.4	**^{63}Cu**	133.8
^{64}Zn	149.3	84.2	102.2	69.5	**^{64}Zn**	147.0
^{66}Zn	110.7	68.2	74.7	56.3	**^{66}Zn**	107.6
^{106}Cd	88.9	80.4	69.7	71.8	**^{106}Cd**	99.2
^{111}Cd	113.8	94.4	89.2	75.1	**^{111}Cd**	127.0
^{114}Cd	114.4	105.0	89.7	84.4	**^{114}Cd**	127.6
^{206}Pb	97.3	77.9	70.8	62.0	**^{206}Pb**	101.4
^{207}Pb	100.0	72.3	73.3	57.4	**^{207}Pb**	105.0
^{208}Pb	100.3	74.3	73.5	59.1	**^{208}Pb**	105.2

Appendix 8. Statistical comparisons of recoveries when using internal standards (t_{table} (degree of freedom=3, 95%) = 3.182)

	WO itnstd (%) (N=4)		**Yb (N=4)**		**WO and Yb**		**Y (N=4)**		**WO and Y**	
	Average	**s**	**Average**	**s**	s_{pooled}	t_{calc}	**Average**	**s**	s_{pooled}	t_{calc}
^{27}Al	27.4	1.5	29.3	1.8	1.7	2.2	26.8	3.6	2.7	0.4
^{52}Cr	54.5	4.6	65.9	5.9	5.3	4.3	47.5	5.1	4.8	2.9
^{55}Mn	107.5	17.3	114.9	20.5	19.0	0.8	106.4	26.9	22.6	0.1
^{57}Fe	87.4	4.8	93.3	5.2	5.0	2.3	85.6	10.0	7.9	0.5
^{59}Co	94.1	3.0	113.9	5.2	4.3	9.3	82.3	5.9	4.7	5.0
^{60}Ni	74.7	5.9	90.4	7.5	6.7	4.7	65.2	7.5	6.8	2.8
^{63}Cu	82.0	15.2	98.7	16.1	15.7	2.1	71.7	14.8	15.0	1.4
^{64}Zn	76.8	5.6	92.7	4.3	5.0	6.3	67.0	5.9	5.8	3.4
^{66}Zn	80.4	7.9	97.1	7.8	7.9	4.2	70.2	8.2	8.1	2.5
^{106}Cd	100.7	9.4	121.6	10.2	9.8	4.3	90.1	8.6	9.0	2.4
^{111}Cd	90.9	8.3	109.8	9.3	8.8	4.3	79.5	8.4	8.3	2.7
^{114}Cd	120.7	12.1	145.7	13.2	12.7	3.9	105.4	12.5	12.3	2.5
^{206}Pb	92.0	6.8	111.2	7.3	7.0	5.4	80.2	5.1	6.0	4.0
^{207}Pb	88.1	3.5	106.5	1.9	2.8	13.1	76.9	4.1	3.8	5.9
^{208}Pb	80.1	4.5	96.7	3.4	4.0	8.4	69.8	4.3	4.4	4.7

Appendix 9. Statistical comparisons between mean mass fractions determined with internal standards (Yb for all elements) and certified mass fractions.

	Experimental results		**Certified results**		**t_{calc}**	**ν**	**t_{table}**
	Mean (µg/g)	s	Mean (µg/g)	kUx			
^{27}Al	17842.7	1124.5	61000.0	109.8	76.397	558004.1	1.960
^{52}Cr	80.4	7.2	121.9	3.8	10.206	36.6	2.060
^{55}Mn	624.8	111.5	544.0	21.0	1.424	5771.1	1.960
^{57}Fe	37028.4	2055.9	39700.0	39.7	2.598	1831584.4	1.960
^{59}Co	15.5	0.7	13.6	0.4	4.578	0.4	12.706
^{60}Ni	38.8	3.2	42.9	3.7	1.683	23.2	2.042
^{63}Cu	97.4	15.9	98.6	5.0	0.149	132.0	2.021
^{64}Zn	378.4	17.7	408.0	15.0	2.550	395.7	1.960
^{66}Zn	396.1	31.8	408.0	15.0	0.678	653.7	1.960
^{106}Cd	3.6	0.3	2.9	0.3	3.044	0.1	1.960
^{111}Cd	3.2	0.3	2.9	0.3	1.442	0.1	1.960
^{114}Cd	4.3	0.4	2.9	0.3	5.534	0.2	1.960
^{206}Pb	166.8	11.0	150.0	17.0	1.661	531.2	1.960
^{207}Pb	159.7	2.8	150.0	17.0	1.126	588.8	1.960
^{208}Pb	145.0	5.0	150.0	17.0	0.563	618.2	1.960

Appendix 10. Mass ratios (ppm) Al measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

	11/1/2021	11/13/2021	12/4/2021	12/20/2021	1/22/2022	2/6/2022	2/27/2022	3/10/2022	3/20/2022
W1	2604.7	3727.6	2488.4	2924.7	2511.5	3541.6	2181.9	2436.6	4461.1
W2	1854.4	2830.5	1873.4	2488.1	2630.5	3132.2	2036.3	2338.1	3387.3
W3	2401.3	4099.1	2114.3	2006.2	1337.4	3673.1	2644	3058.8	3157.2
W4	4086.4	3149.7	3287.3	4132.7	2754.9	2890.4	2218.1	2288.8	2561
C1	15526.8	2293.9	2713.6	2231.5	3361.6	2140.1	2849.7	3350.4	3682.2
C2	1671.8	2996.2	2986.3	1847	1760.2	2730.8	3064.4	2428.1	3112.9
C3	2460.2	3244.4	3175.2	2367.4	2126.9	4107.3	2070.8	2612.4	3372
C4	2020.9	1827.2	2425.2	2616.2	2404.3	3004.7	2884.1	1844.3	3558.7
L1	3396.8	2015.6	1194.2	2636.6	3402.4	3771.2	5239.8	1843	2352.4
L2	2670.7	2447	1952.5	2339.8	3392.5	2684.4	3813.6	1949.8	3041
L3	2620.5	1943	3027.1	1373.5	2535.7	3647.6	3601.2	1512.6	3968.8
L4	2478.6	2801.8	2363.1	2795.3	3299.7	3053.5	1453.4	x	3951.5

Appendix 11. Mass ratios (ppm) Mn measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

Mn	**11/1/2021**	**11/13/2021**	**12/4/2021**	**12/20/2021**	**1/22/2022**	**2/6/2022**	**2/27/2022**	**3/10/2022**	**3/20/2022**
W1	293.2	377.2	291.5	342.0	358.5	567.5	393.7	837.7	672.3
W2	244.7	469.3	240.9	350.9	622.3	530.2	339.3	914.0	638.6
W3	235.3	604.3	277.8	416.7	265.8	843.9	435.4	798.1	503.3
W4	518.2	670.8	330.4	585.8	814.2	603.6	497.3	980.1	405.1
C1	545.7	729.7	432.0	701.9	987.8	502.3	621.7	898.1	844.5
C2	388.1	880.1	499.7	520.8	616.7	691.8	502.3	598.0	706.8
C3	516.4	962.2	595.7	705.9	500.0	922.7	597.5	539.8	992.2
C4	422.0	656.5	484.1	397.6	574.0	705.3	583.9	576.8	862.5
L1	**406.5**	441.1	174.6	471.8	966.3	1364.4	675.3	263.7	605.4
L2	511.5	435.2	283.2	520.9	1725.0	1505.3	460.4	286.0	489.1
L3	314.8	479.6	609.2	302.9	1218.9	1512.4	551.3	292.3	550.2
L4	507.3	460.4	532.5	617.6	877.4	770.9	210.4	x	678.2

Appendix 12. Mass ratios (ppm) Fe measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

	11/1/2021	**11/13/2021**	**12/4/2021**	**12/20/2021**	**1/22/2022**	**2/6/2022**	**2/27/2022**	**3/10/2022**	**3/20/2022**
W1	7211.5	7732.3	9854.7	9559.7	9139.6	13752.1	13554.0	9947.0	13762.1
W2	6960.3	9923.6	6836.3	9897.1	9038.3	9937.4	22967.5	12458.1	12428.9
W3	6872.0	14786.3	6817.9	7594.2	5754.4	13055.3	12016.6	14211.1	10383.3
W4	13490.2	12094.9	8425.3	13287.5	9814.0	11602.7	21804.3	9623.1	9906.0
C1	12629.0	10196.4	10196.7	13695.7	20907.6	7361.1	21578.5	18615.2	14208.0
C2	14936.4	14846.1	11727.0	8732.5	9301.7	9981.5	12110.3	16757.6	14490.7
C3	10825.1	13359.4	10343.9	9315.1	10906.8	15062.4	17444.7	14548.0	15747.7
C4	18420.4	28933.9	11337.5	11059.8	9251.0	9981.3	16922.7	26632.5	21054.9
L1	**15893.2**	13832.8	9745.6	15772.4	13392.5	16284.8	13557.9	6337.0	29841.7
L2	11896.1	11251.3	9201.9	10207.4	37422.1	14408.7	9220.3	7591.1	10331.3
L3	12287.8	8362.0	15521.7	6998.9	43938.4	17918.2	12888.0	11109.4	13090.6
L4	9621.6	11734.2	12923.1	14996.1	21338.6	11817.2	5170.5	x	12599.7

Appendix 13. Mass ratios (ppm) Cr measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

	11/1/2021	**11/13/2021**	**12/4/2021**	**12/20/2021**	**1/22/2022**	**2/6/2022**	**2/27/2022**	**3/10/2022**	**3/20/2022**
W1	4.9	6.6	4.3	4.3	6.5	10.0	10.1	5.6	14.6
W2	3.6	6.5	3.4	4.7	6.5	9.4	11.5	6.4	7.6
W3	3.6	9.9	4.4	4.1	3.0	13.3	7.1	6.6	7.5
W4	5.7	7.9	3.9	9.9	5.4	7.9	37.1	5.2	10.0
C1	16.1	19.9	8.4	13.9	24.5	6.0	16.7	21.2	13.6
C2	17.7	15.0	8.1	5.9	8.3	15.3	7.7	15.9	17.3
C3	7.2	15.3	16.3	6.2	9.3	22.5	16.1	8.6	22.2
C4	21.1	69.4	6.5	10.4	8.8	19.3	12.3	18.0	26.6
L1	**7.8**	16.7	4.7	21.8	11.7	9.6	19.3	4.1	20.2
L2	10.7	7.9	7.4	7.3	33.5	8.0	9.4	5.1	7.5
L3	9.5	14.6	8.2	3.5	60.5	11.0	8.6	6.2	10.9
L4	6.7	9.0	4.6	5.7	12.0	8.2	6.9		11.4

Appendix 14. Mass ratios (ppm) Co measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

	11/1/2021	**11/13/2021**	**12/4/2021**	**12/20/2021**	**1/22/2022**	**2/6/2022**	**2/27/2022**	**3/10/2022**	**3/20/2022**
W1	3.6	4.1	3.5	3.7	5.6	6.3	3.1	4.0	6.6
W2	2.5	4.6	2.8	3.6	4.3	5.9	3.6	4.3	5.7
W3	3.1	7.0	2.9	3.7	2.7	6.2	3.4	5.0	5.4
W4	5.9	5.0	3.5	5.3	4.6	7.2	4.3	4.0	4.5
C1	4.5	3.7	3.5	3.5	5.8	3.4	3.5	4.6	5.3
C2	3.1	4.8	3.5	2.8	3.6	5.2	4.7	3.7	4.9
C3	4.2	5.0	3.3	3.3	3.7	5.7	4.1	6.4	5.4
C4	4.3	5.8	4.5	3.5	5.1	5.7	4.9	4.6	5.8
L1	**4.9**	4.3	1.9	3.9	5.4	7.3	6.1	2.7	6.5
L2	3.9	3.9	2.7	3.3	8.7	6.2	5.8	3.1	4.5
L3	4.4	3.1	3.7	2.7	6.6	6.7	3.6	2.8	5.5
L4	3.6	4.8	3.6	4.9	6.4	5.7	2.5	x	6.2

Appendix 15. Mass ratios (ppm) Ni measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

	11/1/2021	**11/13/2021**	**12/4/2021**	**12/20/2021**	**1/22/2022**	**2/6/2022**	**2/27/2022**	**3/10/2022**	**3/20/2022**
W1	5.4	7.2	5.1	6.1	10.4	11.1	4.2	5.4	14.4
W2	4.1	7.9	4.2	5.5	11.6	9.4	4.6	5.6	10.4
W3	4.3	11.4	5.1	5.2	5.8	10.0	5.5	8.8	8.2
W4	8.6	9.5	5.1	8.3	7.9	15.2	12.0	4.6	8.2
C1	7.3	12.5	6.4	5.4	9.2	6.6	4.1	7.0	9.6
C2	5.4	8.4	6.5	4.4	5.6	8.2	6.2	8.4	8.8
C3	6.1	10.7	5.3	5.6	6.3	9.7	5.0	9.6	12.1
C4	10.6	31.8	5.1	6.1	8.7	9.8	6.3	10.3	12.0
L1	**7.8**	7.3	2.9	6.0	11.8	11.4	8.1	11.6	9.7
L2	6.2	7.3	4.0	5.0	14.7	9.9	7.7	4.2	8.1
L3	7.9	5.6	5.6	3.5	17.3	13.5	5.6	4.1	9.3
L4	5.8	9.0	5.9	7.8	15.4	9.3	3.2	x	10.0

Appendix 16. Mass ratios (ppm) Cu measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

	11/1/2021	**11/13/2021**	**12/4/2021**	**12/20/2021**	**1/22/2022**	**2/6/2022**	**2/27/2022**	**3/10/2022**	**3/20/2022**
W1	4.6	4.7	4.0	5.1	6.2	52.2	4.2	5.3	8.5
W2	3.1	6.5	2.8	5.7	5.5	5.8	4.6	6.2	8.3
W3	3.1	8.3	3.1	5.0	3.0	8.5	4.4	8.9	5.9
W4	6.2	6.9	3.1	7.4	6.6	6.0	4.6	5.9	6.4
C1	6.7	5.5	4.6	18.6	9.9	5.8	6.0	10.2	7.5
C2	26.2	8.8	4.7	5.7	5.5	7.7	6.4	5.9	9.0
C3	6.6	9.4	4.1	5.7	5.8	8.4	7.1	11.1	10.6
C4	15.2	84.4	8.4	10.0	6.5	7.9	7.4	11.9	9.4
L1	8.1	8.8	2.6	5.5	7.2	8.2	12.2	3.5	79.8
L2	4.2	5.1	3.1	4.6	13.7	7.5	9.3	4.2	4.9
L3	4.7	4.8	4.7	3.8	11.9	12.9	8.6	6.0	7.6
L4	4.7	5.5	4.3	6.1	9.3	6.9	3.5	x	7.9

Appendix 17. Mass ratios (ppm) Zn measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

	11/1/2021	**11/13/2021**	**12/4/2021**	**12/20/2021**	**1/22/2022**	**2/6/2022**	**2/27/2022**	**3/10/2022**	**3/20/2022**
W1	33.8	27.2	23.6	33.1	29.5	44.0	16.8	23.6	41.5
W2	21.5	29.1	19.9	30.5	42.9	38.0	18.2	30.9	39.7
W3	24.3	36.2	26.5	28.6	26.4	41.5	17.5	28.9	28.6
W4	43.9	35.0	23.0	41.2	25.5	39.7	19.7	18.3	27.0
C1	38.5	34.2	31.1	42.2	47.6	28.8	19.1	166.0	33.3
C2	29.7	56.3	31.3	39.5	24.9	43.6	28.8	35.3	31.8
C3	34.6	42.4	31.7	38.7	25.4	51.7	23.6	22.1	43.9
C4	36.1	48.1	27.2	42.5	31.5	50.0	39.5	88.1	40.2
L1	56.6	32.6	19.3	34.1	34.2	42.3	45.6	16.7	30.4
L2	39.9	33.5	38.0	26.6	43.1	40.9	40.1	19.6	31.6
L3	40.7	37.2	33.5	20.7	33.7	45.4	33.3	20.6	39.2
L4	39.8	39.0	36.2	43.0	42.5	33.6	19.6	x	37.9

Appendix 18. Mass ratios (ppm) Cd measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

	11/1/2021	**11/13/2021**	**12/4/2021**	**12/20/2021**	**1/22/2022**	**2/6/2022**	**2/27/2022**	**3/10/2022**	**3/20/2022**
W1	0.16	0.07	0.06	0.05	0.04	0.04	0.06	0.04	0.06
W2	0.03	0.01	0.09	0.04	0.12	0.06	0.07	0.08	0.04
W3	0.09	0.05	0.05	0.05	0.04	0.05	0.04	0.08	0.03
W4	0.09	0.03	0.04	0.05	0.04	0.03	0.06	0.04	0.03
C1	0.07	0.03	0.10	0.07	0.06	0.04	0.06	0.24	0.02
C2	0.07	0.03	0.09	0.05	0.03	0.08	0.05	0.10	0.04
C3	0.23	0.03	0.05	0.09	0.04	0.08	0.05	0.04	0.02
C4	0.10	0.05	0.33	0.10	0.04	0.08	0.05	0.06	0.03
L1	0.20	0.11	0.05	0.03	0.03	0.08	0.16	0.02	0.03
L2	0.08	0.00	0.03	0.04	0.07	0.07	0.09	0.14	0.08
L3	0.10	0.05	0.14	0.08	0.08	0.11	0.06	0.03	0.05
L4	0.14	0.04	0.10	0.06	0.06	0.03	0.12	x	0.06

Appendix 19. Mass ratios (ppm) Pb measured in samples collected in Fall 2021, Winter 2022 and Spring 2022

	11/1/2021	**11/13/2021**	**12/4/2021**	**12/20/2021**	**1/22/2022**	**2/6/2022**	**2/27/2022**	**3/10/2022**	**3/20/2022**
W1	4.6	4.3	6.3	5.2	6.0	8.8	3.7	5.0	8.3
W2	3.8	6.2	3.3	4.8	4.1	5.8	5.9	6.0	8.1
W3	3.9	7.0	3.3	5.3	3.4	6.8	4.1	8.4	5.7
W4	6.4	7.3	3.9	7.0	5.1	7.5	5.5	5.2	5.3
C1	18.2	9.2	6.8	6.2	7.4	5.8	7.4	10.6	7.5
C2	7.9	8.1	7.1	5.1	6.1	8.0	7.3	9.0	9.4
C3	7.9	20.3	7.9	78.9	8.2	9.0	11.1	6.4	16.9
C4	42.6	8.3	6.1	9.2	12.7	20.4	11.8	19.1	9.1
L1	11.8	4.5	3.3	10.9	6.3	9.1	11.0	4.0	11.7
L2	7.4	4.7	9.3	5.4	9.0	5.8	8.6	6.3	7.1
L3	5.9	5.4	5.7	4.3	40.5	7.2	11.2	5.2	8.8
L4	9.8	6.2	8.5	13.3	8.2	5.6	3.4	x	8.8

Appendix 20: Mass ratios (%) of elements measured by XRF and ICP-MS

	Al		Mn		Fe		Cr		Cu		Zn	
	XRF	ICP-MS	XRF	ICP-MS	XRF	ICP-MS	XRF	ICP-MS	XRF	ICP-MS	XRF	ICP-MS
W1 11.1.21	7.41	0.26	0.05	0.03	1.46	0.72	0.0022	0.0005	0.0022	0.0005	0.0061	0.0034
W1 11.13.21	6.98	0.37	0.05	0.04	1.21	0.77	0.0030	0.0007	0.0024	0.0005	0.0041	0.0027
W1 12.20.21	6.15	0.29	0.05	0.03	1.74	0.96	0.0054	0.0004	0.0021	0.0005	0.0072	0.0033
W1 1.21.22	5.14	0.25	0.05	0.04	1.33	0.91	0.0008	0.0006	0.0037	0.0006	0.0031	0.0029
W1 2.6.22	7.72	0.35	0.06	0.06	1.85	1.38	0.0023	0.0010	0.0029	0.0052	0.0065	0.0044
W2 11.1.21	7.13	0.19	0.05	0.02	1.60	0.70	0.0045	0.0004	0.0023	0.0003	0.0062	0.0021
W2 11.13.21	7.21	0.28	0.05	0.05	1.34	0.99	0.0030	0.0007	0.0024	0.0006	0.0041	0.0029
W2 12.20.21	6.05	0.25	0.06	0.04	1.85	0.99	0.0042	0.0005	0.0023	0.0006	0.0075	0.0031
W2 1.21.22	5.10	0.26	0.07	0.06	1.30	0.90	0.0008	0.0007	0.0035	0.0006	0.0033	0.0043
W2 2.6.22	7.22	0.31	0.05	0.05	1.58	0.99	0.0021	0.0009	0.0028	0.0006	0.0060	0.0038
W3 11.1.21	7.00	0.24	0.04	0.02	1.25	0.69	0.0016	0.0004	0.0022	0.0003	0.0059	0.0024
W3 11.13.21	7.95	0.41	0.07	0.06	1.85	1.48	0.0025	0.0010	0.0027	0.0008	0.0048	0.0036
W3 12.20.21	6.37	0.20	0.07	0.04	1.73	0.76	0.0046	0.0004	0.0020	0.0005	0.0069	0.0029
W3 1.21.22	4.79	0.13	0.05	0.03	1.29	0.58	0.0012	0.0003	0.0035	0.0003	0.0033	0.0026
W3 2.6.22	7.76	0.37	0.08	0.08	1.71	1.31	0.0025	0.0013	0.0028	0.0008	0.0067	0.0041
W4 11.1.21	7.42	0.41	0.06	0.05	1.64	1.35	0.0025	0.0006	0.0019	0.0006	0.0062	0.0044
W4 11.13.21	7.10	0.31	0.07	0.07	1.45	1.21	0.0047	0.0008	0.0026	0.0007	0.0043	0.0035
W4 12.20.21	6.11	0.41	0.07	0.06	1.75	1.33	0.0049	0.0010	0.0022	0.0007	0.0071	0.0041
W4 1.21.22	5.08	0.28	0.11	0.08	1.53	0.98	0.0012	0.0005	0.0036	0.0007	0.0037	0.0026
W4 2.6.22	7.50	0.29	0.08	0.06	1.73	1.16	0.0027	0.0008	0.0030	0.0006	0.0063	0.0040
C1 11.1.21	5.93	1.55	0.06	0.05	1.59	1.26	0.0030	0.0016	0.0022	0.0007	0.0065	0.0039
C1	7.2	0.23	0.0	0.07	1.7	1.02	0.00	0.002	0.00	0.000	0.00	0.003

	Al		Mn		Fe		Cr		Cu		Zn	
11.13.21	3		9		0		48	0	28	5	52	4
C1 12.20.21	5.18	0.22	0.07	0.07	1.89	1.37	0.0056	0.0014	0.0022	0.0019	0.0065	0.0042
C1 1.21.22	4.34	0.34	0.10	0.10	1.77	2.09	0.0087	0.0024	0.0037	0.0010	0.0042	0.0048
C1 2.6.22	7.35	0.21	0.09	0.05	1.98	0.74	0.0041	0.0006	0.0029	0.0006	0.0069	0.0029
C2 11.1.21	4.94	0.17	0.09	0.04	2.30	1.49	0.0039	0.0018	0.0024	0.0026	0.0067	0.0030
C2 11.13.21	6.94	0.30	0.10	0.09	2.24	1.48	0.0055	0.0015	0.0025	0.0009	0.0092	0.0056
C2 12.20.21	5.61	0.18	0.10	0.05	1.85	0.87	0.0134	0.0006	0.0021	0.0006	0.0072	0.0039
C2 1.21.22	4.91	0.18	0.08	0.06	1.44	0.93	0.0024	0.0008	0.0037	0.0005	0.0042	0.0025
C2 2.6.22	7.50	0.27	0.09	0.07	2.05	1.00	0.0016	0.0015	0.0030	0.0008	0.0075	0.0044
C3 11.1.21	6.72	0.25	0.09	0.05	1.87	1.08	0.0024	0.0007	0.0021	0.0007	0.0073	0.0035
C3 11.13.21	7.43	0.32	0.09	0.10	1.62	1.34	0.0038	0.0015	0.0028	0.0009	0.0048	0.0042
C3 12.20.21	5.35	0.24	0.10	0.07	1.58	0.93	0.0056	0.0006	0.0021	0.0006	0.0070	0.0039
C3 1.21.22	4.71	0.21	0.08	0.05	1.60	1.09	0.0019	0.0009	0.0036	0.0006	0.0039	0.0025
C3 2.6.22	6.96	0.41	0.07	0.09	1.71	1.51	0.0031	0.0023	0.0027	0.0008	0.0063	0.0052
C4 11.1.21	6.21	0.20	0.07	0.04	2.48	1.84	0.0106	0.0021	0.0025	0.0015	0.0076	0.0036
C4 11.13.21	6.38	0.18	0.06	0.07	1.83	2.89	0.0064	0.0069	0.0031	0.0084	0.0070	0.0048
C4 12.20.21	5.69	0.26	0.07	0.04	1.90	1.11	0.0085	0.0010	0.0026	0.0010	0.0084	0.0042
C4 1.21.22	4.45	0.24	0.06	0.06	1.26	0.93	0.0015	0.0009	0.0036	0.0007	0.0034	0.0032
C4 2.6.22	7.33	0.30	0.08	0.07	1.67	1.00	0.0010	0.0019	0.0029	0.0008	0.0066	0.0050
L1 11.1.21	6.62	0.34	0.09	0.04	1.95	1.59	0.0058	0.0008	0.0026	0.0008	0.0074	0.0057
L1 11.13.21	5.66	0.20	0.06	0.04	1.86	1.38	0.0047	0.0017	0.0025	0.0009	0.0039	0.0033
L1 12.20.21	5.37	0.26	0.08	0.05	2.42	1.58	0.0052	0.0022	0.0022	0.0005	0.0076	0.0034
L1 1.21.22	4.34	0.34	0.10	0.10	1.77	1.34	0.0087	0.0012	0.0037	0.0007	0.0042	0.0034
L1 2.6.22	7.86	0.38	0.17	0.14	2.01	1.63	0.0028	0.0010	0.0030	0.0008	0.0054	0.0042

	Al		Mn		Fe		Cr		Cu		Zn	
L2 11.1.21	6.15	0.27	0.06	0.05	1.53	1.19	0.0026	0.0011	0.0021	0.0004	0.0064	0.0040
L2 11.13.21	6.91	0.24	0.06	0.04	1.78	1.13	0.0041	0.0008	0.0025	0.0005	0.0056	0.0033
L2 12.20.21	5.51	0.23	0.07	0.05	1.87	1.02	0.0046	0.0007	0.0019	0.0005	0.0076	0.0027
L2 1.21.22	4.91	0.34	0.08	0.17	1.44	3.74	0.0024	0.0033	0.0037	0.0014	0.0042	0.0043
L2 2.6.22	7.22	0.27	0.18	0.15	1.88	1.44	0.0006	0.0008	0.0028	0.0007	0.0054	0.0041
L3 11.1.21	6.78	0.26	0.06	0.03	2.48	1.23	0.0070	0.0010	0.0022	0.0005	0.0072	0.0041
L3 11.13.21	6.23	0.19	0.06	0.05	1.50	0.84	0.0094	0.0015	0.0026	0.0005	0.0053	0.0037
L3 12.20.21	5.72	0.14	0.06	0.03	1.79	0.70	0.0070	0.0003	0.0022	0.0004	0.0079	0.0021
L3 1.21.22	4.71	0.25	0.08	0.12	1.60	4.39	0.0019	0.0061	0.0036	0.0012	0.0039	0.0034
L3 2.6.22	7.25	0.36	0.13	0.15	1.65	1.79	0.0023	0.0011	0.0029	0.0013	0.0050	0.0045
L4 11.1.21	6.53	0.25	0.07	0.05	1.53	0.96	0.0152	0.0007	0.0020	0.0005	0.0062	0.0040
L4 11.13.21	6.71	0.28	0.06	0.05	1.85	1.17	0.0043	0.0009	0.0026	0.0006	0.0051	0.0039
L4 12.20.21	5.54	0.28	0.09	0.06	2.02	1.50	0.0054	0.0006	0.0022	0.0006	0.0085	0.0043
L4 1.21.22	4.45	0.33	0.06	0.09	1.26	2.13	0.0015	0.0012	0.0036	0.0009	0.0034	0.0042
L4 2.6.22	7.59	0.31	0.10	0.08	1.95	1.18	0.0050	0.0008	0.0031	0.0007	0.0055	0.0034

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