

**MUNICIPAL LANDFILL LEACHATE INORGANIC ANALYSIS
FOCUSING ON DETECTING VALUABLE METALS**

by
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*Dedicated to my wife Madeline, for sticking out a miserable pregnancy and caring for our baby
while I worked on campus.*

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ABSTRACT

Pumped municipal solid waste landfill leachate samples (7 cells from a site in Nebraska, 4 cells from a site in Illinois) have been analyzed for 62 elements using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). A procedure for complete dissolution of solids in the leachate was developed. Complete dissolution aims to reduce material loss in filtration by eliminating the need for filtration, and frees materials entrapped in undissolved solids. The procedure uses centrifugation to separate solid phase matter from the raw sample to maximize the effect of acid, and uses Chloric, Nitric, Fluoric, and Boric acids with microwave digestion to achieve full dissolution. The dissolved solid fraction precipitates yttrium fluoride and some other metals due to over-solubility concentrations; the precipitate is recovered and redissolved for analysis. Platinum, (Post-) Transition, and Lanthanide group metals were positively detected in the landfill leachate. Individual metals from these groups were detected in either/both aqueous or/and solid phases: solid phase metals are usually at least one magnitude of concentration greater than liquid phase metals, unless the solid phase produced no detection of the metal where the liquid phase did. Noteworthy results are: in the solid phase; Al was quantified from 10 to $10^3 \mu\text{g/g}$ of solid mass; Sc, Cr, Ti, and Cu were quantified in the solid phase from 1 to $50 \mu\text{g/g}$ of solid mass; Zr and Eu were quantified from .5 to $\sim 8 \mu\text{g/g}$ of solid mass. In the liquid phase: Ti, Cr, Li, Cu, As, and Zr were quantified mostly between 10^{-2} to $10^{-1} \mu\text{g/g}$ of liquid mass, but occasionally reach out of those bounds; Al, Sc, Pt, Co, and V were quantified mostly from 10^{-3} to $10^{-2} \mu\text{g/g}$ of solid mass. Solid phase metals were positively detected with a minimum Limit of Detection (LOD) usually around $10^{-1} \mu\text{g/g}$ of solid mass, including: In, Ge, Pb, Ru, Sb, Ta, Hf, Bi, Yb, La, Ti, Pd, Lu, Dy, and Tb. Liquid phase metals were positively detected with a minimum LOD usually around $10^{-5} \mu\text{g/g}$ of liquid mass, including: Tm, Ge, Au, Pb, Sb, Ta, Hf, Sm, Nb, Ho, Ga, Bi, Yb, Pd, Er, and Cd.

1. INTRODUCTION

Recent research suggests that waste electronics thrown away by consumers could amount to \$37.5M of potentially recoverable metals in single landfill^{a,1}. Municipal solid waste landfills are a target of interest because of the precious metal content of waste electronics, which are commonly thrown away by consumers^{2,3,4}. The EPA in 2018 reports that 2.51 million tons of nonferrous metals are generated in MSW landfills, which could contain ample opportunity for recovering metals of high economic value⁵.

Tantawi³ analyzed the metals content of smart phones to track the evolution of metals used as technology advances, discovering the presence of various valuable metals as one would expect from electronic devices. Gozun²³ performed surveys and stock analysis of consumer habits regarding their devices and found that the total number of electronic devices disposed of by US households has increased rapidly in the last two decades, reaching a high of 63 million devices disposed to landfills in 2021. These devices were specifically discarded, not recycled at a designated buy-back or recovery type of service. The volume of consumer devices, and therefore the valuable metals within, entering landfills every year may represent a significant opportunity for resource recovery in the US.

Economic landfill recovery analyses such as this are an up-and-coming field of study, currently working on sparse data which can be improved immediately with both more and better data. Research going back decades has well established the magnitude of common ions like sodium, calcium, and ammonium, and heavy metals like iron, lead, and copper in landfills⁶, but do not report on valuable metals. Some research highlights a potential for valuable recoverable resources but the level of data available is still limited. Studies in the field have focused on the contained value of metals^{1,2,7,8,9}, waste incinerator fuel¹⁰, and compost nutrients or fertilizer^{11,12,13}, and combinations of recoverable waste streams¹⁴.

Two general tasks to advance toward landfill metal recovery are 1) improving the lab procedures to detect and characterize the metal content in landfills, and 2) directly improving the library of data by applying the analytical procedures on many samples. One naturally leads to the

^a \$148.2M was associated with 4 landfills.

other, but troubleshooting a procedure takes more work than routinely following an established procedure to expedite results. Both tasks are important contributions.

Current analytical methods leach landfill samples in a combination of hydrochloric and nitric acids (called aqua regia), or in nitric acid alone. This combination of acids solubilizes several elements, but does not completely dissolve the particulates in the sample and requires filtration which fails to perfectly recover all of a sample.

The limitations of the current acid digestion procedure causes a disincentivizing barrier to obtaining solid samples. Drilled cores are difficult to obtain logistically and difficult to process with current separation, digestion, and detection methods. When available, drilled cores would provide much more quantity, range, and better quality of data than pumped leachates because they provide large solid sample sizes and have reduced water content. Water is 99% of the mass in leachates but is not the mass of interest, which results in extra procedural expenses in time, materials, accuracy. In order to justify the difficulty of getting and processing better samples, better methods must be developed first.

The most recent valuable metals analyses are currently limited to the United Kingdom and Sweden^{1,8,14}. Rare and useful metals may have a large variance in presence from one landfill to another depending on factors such as age and waste management policies. As an example of the large variance already known, a landfill in Istanbul has been measured as 76% food waste with little metals content¹¹, while Indiana landfills contain major groups up to 15% food waste, 5% metal, 15% plastic, and 30% paper¹⁵. Landfill contents will naturally be different based on their designation as municipal or industrial, and based on common materials and waste regulations which differ from one location to the next, as seen in the difference between Istanbul and Indiana. A general procedure to process and analyze any given sample based on a generalized concept of waste composition would be ideal to speed up data collection.

1.1 Study scope and objective

This study comprehensively analyzed two landfill sites for 62 metals in United States municipal solid waste (MSW) landfills. An adaptation of current acid digestion procedures used in landfill studies was developed. Preference for ICP-OES analysis is due to its common availability and ease of operation compared to ICP-MS abilities.

To fully quantify the elements within the ICP-OES capabilities, the particulate in the landfill leachate samples should be completely dissolved with an acid solution that can support stable solubilization for all elements. A method using an aqua regia and HF-containing matrix was developed to achieve complete dissolution of landfill particulates.

The choice to analyze for 62 metals is to avoid inadvertently limiting the abilities and results of ICP-OES relative to what may be in landfills. Several elements are not as important for precise quantitation such as Na, Ca, K, and Mg, which are well known to be ubiquitous and little value is gained by precisely quantifying them; a rough measurement is sufficient in exchange for no extra effort.

2. LITERATURE REVIEW

The general procedure used for ICP analysis of leachates does not use HF for complete dissolution due to safety and technical difficulties, rather they opt for nitric acid and/or aqua regia leaching. Samples leached this way require filtering and cannot adequately analyze for a handful of elements which are only soluble in HF. Xiaoli¹⁶ performs full dissolution of a solid landfill sample using HF, HNO₃, and H₂O₂, but only analyzed for heavy metals. Lacking HCl in this method, platinum group metals would be less stable and uncertain for full quantitation¹⁷.

A study performed by Oman⁸ quantified 49 elements in landfill leachate and many organic pollutants. The procedure for particulate acidification included only nitric acid digestion, however, multiple elements which are not aqueously stable in nitric acid were reported. Of particular note, several elements which are typically insoluble in water were detected in the liquid leachate fraction of their sample, which may be an artifact of their sampling preservation method: samples were immediately acidified with 5mL/L of 65% HNO₃, maintained at 4°C within 6 hours, and delivered to the laboratory within 24 hours. This may have provided a dissolving effect on the particulates that would increase the solubilized metals before filtration occurred. The samples were not taken from leachate pumps; instead the runoff from landfill sides, ditches, and collection ponds was collected. This sampling technique may result in various accumulations or additions not typical of the internal contents of the landfill and not comparable to other studies. The method analyzed for tungsten but has no detections; this may be attributed to tungsten being highly resistant to dissolution without HF, but could also be due to a real lack of tungsten in the sample.

Wagland¹⁴ demonstrates the extraction capabilities of nitric acid vs aqua regia on solid landfill samples. The results show that a notable amount of several metals can be recovered using only nitric acid. The common methodology uses aqua regia; comparing both methods shows that more substance is recovered using aqua regia. Methods without aqua regia risk underreporting by a significant margin. Of more importance, their selected metals of interest were positively correlated with fine solids, plastics, and textile fractions of waste; this justifies special interest the particulate fraction of pumped leachate. While the precious metals of interest were correlated with fine solids, Jain¹⁸ and others^{19,20,21,22} have found that heavy metals and organic substances are negatively correlated with fine solids, posing a distinct but not necessarily contradictory mechanism for metal group segregation.

Gutierrez-Gutierrez¹ analyzed drilled core samples from four landfills using the typical aqua-regia based leaching method, and analyzed the samples for 27 valuable metals. The drilled core sample contained solids too large to process and plastics which are virtually impossible to dissolve in acid, which were manually sorted out before obtaining their sample for digestion. Having access to a drilled core allowed them to seek correlations between metals and depth; they found no correlations between metals and depth, showing metal mobility in the landfill is quite low. However, the access to such a large sample size allowed them to estimate 5 tonnes of platinum group metals across the four landfill sites, worth \$148.2M as pure substances. For data purposes, the Wagland¹⁴ study and Gutierrez-Gutierrez¹ studies were different thrusts based on the same sample, with Gutierrez-Gutierrez¹ being the study that first produced the measurements.

Wagner⁷ designs an economic model for landfill metals recovery based on incinerator ash generated from US MSW landfill contents, tangentially exploring the economic difficulties of landfill mining. MSW incinerator ash can contain several percent by weight of Fe, Al, Cu, Zn, and Pb, and would be a plausible candidate for recovery of commonly used metals. The case study detected Al, As, Ba, B, Cd, Ca, Cr, Cu, Pb, Hg, Mo, Ni, Se, Ag, V, and Zn in the ash samples; 6% of ash mass was ferrous, and 1% was non-ferrous metals. The estimated cost per mega-ton (one million tons) of ash processed was \$158, with an expected revenue of \$216 estimating all mass as low grade iron for recycling. Costs of processing landfilled ash, which was wet and required extra excavation and transport steps and caused malfunctions in the process, were more economically routed by sorting the ash before landfilling rather than after.

Xiaoli¹⁶ uses an HF method on landfill solids which was very similar to the one developed here, though their work was discovered after this method was developed. Their method uses less acid relative to the solids in the digestion process than the method developed in this paper, however they also filter the digested sample which is a step that would optimally be avoided. The researchers limited their analysis to heavy metals. The focus of their work was to sequentially strip heavy metals out of the landfill waste to determine the conditions which would cause them to mobilize and become hazardous to the surrounding environment. Heavy metals are mostly highly insoluble under normal conditions, but instances can and have occurred to cause hazardous leachate effluents.

The elements are not all equally stable in solution for accurate analysis; according to Inorganic Ventures¹⁷, Ti, Zr, Nb, Mo, Hf, Si, Ge, Sn, and Sb are best stabilized for analysis when

complexed with F^- ion which is best achieved through HF interactions; Ta and W should have excess HF present for stability; and Ru, Rh, Ir, Pt, and Au require Cl^- ion complexation achieved best with HCl.

Below is a table summarizing the relevant literature to valuable metals content of landfills and analytical notes associated with them (Table 1) and a table of the quantities of metals detected in these studies (Table 2).

Table 1: Summary of literature relevant to metals. For reference, ‘heavy metals’ in landfill contexts typically refers to Al, As, Hg, Cd, Cu, Cr, Fe, Ni, Pb, and Zn which are the most commonly expected and impactful metals in landfills. ‘Valuable metals’ in these contexts refers to everything else but *not* the ubiquitous elements B, C, N, O, F, Na, Mg, Si, P, S, Cl, K, or Ca. This distinction has come about due to environmental studies on landfills generalizing the use of ‘heavy metals’ according to EPA regulated metals, while resource-economic studies are still converging on what metals are ‘critical or valuable’ relative to price, abundance, and political stability^{1,24}.

Author, Year	Location	Details	Key Result
Oman ⁸ , 2008	Sweden	Leachate ponds and slopes sampled, acidified with HNO ₃ , microwaved, filtered, and analyzed by ICP-MS.	A wide range of organic and inorganic substances quantified.
Wagland ¹⁴ , 2019	UK	Aqua regia leached and filtered core samples.	Valuable metals from the Gutierrez-Gutierrez study were correlated with fine fraction of particulates and soil-like organics.
Gutierrez-Gutierrez ¹ , 2015	UK	Aqua regia leached and filtered core samples.	No spatial correlation of valuable metals within landfills determined. \$148.2M of metals were estimated.
Wagner ⁷ , 2015	United States	Case study of metal recovery economics from MSW incinerator ash.	Metals were not refined into useful materials; they were separated and collected as raw materials. Metals were mostly ferrous.
Xiaoli ¹⁶ , 2007	Shanghai	Digged refuse samples and leachates analyzed, H ₂ O ₂ , HCl, and HF leaching of solids.	Common heavy metals content in solids is very slowly responsive to age of landfill, but can be highly responsive to acidity.
Kjeldsen ⁶ , 2002	Not applicable	Fundamental review of landfill science including metals content.	Discusses common heavy metal behaviors, but has no analysis of valuable metals.

Table 2: Reported metals content in recent literature regarding valuable metals. There are a couple of differences between detections between the two studies; this may be an artifact of landfills being heterogeneous, or could be due to the Swedish landfill (Oman⁸) not being sampled from the inside, or due to the abbreviated list of analytes in the UK study (Gutierrez-Gutierrez¹).

Element	Gutierrez-Gutierrez, 2015		Oman, 2008			
	Solid sample Average, ppm	RSD%	Filtered liquid sample Average, ppm	RSD%	Suspended solids Average, ppm	RSD%
Ag	3.4	119%	0.1	110%	0.7	79%
Al	13576.0	49%	209.0	93%	10731.0	93%
As	-	-	5.5	160%	48.0	164%
Au	0.1	122%	-	-	-	-
B	-	-	2580.0	28%	38.0	43%
Ba	-	-	280.0	110%	1029.0	82%
Be	-	-	0.1	100%	3.7	73%
Bi	-	-	0.0	160%	0.3	84%
Br	-	-	4298.0	87%	-	-
Ca	-	-	131000.0	82%	115450.0	80%
Cd	-	-	0.4	170%	2.2	150%
Ce	19.8	35%	-	-	-	-
Cl	-	-	-	-	-	-
Co	11.2	50%	7.7	68%	8.3	82%
Cr	-	-	15.3	84%	55.0	74%
Cu	1632.0	130%	23.0	85%	242.0	230%
Dy	1.2	35%	-	-	-	-
Eu	0.4	33%	-	-	-	-
Er	0.6	34%	-	-	-	-
Fe	-	-	6500.0	150%	105825.0	100%
Gd	1.8	35%	-	-	-	-
Ge	-	-	0.2	100%	1.2	230%
Hg	-	-	0.03	120%	0.4	170%
In	0.1	63%	0.01	180%	0.1	59%
K	-	-	411000.0	190%	3840.0	75%
La	8.8	31%	4.4	87%	29.0	150%
Li	18.1	43%	173.0	125%	23.0	140%
Lu	0.1	35%	-	-	-	-
Mg	-	-	47900.0	63%	3490.0	60%
Mn	-	-	1152.0	120%	1850.0	40%
Mo	-	-	223.0	0%	41.0	62%
Na	-	-	476000.0	79%	2140.0	64%
Nb	-	-	0.8	8%	3.1	150%
Nd	10.0	30%	-	-	-	-
Ni	-	-	0.6	65%	22.0	91%
P	-	-	1.2	94%	-	-
Pb	-	-	4.4	90%	97.0	150%
Pd	0.5	48%	0.1	100%	0.4	95%
Pr	2.2	31%	-	-	-	-
Pt	0.02	76%	0.006	110%	0.0	150%
Rb	-	-	480.0	110%	33.0	74%
Rh	-	-	0.009	140%	0.0	120%
Ru	0.002	114%	-	-	-	-
S	-	-	90800.0	210%	4020.0	100%
Sb	9.7	72%	1.5	120%	2.4	200%
Sc	2.6	35%	0.1	100%	13.0	53%
Se	-	-	27.0	140%	1.5	160%
Si	-	-	-	-	-	-
Sm	1.9	33%	-	-	-	-
Sn	-	-	2.7	29%	41.0	73%
Sr	-	-	1010.0	42%	361.0	29%
Ta	-	-	0.01	11%	0.2	80%
Tb	0.2	34%	-	-	-	-
Te	-	-	0.03	61%	0.0	62%
Th	-	-	-	-	-	-
Ti	-	-	22.0	27%	-	-
Tl	-	-	0.1	180%	0.3	93%
Tm	0.1	35%	-	-	-	-
U	-	-	-	-	-	-
V	-	-	16.0	46%	65.0	38%
W	-	-	-	-	0.5	220%
Y	5.3	34%	4.0	64%	56.0	73%
Yb	0.4	34%	-	-	-	-
Zn	-	-	66.0	140%	482.0	100%
Zr	-	-	7.8	24%	152.0	63%

3. METHODS

3.1 Landfill leachate sampling method

Six pumped leachate samples were collected in 50mL metal-free polypropylene centrifuge tubes from each wellhead sampled, from a total of 11 wellheads; 7 wellheads from the Nebraska site, and 4 wellheads from the Illinois site. The samples were taken sequentially at the wellhead. The centrifuge tubes were supplied to a contractor during leachate sampling events organized by the landfill owners. Each wellhead was located in a distinct cell of the landfill site which keeps parameters of each cell separate from the next. The samples were shipped overnight in a cooler full of ice. When the samples arrived at the lab, they were stored upright in a freezer until analysis; the Nebraska samples were sampled in December of 2021 and the Illinois samples were sampled in December of 2022. Analysis of the Nebraska samples began in September of 2022 and analysis of the Illinois samples began in January of 2023. The landfill operators at the Nebraska site sent the measurements of aqueous parameters such as pH, ammonium, and cell age to the researcher, but the Illinois operators did not. Those parameters for the Illinois site were not determined in the lab. Some of the Nebraska samples were measured for these parameters and were found to have changed considerably despite the storage treatment, therefore measuring these parameters for the Illinois site would not represent their state at the point of sampling.

3.2 Analytical tools and materials

Unique tools used: ICP-OES (iCAP 7400 Duo, Thermo Scientific) equipped with HF-containing sample introduction kit, ICP-MS (Element 2 ICP-MS, Thermo Scientific), centrifuge (Heraeus Multifuge X1R, Thermo Scientific), microwave digester with high-pressure rotor (Ethos UP SK-15 eT, Milestone). General laboratory tools were also used, such as scales accurate to four decimal places, calibrating weights, and pipettes.

Because of metal adhesion to glass, glass tools and containers were not used in contact with samples. Centrifuge tubes, pipette tips, and volumetric flasks were metal-free polypropylene (PP). Trace metal grade concentrated acids purchased from Fisher Scientific; Nitric acid was 67-70% concentrated, fluoric acid was 47-51% concentrated, chloric acid was 34-37% concentrated. Boric acid was made as an oversaturated solution in-lab using Type 1 ultrapure water and solid boric

acid crystals, 99.98% pure. Water was always Type 1 ultrapure, produced in-lab with GenPure Pro UV/UF dispenser by Thermo Scientific. Argon gas used for ICP-OES analysis was commercial grade 99.997% pure.

Inorganic Ventures' yttrium 10000 $\mu\text{g g/mL}$ standard (part number CGY10) was used as a surrogate standard in the samples. ICP-OES was calibrated with Inorganic Ventures' ICP calibration standard series CCS(1,2,4-6). The standard series was used as external standards for calibrating the instrument at initialization. The calibration standards were made in acid matrices identical to the matrices used in sample processing to match the viscosity and background spectra effects of the sample matrices. Internal standards were not used in analysis because any selected element would interfere with the detection of that element naturally occurring in the sample. Using yttrium as the surrogate standard and boric acid in sample preparation already removed the ability to properly analyze for two elements and it was desired not to limit the study further by using an internal standard. Instead, the standard series used for calibration was also sampled periodically throughout run time for accuracy checks.

The sample treatment process was monitored using experimental blanks and digest blanks containing yttrium, and loaded "special" blanks containing each element analyzed. Experimental and digest blanks were made every time the procedure was performed to represent contamination or loss during that iteration of the procedure. The need for special blanks was discovered after several samples were processed when yttrium precipitation was noticed in the acidified samples. The special behavior of yttrium in the matrix prompted the need to analyze each element for special behaviors, since yttrium was not representative as was assumed. Two special blanks were subjected to the same procedure in separate iterations.

3.3 Inorganic analysis - ICP-OES/MS method development

Samples were weighed in their containers. .25mL of 10011ppm yttrium nitrate surrogate standard was added to each sample and shaken and weighed again prior to separation. Approximately 99% of the sample was water, which would require an excessive amount of acid to digest. However, the aqueous fraction did not need an extensive digesting procedure; clarifying in a centrifuge at 10000rpm for 20 minutes and pouring off the supernatant was sufficient to procure a liquid phase sample ready for acidification to 2% HNO_3 for ICP analysis. The remaining pellet (defined; solids retained in the bottom of the centrifuged sample, with a minimal amount of

liquid) was a good size to submit for acid digestion—usually weighing .4-.5g per 40-50g of total sample. This pellet was quantitatively transferred into a Teflon microwave digestion vessel using 24mL of 36% HCl and then 8mL of 70% HNO₃ to wash the original vessel (collecting the wash acid into the Teflon vessel as well). The sample is allowed to degas volatile substances overnight, then 3mL of 50% HF and 15mL of ~5% B(OH)₃ (prepared to oversaturation at room ambient temperature) are added to the Teflon vessel. The vessel is sealed and entered to the microwave digester for three cycles; heating over 25 minutes to 230°C using 1500W, holding 230°C for 25 minutes, cooling over 25 minutes to 60°C, and holding the cooled temperature for 15 minutes, repeated two more times, the whole process lasting approximately 5 hours. This is a longer cycle than prior researchers use, for the purpose of ensuring complete digestion of silicates. It may be possible to reduce the duration. A greater power (1500W) was used than previous studies because many Teflon vessels were entered to the microwave at a time, requiring more power to heat all of them simultaneously per the manufacturer's instructions. The samples were quantitatively transferred with water into 100mL PP volumetric flasks, mixed well, then transferred to 50mL centrifuge tubes. All 100mL of sample were contained in two centrifuge tubes (in the final method).

The 50mL samples were stored on a benchtop for a week to allow precipitation to occur. The samples were closed tightly to prevent evaporation and gas transfer, and were exposed to regular lab conditions such as ambient temperature which is automatically maintained near 20-25°C and fluorescent white lighting during day usage. After a week, the samples were mildly agitated by shaking them by hand, then centrifuged at 600 rpm for 10 minutes to collect the precipitate in the bottom of the tube. The precipitate was collected with a 5mL PP pipette and transferred into a 15mL PP centrifuge tube. The excess liquid in the 15mL tube was pipetted back to the original 50mL container. The agitation, centrifugation, and transfer steps were repeated until no more precipitate was observed when the tube was inverted slowly after centrifugation.

For ICP analysis of the HF containing solutions, dilutions were prepared into 2% HNO₃. ICP calibrations were made with the same acid matrix and treatment as the samples to match the properties of the sample solutions as best as possible, diluted into 2% HNO₃. ICP analysis of the liquid phase supernatant was achieved by adding an aliquot of 70% HNO₃ to the sample to achieve a final 2% HNO₃ concentration with a minimally diluted sample.

Four injections per sample were measured, and wavelengths for analysis were selected to have minimal overlap.

A flowchart describing the overview of the process is shown in Figure 1. The procedure is described in greater detail in Appendix A.

Pictures of samples during various stages of the procedure are located in Appendix C, and troubleshooting operations are located in Appendix D.

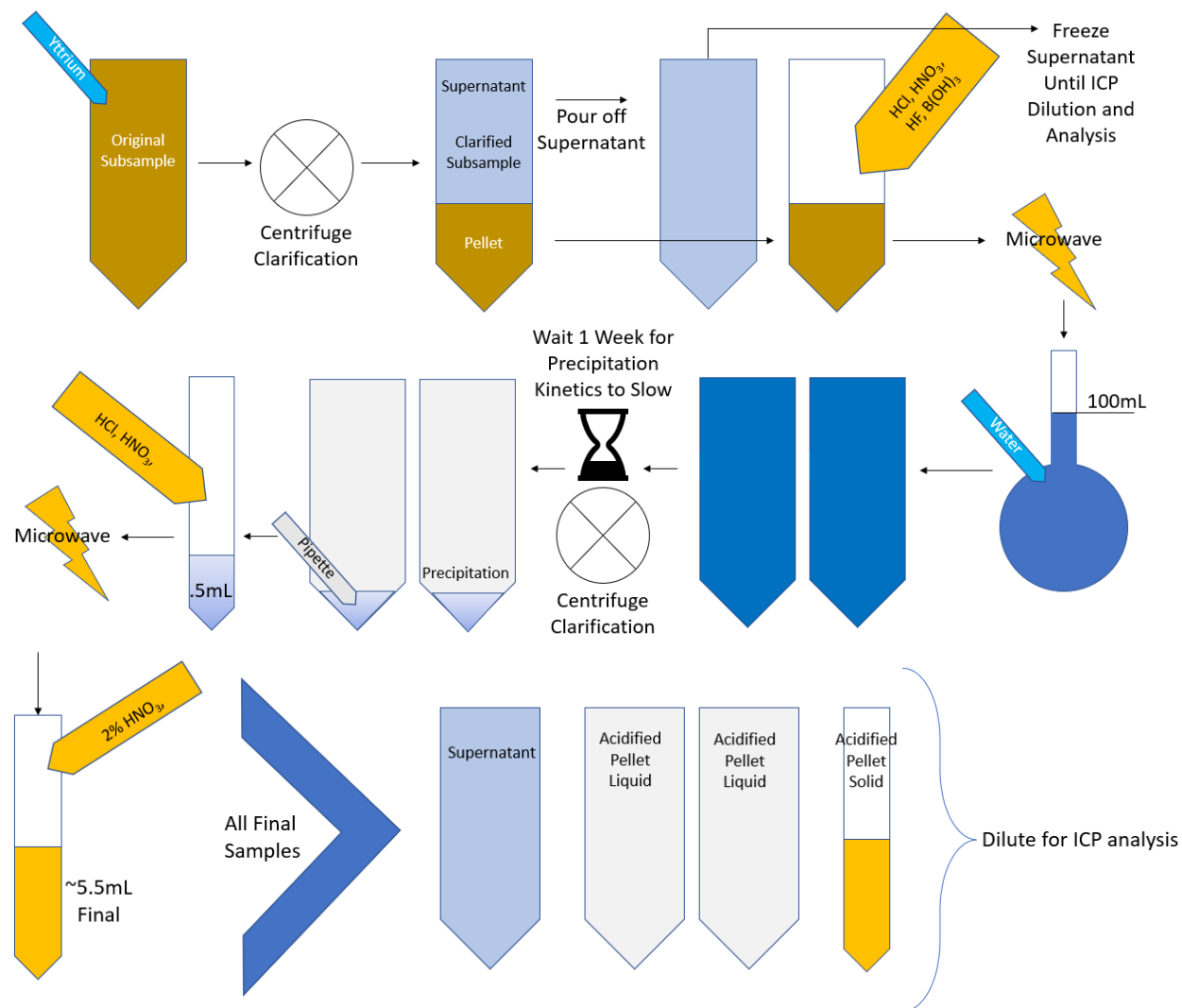


Figure 1: Flowchart describing the general procedure to separate, dissolve, and analyze the solid phase of pumped landfill leachate.

3.4 Sample data processing

Measurements of the samples were filtered based on criteria; the level of detection (LOD) unique to the instance of running the instrument, the level of quantitation (LOQ), the error in the instrument reading elements in the external standards, and the range of the calibration curve. The

LOD of the instrument is internally calculated during calibration. The LOQ suggested by the instrument manual is 10/3*LOD. Positive detections of an element are important, and are treated here as non-zero even if they are not above the LOQ. In the case of a measurement value between the LOD and LOQ, the LOD is taken as the quantity to report. Measurements below the LOD are taken as zero. The external standards were used to determine the accuracy of the instrument by the following formula;

$$\%Error = \left| \left(1 - \frac{C_{ICP}}{C_{Calculated}} \right) * 100\% \right|$$

Where C_{ICP} is the concentration of the element measured by the instrument, and $C_{Calculated}$ is the concentration calculated based on mass, concentration, and volume measurements taken during preparation. If the error exceeded 10%, the sample measurement was flagged. For general reporting in the figures in the discussion, while the external standard was in excess of 10% error the sample measurement was rounded down to its first nonzero digit to provide a conservative magnitude of quantification.

Measurements beyond the calibration curve are reported as measured for calcium, sodium, sulfur, and magnesium. Accurate quantification of those elements are not consequential to this study. Other elements that exceeded the calibration range by less than 10% of the maximum calibration were accepted as valid, otherwise they were re-analyzed with an appropriate calibration range.

After filtering, the data was processed for quantification. The concentration of each subsample was determined separately. The concentration of the sample injection was converted through its dilution factor to the volumetric concentration of the original sample, then was converted to a mass concentration. The general formula for this process is:

$$\begin{aligned} \text{Mass concentration, } \frac{\mu g}{g} &= \Sigma(C_{ICP,ppb,j} * \frac{1L}{1000mL} * DF * V_{mL}/M_g) \\ \text{Standard deviation, } \frac{\mu g}{g} &= \sqrt{\Sigma(C_{ICP,ppb,j}^2) * \frac{1L}{1000mL} * DF * V_{mL}/M_g} \end{aligned}$$

where $C_{ICP,ppb,j}$ is the concentration of the j^{th} subsample measured by the instrument in ppb or $\mu g/L$, $1L/1000mL$ is a conversion factor, DF is the dilution factor of the sample, V_{mL} is the volume of the sample (the volume of the supernatant, 100mL of acidified pellet, or ~5.5mL of precipitate re-digest), and M_g is the mass of the sample (total sample or phase of sample). The j^{th}

subsample is inconsequential for single sub samples, but necessary when combining subsamples into a value for the whole cell. The procedure and math are described in greater detail in Appendix A.

3.5 Method limitations

Gold was not quantifiable by ICP-OES in the solid phase with this method due to the presence of fluorine in the HF added and due to suspected Teflon contamination from the TFM in the digestion process. See Appendix D for troubleshooting details about why fluorine and gold false positive detections are observed.

Boron is not reliably quantified in the solid phase due to lack of precision during acidification, solubility changing with temperature, and extremely high concentrations requiring excessive dilution to measure with ICP-OES. Boron is not a metal of interest, so this does not pose an issue to the remaining analysis.

Silica is not reliably quantified in the solid phase due to fluoric acid and/or fluoroboric acid attacking the glass torch of the instrument and contaminating the plasma during analysis. More discussion of the interactions between fluoric acid, boric acid, silica, and the reason to include boric acid can be found in Appendix D.

Mercury and silver are commonly known not to measure accurately in ICP-OES due to memory effects. Memory effects are effectively contamination remaining adhered to the tubing and other structures in the instrument despite many hours of acid rinsing. Therefore, silver, mercury, and yttrium were not quantified in any sample, and boron, gold, and silicon were not quantified in the acid digested pellet phase samples.

4. RESULTS

4.1 Blanks and surrogate standard recovery

Several metals besides yttrium were detected in the precipitates of the special blanks, potentially due to a combination of complex behavior and surface adsorbance or flocculation effects on the powder. The special blank demonstrates that those elements preferentially segregate >90% into the solid phase, which suggests a similar distribution would occur in the samples if those elements were present. The recovery of elements from two special blank samples are shown below in Table 3. It is particularly concerning that the second sample recovered several elements in the 70-80% range, whereas the first sample had consistently >90% recovery. This would imply that the method cannot be consistently performed to achieve the same results each time.

Table 3: Recovery of special blanks

Total Recovery %			Total Recovery %			Total Recovery %			Total Recovery %		
Special 1	Special 2		Special 1	Special 2		Special 1	Special 2		Special 1	Special 2	
Al	124%	122%	Fe	101%	119%	Na	92%	124%	Sm	88%	71%
As	111%	115%	Ga	113%	115%	Nb	102%	105%	Sn	103%	104%
Au	290%	151%	Gd	91%	72%	Nd	95%	79%	Sr	115%	117%
Ba	112%	115%	Ge	87%	90%	Ni	110%	116%	Ta	103%	105%
Be	105%	106%	Hf	103%	100%	P	69%	68%	Tb	96%	72%
Bi	68%	61%	Hg	97%	94%	Pb	112%	116%	Th	89%	65%
Ca	97%	98%	Ho	96%	72%	Pd	103%	107%	Ti	99%	101%
Cd	104%	113%	In	108%	111%	Pr	96%	80%	Tl	113%	115%
Ce	99%	82%	Ir	77%	91%	Pt	99%	103%	Tm	97%	72%
Co	104%	113%	K	91%	115%	Re	101%	101%	V	104%	107%
Cr	103%	113%	La	90%	82%	Rh	107%	111%	W	101%	103%
Cu	110%	115%	Li	93%	93%	Ru	105%	105%	Y	85%	42%
Dy	94%	73%	Lu	92%	71%	S	98%	100%	Yb	93%	72%
Er	90%	71%	Mg	97%	110%	Sb	105%	104%	Zn	107%	109%
Eu	93%	73%	Mn	110%	116%	Sc	100%	100%	Zr	101%	99%
			Mo	101%	102%	Se	102%	104%			

The experimental blanks and digest blanks behaved differently from each other. The digest blanks all produced a precipitate, but none of the experimental blanks did. This can be explained by recognizing that the “pellet” transferred from the experimental blank was simply an aliquot of liquid water with the yttrium recovery homogeneously mixed in it. Contrast that with the digest blank, which was made with the entire amount of yttrium directly in the digest acids. The concentration of yttrium in the acidified experimental blank was much lower than the others, resulting in no precipitation. When accounting for yttrium based on the concentration of the

experimental-blank water-aliquot, the recovered mass of yttrium in the acid digest was sensible. The experimental blanks tended to recover >90% of yttrium, but the digest blanks recovered only 40-80%. Despite the extreme care taken to ensure a complete transfer of precipitated powder for the redigestion procedure, and despite much better recovery of other elements in the special blanks, the digest blanks failed to recover yttrium well. Table 4 below shows the yttrium recovery distribution of the blank samples.

Table 4: Experimental and digest blanks^b

Digest Blanks						
Yttrium Recovery	DBLK A	DBLK B	DBLK C	DBLK D	DBLK E	
% Recovered	39.7%	64.3%	66.0%	42.9%	88.2%	
Supernatant, ug	NA	NA	NA	NA	NA	
Pellet Liquid, ug	15	51	372	27	52	
Pellet Solid, ug	980	1558	1239	1093	2138	

Experimental Blanks						
Yttrium Recovery	EBLK A	EBLK B	EBLK C	EBLK D	EBLK E	EBLK F
% Recovered	94.2%	92.4%	92.4%	95.8%	91.1%	92.8%
Supernatant, ug	2389	2365	2342	2272	2284	2221
Pellet Liquid, ug	67	44	87	125	102	102
Pellet Solid, ug	NA	NA	NA	NA	NA	NA

The samples themselves fared somewhat better than the digest blanks, but not as consistently well as the experimental blanks. Shown below in Table 5 is a summary of yttrium recovery in the samples. It can be seen that the recovery is sporadically inconsistent with low recovery and large variations among the sub samples. This may be attributable to both the complex chemical profile of all the samples, and the inability to manually replicate the procedure accurately. Knowing from the special blanks that the yttrium recovery is lower than the recovery of other elements, it is likely that the yttrium recovery does not adequately describe the sample recovery. Whatever the case is, low recovery does not invalidate the positive detection of elements in the samples. Therefore, the results obtained are low, but conservative and optimistically indicate that slightly modifying the recovery process would yield better quality of data.

^b The researcher made an error by adding a mixed element standard instead of the Y standard to the DBLK F, resulting in concentrations too low to measure adequately: this sample is not included in the table.

Table 5: Sample yttrium recovery

Samples	NE 1	NE 2	NE 3	NE 10	NE 11	NE 12
Average Recovered, ug	1754	2539	2341	2064	2188	2502
Average % Recovered	75%	101%	92%	83%	83%	100%
RSD Recovered	13%	24%	13%	29%	12%	15%
Average Supernatant, ug	126	141	166	133	255	274
Average Pellet Liquid, ug	387	248	79	177	32	179
Average Pellet Solids, ug	1241	2151	2097	1754	1901	2049

Samples	NE 13	IL 1	IL 2	IL 3	IL 4
Average Recovered, ug	1827	1696	1733	1517	1767
Average % Recovered	73%	72%	71%	64%	75%
RSD Recovered	26%	26%	28%	13%	15%
Average Supernatant, ug	231	145	135	405	190
Average Pellet Liquid, ug	82	107	27	7	19
Average Pellet Solids, ug	1514	1443	1571	1105	1557

4.2 Figures representing sample measurements

Several valuable metals were detected by ICP-OES in the landfill samples. These metals are shown below in Figure 2, Figure 3, and Figure 4. The level of quantitation (LOQ) is defined as 10/3 multiplied by the level of detection (LOD), or the statistical difference between background noise and a known analyte²⁸. For this study, because of the value of positively detected substances, values above the LOD but below the LOQ are taken as the LOD.

An extended set of data is provided in Appendix E.

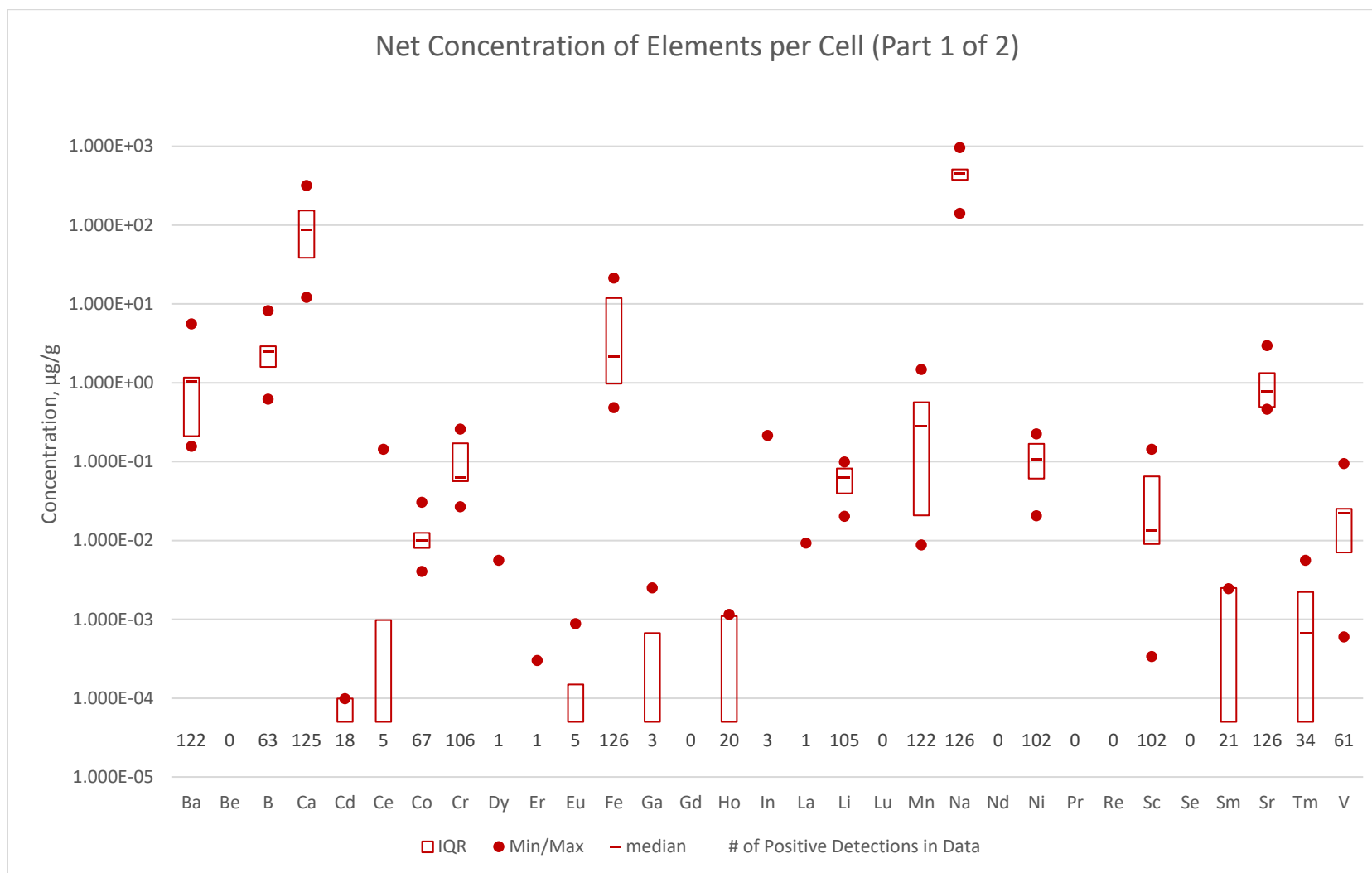
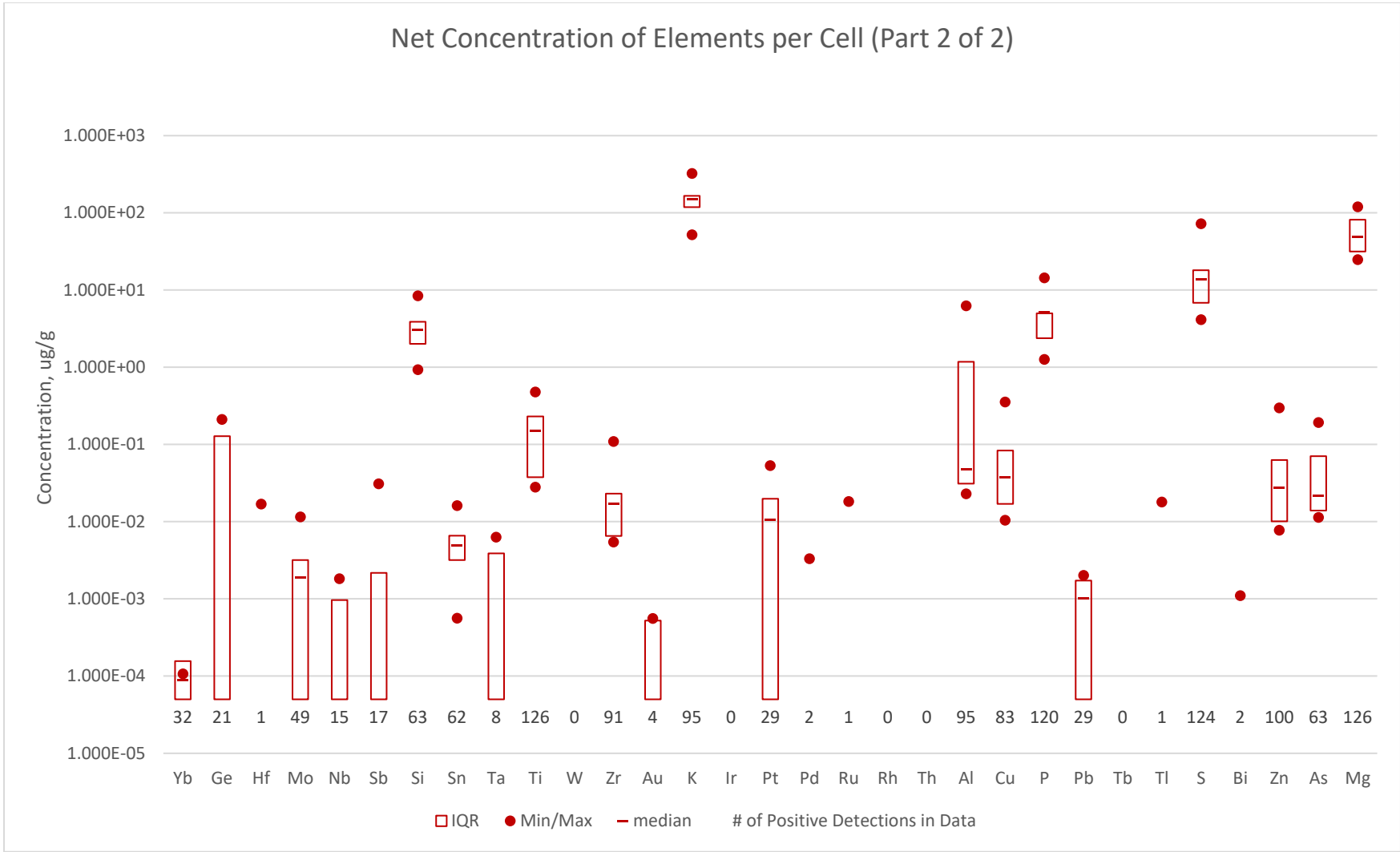


Figure 2: Net Concentration of Elements per Cell (2 Parts): Elements detected in US Midwest pumped landfill leachates. Detections below the LOQ are treated as positive detections of the LOD, and non detections are treated as 0. The sum of mass of an element detected in six sub samples was divided by the sum of mass of the sub samples. The inter-quartile range is truncated at $5\text{E-}5$ for ease of viewing, else the range would extend infinitely on a log scale.

Figure 2 continued



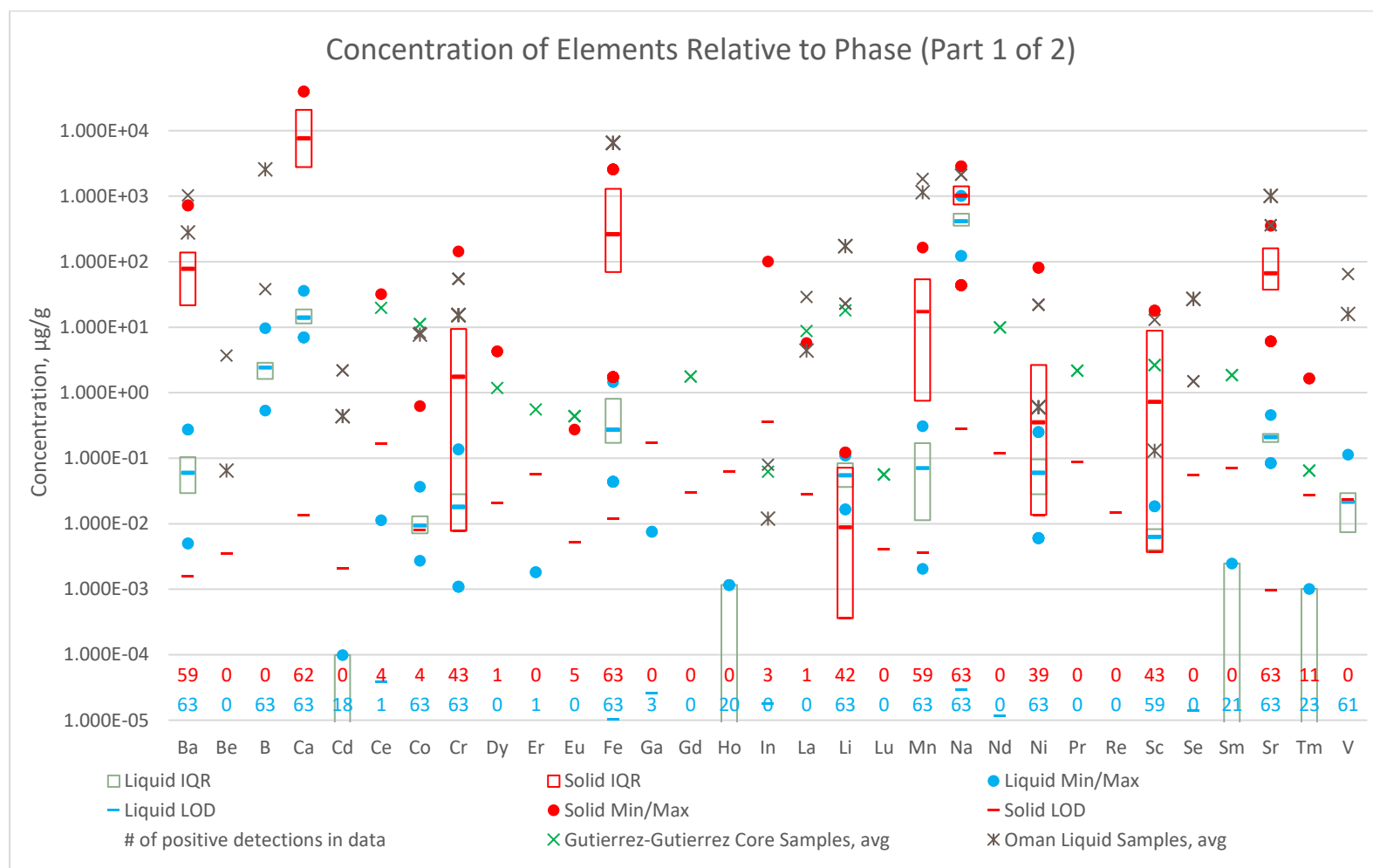
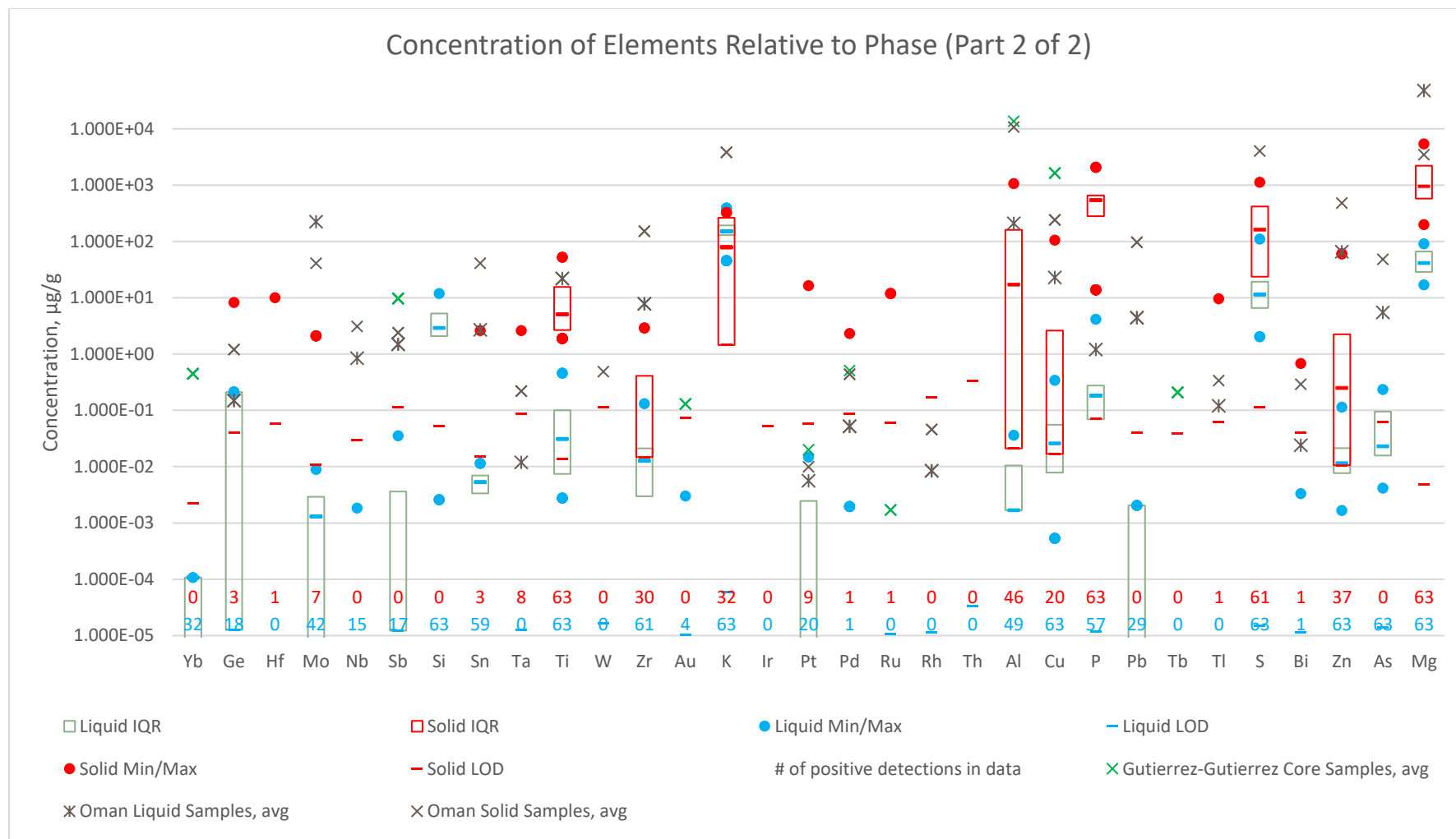


Figure 3: Concentration of Elements Relative to Phase (2 parts): The spread of element concentrations per sub sample. Data below LOQ are treated as detections of LOD. To generate the boxplot, non-detections were taken as 0 but the inter-quartile range was truncated at the LOD for ease of viewing, else the range would extend infinitely on a log scale. Phase data suggests the solid fraction contains metal concentrations magnitudes higher than the leachate, making it a target for mining and recovery. Recall that the Gutierrez-Gutierrez and Oman samples were not pumped leachates; they were core and leachate ponds, respectively, which could explain their frequently higher concentrations.

Figure 3 continued

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H			Solid	Liquid													He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 4: Solid-Liquid Mass Fractions. Notice that although the *concentration* in the solids is much greater, in several cases a large portion of the mass is spread throughout a much larger liquid mass.

5. DISCUSSION

The method was successful at positively detecting a wide range of analytes at low concentrations despite the poor recovery of the yttrium standard. The special blanks suggest that the majority of an element can be recovered despite most yttrium being lost. This is a good indication that with some improvements to the method, detections will also improve.

Many elements were detected in much stronger concentrations in the literature review^{1,8}, with some being found in similar or greater concentrations in this study's leachates, nominally; Ce, Sc, Cr, Eu, In, Ge, Sb, Bi, Tl, Pd, Dy, and Tb were found in the same magnitude, and Pt, Ru, Tm, Ta were found in greater magnitudes. Hf was detected in one sub-sample, which was not previously detected in other studies. The trend for the prior literature to report higher concentrations than this study may be due to the potential low recovery of this study, however that would not result in several magnitudes of difference for some elements and matching magnitudes for others. It is plausible that the differences in sampling are displayed in the results; pumped leachate solids are significantly different than core samples and leachate ponds. Consider that leachate ponds are allowed to evaporate and consolidate material in the sediments, and core samples will contain substantially different materials from the mobile solid fraction of pumped leachate. Due to the substantial differences in sample properties, the data discovered here should be considered distinct from those in the literature until more sample data can validate the parity of core, pond, and wellhead samples.

Correlations between aqueous parameters and each metal were calculated on a cell average basis and metals with a correlation of strength of $R^2 > 0.7$ are shown below in Table 6. Several strong correlations in the liquid phase were found, which is to be expected *a priori*: these parameters are common measurements because of their strong influence on aqueous chemistry. The solid phase has only two strong correlations with aqueous parameters, all other parameters are weakly correlated at best. The turbidity and conductivity are positively correlated with solid phase aluminum and phosphorous. This theoretically makes sense because aluminum is a strong coagulant and phosphate is highly insoluble, thus to increase turbidity and conductivity aluminum and phosphate must be consumed first resulting in solid phase separation.

Liquid phase metals were analyzed for correlation to solid phase samples, but yielded no meaningful results due to the low sample size and several non-detects of metals of interest.

Although some high R^2 values were calculated, fitting one or two data points to another line naturally leads to low variability and high correlation. This analysis could provide useful relations when enough data is available to draw meaningful conclusions.

The consistent medium to strong positive correlation of date of construction to soluble metal content is in line with established research determining that soluble metals decrease with time due to constant washing out^{6,9,18,21,25,26,27}.

Table 6: Correlations between metals, phases, and aqueous parameters (only metals with at least one value of $R^2 > .7$)

Liquid Phase								
Coefficient of Determination (R^2) Direction of Correlation								
Element	pH	Conductivity	Temperature	Turbidity	NH4	COD	BOD	Date of construction
Ba	0.38 -	0.33 -	0.38 -	0.36 -	0.91 -	0.12 -	0.08 -	0.78 -
B	0.68 +	0.71 +	0.38 +	0.05 +	0.56 +	0.03 -	0.06 -	0.77 +
Ca	0.32 -	0.07 -	0.79 -	0 -	0.42 -	0 -	0 -	0.58 -
Ca	0.42 -	0.13 -	0.78 -	0 +	0.45 -	0 +	0 +	0.62 -
Cr	0.57 +	0.46 +	0.34 +	0.09 +	0.76 +	0.02 +	0.01 +	0.68 +
Ho	0.65 +	0.62 +	0.2 +	0.2 +	0.84 +	0.02 +	0 +	0.72 +
Li	0.71 +	0.69 +	0.43 +	0.05 +	0.6 +	0.03 -	0.06 -	0.85 +
Mn	0.48 +	0.79 +	0 +	0.18 +	0.43 +	0 +	0.01 -	0.28 +
Na	0.57 +	0.8 +	0.05 +	0 +	0.2 +	0.15 -	0.23 -	0.31 +
Ni	0.55 +	0.86 +	0.02 +	0.1 +	0.36 +	0.05 -	0.1 -	0.42 +
Sc	0.54 -	0.21 -	0.81 -	0 +	0.46 -	0.01 +	0.02 +	0.67 -
Sm	0.56 +	0.53 +	0.17 +	0.24 +	0.88 +	0.07 +	0.03 +	0.66 +
Tm	0.01 -	0.02 -	0 +	0.42 +	0.3 +	0.78 +	0.74 +	0.02 +
V	0.71 +	0.7 +	0.29 +	0.14 +	0.82 +	0 +	0 -	0.8 +
Y	0.2 +	0.32 +	0.01 +	0.59 +	0.78 +	0.3 +	0.22 +	0.36 +
Yb	0.56 +	0.58 +	0.15 +	0.27 +	0.89 +	0.06 +	0.02 +	0.67 +
Mo	0.55 +	0.8 +	0.08 +	0.06 +	0.33 +	0.09 -	0.15 -	0.51 +
Nb	0.6 +	0.6 +	0.16 +	0.25 +	0.88 +	0.04 +	0.01 +	0.69 +
Sb	0.03 -	0.02 -	0 -	0.58 +	0.32 +	0.86 +	0.83 +	0.03 +
Ti	0.43 +	0.5 +	0.06 +	0.28 +	0.77 +	0.09 +	0.05 +	0.49 +
Zr	0.56 +	0.64 +	0.05 +	0.2 +	0.73 +	0.04 +	0.01 +	0.47 +
K	0.46 +	0.74 +	0 +	0 -	0.08 +	0.23 -	0.32 -	0.15 +
Pt	0.36 +	0.46 +	0.03 +	0.34 +	0.74 +	0.14 +	0.08 +	0.41 +
Al	0.66 +	0.62 +	0.44 +	0.09 +	0.7 +	0.01 -	0.02 -	0.89 +
Zn	0.45 +	0.76 +	0.02 +	0.24 +	0.47 +	0 -	0.02 -	0.47 +
As	0.23 -	0.18 -	0.06 -	0.62 +	0.1 +	0.98 +	0.998, +	0.01 -

Solid Phase								
Coefficient of Determination Direction of Correlation								
Element	pH	Conductivity	Temperature	Turbidity	NH4	COD	BOD	Date of Construction
Al	0.04 -	0 +	0.07 -	0.74 +	0.12 +	0.34 +	0.3 +	0.02 +
P	0.51 +	0.77 +	0.08 +	0.14 +	0.41 +	0.03 -	0.07 -	0.53 +

5.1 Ammonium, humic acid, and the common ion effect

Ammonium, conductivity, and age together have many strong correlations to aqueous metals and have covariance with each other, though ammonium is the most prevalent strongly correlated factor. Ammonium concentration increases with age and contributes to ionic strength and conductivity. Ammonium also forms many soluble complexes with metals which would aid in solubilizing them as the landfill ages and produces more ammonium.

Most elements show a weak positive correlation with pH which is counterintuitive to aqueous modeling, in which low pH tends to increase metal solubility. However, the pH of the landfill leachates were 6.10 down to 4.75. The oldest landfill, at 34 years old, had a pH of 5.2. This is unusually low and may explain why these leachates produced so many positive detections and had abnormal correlations with pH. In the case of these landfill cells, solubility was optimized by the combination of low pH and increasing ammonium providing a strong common ion effect.

The common ion effect is observed when a species in a reaction is also involved in other reactions simultaneously; thus the effect of any one reaction (such as forming a solid) is reduced because some portion of a species is involved in other reactions. Sodium, chloride, and ammonium are ubiquitous in common ion effect interactions because they are plentiful in nature, have multiple possible complexing reactions, and are highly soluble. These parameters together can quickly increase the conductivity or total dissolved solids content of aqueous solutions by spreading out and occupying metals which would otherwise precipitate.

For example, lithium carbonate will form a precipitate under the condition:

$$[\text{Li}^+]^2 * [\text{CO}_3^{2-}] = 8.15 \times 10^{-4}$$

$$\Sigma \text{Li} = 2 * [\text{Li}_2\text{CO}_3]$$

However, lithium also forms an aqueous complex with ammonia. If ammonia is also present in the solution, then the ammonia and carbonate have to share lithium, which will lower the left side of the equation and prevent solid lithium carbonate from forming. Ammonia dissociates a proton to complex with lithium and the system becomes:

$$\Sigma \text{Li} = 2 * [\text{Li}_2\text{CO}_3] + [\text{Li}(\text{NH}_2)_2]$$

As the pH of the solution increases, more ammonia is present relative to ammonium which facilitates the rate of formation of the lithium-ammonia complex. The amount of lithium available to precipitate with carbonate is reduced by the presence of ammonia.

Lee²¹ employed VMINTEQ to model landfill leachate complexation behavior and discusses the complexation behavior of humic substances at medium to high pH. Humic acid is known to have a strong retention ability for metals. Humic acid is generated by microbial activity as well as ammonium, so the correlation between dissolved metals and ammonium may actually be co-correlated to humic acid.

Using VMINTEQ is a good start to modeling landfill chemistry, but the modeling method has barriers. Modeling software such as MINEQL, MINTEQ, and their variants draw on databases such as the IUPAC database, Thermodemmm and Thermochimie online databases, and generally the same research literature. Several of these databases have been deprecated and evolved independently in newer software multiple times. The data quality of any database now is passable for education and basic water chemistry applications, but many reported constants are highly variable from one source to another and some metals have gone largely unmeasured at all. To pursue chemical modeling methods, fundamental research into the limitless permutations of humic acids, organic ligands, and metals possible in landfills would be needed.

5.2 Future improvements

This method can be improved in several ways:

Use less yttrium in the recovery standard to avoid precipitation, losses, and excess manual work. Based on the liquid concentration of yttrium recovered, only 100ug of yttrium should be used instead of 2500ug to avoid precipitation. However, if yttrium is naturally present in the sample, this may make it difficult to differentiate between natural yttrium and standard yttrium.

Optimize the ratio of solids to acid volume to increase low concentration detectability or use ICP-MS to detect low concentrations and positively detect gold.

Compare the HF method to aqua regia methods on the same samples to determine if the HF hazard is worthwhile, or if both methods will produce similar results.

Other future work in the field of landfill metal analysis will benefit from gathering more data to estimate industrial scale recovery values; to do that work, attention to global metal markets and novel recovery methods will be important to produce a viable approach to landfill mining.

Metal mobility and recovery studies involving landfills have been predominantly focused on the effects of pH and humic characteristics. As seen in the optimal pH and ammonium case here, metals may be solubilized readily without risky acids if a synthetic ligand could be designed which

has properties to solubilize metals for pump extraction, but be easily de-coupled in a reactor and recovered.

APPENDIX A. LANDFILL LEACHATE ANALYSIS PROCEDURE

Preliminary Preparation

1. Once all timeframes are known, schedule all instrument use beforehand.
2. Schedule time with HF buddy, schedule MWDR and HF use with lab management. An HF buddy is needed for the period just before microwaving, and just after when HF solutions are handled.
3. The samples received were 50mL metal-free polypropylene centrifuge tubes of pumped landfill leachate. They were shipped on ice and were frozen upon arrival until they could be tested; in this case some were frozen for several weeks and others for months before analysis began.
4. Unfreeze leachate samples under warm water.
5. Dry the outside of the sample vessels with paper towels.
6. Take pictures of the samples. Shake them and take more pictures.
7. Create an Experimental Blank of Type 1 water. Simply add ~40mL of fresh Type 1 water to a metal-free centrifuge tube. The experimental blank will undergo the same entire experimental procedure as the samples. This is 1/2 blanks.
8. Weigh the samples and Experimental Blank with the lid on analytical balance to 0.000X g = M_1 .
9. Add a recovery standard of Yttrium to samples. Record the new mass to accurately determine Y content.
 - a. Use 0.25mL of 10000ug/mL Y standard (part number CGY10, Inorganic Ventures).
 - b. Shake well to mix.

Centrifuge samples and experimental blank for clarifying and solids separation.

10. Balance the samples for the centrifuge using Type 1 water. Re-weigh and record the mass with the lid. Treat the Experimental Blank the same as the samples. When pouring the supernatant of the Experimental Blank into a new tube, leave ~1mL of solution as the “pellet.”
11. Centrifuge at 10000 RPM for 20 minutes, not including start up and slow down phases.
12. Pour the supernatant into a new centrifuge tube.

13. Measure the mass of the pellet phase in the tube with the lid.
14. Freeze all samples until they are needed for their next steps.

Prepare for digestion

15. Prepare the clean and dry TFM digestion vessels.
 - a. Do NOT mark the vessels: use a piece of tape to mark the rack where the vessel is held to keep track of samples.
16. Under a fume hood use 6x 4mL (total 24mL) of concentrated trace metal grade HCl 37% to rinse the walls of the centrifuge tube (containing the pellet) into the TFM digestion vessel (the experimental blank is included). The first two rinses should be poured directly to the TFM. The third rinse and on; add the acid, put the lid on tightly, shake the acid in the tube to fully dislodge any material in the lid and on the walls, then remove the lid and pour into the TFM. Then use 2x 4mL (total 8mL) of concentrated trace metal grade HNO₃ 70% to finish rinsing the centrifuge tube into the TFM.
 - a. Use pipette tips with filters to protect the pipette from acid fumes.
 - b. This wash step simultaneously becomes aqua regia for digestion.
 - c. Close and shake the tubes after most mass is transferred to clean the walls well.
 - d. Volumetric measurement is ok, the samples will be diluted to a 100mL flask later.
17. Prepare a digest blank. Add 0.25mL of 10000ug/mL Y standard (Part number CGY10, Inorganic Ventures) to a TFM and record the mass of Y added. Add the same mixture of acid to this TFM (2/2 blanks).
18. Prepare a matrix blank. The matrix blank will be used to make the calibration curve a similar matrix to the samples. The matrix blank will receive the same mixture of acids in a TFM, no Y standard.
19. Optionally, prepare a special digest blank in another TFM with a known amount of every element. Use .25mL of 10000ug/mL Y standard (Part number CGY10, Inorganic Ventures), and 1.8mL of 100ug/mL standards for the other elements in bottles CCS1, CCS2, CCS4, CCS5, and CCS6 from Inorganic Ventures. This amount of elements results in 100ppb of every element at the point of ICP analysis, which is easily quantified for a full recovery balance.

20. Allow the samples to degas volatile compounds in the fume hood for at least 30 minutes, or overnight. Leave the lid on during degassing—the pressure is not enough to cause a problem.
21. Take pictures of the centrifuge tubes again. Any bits on the walls that wouldn't come off? Make a note of it.
22. Weigh each of the empty dry centrifuge tubes with the lids. This is essential to determine the mass of the pellet.
23. After degassing, open lid to evacuate vapors.

Fully digest samples

24. Microwave and ICP processes will take most of a day; prepare accordingly.
25. Prepare all materials dealing with HF beforehand to reduce time scheduled with buddy:
 - a. Have filtered pipette tips arranged in rack.
 - b. Have Hazardous Waste bag ready.
 - c. Label all containers and arrange them in a carrier/rack.
 - d. Prepare 50mL centrifuge tubes of oversaturated boric acid (so that there is solid phase present). 15mL of boric acid needed per sample (boric acid is soluble to 5.7g/100mL at 25°C).
26. With HF buddy or just before HF buddy arrives: Review HF SOP, set up PPE, hazard warnings, caution tape.
27. With HF buddy present:
 - a. Add 3mL of concentrated trace metal grade 49% HF to each TFM.
 - b. Dispose pipette tip.
 - c. Add 15mL of boric acid.
 - d. One at a time, put TFM into PEEK shield and then into MWDR cartridge. Record which sample is in which cartridge.
 - e. Load vessels into MWDR apparatus, equally spaced around the rotor.
 - f. The area can be reopened; switch the warning sign from lvl 4 to lvl 3. Buddy may leave now.
28. Program the MWDR.
 - a. This is a 4.5 hr cycle.

- b. Use 1500W for 8 TFM. (Important: use lower power if digesting fewer samples. Follow manufacturer suggestions.)
 - c. Heat for 25min, maintain at 230°C for 25min, cool for 25min to 60°C, maintain 15min at cool, repeat a total of 3x. No stirring. Ventilation set at 3 (max).
 - d. Run program.
 - e. HF PPE and buddy restrictions are lifted while samples are in the microwave.
 - f. HF PPE and buddy restrictions must be in place when samples are removed.
 - g. In the first minute of running, the sensor can fail to read the TFM temperature and abort the process. Don't leave the machine until it is confidently proceeding.
29. Stick around and record the temperature of each vessel every 10-15 minutes if possible, this helps determine if the sample didn't reach temp and failed to fully digest.
- a. If the building loses electric power or the vessel ruptures, make everyone leave the lab as a safety measure: in the event of a power outage, the air evacuation system will not be able to remove HF gases.
30. When finished in the MWDR, samples do not need to be removed immediately.
31. With HF buddy present again:
- a. Remove vessels from MWDR.
 - b. Open cartridges slowly: a 1/8th turn or less, then 60 seconds before another turn.
 - c. Visually evaluate samples for full digestion to make sure no solids remain.
 - d. Quantitatively transfer the TFM contents to 100mL volumetric plastic flasks using Type 1 water to rinse, still visually inspecting for solids.
 - e. Add Type 1 water to the 100mL flasks precisely to the 100mL mark, mix well.
 - i. The final sample composition is 8mL 70% HNO₃, 24mL 37% HCl, 3mL 49% HF, 15mL 5.7% B(OH)₃, 50mL H₂O. This contains ~1.5% HF and is safe to handle later without a buddy present.
 - f. Transfer the samples from the 100mL flasks to 50mL centrifuge tubes. Keep all 100mL of the sample; use two tubes per sample.
 - g. The HF buddy can go once all concentrated HF containers are put away and only the dilute samples remain.
 - h. Clean up HF tools etc.
32. Do the cleaning procedure for TFM.

Fluorine complex precipitation recovery

33. The samples will precipitate a significant amount of fluorine complexes within 2 hours and will result in poor accuracy of ICP results and recovery standard. Allow the samples to sit for a week before analyzing them, then proceed to recover the precipitates.
34. Pre-weigh and record 15mL centrifuge tubes with their lids which will receive the precipitate fraction.
35. Use a long pipette tip (5mL) to reach the bottom of the sample: suck the precipitate into the pipette and transfer it to the 15mL centrifuge tube. Ensure that excess volume is taken to transfer all of the precipitate. Transfer the precipitate from both matching sample containers into the same 15mL centrifuge tube.
36. Centrifuge the 15mL containers to re-concentrate the agitated precipitate to the bottom. Use only 600rpm for 10min. This speed is slow enough to feel secure even when the samples are not properly balanced.
37. Use a pipette to carefully remove the supernatant without disturbing the precipitate. Put the supernatant back in the original 50mL tubes.
38. Centrifuge the 50mL tubes at 600rpm for 10min. The increased pressure caused by centripetal forces causes precipitation settling to accelerate. Repeat steps 35-38 until no more precipitate is observed after centrifugation, or if the precipitate observed after centrifugation redissolves in a few minutes after removal from the centrifuge.
 - a. The increased pressure of the centrifuge allows solid phases to exist where they otherwise will not at ambient pressure. What is important is that the final solution does not contain solid phases that would fail to be analyzed by the ICP, while the solid phase is fully recovered for redigestion.
 - b. Slowly invert the 50mL containers with the lid on tightly and watch closely for agitated white precipitate to dislodge from the walls or ridges on the inside of the container. If any precipitate is observed this way, continue steps 35-38.
39. Once all the precipitate has been separated from the solution and the 15mL container contains only the precipitate phase and a small volume of liquid (~.5mL), weigh and record mass of the 15mL tube with the lid and sample.
40. Pour the contents of the vial into a clean and dry TFM. Wash the vial into the TFM using 2x 1mL (total 2mL) of HCl 37% and 1mL of HNO₃ 70%.

41. Microwave the sample: 25min heating to 180°C, 10min held at 180°C, 30min cooling to 30°C.
42. Pour the TFM back into its original 15mL centrifuge tube. Examine the solution to guarantee no precipitate persists.
43. Wash the TFM into the vial with 2x 1mL (total 2mL) of 2% HNO₃. Examine the solution again to guarantee no precipitate persists.
 - a. .5mL sample + 3mL conc. acid + 2mL dilute acid = 5.5mL.
 - b. Acids content: 5.5mL solution / (.5mL acids in sample + 3mL strong acids) = ~1.57x acid dilution.
44. Weigh and record the vial with lid and ~5.5mL sample.
45. The samples are now stable until ICP analysis.

ICP-OES analysis

46. Prepare the ICP dilutions with 2% HNO₃ and the corresponding matrix to make the sample matrix the same as the calibration.
 - a. The leachate supernatant matrix is 2% HNO₃.
 - b. The HF solution and redigested precipitates should accompany calibrations made with the matrix blank.
 - i. The redigested precipitate solution contains large amounts of Calcium-Fluoride and Yttrium-Fluoride complexes. Acidifying these complexes will likely produce HF again in the solution, so continuing to design the ICP injection solution with the same background as the other samples will keep the detection parameters (mainly viscosity) consistent.
47. The dilution designs for each sample type:
 - a. The leachate supernatant samples have a TDS of approximately 1000ppm according to high-dilution samples.
 - b. Most ICP-OES can tolerate TDS of 30%, or 300000ppm. Therefore minimal dilution is desired to achieve the greatest detection sensitivity. Prepare 14.5mL of leachate supernatant in a 15mL centrifuge tube, then in a fume hood slowly

add .43mL of trace metal grade HNO_3 70%. $70\% * .43\text{mL} = 2.01\% * 14.93\text{mL}$.

This acidifies the solution for ICP injection while minimizing the dilution.

- i. The calibration curve for this sample type is simply 2% HNO_3 .
 - c. The 50mL tubes of HF digested solution require 18x dilution for the minimum safe factor to enter the acids to the machine. Assuming the 50mL digest sample contains a maximum of 70% HNO_3 (conservative), then the 100mL flask dilution would contain 35% HNO_3 and an additional 18x dilution with 2% HNO_3 will result in 2% acid solution.
 - i. The calibration curve for this sample type should include an 18x diluted portion of the matrix blank because the fundamental matrix of the sample is identical to the matrix blank.
 - d. The redigested HF precipitate sample requires a dilution of 22x. $22 * 1.57 = 35\text{x}$ acid dilution from the assumed initial 70% HNO_3 , the resulting solution is 2% HNO_3 which is safe for ICP introduction.
 - i. The calibration curve for this sample type should include an 18x diluted portion of the matrix blank because the fundamental matrix of the sample is identical to the matrix blank.
48. Use 10x 0.1mL aliquots in a calibrated pipette to determine the density of the redigested solution in the 15mL vials and the solution in the 50mL vials. Use this density to calculate the exact volume of the solution and the dilution factors. The leachate supernatant density is not significantly different than water.

Establish math

- 49. C_{ICP} = Concentration of the element measured in ICP vial, ng/mL or ppb.
- 50. M_p = mass of pellet sample (heavy phase) transferred to TFM, g.
- 51. M_s = mass of supernatant removed from centrifuged sample, g.
- 52. D = density (g/mL) of the liquid sample. This is established by calibrating the pipette and measuring 10 aliquots of the sample.
- 53. $V_{\text{D,solution}}$ = volume of digested sample prior to dilutions for ICP, L. In this experiment this value is constant and equals 0.1L (100mL plastic volumetric flasks).
- 54. $V_{\text{D,redigested}}$ = volume of the redigested solution, approximately 5.5mL. $V_{\text{D,redigested}} = \text{mass of sample} / D$.

55. DF = dilution factor = Volume of final diluted volume / volume of original sample = (mass of diluted sample/1.01 g/mL) / (mass of original sample, g) / (D g/mL), where 1.01 g/mL is the density of 2% HNO_3 (which the diluted solution approximates).

56. M_{pt} = total mass of element in pellet, in micrograms

$$= (V_{D,solution}(L) * C_{ICP} \left(\frac{ug}{L}\right) + V_{D,redigested} * C_{ICP} \left(\frac{ug}{L}\right)) * DF$$

57. M_{st} = total mass of element in supernatant, in micrograms

$$= C_{ICP} \left(\frac{ug}{L}\right) * DF * (M_s(g) * \frac{1L}{1000g})$$

- a. 1L/1000g is due to the supernatant density being arbitrarily close to the density of water.

58. C_T = total concentration of element in subsample, in micrograms per gram

- a. Total leachate concentration = $(M_{pt} + M_{st}) / (M_p + M_s)$.
- b. Solid phase concentration = $(M_{pt}) / (M_p)$.
- c. Liquid phase concentration = $(M_{st}) / (M_s)$.

59. Average sample concentration = average of C_T measured in all subsamples

- a. Use 0 as C_T for non-detections.
- b. Use the LOD for C_T for <LOQ detections.
- c. It is necessary to report the average as such because several elements are not detected in each subsample, or the quantity cannot be guaranteed. Therefore, the average concentration is lower across the sample than it is measured in one subsample.

60. The standard deviation is found by using the standard deviation of the readings from the ICP, combined as variances. Because the standard deviation of a non-detect cannot be determined, and square root of zero-squared is zero, the standard deviation remains unchanged when substituting 0 for non-detections. As such, the standard deviation cannot adequately describe the total variation across samples with non-detections.

APPENDIX B. TFM CLEANING PROCEDURE

1. Upon emptying the contents of the TFM, immediately place the PEEK shields in one bucket of Type 1 ultrapure water. Place the TFM vessels in a separate bucket of Type 1 ultrapure water.
2. After the samples are secured, remove the shields and vessels from their water baths. Rinse the shields and vessels under running Type 1 water.
3. Place the TFM parts in a large beaker of water. Boil the beaker of water for 15 minutes.
4. Dry the PEEK shields with Kimwipes first, then air dry (or use compressed air). The shields must be dry before they can be microwaved again.
5. Remove the TFM vessels from the boiling water with soft forceps. Dispose of the contaminated water into a sink.
6. Rinse the TFM parts with Type 1 water.
7. Dry TFM parts with Kimwipes, then air dry (or use compressed air).

The process may be halted here and recontinued later if the TFM parts are left in a fresh Type 1 water bath.

8. Add 20mL of aqua regia to TFM vessels, assemble the vessels, and submit to MWDR on the clean cycle.
 - a. MWDR settings: 25min heating to 180°C, 10min held at 180°C, 30min cooling to 30°C.
9. Rinse the beaker with Type 1 water and prepare for another boiling treatment.
10. After the MWDR cycle ends, repeat steps 1, 2, 3, 4, 5, 6, and 7.

The process may be halted here and recontinued later if the TFM parts are left in a fresh Type 1 water bath.

11. Put dry TFM parts in an oven at 140°C for 4+ hours. Place the lids on a flat tray with the insides facing up. Place the vessels standing up on a tray or in jars, not directly on the metal grate of the oven.

APPENDIX C. PICTURES OF SAMPLES

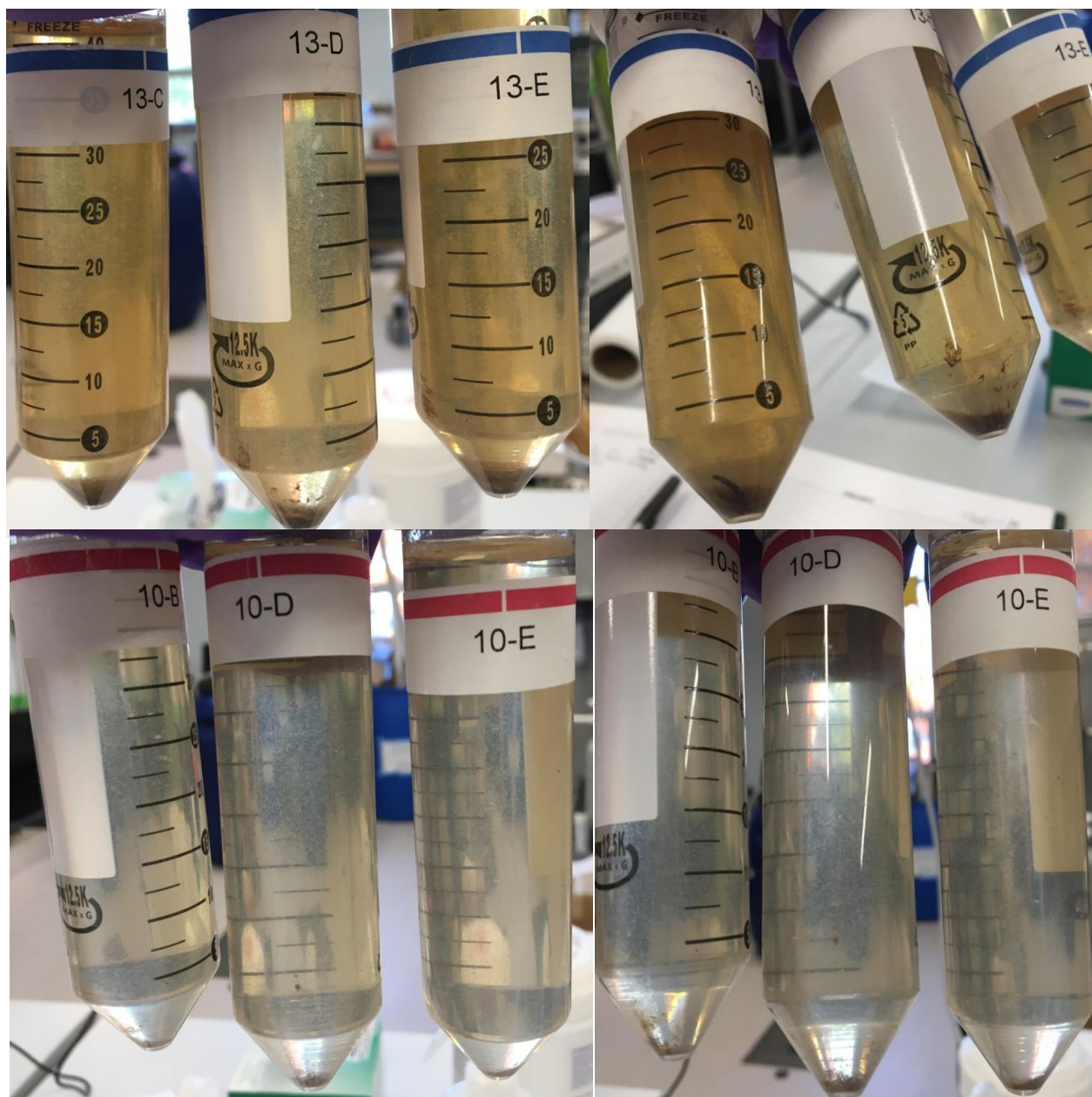


Figure 5: Raw pumped leachate prior to processing.

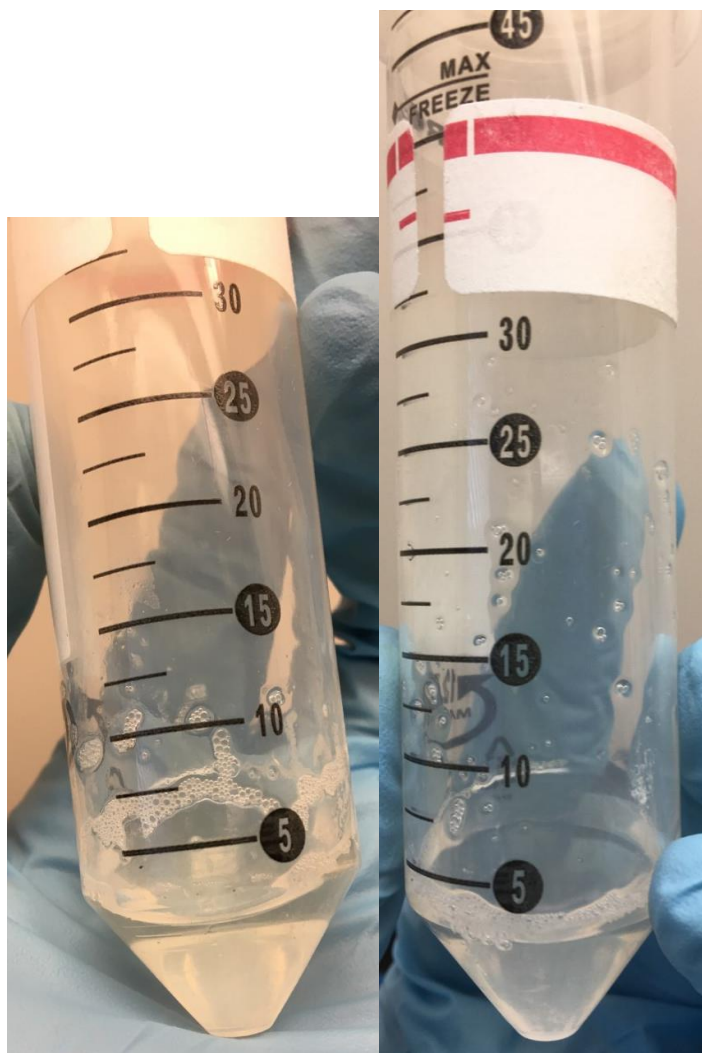


Figure 6: Tubes during acid washing and transfer to TFM



Figure 7: Precipitated powder after MWDR.

APPENDIX D. TROUBLESHOOTING DURING METHOD DEVELOPMENT

Method Limitations to Prevent Excessive Wear on Icp-Oes

Boron is added to the solution in the form of boric acid $B(OH)_3$. Although the solution of boric acid is prepared to saturation, the exact concentration of the solution is susceptible to temperature, which was not measured. The 5mL pipette used to add HF and $B(OH)_3$ is not precise enough to guarantee the final concentration of these in each digestion tube either. It is sufficient to know that the boric acid content is excessive relative to the expected silicon content, as the purpose of boric acid in HF matrices is primarily to prevent volatile H_2SiF_6 from forming. Although chemists have historically used boric acid to neutralize the HF molecule, the notion that fluoroboric acid will save glass from attack is a misconception: fluoroboric acid is still corrosive and attacks glass, and silica determination is not compatible with HF matrices at all²⁹.

For ICP-OES applications with HF matrices, Inorganic Ventures offers a triethanolamine (TEA) product that neutralizes the HF through basifying the solution to a pH greater than 8 while acting as a strong complexing agent to maintain the solubility of other ions. Sodium hydroxide would have a similar basifying effect, but sodium hydroxide also readily attacks glass and would produce the same interference. TEA is an organic compound, which will release a strong green spectrum in the plasma, potentially altering measurements, and leave soot on the torch causing increased maintenance. Ultimately neither option was considered worth investigation. The slight deviation in concentrations of HF and $B(OH)_3$ in each sample resulted in non-constant strength of glass attack. Silicon measurements could not be quantified accurately by subtracting a matrix blank representative. Qualitative analysis of the magnitude of silicon in samples suggests that silica is present at significant quantities in the particulates, which is expected due to landfills using sand to bury layers of trash. Because silica is not a valuable resource for recovery, accurate quantitation was not a further concern. It is sufficient to know that the silica present was fully dissolved by the method, freeing any entrapped or adsorbed elements into solution.

Dealing with Precipitating Samples

The HF-digested leachate samples and digest blanks developed a white precipitate, but not the experimental blanks. The first time this occurred it was noticed at 3 weeks after the digestion procedure; later it was observed within 60 minutes of removal from the microwave, before the samples were ready for ICP analysis. Approximately the same amount of precipitate was visually observed in all samples. No such precipitate was observed in the samples for gold contamination testing (section 4.3.2) even two months after that procedure had been finished. The precipitate did not form in an HF-containing matrix blank that was not microwaved nor had yttrium. The precipitate did not form in an HF-containing matrix blank that was microwaved but did not have yttrium. The precipitate did form in the digest blanks, which were the same HF containing matrix and included yttrium. The precipitate did not form in the experimental blanks, which received a much smaller dose of yttrium due to the original water sample having a homogeneous mix and only transferring a small volume to acid digestion. The samples which precipitated out measured less gold intensity after precipitating for many days than they measured immediately after microwave digestion, which will be addressed in more depth in the following section. These evidences suggested that the precipitate was an yttrium-fluoride complex. Yttrium fluoride is a white powder which is insoluble even in acids.

The yttrium detected in the samples immediately following microwave treatment with no visible particulate was considerably lower than expected. This suggests that yttrium-fluoride precipitates rapidly enough to affect the aqueous concentration but are not visible to the naked eye until later. Nucleation kinetics can occur slowly, so it is possible that solid precipitates smaller than the eye can see are present following microwave treatment. In an attempt to overcome the kinetics, sample dilutions and ICP analysis were prepared immediately after the microwave cycle finished. Precipitates were not observed when the samples were transferred out of the TFM or when they were diluted with water. However, during sample dilution a faint precipitate was observed; the precipitate was possibly visible, but too faint to be certain of approximately 30 minutes after removal from the microwave; the precipitate was certain at about 60 minutes. This time limit made immediate sample analysis unfeasible, and uncertain even if achieved before the 30 minute mark. To combat this, at least one week was given after microwaving to allow the precipitate to settle, then the procedure to redigest the precipitate was developed and analysis was continued.

Several samples had been acid digested prior to discovering the precipitate. Of these samples, only 50mL of the 100mL flask were saved for later analysis under the assumption that they would be stable. Only half of some samples had been lost this way; for example, samples A, B, and C from the same cell were lost this way, but samples D, E, and F were later saved in full. In order to account for the loss of substance in the mass balance, the measured solids were doubled in value, assuming that the liquid was homogeneously mixed in the flask and the 50mL sample was representative of the whole.

A procedure to redigest the precipitate was developed and is reported in Appendix B. The redigested solutions did not produce precipitates again after many days. Calcium and yttrium were confirmed at high levels in the precipitate. Calcium fluoride is also somewhat insoluble in acids and is a white powder, so this result is not surprising. A special blank was designed with 1800ppb of every element and 25ppm of yttrium at the point of 100mL in a flask. Several other metals were detected in the precipitates of the special blank, potentially due to a combination of complex behavior and surface adsorbance or flocculation effects on the powder. The special blank demonstrates that those elements preferentially segregate >90% into the solid phase, which suggests a similar distribution would occur in the samples if those elements were present. The recovery of elements from two special blank samples are shown below in Table 7. It is particularly concerning that the second sample recovered several elements in the 70-80% range, whereas the first sample had consistently >90% recovery. This would imply that the method cannot be consistently performed to achieve the same results each time.

Table 7: Recovery of special blanks

Total Recovery %			Total Recovery %			Total Recovery %			Total Recovery %		
Special 1		Special 2	Special 1		Special 2	Special 1		Special 2	Special 1		Special 2
Ag	1%	1050%	Fe	101%	119%	Na	92%	124%	Si	-7%	-4%
Al	124%	122%	Ga	113%	115%	Nb	102%	105%	Sm	88%	71%
As	111%	115%	Gd	91%	72%	Nd	95%	79%	Sn	103%	104%
Au	290%	151%	Ge	87%	90%	Ni	110%	116%	Sr	115%	117%
B	-6539%	-1717%	Hf	103%	100%	P	69%	68%	Ta	103%	105%
Ba	112%	115%	Hg	97%	94%	Pb	112%	116%	Tb	96%	72%
Be	105%	106%	Ho	96%	72%	Pd	103%	107%	Th	89%	65%
Bi	68%	61%	In	108%	111%	Pr	96%	80%	Ti	99%	101%
Ca	97%	98%	Ir	77%	91%	Pt	99%	103%	Tl	113%	115%
Cd	104%	113%	K	91%	115%	Re	101%	101%	Tm	97%	72%
Ce	99%	82%	La	90%	82%	Rh	107%	111%	V	104%	107%
Co	104%	113%	Li	93%	93%	Ru	105%	105%	W	101%	103%
Cr	103%	113%	Lu	92%	71%	S	98%	100%	Y	85%	42%
Cu	110%	115%	Mg	97%	110%	Sb	105%	104%	Yb	93%	72%
Dy	94%	73%	Mn	110%	116%	Sc	100%	100%	Zn	107%	109%
Er	90%	71%	Mo	101%	102%	Se	102%	104%	Zr	101%	99%
Eu	93%	73%									

The experimental blanks and digest blanks behaved differently from each other. The digest blanks all produced a precipitate, but none of the experimental blanks did. This can be explained by recognizing that the “pellet” transferred from the experimental blank was actually just an aliquot of liquid water with the yttrium recovery homogeneously mixed in it. Contrast that with the digest blank, which was made with the entire amount of yttrium directly in the digest sample. The concentration of yttrium in the experimental blank was much lower than the others, resulting in no precipitation. When accounting for yttrium this way, the recovered mass of yttrium in the acid digest was as expected. The experimental blanks tended to recover >90% of yttrium, but the digest blanks recovered only 40-80%. Despite the extreme care taken to ensure a complete transfer of precipitated powder for the redigestion procedure, and despite much better recovery of other elements in the special blanks, the digest blanks failed to recover yttrium well. Table 8 below shows the yttrium recovery distribution of the blank samples.

Table 8: Experimental and digest blanks^c

Digest Blanks					
Yttrium Recovery	DBLK A	DBLK B	DBLK C	DBLK D	DBLK E
% Recovered	39.7%	64.3%	66.0%	42.9%	88.2%
Supernatant, ug	NA	NA	NA	NA	NA
Pellet Liquid, ug	15	51	372	27	52
Pellet Solid, ug	980	1558	1239	1093	2138

Experimental Blanks

Yttrium Recovery	EBLK A	EBLK B	EBLK C	EBLK D	EBLK E	EBLK F
% Recovered	94.2%	92.4%	92.4%	95.8%	91.1%	92.8%
Supernatant, ug	2389	2365	2342	2272	2284	2221
Pellet Liquid, ug	67	44	87	125	102	102
Pellet Solid, ug	NA	NA	NA	NA	NA	NA

The samples themselves fared somewhat better than the digest blanks, but not as consistently well as the experimental blanks. Shown below in Table 9 is a summary of yttrium recovery in the samples. It can be seen that the recovery is sporadically inconsistent with low recovery and large variations among the sub samples. This may be attributable to both the complex chemical profile of all the samples, and the inability to manually replicate the procedure accurately.

Table 9: Sample yttrium recovery

Samples	NE 1	NE 2	NE 3	NE 10	NE 11	NE 12
Average Recovered, ug	1754	2539	2341	2064	2188	2502
Average % Recovered	75%	101%	92%	83%	83%	100%
RSD Recovered	13%	24%	13%	29%	12%	15%
Average Supernatant, ug	126	141	166	133	255	274
Average Pellet Liquid, ug	387	248	79	177	32	179
Average Pellet Solids, ug	1241	2151	2097	1754	1901	2049

Samples	NE 13	IL 1	IL 2	IL 3	IL 4
Average Recovered, ug	1827	1696	1733	1517	1767
Average % Recovered	73%	72%	71%	64%	75%
RSD Recovered	26%	26%	28%	13%	15%
Average Supernatant, ug	231	145	135	405	190
Average Pellet Liquid, ug	82	107	27	7	19
Average Pellet Solids, ug	1514	1443	1571	1105	1557

^c The researcher made an error by adding a mixed element standard to the DBLK instead of Y standard, this sample is not included in the table.

False Positive Gold Detections Associated with Fluorine and Teflon

A preliminary digestion test was performed on a representative landfill leachate sample to determine the effectiveness of the procedure that was designed. After this test was satisfied, the first real sample was dissolved and measured in ICP-OES. However, upon investigating the ICP results it was discovered that the preliminary landfill sample (test run) from a different location contained very similar concentration of gold to the real sample, which raised suspicion, and the experimental blanks and digest blanks (which should contain only minor contamination from the lab environment) contained the same amount of gold as the samples, which confirmed the suspicion that something was wrong with the tools being used. It was initially hypothesized that the digestion vessels were retaining gold from previous runs, although the vessels are made from Teflon and should not be retaining any substances because they are cleaned with aqua regia and microwaved between every procedure.

To test the hypothesis that the Teflon vessels are transferring gold from one sample to another, a series of contaminating steps and washing steps were performed: First, a 10ppm spike of gold and yttrium was prepared in an acid mix containing HNO_3 , HCl , and B(OH)_3 which mimicked the same mixture used for digestion except for lacking HF due to expedience. The spike solution was split for ICP analysis and microwave digestion; the volume of solution going to the TFM vessels in each stage was 47mL, also mimicking the proper digestion mixture to account for the surface area of the vessel being in contact with the solution. The spike solution was microwaved and measured by ICP. The TFMs were then cleaned three times with the same HNO_3 , HCl , B(OH)_3 mixture. The typical cleaning procedure can be found in Appendix B. Each cleaning solution was sampled for ICP analysis instead of being sent to waste. The test was repeated to determine if the results could be duplicated consistently; although the second test followed a similar trend to the first, the results were not consistent to a point that would alleviate quantitation problems. The second test did not analyze for yttrium because the first test demonstrated that yttrium behaved as expected. The results of the test are displayed in Figure 8 and discussion follows.

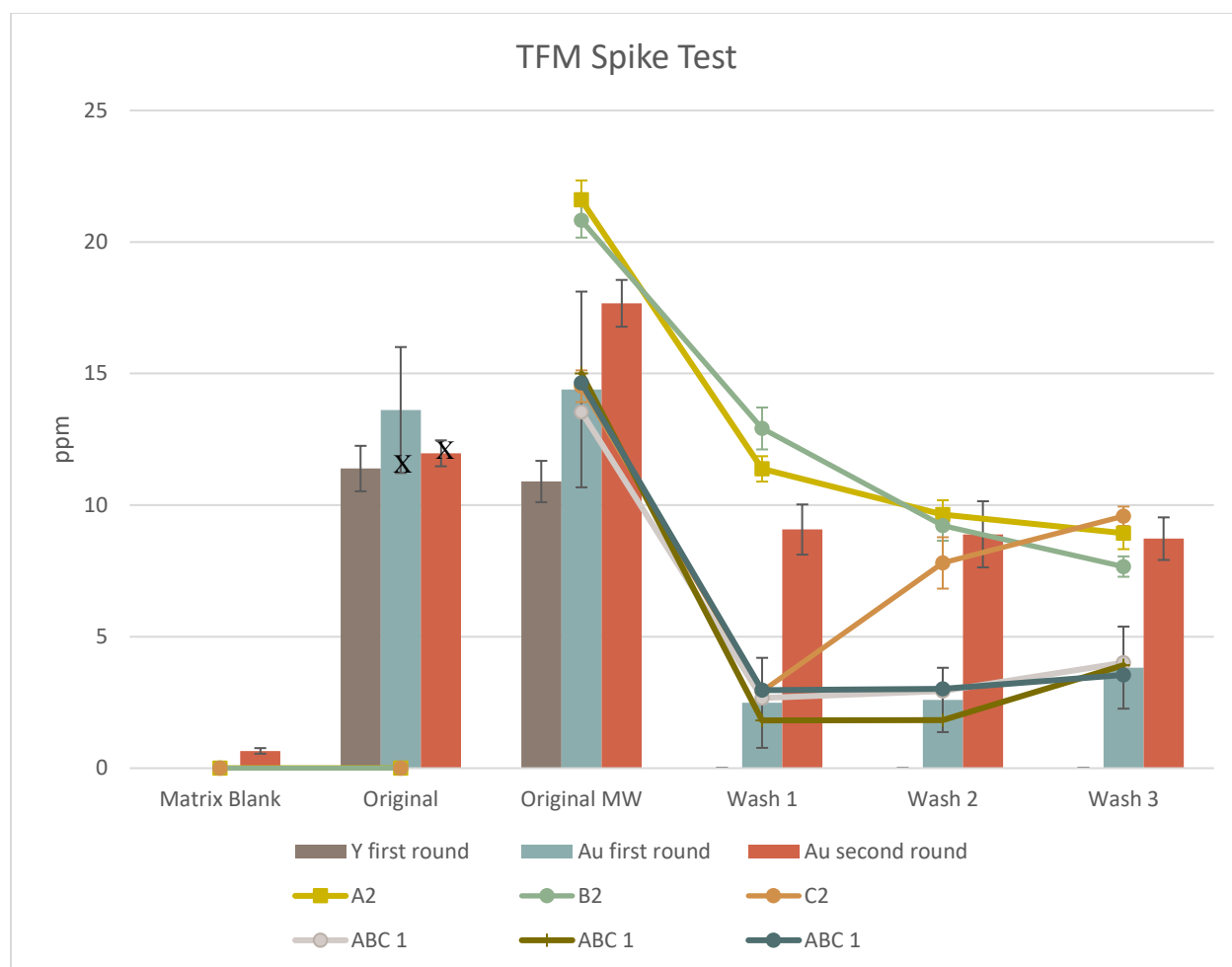


Figure 8: Two runs of the TFM testing procedure for Au detection investigation. “MW” stands for the microwave treatment. The A, B, and C entries were individual TFM vessels tracked on the second run of the test, while “ABC” entries were not tracked individually. The black X’s indicate the mass-calculated concentration of Au in the original spiked mix.

The first set of samples (the spiked samples) resulted in positive detections of gold. The measured concentration of the original mix in the first run was substantially higher than the mass-calculated concentration; the researcher neglected to vigorously shake these three sample dilutions prior to injection resulting in a greater concentration toward the bottom of the vial. The measured concentration of gold in the spiked solution increased noticeably after microwaving, positively indicating that the digestion vessel adds a contaminant. The measured concentration of gold reported for the wash solutions was on the same magnitude as the detected gold in the landfill samples, indicating that real gold detections in the landfill samples could not be distinguished from

false positives caused by the contaminant. The second set of samples demonstrated the same general trend, but with nearly twice the level of contamination detected.

Producing at least 7ppm of gold from an original 10ppm three times in a row from a surface that should not adsorb any metals is inconceivable and serves as convincing evidence that the TFM vessels are not transferring gold from one sample to the next but are actively releasing an interfering substance on every cycle of the microwave. Vessel C changes which trend it follows partway through the second run; this may indicate that the TFM vessel is degrading and Vessel C happened to degrade past a critical point that accelerated its release between Wash 1 and 2 in the second run, clearly resulting in the large standard deviation for the triplicate series. Since the two runs had similar sized standard deviations across triplicate samples yet the individual samples of the second run had smaller standard deviations, it seems plausible that all three TFMs were not synchronized in their stage of degradation at each treatment step in the first run as well.

The treatments were compared to each other using a two-sample T-Test to ensure that the results were significantly comparable. The results of the T-Tests indicate that between the two runs all treatments were significantly different at the $P=.05$ level indicating that despite following the same procedure the test was not repeatable: some parameter changed between the first and second runs. Wash 1 of the first run was significantly different from Wash 1 of the second run (with Vessel C removed as an outlier due to its rapid increase in contamination). The consecutive washes were all significantly different, the same as the first. The hypothesis that gold transfers from one sample to the next can be rejected confidently. The P values are organized in Table 10.

Table 10: Two-sample T-Test assuming equal variances applied to multiple treatments.
Parentheses indicate the first or second run of the test.

Treatment	Treatment		One Tail P	Two Tail P		Significantly different
Original (1)	Original (2)		0.005	0.010		yes
Original MW (1)	Original MW (2)		0.003	0.007		yes
Wash 1 (1)	Wash 1 (2) excl. outlier		0.000	0.000		yes
Wash 2 (1)	Wash 2 (2)		0.001	0.002		yes
Wash 3 (1)	Wash 3 (2)		0.001	0.001		yes
Original (2)	Original MW (2) excl. outlier		0.005	0.010		yes
Wash 1 (1)	Wash 1 (2)		0.056	0.113		no
Wash 1 (2)	Wash 2 (2)		0.422	0.844		no
Wash 2 (2)	Wash 3 (2)		0.492	0.985		no
Wash 1 (1)	Wash 2 (1)		0.421	0.841		no
Wash 2 (1)	Wash 3 (1)		0.492	0.985		no
Original (1)	Original MW (1)		0.131	0.262		no

ICP-MS Gold Contamination Conclusion

To positively determine the presence of gold contamination from the wash samples, the same samples were submitted to ICP-MS analysis (performed by the RIC in the Dept. of Chemistry at Purdue University). The ICP-MS determined that the concentration of gold in the wash sample was below the level of detection; essentially zero. The comparison of the samples read by ICP-OES vs MS is displayed in Figure 9. This evidence proves that the samples are not being compromised entirely by the digestion procedure using the TFM model, and gold can still be accurately quantified using ICP-MS.

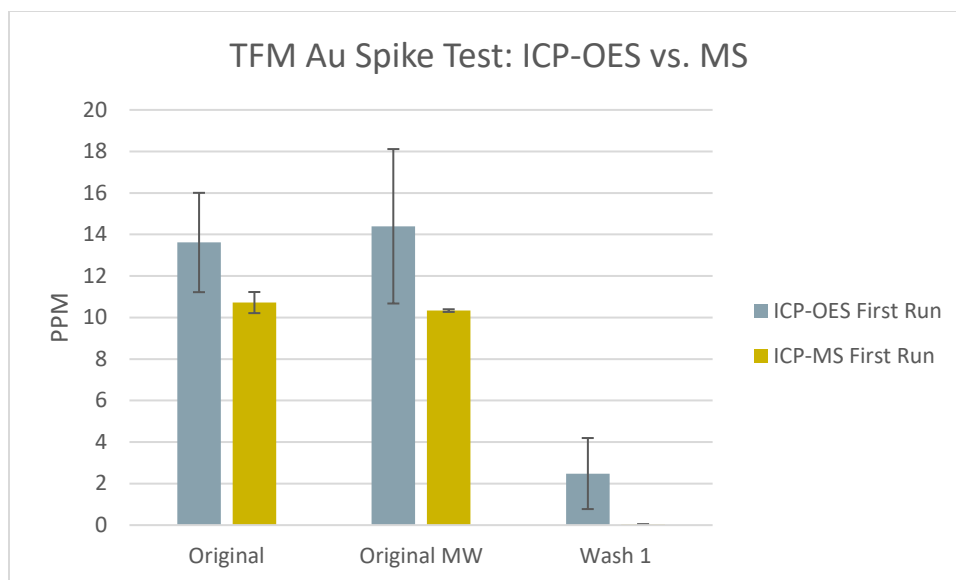


Figure 9: ICP-OES vs. MS Analysis of the Same Samples

ICP-OES Gold False Positive Readings Due to Fluorine

When testing again proceeded to digestion with HF and analyzed in ICP-OES, two blank matrices were created; they contained only the acids and had nothing else added. One set of this matrix blank was submitted to the TFM vessel and microwaved, while the other was not microwaved. After microwaving, they were each diluted up to 100mL in a flask identical to the samples. The matrix blanks were further diluted similar to the samples and measured in ICP-OES. Although they were not supposed to have any gold in them, they both registered high levels of intensity at all wavelengths that gold can be analyzed on: 242.795nm, 267.595nm, 208.209nm, and 197.819nm. By comparing the acid matrices and treatments, shown in Table 11, it seems certain that fluorine in the solution causes significant detections with OES methods. Fluorine apparently can enter the samples via degradation of the Teflon digestion vessel (Teflon is a fluorocarbon), but will also be guaranteed to enter the sample due to the purposeful addition of HF in the digestion matrix. No prior literature or application notes were found describing this influence, nor is fluorine found to have an influence on spectral analysis. Whatever the mechanism is, the presence of fluorine, whether in a fluorocarbon or acid, is associated with strong intensity readings on several wavelengths. Because fluorine is not negotiable in this method, gold is not capable of determination without ICP-MS. Due to availability constraints on the ICP-MS, further testing with ICP-MS was not performed.

Table 11: Sample matrix and treatment associated with false gold positives

False Gold Detections	Aqua regia	Aqua regia + B(OH) ₃	Aqua Regia + B(OH) ₃ + HF
TFM/MWDR	Yes	Yes	Yes
No TFM/MWDR	No	No	Yes

APPENDIX E. SUPPLEMENTAL DATA

Key to interpreting data quality assignments:

OK: Quantifiable data with nearest check standard within 10% error.

Err: Quantifiable data, but the nearest check standard had more than 10% error.

LOQ: The measurement is below $10/3 * LOD$, technically unquantifiable but still positively detected.

CPMax: The measurement is greater than the highest concentration in the calibration curve.

-: Not detected.

On-Site Parameters	NE 1	NE 2	NE 3	NE 10	NE 11	NE 12	NE 13
pH	5.2	5.53	4.75	5.48	5.83	5.81	6.1
Conductivity mS/cm	6.7	8.29	4.63	7.21	8.02	9.1	12.1
Temperature C	16.6	17.7	17.1	24.6	24.8	22	20.9
Turbidity NTU	23	26	272	45	22	228	224
Dissolved oxygen mg/L	0	0	0	0	0	0	0
NH4 mg/L	224	314	410	405	496	740	670
COD mg/L	607	821	3680	507	751	3050	1020
BOD mg/L	30.2	0	2070	36	43.6	1520	38.3
Date of Construction	1989	1990	1991	2003	2004	2007	2010

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