



Metal Content within the Sludge Layer of a Decentralized Wastewater Treatment Plant Serving 80 Homes in Newlands Mashu, South Africa

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Abstract

Metal containments within wastewater effluent severely impact agricultural reuse applications and may not be treated within the wastewater plant. Metals such as Cd, Cr, and Pb are also hazardous to humans resulting in health concerns if exposure occurs. The goal of this research is to identify and quantify the metal content within the sludge layer which accumulates over time. Samples were taken from the beginning, middle, and end of the Anaerobic Baffled Reactors (ABR). Sludge was dried and microwave digested using a concentrated nitric acid solution and an Aqua Regia solution. The digestion methods were compared and showed little difference in quantification of metals. The samples were then run under inductive coupled plasma optical emission spectrometer (ICP-OES). Results showed concentrations of Al and Fe ranging from 26.4 to 32.3 mg/g and 15.0 to 17.1 mg/g respectively. Trace amounts of Cd, Co, Ni and Pb were observed but below the quantification limit.

1. Introduction

1.1 DEWATS

The DEWATS stands for “Decentralized Wastewater Treatment Systems” is an anaerobic gravity flow treatment system used to treat industrial and domestic waste.(BORDA) It is an economical alternative to conventional treatment systems constructed out of concrete and is easy to maintain compared to a traditional centralized treatment system. The DEWATS consists of a (1) settling chamber, (2) a series of anaerobic baffled reactor chambers, (3) a series of anaerobic filters, and (4) a vertical gravity filter. (Figure 1)

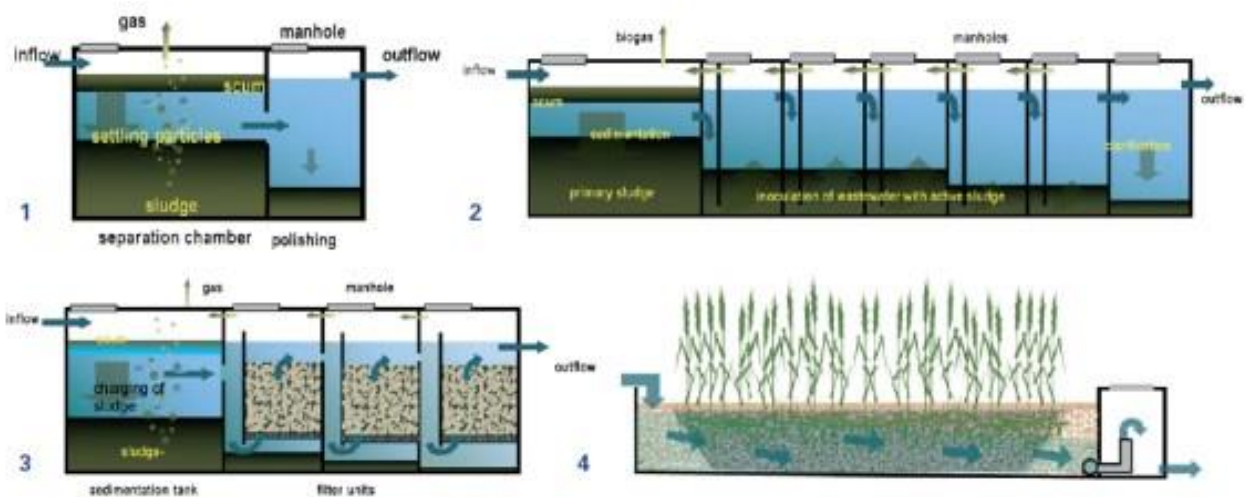


Figure 1. DEWATS System for wastewater treatment. (Image from BOARDA)

1.2 Background

In many countries, especially those with arid climates, water reuse for irrigation purposes is a common practice. (Vergine et al., 2015) Due to the scarcity and availability of water, research into partially treated water for agriculture has risen. Typical treatment trains consist of preliminary treatment to remove large items such as branches, primary treatment to remove solids, secondary treatment to remove dissolved solids, suspended solids, and to disinfect, and tertiary treatment to remove any remaining contaminants within the water. Partially treated water is water which is treated through a portion of the treatment train but does not complete all of the treatment systems and does not achieve the same quality as the water which completes the entire treatment process. There are many benefits when using water reuse for agriculture as it contains many nutrients which are beneficial to plant growth.

However, in excess, some of these nutrients become toxic to vegetation (Farias et al., 2011). Plants such as corn, potato, and rice are aluminum sensitive and root exposure to a concentration of up to 25 μM inhibited root growth. (Sade et al., 2016) Also, with the interference of aluminum in such plant species, nutrient uptake was also inhibited. (Sade et al., 2016) In wetlands, iron toxicity in rice can produce yield losses of 15 % to 30 % of crop loss

from iron toxicity concentrations ranging between 10 to 2000 mg l⁻¹. (Dufey et al., 2014) Additionally, metal toxicity is also hazardous to humans and animal. Human and animal exposure to metals such as lead may cause developmental issues, cancer, hypertension and heart attack. (Hess et al., 2013;; Villiers et al., 2010)

Metals may be present in the wastewater influent due to improper disposal of cadmium-zinc and nickel- cadmium batteries, cosmetics containing trace metals, leaching from pipes due to stagnant water, and surface water intrusion carrying metals from soil into the treatment system. Most wastewater treatment plants (wwtp) are not designed to treat metals. The primary focus is the removal of solids, pathogens and bacteria. Once metals enter a treatment system, an additional treatment process must be added to treat the metals to a safe limit. The research from this investigation into the concentration of metals within the sludge layer throughout the ABR will determine agricultural reuse applications. Should the concentration of a metal exceed the limits of that designated by the World Health Organization, the sludge will need to be treated to remove the excess metals using acid extraction, prior to agricultural use.(Fuerhacker et al., 2012)

Currently, little information is known on which metals are present in the DEWATS. The DEWATS studied throughout this research treats the domestic waste of 80 homes within Newlands Mashu, South Africa. The primary focus of this research is to identify and quantify the metals present throughout the ABR. Understanding the types of metals present and their concentrations throughout the treatment process will aid in assessing water reuse applications.

1.3 Background for sampling location selection

Sampling points were chosen to classify the total metals within the ABR since some metals may be present in the beginning of the treatment process and not at the end. Additionally, the sludge within the ABR accumulates over the course of years making the sludge an ideal sampling choice when observing constituents within the system. It is also hypothesized that the sludge will contain the largest quantities of metals since it may contain elements which metals are bound to.

2. Methods

2.1 Sampling

In order to determine which metals are present in the DEWATS, samples were taken from five sampling points within the anaerobic baffled reactor (ABR) chambers (Figure 2) . Liquid and suspended solid samples were taken from ABR 1 (A), ABR 7 (C), and AF 2 (D). Sludge was taken from the bottom of ABR 1 (A), ABR 4 (B), and ABR 7 (C). Lastly, scum (E) was sampled from the settling chamber.

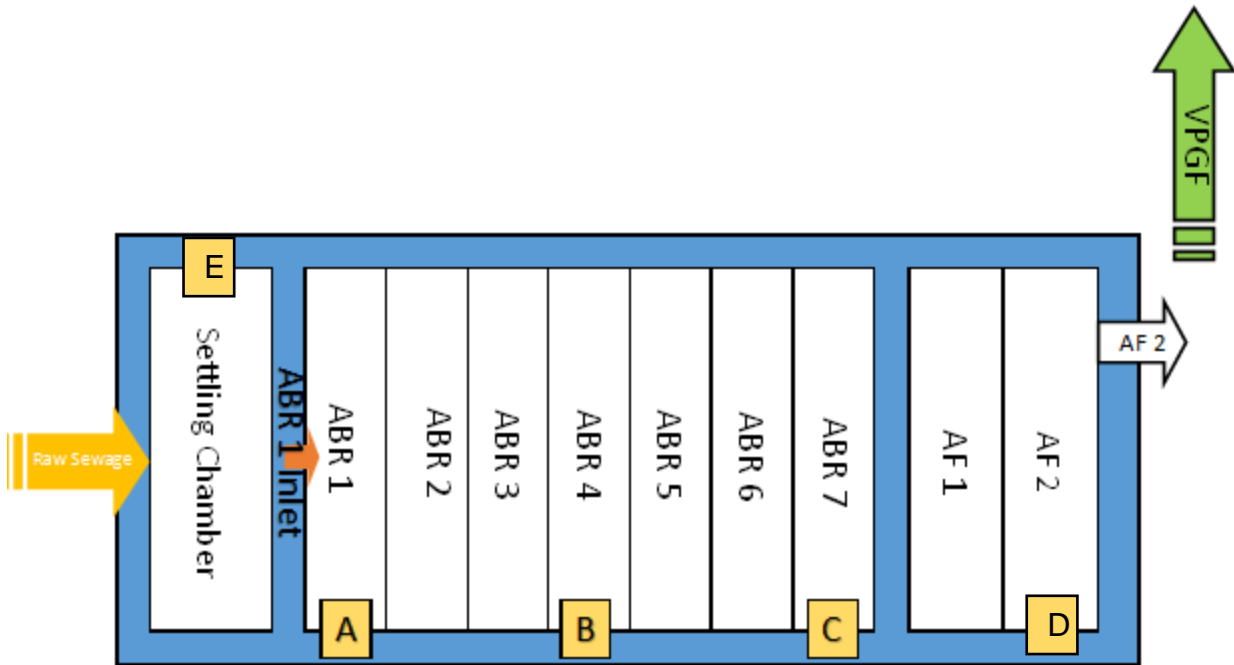


Figure 2. Schematic of sampling locations

2.1.1 Scum sampling

Scum from the settling chamber was sampled from the top of the settling chamber using a piece of wood approximately 3 inches wide, 1 inch thick and 4 feet long. The piece of wood was used to scoop out scum from the middle of the chamber by inserting it approximately 3.5 inches into the scum layer and removing sample.

2.1.2 Sludge sampling

Sludge samples were collected (Figure 2) using field site collection procedures. A sampling tool containing a cylindrical tube with a rubber stopper on one end connected to a metal rod extending to the other end of the cylinder was used to sample the sludge from the bottom of the ABR chambers.

2.2 Sample preparation for digestion

- Samples were placed in 100 mL crucibles
- Dried in an oven at 105 °C for 24 hours.
- After cooling, samples were stored in 50 mL Falcon tubes and placed in a desiccator.
- Approximately 0.2 g of sample were placed into a clean, dry, easy prep digestion vessel. The precise weights were recorded and used in later analysis.

2.3 Digestion Method 1

The first method used an Aqua Regia solution comprised of 25% concentrated hydrochloric acid and 75% concentrated nitric acid. (Sastre et al., 2002) Samples were placed in the digestion vessel followed by the addition of 9 mL of analytical grade, concentrated, nitric acid and 3 mL of analytical grade, concentrated, hydrochloric acid. This was repeated for each of the samples and each sample was completed in multiples of 3. (Figure 3)

2.4 Digestion Method 2

The second method consisted of using only concentrated analytical grade nitric acid for the digestion. Samples were placed in the digestion vessel and 12 mL of analytical grade, concentrated, nitric acid was titrated into each vessel. This was repeated for each of the samples and each sample was completed in multiples of 3. (Figure 3)

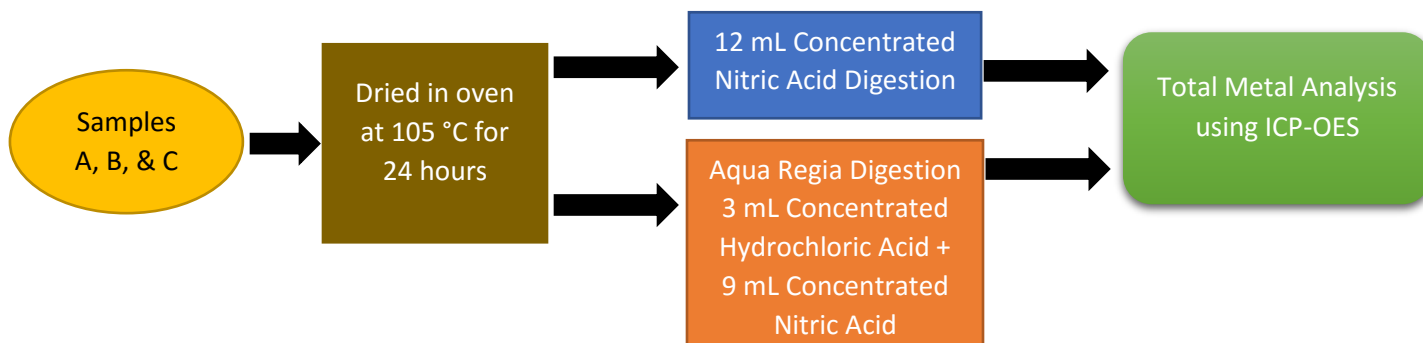


Figure 3. Schematic of method used for total metals analysis

2.5 Microwave Digestion

After addition of the acid, the lids were placed on the digestion vessels and the vessels were undisturbed for 1 hour to predigest. Following pre-digestion, the temperature and pressure sensors were connected to the first digestion vessel. The microwave digester was programmed using an easy prep plus method and 6 samples were digested at a time. The microwave digestion program used for samples was: a ramp time of 15 minutes to reach 190 °C, a hold time of 10 minutes, and a cool down time of 15 minutes.

After digestion, once the vessels cooled to room temperature, the samples were poured into a 100 mL volumetric flask. Approximately 10 mL of deionized (DI) water was poured into the digestion vessel and swirled to remove any sample that may have adhered to the walls of the vessel. The DI water was then poured into the 100 mL volumetric flask containing the sample. This was repeated until the volumetric flask was almost at the 100 mL mark. The volumetric flask was then filled to the 100 mL mark with DI water. Flasks were inverted several times to mix the sample.

2.6 Sample preparation for ICP-OES

A 6 mL syringe with a 0.45 micron syringe filter was used to filter each sample. Prior to filtration to saturate the filter, approximately 5 mL of sample were filter and wasted. Sample was passed through the filter until approximately 14 mL were obtained. Filtrate was collected into clean 15 mL Falcon tube (pre-rinsed with filtered sample). In between samples, the filter was discarded and the syringe washed with soap, water, and DI water. A new filter was used for the next sample and the process was repeated for each sample. Samples were refrigerated between 2 to 5 °C until ICP-OES analysis.

2.7 Standards

Twelve standards were created for 9 metals with concentrations varying from 0.003 to 12 mg/L based on the detection limit of the ICP-OES instrument. The standards were created from 100 ppm stock solution and micropipettes were used to transfer the 100 ppm stock solution into 12 labeled 25 mL volumetric flasks. Each flask contained 4.2 mL of analytical grade, concentrated nitric acid to match the matrix of the samples. DI water was added to the 25 mL mark, all volumetric flasks were inverted for mixing. The standards were filtered using a new syringe and new 0.45 micron syringe filter. Standards were filtered from the lowest to the highest concentration. Before filtering the standards, the filter was rinsed with 5 mL of DI water and 5 mL of standard. A total of 14 mL of filtrated standard were placed into a 15 mL Falcon tube. Every standard was processed following the same procedure. Standards were refrigerated between 2-5 °C until used. Standard curves are shown in Appendix A

2.8 Recovery Studies

Recovery studies were completed to determine which acid digestion was the most repeatable and to verify the accuracy of the results. Approximately 0.2 g of sodium sulfate was oven dried and placed into each of the clean and dry digestion vessels. Each vessel was spiked with the metal standards. Three digestion vessels were digested by adding 12 mL of analytical grade concentrated nitric acid. Three vessels were digested by adding 12 mL of Aqua Regia (9 mL of analytical grade concentrated nitric acid and 3 mL of analytical grade concentrated hydrochloric acid). Samples were predigested for 1 hour before microwave digestion. After digestion, the samples were poured into 100 mL volumetric flasks and filled up to the 100 mL mark with DI water repeating the process used for the samples. Samples were filtered using a 0.45 micron syringe filter and prepared for ICP- OES analysis.

2.9 ICP-OES

Samples were placed in a test tube rack and an auto sampler was used to transfer sample to the instrument. After samples and standards were prepared, ICP-OES (Optima 5300DV) was used to determine the metals within the sludge. Each sample was analyzed three times by ICP-OES. The wavelengths used to measure each metal were as follows:

- Al- 394.401 nm
- Cd- 228.802 nm
- Cr- 205.560 nm
- Cu- 224.700 nm

- Fe- 259.939 nm
- Mn- 259.372 nm
- Ni- 221.648 nm
- Pb- 261.418 nm
- Zn- 213.857 nm

3. Results and Discussion

3.1 ICP-OES Results- A comparison between Aqua Regia and nitric acid digestion throughout the ABR.

The greatest concentration of metals throughout the ABR were Al and Fe with concentration ranging from 26.4 to 32.3 mg/g and 15.0 to 17.1 mg/g respectively. (Figure 4) The greatest concentration of Al is found in the ABR 4 which is located in the middle of the ABR treatment system. Fe had the largest concentration in ABR 1 of 16.09 mg/g using an Aqua Regia digestion and 17.1 mg/g when using a nitric acid digestion. Fe had the smallest concentration of 14.95 mg/g in ABR 4 using a nitric acid digestion.

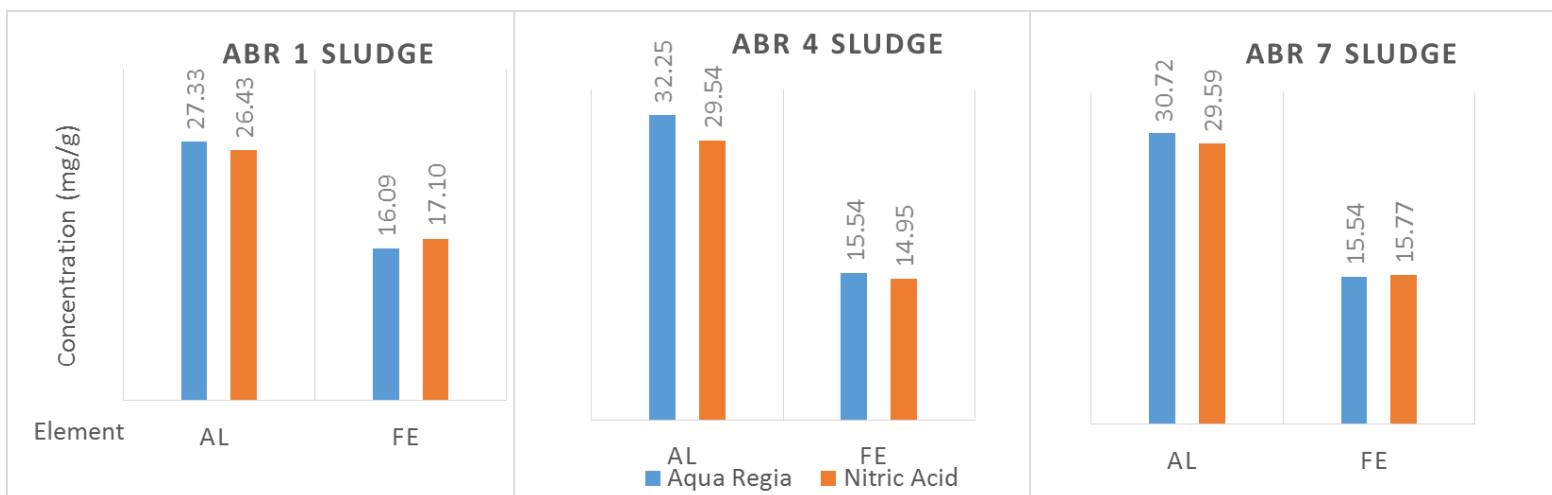


Figure 4. Side by side comparison of aluminum and iron in ABR sludge digested using Aqua Regia and nitric acid.

Metals such as Zn, Cu, Mn, and Cr, had small concentrations compared to the Al and Fe with concentrations ranging from 0 to 1064.43 $\mu\text{g/g}$. Of the metals in Figure 5, the largest concentration of Zn was located in ABR 7 and was 1064.64 and 1081.24 using the Aqua Regia and nitric acid digestions respectively. The largest concentration of Cu and Mn were also found in ABR 7. Cu concentrations were 351.75 $\mu\text{g/g}$ using Aqua Regia and 359.91 $\mu\text{g/g}$ using nitric acid. Mn concentrations were 333.80 $\mu\text{g/g}$ using Aqua Regia and 326.63 $\mu\text{g/g}$ using nitric acid.

The only detectable amount of Ni was in ABR 1 sludge when digested with Aqua Regia. There was very little difference in the concentrations of metals between the nitric acid and aqua regia digestion with the exception of aluminum and iron. Metal concentration were found to be similar in the sludge collected in the studied chambers of the ABR.

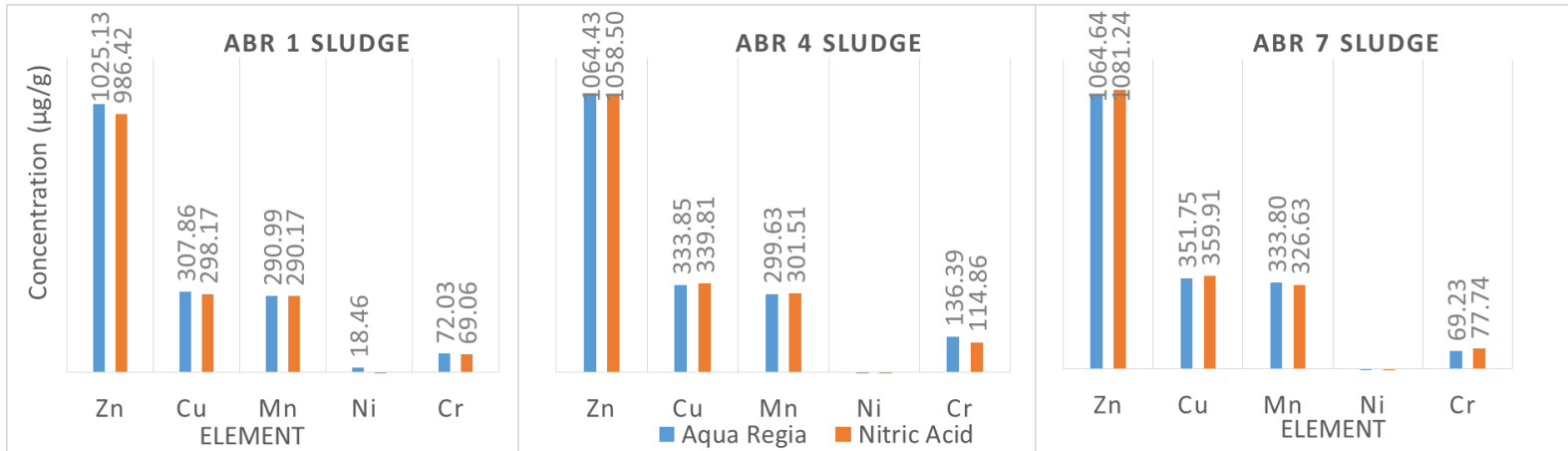


Figure 5. Side by side comparison of Zn, Cu, Mn, Ni, and Cr in ABR sludge digested using Aqua Regia and nitric acid.

3.2 Recovery

The recovery studies showed values greater than 100% for Al, Cr, Mn, and Zn.(Table 1)

Element	Recovery Aqua Regia Digestion (%)	Recovery Nitric Acid Digestion (%)
Al	127.07	126.41
Cr	115.36	139.00
Cu	67.78	51.99
Fe	65.00	77.92
Mn	104.12	94.46
Ni	33.94	32.52
Zn	142.06	161.64

Table 1. Recovery table

3.3 Discussion

Al and Fe may be accumulating within the sludge due to the high concentrations of aluminum and iron within the soils of South Africa entering the system through runoff and storm water intrusion. (Jackson et al., 2013;; Olowoyo and Macheke, 2013) Additionally, metals may also be entering the system through the DEWATS system since the materials for the construction are locally sourced. (BOARDA) Cement contains around 75 % aggregates and if the aggregates used to construct the DEWATS system were locally sourced in South Africa, there may be Al and Fe entering from the system. (Haach et al.,2011)

The similarities between the concentration of metals from both the Aqua Regia and nitric acid digestions indicate that there is little difference between the method's effects on the metal concentration within the sample. From the samples analyzed, neither method provided a consistently different value in concentration. Recovery studies showed that certain metals such as Al, Cr, Mn, and Zn were recovered above 100% indicating possible metal contamination (Table 1). This also may be due to metals within the concentrated acids used for the digestion.

Interestingly, the metals found within the sludge of ABR 1 were similar to the sludge of ABR 4 and ABR 7. This may indicate that the metals entering the system are bound to the same substances within the sludge layer. As the sludge accumulates in each of the chambers the metals accumulate in similar concentrations. It may also indicate that the sludge throughout the ABR is comprised of similar elements and as the sludge begins accumulating in ABR 1, the flow of the system causes some sludge to flow into the next chamber. The hydraulic flow of the system continues to move sludge from one chamber to another causing the elements within the sludge to remain uniform. For most of the metals studied there was no reduction from one chamber to the next and rather for Al, Zn, Cu and Mn, their concentrations increased between ABR 1 to ABR 7.

4. Conclusion

Nutrients and metals are needed to maintain plant, animal, and human health. In proper quantities, metals can be beneficial to plant growth. Characterizing and understanding the metals within the DEWATS system aid in reuse applications. The concentrations of aluminum present in the sludge of the ABR far exceed the plant toxicity values of 25 μ M for Al sensitive plants. Certain plants such as corn, potatoes, and rice which are aluminum sensitive will have extreme difficulty growing in a region with current concentrations present. Additionally, plants which are Fe sensitive will also have difficulty growing as the concentrations of Fe present within the system are greater than the level at which crop losses are upwards of 15 % to 30 %.(Dufey et al., 2014) For metals such as Ni, Co, Pb, and Cd which were below the limit of detection for the ICP-OES. It is recommended to use MP-AES to obtain metal content for these trace metals as the instrument has a lower detection limits.

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Appendix A

Standard Curves for metals

Figure 6. Aluminum measured by ICP-OES at a wavelength of 394.404 nm.

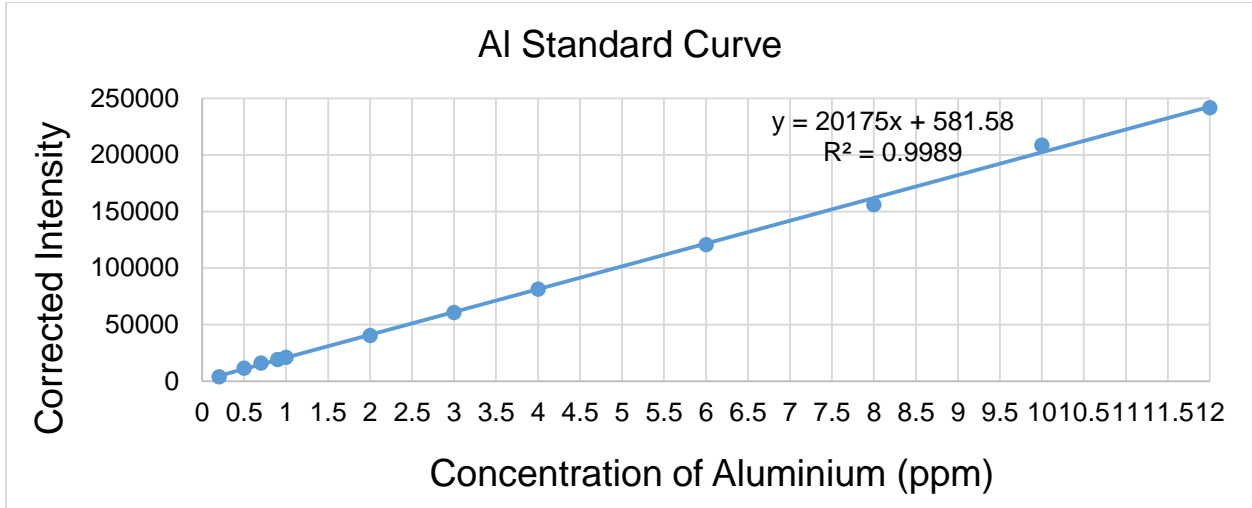


Figure 7. Cadmium measured by ICP-OES at a wavelength of 228.802 nm.

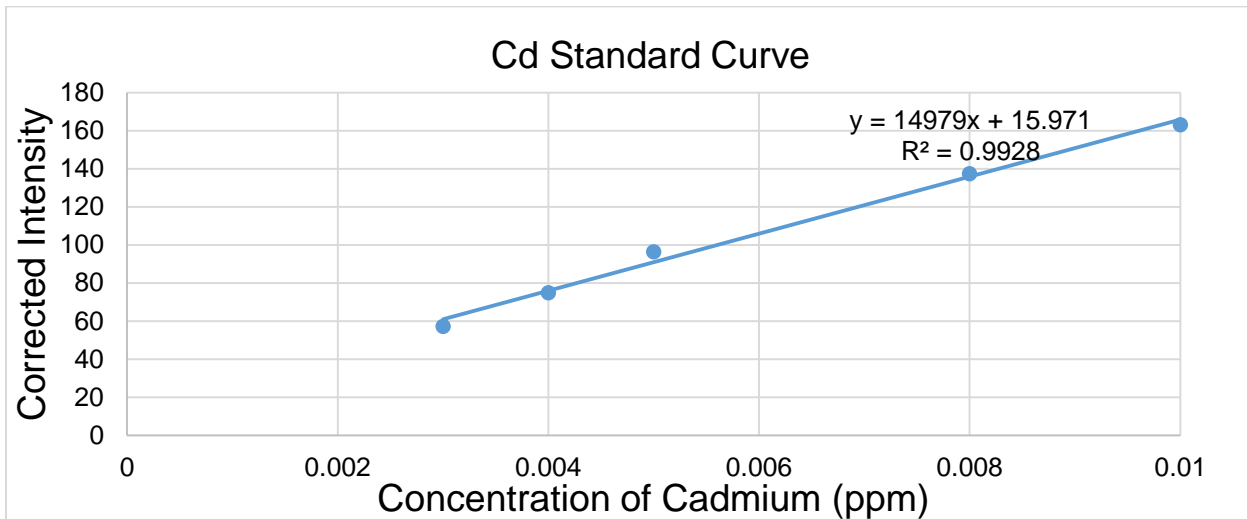


Figure 8. Chromium measured by ICP-OES at a wavelength of 205.560 nm.

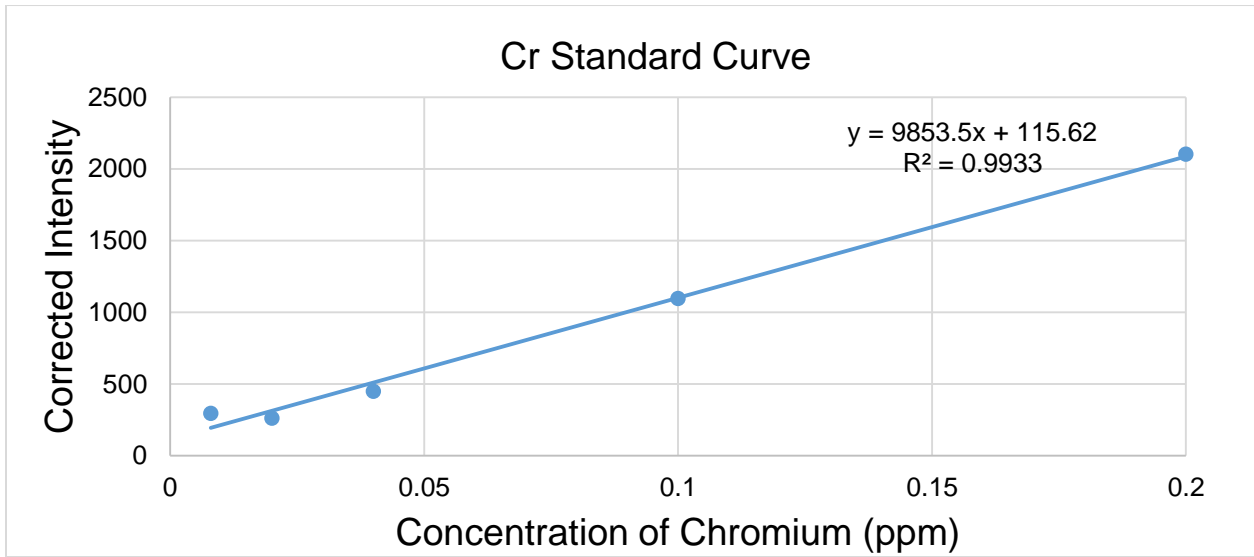


Figure 9. Copper measured by ICP-OES at a wavelength of 224.700 nm.

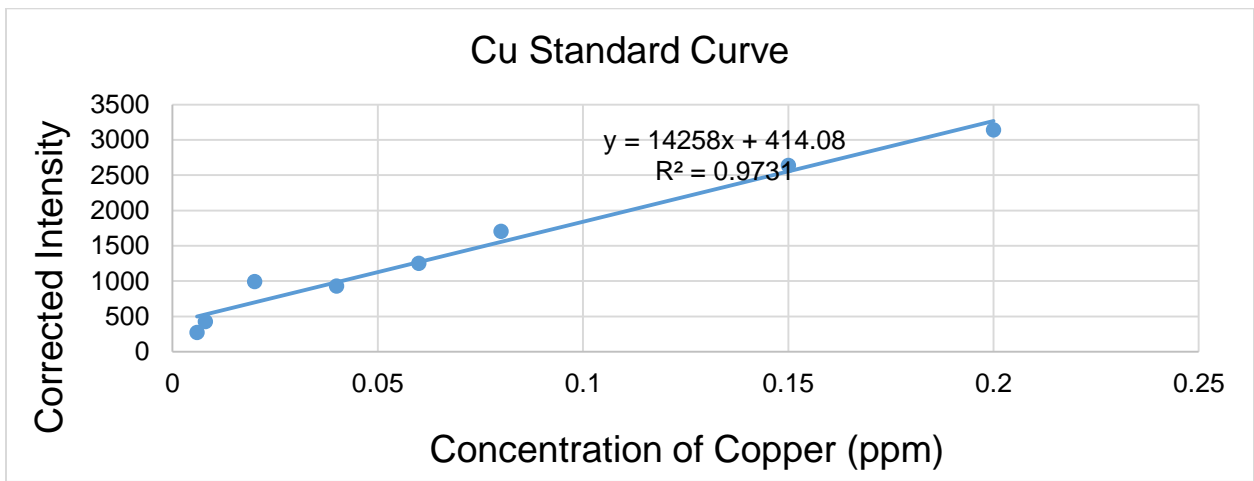


Figure 10. Iron measured by ICP-OES at a wavelength of 259.939 nm.

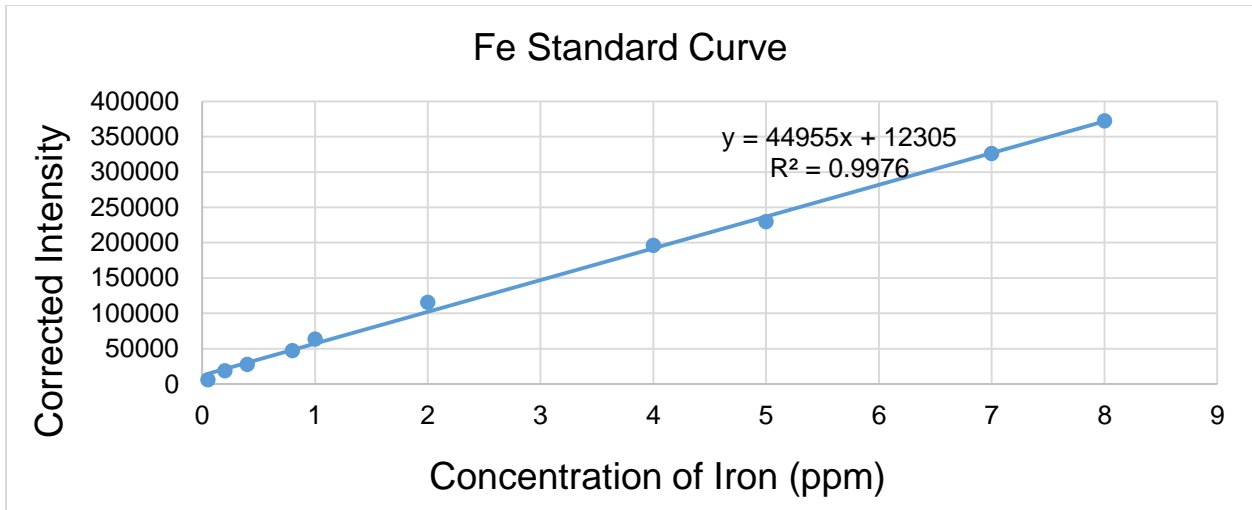


Figure 11. Manganese measured by ICP-OES at a wavelength of 259.372 nm.

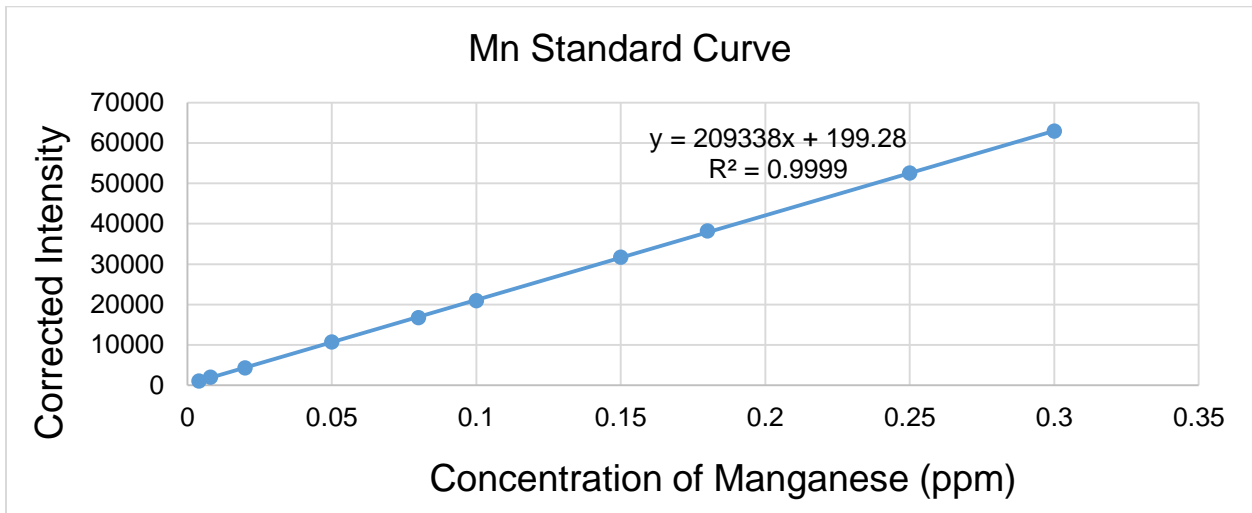


Figure 12. Nickel measured by ICP-OES at a wavelength of 221.648 nm.

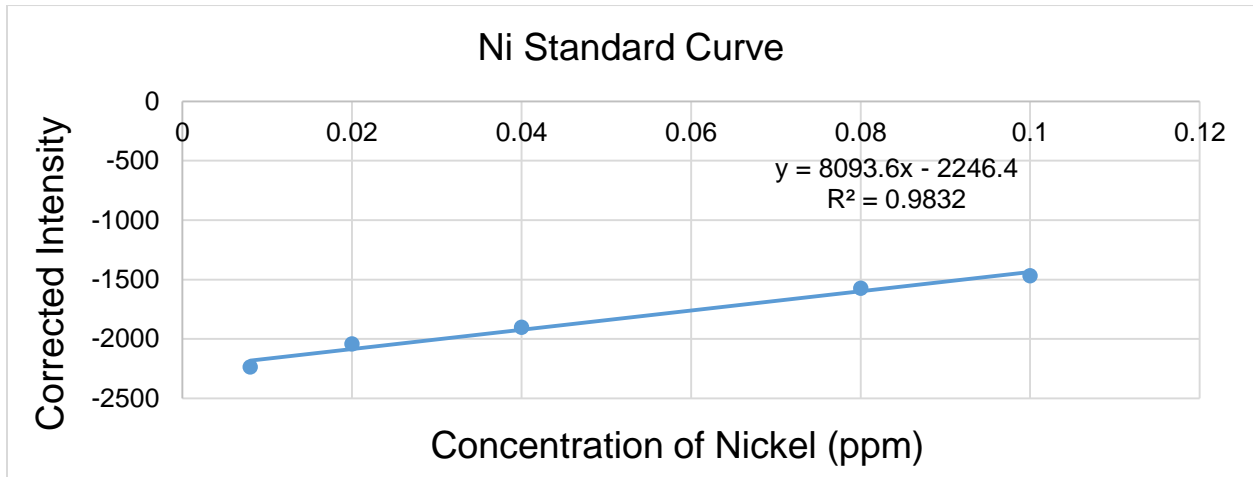


Figure 13. Lead measured by ICP-OES at a wavelength of 261.418 nm.

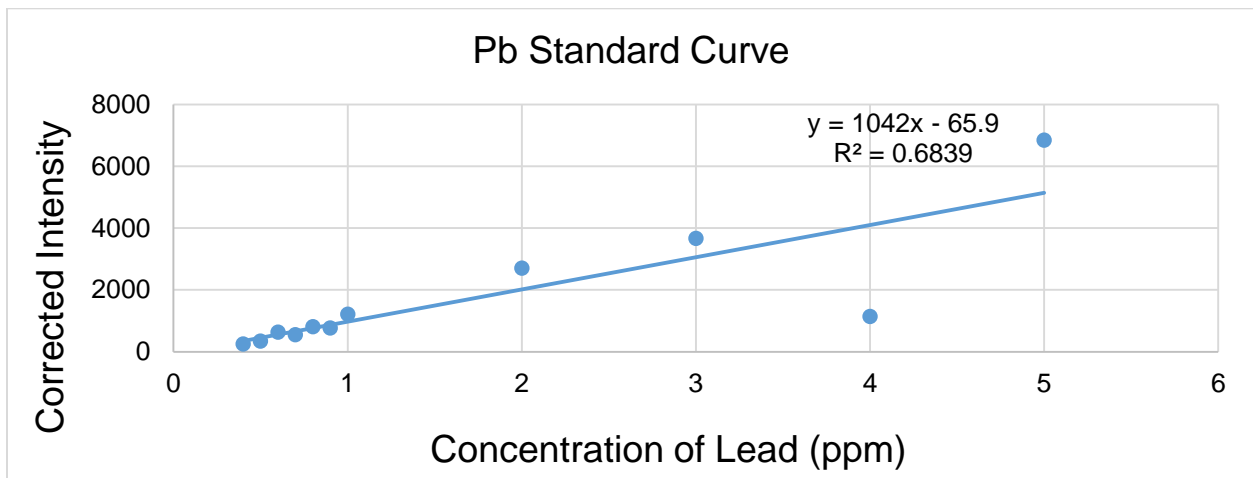


Figure 14. Zinc measured by ICP-OES at a wavelength of 213.857 nm.

