

## **The Effects of Biosludge on Soil in Carroll County**

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There is a large usage of biosludge products on farms in Carroll County, MD. Biosludge, also known as residuals, is the solid waste product from wastewater treatment plants that is used to fertilize farmland. Enviro-Organic Technologies whose products are derived from slaughterhouse waste and McCormick Spice Company supply the residuals used in Carroll County<sup>1</sup>. Residuals improve soil and plant growth at a low cost, but may contain contaminants such as hormones, antibiotics, and metals. Soil samples were collected from ten farms in Carroll County, nine of which use biosludge applications, while one is from an organic (biosludge-free) farm. The Mehlich Extraction, using the LaMotte STH Combined Soil Analysis Kit was performed on all samples. ICP-MS was also used to determine element contaminants. The soils were determined to be mostly of a sandy clay composition, which is typical of the Carroll County area. Results show that the LaMotte Kit results are not as comparable with the ICP-MS as desired. It was found that the biosludge samples have higher metal concentrations than the organic sample, but do not approach EPA restrictions.

Samples were compared to an organic sample from Florida<sup>2</sup> and a biosludge sample from Spain<sup>3</sup>. The data was follows to follow similar trends but varied in element concentrations. Manganese stood out as being in excess in both the Carroll County organic ( $972.2 \pm 4.001$  ppm) and biosludge ( $822.9 \pm 8.962$  ppm) samples, where the average amount found in plants is only 20-200 ppm. Overall it was found that the biosludge sample did not have toxic levels of metals and contaminants and is beneficial to the soil in Carroll County, MD.

### **Introduction**

There is growing public concern about the increasing use of biosludge across the world. In Carroll County, there has been increasing complaints about the odor of biosludge

applied to local farms<sup>1</sup>. Enviro-Organic Technologies Inc. supplies these residuals to local farms. The Maryland Department of Agriculture annually tests and certifies these biosolids<sup>4</sup>. Enviro-Organic is very cost effective; the residuals are completely free to farmers although they have a waiting list for their services. The cost savings on nitrogen alone per acre is as much as \$120.00<sup>4</sup>.

Growing concern over biosludge grows with minimal public understanding and knowledge about the risks and benefits of their application. Due to concerns of the negative side affects of biosolid applications, there have been growing treatments to better cleanse the biosolids of contaminants for land application<sup>5</sup>. This includes the United States Environmental Protection Agency (EPA) creating federal standards in 1993 for appropriate disposal of biosolids to avoid contamination<sup>5</sup>. Federal laws require multiple treatments for sewage<sup>2</sup>. Public acceptance is a major factor in the industry, as the public does not have a good understanding of the risks and benefits of residuals.

In a survey conducted in Tennessee and Virginia, it was found that the majority of interviewed locals understood the nutrient benefits<sup>5</sup>, yet tended to have stronger views on exaggerated risk factors. The residents of both these areas expressed the viewpoint that the benefits do not offset the public risk<sup>5</sup>. Odorous emissions were also found to be key in public stress and concern<sup>5</sup>.

Biosolids come from treated sewage sludge from wastewater treatment plants and are used for agriculture, mine reclamation, forestry, as well as composting<sup>6</sup>. There are increasing amounts of sludge being produced, as well as increasing regulations<sup>7</sup>. Issues arise from how to handle and dispose of this excess waste. This has resulted in companies taking the waste and treating it to form biosolids as an alternative to farmland fertilizers. Enviro-Organic Technologies receives their biosludge from slaughterhouse waste and McCormick spice company<sup>1</sup>. There are two kinds of biosolids: class A and class B. Class B biosolids are treated to greatly reduce the amount of pathogens in the biosolid while Class A are additionally treated to further reduce contaminants<sup>5,6</sup>. Enviro-Organic is a Class B biosolid, which requires special handling.

There are seventeen essential nutrients for plant life<sup>8</sup>, each having a unique role. An element is essential when it is necessary for growth, it cannot be substituted with other elements, or it prevents the plant from completing a life cycle<sup>6</sup>. These nutrients include non-mineral and mineral elements. The non-mineral elements are C, H, and O<sup>8,9</sup>. The fourteen mineral elements are split into macronutrients and micronutrients. The macronutrients are N, P, K, Ca, Mg, and S<sup>8,9</sup>. The micronutrients are Cl, Cu, Fe, Mn, Mo, Ni, Zn<sup>8,9</sup> and B<sup>9</sup>.

Soil pH is vital in availability of these nutrients. Some of these elements are more available at a low pH and some are more available at a high pH<sup>8</sup>. It has been found that the ideal pH range is 5.0-8.5 for plant growth as availability is not only an issue, but some elements can become toxic at a low pH<sup>10</sup>. Nutrients are taken into the plant in their ionic form. All the nutrients are not in their ionic form in soils, but become charged for their uptake through the plant roots.

## **Methods**

Nine soil samples were collected from local farms in Carroll County that use biosludge supplied by Enviro-Organic Technologies, and one additional sample was collected from an organic farm that does not apply any fertilizer or biosolids. Figure 1 displays the locations of each sample collected on a map of Carroll County. Upon collection, it was apparent that some of the soils were freshly tilled and some were not tilled. The tilling does not have an affect on the nutrient uptake as surface application has positive effects on plant growth<sup>11</sup>.

Each sample underwent a percent composition and water content test upon returning to the laboratory after collection. A LaMotte Soil Kit Model AST-15 Code 5412-01<sup>10</sup> was used to determine the concentrations of various nutrients within the soil. These nutrients included nitrates, P, Ca, Mg, S, and many others. The LaMotte Kit utilizes the Mehlich extraction method to make a filtrate for the specific nutrient testing. This extraction method was developed in 1953<sup>12</sup> and has been since adapted. The original method was only used for pH, P, Ca, Mg, K, Na and NH<sub>4</sub> concentration determinations<sup>12</sup>. This extraction method can be utilized via UV-VIS as well as ICP, but

it was used here in the LaMotte Kit. The extraction utilized mixed acid reagent, soil sample, and charcoal suspension to bind to and remove inorganic impurities via filtration.

Dr. Stephen M. Monk collected data using ICP-MS at Towson University. Samples were weighed into Teflon vials with HF and HNO<sub>3</sub> and set on a hotplate at 100°C for 5 days. After running in the ICP-MS, element concentrations were calculated with a standard linear regression calibration curve of standard concentration versus ion counts per second. The curve was made using standards and blanks. The standards were made using a digestion of USGS Standard Reference Material 2709, San Joachin Soil<sup>13</sup>.

## **Results and Discussion**

The soil composition triangle is shown in Figure 2. It shows that the every sample except for sample F being classified as sandy clay, with sample F being characterized as only clay. This soil classification is characteristic of the area. Ideal soils are a mix of the three classifications, sand, silt, and clay. The textures of these soils relates strictly to the size of the minerals<sup>9</sup>. Clay soils, that are dominant in the soil samples, are beneficial in that they are great binding agents in the soil increasing water and nutrient retention due to their large particle size<sup>8,14</sup>. Sandy soils consist of fine particles<sup>14</sup> that have poor retention qualities but more malleable.

The percent moisture of all samples is shown in Table 1. Although the moisture ranges from 17.53% to 39.60%, none of the samples are overly dry or wet. The range can be due to farmers watering schedules. These ranges show that the clay-based soils do retain the water, with the clay-based sample being at the upper end of water percentage with 37.50%.

The pH of the samples was determined with the LaMotte Soil Kit as seen in Table 2. Sample C (organic) and E had replicate trials performed to detect error within the kit. There is evident error within the pH results as the values do vary with a high standard deviation. This error can be due to the LaMotte Kit using color indicators for the pH

determination with an octa-slide bar as seen in Figure 3. Although the pH values are variant and have error, they all fall within the ideal range of 5.0-8.5.

### LaMotte Soil Kit

When overviewing the LaMotte Soil Kit data, Nitrate Nitrogen ( $\text{NO}_3^-$ ), Ammonia Nitrogen ( $\text{NH}_3^+$ ), P, and K are vital. Nitrogen is very important to crop growth as it is in chlorophyll, nucleic acids, and the structure<sup>10,14</sup>. In excess, it can delay crop growth, increase vegetation and decrease fruit growth, as well as produce hazardous nitrate accumulation in plants for consumers<sup>14</sup>. The organic sample has more  $\text{NO}_3^-$  than the biosludge samples by more than an average of 70 ppm while the amount of  $\text{NH}_3^+$  in the biosludge samples is close and comparable with the organic sample. Nitrogen is taken in readily and quickly by plants<sup>10</sup> which can explain the large amount in the organic sample as that sample was taken from a plot that was being prepared for planting and lacked crops.

Low levels of  $\text{NH}_3^+$  are understandable and common in fertile soils due to the ions transforming into more useful nitrogen compounds<sup>7</sup>. Phosphorus levels of biosludge are  $24.2 \pm 11.7$  ppm while the organic sample is 45 ppm. Phosphorus, a vital element in energy storage and found in the nucleus of cells, does not have negative effects with growing amounts<sup>10,14</sup>. The organic sample, for its much larger phosphorous content, should aid in enhancement of plant growth.

Potassium levels in the organic sample (120 ppm) are about double that of the biosludge samples ( $60.0 \pm 38.7$  ppm). Potassium is used in plant functions, but not within the structure itself. The organic sample will better aid crops in cell division and growth as well as keep them healthy as potassium helps defend crops against disease<sup>10</sup>.

A replicate trial of Sample A was performed to determine the accuracy of the LaMotte Kit. The averages and standard deviations are shown in Table 4. The standard deviations are much too large, ranging from 0 to 233 ppm, shows that the test is not as accurate as would be ideal.

## ICP-MS

The ICP-MS tested a wide range of element concentrations: Na, Mg, Al, Si, P, S, Ca, Cr, Fe, Mn, Co, Ni, Cu, Zn, Sr, Cd, I, Pb, and U. The ICP-MS was subsequently studied by looking at all biosludge samples in comparison to the organic sample. Figure 3 displays the metal concentrations in the soil. With the exception of Mn, Pb, and U, there are higher metal concentrations in the biosludge sample than the organic sample. The error bars are minimal and fail to overlap showing the validity of this trend. The trend follows what would be expected that the biosludge has higher metal concentrations. There are very high levels of Mn in both the organic ( $972.2 \pm 4.001$  ppm) and biosludge ( $822.9 \pm 8.962$  ppm) samples. The amount of Mn in plant tissue is only 20-200 ppm<sup>8</sup>, indicating that these values of Mn are incredibly high indicating a large need for lime treatment<sup>10</sup>. Manganese is essential for plant growth as it is used in photosynthesis and germination<sup>10</sup>. Excess Mn toxicity, prevalent in Carroll County soils, can negatively affect crop growth. Mn toxicity can be harmful, but is only minor compared to N deficiency<sup>15</sup>.

The low levels of Fe are reasonable as it, although essential for enzymatic systems, is only used in small amounts by plants<sup>10</sup>. There also appears to be high levels of Zn, which is used in plant metabolism, although these values are consistent with ideal amounts in the plant structure<sup>8</sup>. Zinc levels in biosolids ( $119.0 \pm 0.987$  ppm) and in organic ( $107.8 \pm 0.449$  ppm) easily fall within the ceiling concentration of 7500 ppm as listed by the EPA<sup>16</sup>. Chromium, which is not an essential nutrient in plants and can cause toxicity issues, also has high levels. Cr levels in both biosolids ( $102.4 \pm 1.56$  ppm) and organic soil ( $75.53 \pm 0.4$  ppm) in Carroll County fall below the ceiling concentration of 3000 ppm<sup>16</sup> as stated by the EPA. Figure 4 displays the non-metal element concentrations in the organic sample versus the biosludge samples. These values follow the same general trend as the metals that the majority of elements have higher concentrations in the biosludge than the organic sample. The only exceptions are S and P. There is a very high concentration of S, especially so in the organic sample. Sulfur is used in plant proteins, and is found in the plant structure from 1000-

4000 ppm<sup>8</sup>. The ICP-MS results show that there is 10 fold this amount. The Mg values are low as well, with the biosludge ( $.574 \pm .022$  ppm) being slightly higher than the organic sample ( $0.34 \pm 0.001$  ppm). These values are low as the ideal values are between 1000-4000 ppm.

The organic sample from Carroll County was compared to a literary sample as shown in Figure 5. Sigua studied the effects of continual biosolid application in South Florida<sup>2</sup>. He collected data on a soil sample in 2002 that had not had biosolid application within five years<sup>2</sup>, which was seen as an organic sample. Figure 5 shows that the data is not very comparable. None of Sigua's findings fall within the ICP-MS error bars. Ca and Mn are drastically different as Sigua found very trace amounts of each element in the soil, yet the Carroll County organic sample showed much higher levels. Calcium is necessary in cell division and is found in cell walls<sup>8,10</sup>. In plant tissue, Ca is found from 1000-10,000 ppm<sup>8</sup>. This means that Sigua's values were low and undesirable, while the organic sample from Carroll County falls within the desired levels of Ca. The Carroll County sample, although, has very high levels of Mn while Sigua's sample falls within the desired range.

The biosludge samples from Carroll County were compared to literary values shown in Figure 6 as collected by E. Alonso Álvarez. He collected his samples in Seville, Spain to test sludge samples with varying treatments<sup>3</sup>. In Europe, wastewater treatment is the commonly applied process to produce the sludge placed on farmland<sup>3</sup> which varies from the Enviro-Organic sources. The Carroll County samples were compared with Álvarez's dewatered and digested sludge, as it most closely resembles that of Enviro-Organic Technologies. These values, for the most part, do not closely compare. Zn and Mn, in Álvarez's experiments, opposed the trend that with increased treatment lower metal concentrations were found<sup>3</sup>.

In comparison of ICP-MS data versus the LaMotte Soil Kit, as shown in figure 7, it can be seen that the LaMotte Kit is not very accurate. The ICP-MS data was reproducible with low standard deviations over three trials. In comparison, S stands out most drastically with a significant difference in values. The values range from 100-21,050

ppm. Value's that are more comparable such as Phosphorus ranges from 24.2-122.8 ppm, which is still a significant 134% difference.

In comparing all of the data, as seen in Figure 8, trends can be easily identified. The organic soil data found by Sigua in South Florida have very low values overall. Álvarez's biosludge sample from Spain varied in comparison with Carroll County being much higher in Fe, Cu, Zn, and Pb, but less in Mn, Co, and Cd. The biosolids and organic samples in Carroll County varied. The biosolids tended to have higher metal concentrations and the nonmetals swayed with some having higher and some lower concentrations in the biosolids versus the organic sample.

Overall it can be said that the LaMotte Kit did not reveal statistically strong data and cannot be easily compared with the ICP-MS data. There is an overall trend that the biosolids in Carroll County have higher metal concentrations than the organic samples. None of the Carroll County soils exceed or even near the ceiling concentration regulations described by the EPA<sup>16</sup>. The biosolids overall, seem to have positive contributions to the soil. The only major concern is the Mn, which is high in both the organic and biosludge samples and may be an overall trend in the county or surrounding area.

### **Acknowledgments**

I would like to thank Dr. Mona Becker and the Environmental Science and Chemistry Departments for assisting me in my research. I would also like to thank Gesley Fisher for his help throughout the collections and trials of samples. Thanks to Dr. Stephen M. Monk and Towson University for use of their facilities and collecting my ICP-MS data. My thanks are also extended to the Student-Faculty Collaborative Summer Research Fund at McDaniel College for funding my research.

### **References**

- (1) (2010) Carroll to air dispute over organic farm's odor. *Baltimore Sun*.  
[http://articles.baltimoresun.com/2010-02-16/news/bal-md.briefs161feb16\\_1\\_organic-farm-odor-carroll-county-officials](http://articles.baltimoresun.com/2010-02-16/news/bal-md.briefs161feb16_1_organic-farm-odor-carroll-county-officials) (January 23,



2013)

- (2) Sigua, G.C., Adjei, M.B., and Rechcigl, J.E. (2005) Cumulative and Residual Effects of Repeated Sewage Sludge Applications: Forage Productivity and Soil Quality Implications in South Florida, USA. *Environmental Science and Pollution Research*. **2**, 80-88.
- (3) Alonso Álvarez, E., Callejón Mochón, M., Jiménez Sánchez, J.C. and Ternero Rodríguez, M. (2002) Heavy metal extractable forms in sludge from wastewater treatment plants. *Chemosphere*. **47**, 765-775.
- (4) Enviro-Organic Technologies. [www.enviro-organic-tech.com](http://www.enviro-organic-tech.com) (February 6, 2013)
- (5) Robinson, K.G., Robinson, C., Raup, L., and Markum, T.R. (2012) Public attitudes and risk perception toward land application of biosolids within the south-eastern United States. *Journal of Environmental Management*. **98**, 29-36.
- (6) The United States Environmental Protection Agency.  
<http://water.epa.gov/polwaste/wastewater/treatment/biosolids/genqa.cfm>  
(February 6, 2013)
- (7) Garvey, D., Guarino, C., and Davis, R. (1993) Sludge Disposal Trends Around the Globe. *Water Engineering and Management*. **12**, 17-20.
- (8) Jones, C., and Jacobsen, J. (2001) Plant Nutrition and Soil Fertility. *MSU Extension Services*. **2**,1-11.
- (9) Howell, J. (1997) Soil Basics. University of Massachusetts Extension
- (10) LaMotte Model AST Series Instruction Manual (Code 5410)
- (11) Barbarick, K.A., Ippolito, J.A., McDaniel, J., Hansen, N.C., and Peterson, G.A. (2012) Biosolids application to no-till dryland agroecosystems. *Agriculture, Ecosystems and Environment*. **150**, 72-81.
- (12) Mehlich, A. (1953) Determination of P, Ca, Mg, K, Na, NH<sub>4</sub>. *Short Test Methods Used in Soil Testing Division, Department of Agriculture, Raleigh, North Carolina*
- (13) Mackey, E.A., et. al. (2010) Certification of three NIST renewal soil standard reference materials for element content: SRM 2079a San Joaquin Soil, SRM 2710a Montana Soil I, and SRM 2711a Montana Soil II. *National Institute of Standards and Technology*. 1-39.

- (14) Tucker, M.R. (1985) LaMotte Soil Handbook
- (15) Upjohn, B., Fenton, G., and Conyers, M. (2005) Soil acidity and liming. *Agfact AC. 19. 3*
- (16) (1993) Federal Register. *Environmental Protection Agency*. 40 CFR Part 257, 403, 503 Standards for Use or Disposal of Sewage Sludge

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Figure 1. Map of Carroll County displaying location of soil samples collected.

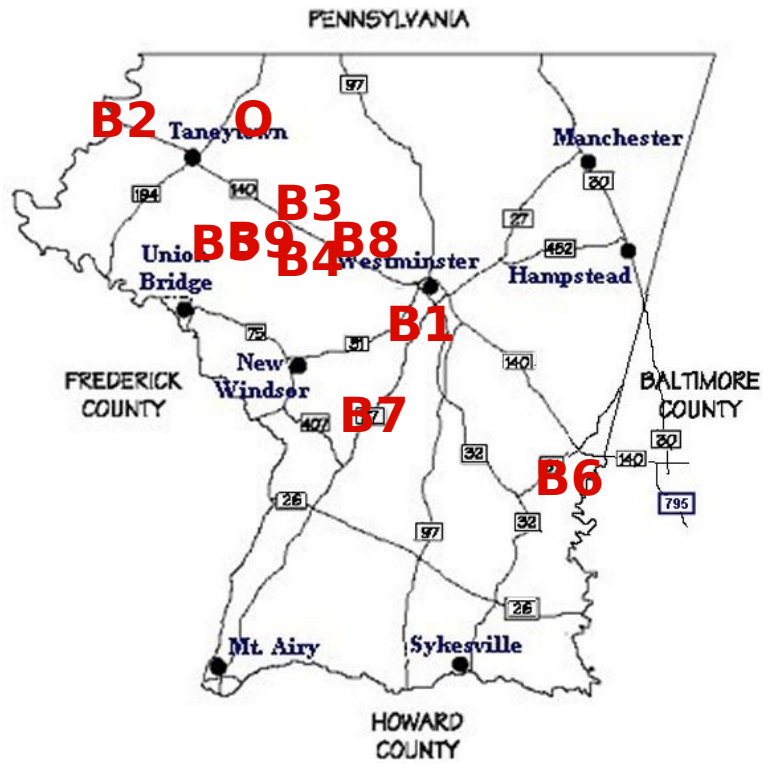


Figure 2. Soil Composition Triangle

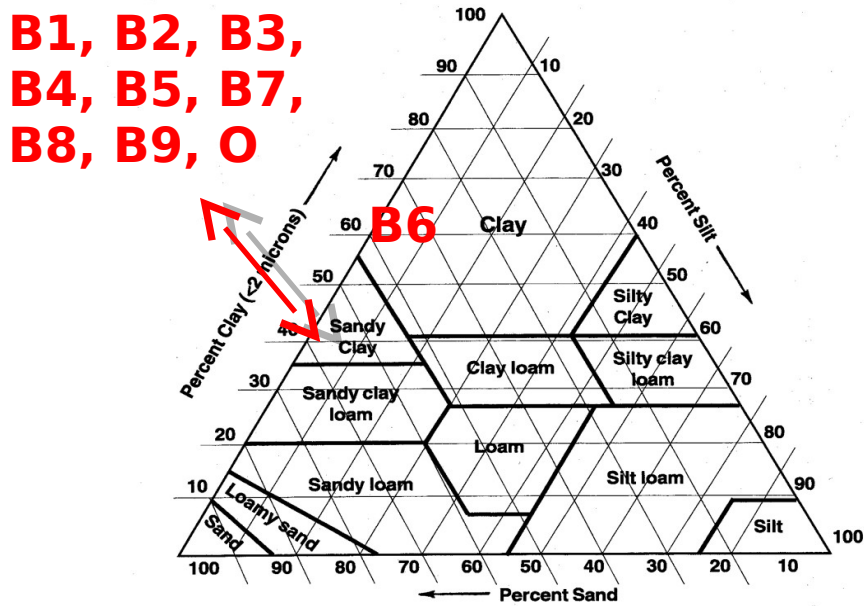


Table 1. Moisture Content

<b>Sample</b>	<b>B1</b>	<b>B2</b>	<b>B3</b>	<b>B4</b>	<b>B5</b>
Moisture (%)	20.50	27.10	30.71	31.89	37.50
<b>Sample</b>	<b>B6</b>	<b>B7</b>	<b>B8</b>	<b>B9</b>	<b>O</b>
Moisture (%)	17.53	36.17	22.13	39.60	36.60

Table 2. pH Results using the LaMotte Soil Kit

<b>Sample</b>	<b>B1</b>	<b>B2</b>	<b>B3</b>	<b>B4</b>	<b>B5</b>
pH	6.5	6.0	6.5	5.3 ± 1.1	7.0
<b>Sample</b>	<b>B6</b>	<b>B7</b>	<b>B8</b>	<b>B9</b>	<b>O</b>
pH	7.0	5.0	6.5	6.5	5.3 ± 0.65

Figure 3. Octa-Slide bar: pH Test



Table 3. LaMotte Soil Kit: Biosludge vs Organic Samples

LaMotte	Biosludge	Organic Sample
% Moisture	29.24±0.079	36.60
% Sand	48.90±0.085	56.5
% Silt	9.200±0.079	5.00
% Clay	41.80±0.088	38.30
pH	6.2±0.75	5.3 ± 0.65
Nitrate Nitrogen (ppm)	10.7±14.1	100.0
Ammonia Nitrogen (ppm)	26.3±17.8	30
Nitrite Nitrogen (ppm)	0.00±0.00	0.0
Phosphorous (ppm)	24.2±11.7	45
Potassium (ppm)	60.0±38.7	120
Potash (ppm)	72.0±46.5	144
Iron (ppm)	25.0±14.6	30.0

Sulfur (ppm)	218.6±285.8	100
Copper (ppm)	0.9±0.517	3.0
Calcium (ppm)	3316.2±2058.1	5696
Magnesium (ppm)	455.5±227.0	1536
Chloride (ppm)	138.3±30.4	120
Aluminum (ppm)	88.3±50.9	125
Manganese (ppm)	29.4±11.84	40

Table 4. Replicate of Sample A using the LaMotte Soil Kit

	Nitrate Nitrogen	Ammonia Nitrogen	Phosphorus	Potassium	Iron	Sulfur
ppm	6.25 ± 5.30	20 ± 7.0	30 ± 0	80 ± 28.3	15 ± 0	235 ± 233
	Copper	Calcium	Magnesium	Chloride	Aluminum	Manganese
ppm	1.25 ± 0.35	1125 ± 205	279 ± 132	160 ± 56.6	43 ± 53	15 ± 14

Figure 3: ICP-MS Results for Metals in Biosludge and Organic Samples  
 \*Mn was divided by a factor of six to fit on scale

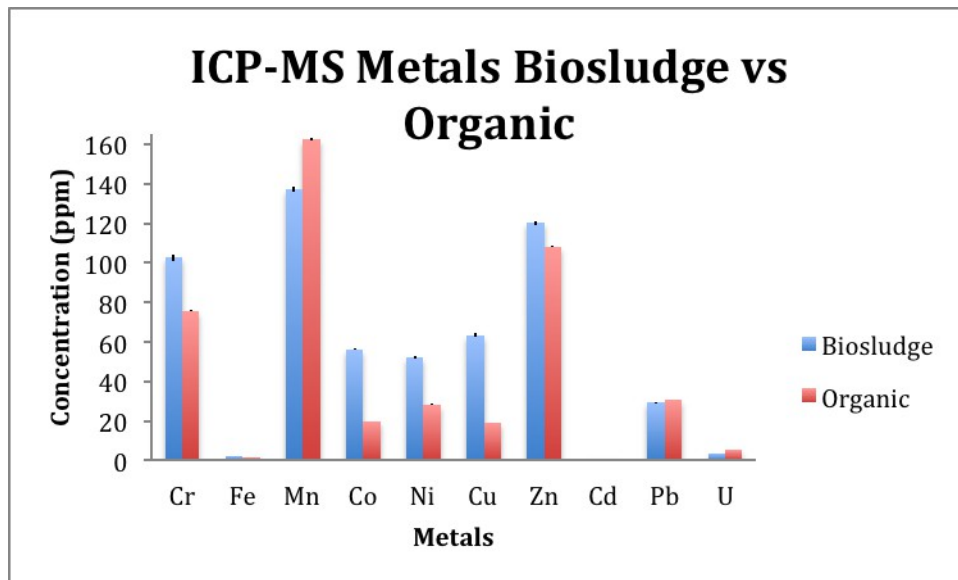


Figure 4: ICP-MS Results for NonMetals in Biosludge and Organic Samples Element Concentrations  
 \*S was divided by a factor of five to fit on scale

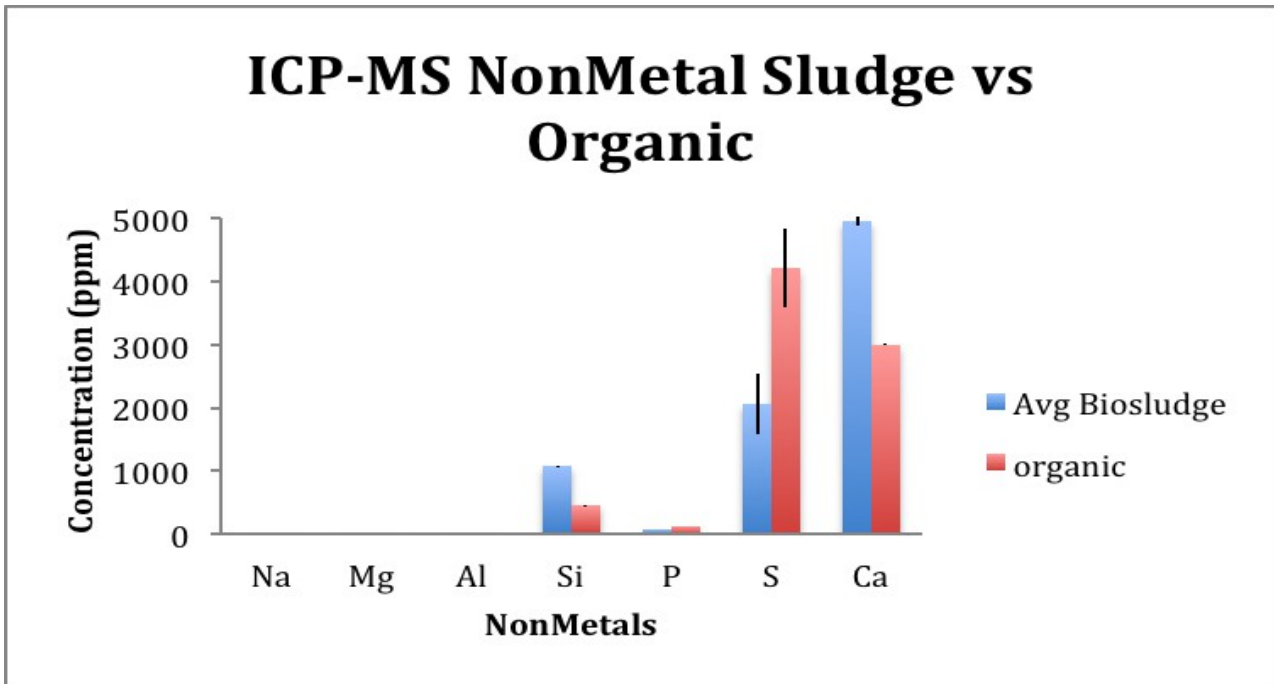
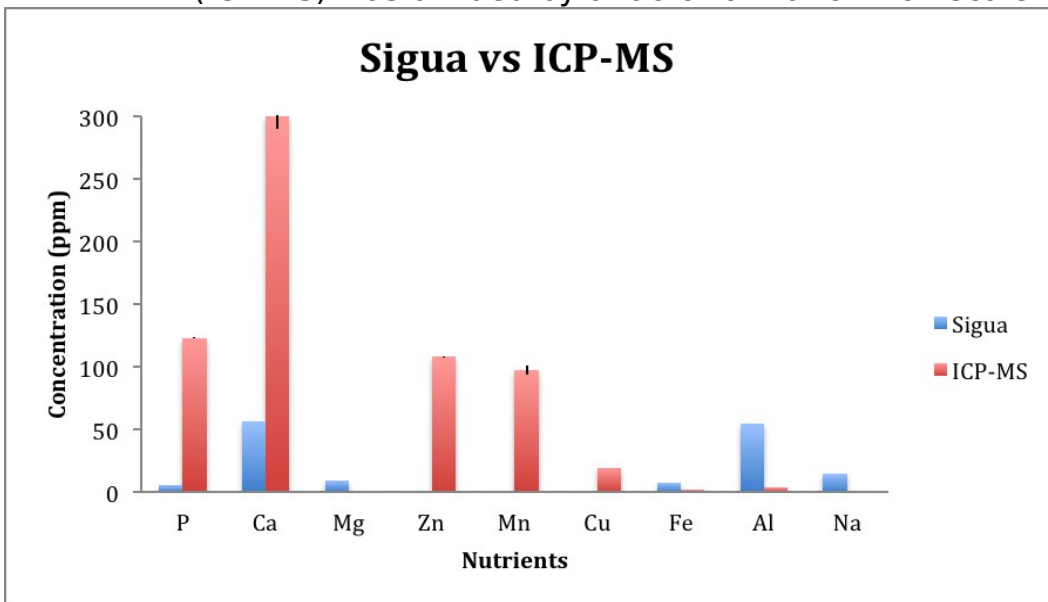
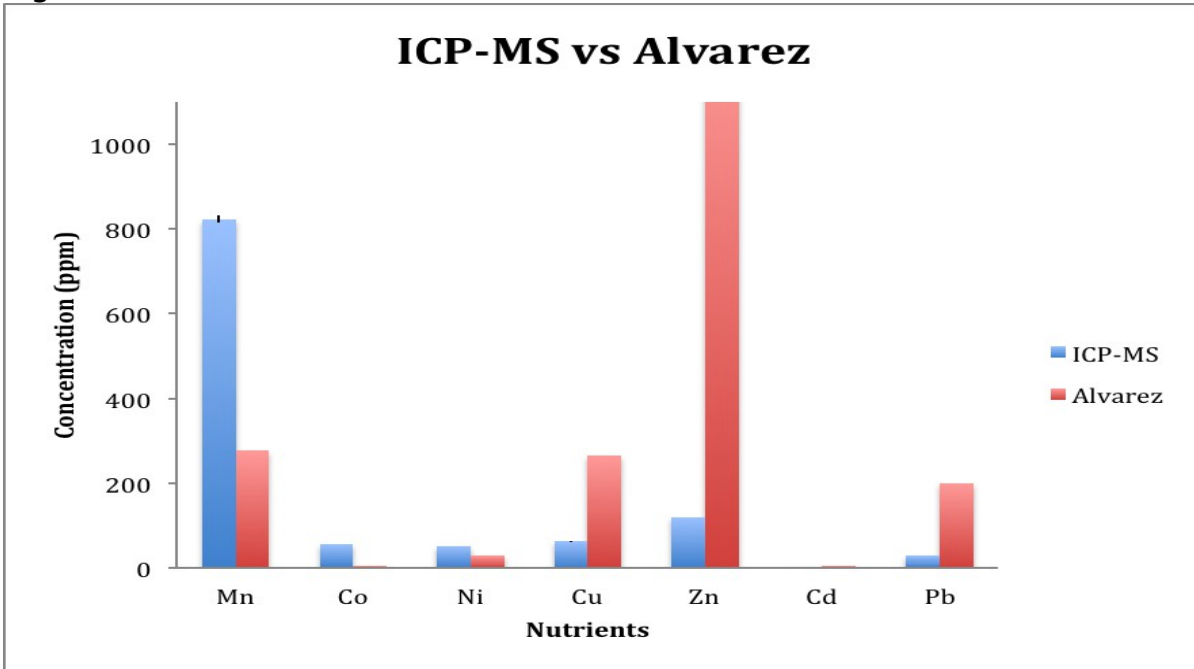


Figure 5: Sigua vs ICP-MS Organic Element Concentrations  
 \*Ca (ICP-MS) was divided by a factor of 10 to fit on scale  
 \*Zn (ICP-MS) was divided by a factor of 10 to fit on scale



\*Sigua Data<sup>2</sup>

Figure 6: Alvarez vs ICPMS Nutrient Concentrations



\*Alvarez Data<sup>3</sup>

Figure 7: ICP-MS & LaMotte Data Comparison

