The Spatial Variability of Total and Bioavailable Metal Concentrations in the Sediments of Mitchell Lake

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Abstract

Century-long disposal of sewage sludge in Mitchell Lake at San Antonio, Texas has resulted in hyper-eutrophic conditions and an excess accumulation of toxic metals in the lake system. To identify the most suitable remedial measure for Mitchell Lake, a baseline study of metal geochemistry in lake water and sediments is currently in progress. The sediment samples were collected from twelve strategic locations, close to possible sources of additional contamination, throughout the lake. Three locations were chosen close to the Leon Creek Effluent Pipeline and from the center of the lake. Two locations were chosen by the Mission Del Lago Golf Course and the SAPD Academy Gun Range. One location was chosen by Polder Pond and the Dam. Samples were tested for their total concentrations of nine common sludge metals, such as Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. To quantify the amount of potentially bioavailable heavy metal concentrations, a widely used chemical extraction scheme, namely, the Olsen method was utilized. Due to the alkalinity of the lake environment, the Olsen method was determined to be an appropriate method for determining the true bioavailability of the metals in the sediments. An ArcGIS map of the lake was created showing the sample locations, their associated total and bioavailable metal fractions, and the elevations. The Geostatistical Analyst exploration tools were used to become familiar with the data. Also, the Geostatistical Analyst tool, Inverse Distance Weighting (IDW), was used to interpolate and to access the spatial variability of the metal concentrations surrounding the sample locations.

Keywords: Bioavailability, Sewage Sludge, Metals, Inverse Distance Weighting, and Spatial Variability.

I. Introduction

In many areas the remediation of lakes once used for sewage sludge disposal is necessary. In the San Antonio Area, Mitchell Lake was used for nearly a century for the disposal of sewage sludge. This sludge has caused hyper-eutrophic conditions, reducing conditions, and an excess accumulation of heavy metals in the lake sediment (Branom and Sarkar, 2004). Also, the lake water has an alkaline pH and has a depth of approximately 2 meters. Extended mudflats that are rich in nutrients have made the lake a migratory stop for over 300 species of birds. The lake is currently owned by San Antonio Water Systems (SAWS) and closed to the general public.

Although an accumulation of metals from the waste is evident and expresses a measure of pollution in the lake, the main concern to citizens is the bioavailable fraction of these toxic metals (Lam et al., 1997). Bioavailability refers to the amount of the metal that is available to organisms, including humans, for uptake from the sediment. A metals bioavailability is highly correlated to the speciation of the metal and pH of the environment (Baruah et al., 1996). Total organic matter in the lake also affects the bioavailability of a metal (Shrivastava et al., 2003).

A study was performed to test the total and bioavailable metal concentrations for nine metals that are common to sewage sludge disposal: Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. The tools available in ArcGIS Geostatistical Analyst were used to interpolate and to access the spatial variability of the metal concentrations throughout the lake.

II. Data Used

2.1 Sampling Method and Locations

Sediment samples were collected from twelve locations in Mitchell Lake by using a van Veen grab and collecting the surface sediments from 0-10 cm (Branom and Sarkar, 2004). The sampling locations were strategically selected to incorporate the potential sources of non-point source pollution into the lake (Branom and Sarkar, 2004). One location, PP1, was located just outside of Polder Pond which was the original location of the sewage sludge disposal. Three sampling locations, C1, C2, and C3, were chosen from the center of the lake progressing from north to south. Two locations, GR1 and GR2, were chosen due to their close proximity to a gun range operated by the city of San Antonio's Police Academy. On the eastern side of the lake, two locations, GC1 and GC2, were selected close to the Mission Del Lago golf course. Three locations, LCE1, LCE2, and LCE3, were located near the Leon Creek Emergency Effluent discharge system. Finally, one location, DAM1, was located by the dam at the south side of the lake (Branom and Sarkar, 2004). Refer to Figure 1, a GIS map, which provides a visual representation of the sampling locations and to Table 1 for the GPS coordinates of each location.

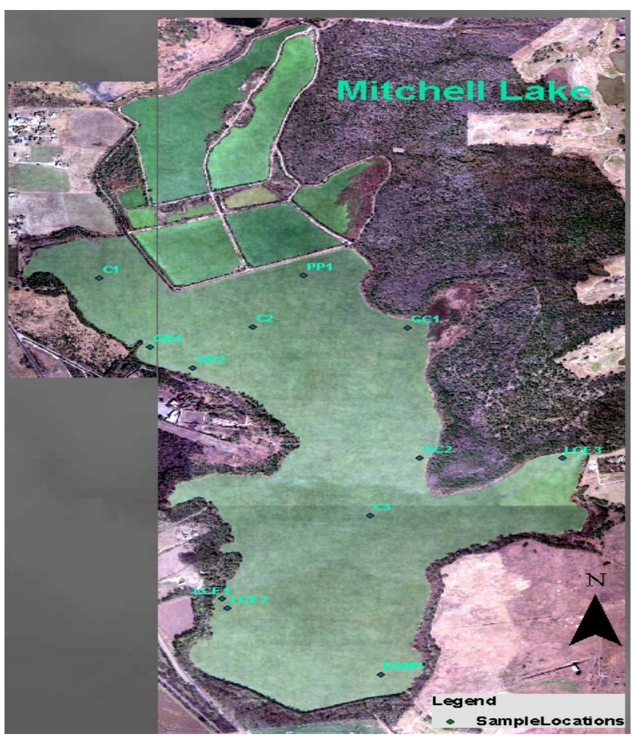


Figure 1. Sampling Locations at Mitchell Lake.

Sample Site	Easting	Northing	Sample Site	Easting	Northing
C1	548639.46	3240411.36	**LCE1**	549070.21	3238696.37
C2	549176.39	3240150.90	**LCE2**	549088.24	3238646.28
C3	549589.11	3239143.15	**LCE3**	550258.28	3239447.68
GC1	549717.34	3240144.89	**GR1**	548815.77	3240044.72
GC2	549759.41	3239449.68	**GR2**	548966.03	3239930.52
PP1	549354.70	3240427.38	**DAM1**	549623.17	3238293.67

Table 1. GPS Coordinates for Sample Locations at Mitchell Lake. Courtesy of Stuart Foote.

2.2 Total Metal Concentrations

The total metal concentration was determined by using the USEPA Method 3050B. 1 g of soil was weighed into a beaker and 10 mL of 1:1 HNO_3 was added. The samples were covered and heated at 95° C for 15 minutes. The samples were then cooled and 5mL of concentrated HNO_3 was added. The samples were again covered and refluxed for 30 minutes. This step was repeated until the reaction was complete which is indicated by the absence of brown fumes. The samples were then refluxed for 2 hours or until approximately 5 mL of solution remained. The samples were cooled followed by the addition of 2mL of DI water and 3mL of 30% H_2O_2. The beakers were returned to the hot plate and heated until effervescence stopped. The samples were removed and cooled. Then 2 mL of H_2O_2 was added and the samples were refluxed until effervescence stopped. This step was repeated until effervescence was minimal, but 10 mL of H_2O_2 was not exceeded. The samples were heated for 2 hours until approximately 5mL of solution remained. The samples were cooled, filtered and diluted to 50mL with DI water. 10mL of this sample was filtered using a 0.2 mm Whatman syringe filter. They were diluted further with DI water and analyzed with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS). All samples were digested in triplicates. Refer to Table 2 which displays the total metal concentrations used in the GIS project.

Sample ID	Chromium	Cadmium	Cobalt	Copper	Zinc	Lead	Nickel	Manganese	Iron
C1	4625.59	46.17	10.03	1566.70	5799.54	5799.54	127.41	482.41	29340.18
C2	684.20	8.70	12.90	223.90	1096.96	1096.96	70.98	568.83	52772.11
C3	1411.52	14.93	12.53	507.22	2388.56	2388.56	101.85	573.29	45974.75
GC1	1735.00	23.38	9.58	645.13	4098.48	4098.48	48.30	556.40	42813.77
GC2	335.34	5.63	3.40	91.30	619.35	619.35	15.80	291.78	9622.19
LCE1	1633.61	16.31	11.62	828.95	2700.99	2700.99	92.37	1031.94	38333.27
LCE2	1614.71	14.60	8.83	914.83	2882.66	2882.66	64.74	1076.66	31703.80
LCE3	689.92	8.70	9.23	202.53	977.88	977.88	62.78	1042.32	29595.96
GR1	497.82	5.34	10.16	148.98	711.11	711.11	45.52	571.27	39670.13
GR2	644.00	6.96	11.61	190.10	891.35	891.35	56.87	553.59	47621.87
PP	3162.64	32.23	11.02	1292.66	5217.52	5217.52	150.98	576.85	39509.92
DAM	2514.69	22.74	11.79	932.73	3638.84	3638.84	100.77	672.34	39913.47

Table 2. Total metal concentrations in parts per million (ppm).

2.3 Olsen Extraction Method (Bioavailable Fraction)

Due to its alkaline pH and the alkaline pH of Mitchell Lake, the Olsen extraction method was determined to be appropriate for accessing the bioavailable fraction of the metals. For this method, 2.5 g of oven dried soil was weighted into a 50mL tube and 50mL of 0.5 M $NaHCO_3$ solution at a pH of 8.5 was added. The samples were shaken for 30 minutes at 180 rpm, centrifuged for 20 minutes at 4000 rpm, and then filtered into new sample tubes. The samples were filtered with a 0.2mm Whatman syringe filter before analysis with the ICP-MS. All samples were extracted in triplicates. See Table 3 which displays the bioavailable fraction of the metals.

Sample ID	Chromium	Cadmium	Cobalt	Copper	Zinc	Lead	Nickel	Manganese	Iron
C1	49.88	0.01	0.16	60.12	0.65	0.04	1.44	0.01	15.47
C2	41.91	0.01	0.21	34.89	0.45	0.08	0.56	0.22	5.14
C3	52.67	0.02	0.21	39.92	9.40	0.49	0.64	1.08	5.61
GC1	43.41	0.01	0.07	31.90	3.76	1.14	0.21	0.68	11.12
GC2	38.68	0.00	0.06	36.17	3.35	0.40	0.15	0.47	6.29
LCE1	42.42	0.01	0.16	38.91	13.25	0.04	0.63	0.12	6.77
LCE2	40.70	0.01	0.13	46.92	4.34	0.24	0.68	0.61	12.41
LCE3	32.14	0.00	0.15	59.29	2.81	0.05	0.59	0.20	4.06
GR1	43.99	0.00	0.20	35.59	0.19	0.10	0.39	0.33	2.67
GR2	46.78	0.01	0.20	36.03	0.33	0.09	0.40	0.01	6.37
PP	37.31	0.01	0.21	53.82	0.51	0.08	1.25	0.02	15.19
DAM	37.17	0.01	0.15	66.29	0.53	0.04	0.50	0.01	6.63

Table 3. Bioavailable metal concentrations in parts per million (ppm).

III. Methods

First of all, a personal geodatabase was created in ArcCatalog. Then, a feature class was created by importing the total metal concentrations for each sample location as XY data, and by using the same method, a feature class was created for the bioavailable metal concentrations. The spatial reference for the area had to be imported into the feature classes, and the GPS easting and northing for each sample location (Table 1) was used as the XY data. Each metal concentration was a separate attribute in the bioavailable and total concentration layers. Then the raster data for Mitchell Lake was downloaded from the City of San Antonio Image Server Website, and the National Elevation Dataset (NED) raster was downloaded from the seamless USGS website.

A map was created in ArcMap by adding the two feature classes, the Mitchell Lake raster data, and elevation (NED) as layers. The data for each metal was explored by using the Geostatistical Analyst exploration tools: Histograms, Normal QQ Plots, Trend Analysis, Semivariance/Covariance Cloud, and Crossvariance Cloud. Then, the Geostatistical Analyst's Inverse Distance Weighting tool was used to interpolate the total and bioavailable metal concentrations surrounding the sample locations and to access the spatial variability of the metals throughout the lake. Normally, a cross-validation would be performed to compare the interpolated results to the known results, but for this study, no results were known except at the sample locations.

IV. Results and Discussion

4.1 ArcMap and NED

Figure 1 shows the final GIS map of the lake with the sample locations labeled. Figure 2 displays the NED for the lake along with the sample locations for reference. The lighter gray indicates higher elevations. The elevation throughout the lake was consistently at 158.191 meters except at the GR1 location which had an elevation of 158.328 meters. The elevation decreases south of the dam to 153 meters, so the water in the lake flows from north to south.

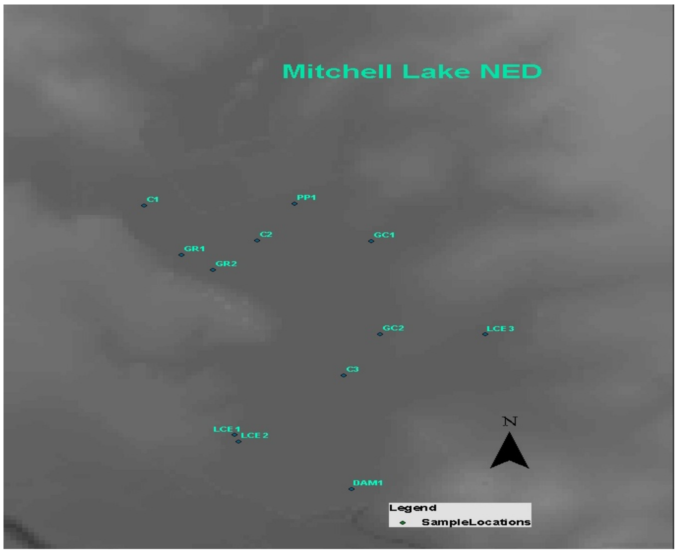


Figure 2. NED layer of Mitchell Lake.

4.2 Exploration of Data

First of all, the results from the histogram analysis for total cadmium levels showed that the total cadmium concentrations were skewed to the right. This means that the frequency of the cadmium concentrations was low. See Figure 3 as an example of the histograms. Also, all the other metals showed this same low frequency in their histograms. The histogram of bioavailable chromium showed a somewhat normal distribution while all the other bioavailable metals were skewed to the right. See Figures 4 and 5.

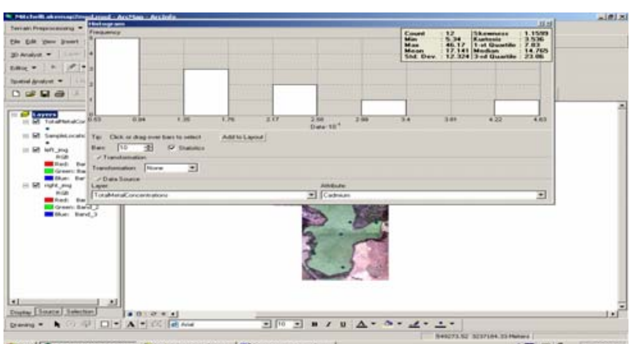


Figure 3. Total Cadmium Histogram. All similar.

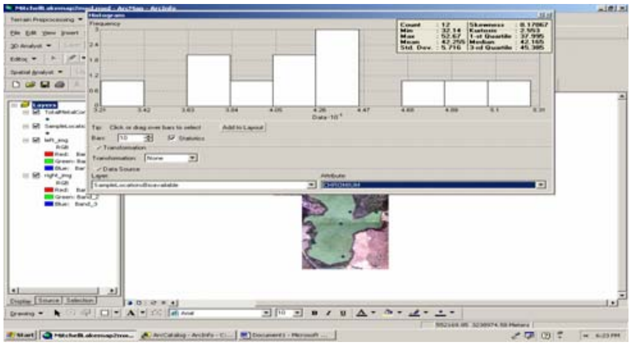


Figure 4. Bioavailable Chromium Histogram.

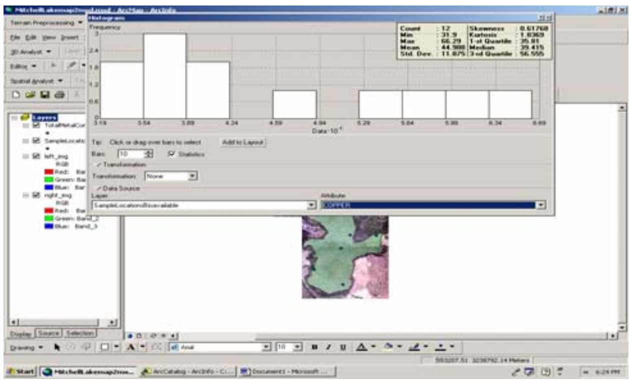


Figure 5. Bioavailable Copper Histogram. All similar.

A trend analysis was performed for each total and bioavailable metal concentration. For the total metal concentrations, a slight trend was determined along the XZ plane and a strong trend was identified along the YZ plane. Refer to Figure 6. The curved line indicates a 2^{nd} order trend. The trend can be attributed to the change of water depth in the lake. The bioavailable metal concentrations showed a 2^{nd} order trend on both planes, and again can be attributed to the differences in water depth. Refer to Figure 7.

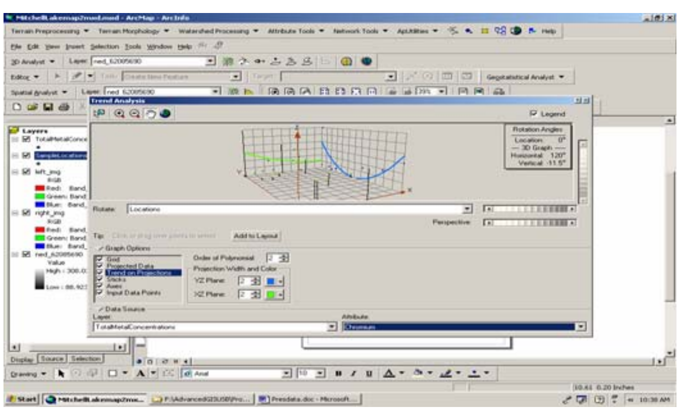


Figure 6. Total Chromium Trend. All others similar.

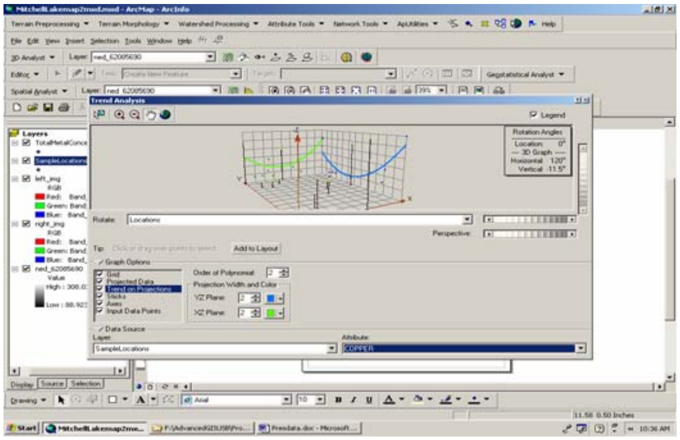
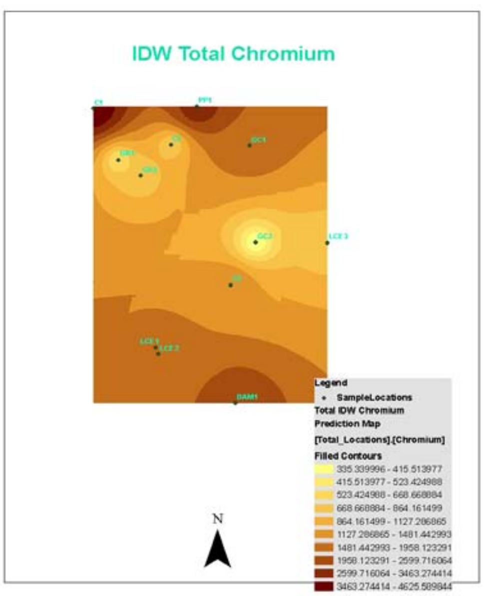


Figure 7. Bioavailable Copper Trend. All others similar.

4.3 Inverse Distance Weighting (IDW)

An IDW interpolation was performed for each total and bioavailable metal concentration. The figures below show the results for each metal with the total and bioavailable concentrations side by side to make it easier for comparisons. Refer to Figures 8-24.

The PP and C1 sites showed the highest total metal concentrations probably due to being closet to the original depositary in the lake. Site, C3, tended to show the highest bioavailable fraction for each metal. For IDW, the closer the distance to the sample location then the more similar characteristics are to that site.



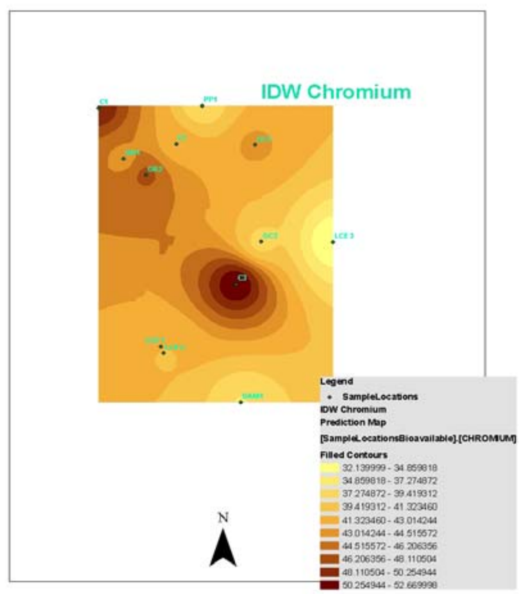


Figure 8. IDW Total Chromium.

Figure 9. IDW Bioavailable Chromium.

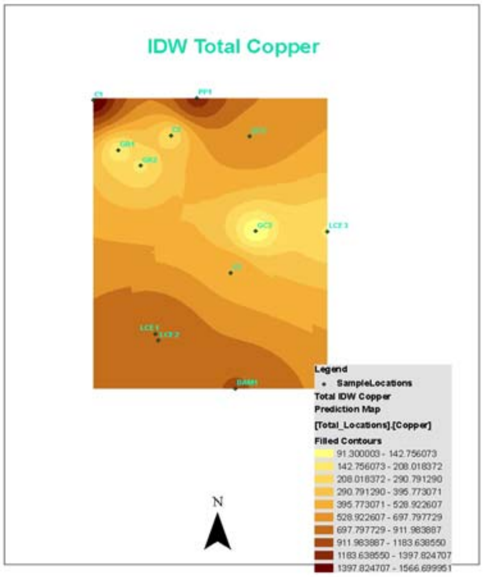


Figure 10. IDW Total Copper.

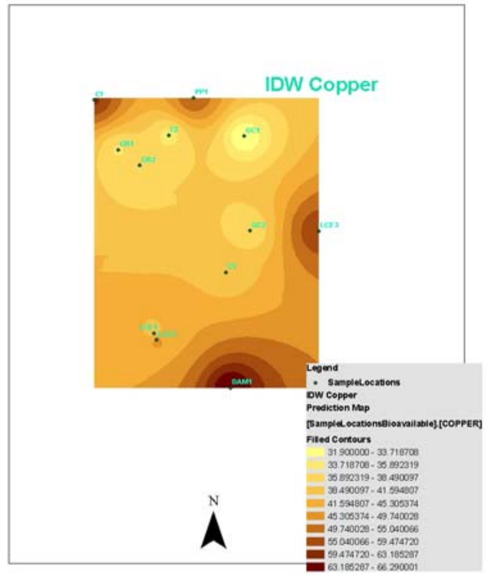


Figure 11. IDW Bioavailable Copper.

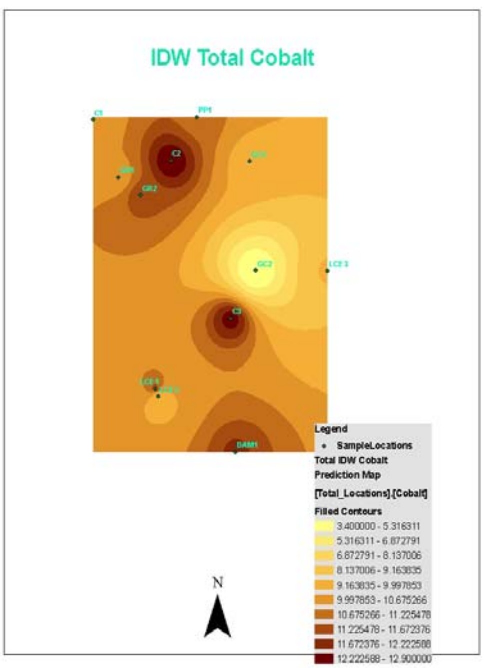


Figure 12. IDW Total Cobalt.

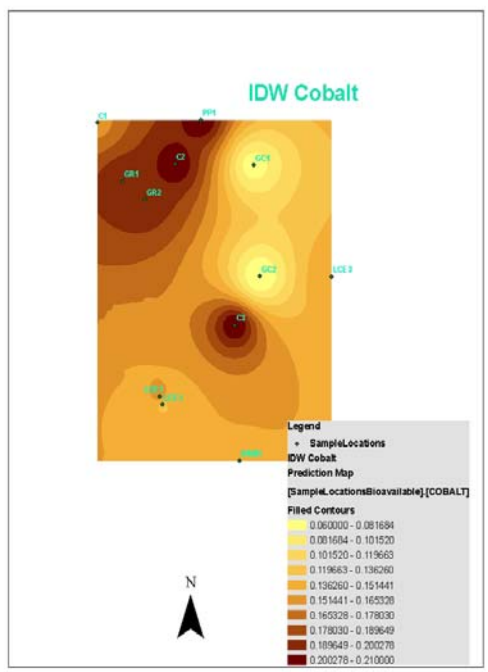
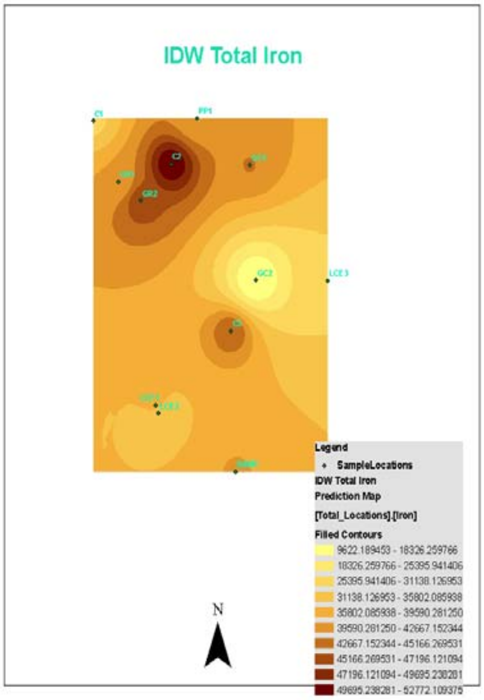


Figure 13. IDW Bioavailable Cobalt.



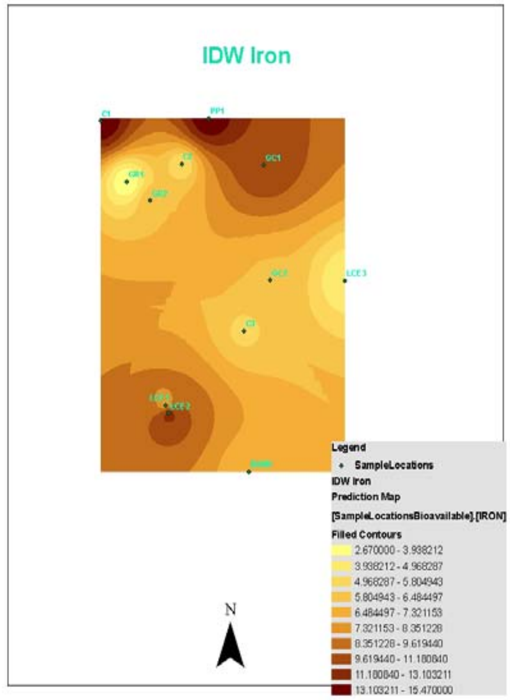
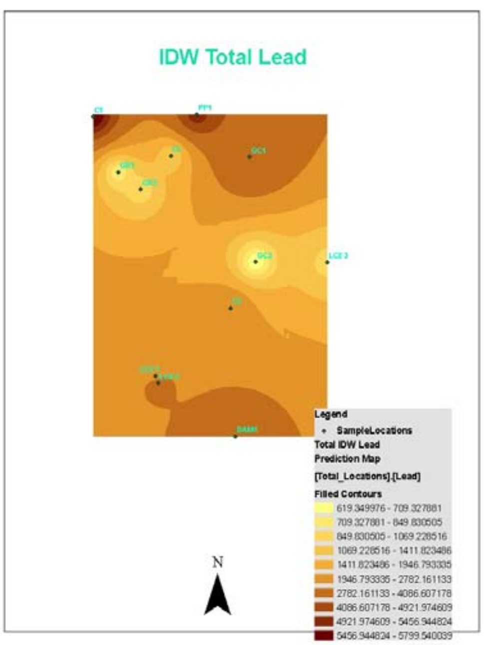


Figure 14. IDW Total Iron.

Figure 15. IDW Bioavailable Iron.



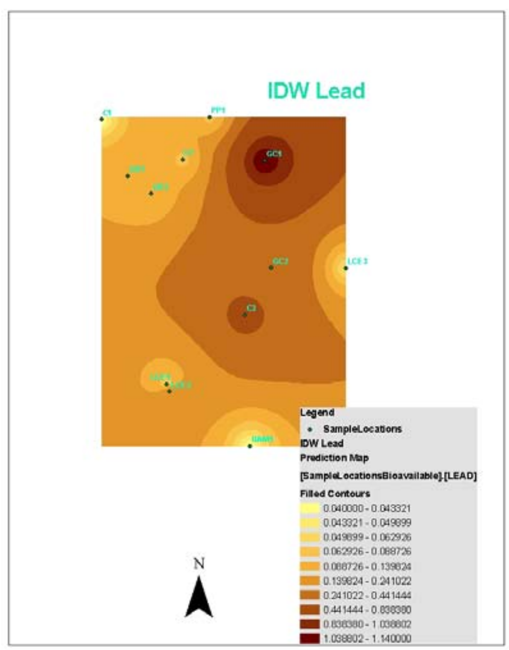


Figure 16. IDW Total Lead.

Figure 17. IDW Bioavailable Lead.

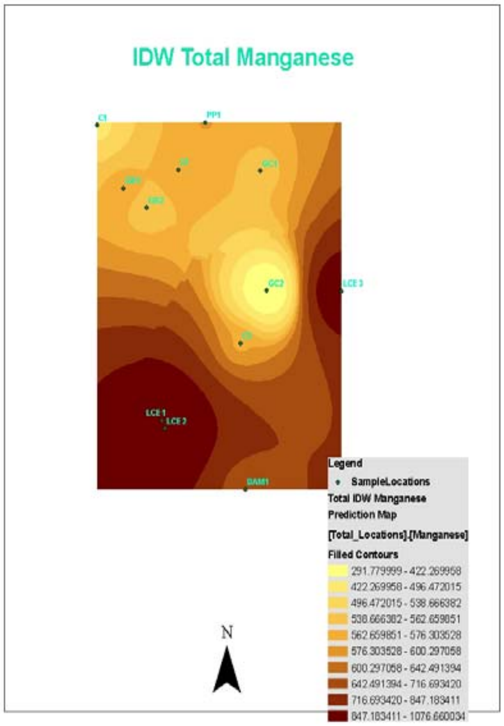


Figure 18. IDW Total Manganese.

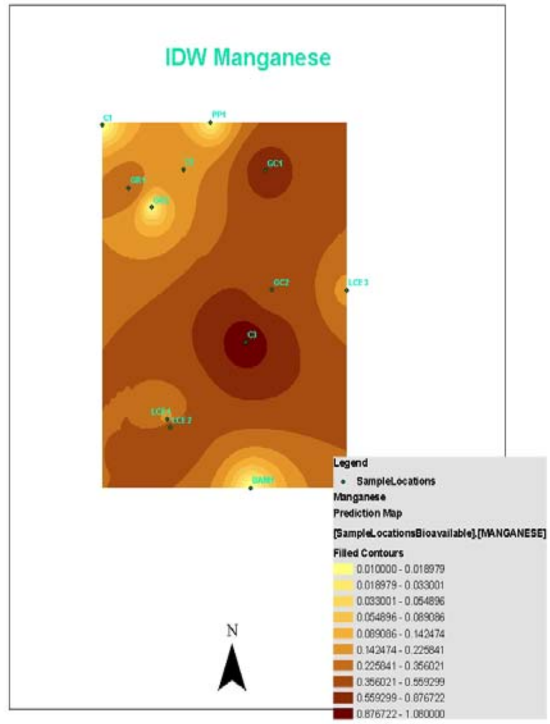


Figure 19. IDW Bioavailable Manganese.

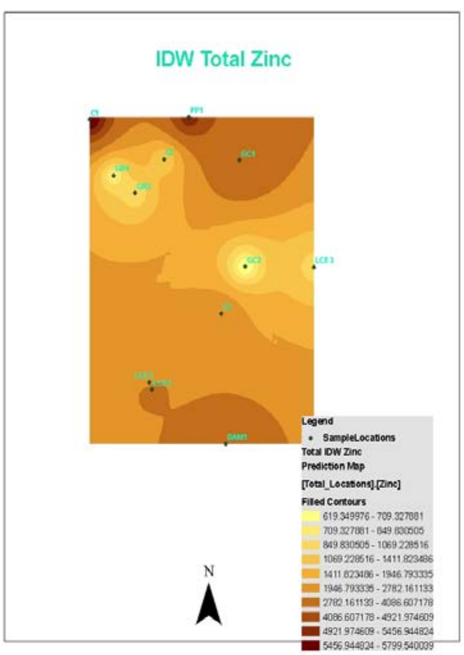


Figure 20. IDW Total Zinc.

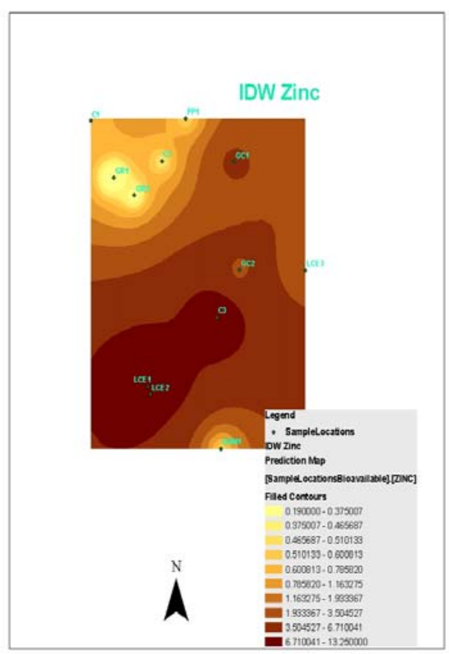


Figure 21. IDW Bioavailable Zinc.

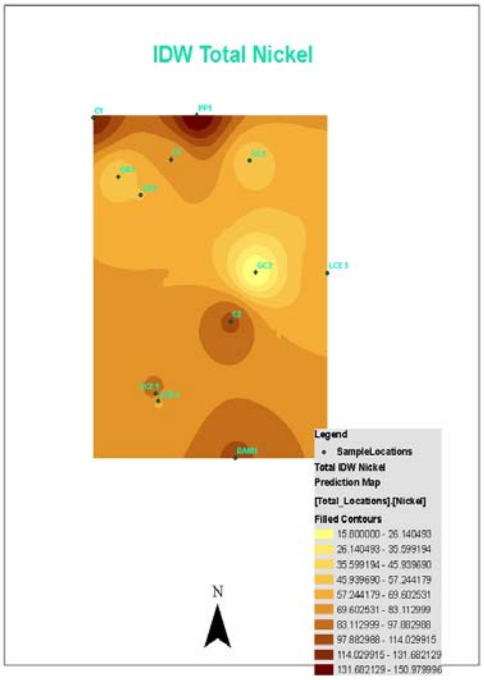


Figure 22. IDW Total Nickel.

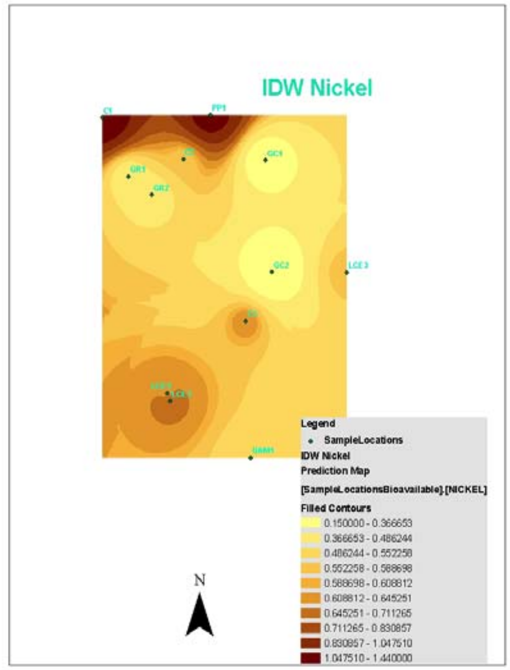


Figure 23. IDW Bioavailable Nickel.

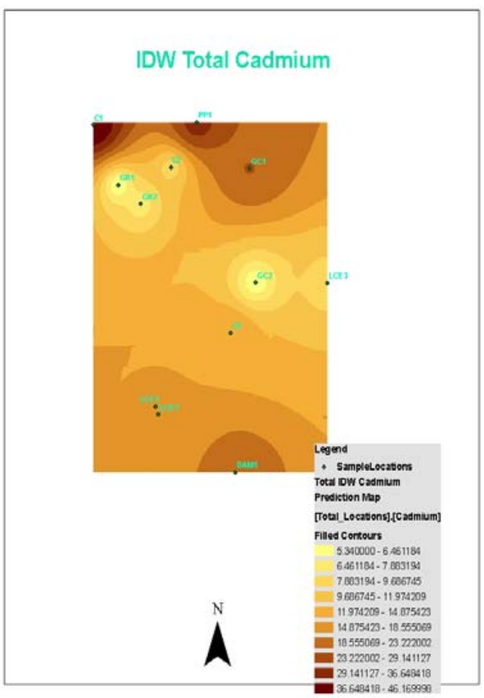


Figure 24. IDW Total Cadmium.
(Due to zero bioavailability, no bioavailable Cadmium IDW shown.)

V. Conclusions

Several conclusions can be reached from the data obtained in this study. First of all, the PP and C1 sites show the highest overall metal concentrations while C3 tended to have the highest bioavailable fraction. Chromium and copper were the metals that were found to have a significant bioavailability. The IDW data shows that the metal concentrations are highly variable throughout the lake. This variability indicates that some metals are more mobile than other metals in the lake. The mobility of metals controls their environmental impact (Baruah et al., 1996). A trend was discovered along the YZ plane for the total metal concentrations. The trend can be attributed to the change in water depth throughout the lake. Overall, the IDW was helpful in interpolating the metal concentrations around the sample locations.

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