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DETECTION OF THE PRESENCE AND CONCENTRATION OF HEAVY METALS IN SELECTED RIVERS IN THE PROVINCE OF SAMAR

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ABSTRACT

Heavy metals has been one of the feared toxins today because of its psychological and physiological effect. This research was designed to determine the heavy metals present in Calbayog and Antiao River and to obtain the concentration of the present heavy metals. This study was conducted based on instrumental analysis which has been accepted in determining the presence and concentration of heavy metals. The environmental parameters were determined first. pH of Antiao and Calbayog River is 7.53 and 7.23, respectively, thus they are slightly basic. Salinity of Antiao and Calbayog is 30 ppt and 34 ppt respectively, which are high. Turbidity of Antiao River and Calbayog are 0.94 m and 0.81 m, respectively, therefore they are quite turbid. Samples are tested for the presence of heavy metal, Mercury (Hg) is present in the two rivers. Cadmium (Cd) is present in the sediment of Antiao River. Concentrations of Cd and Hg was analyzed using AAS, the concentration of the two are below detection limit. The results implied that the levels of heavy metals found in selected rivers are low, though this does not mean that the threat of these metals is absent. Bioaccumulation in living organisms could pose a greater threat.

Keywords:
Heavy metals, rivers, pH, salinity, turbidity, AAS.

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1. INTRODUCTION

Rivers are the cradle of civilization. These rivers are the center of almost all civilization since the antiquity to the present time. The reason behind this was that these rivers provide water for crop for farming which had become a catalyst for growth of each civilization that had sprouted over the time. Without this river, the advancement that we made as a race today would be slower, or ultimately stagnant. Centuries have passed since the first human civilization have been establish in the banks of the fertile crescent in Iraq. Human civilization advances into something that no one of our ancestors, not even in their wildest dream, could have foreseen. But this growth of our race has a major set-back, as we progresses, so was the worsening conditions of the rivers that are

besides a certain human civilization. This happens because an increase in human activity, a careless one, means an increase in man-made wastes that in one ways or the other ends-up in a river. The Province of Samar, formerly known as Western Samar, is the largest and most progressive province in the Island of Samar, it is the only province in the island that has two component cities namely the Calbayog City (1948) and Catbalogan City (2007), which become both the center of politics, commerce and industry in the province. Like most developed and developing civilizations, these two cities resides besides a river which has become polluted over the time because of the amount of human related activities of the people and industries that resides along the banks of its rivers. Pollutants are substance or condition that contaminates air, water, or soil. Pollutants can be artificial substances, such as pesticides and PCBs, or naturally occurring substances, such as oil or carbon dioxide, that occur in harmful concentrations in a given environment. Heat transmitted to natural waterways through warm-water discharge from power plants and uncontained radioactivity from nuclear wastes is also considered pollutants. (Dictionary.com, 2015) Other examples of these pollutants are heavy metals. Over the past two decades, the term "heavy metals" has been used increasingly in various publication and legislation related to chemical hazards and safe use of chemicals. It is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity. (Dufus, 2001). This heavy metals are one of the most feared toxin in the present generation, a toxin whose effects are not entirely known by the scientific community. The vagueness of this toxin causes a stir in our society as more becomes a victim of this ferocious substance without them realizing it until it was too late. Life is lost, life of young ones and those that are still in their mother's womb are ruined because of this heavy metals. For this reason, the researcher is concerned in the detection of heavy metals in the selected rivers in the Province of Samar, to warn the people about the hazards of heavy metal contaminated rivers to the community and help them realize that the immediate resolution to this problem is badly needed.

2. MATERIALS AND METHODS

COLLECTION OF WATER AND SEDIMENTS SAMPLES

The water and sediments samples that have been used in this study were collected directly from the selected rivers. For the collection of water samples, the researcher have someone dive to collect it in the bottom of the rivers.

Samples of water and sediments from three (3) different sites in each river in Calbayog City and Catbalogan City, a total of six (6) samples for each river, a total of twelve (12) samples were analyzed. Arsenic, Cadmium, Chromium, Lead and Mercury are the heavy metals that were detected in the samples used for the experiment.

ANALYSIS OF THE ENVIRONMENTAL PARAMETERS

pH

River pH were measured using a digital pH meter. The pH meter were submerged to the water of the river for a few minutes and the pH was recorded. Three pH readings were taken for each sampling site.

Salinity

Analysis of the saline content of the river water were done using refractometer. A drop of water sample was placed into the refractometer, which then will give a measurement in percentage. The reading was converted from percent to parts per thousand (ppt) using the formula:

$$ppt = \frac{n}{100} \times 100$$

Where; n = percentage seen in the refractometer

Turbidity

In the in determination of Turbidity a Secchi Disk was used. The disk was lowered into the river until its black-and-white color were not clearly seen from the surface. In this position, the knot were marked on the surface of the water and the length to the disk were measured in meters.

QUALITATIVE DETECTION OF HEAVY METALS (GILREATH, 1954)

Arsenic (As)

To the water samples, 3F HCl was added until it is barely acid. Then it was centrifuged and the centrifugate was discarded. Then, on the residue, ten (10) drops of concentrated HCl was added, the solution were stirred and then it was heated in a hot water bath for one (1) minute and then it were centrifuged and the centrifugate were removed. The residue were washed with a mixture of eight (8) drops of water and four (4) drops of concentrated HCl, then it was centrifuged and washing were added to centrifugate of the concentrated HCl treatment. After that, the residue and the centrifugate were separated. The residue was washed with hot water three (3) times, and then four (4) drops of concentrated HNO_3 were added and then it was heated for five (5) in water bath. After heating, five (5) drops of 0.5F $AgNO_3$ were added and it was stirred. To clear the centrifugate, fifteen (15) drops of 2.5F NaAc solution were added. The formation of a reddish-brown precipitation confirms the presence of arsenic.

Cadmium (Cd)

To the samples, ten (10) drops of 3F HNO_3 were added, then it was heated in a water bath for three (3) minutes, and then it was centrifuged. The residue and the centrifugate was separated. The centrifugate was transferred to a casserole and three (3) drops of concentrated H_2SO_4 was added. The solution was evaporated until dense white fume appear and only two (2) or three (3) drops of liquid remains. The solution was cooled thoroughly and then one (1) mL of water was added cautiously, then it was stirred thoroughly and then it was transferred to a centrifuge tube. The casserole was rinsed using with five (5) drops of water and washing will added to the solution, and then it were centrifuge. Then the precipitate and the centrifugate was separated. To the precipitate, concentrated NH_3 was added, with stirring, until the solution becomes basic, and then three (3) drops in excess was added. The solution was centrifuged and the precipitate and the centrifugate were separated. To the centrifugate, sufficient 1F KCN was added to decolorize the solution, then five (5) drops of thioacetamide solution was added and it was placed in a boiling water bath for five (5) minutes. Yellow precipitation indicates the presence of cadmium.

Chromium (Cr)

To the sample, ten (10) drops of saturated NH_4Ac was added, then 3F HAc until acid, and add 3F ammonia until solution is decidedly ammoniacal. Then the solution was centrifuged and then the residue and centrifugate were separated. To the centrifugate, 1F $Ba(Ac)_2$ was added until precipitation is complete. The solution was centrifuge and then the residue and the centrifugate was separated. To the residue, ten (10) drops of 3F HCl was added. Then it was warmed for 1 min in water bath. Then it was centrifuged and the white residue was discarded. Two (2) drops of centrifugate was placed upon a piece of filter paper. Then two (2) drops of H_2O_2 on the same filter paper was added. A formation of a blue color which fades rapidly confirms the presence of chromium.

Lead (Pb)

To the sample, four (4) drops of 3F HCl were added. It were mixed thoroughly and then it were centrifuged. Test for complete precipitation were done by adding another drop of 3F to supernatant liquid. And then solution was centrifuged and then centrifugate was removed with a dropping tube. The precipitate remaining was washed in the test tube with 10 drops of cold water containing one (1) drop of 3F HCl and wash water was discarded. Then ten (10) drops of water was added and it was heated, with stirring, for three (3) min, in water bath. And then it was centrifuged quickly and centrifugate was immediately removed while keeping the mixture hot in a steam water bath. To the centrifugate, four (4) drops of 1F K_2CrO_4 was added. A yellow precipitation confirms the presence of lead.

Mercury (Hg)

To the samples, ten (10) drops of 3F HNO_3 was added and then it was heated in a hot water bath for three (3) min. Then it were centrifuged and the residue and the centrifugate were separated. The centrifugate were discarded and then the residue were dissolved in 4 drops of aqua regia. Then ten (10) drops of water were added in the solution and then it were boiled in water bath for 2 min. The solution were cooled and then 2 drops of $SnCl_2$ (or $BaCl_2$) solution were added. White or gray precipitation will confirm the presence of mercury.

CONCENTRATION OF THE DETECTED HEAVY METALS

Preparation of Samples for AAS Analysis

- **Digestion of Sediments Samples for Cadmium and Mercury Analysis**
  A TFM vessel was placed on the balance plate of an analytical balance, it was tared, 0.2 g of samples was weighed and added. Then the TFM vessel was added in a fume hood, then 9 mL of HCl and 3 mL of HNO_3 was added, the solution was swirled to homogenize the samples with the acids. The vessels was closed and it was introduced into the rotor segment, then it was tighten using the torque wrench.
  The segment was added into the microwave cavity and the temperature sensor was connected. The microwave program was run to completion, the rotor was cold by air until the solution reaches room temperature. The vessels was open, the solution was filtered using #42 Filter paper and the solution was transfer to a marked flask.
- **Digestion of Water Sample for Cadmium Analysis**
  Five hundred (500) mL of water sample was placed to a five hundred (500) mL beaker. Then in a fume hood, five (5) mL of concentrated HNO_3 was added. It was bring to a slow

boil and was evaporated on a hot plate to the lowest volume possible, around 10 – 20 mL, before precipitation occurs. Then it was filtered and placed on a 25 mL flask.

- **Digestion of Water Samples for Mercury Analysis**
  In a flask or a beaker, one hundred (100) mL of water sample was placed, then five (5) mL of concentrated H_2SO_4 was added, after that 2.5 mL of HNO_3 was added. Fifteen (15) mL $KMNO_4$ solution was added and let it stand for fifteen (15) min. Eight (8) mL of $K_2S_2O_8$ solution was added to it and then it was heated for two (2) hours in a water bath. It was cooled into room temperature. And then enough NCl-hydroxylamine solution was added to reduce excess $KMnO_4$.
- **Standard Atomic Absorption Spectrophotometric Analysis**
  The Atomic Absorption Spectrophotometric Analysis was done using steps prescribed in the user manual of Shimadzu AA-6300 Atomic Absorption Spectrophotometer.

3. RESULTS AND DISCUSSIONS

This study determined the presence of the heavy metals, namely Arsenic, Cadmium, Chromium, Lead and Mercury and to determine the concentration of the present heavy metals.

ENVIRONMENTAL PARAMETERS

Prior to the determination of the presence and concentration of heavy metals, the environmental parameters such as pH, salinity and turbidity were done.

pH

The test for pH were done on the laboratory. Prior to the test, the sample have been transported from the sampling sites to the laboratory. The table below shows the pH of the two selected rivers.

Table 1: pH of the Two Selected Rivers

pH						
River	**Sampling Site**	**Test 1**	**Test 2**	**Test 3**	**Average**	**Interpretation**
Antiao River	**1**	7.17	7.18	7.17	7.17	Slightly Basic
	2	7.17	7.15	7.13	7.15	Slightly Basic
	3	8.23	8.29	8.26	8.26	Slightly Basic
			Average		7.53	Slightly Basic
Calbayog River	**1**	7.29	7.30	7.28	7.29	Slightly Basic
	2	7.20	7.17	7.15	7.173	Slightly Basic
	3	7.22	7.26	7.23	7.24	Slightly Basic
			Average		7.23	Slightly Basic

The results indicates that the pH levels of both Calbayog and Antiao Rivers are within the normal range based on where most species of aquatic life on rivers lives [Kemker, 2013], this results clearly shows that even though there are high population density that surrounds this two rivers, its pH is still manageable for life to prosper.

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Salinity

The test for Salinity were done on the laboratory, prior to the test, the sample have been transported from the sampling sites to the laboratory. The table below shows the Salinity of the two selected rivers.

Table 2: Salinity of the Two Selected Rivers

Salinity (ppt)					
River	**Sampling Site**	**Test 1**	**Test 2**	**Test 3**	**Average**
Antiao River	**1**	31.0	32.0	31.0	31.3 ppt
	2	28.0	28.0	28.0	28.0 ppt
	3	30.0	30.0	30.0	30.0 ppt
				Average	29.8 ppt
Calbayog River	**1**	34.0	34.0	34.0	34.0 ppt
	2	34.0	34.0	34.5	34.2 ppt
	3	34.0	34.0	34.0	34.0 ppt
				Average	34.1 ppt

The salinity of this two rivers are quite high because of its geological positions of the sampling sites, of the rivers itself. All the sampling site have a very high salinity, since according to Office of Naval Research, salinity of freshwater river is 0.5 ppt. This could imply that the river's ecosystem is somewhat in danger of deteriorating.

Turbidity

The table below shows the results gathered on the conduct of the study in the determination of the environmental parameters specifically Turbidity.

Table 3: Turbidity of the Two Selected Rivers

Turbidity (m)					
River	**Sampling Site**	**Test 1**	**Test 2**	**Test 3**	**Average**
Antiao River	**1**	0.772	0.775	0.772	0.773
	2	0.996	0.991	0.993	0.993
	3	1.060	1.060	1.054	1.058
				Average	0.941
Calbayog River	**1**	0.792	0.792	0.790	0.768
	2	0.881	0.879	0.881	0.880
	3	0.789	0.790	0.805	0.796
				Average	0.815

The table above shows that the overall results of the salinity of the two rivers. It shows that the Turbidity of this two rivers are almost similar, with little differences. Based on the results, the turbidity of the rivers are quite high, since according to the United States Environmental Protection Agency, the clearer the river, the greater the distance in which the Secchi disk were submerged.

This indicates that maybe the river is losing its ability to support aquatic life, since high turbidity means that the water would be warmer, the photosynthesis would decrease since no or little sunlight penetrates the water, this would lead to the drop of the oxygen levels in the rivers.

QUALITATIVE ANALYSIS OF HEAVY METALS

Test for the Qualitative Analysis of Heavy Metals were done using the procedure of Gilreath (1954). Each Test was performed with three different replications.

Detection of Arsenic

The tables below show the results, gathered during the conduct of the study, for the detection of arsenic. Positive result for the detection of arsenic was indicated with the presence of a reddish – brown precipitate.

Table 4: Presence of Arsenic (As) in Antiao River and Calbayog River

Rivers	Sample	Sampling Site	Test 1	Test 2	Test 3	Remarks
Antiao River	Water	1	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative
	Sediments	1	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative
Calbayog River	Water	1	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative
	Sediments	1	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative

The table above shows a negative results to all the samples for the presence of Arsenic in the two rivers. The negativity of the results might indicate that even though there is a high population density that resides besides the rivers, both rivers might not have contaminants and pollutants that could imply lead contaminations or maybe the tides and the current of the rivers may have carried those materials elsewhere.

Detection of Cadmium

The tables below show the results gathered during the conduct of the study, for the detection of arsenic. Positive result for the detection of cadmium was indicated with the formation of a yellow precipitate.

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Table 5: Presence of Cadmium (Cd) in the Two Rivers

Rivers	Sample	Sampling Site	Test 1	Test 2	Test 3	Remarks
Antiao River	**Water**	**1**	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative
	Sediments	**1**	Positive	Positive	Positive	Positive
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative
Calbayog River	**Water**	**1**	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative
	Sediments	**1**	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative

The table above shows negative results to some of the samples for the presence of Cadmium in the two rivers with only one sampling site turns-out to be positive. The results denotes that there are no Cadmium contaminations in Calbayog River, even though there is a high density of population that resides besides the river. This non-contamination of Cadmium might be the effect of the tide and current of the river that might have carried away the contaminants. Only one sampling site in Antiao River turns out to be positive of Cadmium, this result indicates that each sampling sites may have different contaminants.

Detection of Chromium

The tables below show the results gathered during the conduct of the study, for the detection of arsenic. Positive result for the detection of chromium was indicated with the formation of a blue color which fades away rapidly on the filter paper.

Table 6: Presence of Chromium (Cr) in the Two Rivers

Rivers	Sample	Sampling Site	Test 1	Test 2	Test 3	Remarks
Antiao River	**Water**	**1**	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative
	Sediments	**1**	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative
Calbayog River	**Water**	**1**	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative
	Sediments	**1**	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative

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The table above shows a negative results to all the samples for the presence of Chromium in the two rivers. The results denotes that there are no Chromium contaminations in both the rivers, Calbayog and Antiao even though there is a high density of population that resides besides both rivers, this non-contamination of Chromium might be the effect of the tide and current of the river that might have carried away the contaminants.

Detection of Lead

The tables below show the results gathered during the conduct of the study, for the detection of arsenic. Positive result for the detection of lead was indicated with the formation of a yellow precipitation.

Table 7: Presence of Lead (Pb) in the Two Rivers

Rivers	Sample	Sampling Site	Test 1	Test 2	Test 3	Remarks
Antiao River	Water	1	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative
	Sediments	1	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative
Calbayog River	Water	1	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative
	Sediments	1	Negative	Negative	Negative	Negative
		2	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative

The table above shows a negative results to all the samples for the presence of Lead in the two rivers. The negativity of the results might indicate that even though there is a high population density that resides besides the rivers, both rivers might not have contaminants and pollutants that could lead to lead contaminations or maybe the tides and the current of the rivers may have carried those materials elsewhere.

Detection of Mercury (Hg)

The tables below shows the results gathered during the conduct of the study, for the detection of arsenic. Positive result for the detection of mercury was indicated with the formation of a white or gray precipitate.

Table 8: Presence of Mercury (Hg) in the Two Rivers

Rivers	Sample	Sampling Site	Test 1	Test 2	Test 3	Remarks
Antiao River	Water	1	Positive	Positive	Positive	Positive
		2	Negative	Negative	Negative	Negative
		3	Positive	Positive	Positive	Positive
		1	Negative	Positive	Positive	Positive

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	Sediments	**2**	Negative	Negative	Negative	Negative
		3	Negative	Negative	Negative	Negative
Calbayog River	**Water**	**1**	Negative	Positive	Positive	Positive
		2	Negative	Negative	Negative	Negative
		3	Positive	Positive	Positive	Positive
	Sediments	**1**	Negative	Positive	Positive	Positive
		2	Negative	Positive	Negative	Negative
		3	Negative	Negative	Negative	Negative

The table above shows a positive results to some of the samples for the presence of Mercury in the two rivers. The results might be caused by the high population density in the river sides, where the sampling sites are located, were pollutants and contaminants are directly disposed into the rivers.

Table 9: Summary of the Heavy Metals Present in the Two Rivers

Heavy Metals	**Calbayog River**		**Antiao River**	
	Water	**Sediments**	**Water**	**Sediments**
As	Not Present	Not Present	Not Present	Not Present
Cd	Not Present	Not Present	Not Present	Present
Cr	Not Present	Not Present	Not Present	Not Present
Pb	Not Present	Not Present	Not Present	Not Present
Hg	Present	Present	Present	Present

The table above shows the overall results of the detection of the presence of heavy metals of the two rivers, the two rivers have almost the same positive, with only Cadmium that came up positive at Antiao River. Mercury is the heavy metals that came up with the most positive results. The Calbayog River of Calbayog City and Antiao River of Catbalogan City has almost the same negative and positive results, this is the case since in terms of progress and population, both cities are almost the same, both are center of commerce and industry of the Province of Samar.

QUANTITATIVE DETERMINATION OF THE DETECTED HEAVY METALS

This quantitative analysis of the study uses the Shimadzu AA-6300 Atomic Absorption Spectrophotometer to find out the concentrations of Cadmium and Mercury that came up positive during the conduct of qualitative determination of heavy metals. Before the test proper, the AAS has been calibrated using standard solutions so that it could be the basis of comparison on the absorbance of the heavy metals.

AAS Analysis of Cadmium

For the AAS analysis of the Sediments Samples for Cadmium in the Antiao and Calbayog Rivers, the following standard solution was prepared: (a) 0.0000 ppm, (b) 0.0400 ppm, (c) 0.0800 ppm and (d) 0.0200 ppm. The standard solutions was pre-formulated by the chemist in-charge of the laboratory where this study was conducted.

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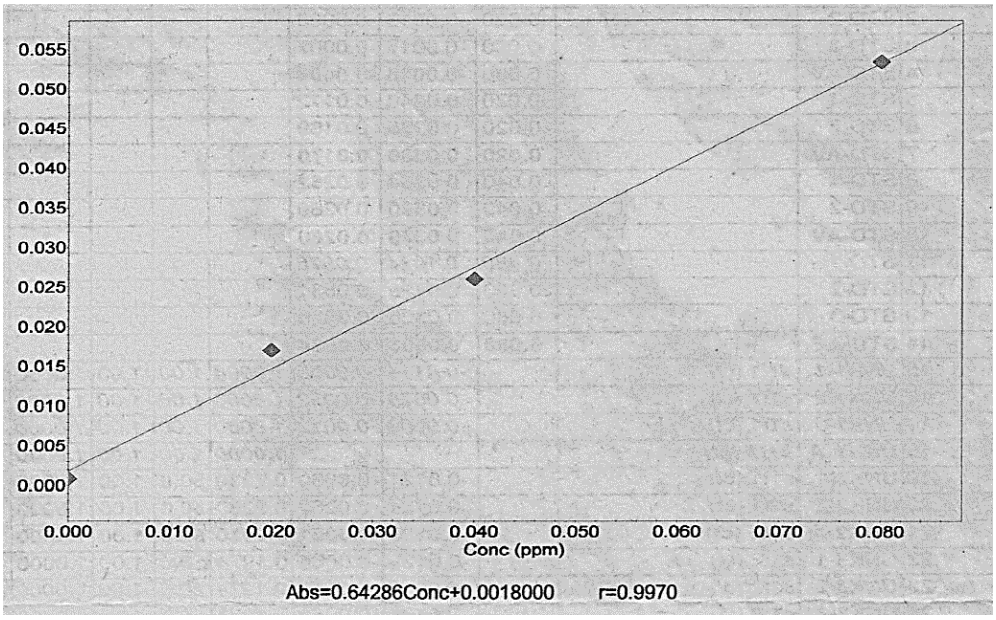

Concentration	Absorbance3
0.0000	0.0008
0.0200	0.0170
0.0400	0.0260
0.0800	0.0534

Figure 1: Calibration Curve for the Standard for the Cadmium Analysis

The figure above shows an acceptable curve, this means that any test for Cadmium in the instrument (AAS) is acceptable. The sediments sample solutions ware subjected to the analysis and it yield results (See Appendix A) that is below detection limit, the detection limit is 1.25 ppm.

AAS Analysis of Mercury

For the AAS analysis of the Water Samples for Cadmium in the Antiao and Calbayog Rivers, the following standard solution was prepared: (a) 0.0000 ppb, (b) 25.0000 ppb, (c) 50.0000 ppb and (d) 100.0000 ppb. The standard solutions was pre-formulated by the chemist in-charge of the laboratory where this study was conducted.

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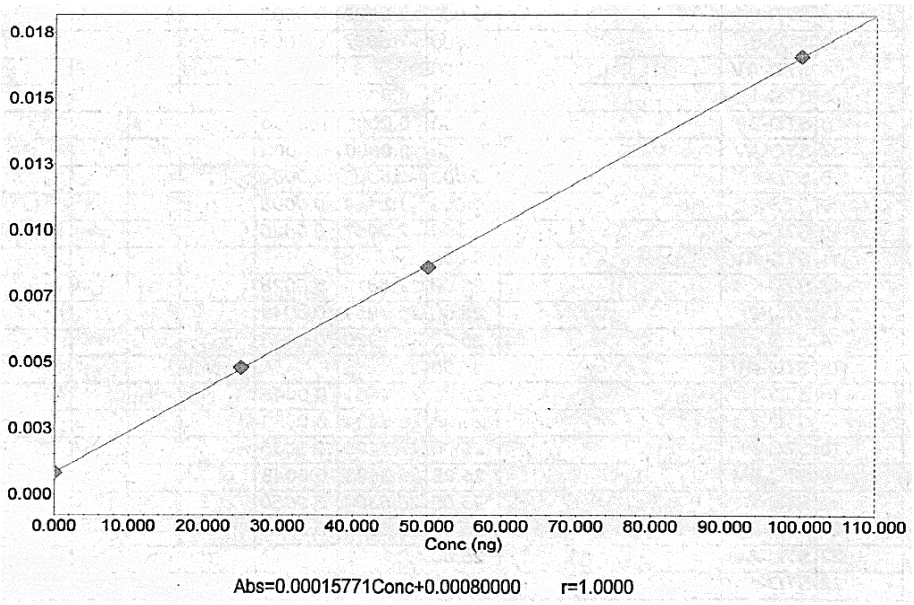

Concentration	Absorbance
0.0000	0.0008
20.0000	0.0048
50.0000	0.0086
100.0000	0.0166

Figure 2: Calibration Curve for the Standard for the Cadmium Analysis

The figure above shows an acceptable curve, this means that any test for Mercury in the instrument (AAS) is acceptable. The water and sediments sample solution was subject to the analysis and it yield results (See Appendix C) that is below detection limit, the detection limit is 125 ppb for the sediments and 0.25 ppb for the water samples.

Table 10: Results of Atomic Absorption Spectrophotometric Analysis

Rivers	Heavy Metals	Samples	Concentrations
Antiao River	**Cadmium**	Water	< 0.00025 ppm
		Sediments	< 1.25 ppm
	Mercury	Water	< 0.25 ppb
		Sediments	< 125 ppb
Calbayog River	**Cadmium**	Water	< 0.00025 ppm
		Sediments	< 1.25 ppm
	Mercury	Water	< 0.25 ppb
		Sediments	< 125 ppb

The results of the AAS analysis indicates that the levels of heavy metals Cadmium and Mercury are below detection limit. This means that the concentration of those two heavy metals are between the limit of detection and 0 concentration.

The results show that the levels of Cd and Hg on water and sediments from the two selected rivers are still very low. But the fact that these heavy metals were detected in the qualitative analysis, this could not mean that these two rivers are safe. The living organisms like fishes and crustaceans living in these rivers might have higher concentrations of Cd and Hg metals due to bioaccumulation.

4. CONCLUSIONS

Based on the results that has been found out in this research work, the following conclusions are formulated: (1) The pH of the two rivers are slightly basic, the salinity is extremely high and the turbidity is also quite high. (2) Cadmium (Cd) and Mercury (Hg) metals are found present in the two rivers. Hg is present in waters and sediments of the two rivers. Cd is present in the sediments of Antiao River. (3) Atomic Absorption Spectrometric analysis of Cd and Hg from water and sediment samples from the two rivers revealed concentrations that are below detection limit. (4) The two rivers have almost similar results.

5. RECOMMENDATIONS

Based on the gathered data in this research work, the following recommendations were formulated to further improve this study: (1) Conduct a more thorough investigation on the presence and concentration of heavy metals in the two rivers using another samples like fishes and crustaceans. (2) Conduct a similar study using another qualitative and quantitative methods to either uphold the current study's validity or nullify it. (3) Conduct a similar study using another instrumentations.

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7. APPENDICES

APPENDIX C

Atomic Absorption Spectrophotometric (AAS) Analysis Results

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AAS Analysis of Cadmium (Sediments)

	Action	Sample ID	True Value (ppm)	Conc. (ppm)	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc Unit	%RSD	SD
1	*STD-1*		*0.000*	*-0.0009*	*0.0012*								
2	STD-2		0.000	-0.0016	0.0008								
3	STD-3		0.000	-0.0017	0.0007								
4	**STD-AV**		**0.000**	**-0.0016**	**0.0008**							**9.43**	**0.0**
5	STD-1		0.020	0.0240	0.0172								
6	STD-2		0.020	0.0235	0.0169								
7	**STD-AV**		**0.020**	**0.0236**	**0.0170**							**1.24**	**0.0**
8	STD-1		0.040	0.0364	0.0252								
9	STD-2		0.040	0.0390	0.0269								
10	**STD-AV**		**0.040**	**0.0376**	**0.0260**							**4.61**	**0.0**
11	*STD-1*		*0.080*	*0.1024*	*0.0676*								
12	STD-2		0.080	0.0798	0.0531								
13	STD-3		0.080	0.0806	0.0536								
14	**STD-AV**		**0.080**	**0.0803**	**0.0534**							**0.66**	**0.0**
15	*UNK1-1*	*s1t1 (ct)*		*-0.0114*	*-0.0055*	*1.0000*	*1.00*	*1.00*	*1.0000*	*-0.0114*	*ppm*		
16	*UNK1-2*	*s1t1 (ct)*		*-0.0078*	*-0.0032*	*1.0000*	*1.00*	*1.00*	*1.0000*	*-0.0078*	*ppm*		
17	*UNK1-3*	*s1t1 (ct)*		*-0.0009*	*0.0012*	*1.0000*	*1.00*	*1.00*	*1.0000*	*-0.0009*	*ppm*		
18	***UNK1-A***	***s1t1 (ct)***				***1.0000***	***1.00***	***1.00***	***1.0000***		***ppm***		
19	UNK2-1	s1t1 (ct)		-0.0121	-0.0060	0.2230	50.0	1.00	1.0000	-2.7205	ppm		
20	UNK2-2	s1t1 (ct)		-0.0124	-0.0062	0.2230	50.0	1.00	1.0000	-2.7902	ppm		
21	**UNK2-A**	**s1t1 (ct)**		**-0.0123**	**-0.0061**	**0.2230**	**50.0**	**1.00**	**1.0000**	**-2.7554**	**ppm**	**2.32**	**0.0**
22	UNK3-1	s1t2 (ct)		-0.0129	-0.0065	0.1974	50.0	1.00	1.0000	-3.2703	ppm		
23	*UNK3-2*	*s1t2 (ct)*		*-0.0143*	*-0.0074*	*0.1974*	*50.0*	*1.00*	*1.0000*	*-3.6249*	*ppm*		
24	UNK3-3	s1t2 (ct)		-0.0126	-0.0063	0.1974	50.0	1.00	1.0000	-3.1915	ppm		
25	**UNK3-A**	**s1t2 (ct)**		**-0.0128**	**-0.0064**	**0.1974**	**50.0**	**1.00**	**1.0000**	**-3.2309**	**ppm**	**2.21**	**0.0**
26	*UNK4-1*	*s1t3 (ct)*		*-0.0151*	*-0.0079*	*0.2460*	*50.0*	*1.00*	*1.0000*	*-3.0668*	*ppm*		
27	UNK4-2	s1t3 (ct)		-0.0138	-0.0071	0.2460	50.0	1.00	1.0000	-2.8139	ppm		
28	UNK4-3	s1t3 (ct)		-0.0143	-0.0074	0.2460	50.0	1.00	1.0000	-2.9088	ppm		
29	**UNK4-A**	**s1t3 (ct)**		**-0.0140**	**-0.0072**	**0.2460**	**50.0**	**1.00**	**1.0000**	**-2.8455**	**ppm**	**2.93**	**0.0**
30	UNK5-1	s3t1 (ct)		-0.0129	-0.0065	0.2097	50.0	1.00	1.0000	-3.0785	ppm		
31	*UNK5-2*	*s3t1 (ct)*		*-0.0143*	*-0.0074*	*0.2097*	*50.0*	*1.00*	*1.0000*	*-3.4123*	*ppm*		
32	UNK5-3	s3t1 (ct)		-0.0131	-0.0066	0.2097	50.0	1.00	1.0000	-3.1156	ppm		
33	**UNK5-A**	**s3t1 (ct)**		**-0.0131**	**-0.0066**	**0.2097**	**50.0**	**1.00**	**1.0000**	**-3.1156**	**ppm**	**1.08**	**0.0**
34	UNK6-1	s3t2 (ct)		-0.0121	-0.0060	0.2159	50.0	1.00	1.0000	-2.8099	ppm		
35	*UNK6-2*	*s3t2 (ct)*		*-0.0135*	*-0.0069*	*0.2159*	*50.0*	*1.00*	*1.0000*	*-3.1342*	*ppm*		
36	UNK6-3	s3t2 (ct)		-0.0114	-0.0055	0.2159	50.0	1.00	1.0000	-2.6298	ppm		
37	**UNK6-A**	**s3t2 (ct)**		**-0.0118**	**-0.0058**	**0.2159**	**50.0**	**1.00**	**1.0000**	**-2.7379**	**ppm**	**6.15**	**0.0**
38	UNK7-1	s3t3 (ct)		-0.0064	-0.0023	0.2380	50.0	1.00	1.0000	-1.3399	ppm		
39	UNK7-2	s3t3 (ct)		-0.0067	-0.0025	0.2380	50.0	1.00	1.0000	-1.4052	ppm		
40	*UNK7-3*	*s3t3 (ct)*		*-0.0051*	*-0.0015*	*0.2380*	*50.0*	*1.00*	*1.0000*	*-1.0784*	*ppm*		
41	**UNK7-A**	**s3t3 (ct)**		**-0.0065**	**-0.0024**	**0.2380**	**50.0**	**1.00**	**1.0000**	**-1.3725**	**ppm**	**5.89**	**0.0**
42	UNK8-1	s1t1(cl)		-0.0118	-0.0058	0.2378	50.0	1.00	1.0000	-2.4857	ppm		
43	UNK8-2	s1t1(cl)		-0.0115	-0.0056	0.2378	50.0	1.00	1.0000	-2.4203	ppm		
44	**UNK8-A**	**s1t1(cl)**		**-0.0117**	**-0.0057**	**0.2378**	**50.0**	**1.00**	**1.0000**	**-2.4530**	**ppm**	**2.48**	**0.0**
45	UNK9-1	s1t2 (cl)		-0.0051	-0.0015	0.2007	50.0	1.00	1.0000	-1.2789	ppm		
46	UNK9-2	s1t2 (cl)		-0.0048	-0.0013	0.2007	50.0	1.00	1.0000	-1.2014	ppm		

	Action	Sample ID	True Value (ppm)	Conc. (ppm)	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc	%RSD	SD
47	*UNK9-3*	*s1t2 (cl)*		*-0.0073*	*-0.0029*	*0.2007*	*50.0*	*1.00*	*1.0000*	*-1.8214*	*ppm*		
48	**UNK9-A**	**s1t2 (cl)**		**-0.0050**	**-0.0014**	**0.2007**	**50.0**	**1.00**	**1.0000**	**-1.2401**	**ppm**	**10.1**	**0.0**
49	UNK10-1	s1t3 (cl)		-0.0028	0.0000	0.2383	50.0	1.00	1.0000	-0.5875	ppm		
50	UNK10-2	s1t3 (cl)		-0.0028	0.0000	0.2383	50.0	1.00	1.0000	-0.5875	ppm		
51	**UNK10-A**	**s1t3 (cl)**		**-0.0028**	**0.0000**	**0.2383**	**50.0**	**1.00**	**1.0000**	**-0.5875**	**ppm**	**0.00**	**0.0**
52	*UNK11-1*	*s3t1 (cl)*		*-0.0103*	*-0.0048*	*0.2065*	*50.0*	*1.00*	*1.0000*	*-2.4859*	*ppm*		
53	UNK11-2	s3t1 (cl)		-0.0090	-0.0040	0.2065	50.0	1.00	1.0000	-2.1846	ppm		
54	UNK11-3	s3t1 (cl)		-0.0086	-0.0037	0.2065	50.0	1.00	1.0000	-2.0716	ppm		
55	**UNK11-A**	**s3t1 (cl)**		**-0.0087**	**-0.0038**	**0.2065**	**50.0**	**1.00**	**1.0000**	**-2.1092**	**ppm**	**5.51**	**0.0**
56	UNK12-1	s3t2 (cl)		-0.0114	-0.0055	0.2057	50.0	1.00	1.0000	-2.7602	ppm		
57	UNK12-2	s3t2 (cl)		-0.0109	-0.0052	0.2057	50.0	1.00	1.0000	-2.6468	ppm		
58	**UNK12-A**	**s3t2 (cl)**		**-0.0112**	**-0.0054**	**0.2057**	**50.0**	**1.00**	**1.0000**	**-2.7224**	**ppm**	**3.97**	**0.0**
59	UNK13-1	s3t3 (cl)		-0.0112	-0.0054	0.1995	50.0	1.00	1.0000	-2.8070	ppm		
60	UNK13-2	s3t3 (cl)		-0.0115	-0.0056	0.1995	50.0	1.00	1.0000	-2.8850	ppm		
61	**UNK13-A**	**s3t3 (cl)**		**-0.0114**	**-0.0055**	**0.1995**	**50.0**	**1.00**	**1.0000**	**-2.8460**	**ppm**	**2.57**	**0.0**

AAS Analysis of Mercury (Water & Sediments)

	Action	Sample ID	True Value (ng)	Conc. (ng)	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc	%RSD	SD
1	*STD-1*		*0.000*	*-0.6341*	*0.0007*								
2	*STD-2*		*0.000*	*-1.9022*	*0.0005*								
3	*STD-3*		*0.000*	*-7.6087*	*-0.0004*								
4	***STD-AV***		***0.000***										
5	STD-1		0.000	0.0000	0.0008								
6	STD-2		0.000	0.0000	0.0008								
7	**STD-AV**		**0.000**	**0.0000**	**0.0008**							**0.00**	**0.0**
8	*STD-1*		*0.000*	*-2.5362*	*0.0004*								
9	*STD-2*		*0.000*	*-10.144*	*-0.0008*								
10	*STD-3*		*0.000*	*7.6087*	*0.0020*								
11	***STD-AV***		***0.000***										
12	*STD-1*		*25.00*	*12.6812*	*0.0028*								
13	*STD-2*		*25.00*	*25.9964*	*0.0049*								
14	*STD-3*		*25.00*	*22.1920*	*0.0043*								
15	***STD-AV***		***25.00***										
16	STD-1		25.00	23.4601	0.0045								
17	STD-2		25.00	26.6304	0.0050								
18	*STD-3*		*25.00*	*17.1196*	*0.0035*								
19	**STD-AV**		**25.00**	**25.3623**	**0.0048**							**7.44**	**0.0**
20	*STD-1*		*25.00*	*26.6304*	*0.0050*								
21	*STD-2*		*25.00*	*28.5326*	*0.0053*								
22	***STD-AV***		***25.00***										
23	*STD-1*		*50.00*	*43.1159*	*0.0076*								
24	*STD-2*		*50.00*	*34.2391*	*0.0062*								
25	*STD-3*		*50.00*	*41.2138*	*0.0073*								
26	***STD-AV***		***50.00***										

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27	*STD-1*		*50.00*	*44.3841*	*0.0078*								
28	*STD-2*		*50.00*	*46.9203*	*0.0082*								
29	***STD-AV***		***50.00***										
30	STD-1		50.00	48.8225	0.0085								
31	STD-2		50.00	49.4565	0.0086								
32	**STD-AV**		**50.00**	**49.4565**	**0.0086**							**0.83**	**0.0**
33	*STD-1*		*100.0*	*89.4022*	*0.0149*								
34	STD-2		100.0	96.3768	0.0160								
35	STD-3		100.0	103.351	0.0171								
36	**STD-AV**		**100.0**	**100.181**	**0.0166**							**4.70**	**0.0**
37	*STD-1*		*100.0*	*105.887*	*0.0175*								
38	*STD-2*		*100.0*	*94.4746*	*0.0157*								
39	*STD-3*		*100.0*	*102.717*	*0.0170*								
40	***STD-AV***		***100.0***										
41	*STD-1*		*100.0*	*109.692*	*0.0181*								
42	*STD-2*		*100.0*	*102.717*	*0.0170*								
43	***STD-AV***		***100.0***										
44	UNK1-1	S1 Water (Calb.)		-1.9022	0.0005	100.00	1.00	1.00	1.0000	-0.0190	ppb		
45	UNK1-2	S1 Water (Calb.)		0.6341	0.0009	100.00	1.00	1.00	1.0000	0.0063	ppb		
46	*UNK1-3*	*S1 Water (Calb.)*		*15.2174*	*0.0032*	*100.00*	*1.00*	*1.00*	*1.0000*	*0.1522*	*ppb*		
47	**UNK1-A**	**S1 Water (Calb.)**		**-0.6341**	**0.0007**	**100.00**	**1.00**	**1.00**	**1.0000**	**-0.0063**	**ppb**	**40.4**	**0.0**
48	UNK2-1	S2 Water (Calb.)		5.7065	0.0017	100.00	1.00	1.00	1.0000	0.0571	ppb		
49	UNK2-2	S2 Water (Calb.)		11.4130	0.0026	100.00	1.00	1.00	1.0000	0.1141	ppb		
50	*UNK2-3*	*S2 Water (Calb.)*		*1.9022*	*0.0011*	*100.00*	*1.00*	*1.00*	*1.0000*	*0.0190*	*ppb*		
51	**UNK2-A**	**S2 Water (Calb.)**		**8.8768**	**0.0022**	**100.00**	**1.00**	**1.00**	**1.0000**	**0.0888**	**ppb**	**29.6**	**0.0**
52	*UNK3-1*	*S3 Water (Calb.)*		*7.6087*	*0.0020*	*100.00*	*1.00*	*1.00*	*1.0000*	*0.0761*	*ppb*		
53	UNK3-2	S3 Water (Calb.)		14.5833	0.0031	100.00	1.00	1.00	1.0000	0.1458	ppb		
54	UNK3-3	S3 Water (Calb.)		10.7790	0.0025	100.00	1.00	1.00	1.0000	0.1078	ppb		
55	**UNK3-A**	**S3 Water (Calb.)**		**12.6812**	**0.0028**	**100.00**	**1.00**	**1.00**	**1.0000**	**0.1268**	**ppb**	**15.1**	**0.0**
56	*UNK4-1*	*S1 Water (Catb.)*		*-2.5362*	*0.0004*	*100.00*	*1.00*	*1.00*	*1.0000*	*-0.0254*	*ppb*		
57	UNK4-2	S1 Water (Catb.)		3.8043	0.0014	100.00	1.00	1.00	1.0000	0.0380	ppb		
58	UNK4-3	S1 Water (Catb.)		5.0725	0.0016	100.00	1.00	1.00	1.0000	0.0507	ppb		
59	**UNK4-A**	**S1 Water (Catb.)**		**4.4384**	**0.0015**	**100.00**	**1.00**	**1.00**	**1.0000**	**0.0444**	**ppb**	**9.43**	**0.0**
60	UNK5-1	S2 Water (Catb.)		3.8043	0.0014	100.00	1.00	1.00	1.0000	0.0380	ppb		
61	*UNK5-2*	*S2 Water (Catb.)*		*10.1449*	*0.0024*	*100.00*	*1.00*	*1.00*	*1.0000*	*0.1014*	*ppb*		
62	UNK5-3	S2 Water (Catb.)		4.4384	0.0015	100.00	1.00	1.00	1.0000	0.0444	ppb		
63	**UNK5-A**	**S2 Water (Catb.)**		**3.8043**	**0.0014**	**100.00**	**1.00**	**1.00**	**1.0000**	**0.0380**	**ppb**	**4.88**	**0.0**
64	UNK6-1	S3 Water (Catb.)		15.2174	0.0032	100.00	0.00	1.00	1.0000	0.0000	ppb		
65	*UNK6-2*	*S3 Water (Catb.)*		*10.7790*	*0.0025*	*100.00*	*0.00*	*1.00*	*1.0000*	*0.0000*	*ppb*		
66	UNK6-3	S3 Water (Catb.)		13.3152	0.0029	100.00	0.00	1.00	1.0000	0.0000	ppb		
67	**UNK6-A**	**S3 Water (Catb.)**		**13.9493**	**0.0030**	**100.00**	**0.00**	**1.00**	**1.0000**	**0.0000**	**ppb**	**6.96**	**0.0**
68	UNK7-1	S1T1Sediments (Calb		19.0217	0.0038	0.2378	1.00	1.00	1.0000	79.990	ppb		
69	UNK7-2	S1T1Sediments (Calb		18.3877	0.0037	0.2378	1.00	1.00	1.0000	77.324	ppb		
70	**UNK7-A**	**S1T1Sediments (Cal**		**19.0217**	**0.0038**	**0.2378**	**1.00**	**1.00**	**1.0000**	**79.990**	**ppb**	**1.89**	**0.0**
71	UNK8-1	S1T3Sediments (Calb		22.8261	0.0044	0.2383	1.00	1.00	1.0000	95.787	ppb		
72	UNK8-2	S1T3Sediments (Calb		20.9239	0.0041	0.2383	1.00	1.00	1.0000	87.804	ppb		
73	**UNK8-A**	**S1T3Sediments (Cal**		**21.5580**	**0.0042**	**0.2383**	**1.00**	**1.00**	**1.0000**	**90.465**	**ppb**	**4.99**	**0.0**
74	UNK9-1	S1T2Sediments(Catb)		-1.9022	0.0005	0.1974	1.00	1.00	1.0000	-9.6361	ppb		
75	*UNK9-2*	*S1T2Sediments(Catb)*		*-6.9746*	*-0.0003*	*0.1974*	*1.00*	*1.00*	*1.0000*	*-35.332*	*ppb*		
76	UNK9-3	S1T2Sediments(Catb)		3.8043	0.0014	0.1974	1.00	1.00	1.0000	19.272	ppb		
77	**UNK9-A**	**S1T2Sediments(Catb**		**1.2681**	**0.0010**	**0.1974**	**1.00**	**1.00**	**1.0000**	**6.4241**	**ppb**	**66.9**	**0.0**
78	UNK10-1	S1T3Sediments (Calb		-4.4384	0.0001	0.2383	1.00	1.00	1.0000	-18.625	ppb		
79	*UNK10-2*	*S1T3Sediments (Calb.*		*-10.144*	*-0.0008*	*0.2383*	*1.00*	*1.00*	*1.0000*	*-42.572*	*ppb*		
80	UNK10-3	S1T3Sediments (Calb		-2.5362	0.0004	0.2383	1.00	1.00	1.0000	-10.643	ppb		

81	UNK10-A	S1T3Sediments (Cal		-3.8043	0.0002	0.2383	1.00	1.00	1.0000	-15.964	ppb	84.8	0.0
82	UNK11-1	S3T1Sediments (Calb.		-5.7065	-0.0001	0.2065	1.00	1.00	1.0000	-27.634	ppb		
83	UNK11-2	S3T1Sediments (Calb		-12.047	-0.0011	0.2065	1.00	1.00	1.0000	-58.339	ppb		
84	UNK11-3	S3T1Sediments (Calb		-12.681	-0.0012	0.2065	1.00	1.00	1.0000	-61.410	ppb		
85	UNK11-A	S3T1Sediments (Cal		-12.681	-0.0012	0.2065	1.00	1.00	1.0000	-61.410	ppb	6.15	0.0
86	UNK12-1	S3T2Sediments (Calb		-5.0725	0.0000	0.2057	1.00	1.00	1.0000	-24.659	ppb		
87	UNK12-2	S3T2Sediments (Calb		-5.0725	0.0000	0.2057	1.00	1.00	1.0000	-24.659	ppb		
88	UNK12-A	S3T2Sediments (Cal		-5.0725	0.0000	0.2057	1.00	1.00	1.0000	-24.659	ppb	0.00	0.0
89	UNK13-1	S3T3Sediments(Calb)		-10.779	-0.0009	0.1995	1.00	1.00	1.0000	-54.030	ppb		
90	UNK13-2	S3T3Sediments(Calb)		-3.8043	0.0002	0.1995	1.00	1.00	1.0000	-19.069	ppb		
91	UNK13-3	S3T3Sediments(Calb)		-5.0725	0.0000	0.1995	1.00	1.00	1.0000	-25.425	ppb		
92	UNK13-A	S3T3Sediments(Calb		-4.4384	0.0001	0.1995	1.00	1.00	1.0000	-22.247	ppb	141.	0.0
93	UNK14-1	S1T1Sediments(Catb)		8.8768	0.0022	0.2230	1.00	1.00	1.0000	39.806	ppb		
94	UNK14-2	S1T1Sediments(Catb)		15.2174	0.0032	0.2230	1.00	1.00	1.0000	68.239	ppb		
95	UNK14-3	S1T1Sediments(Catb)		13.3152	0.0029	0.2230	1.00	1.00	1.0000	59.709	ppb		
96	UNK14-A	S1T1Sediments(Catb		13.9493	0.0030	0.2230	1.00	1.00	1.0000	62.552	ppb	6.96	0.0
97	UNK15-1	S1T3Sediments(Catb)		10.1449	0.0024	0.2460	1.00	1.00	1.0000	41.239	ppb		
98	UNK15-2	S1T3Sediments(Catb)		3.1703	0.0013	0.2460	1.00	1.00	1.0000	12.887	ppb		
99	UNK15-3	S1T3Sediments(Catb)		9.5109	0.0023	0.2460	1.00	1.00	1.0000	38.662	ppb		
100	UNK15-A	S1T3Sediments(Catb		10.1449	0.0024	0.2460	1.00	1.00	1.0000	41.239	ppb	3.01	0.0
101	UNK16-1	S3T1Sediments(Catb)		14.5833	0.0031	0.2097	1.00	1.00	1.0000	69.543	ppb		
102	UNK16-2	S3T1Sediments(Catb)		12.0471	0.0027	0.2097	1.00	1.00	1.0000	57.449	ppb		
103	UNK16-3	S3T1Sediments(Catb)		21.5580	0.0042	0.2097	1.00	1.00	1.0000	102.80	ppb		
104	UNK16-A	S3T1Sediments(Catb		13.3152	0.0029	0.2097	1.00	1.00	1.0000	63.496	ppb	9.75	0.0
105	UNK17-1	S3T2Sediments(Catb)		21.5580	0.0042	0.2159	1.00	1.00	1.0000	99.851	ppb		
106	UNK17-2	S3T2Sediments(Catb)		25.3623	0.0048	0.2159	1.00	1.00	1.0000	117.47	ppb		
107	UNK17-3	S3T2Sediments(Catb)		18.3877	0.0037	0.2159	1.00	1.00	1.0000	85.167	ppb		
108	UNK17-A	S3T2Sediments(Catb		20.2899	0.0040	0.2159	1.00	1.00	1.0000	93.978	ppb	8.95	0.0
109	UNK18-1	S3T3Sediments(Catb)		24.7283	0.0047	0.2380	1.00	1.00	1.0000	103.90	ppb		
110	UNK18-2	S3T3Sediments(Catb)		24.7283	0.0047	0.2380	1.00	1.00	1.0000	103.90	ppb		
111	UNK18-A	S3T3Sediments(Catb		24.7283	0.0047	0.2380	1.00	1.00	1.0000	103.90	ppb	0.00	0.0

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