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Electrochemical Measurement of Toxic Metal Contaminants in the Waters of the Golden Triangle Area

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Abstract

While there are metals that are essential for our body, there are also metals that are harmful to our bio-system. Toxic metals such as lead, copper, cadmium, and arsenic are emitted to the environment in numerous ways. This study is designed to collect and analyze water samples from natural, industrial, and residential sources in the Golden triangle area in Southeast Texas and assess the level of accumulation of heavy metals. The process used in this study is Anodic Stripping Voltammetry (ASV) which takes place in two major steps, first where the metals are deposited on the working electrode and second where they are stripped off from the working electrode. A "Trace Detect nano-band Explorer-II" was used to measure the current needed to deposit each metal separately and it showed the peak height of the current. Some tap water samples from houses in Beaumont and Port Arthur were tested. Water samples from different locations in the Golden Triangle area were also collected, and anodic stripping voltammetry was used for each of the samples to measure the concentration of the heavy metals in them. Peak-Fit program was also used to estimate the concentrations of the metals that are in the sub-ppb levels. The standard deviations for the data set in each location were found.

Keywords: Toxic metals, Neches River, Anodic Stripping Voltammetry

1. Introduction

Metal Contamination in the marine environment is a widespread occurrence, and it heavily impacts coastal regions[1,2]. This research focused on the metal contamination in the Golden Triangle area which is a coastal region of Southeast Texas between the cities of Beaumont, Port Arthur and Orange. Since many petrochemical, polymer, and metal-work industries are located in that region, the presence of toxic metals such as lead, cadmium, copper, and arsenic in drinking water and river fronts should be monitored. The United States Environment Protection Agency (EPA), Texas Commission on Environment Quality (TCEQ) and Lower Neches Valley Authority (LNVA) monitors the quality of water in this area and previously there have been water quality concerns and impairments including presence of heavy metals, elevated bacteria, dissolved oxygen and organic chemicals[2,3]. In order to assess the bioaccumulation pathways of these metals and health impacts that they have, it is crucial to determine their total concentration which leads us to the analytical quantification of metals in water. A wide range of detection techniques are used for the quantification of metallic ions. Laboratory-based techniques include spectrometric techniques such as atomic fluorescence spectrometry, inductively coupled plasma techniques- Atomic emission spectrometry and High performance liquid chromatography (HPLC). Field-deployable techniques include X-ray fluorescence, spectrophotometers and Electrochemical methods such as Cathodic Stripping Voltammetry (CSV) and Anodic Stripping Voltammetry (ASV) [4]. In this study, ASV technique has been used to measure the concentration of metal contaminants in water.

2. Significance

The metals lead, cadmium, copper and arsenic were measured in this study. Each of them has industrial uses which lead to their presence in drinking water, causing a variety of adverse health effects in the human body.

Lead can be found in various types of industrial wastewater such as metal plating facilities, mining operations, metallurgical engineering, production of paints and pigments, and ceramic and glass industries. It can also be emitted into the air from industrial sources and leaded aviation gasoline, and can enter drinking water from plumbing materials. Lead may cause a range of health effects, from behavioral problems and learning disabilities, to seizures and deaths. Lead has toxic effects on many organ systems and physiological processes, such as kidney, cardiovascular system, reproductive system, and probably the most serious aspect is developed in the central nervous system [1,2]. The toxic action of lead is attributed to its affinity for molecular sites of action of calcium and therefore it acts as a substitute for calcium in several intracellular regulatory events [3].

Cadmium causes many public health problems because of its serious toxic effects even at low exposure levels (parts per billion levels). United States Environmental Protection Agency (USEPA) classified cadmium as a probable human carcinogen (Group B1). Cadmium and its compounds are regarded as potential occupational carcinogen by the National Institute for Occupational Safety and Health (NIOSH) [4]. Cadmium emissions to the environment originate from two major source categories, natural sources and anthropogenic sources. Emissions occur to the three major compartments of the environment - air, water, and soil, but there would be considerable transfer between the three compartments after initial deposition. Emissions to air are regarded more mobile than those to water, which in turn are considered more mobile than those to soils [3]. Cadmium emissions to air arise from the combustion of fossil fuels, iron and steel production, non-ferrous metals production, and municipal solid waste combustion [4]. Cadmium emissions to water originate with phosphate fertilizers, non-ferrous metals production, and the iron and steel industry. Cadmium emissions to soils occur, as inputs to agricultural soil and as depositions in controlled landfills.

Copper is one of the most used metals for industrial manufacture as well as household materials. The mining and metallurgy industries are main contribution of anthropogenic copper emission to the environment [5,6]. Copper is widely used in household plumbing materials. At high concentration, copper can be toxic to all life forms but at low concentration copper is a micro nutrient and is essential to all plants and animals. People who drink water containing copper in excess of the action level may, with short term exposure, experience gastrointestinal distress, and with long-term exposure may experience liver or kidney damage [3].

Arsenic is released into the environment from volcanoes and by weathering of arsenic-containing minerals and ores. Arsenic release from iron oxide is one of the most common causes of widespread arsenic concentration in groundwater [3]. Arsenic in drinking water is a significant cause of deaths due to cancer around the world. Agricultural applications, wood preservation, and glass production are the most dominant uses of arsenic metal. Health effects in human who drink arsenic contaminated water include skin and internal cancers, diabetes, and cardiovascular diseases [3].

The river segment joining the Sabine Lake in Orange county and the Neches river, referred to as the Neches River Tidal, is classified as a tidal stream segment with intermediate aquatic life use and recreation use designations [2]. Below the I-10 interstate crossing in Beaumont, the segment is highly industrialized, consisting of a navigation channel through which industrial cargo ships pass and recently, a project to deepen the channel has been proposed to accommodate larger cargo ships, which increases the likelihood of industrial chemicals, which might consist of toxic metals, to be discharged in the water [2]. The current maximum permissible limit set by EPA of Cd, As, Pb, and Cu in drinking water are 5ppb, 10ppb, 15ppb and 1300 ppb, respectively [4]. The presence of these toxic metals needs to be monitored, specifically in the Golden Triangle area because many petrochemical and metal-work industries are located there. In this research, the concentration of four different metals lead (Pb), Copper (Cu), Cadmium (Cd), and Arsenic (As) in the waters of the Golden Triangle Area was measured by collecting water samples from upstream and downstream of Neches and Sabine river joining Sabine lake. The primary goal was to measure the level of accumulation of heavy metal contaminants in waters of Golden Triangle area. Additional goals were to get exposure to water analysis and treatment processes through this research.

3. Experimental Procedure

3.1. Instrumentation And Analysis:

Electrochemical Anodic Stripping Voltammetry (ASV) technique was used for the analysis of aqueous heavy metals in the water samples. ASV works in the following three steps: plating the electrode by a thin film of gold or mercury, conditioning the plated electrode by buffer solution, and placing the conditioned electrode in the sample for measurement.

The ASV system gives reasonably accurate, precise and reliable for heavy metal analysis of real water samples. It can measure large linear concentration ranging from few mg/L to 0.1µg/L and has a sensitivity of less than 0.1 ppb. Moreover, ASV is extremely safe for monitoring and hence it does not require vigorous heating or concentrated acid and gives rapid and inexpensive analysis [7].

The Explorer Portable system (Figure 1a) used in the present work includes: Nano-Band™ Explorer Portable instrument, Explorer software to operate the instrument, Iridium or carbon Nano-Band™ TriTrode including Platinum auxiliary electrode and Ag/AgCl Reference electrode (Figure 1b), Temperature sensor, pH probe, Hot plate with magnetic stirrer. Iridium tritrode was used for analyzing lead, cadmium, and copper. Carbon TriTrode was used to analyze arsenic. This instrument has a sensitivity of less than 0.1 ppb for analyzing lead, cadmium, copper and arsenic in water. This rapid analysis is selective due to the reduction of the analyte at known potential followed by oxidation at specific potential.

(a) (b)

Figure 1. components of NanoBand Electrochemical System. (a) shows the whole system, and (b) shows the parts of the TriTrode.

ASV takes place in two principle steps- the deposition step and the stripping step. The particular dissolved metals (in this case lead, copper, cadmium and arsenic) were reduced and deposited as a layer on the conditioned electrode that is subsequently oxidized.

Deposition step:

$$Pb^{2+} + 2e^- \rightarrow Pb^0$$
$$Cd^{2+} + 2e^- \rightarrow Cd^0$$
$$Cu^{2+} + 2e^- \rightarrow Cu^0$$
$$As^{3+} + 3e^- \rightarrow As^0$$

Stripping step:

$$Pb^0 \rightarrow Pb^{2+} + 2e^-$$
$$Cd^0 \rightarrow Cd^{2+} + 2e^-$$
$$Cu^0 \rightarrow Cu^{2+} + 2e^-$$
$$As^0 \rightarrow As^{3+} + 3e^-$$

The amount of current needed to remove the metal on the electrode by oxidation was measured. The metal concentration in the sample was determined by comparing electrochemical response of the sample to that of external standards.

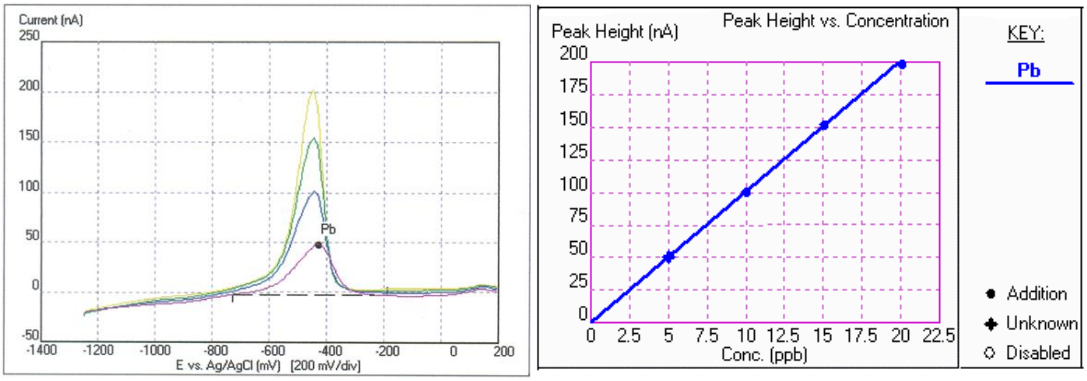

Figure 2. voltammograms for lead standards in the range of 5 ppb to 20 ppb, and the calibration curve (right). The correlation coefficient of the curve (R^2) is more than 0.99.

3.2. Sampling

Samples were collected from different locations in the Golden Triangle area. From both upstream and downstream Neches River, samples were collected as shown in the Fig. 3. The pH, conductivity, and the amount of dissolved materials known as Total Dissolved Solid (TDS) in the aqueous solution were measured. Conductivity is a measure of the electrical current that can pass through the water and can therefore give an indirect measure of the metal ions present in the sample water [8]. Nitric acid was added to all the samples until the pH was 2. Acidification of the samples is important because higher acidity increases the ability of the metal ions to be dissolved in the water. Before analysis, the water samples were filtered to remove some insoluble particles.

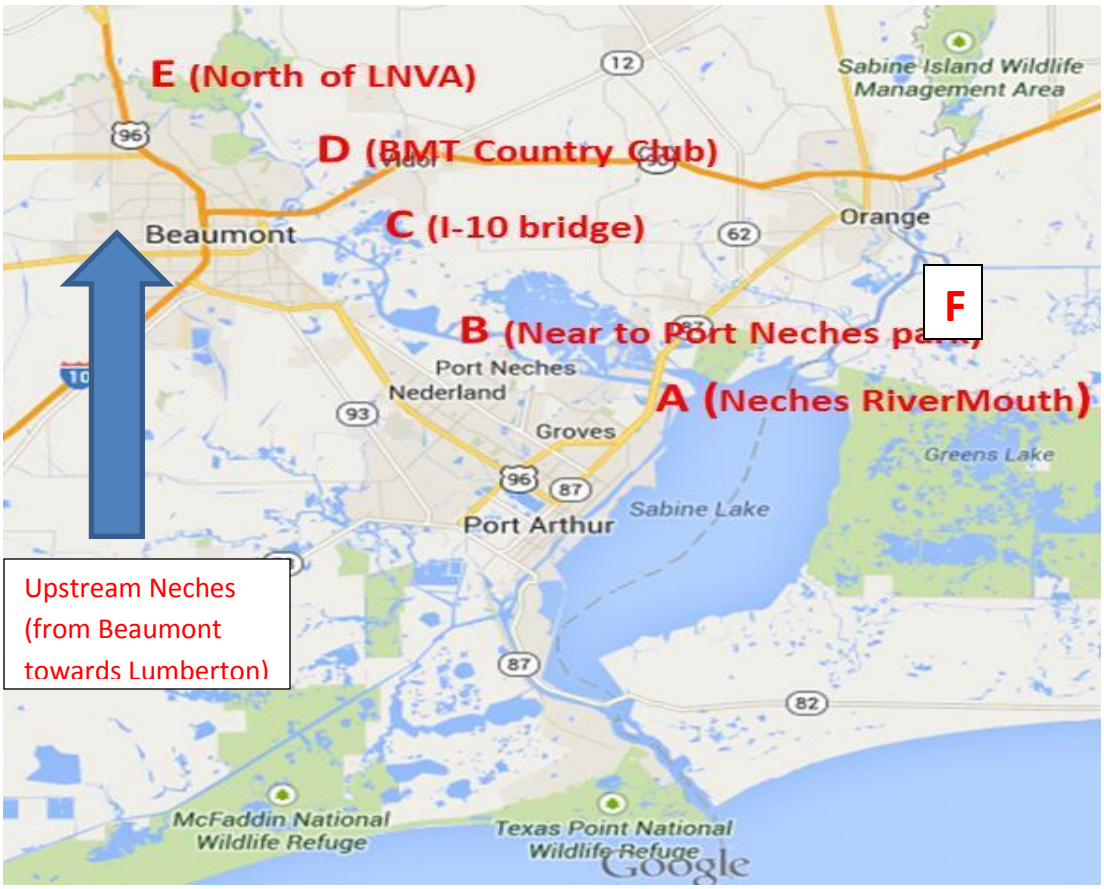

Figure. 3. map of the sampling sites. Samples (A-E) are Neches river samples collected from the locations mentioned above (about every 5 miles upstream). Sample F was collected from Sabine Lake

3.3. Peak Fit Deconvolution

Peak Fit is a software that enables one to detect, separate and quantify the hidden peaks. Hidden peak is a peak that is not responsible for a local maximum in a data stream, however in some cases, it barely misses producing a local maximum[9]. In particular, Cadmium gives hidden peaks due to its very low concentration in the samples which causes low levels of signal to noise ratios. Peak Fit helps to estimate the intensity of the peaks at very low levels of signal values. Deconvolution is the mathematical process that broadens the peaks and helps to show a local maximum that would otherwise be hidden. We took help of this software, especially for the analysis of cadmium concentration in our water samples.

4. Results and Discussion:

Table 1 shows analytical results for lead, cadmium, and copper in the waters from five sampling sites of Neches River and one sampling site for Sabine lake. Although the presence of these metals is under the maximum permissible levels of EPA, certain samples have a considerable amount of dissolved metals in them. Arsenic could not be detected in any of the samples, and since no peaks were found for arsenic, it was assumed that the concentration of arsenic was below the detection limit of the instrument. Three samples were collected and measured from each location, and the standard deviation for every data set was found. Table 1 also shows the analysis of these metals in the tap waters used in the residential areas from the city of Beaumont, and the city of Port Arthur. The analysis for the tap water samples were repeated three times as well. The Standard Deviation for every data set has been shown under each particular metal. Following the data closely, it can be noticed that Sample D

(collected close to the BMT country club) has the highest concentration of the three metals. Although the exact reason behind that is not yet known, the inconsistency of the river feature (i.e, the depth or the width) in that particular region compared to the surrounding locations, or additional industrial discharge could possibly be a reason for the heavy metals to be accumulated there. It is also observed from the data in Table 1 that the water quality of Beaumont is slightly better than that of Port Arthur area.

Table 1. Concentration of heavy metals found in water samples in parts per billion (ppb).

A through F represents the sample locations (A-F) shown in Figure 3. Three samples from each location were collected and the concentration of each of the metal was measured. The best values from every data set have been given. Standard deviation (S.D) for the data set in every location has been shown under each particular metal.

MPL: Maximum Permissible Limit
BDL: Below Detection Level

Metal	A (ppb)	B (ppb)	C (ppb)	D (ppb)	E (ppb)	F (ppb)	Beaumont Tap Water (ppb)	Port Arthur Tap water (ppb)	MPL (ppb)
Pb S.D	3.4 0.3	2.8 0.2	4.2 0.3	8.1 0.3	4.9 0.2	11.8 0.4	2.9 0.2	4.2 0.2	15
Cd S.D	BDL -	BDL -	0.004 0.0001	0.075 0.0002	BDL -	0.510 0.0020	BDL -	BDL -	5
Cu S.D	379.4 91.0	168.0 54.2	573.5 103.4	686.2 124.5	298.3 95.3	500.6 98.5	312.7 89.0	483.6 96.5	1300

Similar to most new technologies, there are limitations to the instrumentation and method of detection used. As it was mentioned earlier, ASV gives hidden peaks for metals present in very low concentration which is why the peakfit software was used. ASV scans also give copper interference peaks while measuring other metals like lead or cadmium because the concentration of copper in drinking water is much higher than other metals. Potassium iodide solution was used to remove the interfering metal cations. Peakfit software was also used to remove interference peaks. There could have been errors while shifting data from the detector to the Peakfit software. However, the low standard deviation of the measured concentrations, as shown in Table-1, proves that the errors were negligible and that the laboratory techniques used were reliable.

5. Conclusion

Heavy metals such as lead, cadmium and copper are present in both river and tap water samples in the Golden Triangle area. However, their concentration is within the EPA determined permissible limit. Arsenic could not be detected in any of the samples which prove that the presence of arsenic in that area is negligible. For every sample, the analysis for each metal was done three times and the standard deviation shows that the values received were quite consistent. This indicates that there is no immediate danger of metal contamination in this area but works should be continued to monitor the waters in these areas, and also steps should be taken to minimize these concentrations.

Presently and into the future, we continue to collect samples and gather experimental data. We plan to extend this research outside of Golden Triangle Area in South Texas, and develop other analytical techniques for water analysis with more user-friendly procedure to detect and quantify not only inorganic metals but also organic chemicals in water.

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