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Determination and comparison of heavy metals in selected seafood, water, vegetation and sediments by inductively coupled plasma-optical emission spectrometry from an industrialized and pristine waterway in Southwest Louisiana

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Abstract

Samples of crab, fish, sediments, vegetation and waters were collected from a pristine (Rockefeller Wildlife Refuge) and historically polluted (Bayou d'Inde) waterway in Southwest Louisiana. After sample preparation via microwave digestion to obtain a solution, cadmium, mercury, nickel and lead were determined by inductively coupled plasma-optical emission spectrometry. A comparison of results showed that there was very little difference in concentrations for the four metals between the two areas, typically in the 10 μg/g range for crabs and fish, around 0.05 μg/mL or lower for waters, and somewhat higher for sediments and vegetation of around two to three times.

Keywords: Metals; ICP-OES; Crabs; Vegetation; Fish; Sediments; Waters

1. Introduction

Southwest Louisiana is one of the most productive areas in the continental USA for fishing, both commercial and recreational. Because of its remoteness and nearness to water in the 1940's it was chosen as an area for fossil fuel refining and production of associated petrochemicals. None or poorly enforced environmental laws resulted in widespread pollution, particularly from heavy metals such as cadmium, mercury and lead. While the introduction and enforcement of environmental laws has significantly improved from the early 1970's, the possibility of heavy metal contamination and sources of previously polluted waterways still exist in Southwest Louisiana [1].

The object of this study was to compare the concentration of selected heavy metals (cadmium, mercury, nickel, and lead) in two quite different waterways: one on a well documented and historically polluted waterway and the second a more pristine waterway. Of particular interest was the concentration of these metals in crabs, fish, vegetation, sediments and waters. Crabs and fish are frequently caught and consumed by recreational fisherman, often a family tradition [2].

2. Experimental

2.1. Sampling sites and collection

The two areas investigated are on the heavily industrialized and historically polluted Bayou d'Inde waterway, and the more pristine Rockefeller Wildlife Refuge, both located in Southwest Louisiana.

Bayou d'Inde is located approximately one mile west of the city of Lake Charles, Louisiana. The waterway empties into Lake Charles. Bayou d'Inde is located in the northern part of the Calcasieu Estuary, west of the city of Lake Charles in Calcasieu Parish, Louisiana [1,2]. Bayou d'Inde's headwaters originate in

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Table 1
Sampling location on Bayou d'Inde

Site	GPS (coordinates)	Samples taken
1	N 30° 12.289′ W 93° 20.566′	Water, vegetation, sediment, crab, fish
2	N 30° 12.102′ W 93° 19.7771′	Water, vegetation, sediment, crab, fish
3	N 30° 12.129′ W 93° 19.490′	Water, vegetation
4	N 30° 12.720′ W 93° 18.632′	Water, vegetation
5	N 30° 12.429′ W 93° 18.368′	Water, vegetation
6	N 30° 12.480′ W 93° 17.841′	Water, vegetation

the western part of Sulphur, Louisiana and flow primarily east-southeast through heavy commercial and industrial areas emptying into the Calcasieu Ship channel west of Lake Charles.

Bayou d'Inde is a tidally influenced wetland bayou that flows through or adjacent to property owned by Citgo Petroleum (Citgo), OxyChem Corporation (OxyChem), Firestone Synthetic Rubber and Latex Company (Firestone), Westlake Polymers Corporation (Westlake Polymers), Browning-Ferris Industries (BFI), Certain-Teed Products Corporation (Certain-Teed), and Pittsburgh Paint and Glass Industries (PPG). These facilities are all active.

The land around Bayou d'Inde includes undeveloped wooded marshland, rural residential, commercial, and heavy industrial property. Rural residential and underdeveloped woodland areas border the Bayou northwest and up gradient of the industrial area. Heavy industry dominates the middle and southern reaches of Bayou d'Inde on both sides. Several of the industries have wastewater outfalls permitted under the National Pollutant Discharge Elimination System (NPDES). Permitted discharges to Bayou d'Inde include outfalls belonging to Citgo, OxyChem, Firestone, Westlake Polymers, BFI, Certain-Teed, and PPG.

In addition, PPG discharges wastewater to Bayou d'Inde via the PPG Canal, which enters the bayou approximately one mile upstream of the Calcasieu Ship Channel. These discharges (current and historic), storm-water runoff, and accidental releases have contributed to organic and inorganic impacts to surface water, sediment, and biota within the Bayou d'Inde area of concern.

Although Bayou d'Inde is not used as a drinking water source, the estuary surface waters have been designated by the Louisiana Department of Environmental Quality as supporting primary contact recreation, secondary contact recreation, and fish and wildlife propagation. Bayou d'Inde supports recreational fishing and has several delineated wetlands that are considered sensitive environments. Health advisories warning of contaminated fish consumption have been issued for the Calcasieu Estuary including Bayou d'Inde.

The Bayou d'Inde area of concern has not been proposed for inclusion on the National Priorities List (NPL), but the entire Calcasieu Estuary has been the subject of environmental studies dating back to the early 1970's.

The sampling of this project involved six locations throughout the Bayou D'Inde area. A global positioning system (GPS) was used to establish the exact location of each site and shown in Table 1. The sampled substances to be tested included: (1) Fish (mullet), (2) Crab (Blue Crab, *Callinectes sapidus*), (3) Vegetation, (4) Water, and (5) Sediments. The samples were collected on two different dates, 01/26/06, temperature of 20 °C, samples 51–79 (water, sediments and vegetation) and 05/30/06, temperature of 33 °C, samples 1–50 (samples 42–50 from sampling Site 1 of whole crab were contaminated and results not presented in this work).

The water samples were collected by scooping a plastic container into the water in the sampling area in a 50 mL plastic container. The soil was collecting by using a four foot PVC pipe about 5 ft from the shoreline. The pipes were labeled and stored in cold storage room (0 °C). The vegetation was collected from the shoreline using a catch and grab method. Flora was stored in Ziploc bags, labeled and stored at −20 °C. The crabs and fish were collected using a hybrid fish/crab trap. Fish and crabs were individually stored in Ziploc bags, labeled and stored at −20 °C. The crabs collected were only found in Site 1 and 2. The other sites did not produce crabs. The fish collected were only found in Site 1 and 2.

Rockefeller Wildlife Refuge is a federally protected refuge, and harbors various types of wildlife. It is located in eastern Cameron and western Vermilion Parishes, South of Lake Charles (approximately 40 miles) and is owned and maintained by the State of Louisiana. This area, of approximately 76,000 ac borders the Gulf of Mexico for 26.5 miles and extends inland toward the Grand Chenier ridge, a stranded beach ridge, and 6 miles from the Gulf. It is remote from industry and is regarded as a pristine area with various wildlife studies such as alligator research in progress. Detailed information about Rockefeller Refuge can be found elsewhere [3]. The samples were acquired from the Wildlife Employees located at Rockefeller Refuge testing complex. The whereabouts of these samples are not exact. Samples are known to be caught near the middle of the refuge. The samples were acquired on 08/03/06. Acquisitions included blue crab and fish. Samples acquired were labeled 80–117.

2.2. Sample preparation

Sample preparation was similar to that described previously [4]. A few drops of concentrated nitric acid was added to all water samples and stored in at 4 °C prior to determination by inductively coupled plasma-optical emission spectrometry (ICP-OES). The vegetation was removed from cold storage and placed in a mortar and dried overnight at 70 °C in an oven. The sample was ground with the pestle and approximately 0.3000 g accurately weighed into the microwave digestion tube, and 4 mL of concentrated nitric acid and 2 mL of hydrogen peroxide then added. The sample was microwaved on power 3 for 3 min, and removed and placed under a hood for 5 min. A microwave of a further 5 min at microwave power of 3 was followed by a 5 minute cool down in a hood. The microwave digestion was vented for 5 min. The contents were filtered into a