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A STUDY OF THE MERCURY CONCENTRATIONS  
OF THE RED MANGROVES OF THE  
SOUTH AND WEST COASTS OF PUERTO RICO

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## INTRODUCTION

The presence of mercury in a primary producer is a potentially hazardous situation when the resultant food web leads to man. The importance of mangrove detritus as an energy source has already been established (Oden and Heald, 1972), and since mangroves have the ability to acquire contaminants from the environment and then pass them on in the detritus (López and Teas, 1978) they can serve as a source of contamination for the entire food web.

The purpose of this study is to determine the average mercury content of mangroves in areas where pollution is not suspected. The Red Mangrove, (*Rhizophora mangle*), was studied in 4 areas on the western and southern coastline of Puerto Rico. These areas represent fairly clean locations with little, if any, industrial or commercial pollution. The determination of the mercury levels in the Red Mangrove of these areas gives an indication of the amount of mercury which can be expected to be found in non-contaminated coastal waters of Puerto Rico.

Samples collected from Laguna Joyuda and Punta Ostiones on the western shore, and Guanica Bay and Phosphorescent Bay on the southern shore were chopped, dried, and ground into a powder, then analyzed for their mercury content.

## FIELD METHODS

In order to give a representative cross section of each study area (Laguna Joyuda, Punta Ostiones,...), two or three sampling sites were chosen for obtaining samples. Each sampling

site consisted of a 20 yard long stretch of fringing mangrove forest from which the samples were collected. Five components of the mangrove tree were selected for analysis. These were the leaves, wood, aerial roots, feeding roots, and propagules. The sampling was performed so that the characteristics of each component were consistent for all the sites. That is, only large, green, healthy looking leaves were selected; the hard wood sample consisted of a piece approximately 30-35 cm in length and 3-5 cm in diameter; aerial roots were the roots which extended from a branch to either air or water, but were not touching the mud; feeding roots, (included rhizomes), were selected only from portions of the root submerged in the mud; and finally, only mature propagules approximately 20-30 cm in length were picked. Leaves and propagules were picked by hand, while both roots and the wood were chopped off the tree with a stainless steel butcher's cleaver. Samples from each site consisted of 100 leaves picked alternately from upper, middle, and lower sections of the tree, one piece of wood as described above, approximately 1.5 m of aerial root from 2 or 3 different locations in the site, 2 or 3 feeding roots, and 20 propagules. Each component, (leaves, wood,...), was placed in its own plastic bag, combining the collections from sites of the same study area, so that the samples were representative of the mangroves from each study area.

Care was taken to avoid contamination from metallic objects. If possible, the samples were handled only with plastic, glass, or porcelain objects. When this proved

impractical, a control experiment was established in order to test for contamination in the procedure.

#### LABORATORY METHOD

After collection from the field, the samples were stored under refrigeration at about 4°C. They were then chopped into smaller pieces with the butcher's cleaver and placed in glass dishes to be dried at 60°C for at least 48 hours. Prior to chopping, the mud and barnacles were washed with tap water from the feeding root. Also, the leaves were ripped by hand into halves or thirds rather than chopped with the cleaver. In order to test if the cleaver was contaminating the samples, a control was performed where a 50 cm section of aerial root was split lengthwise in half using a plastic knife, then one-half was cut up with the plastic knife while the other half was chopped up with the cleaver. The material obtained for the control was then dried, and ground with a porcelain mortar and pestle prior to analysis for mercury.

After drying the samples, a subsample of approximately 25 grams was removed for grinding. Grinding with a mortar and pestle proved too time consuming for this study, so an osterizer was used to grind the subsample. A second control was established to determine if the stainless steel blades or lubricant of the osterizer contaminated the sample. For this purpose, two 25 g subsamples were removed from the leaves and wood from Laguna Joyuda so that one subsample could be pulverized with a mortar and pestle while the other subsample was chopped up in the osterizer.

The standard U.S. EPA (1974) method for mercury analysis in sediments was used for determining the mercury content of the samples. Duplicate 0.5 g portions of each samples was weighed into 300 ml MOD bottles, then digested in 10 ml of concentrated  $H_2SO_4$  and 5 ml of concentrated  $HNO_3$  for 30 minutes at  $80^\circ C$ . After allowing the samples to cool, 5%  $K MnO_4$  was added to the samples until an excess of permanganate was achieved. The samples were then digested an additional 30 minutes, taking care that the solution remained dark throughout the second digestion. After diluting the solution to 100 ml with distilled water, the excess permanganate was reduced by the addition of 6 ml of 1.5%  $NH_2OH HCl$  solution plus  $NH_2OH HCl$  crystals if necessary. Finally, the mercuric ions in solution were reduced to the volatile elemental form by the addition of 5 ml of saturated  $Sn Cl_2$  solution. The solution was then aerated and the gasses were swept into a Coleman/Perkin-Elmer MAS 50 mercury analyzer. This instrument used the flameless atomic absorption technique to determine mercury content and displayed the level detected as percent transmittance (% T).

#### Calculations

The instrument was calibrated each time a set of samples was analyzed using solutions of known mercury concentrations prepared from a stock mercury solution containing 1.0 mg/ml Hg. Calibration of the relationship between absorbance and mercury concentration was done by running standard solutions of 0, 0.5, 1.0, 2.5, 5.0, and 10.0 ppb mercury and determining the percent transmittance. To convert % T to absorbance, (A),

Beer's Law:

$$A = \log \frac{1}{T}$$

where  $T = (\%T)(100)$  is the transmittance, was used.

After correcting for the standard blank:

$$A' = A \text{ Standard} - A \text{ blank}$$

a linear regression was performed on the data  $(x,y) = (C,A')$ , where C is the known concentration in ppb, to find the best fit line. The formulas used in the linear regression were:

$$m = \text{slope} = \frac{ss(xy)}{ss(x)} = \frac{\sum xy - \frac{\sum x \sum y}{n}}{\sum x^2 - \frac{(\sum x)^2}{n}}$$

$$b = \text{intercept} = \frac{\sum y - m \sum x}{n}$$

where x was the concentration, y was the absorbance, and n was the number of data points.

Concentrations of mercury (ug/l) in the samples were found by using the slope and intercept values determined in the calibration, then solving for x in the equation

$$A = mx + b \rightarrow x = \frac{A-b}{m}$$

where A is the absorbance for the sample, and x is the concentration of Hg in the sample. Slope and intercept values, along with the concentrations in the samples, were determined automatically on a Texas Instruments SR-51A calculator.

The values for concentration of mercury were converted to ug/g or ppm Hg in the sample using the formula

$$\text{ppm Hg} = \frac{(x - \text{blk } x) (.1)}{\text{sample wt in grams}} = \frac{\text{ug}}{\text{g}} \text{ Hg}$$

where x is the sample concentration (ug/l) and blk x is the concentration in the blank as calculated above.

## RESULTS

The data from the control experiments and the mercury analysis of the samples are recorded in Tables 1, 2, and 3, respectively. The standard deviation is in parentheses.

TABLE 1. Control (Cleaver)

| MATERIAL                            | ug/g | ug/g  | Mean | $\sigma$ |
|-------------------------------------|------|-------|------|----------|
| Root chopped with plastic knife     | .010 | .017  | .014 | (.005)   |
| Root chopped with butcher's cleaver | .017 | <.002 | .009 | (.012)   |

TABLE 2. Control (Osterizer)

| MATERIAL                   | ug/g | ug/g | Mean | $\sigma$ |
|----------------------------|------|------|------|----------|
| Wood ground in mortar      | .034 | .017 | .026 | (.012)   |
| Wood ground in osterizer   | .027 | .043 | .035 | (.011)   |
| -----                      |      |      |      |          |
| Leaves ground in mortar    | .044 | .027 | .036 | (.012)   |
| Leaves ground in osterizer | .027 | .027 | .027 | -        |

As we can see, the range of the determinations is overlapped and thus the mean values show no significant difference in Hg content. The precision allowed by the instrument is at best  $\pm 0.2\%T$  which is equivalent to  $\pm 0.007$  ug/g Hg. Hence, the tests for contamination by the procedure show that the



values are within the limits of precision, and that no appreciable amount of mercury is added using these stainless steel utensils for preparing the samples.

TABLE 3. Mercury Content (ug/g) in the samples\*

| COMPONENT     | LAGUNA<br>JOYUDA | PUNTA<br>OSTIONES | GUANICA<br>BAY   | PHOSPHORESCENT<br>BAY |
|---------------|------------------|-------------------|------------------|-----------------------|
| Leaves        | 0.031<br>(0.001) | 0.033<br>(0.002)  | 0.066<br>(.001)  | 0.042<br>(0.004)      |
| Wood          | 0.030<br>(0.011) | 0.019<br>(0.002)  | 0.042<br>(0.004) | 0.033<br>(0.009)      |
| Aerial Roots  | 0.031<br>(0.005) | 0.020<br>(0.004)  | 0.022<br>(0.006) | 0.026<br>(0.004)      |
| Feeding Roots | 0.017<br>(0)     | 0.031<br>(0.019)  | 0.066<br>(0)     | 0.060<br>(0.009)      |
| Propagules    | 0.018<br>(0.012) | 0.026<br>(0.008)  | 0.040<br>(0.001) | 0.013<br>(0)          |

\*(Standard deviation is given below the mean in parentheses.)

The highest mercury concentration was found in most of the components from Guánica Bay. While even the highest level, (0.066 ug/g), is well below the adopted limit of 0.05 ug/g considered safe for human consumption, the presence of mercury in the trophic level of primary producer should not be ignored. More research would need to be conducted in order to determine the actual bioavailability of the mercury and its impact on the food web.

## DISCUSSION

As stated before, mangrove detritus serves as a major nutritional source for aquatic ecosystems. The U.S. EPA "Quality Criteria for Water" (1975) summarizes findings which indicate that mercury compounds are made available to a food web by absorption of the mercury by aquatic plants, then ingestion of the plant detritus by other organisms. It is known that microorganisms which feed on the detritus can convert inorganic mercury to highly toxic methyl or dimethyl mercury and then contaminate any organism which feeds on it (U.S. EPA, 1975). Thus, the analysis of total mercury present in the Red Mangrove is justified, even though the mercury might occur in less toxic forms.

Once a source of mercury is made available to a food web, organisms from higher trophic levels accumulate the mercury into higher concentrations by the process of biomagnification. That is, the rate at which the mercury is incorporated into the body of an organism exceeds the rate at which the organism can expel the mercury. Determining the mercury content in the Red Mangrove provides a point of reference for comparing mercury levels, (and hence an indication of availability), in polluted and non-polluted areas.

A previous study of mercury content of the Red Mangrove in Guayanilla Bay was conducted by López and Teas (1978), showing a significantly higher concentration of mercury than was found in this study. Guayanilla Bay has known sources of mercury pollution from industrial waste and has apparently

been affected by such activity. Some mercury levels in Guayanilla Bay were as much as 10 times higher than the highest mercury level determined here. While the significance of the mercury concentrations in Guayanilla Bay is still not clearly understood, the findings of this report show that apparently the mercury found in Guayanilla Bay is more abundant than what would normally be expected of coastal waters in Puerto Rico.

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