CEER-MA3 August 1979 A STUDY OF THE MERCURY CONCENTRATIONS OF THE RED MANGROVES OF THE SOUTH AND WEST COASTS OF PUERTO RICO CENTER FOR ENERGY AND ENVIRONMENT RESEARCH

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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 (Lopez 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 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

Feeding roots and propagules were included in the sampling. The sampling was performed to ensure the consistency of each component across all sites. That is, only large, green, healthy looking leaves were selected. The hardwood sample consisted of a piece approximately 30-35 cm in length and 3-5 cm in diameter. Aerial roots were those that extended from a branch to either air or water, but were not touching the mud. Feeding roots, which included rhizomes, were only taken from portions of the root submerged in the mud. Finally, only mature propagules approximately 20-30 cm in length were picked. Leaves and propagules were picked by hand, while both roots and 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, etc.) was placed in its own plastic bag, combining the collections from sites of the same study area, to ensure 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 to test for contamination in the procedure.

Laboratory Method: After collection from the field, the samples were stored under refrigeration at approximately 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 off the feeding root with tap water. Also, the leaves were torn by hand into halves or thirds rather than being chopped with the cleaver. In order to test if the cleaver was contaminating the samples, a control was performed where a 50 cm section...

An aerial root was split lengthwise into two halves using a plastic knife. One half was cut up with the plastic knife, while the other half was chopped up with a cleaver. The material obtained for 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 to be 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-gram 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-gram portions of each sample were weighed into 300 ml MD bottles, then digested in 10 ml of concentrated H2SO4, and 5 ml of concentrated HNO3 for 30 minutes at 60°C. After allowing the samples to cool, potassium permanganate 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 10% HCl solution plus NH4Cl crystals. Finally, the mercuric ions in the solution were reduced to the volatile elemental form by the addition of 5 ml of saturated SnCl2 solution. The solution was then aerated and the gases 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.

Each time a set of samples were analyzed, they were calibrated using solutions of known mercury concentrations. These were prepared from a stock mercury solution containing 1.0 mg/ml. 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 to absorbance (A), Beer's Law was used: $1 \text{ A} = \log \text{ F}$, where T = (#7) (109) is the transmittance. After correcting for the standard blank, the following was used: AY = A Standard - A blank. A linear regression was performed on the data (x, y) = (C, A'), where C is the known concentration in ppb. The formulas used in the linear regression were as follows: y = mx + b.

Here, x was the concentration, y was the absorbance, and n was the number of data points. Concentrations of mercury ($\mu g/I$) in the samples were determined by using the slope and intercept

values in the calibration, then solving for x in the equation A = mx + b. Here, A is the absorbance for a 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-S1A calculator. The values for concentration of mercury were converted to μ g/g or ppm Hg in the sample using the formula ppm = (μ g/I)*(1/sample wt in grams), where x is the sample concentration (μ g/I) and blank 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 | µg/g | µg/g | Mean

Root chopped with plastic knife | 0.010 | 0.017 | +0.014 (0.005)

Root chopped with butcher's cleaver | 0.017 | <0.002 | +0.008 (0.022)

TABLE 2. Control (Osterizer)

MATERIAL | µg/g | µg/g | Mean

Wood ground in mortar | +0.034 | 0.07 | 0.026 (0.022)

Wood ground in.

Osterizer - 027 043 035° (0.011) Leaves ground in mortar 1084 - 027 1036 (0.012) Leaves ground in Osterizer 027 027 027 - As we can see, the range of the determinations overlaps, and thus the mean values show no significant difference in lig content. The precision allowed by the instrument is at best + 0.287, which is equivalent to + 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:

Compor BAY"	nent LAGU	NA PU	NTA GUAN	IICA P	HOSPHC	RESCE	ENT JC	YUDA,	ostionrs "	PAY
		.								
Leaves	0.032 (0.	002) 0	.033 (0.002)	0.066	(0.008) (0.042				
Wood	0.030 (0.	002) 0.	.019 (0.002)	0.042	(0.004) ().033 (C).003)			
Roots	0.031 (0.0	005) 0.9	920 (0.004)	0.022 (0.006) 0	.026 (0	.004)			
Foots	0.017 (0.0	0.0 (0.0	066 0.060	0.013						

| Propacules| 0.018 (0.022) | 0.026 (0.008) | 0.040 (0.002) | 0.013 |

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

The highest mercury concentration was found in most of the components from Guanica 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

Organisms which feed on it (U.S. EPA, 1975). Thus, the analysis of total mercury presence in 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 Lopez 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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