

POTENTIALLY TOXIC ELEMENTS IN MANGANESE NODULES

Environmental Implications  
for a Land-Based Processing Industry

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By

Carol A. Feldman

Thesis Committee:

Keith E. Chave, Chairman  
Stanley W. Margolis  
James E. Andrews

SUMMARY

The results of the present study can be summarized as follows:

(1) The presence of potentially toxic metals in manganese nodules from the East Pacific mining belt has been confirmed. Arsenic, selenium, cadmium, thallium, and lead have been detected in all nodules from this region. Using semi-quantitative analysis by Proton Induced X-ray Emission (PIXE) the range of concentrations for these elements was found to be: As = 75-116 ppm; Se = 17-23 ppm; Cd = 27-44 ppm; Tl = 157-189 ppm; Pb = 407-540 ppm. These concentrations generally fall within the range of previously reported values, except for Se and Cd, which are probably too high in the PIXE data. Analysis of Cd and Pb in the same samples by atomic absorption spectrophotometry produced slightly lower values for these elements: Cd = 9-15 ppm; Pb = 378-448 ppm.

(2) The "availability" of these toxic metals, that is, the ease with which they can be removed from nodules by natural processes, has been tested by a series of leaching experiments using deionized water, acidified deionized water (simulated "acid rain") and neutral 1N  $\text{NH}_4\text{OAc}$  solution. Concentrations of Cd and Pb were determined in the liquid leachates by atomic absorption, and the solid leached residues were analyzed semi-quantitatively by PIXE for As, Se, Cd, Tl, and Pb.

The following observations were made:

(a) Arsenic was found to be substantially depleted in all solid residues regardless of the leaching solution used.

(b) Selenium showed erratic behavior, sometimes becoming depleted in residues and, in other cases, showing substantial enrichment. This inconsistent response is probably a function of the PIXE technique, as selenium emits X-rays in a region occupied by X-rays of several other elements, and there is some difficulty in sorting out the X-rays produced by selenium.

(c) Cadmium concentrations generally decline in the leached residues. However, only small amounts of Cd could be detected in the leachates themselves. Deionized water extracts contained the greatest amount of Cd, removing an average 3.6 per cent of the total Cd. Acidified deionized water extracts contained only about 1.2 per cent of the total Cd, and no Cd was detectable in  $\text{NH}_4\text{OAc}$  extracts. PIXE is not sensitive to Cd at the levels found in nodules, and therefore the results of the semi-quantitative PIXE analysis of Cd in nodules and solid residues cannot be used with a great deal of confidence.

(d) Thallium, according to PIXE analysis of leached residues, does not behave in a consistent manner during leaching. It appeared to be depleted in some residues and enriched in others, although the total magnitude of the changes was less than about 25 per cent of the Tl present.

(e) Lead could not be detected in any liquid extracts, and in the solid residues it was only slightly depleted or slightly enriched.

The difference between apparent depletion in the residues and the actual amount of an element that has been carried off by the extracting solution must be appreciated. The change in composition in the residue does reflect the removal of elements, but it cannot reveal the absolute concentration of any element in solution.

(3) Basalts and soils from the Island of Hawaii have been qualitatively examined by PIXE for baseline information on toxic metals in the local environment. As, Cd, and Tl were not detected in any rocks or soils by PIXE and Cd could not be detected by atomic absorption. Selenium may be present in undetermined quantity, and low concentrations of Pb occur in all samples. There is evidently no consistent pattern of lead enrichment in rocks relative to soils, or vice versa. Selenium appears to be more abundant in basalts than in soils.