PRELIMINARY MASS BALANCE CALCULATIONS FOR CADMIUM IN SOUTHERN LAKE MICHIGAN

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Cadmium is a relatively volatile element, one that is highly enriched on atmospheric particles relative to its average abundance in the earth's crustal rocks.* This characteristic suggests that cadmium is among those elements whose fluxes from the atmosphere are important, and perhaps comparable in magnitude to tributary inputs.[1]

Cadmium borne into the lake by both tributaries† and atmospheric particles[3] appears to be relatively soluble under oxic conditions. This property may result in heightened biological availability and also lead to a slow rate of removal on settling particles. In most areas, the surface sediments of southern Lake Michigan remain oxic to a depth of several centimeters.[4] Under these conditions, the concentration of cadmium in the interstitial fluid appears to be controlled by the solubility of cadmium carbonate, rather than the far less soluble cadmium sulfide found under anoxic conditions.[5] This situation creates the possibility that cadmium returns from the sediments to the water column by diffusion and/or resuspension.

The present concentration of cadmium dissolved in Lake Michigan is so low that to sample, handle, and measure it challenges the state of the art. Present concentrations in offshore waters are < 30 ng L^{-1}.[6] However, cadmium is very toxic to aquatic organisms, and Marshall[6] has shown that even levels below 100 ng L^{-1} can affect natural zooplankton communities adversely. Thus, despite the ultratrace amounts now present, it is important to know whether cadmium concentrations are likely to increase, and if so, at what rate.

Our approach to answering this question is to compare the sum of input rates from the major sources to the sum of removal rates to the major sinks.

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*We measured an average enrichment factor for Cd of 340 in 22 samples of airborne particulate matter collected over Lake Michigan.

†The average ratio of dissolved to suspended loads in the rivers we sampled was 2.0. See also Ref. 2.

As sources we considered rain and snow, dry deposition from the atmosphere, shore erosion, tributaries, and runoff from the land; as sinks, natural outflow sedimentation.

To establish the present concentration of cadmium in Lake Michigan, we collected and analyzed twelve samples from various locations in the southern basin. The average value for cadmium in these samples was 26×10^{-9} g L^{-1} (N = 12, $\sigma = 8.5$, range: 11 to 46×10^{-9} g L^{-1}). These values were substantiated by a separate determination using mass spectrometric isotope dilution.

Cadmium Input

Rain Water

Twenty-nine rain events were sampled with a Battelle automatic rain collector at ANL during the period March to September 1978. The rain was frozen until it could be analyzed by graphite furnace atomic absorption spectrophotometry (GFAA). The average cadmium concentration weighted according to rainfall amount was 0.32 ppb.* The range of values was 0.07 to 1.1 ppb.

The average total annual precipitation over Lake Michigan is about 29.2 inches or 74 cm.[7] Assuming a surface area over the southern basin of 1.8×10^4 km^2, approximately 1.33×10^{13} L of precipitation falls on the lake surface each year. If one takes the average concentration of cadmium in rain at ANL to be representative of precipitation falling on the lake, wet deposition accounts for a cadmium input rate of 4.3×10^6 g/yr.

Dry Deposition

Particles were collected from large volumes of air on 20 × 25 cm Whatman 541 filters at the 68th Street water intake crib. A quarter of each filter was leached into 0.1 N nitric acid and analyzed by GFAA using the method of Janssens and Dams.[8] Four portions of the same filter showed the method to have a precision of ∿7%. The average airborne cadmium concentration from the analysis of 28 filters collected between August and November was 1.9 ng/m^2. The values

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*The precipitation-weighted average is given by: $\Sigma C_i \times Q_i / \Sigma Q_i$, where C_i is the Cd concentration and Q_i is the amount of rain for each event.

ranged from 0.43 to 5.0 ng/m^3.

Estimates of the dry deposition velocity of cadmium to the lake surface vary from 0.1 cm/sec in the summer to 0.5 cm/sec in the winter. The annual average is probably close to 0.2 cm/sec.[9] This latter value leads to a dry deposition rate over the southern basin of 2.2×10^6 g/yr, or about half the rainwater input rate. Because cadmium is predominately on the surface of atmospheric particles, it is probably very accessible to leaching and therefore, easily placed in solution.[3] The total atmospheric contribution from wet and dry deposition is thus predicted to be 6.5×10^6 g/yr.

Shoreline Erosion

Approximately 1.0×10^{13} g/yr of material is expected to erode from the shoreline into the southern basin.[10] The average crustal cadmium concentration is 0.1 μg/g according to Wedepohl.[11] These values lead to an erosion contribution of 1.0×10^6 g/yr. This will be an overestimate if sand with low trace metal levels is the predominant material washed into the lake.

Tributaries

Water was collected from the major tributaries in the spring and fall of 1978. These samples were filtered immediately after collection using 0.45 μm membranes to separate the soluble portion from suspended solids. The soluble portion was analyzed by GFAA. The suspended solids were leached in 0.1 N HNO_3 and analyzed by GFAA. The soluble inputs are listed in Table 1. The concentration value for Burns Ditch was taken from the work of Wahlgren et al., who used spark source mass spectrometry.[12] The uncharted runoff figure is calculated from a total discharge to the whole lake of 3.84×10^{13} L/yr, or 1.28×10^{13} L/yr into the southern basin.[13] The difference between this value and the known river discharge is referred to as uncharted runoff. An intermediate concentration of 0.09 ppb is assigned to it.

The cadmium on suspended solids is summarized in Table 2. The total estimated input from tributaries is 3.1×10^6 g/yr, or about one-half the atmospheric input rate. This indicates that atmospheric sources of cadmium to Lake Michigan are indeed quite important.

Table 1. Tributary inputs of soluble cadmium.

Sampling site	Tributary flows 10^{11} L/yr	Cd concentration, $\mu g\ L^{-1}$ Spring 1978	Fall 1978	Cd input, 10^5 g/yr
St. Joseph	30.4	0.08	0.10	2.73
Kalamazoo	11.6	0.07	0.07	0.81
Grand	30.0	0.19	0.095	4.3
Muskegon	17.0	0.05	0.06	0.94
Burns Ditch	1.2	0.40[a]		0.48
Milwaukee	3.4	0.25		0.85
Uncharted	31	0.09[b]		2.8
	125			12.9

[a]Ref. 13.
[b]Estimated concentration.

Table 2. Tributary inputs of cadmium on suspended solids

Sampling site	Cd concentration, $\mu g\ L^{-1}$ Spring 1978	Fall 1978	Cd input, 10^5 g/yr
St. Joseph	85	140	3.4
Kalamazoo	65	60	0.73
Grand	130	740	13
Muskegon	17	8	0.21
Milwaukee	100	—	0.34
			17.7

Cadmium Removal

Outflow

One removal mechanism for cadmium is the outflow of lake water. If the total volume of the lake is assumed to remain constant, the outflow will equal the sum of runoff plus rainfall minus evaporative losses. The runoff amounts to 1.25×10^{13} L/yr. The rainfall is 74 cm annually and the evaporative losses amount to about 84 cm a year. For the southern basin the net outflow is calculated to be 1.07×10^{13} L/yr. The cadmium concentration in lake water has been measured at 0.016 ppb, leading to a predicted net outlfow rate for cadmium of 2.8×10^5 g/yr.

Sedimentation

The rate of removal of cadmium by sedimentation was estimated using the sediment deposition rates proposed by Edgington and Robbins.[14] They found an average cadmium concentration of 3.0 ppm in the upper centimeter of 41 cores collected in the southern basin.[15] The sedimentation calculations are shown in Table 3. Rather than take an average sedimentation rate for the entire basin, we adopted Edgington and Robbins' values for the areal extent of sedimentation rates lying within a given range, multiplied each by the value 3.0 ppm, and summed the products to obtain the total annual cadmium deposition. Sedimentation accounts for the removal of 3.75×10^6 g/yr of cadmium. This may be an underestimate if the top centimeter of sediment covers a large time span and the deposition rate is rapidly increasing. However, the average concentration in pre-cultural sediment was 1.5 ppm so the cadmium deposition does not appear to be increasing rapidly.

Balance

The sources and sinks of cadmium in southern Lake Michigan are summarized

Table 3. Loss of cadmium to sediments

Mean mass sedimentation rate, $g/cm^2/yr$ [a]	Area of southern basin affected[a] 10^{13} cm^2	Total Cd flux, 10^7 g/yr [b]
0.0	10.6	0
0.01	0.5	0.015
0.006	3.5	0.063
0.015	1.6	0.072
0.030	1.2	0.108
0.050	0.5	0.075
0.070	0.2	0.042
		0.375

in Table 4. According to this estimate, cadmium is being added to Lake Michigan two to three times faster than it is being removed. This suggests that cadmium is accumulating in the water column. Assuming a maximum concentration of 0.026 ppb cadmium at present in the lake and a volume of 1600 km^3, the cadmium in the water column in the southern basin is 42×10^6 g. If the net accumulation of cadmium is 6.5×10^6 g/yr, the approximate doubling time of cadmium is 7 yr. Owing to its toxicity, apparent buildup of cadmium in Lake Michigan may be cause for concern.

Table 4. Mass balance of cadmium.

Sources		Sinks	
Rain	4.3×10^6 g/yr	Outflow	0.28×10^6 g/yr
Dry	2.2	Sedimentation	3.8
Erosion	1.0		4.08
Tributaries	1.3		
Suspended	1.8		
	10.6		

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