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## Mass Independent Fractionation of Mercury Isotopes as Source Tracers in Sediments

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### Abstract

Since the discovery of isotopic fractionation of mercury in nature, mass dependent fractionation (MDF) and mass independent fractionation (MIF) of mercury isotopes are used as a tracer to understand the mercury cycle. MIF is a powerful tool in understanding the Hg transformations and reaction mechanisms. Here we look into the MIF of the two odd isotopes of mercury (<sup>199</sup>Hg and <sup>201</sup>Hg) in sediment samples collected from lakes and springs of Florida, Lake Erie, and Yucatan Peninsula. The  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  of the sediments range from +0.52‰ to -0.48‰. From the isotopic signature we interpret the possible source of Hg in the Yucatan Peninsula carbonate to be Hg(II) from the water column. Hg in the Florida lakes and spring sediments primarily comes from litterfall. Lake Erie appears to have an anthropogenic source. This study suggests that the MIF signature of Hg isotopes can be used to qualitatively determine the primary source(s) of Hg in sediments.

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### 1. Introduction

The discovery of MDF and MIF of mercury isotopes in natural samples like fish [1,2,3,4,5] human hair from gold mining communities [6], epiphytes [7,8], peat cores and coal bearing formations [7,9,10] cinnabar ore [11,12], source rocks in the upper crust [12], hydrothermal systems [12,13,14], arctic snow [15], Great Lake rain and vapour

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[16], atmospheric Hg species [17] and sediments [2,18,19,20,21,22,23] has provided new insights into the cycling of this toxic element in the environment. Hg isotopic composition in sediments can provide varied information regarding source, changing physicochemical condition, paleo-environment etc. In this study we evaluated the feasibility of using the Hg isotopic signature in sedimentary records to qualitatively assess the primary sources of mercury in sediments. For this purpose we used the isotopic signature of a large variety of natural samples reported in the literature and the results of experimental studies to characterize the Hg sources.

## 2. Sampling and Methods

Sediments from 2 lakes (Snag and Marquis), 6 springs (Big Spring, Bluehole, Mill Pond, Madison Blue, Manatee and Wacissa) in Florida, Lake Erie (Ohio) and carbonate sediments from the Celestium Lagoon on the Yucatan Peninsula were analysed for Hg concentrations and Hg isotope ratios. Samples from the Celestium Lagoon were collected using acrylic push cores [24]. Lake Erie samples were collected using a mini box core. Sediment cores from the Florida lakes were collected using a polycarbonate push core to preserve the sediment–water interface. For the Florida springs, bedload sediments were collected from the sediment-water interface using a drag bucket by the Florida Department of Environmental Protection.

1-5 grams of wet sediment was leached in aqua regia and 30% H<sub>2</sub>O<sub>2</sub> in a tightly capped 120 ml Savillex PFA container at room temperature for 24 hrs, placed on a platform shaker for 2 hours, ultrasonicated and filtered. The same technique was applied to SRM NIST 2704 Buffalo River Sediment to confirm >98% recovery of mercury. The samples were analysed for Hg concentrations and isotope ratios using a cold-vapor introduction system (CETAC HGX – 200) interfaced to a MC-ICP-MS. Inside HGX-200, the sample solutions were mixed with 5% w/v% SnCl<sub>2</sub> in 1 N HCl to generate cold Hg vapour. Typical instrument sensitivity was 200 mV on <sup>202</sup>Hg on 1 ppb NIST SRM 3133 Hg standard with an uptake rate of 350 µl min<sup>-1</sup> at 6 rpm pump speed. Washout time was ~10 min until the wash signal stabilize at <1% of the preceding measured solution. The SnCl<sub>2</sub> solution was prepared daily from a 98% pure SnCl<sub>2</sub>·2H<sub>2</sub>O salt (ACROS) in 1 M HCl and purged with argon gas for 30 min to remove any traces of Hg. HNO<sub>3</sub> and HCl used for the experiments were all purified in-house through sub boiling, double distillation. The total procedural blank, including instrumental background is <10 pg, and insignificant relative to the amounts of Hg extracted from the samples. Instrumental mass bias correction was done using matrix matched sample-standard bracketing technique [3,17]. The isotopic compositions of Hg were measured using single block of 50 cycles with 8s integration/cycle. The mercury isotope ratios are expressed relative to the NIST 3133 Hg standard reference material in δ (‰) notation:  $\delta^A\text{Hg} = \left[ \frac{(^A\text{Hg}/^{198}\text{Hg})_{\text{sample}}}{(^A\text{Hg}/^{198}\text{Hg})_{\text{NIST3133}}} - 1 \right] \times 1000\text{‰}$ . MIF is reported as Δ notation as the difference between the measured and the theoretical MDF value [25].

Total Hg concentrations of wet sediments measured in the MC-ICP-MS were calculated by comparing the signal intensity of <sup>202</sup>Hg of 1 ppb bracketing standards with the sample. The total Hg concentrations for the Snag Lake sediments were compared to the values obtained by analysing the samples by Cold Vapor Atomic Fluorescence Spectrometry using a Tekran 2600 Mercury Analyzer (EPA method 1631). The maximum differences in concentration obtained by these two different methods were ≤10%. Given the fact that the measurements were made on different sample splits using different analytical techniques, we consider the agreement to be quite acceptable.

## 3. Results and Discussions

All the sediment samples show MDF and MIF of <sup>199</sup>Hg and <sup>201</sup>Hg isotopes, with Δ<sup>199</sup>Hg and Δ<sup>201</sup>Hg values ranging between -0.46 to 0.52 ‰. We did not observe any MIF of <sup>200</sup>Hg as has been observed in atmospheric samples in some studies [16, 17, 26]. The top 20 cm of the Lake Erie sediments show positive δ<sup>202</sup>Hg whereas all the other sediments show negative δ<sup>202</sup>Hg. Sediments from Florida lakes and springs show negative MIF whereas those from Lake Erie and the Yucatan Peninsula show positive MIF of the odd isotopes (Table 1).

The primary source of mercury to most aquatic systems (including their watersheds) is from the atmosphere through wet and dry deposition, urban and industrial discharges and catchment weathering. Catchment erosion contributes a small fraction of the total mercury in the sediments unless the bedrock in the catchment area is Hg bearing ore [27].

Variations in the isotopic composition of Hg in the sediments are likely due to a combination of processes: different sources of Hg and the subsequent effects from various physicochemical reactions in the water column and sediments. We assumed that the primary sources of mercury in the sediments could be 1. Direct deposition of anthropogenic mercury from local point sources, 2. Direct deposition of atmospheric mercury from regional and far-distant sources, 3. Residual mercury in the form of Hg(II) scavenged from water column after partial photoreduction of Hg(II) and methylmercury 4. Mercury associated with litterfall from terrestrial plants surrounding the water body. Once mercury gets deposited in the sediments, bacterial methylation and demethylation of Hg(II) inside sediments are thought to be significant processes [28,29,30] that can cause isotopic fractionation. Experimental studies demonstrated that methylation-demethylation can only produce MDF but not MIF [31,32,33,34]. However bacterial methylation-demethylation causing MIF in lake sediments have been postulated by previous studies [35] based on the argument that bacterial communities in natural habitats can have numerous combinations of species and strains interacting with each other and the few that can be cultured yield only limited or misleading information. MIF of mercury has been observed during dark abiotic reduction experimental studies [36] which can be a possible *in situ* process in the sediments and such processes can be identified from the distinctive  $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$  slopes. For our study we use the interpretations from experimental results,  $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$  slopes and Hg isotopic signature of varied natural samples to understand the observed Hg isotopic signature of the sediments.

Table 1. Hg isotopic ratios and Hg concentrations (wet weight) of sediment samples.

	Hg <sub>T</sub> (ppb)	$\delta^{202}\text{Hg}\text{‰}$	$\Delta^{199}\text{Hg}\text{‰}$	$\Delta^{200}\text{Hg}\text{‰}$	$\Delta^{201}\text{Hg}\text{‰}$
Madison Blue	1	-0.21	-0.22	-0.04	-0.26
Mill Pond	1	-1.75	-0.22	0.05	-0.28
Bigspring-1	6	-0.78	-0.14	0.04	-0.15
Bigspring- 2	7	-0.49	-0.19	0.03	-0.16
Bigspring- 3	6	-0.63	-0.16	0.03	-0.16
Bluehole Spring	6	-1.14	-0.19	0.03	-0.23
Manatee Spring-1	3	-1.52	-0.16	0.05	-0.21
Manatee Spring-2	3	-1.16	-0.24	0.02	-0.20
Wacissa Spring	6	-0.54	-0.16	-0.01	-0.14
Marquis 0-1	11	-1.18	-0.28	0.05	-0.17
Marquis 2-3	13	-0.67	-0.29	0.07	-0.18
Marquis 12-13	10	-1.08	-0.34	0.02	-0.22
Marquis 22-24	3	-0.93	-0.40	0.04	-0.46
Cypress leaves	2	-1.52	-0.17	0.02	-0.25
Snag 1-2	50	-1.21	-0.24	0.07	-0.19
Snag 2-3	50	-0.40	-0.24	0.02	-0.26
Snag 3-4	45	-1.02	-0.18	0.08	-0.17
Snag 5-6	47	-0.69	-0.24	0.08	-0.20
Snag 12-14	45	-0.60	-0.26	0.06	-0.21
Snag 18-20	39	-0.51	-0.33	0.03	-0.31
Snag 20-22	45	-0.46	-0.45	0.02	-0.41
Snag 22-24	18	-0.98	-0.34	0.06	-0.37
Snag 24-26	22	-1.79	-0.37	0.00	-0.44
Snag 26-28	20	-0.48	-0.31	0.03	-0.35
Cypress leaves	2	-1.73	-0.58	0.07	-0.49
Yucatan 1-2	3	-1.16	0.42	0.00	0.35
Yucatan 2-4	3	-1.17	0.33	-0.01	0.30

Yucatan 10-12	2	-2.52	0.51	0.04	0.46
Yucatan 20-22	1	-2.91	0.51	0.01	0.49
Yucatan 32-34	3	-1.74	0.52	0.05	0.42
Erie 2-3	46	0.14	0.06	-0.01	0.10
Erie 6-7	48	0.14	0.07	0.00	0.08
Erie 8-9	46	0.34	0.15	0.00	0.10
Erie 9-10	46	0.50	0.11	0.03	0.11
Erie 15-20	58	0.50	0.09	0.05	0.10
Erie 25-30	12	-0.12	0.29	-0.06	0.19
Erie 30-35	9	-0.40	0.20	0.05	0.16
Erie 35-40	6	-1.06	0.17	0.00	0.12

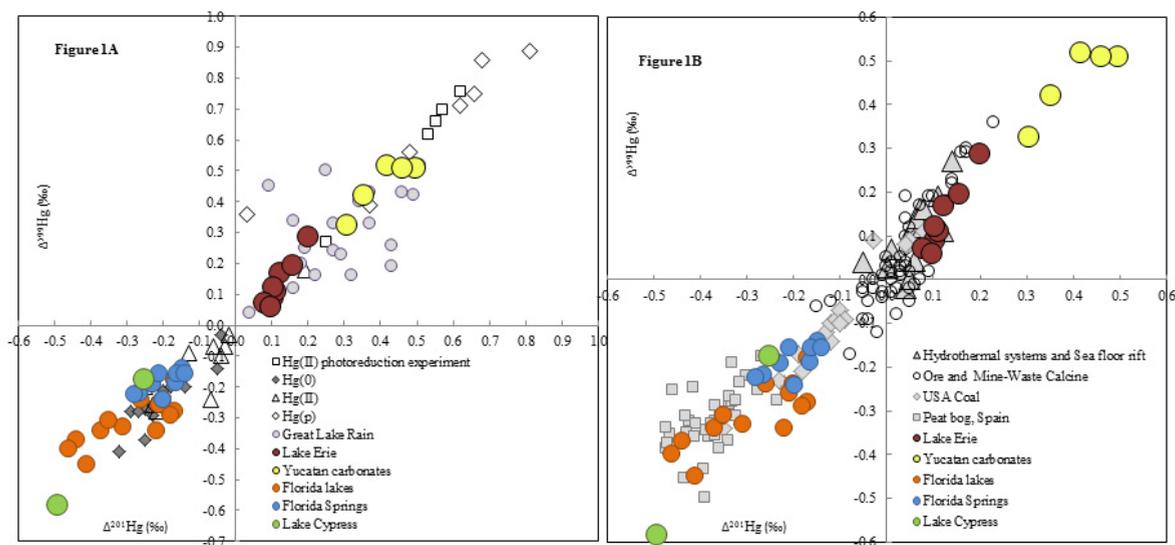


Fig. 1. Hg isotope MIF ( $\Delta^{201}\text{Hg}\%$  vs.  $\Delta^{199}\text{Hg}\%$ ,  $2\text{SD} = 0.1\%$ ) of sediment samples compared with (A) atmospheric Hg species [ $\text{Hg}(0)$ ,  $\text{Hg}(\text{II})$  and  $\text{Hg}(\text{p})$ ] [17], rain [16] and aqueous  $\text{Hg}(\text{II})$  from photoreduction experiment with a  $\text{Hg}/\text{DOC}$  mass ratio of 34.6 [33]; and (B) natural samples like coal [9], peat [7], ore, and mine waste calcine [42] and hydrothermal systems [14].

Snag Lake near Pensacola in Santa Rosa County, Florida is an open basin off the Big Simpson River. Marsh plants and cypress trees surround the basin. The water depth is shallow (~ 1 meter) with very soft sediments rich in organics. The lake sediments are potentially impacted by anthropogenic mercury from the nearby Gulf Power Company's Crist Plant, a coal-fired power plant. The  $\delta^{202}\text{Hg}$  ranges from -0.40 to -1.79 and  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  values range from -0.18 ‰ and -0.17 ‰ to -0.45 ‰ to -0.41 ‰ respectively with more negative MIF values in the deeper part of the core. Lake Marquis is an isolated basin off the Blackwater River, in Santa Rosa county of Florida. The water depth in Marquis is approximately 0.6 meters. The sediments are hard, and peaty. Saw grass is abundant in the area. Cypress domes are well developed around the lake. Lake Marquis shows a similar trend to Snag Lake, with mercury concentrations decreasing with depth, although the total Hg concentrations are much lower. The  $\delta^{202}\text{Hg}$  ranges from -0.67 to -1.52,  $\Delta^{199}\text{Hg}$  range from -0.28 ‰ to -0.40 ‰ and  $\Delta^{201}\text{Hg}$  from -0.17 ‰ to -0.46 ‰, once again with the most negative MIF values in the deeper part of the core. Cypress leaves collected from cypress domes in and around the two lakes shows  $\delta^{202}\text{Hg}$  values of -1.52 and -1.73 and depleted in the two odd Hg isotopes (Table 1). The bedload sediment samples collected from the sediment-water interface of the Florida Springs are slightly depleted (-0.14 to -0.28 ‰) in  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  and  $\delta^{202}\text{Hg}$  ranging between -0.21 and -1.75, similar to the lake sediments. Replicate samples are collected from different locations (approximately 50 m apart) in Big Spring and Manatee Spring to ensure absence of any local inhomogeneity in the observed MIF. The triplicate analyses are

within 0.1‰ demonstrating the excellent precision of these measurements.

The EPA's REMSAD model suggests that in Pensacola area only 7.2% of the total Hg deposition comes from the Crist Plant coal combustion whereas 78% comes from the “global background”. Hence in the absence of a dominant anthropogenic point source for the lake and spring sediments of Florida, we assume that the observed Hg isotopic signature is a combination of atmospheric deposit of “global background Hg”, Hg scavenged from the water column, bacterial methylation-demethylation, dark abiotic in situ reductions and Hg associated with litter fall. Both  $\text{Hg}^{\text{II}}_{(\text{g})}$  (Reactive Gaseous Mercury/RGM) and  $\text{Hg}_p$  (Particle Bound Mercury/PBM) are readily washed out of the atmosphere by rainfall and are the forms that contribute to wet deposition. Because it is generally associated with fine particles,  $\text{Hg}_p$  has a relatively low apparent dry deposition velocity, on the order of 0.1 cm/sec. RGM is thought to behave like nitric acid vapor, has an apparent dry deposition velocity of 2 cm/sec, and will adsorb especially well to wet surfaces such as surface waters and dew-covered vegetation. Because of the slow oxidation rate of  $\text{Hg}^0_{(\text{g})}$  (Gaseous Elemental Mercury/GEM), and the rapid deposition rates for RGM and  $\text{Hg}_p$ , only the emission of these latter two forms is expected to contribute to atmospheric Hg deposition around point sources. Isotopic composition of  $\text{Hg}^0_{(\text{g})}$ ,  $\text{Hg}^{\text{II}}_{(\text{g})}$  and  $\text{Hg}_p$  measured in the coastal environment of Grand Bay, Mississippi, USA, showed positive MIF for  $\text{Hg}_p$  and negative MIF for  $\text{Hg}^0_{(\text{g})}$ ,  $\text{Hg}^{\text{II}}_{(\text{g})}$  [17]. The RGM was enriched in the heavy isotopes ( $\delta^{202}\text{Hg}$  0.51 to 1.57) whereas GEM and PBM were depleted in the heavy isotopes ( $\delta^{202}\text{Hg}$  -0.12 to -3.88). Rain samples from near the Great Lakes showed positive MIF and negative  $\delta^{202}\text{Hg}$  [16] (Figure 1A). Modelled data for Hg isotopes in emissions from coal-fired power plants show modern-day mean  $\delta^{202}\text{Hg}$  and  $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$  values of  $-1.2 \pm 0.5\%$  and  $0.05 \pm 0.06\%$  respectively [10]. Dark abiotic reduction of Hg can produce MIF with a distinctive  $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$  slope of 1.61.  $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$  slope of our Florida lake and spring samples is 0.94 ( $R^2=0.67$ ) similar to photochemical reduction reactions ( $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$  ranges from ~1.0-1.3) at different Hg/DOC ratios [37]. Hence we rule out dark abiotic reduction as a primary ongoing process in the sediments to explain observed isotopic signature. Bacterial methylation-demethylation does not cause any MIF however it leaves the reactor, sediment in this case enriched in the heavy isotopes. Laboratory experiments on photoreduction of Hg(II) and MeHg showed that the water column gets progressively enriched in  $^{199}\text{Hg}$  and  $^{201}\text{Hg}$ , hence sediments scavenging Hg from the water column should have positive MIF [1]. Previous research reported the accumulation of atmospheric Hg on leaves of the Brazilian Pepper (*Schinus teribinthifolius*) in the Everglades National Park, and estimated that the annual average Hg flux associated with litterfall was approximately 70% of the wet deposition flux [38]. This suggests that litterfall may be a significant vector for deposition of atmospheric Hg to the sediments in water bodies, and may be especially important in Marquis Lake and Snag Lake where the sediments are high in organic matter derived from the vegetation surrounding the lakes. The negative MIF in the lake and spring sediment samples could be due to a more negative source (plants in these cases) mixing with scavenged Hg(II) from water column with positive MIF. The observed MDF can be caused by more complex interactions including in situ processes like bacterial reductions.

The Celestun Lagoon is located on the west coast of the Yucatan Peninsula, Mexico. The lagoon is relatively pristine and undisturbed by pollution originating from the port of Celestun situated on the barrier peninsula [24]. The local geology is that of a karst terrain and hence surface run off is nearly absent; rivers are not the primary source of the mercury. The mercury concentrations in the sediments (>98% calcium carbonate) do not show much variability and range from 1 to 3 ppb. The concentrations do not show any obvious correlation with depth. The enrichment in the odd isotopes of Hg also show little variability with depth and ranged from 0.30 to 0.52 ‰.  $\delta^{202}\text{Hg}$  ranges from -1.16 to -2.91 ‰. We do not know the exact incorporation site or the actual species of mercury in carbonate rock; it could be mercury carbonate ( $\text{HgCO}_3$ ) or any other compounds of Hg(II) that co-precipitate with the calcium carbonate or are bound to the organic matter. In this case, since the percent of OM in the sediments is low, we make the assumption that the mercury in the carbonate material has been scavenged from the water column. In a plot of  $\Delta^{199}\text{Hg}$  vs.  $\Delta^{201}\text{Hg}$ , the carbonate samples have a linear relationship with a slope of 1.2. This value is similar to that observed in Hg(II) photoreduction experiment conducted with a Hg(II)/DOC mass ratio of 34.6 (Figure 1A) [37]. Hence we conclude that the Hg MIF signature of the carbonates is representative of the water column composition, consistent with previous Hg isotopic measurements in natural water [39].

Lake Erie sediments were contaminated by mercury released from the Dow Chemical Chlor-Alkali Plant in Sarnia, Ontario (operating since 1949). The plant released very large amounts of mercury to the atmosphere as well as St.

Clair River, which flowed downstream to contaminate Lake St. Clair, the Detroit River and Lakes Erie and Ontario. Hg concentrations in the top 3 cm of the sediments measured in 1971 ranged from 8 to 2929 ppb (dry weight) with the highest levels recorded in the Western basin adjacent to the Detroit River [40,41]. In the present study the top 20 cm of Lake Erie sediment shows high Hg concentrations, is characterized by slight enrichment of  $^{202}\text{Hg}$  ( $\delta^{202}\text{Hg}$  from 0.14 to 0.5 ‰) and up to 0.15 ‰ enrichment of the odd isotopes. The bottom “unpolluted” horizons have low Hg concentrations,  $\Delta^{199}\text{Hg}$  up to 0.29 ‰ and depleted in the heavy isotopes ( $\delta^{202}\text{Hg}$  -0.12 to -1.06‰) similar to other sediments reported in this study. A logical approach of understanding source attribution is to investigate isotope signatures of Hg of the point source(s). However in the absence of mercury samples used in the chlor alkali plant we use Hg ore data from literature to understand the observed isotope ratio of the contaminated sediments. MDF and MIF was observed in Hg bearing minerals [14,42]. While the MDF showed a huge range ( $\delta^{202}\text{Hg}$  from 2‰ to -2‰) MIF signatures were more distinctive. Hypogene cinnabar, Hg-bearing ore minerals, and mine waste calcine from Texas showed MIF, with  $\Delta^{199}\text{Hg}$  ranging from -0.09 to 0.36‰ [42]. Fluid and sinter samples collected from Ojo Caliente hot spring in the Yellowstone National Park showed a small yet consistent enrichment of the odd isotopes ( $\Delta^{199}\text{Hg}=0.13\text{‰}\pm 0.06\text{‰}$  2SD) possibly inherited from the photoreduction of Hg(II) in the water column [14]. In a plot of  $\Delta^{199}\text{Hg}$  vs.  $\Delta^{201}\text{Hg}$ , Lake Erie sediments fall in the same field as the fluid and sinter samples from Ojo Caliente and Cinnabar, Hg ore minerals, mine waste calcine and leachates from Terlingua district and McDermitt mine (Figure 1B). We do not know the exact isotopic composition of the anthropogenic discharge to Lake Erie. The ore samples have a MIF range from slightly negative to zero to positive. We infer the Hg isotopic signature at the top polluted part of the sediment resulted from combination of discharge from chlor alkali plant (probably with a MIF signature close to zero), atmospheric fall out ( $\Delta^{199}\text{Hg}$  close to zero) and adsorption from water column (positive MIF). The bottom, relatively pristine part of the sediment possibly sourced Hg from background atmospheric deposition and adsorption from water column.

Hg isotope signatures are potentially useful tools for tracing environmental Hg sources of contamination. But major limitation lies in the fact that 1. the original isotopic signatures are altered by natural processes 2. mixing of variable quantities of Hg from different sources may obscure individual signatures. In this study we qualitatively evaluate the potential sources of Hg of a variety of sediments by using MIF signatures. Overall, we surmise that sediments will reflect the Hg isotopic composition of the primary source, whether that be from local anthropogenic pollution, local vegetation, or uptake from the water column.

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