Use of $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ To Identify Slag-Affected Sediment in Southern Lake Michigan

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Slag is a ubiquitous byproduct of the iron-smelting industry and influences geochemistry and water quality in adjacent geologic units, ground and surface water. Despite extensive slag deposition along the Indiana shoreline of Lake Michigan, definitive evidence that slag has affected lakebed sediments has not been established. Concerns for the protection of water and ecosystem resources in the Great Lakes motivated this study to determine if strontium and boron isotopes could be used to identify and delineate slag-affected bed sediment in Lake Michigan. Sixty-five samples of bed sediment were acquired from the southern lobe of Lake Michigan and analyzed for $^{87}Sr/^{86}Sr$ and $\delta^{11}B$. Samples immediately offshore from Indiana steel mills and slag-disposal sites contained higher median $^{87}Sr/^{86}Sr$ values (0.70881) than shoreline sediments collected elsewhere in the basin (0.70847) and uniquely decreased with increasing distance from the shoreline. The highest $\delta^{11}B$ values occurred in sediments from the Indiana shoreline ($+12.9$ to $16.4^o/_{oo}$) but were also elevated in sediments collected offshore from three Lake Michigan cities ($+11.7$ to $12.7^o/_{oo}$). Contoured isotope data indicated that $82-154$ km^2 of bed sediment along the Indiana shoreline had elevated $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ values relative to shoreline sediments elsewhere in southern Lake Michigan.

Introduction

Ground and surface water in contact with slag acquires chemical characteristics that are distinctly different from the background water quality (*1−4*). A previous study of water from 137 observation wells in northwestern Indiana determined that groundwater in slag contains higher pH, specific conductance, and concentrations of alkalinity, dissolved solids, suspended solids, total organic carbon, calcium, potassium, sodium, chloride, aluminum, barium, magnesium, sulfate, chromium, cobalt, copper, cyanide, manganese, mercury, nickel, and vanadium than water unaffected by slag (*1*). Geochemical models, scanning electron microscope, and electron microprobe data have shown that slag-affected water precipitates carbonate and sulfate minerals and dissolves native silicate minerals (*1, 4, 5*). Active precipitation of calcite and dolomite has been documented where slag-

affected ground and surface water discharged to a freshwater lake in northwestern Indiana and air photography indicates that slag drainage and slag-related precipitates may be discharged to Lake Michigan along the Indiana shoreline ((*1*) Figure 1). Although column-leaching studies of slag samples from northern Indiana deposits have produced fluids that are nontoxic to *Daphnia magna* or *Selenastrum capricornutum*, slag-related mineral precipitation may cause bed sediment armoring that degrades benthic habitats (*1, 5−7*). An environmental tracer is needed to ascertain whether slag is affecting bed-sediment chemistry along the southern shoreline of Lake Michigan.

Slag is a nonmetallic byproduct of the iron and steel beneficiation processes. The geochemical composition of slag is determined by the source of iron ore and carbonate material combined during metal refining, the manufacturing processes employed, and the method used to cool the molten slag. Blast-furnace slag, the most abundant form of slag in northwestern Indiana, is approximately 95% silicates and aluminosilicates of calcium and magnesium and 5% iron, manganese, sulfur compounds, and other iron-ore impurities (*8*). Typical minerals in blast-furnace slag include melilite $(Ca,Na)_2(Al,Mg,Fe^{2+})(Si,Al)_2O_7$, oldhamite $(Ca,Mg,Fe,Mn)S$, and merwinite $Ca_3Mg(SiO_4)_2$ (*9*). Glass accounts for $80-95\%$ of the volume of slag (*9*).

Slag deposition on the southern Lake Michigan shoreline has been continuous since Chicago steel mills began operations during the 1830s (*1*). To dispose of rapidly accumulating stockpiles, slag was hauled from Chicago steel mills to northwestern Indiana and dumped along the southern Lake Michigan shoreline to provide erosion protection for railways that followed the beach line (*1*). Interdunal wetlands and other low-lying lands in northwestern Indiana were extensively used for slag disposal (*10*). Slag was later used for roadway aggregate and highway-overpass approaches and dumped on the steel-mill properties, in offsite dumps and directly into Lake Michigan. As a result of slag deposition on the Lake Michigan shoreline, the State of Indiana has accumulated more than 27 km^2 of land-surface area (*11*). By 1996, 3.7×10^8 m^3 of steel-industry waste (mostly slag) covered more than 79 km^2 of the Lake Michigan drainage in northwestern Indiana and northeastern Illinois (*10*). The extent of deposited slag in the United States and worldwide is uncertain, but estimates indicate that millions of tons of slag are produced annually in the United States (*12*).

The isotopic abundances of strontium (Sr) and boron (B) may have potential as tracers of slag-affected bed sediments because Sr substitutes for Ca and was likely to occur in slag-related precipitates, and B is minor trace constituent in many minerals (*13, 14*). Strontium is an alkali earth metal that has four stable naturally occurring isotopes—^{84}Sr (0.56%), ^{86}Sr (9.86%), ^{87}Sr (7.0%), and ^{88}Sr (82.58%) (*15*). Strontium isotopes were naturally fractionated during primordial nucleosynthesis. Although ^{87}Sr additionally is produced by the radioactive decay of ^{87}Rb, the half-life of the reaction is 48.8 billion years; consequently this process had no noticeable effect on the abundance of ^{87}Sr during the course of this study (*15*). Strontium is a common constituent of most rocks, but anthropogenic sources of strontium are uncommon (*16, 17*).

The ratio of strontium-87 to strontium-86 ($^{87}Sr/^{86}Sr$) is typically used in geologic and hydrologic investigations to distinguish different rock sources. The $^{87}Sr/^{86}Sr$ ratio in a water sample can be modified by mineral dissolution or cation exchange. The ratio in rock can be modified by mineral precipitation or cation exchange (*18*). Values of $^{87}Sr/^{86}Sr$ in terrestrial rocks generally range from 0.704 to 0.720 (*19*).

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FIGURE 1. Aerial photograph showing a plume emanating from a large slag deposit through or beneath a retention wall into Lake Michigan in northwestern Indiana.

TABLE 1. Values of $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ in Terrestrial Rocks[a]

rock type	$^{87}Sr/^{86}Sr$
siliclastic − silicate fraction	0.71185−0.72015
carbonate − carbonate fraction	0.70775−0.70870
carbonate − whole rock	0.70869−0.70934
siliclastic − whole rock	0.70919−0.70998

rock type	$\delta^{11}B$
evaporites	$-31 - +50^0/_{00}$
metamorphic rocks	$-34 - +22^0/_{00}$
igneous rocks	$-17 - +15^0/_{00}$
calcite and limestone	$+15 - +32^0/_{00}$
aragonite	$+23 - +27^0/_{00}$

[a] Sources: refs 22, 24, 41−43, and 61; http://wwwrcamnl.wr.usgs.gov/isoig/.

Values of $^{87}Sr/^{86}Sr$ in silicate and carbonate sedimentary rocks, commonly encountered in the Lake Michigan drainage, are shown in Table 1. The values of $^{87}Sr/^{86}Sr$ are not affected by mass fractionation or interaction with gas phases (20). It was hypothesized that $^{87}Sr/^{86}Sr$ in Lake Michigan bed sediments, where slag-affected ground and surface water discharges to the lake, would bear an isotopic signature identical to the signature present in the slag itself (20−22), the slag signature being determined by the silaceous ore rock and carbonate flux used to manufacture the slag.

Strontium isotopes have been applied to studies of watershed hydrology (23), groundwater evolution (24−28), and historical environmental conditions (29, 30). Hydrologists have used $^{87}Sr/^{86}Sr$ to distinguish sources of water in freshwater springs (30), regional carbonate aquifers (31, 32), bedrock aquifers (33), and rivers (34). There has been extensive use of the $^{87}Sr/^{86}Sr$ in various aspects of saline surface and groundwater hydrology (35, 36) and as a tracer in studies of groundwater/surface water interaction (37−40). Strontium isotopes have not been measured in slag or used previously to trace slag-affected water or sediment.

Boron is a naturally occurring element that is not abundant but is widely distributed in groundwater, surface water, and geologic sediments (41, 42). Boron has two naturally occurring stable isotopes, ^{11}B (80.1%) and ^{10}B (19.9%) (43). Natural sources of B include thermal springs, volcanically influenced water, volcanic gases, and evaporite deposits (17). Anthropogenically, boron is used to manufacture cosmetics, disinfectants, photochemicals, fertilizers, preservatives, glass, and enamels (42). Anthropogenic sources include landfill leaching, coal mining, coal burning, fly ash drainage, municipal sewage, and industrial wastewater disposal (43−46). Boron isotopes have not been used previously to trace slag-affected water or sediment.

Boron isotopes are fractionated by mineral crystallization, H_2O phase changes in hydrothermal systems, and hydrothermal alterations of rock (47−49). Boron can be adsorbed by clay minerals and undergo isotopic fractionation, the lighter ^{10}B being preferentially and nonexchangeably adsorbed (50−52). A general range for $\delta^{11}B$ values in terrestrial rocks is −34 to +59$^0/_{00}$ ((42, 53) Table 1). The $\delta^{11}B$ values for sources of environmental contamination by municipal wastewater range from 5 to 13$^o/_{oo}$ (43, 53).

The wide range of boron isotope abundances in natural and anthropogenic materials is the foundation of its utility to hydrologic investigations (15). Boron isotopes have been used to identify sources of water to aquifers, streams, and lakes (54), to track the evolution of brines (55−57), to determine the origin of evaporite minerals (58, 59), and to examine hydrothermal flow systems (48). Boron isotopes have been widely used to delineate groundwater contamination by municipal and industrial wastewater (31, 53, 60), injected wastewater (43), irrigation (43), and landfill leachate (44). Boron isotope data have also been used to provide historical context for water pH (61), seawater composition (50), temperature, and atmospheric CO_2 (62). Boron isotopes have not been used previously to trace slag effects on ground and surface water.

The purpose of this study was to explore the feasibility of using $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ to trace slag-influenced bed sediments along the Indiana shoreline of Lake Michigan. The study area included the entire southern lobe of Lake Michigan with the expectation that the influence of slag would not exceed these boundaries, and the background isotope distribution for the region could be established. Sample collection and analysis focused on the Indiana shoreline, but generally included a population that was well distributed throughout the study area.

Methods

Sixty-five Lake Michigan bed-sediment samples were acquired for this investigation (Table 2, Figure 2). Samples were selected from archived collections and from new samples collected as part of this study.

Twenty sediment samples were acquired from an archived collection maintained by the U.S. Geological Survey (USGS) at Woods Hole, MA (Table 2). The Woods Hole archive samples that were eventually analyzed for this study were primarily collected in 1988−1989 along the southwestern Michigan shoreline of Lake Michigan. These samples were collected using a box core at the sediment−water interface. The Woods Hole samples were collected for the Southern Lake Michigan Coastal Erosion Study; that study focused on coastal geomorphology (63), littoral drift sand deposits along the Indiana and Illinois shoreline (64), sediment budgets (65), historical lake-level fluctuations (66), and climatic history (67). Upon collection, the samples were immediately subsampled, containerized, and refrigerated.

Twenty-five samples were acquired from an archived collection maintained by National Oceanic and Atmospheric Administration-Great Lakes Environmental Research Laboratory (NOAA-GLERL) at Ann Arbor, MI (Table 2). The archived NOAA-GLERL samples were collected in 1995 as

TABLE 2. Sample Source, Water Depth, and Isotope Data

sample ID	source	depth (m)	distance (km)	$^{87}Sr/^{86}Sr$	$\delta^{11}B$ (‰)
1	USGS−I[a]	6.0	2.630	0.70839	
2	USGS−I	3.3	1.710	0.70954	
3	USGS−I		2.009	0.70954	
4	USGS−I	8.8	1.545	0.70968	15.2
5	USGS−I		2.781	0.70926	8.49
6	USGS−I		1.970	0.70961	
7	USGS−I	8.0	.837	0.70881	14.9
8	USGS−I	5.0	.270	0.70994	
9	USGS−I	6.0	.365	0.70931	13.4
10	USGS−I	9.7	.231	0.70856	
11	USGS−I	7.6	.058	0.70894	
12	USGS−I	10	.433	0.70855	
13	USGS−I	11	.652	0.70847	11.7
14	USGS−I		.026	0.70924	7.74
15	USGS−I	14	1.722	0.70869	12.9
16	USGS−I	4.2	.216	0.70844	
17	USGS−I		.026	0.70854	
18	USGS−I	9.4	1.353	0.70875	
19	USGS−W[b]	12		0.70881	
20	USGS−W	18	1.807	0.70858	
21	USGS−W	14	.543	0.70847	
22	USGS−W	13	.815	0.70835	
23	USGS−W	20	2.990	0.70868	9.49
24	USGS−W	27	6.267	0.70880	9.24
25	USGS−W	30	9.269	0.70901	12.7
26	USGS−W	21	5.152	0.70899	11.7
27	USGS−W	21	5.152	0.70992	
28	USGS−W	17	1.740	0.70840	8.24
29	USGS−W	15	.708	0.70892	
30	USGS−W	16	3.745	0.70835	
31	USGS−W	21	6.750	0.70771	3.00
32	USGS−W	26	9.119	0.70904	7.49
33	GLERL[c]	6.0		0.70837	
34	GLERL	20	16.403	0.70915	
35	GLERL		9.940	0.70905	6.49
36	GLERL	8.0	1.376	0.70834	11.7
37	GLERL	17	1.399	0.70863	
38	GLERL	55	15.630	0.70935	0.25
39	GLERL	51	23.596	0.70956	−3.00
40	GLERL	83	42.268	0.70988	−6.49
41	GLERL	79	20.151	0.70947	
42	GLERL	45	10.985	0.70913	3.75
43	GLERL	125	42.250	0.70998	−2.25
44	GLERL	147	50.310	0.71011	−5.49
45	GLERL	84	23.906	0.71003	2.25
46	GLERL	80	21.953	0.71002	−3.00
47	GLERL	28	4.484	0.70933	
48	GLERL	86	12.864	0.70993	.50
49	GLERL	80	20.040	0.70935	
50	GLERL	18	4.355	0.70879	2.75
51	GLERL	125	41.633	0.70947	−6.49
52	GLERL	17	2.132	0.70842	10.2
53	GLERL	51	15.343	0.71018	−4.00
54	GLERL	93	40.717	0.70950	3.75
55	GLERL	28	.448	0.70912	
56	GLERL	89	26.221	0.70968	−6.99
57	GLERL	86	53.462	0.70992	−8.49
58	USGS−W	160	59.908	0.70965	2.25
59	USGS−W	79	20.640	0.70972	−5.99
60	USGS−W	148	48.738	0.70985	5.74
61	USGS−W	90	25.713	0.70940	−1.50
62	USGS−W	64	15.567	0.70922	1.25
63	USGS−I	33	5.759	0.70876	9.99
64	USGS−I	36	7.197	0.70834	16.4
65	USGS−W	- -	8.436	0.70864	10.2

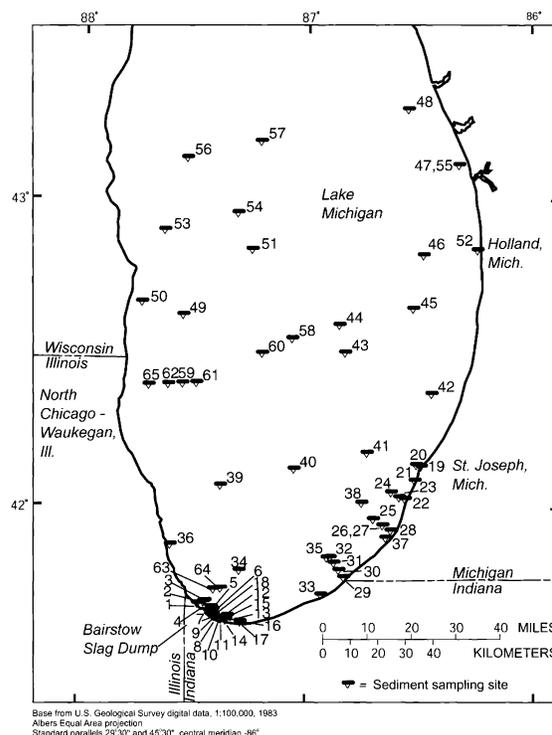[a] USGS−Indianapolis District. [b] USGS−Woods Hole. [c] NOAA-GLERL.

FIGURE 2. Lake Michigan sites where sediment samples were collected.

Samples for the present study were taken from the 0−1 cm interval of each core. At the remaining NOAA-GLERL sites, where box cores were not collected, the 0−1 cm interval of lakebed sediment was collected with a Ponar sampler. All samples were frozen upon collection, freeze-dried, ground, and stored at 0 °C. The NOAA-GLERL samples analyzed as part of this study were spatially distributed throughout the southern lobe of Lake Michigan.

The USGS collected an additional 20 samples along the Indiana shoreline of Lake Michigan during 2000−2001 (Table 2). The samples were collected primarily offshore from slag dumps and steel mills. Samples were collected from the water−sediment interface using a stainless steel, Ponar sampler. Samples were immediately transferred to glass jars with plastic lids. The latitude and longitude of each sample site was determined and recorded with a global positioning system (GPS).

A leaching procedure was used on all samples to address the possibility of mineral precipitation and ion exchange related to slag drainage. Samples were leached for 24 h with 1 N HCl to extract Sr and B structurally bound in calcite and dolomite and adsorbed to exchangeable sites in clay minerals. Some oxides, hydroxides, and silicates that are easily solubilized in weakly acidic solutions may have been dissolved by the leaching procedure. The leachate was analyzed for ^{87}Sr, ^{86}Sr, ^{11}B, ^{10}B, total Sr, total B, Ca, Mg, and Si (Tables 2 and 3). For purposes of this study, strontium and boron isotopes are reported as $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ (the per mil deviation of the $^{10}B/^{11}B$ ratio of the sample from that of NIST 951). The Lake Michigan bed-sediment samples were analyzed in 2002.

Strontium isotopes were measured in the bed-sediment leachates using positive thermal ionization mass spectrometry (PTIMS). The strontium was purified using cation-exchange chromatography in a clean laboratory environment with Teflon-distilled reagents. Samples were loaded on tantalum (Ta) filaments, and isotope ratios were measured using a Finnigan MAT 261 multicollector PTIMS instrument. NIST 987, an Sr standard reference metal, was analyzed daily

part of a lake-wide sediment sampling effort for the Lake Michigan Mass Balance Program (http://www.epa.gov/glnpo/lakemich/index.html). Samples from stations 41−46 were collected by box core (68). Subcores with 8−10 cm diameter and 50 cm long were extruded from each box.

TABLE 3. Elemental Concentrations in Lake Michigan Bed Sediments

sample ID	B (μg/g)	Mg (mg/g)	Si (mg/g)	Ca (mg/g)	Sr (μg/g)
1	1.338	34.13	0.195	64.31	22.02
2	<0.040	0.144	0.014	95.50	119.9
3	0.049	0.500	0.024	98.91	126.5
4	3.936	19.05	0.703	49.96	43.80
5	5.441	31.87	0.861	83.16	51.64
6	<0.040	0.210	0.025	93.09	122.9
7	1.406	29.51	0.282	59.07	22.84
8	3.228	3.489	1.937	87.71	104.39
9	2.804	27.18	1.784	100.92	68.95
10	1.582	36.95	0.240	71.69	24.40
11	1.855	33.87	0.875	76.60	35.37
12	1.549	34.31	0.235	69.30	25.56
13	1.823	23.69	0.248	42.51	16.13
14	3.269	30.99	2.417	71.72	39.73
15	2.754	31.436	0.361	70.70	29.84
16	0.616	10.09	0.255	22.44	12.36
17	0.271	8.124	0.160	17.08	8.475
18	1.618	28.99	0.352	59.16	24.86
19	<0.040	3.903	0.091	8.988	5.070
20	1.195	5.897	0.250	11.97	6.607
21	0.473	11.12	0.240	25.16	13.58
22	0.963	5.025	0.124	10.19	5.273
23	2.095	23.92	1.154	55.04	31.74
24	2.453	36.51	0.664	70.72	28.95
25	2.860	39.60	0.838	75.89	31.80
26	2.137	32.94	0.424	65.79	29.25
27	<0.040	3.189	0.280	5.697	2.986
28	0.669	12.73	0.177	24.61	11.88
29	0.200	5.783	0.163	11.63	5.839
30	<0.040	2.924	0.251	8.485	4.203
31	1.255	6.913	0.340	11.81	6.282
32	1.695	22.61	0.845	42.57	18.47
33	0.468	12.47	0.126	33.84	20.77
34	0.399	8.308	0.198	14.32	7.854
35	2.365	17.09	0.426	30.99	14.09
36	2.244	24.55	0.158	43.47	15.61
37	0.778	14.57	0.322	28.03	13.84
38	4.333	34.23	0.883	73.44	38.51
39	1.820	7.705	0.580	12.79	8.10
40	5.330	18.48	1.486	43.72	34.56
41	4.900	31.17	0.976	64.29	37.67
42	4.291	33.61	1.109	72.10	40.83
43	5.578	17.63	<0.010	59.25	47.46
44	5.783	15.00	2.268	62.63	50.55
45	5.525	20.49	1.946	57.79	43.80
46	5.340	21.43	1.969	55.44	42.55
47	0.671	7.779	0.424	14.37	8.704
48	5.169	23.29	1.754	51.55	38.84
49	0.969	8.101	0.395	14.11	9.70
50	2.795	28.73	0.446	61.25	30.73
51	5.057	14.60	1.450	46.92	39.35
52	0.133	5.447	0.096	9.951	4.535
53	<0.040	2.699	0.241	4.478	3.634
54	3.497	11.58	0.779	31.95	25.67
55	0.668	6.936	0.240	13.12	8.094
56	1.085	6.610	0.548	13.66	10.50
57	1.448	4.293	0.607	9.980	9.446
58	4.354	9.975	1.230	60.85	45.21
53	1.463	11.71	0.700	19.64	12.01
60	4.510	10.34	1.378	54.31	39.70
61	3.062	18.53	0.642	36.34	21.50
62	1.637	19.26	0.456	31.53	16.51
63	0.123	0.715	0.024	2.495	2.044
64	1.046	17.62	0.047	30.33	9.451
65	1.109	21.96	0.201	37.45	13.57

during the analyses; samples were analyzed only if the reported Sr isotope ratio for NIST 987 was within the long-term (5-year) 2-sigma range of replicate values ($^{87}Sr/^{86}Sr = 0.71024 \pm 0.00002$). Analytical precision typically was better than $\pm 0.03^0/_{00}$ (per mil) at the 95-percent confidence level.

Boron (B) isotopes were measured in 40 Lake Michigan bed-sediment samples using negative thermal ionization mass spectrometry (NTIMS). An amount of sample sufficient to provide approximately 2 ng of B was loaded directly on rhenium (Re) filaments. Isotope ratios were measured using a Finnigan MAT 261 multicollector NTIMS instrument. NIST 951, a synthetic boric acid, and seawater were measured daily during the analyses; samples were analyzed only if the reported B isotope ratio for seawater relative to NIST 951 was within the long-term (5-year) 2-sigma range of replicate values ($\delta^{11}B = + 39.2 \pm 0.5^0/_{00}$). Analytical precision was typically better than $\pm 0.1^0/_{00}$ at the 95-percent confidence level. All samples were analyzed at least twice to ensure reproducibility within $1^0/_{00}$.

The isotope and geochemical data collected for this study were examined statistically and graphically. Summary statistics and correlation coefficients were computed using S-Plus 2000. Initial data exploration indicated that samples collected along the Indiana shoreline might contain trends that opposed data trends observed throughout the remainder of the basin. To accommodate this initial evaluation, the data set was split into "Indiana shoreline" and "basin" subsets prior to computing the correlation coefficients (Table 4).

The coefficient of correlation ρ, for two random variables X and Y, is defined by the equation

$$\rho_{XY} = \sigma\{X,Y\}/\sigma\{X\}\sigma\{Y\}$$

where $\sigma\{X\}$ is the standard deviation of X, $\sigma\{Y\}$ is the standard deviation of Y, and $\sigma\{X,Y\}$ is the covariance of X and Y (69). Values of ρ_{XY} range between -1 and 1, where values closer to ± 1 indicate a greater degree of linear statistical relation, and values closer to zero indicate less linearity. The sign ($+$ or $-$) that accompanies the ρ_{XY} value indicates a positive or negative slope of a regression line fitted to the data.

A geographic information system data set was built with ARC/INFO, and internal contouring routines were utilized to contour isotope data in Lake Michigan. Visual inspection of the contoured maps indicated that an inverse-distance weighted method provided the most faithful rendering of the data. ARC/INFO system commands were used to compute the lakebed areas delineated by specific data contours and representing areas potentially affected by slag discharges.

Results

The values of $^{87}Sr/^{86}Sr$ in Lake Michigan bed-sediment samples ranged from 0.70771 to 0.71018 (median = 0.70912, $n = 65$) (Table 2). Higher values of $^{87}Sr/^{86}Sr$ generally occurred in the northern and central parts of the basin and became progressively lighter to the south and closer to the shoreline (Figure 3). The range and median $^{87}Sr/^{86}Sr$ of seven samples collected within 2 km of shore, excluding the Indiana shoreline samples, were 0.70834−0.70892 and 0.70847, respectively, and were slightly less than the range and median in Indiana shoreline samples collected within 2 km of shore which was 0.70844−0.70994 and 0.70881, respectively (Table 2). The Kriged contour of $^{87}Sr/^{86}Sr = 0.70900$, which is proposed herein as an operational boundary of elevated $^{87}Sr/^{86}Sr$ values along the Indiana shoreline, encompassed 154 km^2 of Lake Michigan bed sediment.

The values of $\delta^{11}B$ in Lake Michigan bed sediments ranged from -8.49 to $+16.48^0/_{00}$ (median = 4.74, $n = 40$) (Table 2). The $\delta^{11}B$ values were generally distributed with isotopically lighter values in the northern and central parts of the basin and progressively heavier values to the south and closer to the shoreline (Figure 4). Four areas of relatively heavier $\delta^{11}B$ areas ($> +8.0^0/_{00}$) occurred near Holland, MI (84 km^2), the Indiana steel mills (1369 km^2), Waukegan, IL (118 km^2), and southwest of St. Joseph, MI (360 km^2). The area enclosed by the $+13^0/_{00}$ contour, an area of uniquely elevated $\delta^{11}B$ along

TABLE 4. Correlation Coefficients for Lake Michigan Bed-Sediment Data[d]

	depth[a]	distance	87Sr/86Sr	$\delta^{11}B$	B[b]	Mg[c]	Si	Ca	Sr
depth		*0.902*	*0.775*	*−0.630*	*0.639*	*−0.324*	*0.677*	*0.149*	*0.559*
distance	0.657		*0.743*	*−0.658*	*0.544*	*−0.391*	*0.554*	*0.043*	*0.428*
87Sr/86Sr	−0.585	0.144		*−0.716*	*0.676*	*−0.097*	***0.751***	*0.213*	*0.558*
$\delta^{11}B$	−0.490	0.274	0.696		*−0.423*	*0.336*	*−0.499*	*0.147*	*−0.229*
B[b]	−0.036	0.514	**0.806**	0.328		*0.306*	***0.902***	*0.670*	***0.922***
Mg[c]	0.297	−0.034	−0.565	−0.199	−0.546		*0.149*	***0.836***	*0.478*
Si	−0.662	−0.466	0.598	0.096	0.401	−0.078		*0.534*	***0.856***
Ca	−0.382	−0.338	0.270	0.013	0.139	0.465	**0.839**		***0.853***
Sr	−0.607	−0.247	0.739	0.258	0.576	−0.120	**0.969**	0.814	

[a] Depth is water depth in meters. [b] B and Sr are concentrations expressed as $\mu g/g$. [c] Mg, Si, and Ca are concentrations expressed as mg/g. [d] Italicized numbers are correlation coefficients for basin samples excluding Indiana shoreline samples. Nonitalicized numbers are correlation coefficients for Indiana shoreline samples.
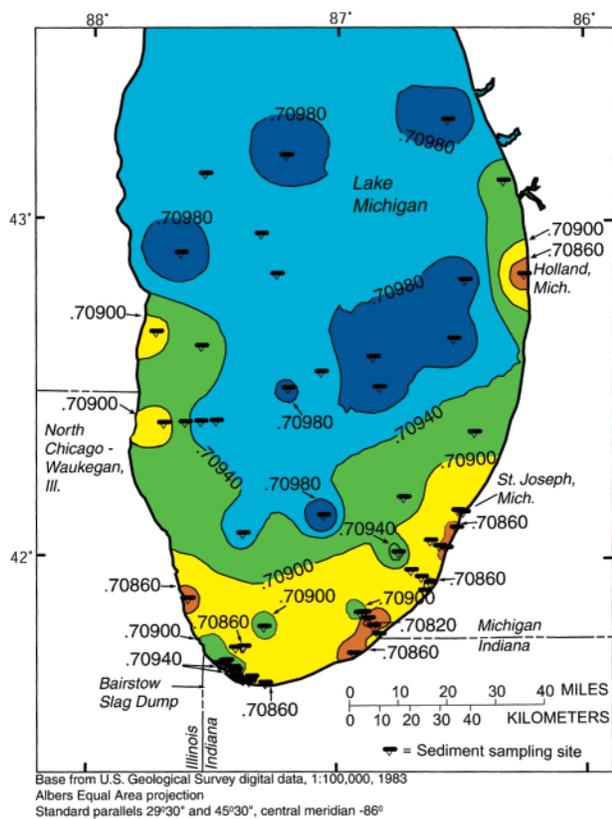
FIGURE 3. Inverse-distance weighted contour of 87Sr/86Sr in bed sediment of Lake Michigan. [Contour interval is 0.00040.]

FIGURE 4. Inverse-distance weighted contour of $\delta^{11}B$ in bed sediment of Lake Michigan. [Contour interval is 4‰.]

the Indiana shoreline, encompassed 82 km² of Lake Michigan bed sediment potentially affected by slag.

Elemental concentrations of B, Ca, Mg, Si, and Sr in Lake Michigan bed sediments are shown in Table 3. Correlation coefficients for possible data relations between water depth, distance from shore, 87Sr/86Sr, $\delta^{11}B$, B, Mg, Si, Ca, and Sr are shown in Table 4. The correlation coefficients ranged from −0.716 to +0.969. Four correlation coefficients exceeded |±0.900| and 12 exceeded |±0.750|. Indiana shoreline and Lake Michigan basin samples showed high positive correlations between strontium, calcium, and silicon. 87Sr/86Sr and $\delta^{11}B$ were negatively correlated in Lake Michigan basin samples (−0.716) but positively correlated in Indiana shoreline samples (+0.696).

Discussion

Management and protection of the Great Lakes is a growing source of international concern. One-fifth of the world's freshwater is held in the Great Lakes, and 33 million people utilize the lakes for d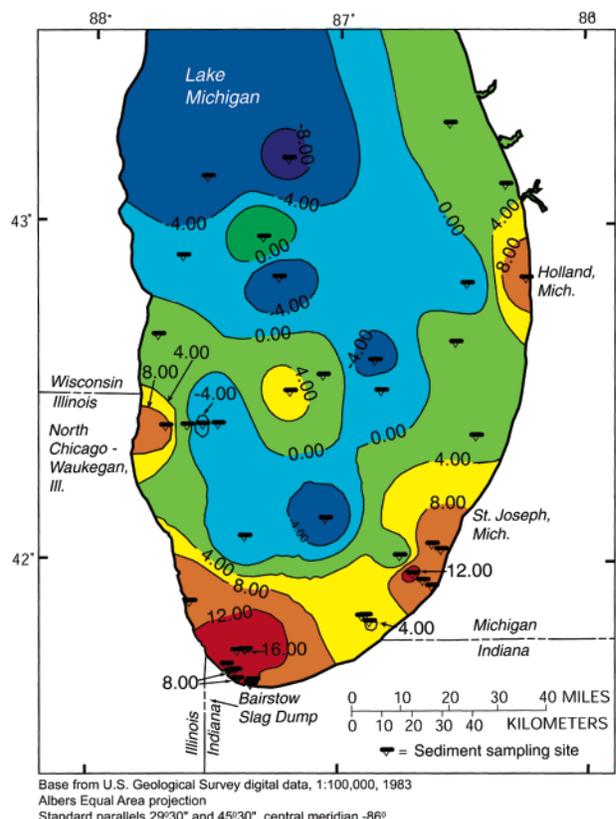rinking water (72). Revenues from sport and commercial fisheries in the Great Lakes exceed 4 billion dollars per year and the value to manufacturing industries in the region is immeasurable. Desires to export water beyond the Great Lakes drainage divide further increases concern for the Great Lakes resource.

The data collected for this study provided some evidence to support the hypothesis that Sr and B isotopes can be used to identify slag-affected bed sediments. This evidence included the following: (1) elevated 87Sr/86Sr in Indiana shoreline samples relative to values in nearshore samples from elsewhere in the basin, (2) a negative relation of 87Sr/86Sr with distance through Indiana shoreline transects compared with a positive relation of 87Sr/86Sr with distance through shoreline transects elsewhere in southern Lake Michigan, and (3) uniquely high $\delta^{11}B$ in Indiana shoreline samples. In addition to exploring the testable hypothesis concerning the use of 87Sr/86Sr and $\delta^{11}B$ to trace slag influence on bed sediments, a regional distribution of the isotopes throughout the southern lobe of Lake Michigan was produced
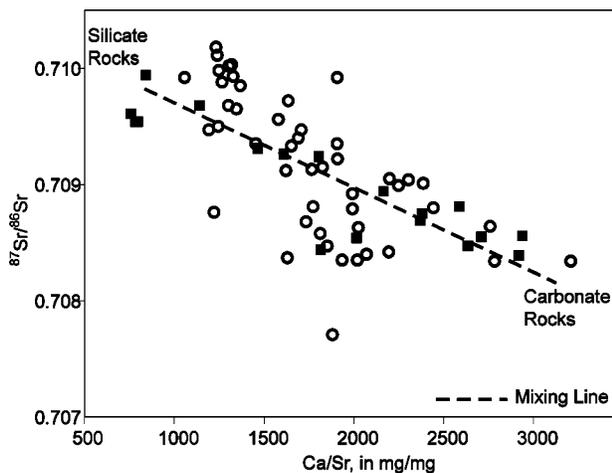
FIGURE 5. Plot $^{87}Sr/^{86}Sr$ with Ca/Sr for samples of bed sediment from the southern Lake Michigan basin (○) and the Indiana shoreline (■) along a mixing line between generalized silicate and carbonate-rock end members.
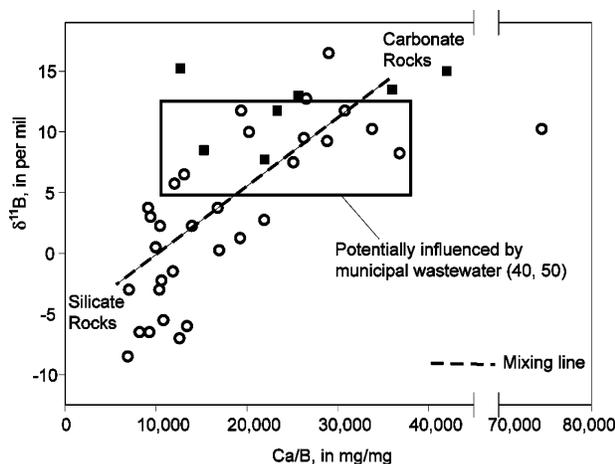

FIGURE 6. Plot $\delta^{11}B$ with Ca/B for samples of bed sediment from the southern Lake Michigan basin (○) and the Indiana shoreline (■) relative to a mixing line between generalized silicate and carbonate-rock end members.

that could have applications for many other studies in the basin.

The distribution of $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ in southern Lake Michigan bed sediments is predominantly a reflection of the regional geology and the pervasive current patterns that transport sediment in the southern lobe of the lake. Bedrock geology in the northern Great Lakes chiefly consists of Precambrian igneous and metamorphic rocks (70). Conversely, the bedrock geology of the Lake Michigan drainage is largely dominated by Paleozoic carbonate rocks and unconsolidated glacial materials (70). Table 2 illustrated the isotope differences between these two rock groups. In addition to geologic inputs, the distribution of $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ is affected by currents that transport sediment from north to south along the east and west shorelines of the lake (71). The currents converge in southern Lake Michigan and force sediment transport to deeper basins located near the central and southeastern parts of the lake (71).

Plots of $^{87}Sr/^{86}Sr$ with Ca/Sr and $\delta^{11}B$ with Ca/B showed that samples analyzed for this study were evenly distributed along mixing lines between silicate and carbonate-rock end members, indicating that the isotopic signatures are largely a result of mixed rock sources (Figures 5 and 6). The trend for lower $^{87}Sr/^{86}Sr$ and higher $\delta^{11}B$ to the south and with proximity to the shoreline indicates that the geologic sources

for shoreline sediments in southern Lake Michigan are carbonate bedrock and carbonate bearing glacial deposits (Figures 5 and 6). Although the majority of samples used to portray the regional distribution of $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ in southern Lake Michigan were collected during two discrete time periods 1988−1989 and 1995, the long-term controls on distribution are believed to be near steady state. This near steady-state condition allowed for a seamless interlacing of these two data sets that was not contradicted by data contouring.

Higher $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ in sediments from the Indiana shoreline, relative to elsewhere in southern Lake Michigan, provided evidence that slag-affected discharges might be locally altering the isotopic composition of bed sediments. Lake Michigan bed-sediment samples collected along the Illinois, Michigan, and Wisconsin shorelines had a more limited range and lower median value than the Indiana shoreline samples. Although the median $^{87}Sr/^{86}Sr$ in Indiana shoreline samples was higher than shoreline samples elsewhere in southern Lake Michigan, the values did not define a distinct subset of the data. The result is not surprising given that the $^{87}Sr/^{86}Sr$ in Indiana shoreline samples includes strontium from slag as well as sediment and water transported to the Indiana shoreline from elsewhere in the basin. A sampling strategy that targets areas where slag is believed discharging to Lake Michigan, rather than sampling transects at regularly spaced intervals along the shoreline, might result in a distinctly higher $^{87}Sr/^{86}Sr$ values in Indiana shoreline samples relative to elsewhere in the basin.

Decreasing values of $^{87}Sr/^{86}Sr$ in bed sediments with increasing distance from slag disposal sites, a trend not observed elsewhere in the basin, provided further support for the hypothesis that slag was affecting bed sediment composition along the Indiana shoreline (Figure 7). The $^{87}Sr/^{86}Sr$ in samples from seven transects oriented perpendicular to the Indiana shoreline and four transects perpendicular to the southwestern Michigan shoreline was compared. Plots showed that $^{87}Sr/^{86}Sr$ decreased with distance from the Indiana shoreline but generally increased with distance from the Michigan shoreline. The trends observed in the Indiana shoreline data were consistent with a source-plume relationship.

The uniquely high $\delta^{11}B$ values along the Indiana shoreline may be related to slag discharges. The Lake Michigan watershed is heavily industrialized in northwestern Indiana, and various manufacturers may be discharge boron to Lake Michigan. Boron is probably discharged to the lake by municipal wastewater-treatment facilities as well. As a result, $\delta^{11}B$ values along the Indiana shoreline likely represent a combination of sources. The transcendence of literature values for $\delta^{11}B$ in wastewater (+5 to +13‰) by three of seven Indiana shoreline samples, however, may indicate a source of boron related to slag.

The $\delta^{11}B$ was additionally high at three Illinois and Michigan shoreline sites, relative elsewhere in the basin. At two sites located offshore from Holland, MI and Waukegan, IL the $\delta^{11}B$ exceeded 10‰. The values may indicate that wastewater was influencing bed-sediment chemistry when samples were collected in 1988−1989 and 1995, respectively. A third area located southwest of St. Joseph, MI, included four values that exceeded 9‰ and two values greater than 11‰. A long-term depositional basin for Lake Michigan sediment exists in this vicinity, and the $\delta^{11}B$ values may indicate wastewater, slag, or other influences on bed sediment in 1988−1989.

The $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ data were used to estimate the amount of Indiana shoreline bed sediment affected by slag drainage. The estimates utilized only the data for samples collected in 2000−2001. Contour values delineating the extent of slag-affected sediment were selected where the non-
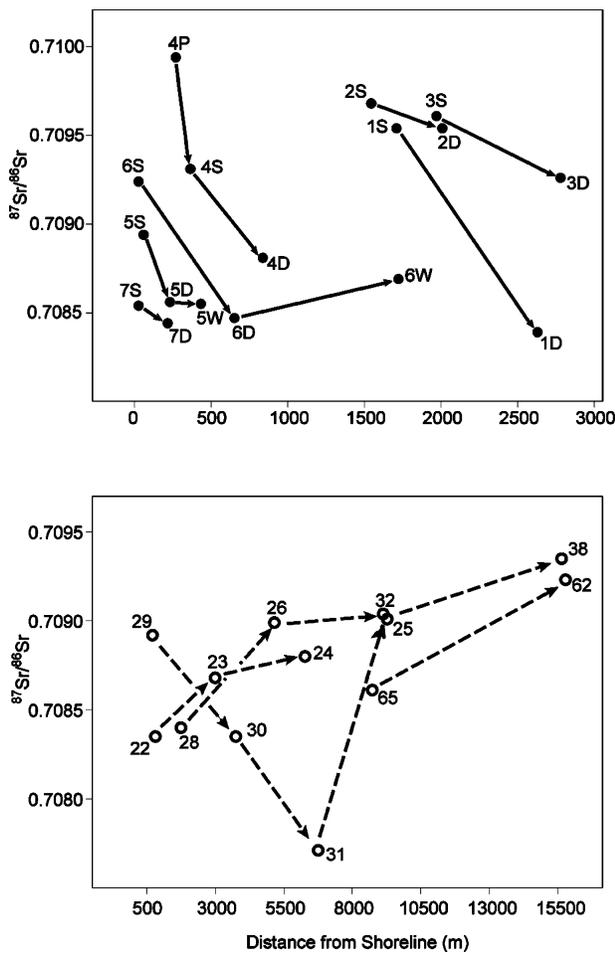
FIGURE 7. Plots showing $^{87}Sr/^{86}Sr$ with distance from shoreline for sample transects along the Indiana shoreline samples (●) and elsewhere in southern Lake Michigan (○). Values of $^{87}Sr/^{86}Sr$ along Indiana shoreline transects generally decreased with distance from shore but increased along transects elsewhere in southern Lake Michigan.

Indiana shoreline maximum $^{87}Sr/^{86}Sr$ and the maximum $\delta^{11}B$ for municipal wastewater were exceeded. Recognizing these assumptions, the areas of slag-affected sediments along the Indiana shoreline were estimated to range from 82 km² ($\delta^{11}B \geq 13^0/_{00}$) to 154 km² ($^{87}Sr/^{86}Sr \geq 0.70900$). These estimates were qualified by (1) scarcity of data, (2) the use of an arbitrarily selected contour value to define the boundary of the affected area, (3) possible inclusion of elevated $\delta^{11}B$ values generated by other sources of anthropogenic contamination, (4) inherent inaccuracies in the numerical methods used to contour the data and estimate the area of contour-delimited trapezoids, and (5) the premise that unique distributions of $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ are related to slag-affected discharges.

There is some evidence to indicate that the estimated areas of slag-affected sediments represent only an annual, rather than historical, accumulation. Studies have shown that there is no net annual accumulation of sediment in southern Lake Michigan between the Illinois–Wisconsin State line and the Indiana–Michigan State line (66). Episodic redistribution of sediments occurs annually in response to late-winter storms and spring ice break-up (71). During these events, huge quantities of Indiana shoreline sediments are resuspended and transported to long-term depositional basins located offshore from southwestern Michigan (66). Sediment scour to glacial-till units that underlay transient shoreline sediments has been described (71). This implies that a much larger quantity of sediment than was estimated herein, may have been historically effected by slag.

If $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ are useful tracers of slag-affected sediment, then a more significant question is whether isotope alterations infer chemical changes that could affect ecological habitats or human usability of the water resources. Previous studies have determined that sediments in contact with slag-affected groundwater have higher concentrations of most trace elements relative to control samples and indicate that the potential exists for chemical modification of lakebed sediments (1). Correlation coefficients of cation data collected for this study, however, did not indicate a strong relation between chemical concentration and distance from slag-disposal sites, as might be expected if slag were significantly affecting sediment chemistry. A complete chemical characterization of samples used in this investigation was beyond the intended scope of this project but represents an important step in assessing the environmental implications of slag discharges to southern Lake Michigan.

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