

THE COPPER, IRON, ZINC, MAGNESIUM, MANGANESE, AND CALCIUM CONTENT OF THE WESTERN BASIN OF LAKE ERIE¹

FRANK J. VARGA AND BRUNO J. KOLODZIEJ

Department of Microbiology, The Ohio State University, Columbus, Ohio 43210

ABSTRACT

Water samples from the western basin of Lake Erie were filtered to restrain suspended particles larger than 4 μm and were analyzed for copper, iron, zinc, manganese, magnesium, and calcium by atomic absorption spectrophotometry. Samples were collected at weekly intervals during July-August and with less frequency in September, October and November (1970). Mean seasonal and range of concentrations for elements considered did not vary with depth. Mean seasonal and range of concentrations for soluble elements from 4.5 m depth were ($\mu\text{g}/\text{ml}$): copper, 0.091 (0.04-0.20); iron, 0.284 (0.06-0.050); zinc, 0.087 (0.06-0.11); manganese, 0.039 (0.025-0.063); magnesium, 10.38 (6.54-13.54); and calcium, 35.78 (30.30-43.60). Solvent extracted elements from suspended particulates were present in mean seasonal and range of concentrations ($\mu\text{g}/\text{ml}$) for copper, 0.014 (0.003-0.038); iron, 0.550 (0.30-1.00); and zinc, 0.050 (0.020-0.150). Manganese content was below detectable limits, while magnesium and calcium were non-extractable. Except for calcium, the mean seasonal concentration varied for elements considered from those reported previously for either Lake Erie or for the western basin. A close association existed between the levels of soluble and particulate copper, iron and zinc.

Concentrations of copper, iron, zinc, manganese, magnesium and calcium were measured by atomic absorption spectrophotometry in water samples removed and filtered (0.45 μm pore size) from an area in the western basin of Lake Erie. The area was located between Rattlesnake, Middle, and South Bass islands (approximately 83°50' W; 41°40' N). Element content was determined on water samples taken from 0, 4.5, and 9.0 m depths. Values for calcium concentrations of Lake Erie date back to 1854 (Ayers 1962) and for calcium and magnesium concentrations to 1906-1907 (Beeton 1965). The conclusions reached by Beeton (1965) from available data spanning the years 1906 to 1959 were that calcium increased in concentration from 31 to 39 $\mu\text{g}/\text{ml}$ with eutrophication while magnesium was unaffected (9.0 $\mu\text{g}/\text{ml}$). The only values observed in the literature on trace metals copper, manganese and zinc concentrations of Lake Erie were those of Weiler and Chawla (1968). However, this latter work was concerned with water taken from a single depth and assayed for elements without any distinction between soluble and particulates suspended in it. It was our contention that suspended particulates would contribute to increased or decreased values of trace elements in Lake Erie. Hence, eutrophication would be associated with increases in particulates which, in turn, would influence the concentrations of trace metals at the time of analysis.

METHODS

All water samples were collected with a Kemmerer sampler and dispensed into scrupulously cleaned polypropylene jars. The samples were immediately cooled in ice. Within an hour, 750 ml of each sample were filtered through a 0.45 μm millipore filter. The filters containing the suspended particulate material were stored in polyethylene bags (at -20°C). The pH of the filtrate was adjusted to pH 3.5. This reduced cation adsorption by the inner surface of the container and deterred precipitation by auto-oxidation. All water samples were analyzed either the day of collection or stored at -20°C. All collecting jars were pre-cleaned with a concentrated nitric-sulfuric acid solution (1:1) and rinsed with double distilled (glass) water.

The concentrations of soluble and particulate copper, iron, zinc, manganese, magnesium and calcium were determined by a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer (AAS). These elements were present in the filtrate (soluble) in quantities detectable by the instrument. This eliminated the necessity of sample dilution or element concentration

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by organic solvent extraction. The atomic absorption spectrophotometer was calibrated for each element by diluting a standard stock solution (ARRO Scientific Laboratories, Inc.) in demineralized double distilled (glass) water. Specifications for the linear working range for each element was that described in Perkin-Elmer Analytical Methods for AAS (1966). A single hollow cathode tube (Perkin-Elmer Intensitron Lamp) was utilized for each element. In the determination of concentrations of calcium and magnesium, lanthanum oxide (Sigma Chemical Co.) was added to reduce chemical interference introduced by the presence of sulfates and phosphates. For these analyses, all water samples and standards were prepared to contain 2% La_2O_3 .

The particulates were prepared for element analysis by adapting the ammonium pyrrolidine dithiocarbamate (APDC)-methyl isobutyl ketone (MIBK) organic solvent extraction system of Brooks *et al.* (1967). Here APDC served as a chelating agent and MIBK as an extracting solvent. The filters were dried, weighed, and hydrolyzed with 6N HCl at 70°C for 1 hr (2 ml in 50 ml volumetric flask). After pH adjustment to 4.0 (6.0 N KOH), 2 ml APDC (Eastman Chemicals) were added and volume raised to 50 ml with MIBK (Fisher Scientific Co.). The instrument was calibrated with standards prepared by extracting 250 ml of 2 $\mu\text{g}/\text{ml}$ standard solution with 20 ml MIBK after the addition of 2 ml APDC. The solution was then extracted again with another 20 ml MIBK. The two combined MIBK extracts were raised to the 50 ml volume. The technique was not suitable for extraction of calcium and magnesium.

Visibility (turbidity) was measured by means of a standard Secchi disc suspended by a calibrated chain. Dissolved oxygen content was measured with a YSI-Model 54 oxygen meter equipped with probe number 5419. The probe was also equipped to measure temperatures. The pH was measured with a Corning Model 7 pH meter. Microscopic identification of blue-green alga within the bloom was made with a Nikon phase contrast microscope using phase dark-low-low objectives.

RESULTS AND DISCUSSION

In general, the concentrations of soluble calcium, copper, iron, magnesium, manganese and zinc in water from the collecting area did not fluctuate extensively with depth. Neither did the concentrations of particulate copper, iron and zinc. Undoubtedly, this was due to shallowness (avg. depth 10 m) and continuous circulation throughout the sampling period due to currents and wind action. Since element concentrations varied slightly with depth, only the 4.5 m values are presented (table 1). The mean seasonal concentration (MSC) for each element

TABLE 1
*The soluble copper, iron, zinc, calcium, magnesium, and manganese concentrations in 4.5 m depth water samples from western basin of Lake Erie**

Date (1970)	Cu	Fe	Zn	Ca	Mg	Mn
7/2	0.20**	0.50	0.11	43.60	10.06	—
7/17	0.17	0.37	0.06	23.38	6.54	—
7/24	0.12	0.28	0.08	33.50	10.00	—
7/31	0.04	0.06	0.20	37.50	11.10	0.025
8/7	0.06	0.34	0.07	39.30	11.70	0.043
8/14	0.04	0.34	0.06	36.50	11.48	0.063
8/21	0.04	0.31	0.06	30.30	10.08	0.029
8/28	0.08	0.27	0.06	35.25	6.83	0.044
9/11	0.06	0.20	0.07	33.30	11.50	0.055
9/25	0.09	0.36	0.09	33.80	10.75	0.050
10/23	0.12	0.28	0.09	39.00	12.10	0.047
11/9	0.08	0.25	0.10	43.25	13.54	0.055

*Samples collected from a single station.

**Data are in $\mu\text{g}/\text{ml}$.

at 0, 4.5, and 9.0 m depths over the entire sampling period was cited in table 2. The MSC for magnesium, copper, manganese, iron and zinc for Lake Erie differed from first values. The use of MSC for comparisons could be questioned since some of the previously reported data were not of seasonal sampling. Because of

this difference and the use of different analytical methods, variances between our and previously reported values for the same elements were anticipated. Also, Weiler and Chawla (1968) concluded from their studies on the chemical composition of Lake Erie that it was quite homogenous in content of various metal ions except for the western basin and certain areas close to the shore. Since the sampling area was within the western basin, this conclusion was taken into consideration.

TABLE 2
*The mean seasonal concentrations of soluble copper, iron, zinc, calcium, magnesium, manganese and particulate material in western basin of Lake Erie**

Element	Soluble			Particulate		
	0 m	4.5 m	9.0 m	0 m	4.5 m	9.0 m
Cu	0.106**	0.091	0.097	0.021	0.014	0.015
Fe	0.287	0.284	0.309	0.570	0.550	0.900
Zn	0.078	0.087	0.118	0.090	0.050	0.084
Ca	34.50	35.78	33.23	---	---	---
Mg	10.07	10.38	9.89	---	---	---
Mn	0.045	0.039	0.049	---	---	---

*Samples collected from a single station.

**Data are in $\mu\text{g/ml}$.

Beeton (1965) in his review on the eutrophication of the Great Lakes discussed the relationship between the concentration of magnesium and calcium during recent eutrophication of Lake Erie. The data cited were from a number of reports spanning the years 1907 to 1959. During this period the magnesium concentration averaged between 7.6 to 8.0 $\mu\text{g/ml}$. There were no apparent changes in magnesium concentrations during these years. With calcium the reverse was observed with progressive increases from 31 to 39 $\mu\text{g/ml}$. Subsequently, Kramer (1961) reported that the average magnesium concentrations of Lake Erie were 7.8 (mid-summer) and 8.8 $\mu\text{g/ml}$ (mid-autumn); and that the average calcium concentrations were 39.2 (mid-summer) and 37.1 $\mu\text{g/ml}$ (mid-autumn). Furthermore, Weiler and Chawla (1968) reported that the mean seasonal magnesium concentrations between the western, central, and eastern basin of Lake Erie were 7.6, 8.0, and 8.0 $\mu\text{g/ml}$, respectively; and for calcium they were 32.4–34.5, 38.3–39.1, and 38.3–40.9 $\mu\text{g/ml}$, respectively. Our data showed a mean seasonal magnesium concentration of 10.38 $\mu\text{g/ml}$ with a seasonal range of concentrations between 6.54 and 13.54 $\mu\text{g/ml}$. Also, a mean seasonal calcium concentration of 35.78 $\mu\text{g/ml}$ with a seasonal range of concentrations between 30.30 to 43.60 $\mu\text{g/ml}$. In this study, the values for magnesium are somewhat higher, and for calcium somewhat lower than those previously reported. These differences could be attributed to area of sampling, the use of mean seasonal concentration values for comparisons, or the precise analytical device utilized.

Our value for copper concentration of 0.091 $\mu\text{g/ml}$ differed from Weiler and Chawla's (1968) value of 0.012 to 0.015 $\mu\text{g/ml}$ for the western basin of Lake Erie. Both studies utilized identical analytical instrumentation; however, there was a difference in the analytical procedure. Our analyses for copper, iron, manganese, and zinc, did not include solvent extraction (Mulford, 1966) as utilized by Weiler and Chawla (1968). Therefore, we did not treat the water samples except for pH adjustment to avert element precipitation before analysis. In reference to manganese, the MSC was 0.039 $\mu\text{g/ml}$. This was somewhat higher than the 0.016 and 0.017 $\mu\text{g/ml}$ assessed by Weiler and Chawla (1968) for two stations, and somewhat lower than the 0.082 $\mu\text{g/ml}$ detected in a third station in the western basin. In relation to iron, the MSC was 0.284 $\mu\text{g/ml}$ with a seasonal range of con-

centrations between 0.060 and 0.500 $\mu\text{g}/\text{ml}$. Weiler and Chawla (1968) reported that the mean seasonal iron concentrations in water from three different stations in the western basin were 0.339, 0.320, and 0.419 $\mu\text{g}/\text{ml}$. The MSC of zinc was determined as 0.087 $\mu\text{g}/\text{ml}$, and showed an MSC of the western basin as 0.012–0.015 $\mu\text{g}/\text{ml}$.

This study included analysis of particulates restrained by millipore filtration. The MSC of copper, iron, and zinc extracted from particulates (from 4.5 m) were assessed as 0.014, 0.55 and 0.050 $\mu\text{g}/\text{ml}$, respectively (table 3). Manganese was

TABLE 3

*The particulate copper, iron and zinc concentrations from 4.5 m depth water samples from western basin of Lake Erie**

Date (1970)	Cu	Fe	Zn
7/2	0.011**	0.30	0.025
7/17	0.011	0.70	0.020
7/24	0.010	0.50	0.045
7/31	0.002	0.50	0.080
8/7	0.005	0.40	0.030
8/14	0.025	0.45	0.130
8/21	0.003	0.55	0.150
8/28	0.020	0.60	0.150
9/11	0.018	1.00	0.120
9/25	0.038	0.55	0.150
MSC***	0.014	0.55	0.050

*Samples collected from a single station.

**Data are in $\mu\text{g}/\text{ml}$.

***Mean seasonal concentration.

extractable by the procedure but could not be detected. No general relationships were noted upon considering the range of concentrations and depth of visibility cited in tables 1, 3 and 4, but minor associations were apparent. For example, particulate copper and zinc concentrations during the second month of sampling were twice the values obtained in the first month. Also, a bloom appeared during the weeks of August 7th and 14th 1970, and the phytoplankton associated with it

TABLE 4

Physical parameters associated with water sampling at 4.5 m depth.

Date (1970)	Visibility*	Bloom	Temperature**	pH	Oxygen***
7/2	1.20	none	21	8.30	—
7/17	1.00	none	23	8.20	—
7/24	0.75	none	23	8.45	—
7/31	3.00	none	24	8.60	8.4
8/7	1.50	yes	25	9.20	8.2
8/14	1.00	yes	25	8.90	8.0
8/21	1.00	none	26	8.50	6.5
8/28	1.20	none	23	8.60	8.7
9/11	0.60	none	21	8.55	7.8

*Meters (Secchi estimation).

**Degrees Centigrade.

***Parts per million dissolved oxygen.

was identified as *Microcystis* sp. The depth of visibility of the sampling area increased sharply to 3 m a week before the appearance of the bloom (7/31/70). This was associated with a decrease in concentrations of soluble copper and iron and in particulate copper. The presence of bloom was associated with an increase of soluble iron and manganese and with a decrease in calcium and zinc. Also evident was an increase in particulate zinc. The period immediately following bloom was associated with an increase in particulate copper and iron and with a decrease in soluble iron and magnesium. It was difficult to conclude from these data that any of these associations were solely in response to the bloom since the western basin was not a sterile system but one teeming with a variety of microflora and -fauna.

Our mean seasonal values of trace elements copper, iron, manganese, and zinc differed somewhat from those reported by Weiler and Chawla (1968); but these were anticipated. We were considering and comparing nanogram quantities; therefore, small increases or decreases of animate or inanimate material in an open water system such as Lake Erie would have an influence on concentrations of trace elements present in either soluble or particulate form.

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