9 Temporal Trends of Inorganic Elements in Kentucky Lake Sediments

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9.1 INTRODUCTION

Sediments are the ultimate reservoir for the numerous potential chemical contaminants that may be contained in effluents originating from urban, agricultural, and industrial lands and recreational activities [1–3]. Contaminated sediments in streams, rivers, lakes, and estuaries have the potential to pose ecological and human health risks [1,3]. Metals are a ubiquitous class of contaminants in aquatic sediments. Concentrations of certain metals such as cadmium, copper, nickel, lead, zinc, and other metals often are elevated above background levels in sediments that have been affected by human activity [4]. Earlier studies have correlated elevated concentrations of certain inorganic elements in sediments of rivers, estuaries, and coastal regions with increased industrial growth, agricultural operations, land use, etc. [5,6].

The sediment record, as revealed in sediment cores, has been used by many groups of investigators to reconstruct the history of contaminant input to reservoirs, lakes, rivers, and oceans throughout the world [7–9]. The basic assumptions are that contaminant inputs equilibrate relatively rapidly with sediment inputs and that the sediment column represents a continuous sequence, of sedimentation and associated contaminant accumulation. Using radiochemical chronologies, it is possible, theoretically, to date sediments over a period corresponding to the half-lives of two radiotracers: ^{210}Pb and ^{137}Cs. Ages can be assigned to different depth intervals within by use of the radiotracers. Reservoirs exhibit sedimentation rates that range from 10 to 200 mm/year [7]. Greater sedimentation rates convey several advantages to reconstructing temporal trends.

Although a large volume of literature exists on the levels and long-term trends of inorganic elements in sediments of natural lakes and coastal and oceanic environments, very limited information is available on the temporal trends of inorganic elements in manmade reservoirs or lakes. Reservoirs, particularly large river impoundments, are human-constructed ecosystems created and used for multiple purposes, including generation of hydroelectric power, water supply, flood control, transportation, and recreation. Therefore, the need to better understand the influence of human activities on these manmade ecosystems is obvious.

Kentucky Lake is the largest manmade lake in the southeastern U.S. (Figure 9.1). It is the ultimate repository of substances entering this watershed from portions of seven southeastern states, which include a sizable fraction of U.S. chemical processing, agricultural chemical products, and electronic manufacturing. Kentucky Dam tailwater, which connects the Ohio River, receives discharges from industries in the Calvert City Industrial Complex. During the past two decades, mass mortalities of mussels have been encountered in these regional waters; the causes have not been fully elucidated. In some cases, the quality and quantity of mussels harvested for the pearl industry have been substantially reduced [10].

Furthermore, a recent Public Advisory Committee Report [11] identified diminished air quality due to high levels of release of air pollutants from a variety of industries (chemical, metallurgical, and paper mills) in this region. Earlier studies have detected several metals and organics in sediments and freshwater mussel tissues collected from Kentucky Lake and Kentucky Dam tailwater [12,13]. These observations indicated the historical contamination of inorganic and organic pollutants in Kentucky Lake.

To the authors' knowledge, no comprehensive study has been conducted to describe historical contamination and trends of inorganic elements in this lake. This study measured the concentrations of chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), silver (Ag), cadmium (Cd), tin (Sn), antimony (Sb), lead (Pb), and mercury (Hg). It reconstructed the history of inorganic element input into Kentucky Lake over a 50-year period using the sedimentary record, as revealed in sediment core collected from Ledbetter embayment of Kentucky Lake.

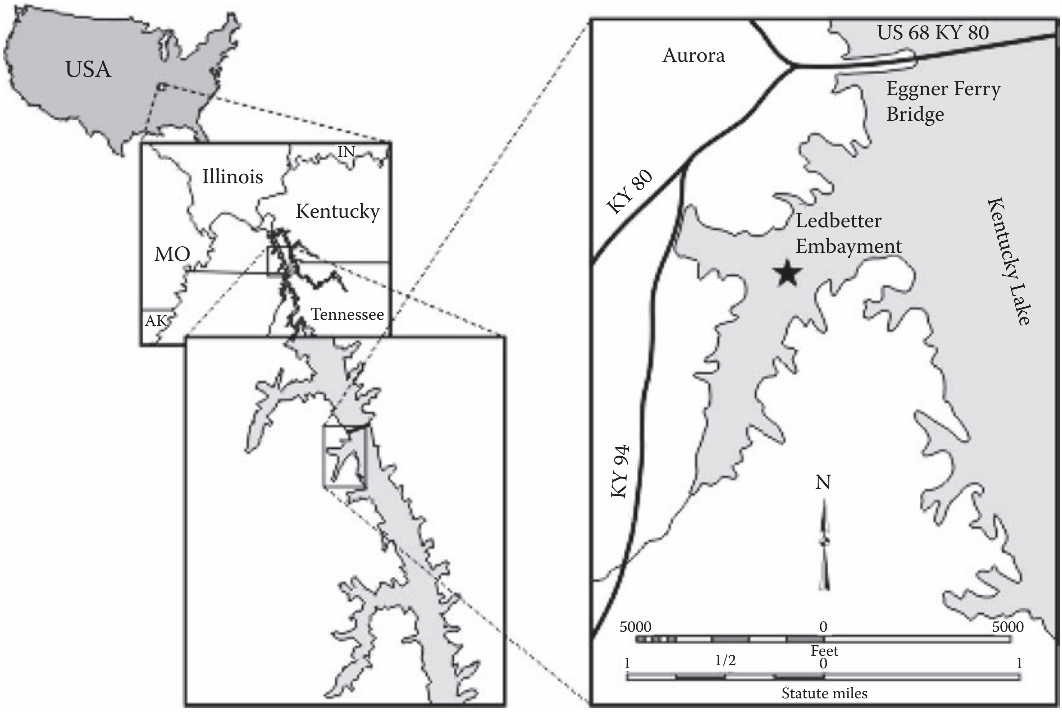

FIGURE 9.1 Map showing sediment core sampling location (* indicates sampling site).

9.2 SAMPLING AND ANALYSIS

The Ledbetter embayment of Kentucky Lake (Figure 9.1) was selected for this study. The sampling site (lat. 36° 45′ 02″ N; long. 88° 08′ 19″ W) in the Ledbetter embayment is situated apart from the mainstream of water current in Kentucky Lake so that the natural sedimentation process is not disturbed. The sediment core collected from this location should thus represent a continuous sequence of sedimentation and consequent accumulation of contaminants over the time frame of interest. A stainless steel inner liner (6 ft long and 2 in. in diameter) was used to collect the sediment core. The inner liner was inserted into a custom-made cast-iron sediment core sampler. It was pushed manually from a boat through the sediment under water to collect the sediment core. The sediment core collected was about 1 m long.

After collecting the sediment core, the inner liner was taken out of the core sampler and immediately transported to the laboratory. A stainless steel iron rod was used to push the sediment core out of the inner liner. The cores were cut into 5-cm sections and were collected in preweighed wide-mouth glass bottles. For chemical analysis, an aliquot of each core section was freeze-dried using a Freezone Freeze Dry System (model: 77535) for 60 h. Aliquots of each section were used for total organic carbon and radiochronological study.

9.2.1 CHEMICAL ANALYSIS

Sediment samples were digested with nitric, perchloric, and hydrofluoric acids. After digestion, the samples were analyzed for Cr, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, Sb, and Pb. The samples were analyzed using Fisons/VG Model PQII+ inductively coupled plasma-mass spectrometry (ICP-MS). Indium was used as an internal standard because it has a major isotope at mass 115, which is approximately in the middle of the mass range (0 to 240 amu). Also, its natural occurrence in environmental samples is negligible. The concentration of the internal standard was in the range of 10 to 100 times greater than the other analytes in the sample.

All standards and samples were spiked with the internal standard of known concentrations. The samples were concentrated or diluted so that all analytes were bracketed by the calibration standards. Each sample batch of 20 samples included one or more certified reference standards, matrix spike and matrix spike duplicate, and continuing calibration standards. Total mercury in sediment was determined by isotope dilution-cold vapor (ICPMS) as described by Smith [14]. The samples are spiked with an enriched ^{201}Hg isotope prior to microwave digestion with HNO_3. An aliquot of the digest was reduced with sodium borohydride and the resulting mercury vapor was swept into the torch of the ICPMS.

9.2.2 ORGANIC CARBON AND NITROGEN

The sample preparation for the organic carbon and nitrogen analysis in sediments was performed following the procedure described by Wong et al. [15]. The analysis was carried out using a CHN analyzer (Perkin Elmer Series II CHNS/O Analyzer-2400 Series II with Perkin Elmer Auto Balance-AD4). Blanks (tin cups), conditioning reagents (sulfamic acid; Perkin Elmer-N241-0501), and standards (CHN standard; acetanilide; organic analytical standard; 0240-121; C = 71.09%, H = 6.71%, O = 11.86%, and N = 10.38%) were run to meet the analytical quality control and quality assurance criteria. After every ten samples, a duplicate, a blank, and a standard were run to verify the instrumental quality control criteria.

9.2.3 RADIOCHRONOLOGY

An aliquot of each of the 5-cm sections of the sediment core from the Ledbetter embayment site were collected in preweighed glass beakers and weighed and dried in an oven at 60°C for 72 h. The activity of ^{210}Pb and ^{137}Cs within each sample was determined concurrently using two lowbackground, planar intrinsic germanium detectors, a computer-based multichannel analyzer, and Maestro-II analysis software [5]. The sediment accumulation rate was calculated by producing a depth profile of total ^{210}Pb activity within the sediment core. The calculated ^{210}Pb accumulation rate was verified using ^{137}Cs as a complementary radiotracer.

9.3 TEMPORAL TRENDS OF INORGANIC ELEMENTS

Table 9.1 shows the concentrations of various inorganic elements detected in different sections of the sediment core. Cr, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, Sb, Pb, and Hg were detected in all sections of the core sediment. Table 9.2 presents geochronology (ages) of different sections of core sediment up to 30 cm, percent organic carbon, and nitrogen contents.

Percent carbon and percent nitrogen ranged from 0.56 to 1.1 and 0.06 to 0.14, respectively. Among the various elements measured, Zn and Hg were found to be the highest (80 μg/g dry sediment) and lowest concentrations (0.02 μg/g dry sediment) detected in Ledbetter embayment core sediment, respectively. In general, Cr, Ni, Cu, Zn, and Pb concentrations in various sections of the core sediment were comparatively higher than As, Se, Ag, Cd, Sn, Sb, and Hg. Except for Pb, most elements measured showed elevated concentrations in the surface sediments and the concentrations decreased with depth up to 25 to 30 cm and then maintained a fairly steady state up to 110 cm.

Inorganic elements accumulate naturally in riverine sediments, associated with clays and other debris carried into the river. Because natural metal inputs are relatively constant, changes in metal concentrations are generally due to human activities [5]. Several investigators [16–19] have used aluminum as a proxy for the concentrations of aluminosilicate minerals. For natural sediments, the concentrations of metals covary with the concentrations of aluminum, thus providing a tool (Al) to normalize the results of metal analysis to identify natural and anthropogenic enrichments. In this study, Al was not determined; therefore, Al normalization could not be done. However, metals such as Cr, Ni, Cu, Sn, and As exhibited relatively higher concentrations in the surface sediments (0 to 5cm = years: 2000.6 to 1986.3) and the concentrations decreased with increasing depth (25 to 30 cm = years: 1929.2 to 1914.9). Then, a steady state was present in the deeper sections up to 110 cm (Table 9.1 and Figure 9.2). Age determination was not done for core sections below 30 cm.

The trends revealed relatively increased input of these chemicals from the early 1900s to 2000. However, Pb showed a gradual declining trend from the early 1970s to 2000 (Figure 9.2). Pb and Zn have been used by humans for a variety of purposes throughout the 19th and 20th centuries [20]. Point source inputs pf Pb and Zn to aquatic systems (streams, lakes, and reservoirs) include industrial effluents, municipal wastewater effluents, and fossil fuel combustion [21].

From 1950 to the 1970s, automobile use increased in response to economic and population growth, and the predominant source of Pb became automobile exhaust emission of tetraethyl Pb [22]. Population growth has continued to the present, but Pb concentrations have declined slowly, probably due to the removal of leaded gasoline. Temporal trend of Pb in Ledbetter embayment clearly reflected the use pattern. Similar trends were also reported by Callender and Rice [20]. Environmental Zn concentrations remained elevated, probably because of lack of specific regulatory actions regarding Zn [20].

Surface sediment (0 to 5 cm) metal concentrations represent current input of contaminants. Most of the new anthropogenic Pb and Zn additions to the environment may come from material sources. Pb is used in paper, plastics, and ceramics [23]. Zn is used in most commercial metal products, including brass, bronze, castings, and galvanized metal and is added during the manufacture of automobile tires, in the form of zinc oxide (ZnO), as an accelerator in the vulcanization process [24].

In addition, Zn is a common contaminant in agricultural and food wastes. Fossil fuel combustion is the main contributor to worldwide anthropogenic emissions of Zn [25]. Furthermore, atmospheric deposition of Pb, Zn, and other elements cannot be ruled out. Baker et al. [26] reported a number

TABLE 9.1
Inorganic Element Concentrations in Various Sections of a Sediment Core Collected at Ledbetter Embayment of Kentucky Lake, U.S.

Sample depth (cm)	Chromium (μg/g)	Nickel (μg/g)	Copper (μg/g)	Zinc (μg/g)	Arsenic (μg/g)	Selenium (μg/g)	Silver (μg/g)	Cadmium (μg/g)	Tin (μg/g)	Antimony (μg/g)	Mercury (μg/g)	Lead (μg/g)
0–5	46.9	20.4	19.2	79.9	3.80	0.46	0.20	0.25	1.33	0.70	0.11	21.3
5–10	46.1	19.4	18.1	75.6	3.43	0.64	0.27	0.26	1.55	0.71	0.14	22.8
10–15	45.7	18.0	17.4	70.7	3.11	0.51	0.20	0.24	1.18	0.53	0.17	23.2
15–20	43.1	17.4	16.1	68.6	2.99	0.54	0.19	0.21	1.01	0.50	0.21	22.5
20–25	40.2	16.4	15.7	62.6	3.04	0.46	0.22	0.17	1.37	0.59	0.11	20.1
25–30	80.2	13.7	13.4	48.9	2.71	0.41	0.20	0.10	1.02	0.51	0.05	17.1
30–35	50.9	11.9	11.8	41.0	2.43	0.28	0.17	0.07	0.74	0.34	0.02	15.6
35–40	33.0	12.2	11.8	40.1	2.71	0.45	0.16	0.07	0.61	0.33	0.02	15.6
40–45	30.6	11.2	10.7	37.1	2.40	0.43	0.14	0.06	0.53	0.30	0.02	14.6
45–50	29.6	11.7	10.4	36.9	2.55	0.29	0.18	0.06	0.64	0.31	0.02	14.6
50–55	34.9	13.7	12.8	44.1	2.98	0.61	0.15	0.06	0.57	0.29	0.02	16.5
55–60	28.0	12.2	10.6	38.7	2.46	0.39	0.13	0.05	0.54	0.31	0.02	14.4
60–65	27.2	12.7	10.2	38.4	2.16	0.42	0.09	0.05	0.23	0.21	0.02	14.3
65–70	76.8	12.7	10.8	39.7	2.18	0.40	0.14	0.05	0.37	0.30	0.02	15.0
70–75	25.5	11.5	9.8	36.3	2.17	0.37	0.13	0.04	0.33	0.20	0.02	13.2
75–80	23.1	9.8	8.6	35.3	2.00	0.28	0.13	0.04	0.43	0.29	0.02	11.3
80–85	24.9	11.1	9.5	36.8	2.07	0.53	0.10	0.04	0.30	0.28	0.02	12.2
85–90	29.5	11.5	11.1	40.4	2.37	0.63	0.17	0.04	0.67	0.29	0.02	13.6
90–95	29.2	11.2	11.1	39.1	2.45	0.52	0.17	0.03	0.63	0.36	0.02	13.7
95–100	30.5	10.9	10.7	39.9	2.53	0.43	0.13	0.03	0.48	0.32	0.02	14.2
100–105	31.0	10.1	9.9	35.0	2.32	0.41	0.10	0.02	0.31	0.23	0.02	13.1
105–110	30.1	9.5	8.7	33.6	2.24	0.39	0.09	0.02	0.23	0.20	0.02	12.5

TABLE 9.2
Total Organic Carbon, Nitrogen, and C/N Ratio in Selected Sections of a Sediment Core from Ledbetter Embayment, Kentucky Lake

Sample ID	Depth (cm)	Year	Percent carbon	Percent nitrogen	C/N ratio
LE 0–5	0–5	2000.6–1986.3	1.10	0.14	7.86
LE 5–10	5–10	1986.3–1972	0.84	0.09	9.33
LE 10–15	10–15	1972–1957.7	0.65	0.06	10.83
LE 15–20	15–20	1957.7–1943.4	0.63	0.06	10.5
LE 20–25	20–25	1943.4–1929.2	0.62	0.06	10.33
LE 25–30	25–30	1929.2–1914.9	0.56	0.06	9.33

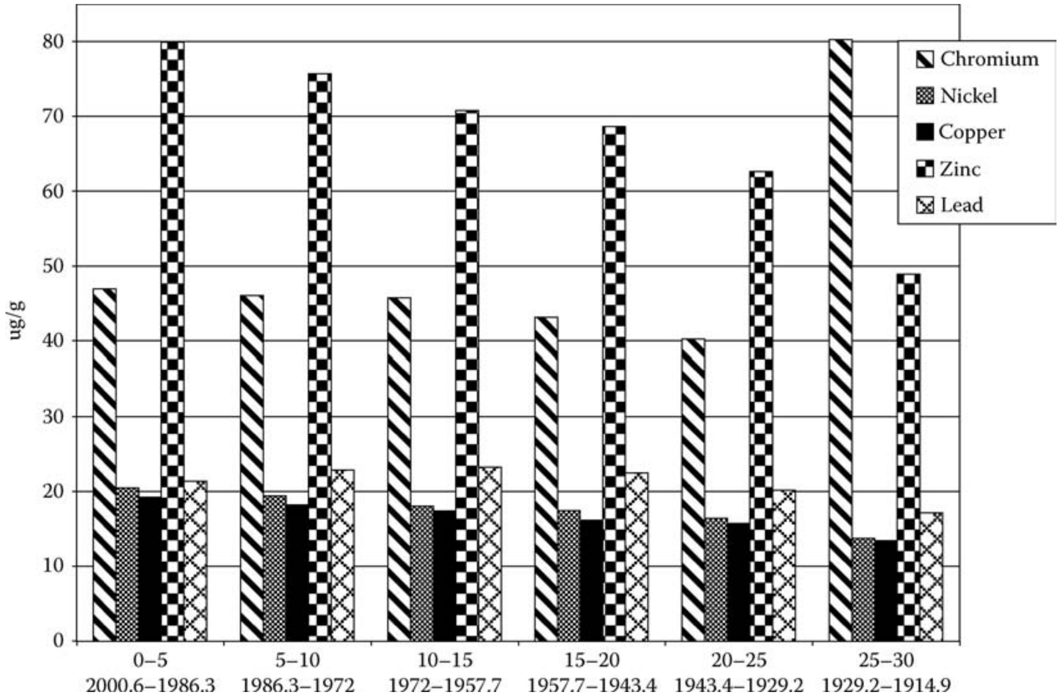

FIGURE 9.2 Temporal trends of selected inorganic elements in sections of a core sediment collected from Ledbetter embayment of Kentucky Lake, U.S.

of elements (Al, As, Br, Cd, Cu, Fe, Mn, Ni, Pb, S, Se, and V) including significant amount (over 10 μg/m^3) of Zn in aerosol particles and over 1.5 μg/L Zn in precipitation samples collected at the three Chesapeake Bay Atmospheric Deposition Study sites in 1991 and 1992.

9.4 CONCLUSIONS

Very few studies have reported temporal trends of inorganic elements in an aquatic ecosystem constructed by humans. Vertical profile of inorganic elements in Ledbetter embayment of Kentucky Lake revealed increasing accumulation of Cr, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, Sb, and Hg from the 1900s to the present. Pb has showed a gradual declining trend in recent years. In general, the profiles of the inorganic elements reflected production and usage trends of the respective chemicals.

Although the elemental concentrations of Ledbetter sediments do not seem to affect the living resources negatively, continued monitoring of theses elements is essential in order to prevent further contamination and harmful effects.

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