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Holocene Record of Major and Trace Components in the Sediments of an Urban Impoundment on the Mississippi River: Lake Pepin, Minnesota and Wisconsin

Open-File Report 2009–1238

U.S. Department of the Interior
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Cover photograph of Lake Pepin. Today Lake Pepin is wide spot on the Mississippi River, but the sediments beneath the lake contain a 10,600 year history of climatic and environmental change.

Holocene Record of Major and Trace Components in the Sediments of an Urban Impoundment on the Mississippi River: Lake Pepin, Minnesota and Wisconsin

By Walter E. Dean

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Holocene Record of Major and Trace Components in the Sediments of an Urban Impoundment on the Mississippi River: Lake Pepin, Minnesota and Wisconsin

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Abstract

Lake Pepin is a natural impoundment formed by damming of the Mississippi River about 9,180 radiocarbon years ago (10,600 calendar years) by an alluvial fan deposited by the Chippewa River, a tributary of the Mississippi in Wisconsin. Unique among 26 Mississippi River impoundments, Lake Pepin has stratigraphically preserved Holocene materials, including pollutants, that have been transported down the Mississippi. This natural Holocene record can then be compared to changes that have occurred since European settlement (ca. AD 1830), and since enactment of clean air and water legislation. The most immediate response to settlement in the sediments of Lake Pepin was an increase in bulk-sediment accumulation rate. This was accompanied by gradual increases in concentrations of phosphorus (P), and organic carbon (OC), followed by dramatic increases in these elements beginning about 1940. The increase in P was far greater than any of the minor fluctuations in P that occurred throughout the Holocene, but the increase in OC was comparable to an increase in OC that occurred in the mid-Holocene. The concentrations of several metals (for example, cadmium [Cd], and lead [Pb]) also are elevated in recent sediments. Increased Cd concentrations lasted only about two decades during the industrial era between World War II and the enactment of clean water standards in the 1970s. Increased Pb emissions, on the other hand, occurred over more than 100 years, first from burning of coal and smelting of lead ores, and then, beginning in the 1930s, burning of leaded gasoline. Concentrations of Pb in the sediments of Lake Pepin decreased to about two times preindustrial levels within a decade of enactment of unleaded gasoline restrictions.

Introduction

As the Laurentide ice sheet in Canada began to melt at the end of the last glaciation, many proglacial lakes formed along the southern margin (Teller, 1985; 1987). One of the largest of these was Lake Agassiz in eastern North Dakota, northwestern Minnesota, and adjacent Canada with an embayment down the valley of the present Red River of the North (fig. 1). Drainage from Lake Agassiz initially flowed southward down the Minnesota River valley as glacial River Warren beginning about 11.6 ka (Wright and others, 1998; Blumentritt and others, 2009). By about 9.5 ka, the ice sheet had retreated far enough that Lake Agassiz was able to drain eastward into Lake Superior, thence through the other Great Lakes into the Gulf of St. Lawrence. At that time, the combined flow down the Minnesota-Mississippi River system, augmented by flow down the St. Croix River, was much reduced and could not transport the sediment delivered by tributary streams. As a result, alluvial fans segmented

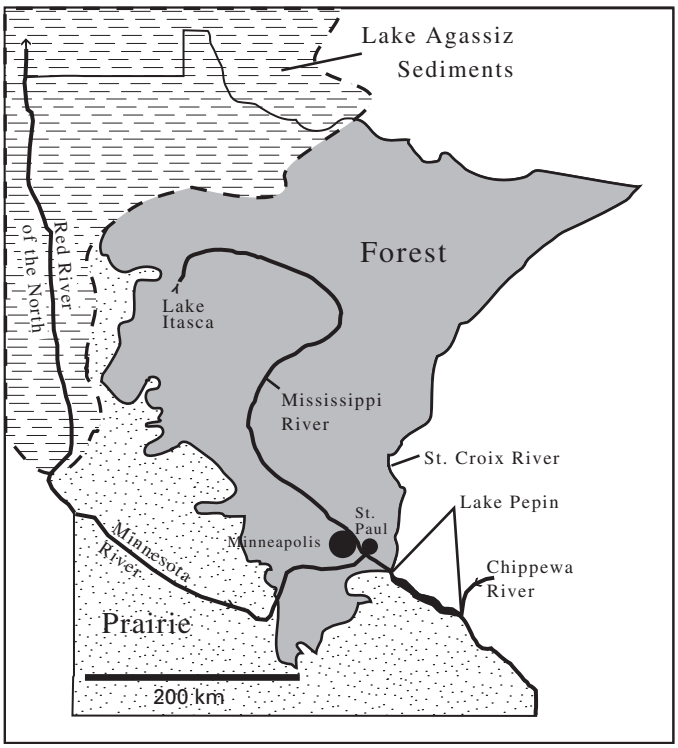

Figure 1. Lake Pepin relative to the Mississippi, Chippewa, and Minnesota Rivers; extent of sediments deposited in glacial Lake Agassiz; and present forest/prairie border.

portions of the valley, forming long riverine lakes (Wright and others, 1998; Blumentritt and others, 2009). One of these lakes formed by an alluvial fan created by the Chippewa River entering the Mississippi from Wisconsin was Lake Pepin, which forms the boundary between Minnesota and Wisconsin (fig. 1).

The Mississippi River at the outlet of Lake Pepin has been modified somewhat by dredging for navigation, and the lake is considered one of the 26 navigation pools along the Mississippi from St. Paul to St. Louis (Meade, 1995). However, Lake Pepin is unique among these navigation pools in that it has a 9.2-ky lacustrine sedimentary history (Wright and others, 1998).

Lake Pepin receives water from three rivers: the Minnesota, the upper Mississippi, and the St. Croix (fig. 1), with a total catchment of 122,000 km^2 and a maximum depth of about 8.5 m (Balogh and others, 1999). Kelly and others (2006) estimated that 82 percent of the 876,000 Mg yr^{-1} sediment load to Lake Pepin is delivered by the Minnesota River draining farmland in southwestern Minnesota, and only 18 percent from the Mississippi and St. Croix Rivers combined.

A total of 25 short cores (most 2–4 m long) were collected along five transects (fig. 2) to investigate the whole-basin recent history of nutrient loading to the Mississippi (Engstrom and others, 2009). These cores were dated and stratigraphically correlated using ^{210}Pb, ^{137}Cs, magnetic susceptibility, pollen analysis, and loss-on-ignition data. In this paper, I present analytical data for one of these cores (core 3 on transect II; II-3, fig. 2). A core collected by H.E. Wright, Jr., from the center of Lake Pepin opposite Lake City, Minnesota, recovered 16 m of lacustrine sediment with a bottom age of 9180 ± 70 radiocarbon years (10,600 calendar years) (Wright and others, 1998; Blumentritt and others, 2009), which marks the beginning of Lake Pepin. In 1997 a 12-m-long Livingstone piston core (P97) was collected off Lake City, Minnesota in the deepest part of transect III (Brachfeld, 1999; fig. 2). A depth-age model for P97 was constructed using a combination of radiocarbon dates and correlation of magnetic secular variation curves with those from Lake St. Croix (Lund and Banerjee, 1985). This age model showed that the base of the 1997 core was 7000 radiocarbon years old (Brachfeld, 1999; Brachfeld and Banerjee, 2000).

Analytical Methods

Samples were analyzed for weight percentages of total carbon (TC) and total inorganic carbon (TIC) using a carbon-dioxide coulometer (Engleman and others, 1985). Percent organic carbon (Corg) was calculated as the difference (TC – TIC), and percent $CaCO_3$ was calculated as

$$CaCO_3 = TIC/0.12,$$

where 0.12 is the mole fraction of carbon in $CaCO_3$. The accuracy and precision of this method, determined from hundreds of replicate standards, usually are better than 0.10 wt percent for both TC and TIC.

Samples were analyzed for 40 major, minor, and trace elements by inductively coupled, argon-plasma, atomic emission spectrometry (ICP–AES) by SGS Laboratories, Toronto, Canada. Rock standards (USGS) were included with the

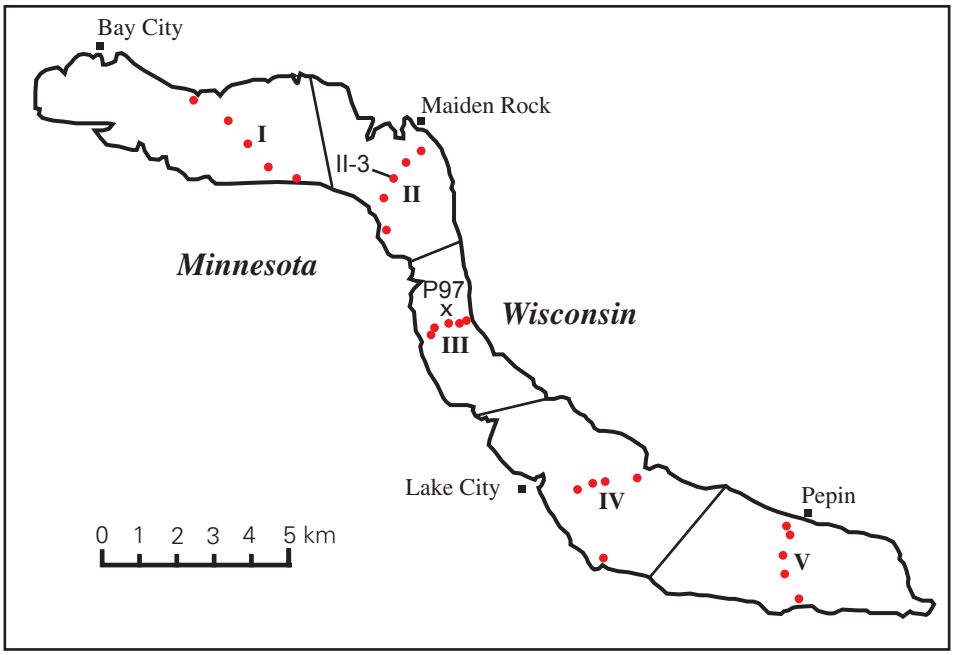

Figure 2. Lake Pepin core sites and depositional regions.

sediment samples, and 10 percent of the samples were duplicated. The precision, determined by analyzing rock standards and duplicate sediment samples, is better than 10 percent, and usually is better than 5 percent, at a concentration of ten times the limit of detection. Analytical results for core II-3 are given in table 1, and for core P97 in table 2.

Pyrolysis of organic matter was performed using a Rock-Eval pyrolysis instrument. The Rock-Eval pyrolysis method provides a rapid determination of the hydrocarbon type and abundance in sediments and sedimentary rocks (Tissot and Welte, 1984). Programmed heating of a sample in a helium atmosphere results in generation of hydrocarbons and CO_2. The hydrocarbons generated are measured with a flame ionization detector, and the CO_2 yield is monitored by a thermal conductivity detector. The yield of free or adsorbed hydrocarbons is determined by heating the sample in flowing helium 250°C, and is recorded as the first characteristic peak on a pyrogram (S1; mg HC/g sample). The S1 peak is roughly proportional to the content of organic matter that can be extracted from the rock or sediment with organic solvents. A second peak is composed of pyrolytic hydrocarbons (HC) generated by thermal breakdown of kerogen as the sample is heated from 250°C to 550°C (S2, mg HC/g sample). The data are expressed in terms of a hydrogen index (HI) in which the S2 peak is normalized to the OC content of the sample (mg HC/g OC). The HI is essentially equivalent to an H/C ratio.

Stable-carbon isotope ratios were determined using standard techniques (Dean and others, 1986). Powdered samples for carbon-isotope determinations of organic carbon were oven dried at 40°C and reacted with an excess of 0.5N HCl for 24 hours to dissolve carbonate minerals. The washed residue from each sample was combusted at 1,000°C under oxygen pressure in an induction furnace. The resulting CO_2 was dehydrated and purified in a high-vacuum gas-transfer system. All carbon-isotope ratios in the purified CO_2 were determined using an isotope-ratio mass spectrometer. Results are reported in the standard per mil (‰) δ-notation relative to the Vienna Pee Dee belemnite (VPDB) marine-carbonate standard,

$$\delta^{13}C\ ‰ = [(R_{sample}/R_{VPDB}) - 1] \times 10^3,$$

where R is the ratio (^{13}C:^{12}C). Analytical precision of these analyses is ±0.2‰.

Analytical results for HI and $\delta^{13}C$ in samples from core II-3 are given in table 3. Analytical results for $\delta^{13}C$ in samples from core P97 are given in table 4.

Anthropogenic Changes

Whole-basin studies of Lake Pepin based on 25 short cores show that bulk-sediment loading to Lake Pepin from the Mississippi River has increased by an order of magnitude since European settlement and land clearing beginning in 1830 (Engstrom and others, 2009). Although gradual increases in nutrient and sediment inputs began with European settlement, the most dramatic changes have occurred since 1950. This can be seen clearly in figure 3 (A–D) in the mass accumulation rates (MARs) and concentrations of P, OC, Cd, and Pb. Similar patterns can be seen for concentrations of other trace metals such as silver (Ag), copper (Cu), nickel (Ni), vanadium (V) and zinc (Zn) (fig. 4). Profiles of eight trace metals, including Cd and Pb, are presented by Balogh and others (2009) for 10 of the 25 cores collected by Engstrom and others (2009).

The slow initial increase in P-loading to the sediments of Lake Pepin is related to land clearing and increased erosion beginning in the 1830s. Sediment loading to Lake Pepin has increased by an order of magnitude, and P accumulation has increased 15-fold since 1830 (Engstrom and others, 2009). The increase in OC at the same time is likely the result of a combination of increased influx of terrestrial organic matter and increased autochthonous algal productivity stimulated by increased nutrient loadings (cultural eutrophication). An increase in Rock-Eval hydrogen index (HI in g hydrocarbons per g OC) from 100 in sediments deposited about 1880 to 250 in sediments deposited about 1990 (table 3) indicates an increase in H-rich, algal organic matter. This conclusion is supported by a decrease in the ratio of OC to nitrogen over the same period from 10.5 to 8.2. However, the stable-carbon isotopic composition of organic matter became enriched in ^{13}C ($\delta\ ^{13}C$ increased from –28.2 ‰ to –26.7 ‰ (table 3; fig. 4E) suggesting a greater influx of terrestrial organic matter. For reference, the most algal-rich surface sediments in Minnesota lakes have $\delta\ ^{13}C$ values of about –29 ‰ to –31 ‰ (Dean and Stuiver, 1993; Dean, 2006), similar to values in Eocene algal-rich, lacustrine Green River oil shale (Dean and Anders, 1991). Values of $\delta\ ^{13}C$ in C4 plants, such as prairie grasses, are usually around –10 ‰ to –20 ‰ (O'Leary, 1988; Cerling and Quade, 1993).

The effects of cultural eutrophication (increased algal organic matter) in the post World War II decades of industrialization, urbanization, and population growth are clearly shown by the significant increases in MARs of P and OC during the 1950s and 1960s (figs. 3A and B). The effects of the Clean Water legislation in the1970s and through the 1980s, which prompted improved wastewater treatment (Engstrom and others 2009), are shown by the dramatic decrease in P MAR and the less dramatic decrease in OC MAR.

The loading of Cd to rivers and lakes is almost entirely due to influx of industrial wastes. Historically, Cd has been used as a protective coating on iron and steel, as a brightener in paint, and, most recently, in Ni-Cd batteries. Following the Clean Water Act, the use of Cd in industrial products decreased markedly. Improved wastewater treatment also resulted in reduction of discharges of many metals (Balogh and others, 2009). Today, Cd is used mainly in Ni-Cd batteries, and there are vigorous recycling programs for these batteries. As a result, the high Cd concentration in the sediments of Lake Pepin lasted only about 20 years, and serves as a distinctive industrial marker (fig. 3C), as does that of Ag (fig. 4).

Whereas the Cd story is clearly related to industrial wastes entering rivers and lakes directly, the Pb story is more

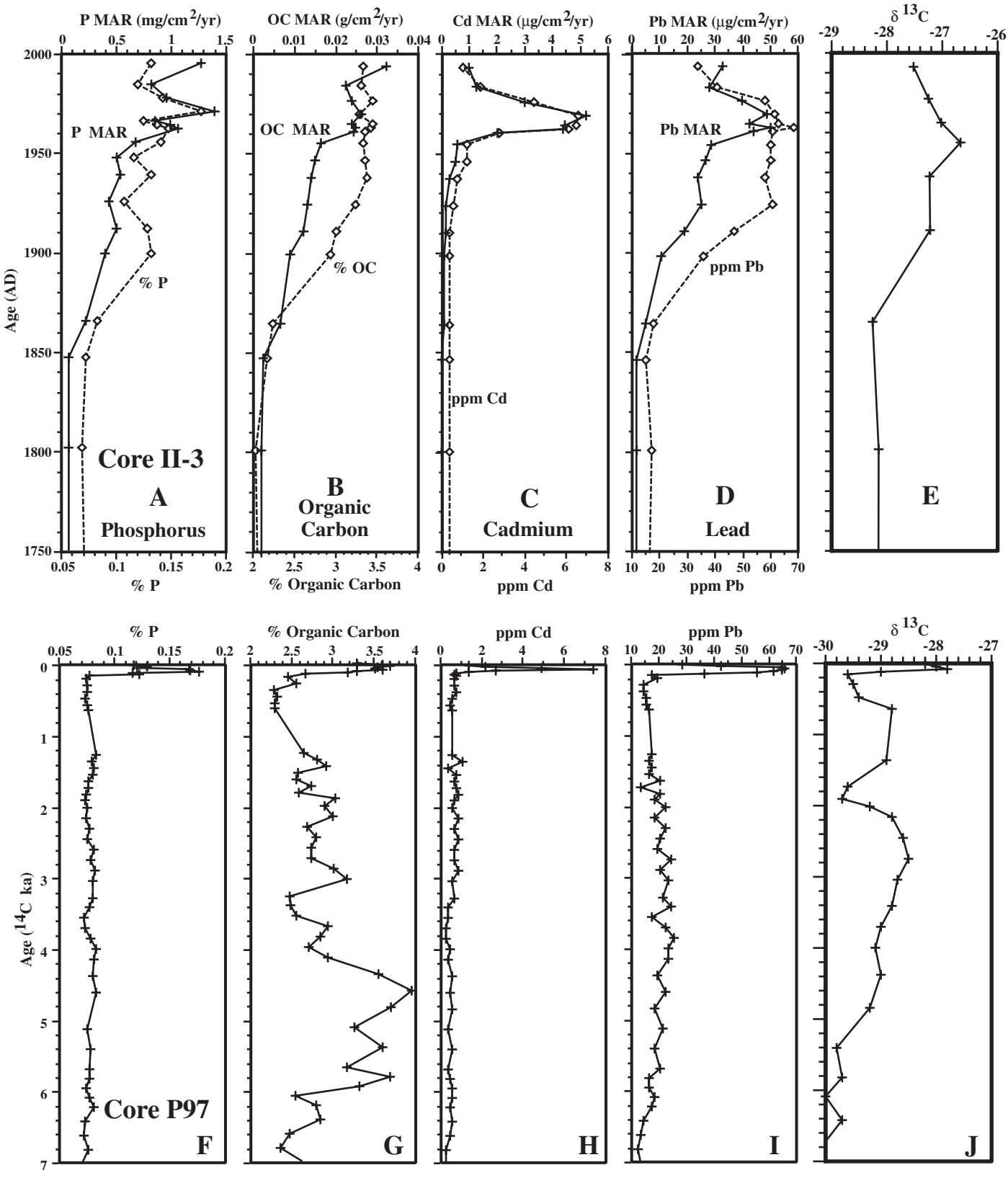

Figure 3. Profiles compared to time of concentrations and mass accumulation rates (MAR) of (A) phosphorus (P), (B) organic carbon (OC), (C) cadmium (Cd), and (D) lead (PB); and (E) values of $\delta^{13}C$ in samples from short core II-3 from Lake Pepin. Profiles compared to time of concentrations of (E) P, (F) OC, (G) Cd, and (H) Pb; and (J) values of $\delta^{13}C$ in samples from long core P97 from Lake Pepin.

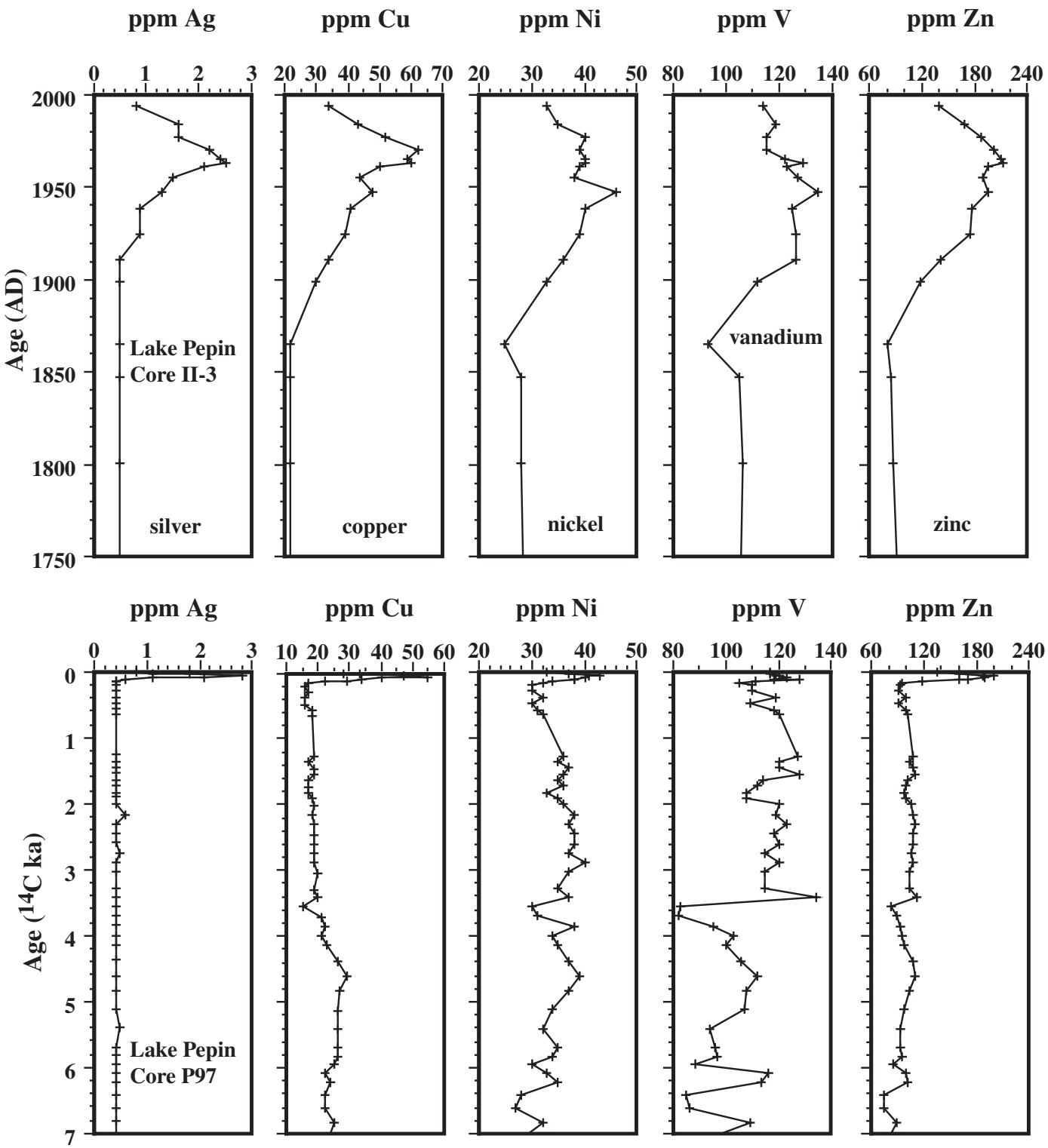

Figure 4. Profiles compared to time of concentrations of silver (Ag), copper (Cu), nickel (Ni), vanadium (V), and zinc (Zn)) in samples from short core II-3 and long core P97 from Lake Pepin.

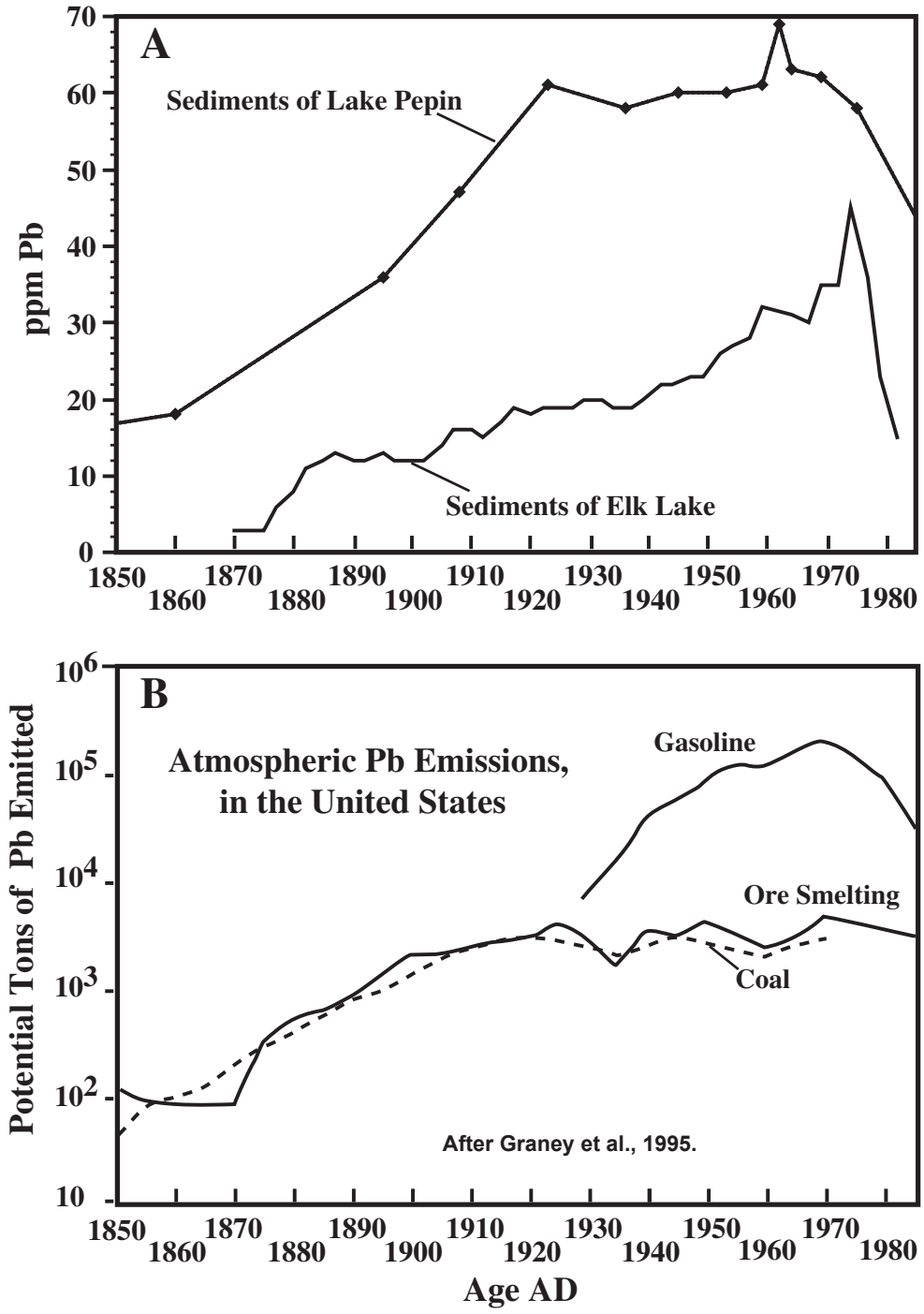

Figure 5. Concentrations of lead in sediments in Lake Pepin and Elk Lake, Minnesota, deposited since 1850 (A); calculated amount of lead emitted from various sources to the atmosphere over the United States since 1850 (B).

complex. The concentration of Pb in sediments of Lake Pepin deposited since 1850 is replotted at a different time scale in figure 5A along with the Pb concentration in the annually laminated (varved) sediments of Elk Lake, northwestern Minnesota (Dean, 1993). Elk Lake is located in forested Itasca State Park, and its outlet enters Lake Itasca, the designated headwaters of the Mississippi River (fig. 1). As part of their study of the Pb-isotope signature on Pb loadings to the sediments of lakes in the Great Lakes region, Graney and others (1995) calculated the potential emissions of Pb to the atmosphere in the United States from 1850 to 1985. Their results are shown in figure 5B. The slow increases in Pb emissions between 1850 and 1930 were due to increased burning of coal and increased ore smelting. The introduction of leaded gasoline in the1930s resulted in an increase in Pb emissions by several orders of magnitude. All of these increases in atmospheric Pb emissions are reflected in the concentrations of Pb in sediments of Lake Pepin and Elk Lake. This indicates that Pb enters the waters and sediments of rivers and lakes through the atmosphere. The slow decline in atmospheric Pb emissions following the restriction of leaded gasoline, mandated by the Clean Air Act of 1970, is reflected in remarkably sharp decreases in Pb concentrations in lake sediments to 1900 levels (in Elk Lake) within one decade (fig. 5A). The decrease in Pb concentration in the sediments of Lake Pepin continued into the 1990s (fig. 3D) to concentrations that are about twice those in sediments deposited prior to 1830 (Balogh and others, 2009).

The mercury (Hg) profile in Lake Pepin sediments looks much like that of Pb, with a gradual increase from less that 50 ppb in sediments deposited in 1850 with maximum values in sediments deposited during the 1950s and 1960s, decreasing during the 1970s based on data from 10 of the cores collected by Engstrom and others (2009) (Balogh and others, 1999; 2009). As with Cd and other metals, some of this decrease in Pb is due to improved wastewater treatment. That this is a regional signal delivered by the atmosphere is indicated by similar anthropogenic increases in Hg in the sediments in most of the 55 lakes studied by Engstrom and others (2007).

Sediments from Elk Lake, Minnesota show a similar anthropogenic increase in Hg, increasing from 55 ppb in sediments deposited during 1860 to a peak of 200 ppb in 1970 (Cannon and others, 2004), similar to Hg profiles in 55 lakes in the Itasca region studied by Engstrom and others (2007). I do not have Hg analyses in Holocene sediments in core P97, but in Elk Lake high concentrations of Hg also occur in mid-Holocene sediments with a peak of 340 ppb in sediments deposited at 8 cal ka, the start of extreme windy conditions that mark the beginning of the prairie period in Minnesota (Dean and others, 2002).

Holocene Changes

As shown in figure 3F, the recent increase in P concentrations in the sediments of Lake Pepin is clearly unprecedented in the past 7,000 years. However, the OC contents of sediments deposited in Lake Pepin during the mid-Holocene (6–5 ka) were as high or higher than in sediments deposited during the last 50 years (fig. 3G). This is probably due to an increase in the influx of terrestrial organic matter during the mid-Holocene "prairie period" in Minnesota when the prairie-forest border migrated at least 100 km east of its present position (Whitlock and others, 1993). At the base of the core, values of $\delta\,^{13}C$ are about 30 ‰ (fig. 3J), similar to values of algal-rich surface sediments from Minnesota lakes (Dean and Stuiver, 1993), then slowly increase during the prairie period due to the increase of more ^{13}C-enriched prairie vegetation.

The "industrial spike" in Cd concentration in the sediments of Lake Pepin, like the more gradual and still present increase in P concentration, is unprecedented in the past 7,000 years. Concentrations of Pb are slightly elevated in sediments deposited between 6 and 2 ka (fig. 3I), but not as high as in sediments deposited during the last century. However, concentrations of Ni and V in mid- to late Holocene sediments in Lake Pepin are comparable to those deposited during the 1990s (fig. 4). The concentrations of Pb, Ni, and V in Holocene sediments of Elk Lake, Minnesota are as high or higher than those in 20th century sediments (Dean, 1993).

Conclusions

The mass accumulation rates of P and OC in the sediments of Lake Pepin have increased more than 15 times since AD 1830, and most of these increases have occurred since 1950. The Cd concentration in the sediments increased dramatically due to industrial contamination to the Mississippi River after World War II, but decreased after 1970 in response to the Clean Water Act. The concentration of Pb in sediments increased slowly between 1850 and 1930 through the atmosphere due to burning of coal and Pb smelting, but increased dramatically after 1930 due to leaded gasoline. The anthropogenic increase in P concentration is unprecedented in the past 7,000 years, but the mid-Holocene OC concentration was as high or higher than during the last 50 years, likely due to influx of terrestrial organic matter during the mid-Holocene "prairie period" in Minnesota. Concentrations of several trace metals, notable Ni and V, are as high in Holocene sediments as those in recent sediments.

Acknowledgments

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Table 1. Geochemical Data for core II-3.

Depth (centimeters)	Age (years AD)	Aluminum (percent)	Iron (percent)	Magnesium (percent)	Calcium (percent)	Potassium (percent)	Titanium (percent)	Phosphorus (percent)	Manganese (ppm)	Silver (ppm)	Cadmium (ppm)	Copper (ppm)	Nickel (ppm)	Lead (ppm)	Strontium (ppm)	Vanadium (ppm)	Yttrium (ppm)	Zinc (ppm)	Nitrogen (percent)	Organic C (percent)	$CaCO_3$ (percent)	Organic Carbon Nitrogen
10	1994	5.28	3.75	1.54	3.65	1.44	0.25	0.133	1662	0.8	1.1	34	33	34	134	114	17	139	0.40	3.33	10.77	8.3
30	1984	5.50	3.83	1.49	3.50	1.53	0.26	0.121	1128	1.6	1.9	43	35	41	132	119	18	168	0.37	3.30	10.52	8.9
42	1977	5.71	3.93	1.38	2.90	1.56	0.27	0.143	1212	1.6	4.5	52	40	58	125	115	18	187	0.36	3.44	7.87	9.6
54	1970	5.60	3.81	1.38	3.05	1.52	0.26	0.178	1414	2.2	6.7	62	39	62	127	115	18	202	0.34	3.28	8.56	9.6
62	1965	5.91	3.73	1.40	2.61	1.62	0.28	0.126	1102	2.4	6.6	59	40	63	115	122	18	209	0.35	3.43	7.15	9.8
66	1963	6.03	4.15	1.39	2.73	1.65	0.30	0.137	1172	2.5	6.2	60	40	69	118	129	19	212	n.a.	3.42	7.09	
70	1961	5.94	4.09	1.26	2.11	1.64	0.28	0.148	1190	2.1	2.9	50	39	61	110	123	19	195	0.38	3.34	5.40	8.8
78	1955	6.38	4.41	1.27	1.56	1.78	0.31	0.141	1137	1.5	1.3	44	38	60	108	127	19	190	0.36	3.33	3.48	9.3
86	1947	6.46	4.38	1.25	1.64	1.84	0.31	0.117	1072	1.3	1.3	48	46	60	117	135	21	196	0.35	3.35	3.59	9.6
94	1938	6.14	4.30	1.08	1.19	1.85	0.30	0.132	1111	0.9	0.8	41	40	58	107	125	20	176	0.36	3.36	2.12	9.3
106	1925	5.84	4.33	1.21	1.31	1.74	0.28	0.108	1118	0.9	0.6	39	39	61	104	126	19	174	0.34	3.23	3.01	9.5
118	1911	5.80	4.28	1.38	1.79	1.72	0.28	0.129	1431	0.5	0.5	34	36	47	115	126	20	142	0.30	3.00	4.96	10
126	1899	5.78	4.21	1.44	1.76	1.77	0.29	0.132	1545	0.5	0.5	30	33	36	123	112	19	119	0.28	2.93	5.17	10.5
142	1865	4.96	3.34	1.89	2.63	1.54	0.26	0.083	1151	0.5	0.5	22	25	18	133	93	17	80	0.21	2.22	10.50	10.6
154	1847	5.16	3.58	2.00	3.01	1.53	0.26	0.074	1288	0.5	0.5	22	28	15	133	105	17	85	0.22	2.17	11.39	9.9
166	1801	5.04	3.45	1.89	3.08	1.48	0.25	0.070	1303	0.5	0.5	22	28	17	126	106	16	87	0.20	2.03	11.52	10.2
198	1667	5.04	3.62	1.92	2.96	1.48	0.25	0.076	1330	0.5	0.5	22	29	16	122	105	17	99	0.19	2.06	11.11	10.8
230	1462	5.18	3.69	1.93	2.94	1.49	0.24	0.085	1398	0.5	0.5	23	32	15	134	113	18	92	n.a.	1.94	11.75	

ppm = parts per million
na = not analyzed

Table 2. Geochemical data for core P97.

Depth (centimeters)	Age (^{14}C yr BP)	Aluminum (percent)	Iron (percent)	Magnesium (percent)	Calcium (percent)	Potassium (percent)	Titanium (percent)	Phosphorus (percent)	Manganese (ppm)	Silver (ppm)	Cadmium (ppm)	Cobalt (ppm)	Chrome (ppm)	Copper (ppm)	Lithium (ppm)	Nickel (ppm)	Lead (ppm)	Strontium (ppm)	Vanadium (ppm)	Yttrium (ppm)	Zinc (ppm)	Total C (percent)	Inorganic C (percent)	Organic C (percent)	$CaCO_3$ (percent)
11	9	5.97	3.83	1.36	3.65	1.41	0.27	0.118	1719	0.8	1.4	11	72	28	35	33	28	122	117	18	136	4.45	1.14	3.31	9.52
31	27	6.09	3.99	1.35	3.74	1.47	0.28	0.130	1272	1.1	2.2	11	83	33	34	37	42	123	117	19	159	4.66	1.05	3.62	8.72
51	45	6.43	4.01	1.22	2.80	1.56	0.30	0.121	1152	1.8	4.9	12	100	47	36	43	64	113	120	21	188	4.40	0.69	3.71	5.75
71	63	6.40	4.00	1.19	2.62	1.53	0.30	0.168	1328	2.8	7.4	12	123	55	34	41	65	110	119	20	200	4.23	0.67	3.56	5.56
91	81	6.71	4.50	1.10	1.92	1.65	0.32	0.169	1344	2.1	2.7	14	84	40	36	40	64	109	123	22	189	3.90	0.37	3.53	3.06
111	99	6.66	4.59	0.99	1.37	1.68	0.31	0.177	1488	1.1	1.4	14	81	34	37	38	61	102	118	22	171	3.81	0.19	3.62	1.54
131	118	6.70	4.77	1.20	1.79	1.68	0.31	0.117	1521	0.6	0.8	15	73	29	42	38	55	107	128	21	160	3.72	0.41	3.31	3.40
151	136	6.17	4.26	1.21	1.64	1.62	0.30	0.123	1702	0.4	0.7	13	66	22	35	34	36	105	111	20	118	3.67	0.48	3.20	3.96
171	154	5.87	3.95	1.71	2.63	1.56	0.28	0.078	1366	0.4	0.8	12	65	17	31	32	17	124	105	19	95	3.68	0.99	2.69	8.24
191	198	5.93	3.95	1.80	3.03	1.51	0.29	0.075	1421	0.4	0.7	12	50	16	33	30	19	120	110	19	94	3.62	1.14	2.48	9.53
211	291	5.85	3.94	1.76	3.09	1.48	0.28	0.076	1576	0.4	0.7	12	62	17	35	30	14	117	110	18	92	3.44	0.86	2.58	7.20
231	384	6.14	4.18	1.71	3.09	1.51	0.29	0.076	1662	0.4	0.8	13	68	16	34	32	14	116	119	19	100	3.44	1.13	2.31	9.41
251	477	5.86	4.04	1.76	2.95	1.50	0.28	0.074	1671	0.4	0.6	12	64	16	32	30	15	117	109	18	91	3.44	1.09	2.35	9.08
271	570	6.09	3.96	1.68	3.18	1.51	0.28	0.076	1688	0.4	0.5	12	62	18	33	31	15	116	118	19	99	3.38	1.07	2.32	8.88
286	640	6.12	4.07	1.67	2.92	1.52	0.29	0.077	1721	0.4	0.6	12	68	18	34	32	16	114	120	20	101	3.35	1.03	2.32	8.55
421	1268	6.62	4.83	1.77	2.57	1.58	0.30	0.084	2284	0.4	0.6	15	60	19	37	36	17	117	127	20	108	3.60	0.92	2.67	7.69
441	1361	6.16	4.86	1.69	2.46	1.49	0.28	0.080	2307	0.4	1.1	15	70	17	33	35	16	107	120	20	104	3.75	0.93	2.83	7.74
461	1454	6.38	5.20	1.70	2.35	1.53	0.30	0.082	2239	0.4	0.4	15	74	19	33	37	17	112	120	21	107	3.71	0.77	2.94	6.43
481	1547	6.63	4.80	1.73	2.48	1.60	0.30	0.081	2115	0.4	0.8	14	72	19	37	36	16	112	128	21	111	3.50	0.91	2.60	7.55
501	1640	5.99	4.83	1.61	2.37	1.54	0.28	0.077	2691	0.4	0.7	15	69	17	33	35	20	113	114	21	101	3.46	0.88	2.58	7.35
521	1733	6.01	5.07	1.64	2.32	1.51	0.28	0.077	2936	0.4	0.8	14	65	17	32	36	13	112	112	21	100	3.62	0.87	2.76	7.24
541	1826	5.95	4.64	1.76	2.55	1.55	0.29	0.075	2147	0.4	0.9	14	67	17	34	33	20	116	108	21	98	3.54	0.93	2.61	7.78
561	1905	5.85	4.85	1.67	2.42	1.51	0.28	0.074	2192	0.4	0.7	15	61	18	31	35	18	111	108	21	100	3.84	0.79	3.05	6.60
581	2012	6.25	5.21	1.71	2.33	1.51	0.29	0.076	2321	0.4	0.6	14	73	19	35	36	22	105	120	21	106	3.82	0.90	2.92	7.47
601	2159	6.12	5.18	1.67	2.30	1.48	0.27	0.075	2338	0.6	0.9	15	74	18	36	38	18	102	119	21	108	3.86	0.84	3.02	7.02
621	2306	6.36	4.96	1.76	2.62	1.55	0.29	0.078	2878	0.4	0.7	15	74	19	36	37	22	108	123	21	110	3.58	0.87	2.71	7.28
641	2453	6.29	5.15	1.75	2.38	1.56	0.29	0.076	2488	0.4	0.9	15	74	19	33	38	20	108	118	21	107	3.73	0.90	2.82	7.54
661	2600	6.38	5.00	1.78	2.46	1.60	0.30	0.082	2508	0.4	0.7	15	73	19	35	38	19	110	120	20	107	3.66	0.91	2.76	7.55
681	2747	6.19	4.95	1.80	2.52	1.56	0.29	0.079	2638	0.5	0.7	15	71	19	36	37	24	111	115	19	105	3.78	1.01	2.76	8.45
701	2894	6.37	5.25	1.75	2.45	1.60	0.30	0.083	4874	0.4	0.9	17	74	19	34	40	20	112	120	20	108	3.94	0.91	3.03	7.59
721	3041	6.19	4.88	1.65	2.42	1.58	0.28	0.081	3201	0.4	0.6	15	70	20	35	37	23	113	115	20	104	3.79	0.60	3.19	4.99
754	3284	6.05	4.49	1.68	2.69	1.58	0.29	0.081	3025	0.4	0.7	14	68	19	35	35	21	114	115	20	103	3.54	1.05	2.50	8.71
771	3409	6.77	4.40	1.61	2.87	1.69	0.31	0.078	2819	0.4	0.4	15	76	20	37	37	24	119	134	21	113	3.15	0.64	2.51	5.32
791	3556	5.05	3.96	1.58	2.49	1.54	0.27	0.073	3679	0.4	0.4	13	57	15	23	30	17	120	83	19	82	3.67	1.09	2.58	9.08
811	3703	5.10	3.97	1.62	2.64	1.59	0.27	0.074	3342	0.4	0.3	13	71	21	27	31	22	129	82	19	89	3.88	0.92	2.96	7.63
831	3850	5.42	4.39	1.61	2.45	1.59	0.28	0.079	4619	0.4	0.3	16	77	22	27	38	25	123	95	20	93	3.86	0.99	2.87	8.22
851	3997	5.66	4.30	1.62	2.56	1.57	0.28	0.084	3239	0.4	0.5	13	78	21	30	34	23	120	103	19	96	3.66	0.93	2.73	7.75
871	4144	5.54	4.64	1.49	3.91	1.53	0.27	0.082	5111	0.4	0.4	14	78	23	31	35	23	127	100	19	98	4.42	1.46	2.96	12.18
891	4377	5.84	5.06	1.48	3.55	1.57	0.28	0.081	3989	0.4	0.6	15	83	26	33	37	19	122	106	20	107	4.73	1.16	3.57	9.69
911	4609	5.78	5.33	1.47	3.85	1.52	0.26	0.084	3730	0.4	0.5	16	84	29	32	39	22	126	112	21	110	5.28	1.30	3.97	10.86
931	4842	5.51	5.72	1.42	5.49	1.48	0.25	0.363	4660	0.4	0.6	14	81	27	31	37	18	137	108	20	104	5.64	1.92	3.72	16.00
951	5124	5.48	4.50	1.36	5.97	1.42	0.25	0.076	3073	0.4	0.4	13	78	26	31	34	21	138	107	19	98	5.41	2.13	3.28	17.73
971	5405	5.03	4.37	1.35	7.36	1.38	0.24	0.079	3237	0.5	0.6	13	74	26	27	32	18	151	94	18	93	6.15	2.54	3.62	21.16
991	5687	5.13	4.41	1.35	7.53	1.42	0.24	0.078	3416	0.4	0.4	14	74	26	30	35	20	153	96	19	94	5.85	2.66	3.19	22.16
1011	5820	5.07	4.63	1.33	7.89	1.38	0.23	0.078	3077	0.4	0.5	14	74	26	29	34	16	155	97	19	96	6.36	2.65	3.71	22.05
1031	5954	4.61	4.05	1.19	10.11	1.25	0.21	0.075	3071	0.4	0.6	11	65	25	28	30	16	172	88	17	85	6.88	3.54	3.34	29.48
1051	6087	5.94	4.21	1.57	5.00	1.49	0.28	0.078	2138	0.4	0.6	13	80	22	34	33	18	135	116	19	99	4.36	1.79	2.57	14.91
1071	6220	5.54	4.22	1.34	8.16	1.40	0.24	0.082	3034	0.4	0.5	13	77	24	35	35	17	156	113	19	101	5.68	2.86	2.82	23.83
1091	6420	4.25	3.33	1.06	12.48	1.10	0.18	0.074	2425	0.4	0.6	10	59	22	25	28	14	190	85	16	75	7.38	4.51	2.87	37.55
1111	6620	4.18	3.14	1.06	13.04	1.07	0.18	0.073	2268	0.4	0.5	9	59	22	27	27	13	196	86	15	74	7.20	4.70	2.50	39.17
1131	6820	5.21	3.45	1.18	10.16	1.29	0.22	0.077	2014	0.4	0.3	11	71	25	32	32	12	173	109	18	90	5.94	3.56	2.39	29.65
1151	7020	4.71	3.18	1.09	11.19	1.19	0.21	0.071	1570	0.4	0.3	10	55	24	32	29	13	181	97	17	81	6.58	3.91	2.67	32.58
1171	7220	5.45	3.43	1.20	9.79	1.34	0.23	0.072	1522	0.4	0.4	12	65	26	37	33	18	172	115	19	92	5.92	3.29	2.63	27.39
1191	7420	3.39	2.67	0.95	15.82	0.98	0.15	0.068	1501	0.4	0.3	8	51	23	21	25	12	219	66	14	59	8.77	5.49	3.27	45.78

ppm = parts per million

Table 3. Rock-Eval hydrogen index (HI) and stable carbon isotope results for core II-3.

Depth (centimeters)	Hydrogen Index (mg HC/gOC)	delta ^{13}C (per mil, VPDB)
10	250	-27.6
42	171	-27.3
62	186	-27.0
78	150	-26.7
94	169	-27.2
118	119	-27.2
142	120	-28.2
166	118	-28.1
198	101	-28.2
230	98	-27.8
258	107	-28.2

Table 4. Stable carbon isotope results for core P97.

Depth (centimeters)	Age (^{14}C yr BP)	delta ^{13}C (per mil, VPDB)
11.5	9	-28.2
51.5	45	-28.0
91.5	81	-27.8
131.5	118	-29.0
171.5	154	-29.6
211.5	291	-29.5
251.5	477	-29.4
286.5	640	-28.8
441.5	1361	-28.9
481.5	2012	-29.2
521.5	1733	-29.6
558.5	1905	-29.7
601.5	2159	-28.8
641.5	2453	-28.6
681.5	2747	-28.5
721.5	3041	-28.7
771.5	3409	-28.8
811.5	3703	-29.0
851.5	3997	-29.1
891.5	4377	-29.0
931.5	4842	-29.2
971.5	5405	-29.8
1011.5	5820	-29.7
1051.5	6087	-30.0
1091.5	6420	-29.7
1131.5	6820	-30.1
1171.5	7220	-29.9