of impact features, such as shatter cones in the surrounding country rocks and shock lamellae within quartz and feldspar fragments of the Onaping Formation. Furthermore, the model Nd-ages of all the rocks analyzed in this study define a narrow range of 2.56 ± 0.13 billion years, similar in age to the early Proterozoic metavolcanic and metasedimentary rocks of the Huronian Supergroup and of the Archean Superior Province-style basement that underlies the Sudbury structure. We propose that this package of metavolcanic, metasedimentary, and plutonic rocks was melted by an impact event some 1840 million years ago to produce the Sudbury Complex.

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$$\epsilon_{Nd} = \left[\frac{(^{143}Nd/^{144}Nd)_{measured}}{(^{143}Nd/^{144}Nd)_{bulk\ earth}} - 1\right] \times 10^4$$

Similarly, the initial ^{143}Nd/^{144}Nd for a sample of age *T* can be presented as the deviation from the bulk earth in parts in 10^4 at the time of its formation.
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A Decline in Lead Transport by the Mississippi River

Abstract. *Inputs of pollutant lead to the Gulf of Mexico from the Mississippi River have declined by about 40 percent within the past decade. This decrease has been determined from annual lead loads of the Mississippi River and from the lead record in Mississippi Delta sediments. The observed trend is consistent with reduced consumption of lead in gasoline in the United States. More than 90 percent of the riverborne lead is associated with suspended sediments. Most of this particle-bound lead is deposited within 50 kilometers of the river mouth and is not easily leached at pH values above 3.*

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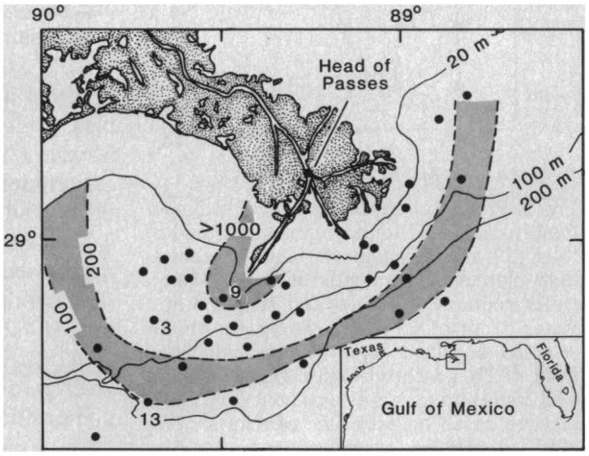
A decade has passed since regulations limiting lead additives in gasoline were put into effect in the United States (*1*). Already, several instances of decreased lead concentrations in the atmosphere, roadside soil, and human blood have been reported (*2*). To assess more completely the effectiveness of this costly regulation (*1*), we must identify and study systems that, by their size and importance, are useful indicators of contaminant transport. The Mississippi River system provides one such frame of reference because it drains more than 40 percent of the contiguous United States and carries more than half of the total sediment and water borne by U.S. rivers (*3*). Most of the Mississippi River burden of sediments and associated contaminants is deposited on the river's expansive delta. At present, the waters of this river and the sediments on its delta show a trend of declining lead inputs to the Gulf of Mexico.

Water, suspended particles, and bottom sediments were collected from the Mississippi River and Delta (Fig. 1) during May and September 1982 and April and November 1983. These efforts complement our work from 1974 and 1975 (*4*). To optimize conditions for trace metal collection and analysis, we used a clean laboratory and clean sampling techniques at sea and ashore during both the 1974–75 and 1982–83 studies. Metal analyses of water, suspended matter, and sediment were by flame or flameless atomic absorption spectrophotometry (*4*, *5*). Extreme care and attention to detail were practiced throughout the study (*6*).

In the Mississippi River, suspended particles play a primary role in lead transport because they typically carry more than 95 percent of the total river lead load. An exception to this trend occurs during the fall when levels of suspended matter often decrease from more than 200 mg/liter to less than 20 mg/liter, and then 80 percent or less of the total lead is particle-bound.

Lead concentrations for all suspended-matter samples (n = 29) collected at Head of Passes (Fig. 1) during 1982–83 were consistent at 32 ± 3 μg/g (mean ± standard deviation) despite a range of values for total suspended matter (TSM) of 200 mg/liter during spring runoff to 20 mg/liter during late fall (*7*). This trend of spatial and seasonal uniformity in particulate lead concentrations is comparable to our previously reported Mississippi River data (*4*) and is primarily due to the

Fig. 1. Map of lower Mississippi River and Delta. (●) Station locations with numbers for sites referenced in text; (——) depth contours (in meters); (------) contours for vertically integrated sediment pollutant lead burdens (in micrograms of pollutant lead per square centimeter of sediment). Shaded portions indicate areas where integrated values for sediment pollutant lead are either greater than 1000 or 100 to 200 μg/cm². Gulf of Mexico map (inset) shows the study area (small rectangle).



homogeneous composition of the abundant suspended matter in the river.

Particle dominance of lead transport by the Mississippi River is reflected in low dissolved lead concentrations of 110 ± 50 ng/liter for all samples collected at Head of Passes during 1982 and 1983. Values for dissolved lead reached a peak of 190 ng/liter during November 1983, when dilution and scavenging processes were inhibited by low water flow and low sediment loading (*7*). These concentrations are high relative to estimates of less than 20 ng/liter for natural river water and 6 to 50 ng/liter for remote streams in the United States (*8*). Nevertheless, values for dissolved lead in the Mississippi River are much lower than previously reported for most rivers (*8*).

To describe the relation between dissolved and particulate lead in the Mississippi River, we calculated distribution coefficients (K_d) (*9*). Ideally, K_d values provide an approximation of element partitioning between dissolved and particulate phases. Relatively constant ionic strength and *p*H, uniform particle composition, and good mixing combine to favor this approach in the Mississippi River. Samples from Head of Passes for 1982–83 had log K_d values for lead of 5.49 ± 0.18 ($n = 15$). This K_d value indicates a strong affinity between dissolved lead and river particles.

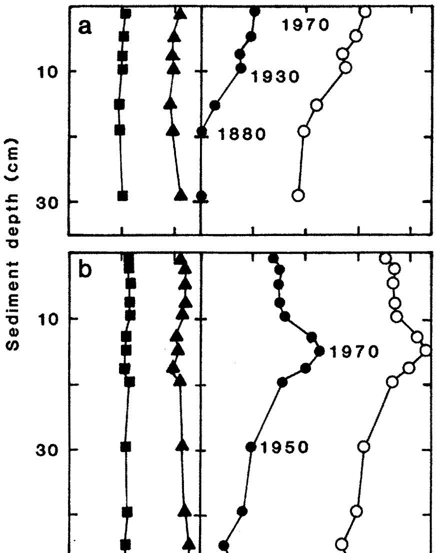


Fig. 2. Profiles of concentrations of sediment total iron (■) and total aluminum (▲) and of total (○) and pollutant (●) lead concentrations plotted against depth for station 13 at a water depth of 107 m (a) and station 3 at a water depth of 69 m (b). Dates shown for selected sediment depths were calculated from ^{210}Pb geochronologies (*12*). Pollutant lead concentrations are calculated from Eq. 1 and are based on estimates of natural, pre-1850 sediment lead concentrations.

To test field K_d values, we treated samples of unfiltered river water, collected from Head of Passes in November 1983, with dissolved lead at concentrations two, three, and ten times higher than average values. Triplicate aliquots of each of the three treated waters plus an unaltered sample were equilibrated for 0.5, 1, 2, 8, and 24 hours at constant river *p*H (8.0) to measure uptake of dissolved lead by particles. The 24-hour laboratory values of log K_d for lead (5.61 ± 0.13; $n = 15$ for treated and untreated samples) compared well with field observations. The results of this experiment suggest that, if dissolved lead is added at ten times normal levels when TSM is at 100 mg/liter and log K_d is 5.6, then 98 percent of the additional lead will adsorb on particles and only 2 percent will remain dissolved (*9*). Such partitioning in the Mississippi River lessens the chance for large increases of the more biologically available dissolved phase.

Estimates of lead transport from the Mississippi River to the Gulf of Mexico show that 1982 and 1983 average annual burdens of pollutant lead (2100 metric tons per year) are about 40 percent lower than the average of 3600 metric tons carried per year for 1974 and 1975 (*10*). Values for total lead in river suspended matter for 1982–83 (32 ± 3 µg/g, $n = 29$) were also lower than those for 1974–75 (44 ± 5 µg/g, $n = 43$) but were still higher than prepollution (circa 1850) levels in delta sediments (~20 µg/g). Pollutant lead concentrations were calculated from Eq. 1.

$$(M_{\mathrm{Pb}})_{\mathrm{p}} = (M_{\mathrm{Pb}})_{\mathrm{t}} - [(M_{\mathrm{Pb}}/M_{\mathrm{Al}})_{1850} \times (M_{\mathrm{Al}})_{\mathrm{t}}] \qquad (1)$$

where $(M_{\mathrm{Pb}})_{\mathrm{p}}$ is the level of pollutant lead, $(M_{\mathrm{Pb}})_{\mathrm{t}}$ is the total level of lead in the sample, $(M_{\mathrm{Pb}}/M_{\mathrm{Al}})_{1850}$ is the ratio of lead to aluminum in pre-1850 sediments, and $(M_{\mathrm{Al}})_{\mathrm{t}}$ is the total level of aluminum in the sample. We have estimated that $(M_{\mathrm{Pb}}/M_{\mathrm{Al}})_{1850}$ is $(2.5 \pm 0.2) \times 10^{-4}$ ($n = 42$) from data for many subsurface samples from the delta and open Gulf of Mexico (*11*). Equation 1 is based on the assumption that remobilization of sediment lead and aluminum is negligible. Total concentrations of iron and aluminum in sediment were generally constant with depth throughout the delta and averaged 4.2 and 8.4 percent, respectively (Fig. 2). This uniformity implies that river particles have been similar in basic composition over at least the past century.

Data for Mississippi Delta sediments also indicate recent decreases in lead inputs to the Gulf of Mexico. At offshore delta sites such as station 13 (Fig. 1), sedimentation rates determined by ^{210}Pb geochronometry are about 0.2 cm/year (*12*). Here, the lead record (Fig. 2a) shows an increase in the concentration of bottom sediment lead during the late 1800's, which is consistent with commencement of lead mining in the Missouri valley and the industrial revolution in the United States. Lead inputs increased steadily, probably augmented by the introduction of lead additives to gasoline during the 1920's. Sediment mixing in the top 2 to 3 cm and a low sedimentation rate at station 13 have obscured details in the lead profile for the past few decades.

Nearer the river mouth, where sedimentation rates exceed 1 cm/year, the lead record is better defined for the past 30 years. The record for station 3 (Fig. 2b) (*12*) shows that concentrations of pollutant lead in bottom sediment, which peaked at more than 20 µg/g, have decreased to less than 13 µg/g in the most recent deposits. The observed trend is

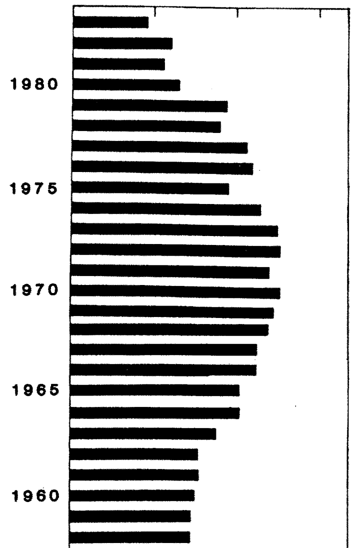


Fig. 3. Annual consumption of lead in gasoline additives in the United States from 1942 to 1983 (*14*).

independent of annual variations in river sediment load (*10*) and is consistent with a decrease in concentrations of lead in suspended matter in the Mississippi River. Mixing of surficial sediment at station 3 (*12*) has probably distorted and diminished the thickness of the layer of maximum pollutant lead (Fig. 2b). This observation is based on the ^{210}Pb distribution at this site and sediment lead profiles from the same area taken during 1974–75. The 1974–75 profiles show total lead concentrations of more than 40 μg/g over the top 10 cm of sediment (*4*).

Comparison of the sediment lead profile for station 3 (Fig. 2b) with the annual consumption of lead in gasoline in the United States (Fig. 3) shows a general decreasing trend for both in recent years. Use of lead in gasoline exceeded 200,000 metric tons per year from 1964 to 1977, with a decrease since peak values during 1969–74 (Fig. 3). Our 1974–75 sampling was carried out during the high-use period. The next sampling period (1982–83) was well after the trend of decreased consumption began. Although no direct year-by-year correlation of gasoline lead use and sediment or suspended-matter lead distributions can be made because of difficulties in estimating lag times for lead on the continent and the limitations of sediment ^{210}Pb data, a trend of declining lead inputs is observed.

Much of the particle-bound lead is deposited close to the river mouth, where sedimentation rates may exceed 5 cm/year and particle-bound contaminants are rapidly buried. When pollutant lead concentrations in nearshore sediments are integrated throughout the sediment column, values can exceed 1000 μg/cm^2 (Fig. 1). These values decrease to less than 100 μg/cm^2 by 30 to 40 km offshore. Beyond the area shown in Fig. 1, pollutant lead values of less than 50 μg/cm^2 were found to depths of less than 10 cm.

Selective leaching of sediments at environmentally or biochemically realistic *p*H values may provide one means for assessing the reactivity and biological availability of sediment metals. When Mississippi Delta sediment from station 9 was treated with buffers of various *p*H (*13*), less than 1 percent of the total lead content (31.7 ± 0.5 μg/g) was leached over 48 hrs at *p*H 5.1 and 6.3 (Fig. 4). At *p*H values below 3, lead release increased greatly (Fig. 4). Within the *p*H boundaries (4 to 8) of digestive systems in most benthic organisms and sediment interstitial water (*13*), relatively little lead would be expected to be released from delta sediment on the basis of *p*H factors alone. Reasonably good comparison of lead concentrations in river suspended matter and delta sediment concentrations for 1982 and 1983 versus 1974 and 1975 (*4*) support the permanence of lead burial. The Mississippi River and Delta thus combine to serve as an efficient filter and sink, respectively, for lead.

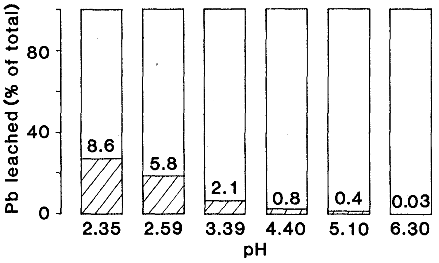


Fig. 4. Results of *p*H leaching experiments for lead from station 9 sediment. Numbers above the bars give the amount of metal leached (in micrograms of lead per gram of sediment at each *p*H). Total lead was 31.7 ± 0.5 μg/g (n = 3).

An observed trend of decreasing pollutant lead transport by the Mississippi River within a decade after partial regulation of lead additives in gasoline is striking. When considering the various options available to reduce lead inputs to the environment, regulation of gasoline lead additives in the United States seems to have been effective.

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6. Surface river water was collected directly in conventional polyethylene bottles from the bow of a small boat moving upriver. The bottles were cleaned according to the methods of Patterson and Settle [in *Accuracy in Trace Analysis*, P. LaFleur, Ed. (National Bureau of Standards, Washington, D.C., 1976)]. Filtration was carried out immediately in the shipboard clean laboratory. Each sample was acidified with HNO_3 (redistilled from Vycor). Analytical precision (coefficient of variation) for sediment and suspended matter averaged 1.4 percent for 1982 and 1983 samples and 3.4 percent for 1974 and 1975 samples. Procedural blanks were less than 2 percent of the total sample signal. Analysis of U.S. Geological Survey standard rocks G-2 and GSP-1 (at 10 to 400 mg quantities) for lead yielded 30.5 ± 1.0 (n = 5) and 51.2 ± 1.4 μg/g (n = 8), relative to accepted values of 31 and 51 μg/g, respectively [F. J. Flanagan, *U.S. Geol. Surv. Prof. Pap. 840* (1976)]. National Bureau of Standards SRM 1646 (estuarine sediment) was found to contain 27.9 ± 1.2 μg of lead per gram (n = 8) relative to a certified value of 28.2 ± 1.8 μg/g. Precision for dissolved lead analysis ranged from 5 to 15 percent as a function of lead content. The procedural blank for dissolved lead was consistently less than 10 percent of the total sample signal. J.H.T. participated in an intercalibration for lead in seawater at the California Institute of Technology [*Mar. Chem.* **2**, 69 (1974)].
7. Data summary for Head of Passes, 1982–83, is as follows. May 1982 (n = 5): suspended matter lead (Pb_{sm}), 34.3 ± 1.3 μg/g; dissolved lead (Pb_d), 110 ± 10 ng/liter; TSM, 110 mg/liter; water flow (WF), 14 × 10^6 liter/sec. September 1982 (n = 9): Pb_{sm}, 34.4 ± 1.7 μg/g; Pb_d, 90 ± 10 ng/liter; TSM, 85 mg/liter; WF, 11 × 10^6 liter/sec. April 1983 (n = 5): Pb_{sm}, 29.8 ± 4.2 μg/g; Pb_d, 70 ± 10 ng/liter; TSM, 200 mg/liter; WF, 30 × 10^6 liter/sec. November 1983 (n = 10): Pb_{sm}, 31.4 ± 1.5 μg/g; Pb_d, 190 ± 10 ng/liter; TSM, 21 mg/liter; WF, 8 × 10^6 liter/sec.
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9. $$K_d = \frac{\text{mass of particulate metal/gram of solid}}{\text{mass of dissolved metal/gram of water}}$$
The percent of total metal associated with the particulate phrase varies as a function of TSM values. With TSM at 10 mg/liter and a log K_d of 5.6 for lead, 80 percent of the total lead will be in the particulate form. If log K_d is held constant and TSM is increased to 100 mg/liter, particles carry 98 percent of the total lead.
10. River lead loads are based on average dissolved and particulate lead concentrations determined from this study and from data for suspended sediment loads and water flow for the river at Tarbert Landing, Mississippi [data from *Water Resources Data for Louisiana* (U.S. Geological Survey, Baton Rouge, La., 1974–83)]. Tarbert Landing is below the channel that diverts about 30 percent of the river flow to the Atchafalaya River. The annual data are as follows. 1974: WF, 5.6 × 10^{14} liters; sediment load (SL), 1.8 × 10^{14} g; pollutant lead load (Pb_p), 3900 metric tons. 1975: WF, 5.0 × 10^{14} liters; SL, 1.5 × 10^{14} g; Pb_p, 3300 metric tons. 1982: WF, 4.4 × 10^{14} liters; SL, 1.7 × 10^{14} g; Pb_p, 2000 metric tons. 1983: WF, 6.1 × 10^{14} liters; SL, 1.9 × 10^{14} g; Pb_p, 2200 metric tons.
11. The pre-1850 lead:aluminum ratio [(2.5 ± 0.2) × 10^{-4}] was calculated from data for subsurface sediment from the Mississippi Delta and outer shelf and slope of the Gulf of Mexico during 1974–75 (n = 16) and 1982–83 (n = 26).
12. Sediment ^{210}Pb concentrations were determined by measuring the activity of ^{210}Po after sufficient time had passed for the ^{210}Po:^{210}Pb activity ratio to become unity. Samples were acid-treated, and ^{210}Po (along with a ^{208}Po tracer) was plated on silver disks [R. Carpenter *et al.*, *Geochim. Cosmochim. Acta* **45**, 1155 (1981)]. Excess ^{210}Pb was determined from ^{226}Ra data and from ^{210}Pb values for subsurface sediments. Stations 3 and 13 were located 28 and 46 km from the river mouth at water depths of 69 and 107 m, respectively. At these locations, the influence of high sediment loading and slumping found closer to the river mouth is reduced. At station 13, the ^{210}Pb profile shows a mixed layer of 2 to 3 cm with an exponential decrease in excess ^{210}Pb to 0 by 30 cm. Dates for station 13 derived from sedimentation rates are consistent with trends for pollutant lead accumulation at this site. At station 3, the ^{210}Pb profile supports sediment mixing to a depth of 8 cm. This is consistent with the stable lead profile. Below the mixed layer, the ^{210}Pb curve shows exponential decay.
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15. We thank D. Atwood, S. Piotrowicz, and G. Harvey for help in planning the cruises and discussions of the manuscript; T. Vetter, R. Bewig, N. Iricanin, S. Holbrook, C. Panico, J. Windsor, and I. Duedall for help at sea and ashore; and M. Champ and C. Patterson for comments on the manuscript. Funded by the National Oceanic and Atmospheric Administration, Project P-PRIME (contracts NA83RAC-00036 and NA84WCC06130). Contribution No. 65, Department of Oceanographic and Ocean Engineering, Florida Institute of Technology.

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