(Cambridge Univ. Press, Cambridge, England, 1962), p. 210.

7. We thank E. Barreto, D. C. Blanchard, N. R. Gokhale, and C. W. McCutchen for their helpful comments and suggestions, and E. Nagle for making the dilatometers. Supported in part by Office of Naval Research contract N00014-71-C-0156; in part by Air Force Cambridge Research Laboratories, Office of Aerospace Research, contract F19628-68-C-0057; and in part by National Science Foundation grant GI-34732.

9 February 1973; revised 16 April 1973 ■

Lead Pollution: Records in Southern California Coastal Sediments

Abstract. *The present anthropogenic lead fluxes into sediments from the Santa Monica, San Pedro, and Santa Barbara basins of Southern California are, respectively, 0.9, 1.7, and 2.1 micrograms of lead per square centimeter of sea bottom per year; the natural (prepollution) rates for these three basins were, respectively, 0.24, 0.26, and 1.0 microgram of lead per square centimeter per year. Studies of isotopic composition indicate that lead pollutants in coastal sediments are derived mainly from the combustion of lead additives in gasoline.*

The sedimentary deposits of coastal areas may well constitute historical records of the atmospheric burden of particulates, such as the lead-containing species produced from the combustion of lead alkyls in gasoline. The basins off the coast of Southern California are especially promising for such studies. Their sediments accumulate at rates of millimeters per year, annual layers are occasionally available for analysis, and there is a very rapid removal of lead to them from the overlying waters (*1*). These basins (Fig. 1), situated near an area of substantial leaded gasoline combustion (*2*), are the basis for several recent models of the sources and dispersion of pollutants introduced to the atmosphere (*2, 3*). The investigation presented here is aimed at the development of the sedimentary records of lead accumulation over the past century, similar to those held in the Greenland snow strata (*4*). Since sedimentation rates vary from place to place along the California coast, the absolute concentrations of man-generated materials in the deposits are often less useful than their fluxes. The time parameter is readily introduced into these sediments (*1*), and thus the rates of deposition of lead can be sought as well as the absolute concentrations.

Sediments from three inner basins near the Los Angeles area were obtained with box-coring equipment which retained the uppermost strata. These three shallowest basins of the group (core water depth at San Pedro, 890 m; at Santa Monica, 930 m; and at Santa Barbara, 575 m) were selected because their sediments are anoxic and thus relatively free from biological disturbances. In the case of the Santa Barbara Basin annual varves can be recognized. A similarly anoxic deposit in the Soledad Basin (520 m) off the coast of Baja California (25°13.8′N, 112°40.6′W) was used as a control. This more southerly sample, remote from the prevailing wind patterns off Southern California and free from its waste discharges, is intended to provide a base-line set of samples. A fifth core was taken off the Los Angeles County waste outfall (75 m) at Whites Point to provide sediments containing domestic and industrial wastes. These Whites Point deposits are accumulating so rapidly that only a recent age can be assigned to them on the basis of both ^{210}Pb and ^{228}Th/^{232}Th chronologies.

The lead isotopic compositions and concentrations were determined by mass spectrometry on all samples except those from the Santa Monica Basin. The lead concentrations were also determined by atomic absorption. In different subsections of the cores at equivalent depths where both mass spectrometry and atomic absorption determinations were carried out, the results usually were in agreement to within 10 percent. The atomic absorption lead values (Fig. 2) are given for the Santa Monica and Santa Barbara samples; the other lead data are isotopic dilution results. The aluminum values were obtained by atomic absorption. The aluminum was used as a normalization factor that reasonably represents a measure of the detrital minerals that are assumed to have had a uniform input over the past century. The ages of the sedimentary levels were determined by ^{210}Pb and ^{228}Th/^{232}Th geochronologies. In Fig. 2, the lead values are given both as concentrations on 110°C dry-weight basis and as the lead/aluminum ratios. In general, both the lead values and lead/aluminum ratios give similar curves as a function of depth in the sediments. The exceptions involve the surface sediments which contain high water and high salt contents because these sediments are subject to less compaction than the deeper deposits. As a result, the absolute concentrations of lead in surface sediments are diminished.

The isotopic compositions of the leads in these sediments are indicative of their sources (*5*). The surface deposits of the Soledad Basin contain lead with isotopic ratios similar to those of the weathering products from the Baja California province (*6*). The Whites Point deposits contain lead with isotopic ratios comparable to those found in gasoline sold in Southern California (*7*). The isotopic compositions of lead in the surface sediments of the inner California basins (*5*) are distinctly less radiogenic than those in the deep sections of the cores which

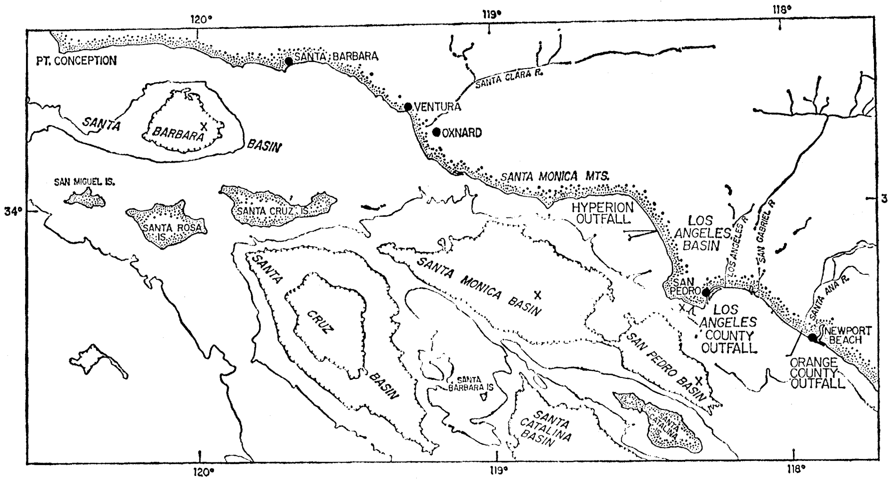

Fig. 1. The inner basin region off the coast of Southern California; X, coring site.

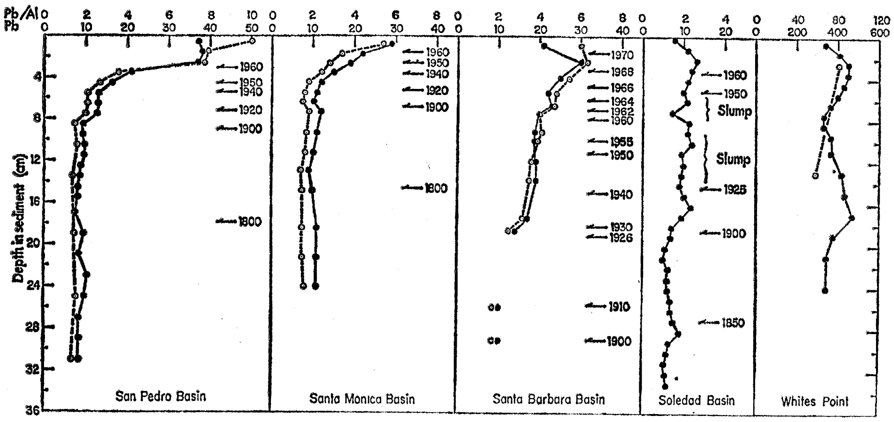

Fig. 2. Lead concentrations (in parts per million) (solid circles) and lead/aluminum ratios ($\times 10^{-4}$) (open circles) in sediments from the Santa Monica, San Pedro, and Santa Barbara basins off Southern California, from the Soledad Basin off the coast of Baja California, and from a site near the Whites Point Los Angeles County outfall.

represent the prepollution drainage. These differences are proportional to the influx of lead pollutants (Fig. 2), mainly from the combustion of gasoline additives.

The rates of lead accumulation began to increase in the basins off the Southern California coast in the 1940's. The much higher sedimentation rate in the Santa Barbara Basin, diluting the anthropogenic lead input, accounts for its lesser slope. The lead concentrations in the Soledad Basin are essentially constant with depth, and thus we feel justified in using such sediments as a base line.

The extremely high concentrations of lead in the sediments off the Whites Point outfall reflect the input of domestic and industrial wastes. The ages of the upper 24 cm of sediment were indistinguishable from one another on the basis of their ^{210}Pb and $^{228}Th/^{232}Th$ geochronologies, an indication that the deposition most probably took place within the last few years or that it was caused by slumping.

We determined extrapolated surface values (to 1971) of the anthropogenic lead fluxes by subtracting the prepollution concentration of lead accumulated per year from the value computed from an extrapolation of the curve to surface depth (the 1970 value was used for the Santa Barbara Basin). The anthropogenic fluxes for the Santa Barbara, San Pedro, and Santa Monica basins are 2.1, 1.7, and 0.9 μg of lead per square centimeter per year compared to natural fluxes of 1.0, 0.26, and 0.24 μg of lead per square centimeter per year, respectively.

Of the 24.3 metric tons of lead burned daily as lead alkyls in internal-combustion engines in the Los Angeles area, Huntzicker and Friedlander (*3*) estimate that 18.4 tons issue from automotive exhausts. The remainder is incorporated in the oil, oil filter, engine, exhaust system, and muffler. Out of this amount of exhaust, 14 tons are computed to fall out over the land and coastal waters with about 4.4 tons transported by the wind out of the Los Angeles air basin. About 8 tons fall out in the vicinity of the roadway.

The winds in the area are prevailing westerlies. However, during "Santa Ana" conditions, easterly winds dominate. Rain collected at Santa Catalina Island (Fig. 1) gave an average flux of 1.3 μg of lead per square centimeter per year in 1966–1967 (*8*), in reasonable agreement with our measured values for the sediments.

Huntzicker and Friedlander (*3*) have calculated that 0.4 ton of lead falls out daily from the atmosphere to a coastal area of 12,000 km^2 off Los Angeles. Using an average flux value from our three stations of 1.5 μg of lead per square centimeter per year to be representative of this coastal area, we compute the daily lead fallout to be 0.5 ton. It should be emphasized that the fluxes in the basins over the adjacent zones may be enhanced if these formations act as sediment traps Hence, our average flux value may be an upper limit.

The lead discharged through the municipal waste outfalls is estimated to be 0.55 ton per day, and the average storm and river runoff of lead is about 0.24 ton per day (*9*). These values are quite similar to the values obtained for the daily atmospheric fallout of lead.

Heavy metals such as lead and mercury are removed from waters very quickly after they enter the marine environment from sewer outfalls or rivers and associate with the sediments within several kilometers of the input site to the marine environment (*10*). Hence, only a fraction of the waste, storm, and river runoff would be expected to reach the basins.

Although this agreement with the total atmospheric fallout value is satisfying, our data do not allow insight into the relative contributions of river, sewer, and storm runoffs and of atmospheric fallout to the lead burden of the sediments. One way to resolve this problem may be to carry out similar flux measurements in the outer basins off the coast of California. If these basins have fluxes similar to those of the inner ones, then atmospheric transport would appear to be dominant. If the fluxes are different, then contributions from direct land discharges would predominate.

TSAIHWA J. CHOW
KENNETH W. BRULAND
KATHE BERTINE
ANDREW SOUTAR
MINORU KOIDE, E. D. GOLDBERG
Scripps Institution of Oceanography,
University of California, San Diego,
La Jolla 92037

References and Notes

1. M. Koide, A. Soutar, E. D. Goldberg, *Earth Planet. Sci. Lett.* **14**, 442 (1972); M. Koide, K. Bruland, E. D. Goldberg, *Geochim. Cosmochim. Acta* **37**, 1171 (1973).
2. S. K. Friedlander, *Environ. Sci. Technol.* **7**, 235 (1973).
3. J. J. Huntzicker and S. K. Friedlander, personal communication.
4. M. Murozumi, T. J. Chow, C. C. Patterson, *Geochim. Cosmochim. Acta* **33**, 1247 (1969).
5. The isotopic ratios of $^{206}Pb/^{204}Pb$, $^{206}Pb/^{207}Pb$, and $^{206}Pb/^{208}Pb$, respectively, for the sediments are as follows: San Pedro, 0 to 2 cm: 18.36, 1.176, and 0.4782; San Pedro, 30 to 32 cm: 19.11, 1.208, and 0.4845; Santa Barbara, 1960–1970: 18.73, 1.189, and 0.4812; Santa Barbara, 1850–1860: 19.17, 1.219, and 0.4872; Soledad, 0 to 2 cm: 18.56, 1.180, and 0.4814; Whites Point, 0 to 1 cm: 18.09, 1.166, and 0.4801; Whites Point, 22 to 26 cm: 18.06, 1.152, and 0.4744.
6. T. J. Chow and C. C. Patterson, *Geochim. Cosmochim. Acta* **26**, 263 (1962).
7. The average isotopic ratios of lead additives in gasoline sold in Los Angeles in 1964 were as follows: $^{206}Pb/^{204}Pb = 17.92$; $^{206}Pb/^{207}Pb = 1.145$; and $^{206}Pb/^{208}Pb = 0.4728$ [as reported by T. J. Chow and M. S. Johnstone, *Science* **147**, 502 (1965)]; in 1968 the average isotopic ratios were as follows: $^{206}Pb/^{204}Pb = 18.08$; $^{206}Pb/^{207}Pb = 1.155$; and $^{206}Pb/^{208}Pb = 0.4756$ [as reported by T. J. Chow, in *Proceedings of the 2nd International Clean Air Congress*, H. Englund, Ed. (Academic Press, New York, 1971), pp. 348–352].
8. A. L. Lazrus, E. Lorange, J. P. Lodge, Jr., *Environ. Sci. Technol.* **4**, 55 (1970).
9. Southern California Coastal Water Research Project, "The Ecology of the Southern California Bight: Implications for Water Quality Management" (October 1972), vol. 1.
10. D. H. Klein and E. D. Goldberg, *Environ. Sci. Technol.* **4**, 765 (1970).
11. This work was sponsored under AEC grant AT (04-3)-34 P.A. 84 and NSF grant GA-26301. We thank C. Snyder for technical assistance.

18 April 1973