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LARGE-SCALE MASS BALANCE FOR LEAD IN SOUTHERN LAKE MICHIGAN

by

Allen C. Cogley
Department of Energy Engineering
University of Illinois, Chicago Circle
Chicago, Illinois 60680

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UNIVERSITY OF ILLINOIS
WATER RESOURCES CENTER
2535 Hydrosystems Laboratory
Urbana, Illinois 61801
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ABSTRACT

LARGE-SCALE MASS BALANCE FOR LEAD
IN SOUTHERN LAKE MICHIGAN

A large-scale, order-of-magnitude mass balance for lead in the near field of Chicago (the source) is presented. Both experimental data and simple physical modeling are used to estimate the transport of lead from the major sources to the near-field sinks of Southern Lake Michigan, its watershed soil, and the surroundings (losses from the system under question). The results show that atmospheric transport of lead aerosols to a sink like Lake Michigan is about two orders of magnitude greater than other transport mechanisms. To perform a detailed (small-scale) mass balance for lead, in support of the large-scale results, a complete model of atmospheric, aerosol transport and deposition is necessary and dominant. Although much work has been done on (free) turbulent dispersion of aerosols and aerosol deposition through precipitation, little is known about the dry deposition of aerosols from a turbulent boundary layer. An aerosol, turbulent dispersion model with a realistic boundary condition at the fluid-ground interface needs to be developed. A coordinated experimental program for measuring (dry) aerosol flux to the ground (and Lake) should be initiated.

Allen C. Cogley
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INTRODUCTION

Lead additives in gasoline result in large quantities of lead being released in the atmosphere as a highly mobile aerosol. Gasoline uses about 20%[1] of all lead, is responsible for about 47% of the lead wasted in the environment, and is the source of about 95% of the lead found in the atmosphere. Other lead uses such as in batteries, paints, ammunition, and manufacturing processes make up the sources for the remaining 53% of the metal wasted in the environment. The mechanical mobility of this lead is difficult to state, but should be much less than that in aerosol form.

The toxicity, quantity, and mobility of lead is cause for concern as to its effects on the environment. This report represents an effort to organize, quantify, and model the transport of lead as it "flows" in the environment from sources to sinks. Such work constitutes input information for other researchers involved in more detailed transport studies or finding any possible hazards associated with lead, in some quantity and form, being found at some location.

As a first step in modeling the transport of lead, the Chicago area was chosen as a particular example. Chicago is a city with large quantities of lead released each year, located next to a large lake, and where many lead measurements have and are being made. This allowed a large-scale, order-of-magnitude mass balance to be carried out for lead in the near field of a large source (Chicago). Such a balance is necessary in determining which transport mechanisms are important so they can be further refined for the needed small-scale (detailed) studies.

In order to have a definite region on which to perform the mass balance, Southern Lake Michigan (south of 43^{o} parallel), its drainage area, and the above atmosphere was selected.[2] For this system, with a water surface area of 6,470 $mi.^2$ and a watershed area of 13,090 $mi.^2$, the magnitude of the various mechanisms for lead transport, as indicated in the schematic diagram of Figure 1, were calculated. The procedure for obtaining the numbers appearing on this diagram are discussed throughout the rest of the report under their respective headings. In all cases enough information is given to allow the results to be recalculated if further study or data reveals that an incorrect assumption or number has been used.

Most of the Chicago metropolitan area is not, strictly speaking, in the watershed of Lake Michigan. This region is, of course, the source of most of the lead and was therefore included in the system studied.

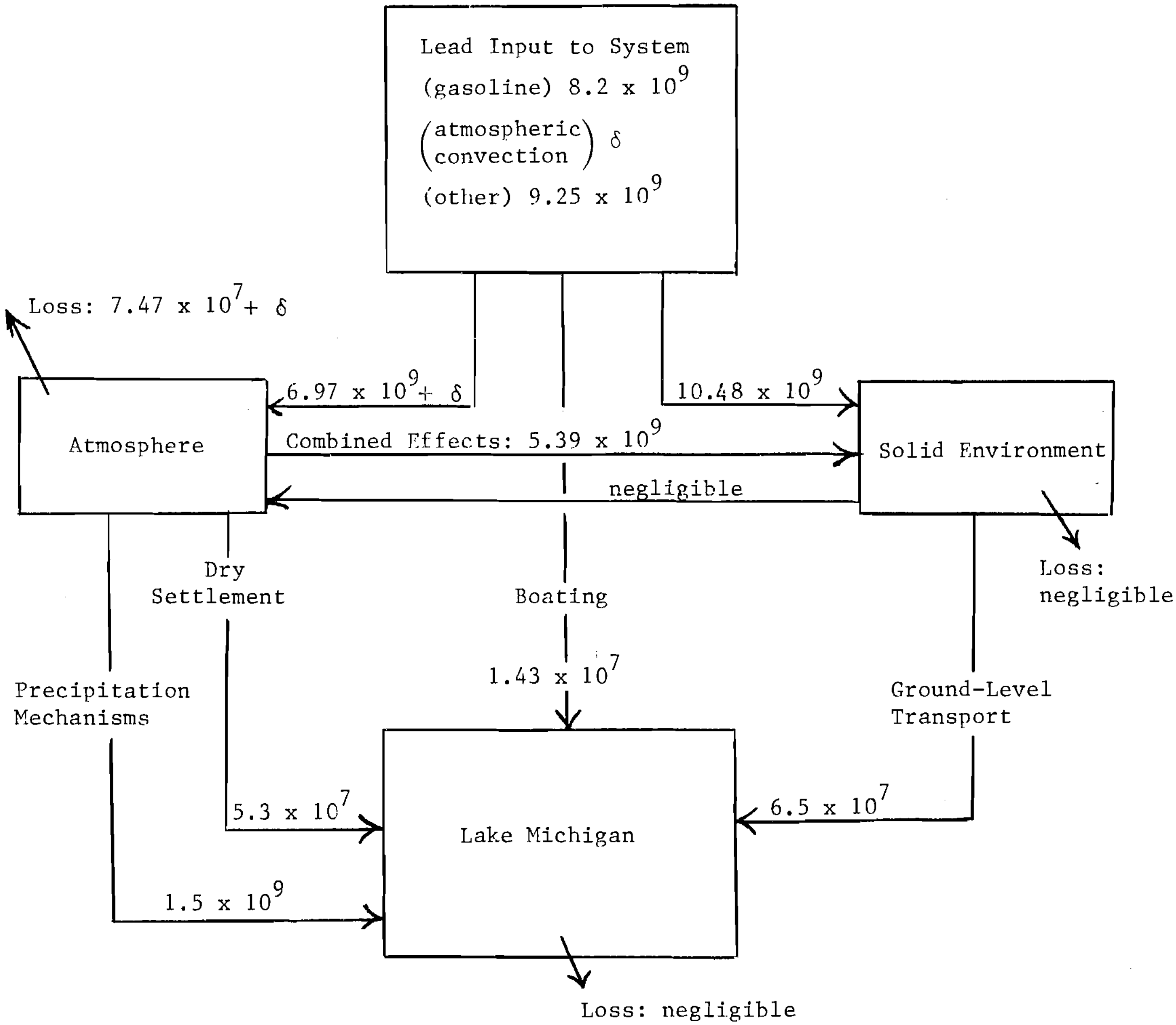

Figure 1: Schematic Diagram of Lead Transport in Grams Per Year for the Chicago Area (Data based on 1968-1973 time span).

LEAD SOURCE

The amount of lead released in the system per year from the automobile is estimated from data on gasoline sold. Gasoline consumption on an area basis can be fairly well estimated from reports of total state taxes collected[3] weighted (distributed) by either county motor-registration fees or population. The former distribution method was used here. Of the total of 3.285×10^9 gallons/year (based on 1972 data) used in the region of concern, 2.58×10^9 is from Cook County. To show the range that can be expected in reported numbers, the City of Chicago[4] lists the consumption of 4.24×10^9 gallons/year of gasoline in 1970. Gallons of gasoline was converted to grams of lead by the factor of 2.5 grams/gallon.

The non-automotive lead wasted in the system from fixed sources was estimated by using the national distribution of lead wasted in the environment according to reference (1). This distribution is referenced to the calculated gasoline consumption for the area. This leads to a figure of 9.25×10^9 grams/year of lead associated with non-automotive sources, all of which we associate with the solid environment.

The lead being convected by the atmosphere into the system cannot be estimated with any accuracy. We denote this by an unknown amount δ and treat it as part of the net lead lost to (or gained from) the surrounding by atmospheric transport.

Of the lead associated with gasoline consumption, a part is retained in the automobile that is part of the solid environment. A number for this retention factor has been reported by several investigators.[1],[5] Even-though the amount retained varies widely with the operational mode and condition of the vehicle, we consider that 15% of the gasoline lead goes directly to the solid environment.

These results are listed in Figure 1 where $6.97 \times 10^9 + \delta$ grams of lead per year go into the atmosphere while 10.48×10^9 grams per year are contributed to the solid environment. Several numeric places are included in these numbers only to indicate they come from calculations. The degree of confidence is only in their order of magnitude.

BOATING

Since the Lake was treated as a sink in the system, consideration was given to lead input due to the direct use of gasoline. The amount of gasoline consumed by boats operating on the Lake can be estimated from state tax data[3] to be approximately 2.7×10^7 gallons/year. References (6) and (7) estimate about 0.53 grams/gallon are put directly into the water by motorboat operations. We, therefore, have a boating input of lead to Southern Lake Michigan of 1.43×10^7 grams/year. This figure agrees with nation-wide estimates weighted by population for the region of concern.[7] This number is most likely an overestimation of the mechanism, but it is based on the best available information. A more detailed estimate based on number of boats registered and motorboat-use statistics is not called for in the present order-of-magnitude mass balance.

ATMOSPHERIC TRANSPORT

Precipitation Mechanisms: Precipitation (or wet) removal means here all removal of lead aerosols associated with precipitation. Such mechanisms are associated with aerosols acting as condensation sites (rainout) and the collision of aerosols with raindrops below the cloud (washout). These processes are extremely complex and one is forced to perform certain overall calculations to obtain transport numbers. The most direct method for obtaining wet removal rates is to measure the lead content in precipitation on a yearly and regional basis. Such data was taken for two locations in the Chicago area between September 1966 and March 1967.[8] The results of this study gave an average figure for Chicago of 24.5 grams of lead per hectare per centimeter of precipitation. Combining this information with an average yearly rainfall of 74 centimeters,[2] one can calculate 3×10^9 grams/year of lead into Southern Lake Michigan and 6.1×10^9 grams/year on the corresponding watershed. Of course, one must remember the data comes from city measurements which are not representative of the entire area.

To check the above data, a second approach can be used to estimate removal rates. Ignoring many complexities, one can write a simple relationship between air and precipitation lead-concentrations as

$$K = WC. \qquad (1)$$

Here K is the precipitation lead-concentration in μg/g, C is the air lead-concentration in μg/g, and W represents the "washout" efficiency (ratio). Using K = 0.245 μg/g from reference (8) and $C = 1.25 \times 10^{-3}$ μg/g, which is a typical city reading,[9] one obtains W = 196. Gatz[10] has also determined W from work in St. Louis and obtained values between 138 and 199 for lead. Even though the washout ratio is a function of many undetermined parameters, this agreement leads to some confidence in the data of reference (8).

Ter Haar[11] has also reported lead concentrations in precipitation at Argonne (30 miles southwest of Chicago) and in rural Michigan (about 90 miles northeast of Chicago). This data, taken between July and September 1966, showed a concentration that was more than a factor of ten less than that for rain collected in Chicago. However, atmospheric lead readings at these sites are only about a factor of two[12] less than Chicago. Therefore, this data is not in agreement with equation (1) and the reported W factors. We thus considered data of reference (8) to be more representative for the system.

To obtain the numbers appearing on Figure 1, we merely took one-half the calculation based on Chicago data and said that would represent the entire area of interest. A more detailed calculation (integration over the area with measured values for C and constant W) could be performed, but there is no doubt that the results represented the correct order of magnitude.

Dry Settlement: The size characterization of the lead aerosols from automotive exhausts, that make up the 6.97×10^9 grams/year atmospheric input, is the key in determining dry settlement figures. Large particles (greater than 10μ in equivalent diameter*) should settle out rapidly by gravity while smaller particles can be transported for large distances. Several investiga-

*Diameter figures refer to the diameter of a sphere that exhibits the "same" aerodynamic drag characteristics. This is a rather poorly defined parameter.

tors have reported experimental measurements of lead aerosol size distributions from automobile exhausts, [for example, reference (5) and (13)]. Their experiments were performed differently, and unfortunately, their reported data covers a wide range. Lee, et.al., concludes that 95% of the lead is below 0.5μ while Habibi's work gives average median equivalent diameters that vary from 0.6μ to 5.7μ. These latter data are for vehicles of different age and operating conditions. In reviewing the available data, it is reasonable to take 30% by weight of the emitted lead as having equivalent diameters greater than 3μ. We consider this lead to fall out very close to the source and to be returned immediately to the solid environment.

Most atmospheric measurements of lead aerosol size distributions,[1] on the other hand, seem to agree that approximately 95% by weight is below 0.5μ in diameter with a mass mean diameter of about 0.25μ. This information is used to estimate the dry settlement from the atmosphere when transport is beyond, say, 100 feet from the source.

The removal of small (less than a micron in diameter) aerosol particles from a turbulent flow field is not well understood.[14] Many dispersion models have been formulated and solved for the release of aerosols into the atmosphere from point and line sources. All these models ignore the question of a realistic boundary condition representing the loss of aerosols to the ground. This boundary condition is extremely difficult to formulate. The most researchers have accomplished is to include a gravitational settling term in the dispersion equation. Furthermore, no experimental data is available for our system on lead flux to the ground by dry settlement and impingement.

To obtain some idea about the importance of this mechanism, one can calculate terminal velocities for spheres of a typical diameter of lead aerosols. Table 1 gives some data taken from reference (14).

Diameter (microns)	Relaxation Time (seconds)	Velocity of Fall V_s (cm/sec)
0.2	2.6×10^{-6}	0.00254
0.3	4.85×10^{-6}	0.00475
0.5	1.13×10^{-5}	0.0135

Table 1. Relaxation Times and Terminal Velocities of Lead Spheres in Air at One Atmosphere and 20°C.

To put this information in perspective, one can calculate an effective fallout velocity $V_{s,p}$ due to precipitation. The relationship is

$$V_{s,p} = \frac{L}{CA} ,$$

where L is the lead per unit time falling on an area A with an air lead-concentration of C. Using the sourthern lake area, $L = 1.5 \times 10^9$ grams/year, and $C = 0.75\ \mu g/g^3$, one obtains $V_{s,p} = 0.382$ cm/sec. Taking the worst possible case that all lead aerosols are 0.5μ in diameter, one concludes the dry gravitational settlement is about 30 times less effective than precipitation mechanisms. These were the data used to estimate the numbers appearing on Figure 1 . As pointed out earlier, these dry settlement calculations ignore turbulent impingement mechanisms and represent a lower bound on this process.

GROUND-LEVEL TRANSPORT

The two main contributions of lead to Southern Lake Michigan by ground-level transport are sediment inflow by major rivers* and waste disposal directly into the lake by numerous small communities†. The sediment inflow of the three major rivers amounted to 7.5×10^5 tons/year.[15] With an average lead sediment-concentration of 28 μg/g, this sediment inflow contributes approximately 1.6×10^7 grams/year of lead to Southern Lake Michigan.

A compilation of waste water discharge into Lake Michigan has been reported.[16], [17] For Southern Lake Michigan the total waste sums to 3.7×10^8 gallons per year. Using an average lead content of 98 μg/liter, one obtains approximately 4.9×10^7 grams of lead per year from this source.

If lead is continued as a gasoline additive, lead concentrations in river sediments and waste will increase over the years. Thus, ground-level transport should be an increasing function of time. One should note that Figure 1 indicates a large lead accumulation in the solid environment in contrast to the fact that no evidence exists that the atmosphere is accumulating lead at a measurable rate.

*Grand, Kalamazoo and St. Joseph Rivers.

†The water inflow itself does not constitute an inflow of lead since its lead concentration is low and approximately equal to that for water in Lake Michigan.

SUMMARY

The results of the overall lead balance of Southern Lake Michigan is given in Figure 1 . It can be seen that atmospheric transport of automotive lead aerosols with precipitation washout is the most important mechanism for lead input to the Lake. It is almost two orders of magnitude greater than the other mechanisms. These figures are based on 1968-73 data and therefore represent an averaged result for a phenomenon which is most likely a function of time. With time one would predict, assuming air readings remain constant, increasing ground-level transport due to accumulation of lead in the solid environment.

Although measurements of lead in the sediments and waters of Lake Michigan[18],[19] show increasing amounts of lead in the sediments, it is not possible to compute the extent of this increase or the total amount present. One is thus not able to close the lead balance as a check on the predicted inflow of lead. The same is true for the solid environment [see reference (20)].

The purpose of this investigation was to answer the question of how much lead is transported through the atmosphere from its basic sources in the urban area of Chicago to Southern Lake Michigan. With the available data, this task was accomplished in the sense that the results are correct to their order of magnitude. A more detailed lead mass balance would involve a great deal of additional experimental and theoretical work. The weak link in the presented arguments is the work on dry deposition. To better understand this mechanism, a Master's thesis was written on the modeling of aerosol deposition by impingement in turbulent boundary layers. This work is not complete, but we have shown that simple mixing-length turbulent modeling cannot predict the important physics. The modeling has thus gone to statistical modeling of the turbulent flow that can predict impingement deposition. This work continues but will constitute a long-term research project.

One should be cautioned that the present lead mass-balance is performed with many argumentive assumptions. One should therefore not attempt to give the results more credence than the presentation and discussion merits.

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