Mass Balance for Lead in the California South Coast Air Basin: 
An Update¹

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A mass balance for lead for the year 1989 in the South Coast Air Basin has inputs to the atmosphere of 600 ± 190 kg/day and outputs of 580 ± 160 kg/day, showing rough agreement. Stationary sources are responsible for only about 5% of the total lead emissions. The bulk of the lead is emitted from vehicles using leaded gasoline (37%) and unleaded gasoline (15%), as well as from resuspension of previously deposited lead on roads (43%). Over half of the total emitted lead deposits on roads and nearby soil, while about one-third is carried out of the basin by wind. A small amount, less than 10%, is deposited on surfaces throughout the basin. These percentages are approximately the same as those in a mass balance for the same region calculated for 1972, when lead emissions from leaded gasoline were about a factor of 70 greater than leaded gas emissions in 1989. When the lead emissions are used as inputs to a simple continuously stirred flow reactor model for the basin, reasonable agreement is obtained between calculated and measured concentrations.

INTRODUCTION

Over the past 20 years the concentration of lead in the atmosphere in the U.S. has been significantly reduced, notably through the gradual phasing out of lead in gasoline. The ingestion of lead has been decreased by bans on lead solder for food cans and gradual replacement of lead pipes used for drinking water. Paint has also been regulated as a key step to further decreasing exposure to lead (SCAQMD, 1992). However, lead is currently used in processes such as soldering, electroplating, and manufacturing storage batteries. Lead is also present as a trace contaminant in fuel and in raw materials for processes such as cement manufacturing and waste incineration (CARB, 1997).

A mass balance for lead for 1972 was conducted for the South Coast Air Basin by Huntzicker et al. (1975). At that time the major contributor of atmospheric lead was the combustion of leaded gasoline, and Huntzicker et al. considered vehicle emissions to be responsible for essentially all of the atmospheric lead found in the basin. By 1989, however, the use of leaded gasoline had been greatly reduced. In this paper we report on an updated mass balance for lead in the same region. We have constructed the mass balance for the most recent year for which the various input data are all available, 1989.

THE NATURE OF LEAD EMISSIONS

Lead from both natural and anthropogenic sources is transported through the atmosphere primarily in the form of fine and coarse particles; only a small fraction is in the vapor phase. Fine particles are those with a diameter of less than 2.5 μm and are often emitted from combustion sources or are the result of gas-to-particle conversion. Coarse particles have a diameter greater than 2.5 μm and are usually generated by mechanical abrasion processes such as crushing and grinding; for example, soil particles released by wind erosion. Atmospheric lead is primarily found in fine particles, with a smaller fraction associated with coarse particles (Milford and Davidson, 1985; CARB, 1997). During transport, chemical transformations from one species to another can

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occur. The direction and distance that lead particles travel through the atmosphere are determined by several related factors such as wind currents, particle size, atmospheric mixing, and wet and dry deposition (CARB, 1997).

The size and composition of emitted lead can vary greatly from source to source. For example, lead emissions from nonferrous metal melting operations are predominantly fine particles of lead oxides and dioxides. Particle size distribution studies of emissions from an aluminum foundry have shown that approximately 80% of the total particulate matter emitted, which includes significant amounts of lead, is less than 1 \( \mu \text{m} \) in diameter (CARB, 1977). The majority of particulate emissions from stationary fuel combustion sources is also less than 1 \( \mu \text{m} \). Soil dust from unpaved urban areas and paved road dust are significant sources of lead with a wide range of particle diameters. Emissions from combustion of gasoline also include a range of particle sizes.

### SOURCES OF LEAD EMISSIONS

The South Coast Air Basin (SOCAB) includes Orange County and the non-desert sections of Los Angeles, Riverside, and San Bernardino Counties (SCAQMD, 1992; CARB, 1995). The California Air Resources Board (CARB) considers the major sources of outdoor lead emissions in the basin to include aircraft fuel combustion, stationary point and area source fuel combustion, autobody refinishing, secondary lead recycling, cogeneration plants, sawmills and paperboard mills, incineration, foundries and steel mills, paint and coatings, battery manufacturing, cement manufacturing, and sand and gravel (SCAQMD, 1992; CARB 1997).

CARB reports that 149 tons of lead were added to aviation fuel in California in 1990, equivalent to 370 kg/day; data are not available for 1989 (CARB, 1997). Relative to other sources we assume that a negligible amount of this lead is emitted below the mixing height in the SOCAB. In 1989 over 700 facilities in the basin used or processed lead or lead-containing materials (SCAQMD, 1992). Approximately 75 of those facilities used between 2 and 10 tons (1.8 and 9.1 metric tons) of lead per year, and 150 facilities processed 10 tons (9.1 metric tons) or more of lead each year. Many sources emit lead due to the handling of melted metals or mechanical processing of other materials. Metal melting operations that emit lead include galvanizing, tinning, soldering and brazing, and casting of type for printing. In other processes, lead or a lead-containing material is used in the manufacture of a product. Other nonvehicular sources of lead emissions include the production of leaded glass, aluminum powder production, lead oxide production, and the use of lead in target ranges (SCAQMD, 1992).

Vehicular emissions can result from the combustion of leaded gasoline and from the combustion of unleaded gasoline that contains trace amounts of lead. Although use of leaded gasoline in the SOCAB had been greatly reduced by 1989 relative to use in previous decades, the amount was nevertheless still significant.

### LEAD EMISSIONS DATA

Data on stationary source lead emissions for 1989 were obtained from the South Coast Air Quality Management District. These data were compiled through the Air Toxics “Hot Spots” Information and Assessment Act (AB 2588) Inventory Reports, which are biennial reports of toxic air pollutants from facilities (SCAQMD, 1992). Figure 1 presents the stationary source data used in the mass balance calculations in this paper. The total of these emissions is 34 kg/day. Throughout the paper, many of the calculations justify one or at most two significant digits. However, we use two or three significant digits in our calculations for bookkeeping purposes.

Data on the 1989 lead content of gasoline has been obtained from the California Air Resources Board (CARB, 1989a). CARB has tested gasoline samples from numerous gas stations in the Los Angeles area; the data have been subjected to rigorous quality assurance procedures. From these data, 94 samples of regular leaded gasoline have an average lead concentration of 0.065 \( \pm 0.029 \) g/gal (17 \( \pm 7.7 \) mg/L) (average value \( \pm \) standard deviation). The average lead concentration of 279 samples of unleaded gasoline has been calculated by two different methods. In the first method, all concentration entries of “< 0.02 g/gal” and “BDL” (below detection limits) are assigned a value of zero (151 samples), and the data have then been averaged to give a lower bound value of 0.0024 \( \pm 0.0036 \) g/gal (0.64 \( \pm 0.96 \) mg/L) for the average and standard deviation. In the second method, entries of “< 0.02 g/gal” are assigned a value of 0.02 g/gal (41 samples), and entries of “BDL” (110 samples) are assigned a value of 0.01 g/gal, which is the detection limit in these tests. The resulting value is 0.0095 \( \pm 0.0054 \) g/gal (2.5 \( \pm 1.4 \) mg/L), which may be considered an upper bound. The average of the lower and upper bounds is 0.0059 \( \pm 0.0065 \) g/gal (1.6 \( \pm 1.7 \) mg/L), where the uncertainty represents the compounded uncertainties of the two values. Compounding of uncertainties
in this and subsequent calculations assumes independence in the input values and is calculated as in Holman and Gadja (1989).

CARB has also issued quarterly reports on the lead content of both leaded and unleaded gasoline based on surveys from California refineries and gasoline blenders (CARB, 1989b). These surveys give a 1989 average lead content of 0.08 g/gal (21 mg/L) for leaded gasoline and an average lead content of 0.013 g/gal (3.3 mg/L) for unleaded gasoline. The American Automobile Manufacturers Association (AAMA) listing of its recommended specifications for high-quality commercial unleaded gasoline for sale in the U.S. includes a specification for lead; the limit is 0.01 g/gal (2.6 mg/L) maximum and requires no intentional addition of lead (AAMA, 1997). This value is comparable to both the measured data and the survey data. The source of the lead is not given, although one possible source is lead in the crude oil. In this paper, the data on the lead content of gasoline from the testing of gasoline samples have been used instead of the survey data.

To determine the total amount of lead in emissions in the SOCAB, we use data from the same survey showing the amount of gasoline produced and imported for California consumption in 1989. We consider all of this gasoline to be consumed within California in 1989. The ratio of leaded gasoline to unleaded gasoline produced for California consumption for these data is 0.185.

The California Department of Transportation (Caltrans) data show 316 million daily vehicle miles (510 million vehicle kilometers) traveled (VMT) each day in the SOCAB in 1989 (Caltrans, 1989). Using this Caltrans daily VMT and the 1989 average value of 17.4 miles per gallon (7.4 km/L) (Caltrans, 1989) yields 18.1 million gallons (69 million liters) used daily. With the above ratio of leaded to unleaded gasoline, this corresponds to 3.36 million gallons (13 million liters) of leaded gas and 14.8 million gallons (56 million liters) of unleaded gas used daily in the SOCAB. Huntzicker et al. (1975) used a factor of 25% lead retained in the automobile upon the combustion of gasoline, although they specified that this percentage applies only to 1972. Here we assume that all of the lead in gasoline is emitted to the atmosphere, although the actual amount must be somewhat less than this. The total daily lead emissions in the SOCAB are then 220 ± 97 kg/day for leaded gasoline and 90 ± 96 kg/day for unleaded gasoline; the sum is 310 ± 140 kg/day.

The amount of lead reentrained from road dust in 1989 has also been estimated by the California Air Resources Board. The CARB staff used a particulate matter emission estimate of 1.17 million tons (1.06 million metric tons) based on a report by the U.S. EPA (1988) and a measured particulate matter lead weight fraction of 0.000199 to estimate that 209 metric tons of lead were resuspended from all of the major paved roads in California during 1989 (CARB, 1997). This is equivalent to 570 kg/day of
lead reentrained. The amount of lead reentrained in the SOCAB has been calculated using the ratio of SOCAB VMT to California VMT, a value of 0.458. This gives 1989 daily lead emissions from reentrainment of 260 ± 130 kg/day, where an uncertainty of 50% has been applied; the true uncertainty may be even greater. Note that lead deposited on soil near roadways may also be reuspended and may contribute to airborne lead, although this contribution is unknown. Here we assume that reuspended road dust includes lead from both streets and soil. The emissions resulting from the combustion of leaded and unleaded gasoline and the reentrainment of lead in road dust are shown in Fig. 2. Calculations of the fractions in small and large particles are described in the next section.

NEAR DEPOSITION OF AIRBORNE LEAD

“Near deposition” is considered to be those particles that deposit in the immediate vicinity of a source (Huntzicker et al., 1975). While large particles are rapidly removed from the atmosphere and will deposit close to their source, small particles are more likely to remain suspended and to be inhaled (Nicholson and Branson, 1992). Here we assume that none of the emissions from stationary sources are deposited near the source, due to several previous studies showing the dominance of small particles in such emissions (CARB, 1997; Nriagu, 1978).

For the lead emitted from the combustion of both leaded and unleaded gasoline, we follow the calculations of Huntzicker et al. (1975), who considered that 57% of lead emissions from motor vehicles deposits near the roadways based on the size distribution data of Habibi (1970, 1973). This is the percentage of lead in emissions associated with particles greater than 9 μm aerodynamic diameter. For the 1989 data, this gives 180 ± 77 kg/day emitted from the combustion of gasoline and deposited near the source.

Vehicular movement as well as wind action can cause resuspension of particles in urban areas. Nicholson and Branson (1992) have shown that reuspended dust from paved roads is primarily coarse particles, and these redeposit quickly in the vicinity of the road. Eldering and Cass (1996) have reported that about 60% of the total suspended particulate mass (TSP) from paved road dust in Los Angeles is associated with particles greater than 10 μm aerodynamic diameter. They also report that about half of the emissions from noncatalyst cars are associated with particles in this size range; this is consistent with the data of Habibi (1970, 1973) cited above. Thus lead in road dust is expected to include an appreciable fraction of large particles. Here we assume that the 60% value for TSP also applies to lead in road dust. We therefore calculate that 160 ± 70 kg/day of the lead from reuspended road dust is associated with large particles and contributes to near deposition in the basin. Forty percent of the lead in road dust, 100 ± 52 kg/day, remains airborne and contributes to the basin-wide atmospheric concentration of lead. Using figures that have not been rounded, the total near deposition from the combustion of leaded and unleaded gasoline and

FIG. 2. Emissions resulting from the combustion of leaded and unleaded gasoline and from reentrainment of lead in road dust. Error bars show uncertainties in the total emissions of small plus large particles in each of the three source categories.
from resuspended road dust is $330 \pm 110$ kg/day. Note that the large particles assumed to be responsible for near deposition are those greater than 9 or 10 $\mu$m, as opposed to coarse particles defined earlier in the paper which refer to those with diameter greater than 2.5 $\mu$m.

**FAR DEPOSITION OF AIRBORNE LEAD**

"Far deposition" is considered to be particles that deposit outside the immediate vicinity of a source (Huntzicker et al., 1975). The deposition flux $F$ (kg/day) in the SOCAB is given by the equation $F = V_d \times A \times C$, where $V_d$ is the deposition velocity, $A$ is the area available for deposition within the SOCAB, and $C$ is the airborne concentration. Several approaches suggest that the deposition velocity of lead in the SOCAB should be about $0.2 \pm 0.1$ cm/s. Huntzicker et al. (1975) report deposition rates of flat Teflon plates along with airborne concentrations that imply a deposition velocity of approximately 0.18 cm/s. Friedlander et al. (1986) found that Pb/CO airborne concentration ratios in tunnels (considered to be characteristic of source emissions) were greater than values of this ratio in ambient air since Pb is deposited while CO is conserved. This information was used with the average residence time in the SOCAB to deduce a deposition velocity of 0.26 cm/s. Davidson and Wu (1990) summarize lead deposition velocities in the literature and report that most values are in the range 0.1–1.0 cm/s. Note that all of these values refer to dry weather, which dominates the annual flows of lead in the SOCAB (Huntzicker et al., 1975).

In the 1972 mass balance of Huntzicker et al. (1975), the area of the SOCAB was assumed to be 4430 km$^2$, as shown in Fig. 3. Between 1972 and 1989, the basin experienced growth in regions to the east of central Los Angeles. This recently built-up area extends several tens of kilometers eastward. Since winds are predominantly from the west, we might expect sources to contribute continually to atmospheric lead levels along a west-to-east trajectory. This "pipe flow" model would predict steadily increasing airborne concentrations along the trajectory. However, airborne lead data show roughly similar concentrations throughout the SOCAB (CARB, 1989c). This is probably because emissions in the new areas are somewhat lower than those in central Los Angeles due to the lower population density. Therefore we assume that the area of the SOCAB in 1989 is the same as that in 1972. Because of the uniformity in airborne concentrations, we choose to model the basin as a continuously stirred flow reactor, as did Huntzicker et al. We thus calculate far deposition $F$ using an airborne lead concentration of $0.065 \pm 0.022 \mu$g/m$^3$ (average $\pm$ standard deviation based on data from 11 sites (CARB, 1989c)) and the values of $V_d$ and $A$ given above. The result is $50 \pm 30$ kg/day. Note that although far deposition is based on an airborne concentration that is primarily small particles, the deposited lead mass is expected to have a disproportionate share from the fraction of large particles present in the atmosphere. The deposition velocity of 0.2 cm/s is an aggregate value based on the full size distribution of airborne lead.

**REMOVAL OF AIRBORNE LEAD BY WIND**

Huntzicker et al. (1975) assumed that the removal of lead from the SOCAB by wind could be estimated by considering the flow of CO as a conservative tracer emitted from the same source, namely the automobile tailpipe. Although lead and CO no longer had identical sources in 1989, it is still possible to use CO data to estimate the ventilation rate of air leaving the basin each day. The total flow of lead out of the basin is then merely equal to the ventilation rate in m$^3$/day multiplied by the airborne lead concentration.

Modeling the SOCAB as a continuously stirred flow reactor in steady-state, the ventilation rate

![Diagram of the portion of the South Coast Air Basin used in this study. Modified from Huntzicker et al. (1975).](image-url)
Q (m³/day) is equal to the total emissions (g/day) divided by the airborne concentration of CO (g/m³). The CO emissions rate has been calculated by the Southern California Association of Governments for 1987 and 1990 using two models that are the result of a joint effort by CARB and Caltrans (SCAG, 1994). The value interpolated for 1989 is 3980 metric tons/day (SCAG, 1990). In another study, measurements by Pierson et al. (1990) in a tunnel in the Los Angeles area show average emissions of 25 ± 3 g CO/mile (16 ± 2 g/km). When multiplied by the Caltrans daily VMT discussed earlier, their resulting CO emissions are 7890 ± 950 metric tons/day; this is one of the only available emissions estimates made on the basis of actual field measurements. Nevertheless, it must be recognized that the Pierson et al. value is not representative of the wide variety of driving conditions encountered. In this study we adopt the average of these two emissions estimates, or 5930 ± 1960 metric tons/day (average ± range of values). Note that the CO emissions standard for California for 1989 was 7 g per mile (4 g/km) for gasoline and diesel passenger cars (CARB, 1994), illustrating that the standard was being greatly exceeded.

In 1989 the annual average measured concentration of CO was 2.0 ± 0.65 mg/m³ (average ± standard deviation based on data from 23 sites, 11 of which are the same as those for lead (CARB, 1989c)). The average CO concentration for those 11 sites is 2.2 ± 0.70 mg/m³, suggesting that both lead and CO are roughly uniformly mixed across the basin. When the average emissions rate is divided by the average airborne concentration, the result is $Q = 3.0 \times 10^{12} \pm 1.4 \times 10^{12}$ m³/day. This ventilation rate is then multiplied by the average measured airborne lead concentration cited in the previous section to yield 200 ± 110 kg/day for the amount of lead removed by wind. The same analysis with the 1972 CO emissions and airborne concentration data from Huntzicker et al. (1975) gives a ventilation rate of $2.2 \times 10^{12}$ m³/day. We expect the values in 1972 and 1989 to be identical if the wind speed, mixing height, and width of the basin are the same in both years. Given the uncertainties in the CO data, the meteorology, and the assumed size of the basin, the agreement is reasonable.

Figure 4 summarizes the near deposition, far deposition, and removal by wind for lead.

**COMPLETE MIX MODEL**

We assume that the average atmospheric concentration of the basin can be described by a complete mix model. At steady-state, the atmospheric concentration is given by the equation

$$C = \frac{S_a + S_e (1 - f_e) + S_t (1 - f_t)}{Q + V_d A}$$

where $C$ is the concentration, $S_a$ is the emissions from stationary sources, $S_e$ is the emissions from the combustion of gasoline, $S_t$ is the emissions from the reentrainment of lead in road and soil dust, $f_e$ is the fraction of lead from the combustion of gasoline that is deposited nearby, $f_t$ is the fraction of reentrained lead from road and soil dust that is deposited nearby, $Q$ is the ventilation rate, $V_d$ is the deposition velocity, and $A$ is the land area.

As previously discussed, values $f_e$ and $f_t$ are 0.57 and 0.6, respectively. Using the stationary source emissions, gasoline emissions, ventilation rate, and previously discussed values for deposition velocity and area, Eq. (1) gives an estimated average atmospheric concentration of $0.071 \pm 0.035 \mu g/m^3$. This is in reasonable agreement with the 1989 measured average atmospheric concentration of $0.065 \pm 0.022 \mu g/m^3$.

**RESULTS AND DISCUSSION**

The results of these calculations are summarized in Table 1. Automobile-emitted lead (including resuspension of previously deposited road dust lead) is responsible for approximately 95% of the total lead emitted into the SOCAB atmosphere in 1989. Note that the amount of resuspended material is substantial. Emissions from the combustion of unleaded gasoline are also significant, although there is considerable uncertainty in the estimate.

Table 1 shows rough agreement between inputs and outputs of lead in the SOCAB. Over half of the lead is deposited on or near roadways, with less than
10% depositing on soil, vegetation, and other surfaces throughout the basin. About one-third is carried out of basin by wind. Despite the fact that emissions from leaded gasoline in 1989 are a factor of 70 smaller than those reported by Huntzicker et al. (1975) for 1972, the fractions of lead in near deposition, far deposition, and removal by wind in the Huntzicker study are similar to those in this paper: values for 1972 are 9500 ± 2200, 2000 ± 1000, and 5300 ± 3000 kg/day, respectively. Note that the annual average measured airborne concentration of lead in 1972 (SCAQMD, 1978) was 2.9 μg/m², a factor of 45 greater than that in 1989.

Although Table 1 shows rough agreement between inputs and outputs, it must be acknowledged that the uncertainties are large, and thus the possibility of additional sources of lead cannot be ruled out. There are a number of sources that could be considered. Cars fueled with leaded gasoline in Mexico and driven to the Los Angeles area may result in additional emissions. Many older cars in the SOCAB using unleaded fuel previously used leaded gasoline; these may emit lead that was deposited on pipes in the exhaust system (Silva and Prather, 1997; Hildeman et al., 1991). Although the analysis here attempts to account for resuspended road dust, the surface soil throughout the SOCAB is also likely to contain deposits of lead that accumulated for decades, and this lead may be resuspended into the atmosphere. Lead in flaking paint from buildings, bridges, and other structures has not been included in this analysis.

### CONCLUSIONS

A mass balance for lead has been constructed for the South Coast Air Basin in California for the year 1989. Inputs to the basin include stationary sources, vehicles using leaded gasoline, vehicles using unleaded gasoline, and resuspended road dust. Outputs include deposition near sources, deposition throughout the basin far from sources, and removal from the basin by wind.

A total of 600 ± 190 kg of lead is emitted into the SOCAB atmosphere each day. This is in rough agreement with the estimated outputs, which total 580 ± 160 kg/day. Stationary sources are responsible for only about 5% of the total input to the atmosphere; the remaining lead is contributed as primary emissions from vehicles or as resuspended road dust. More than half of this lead is deposited on or near the roads, and about one-third is removed from the basin by wind. The remaining lead, less than 10%, deposits on surfaces throughout the basin.

It is of interest to consider the likely current sources of lead in 1997 in the SOCAB. Stationary point source lead emissions for California listed in a recent report total 65 kg/day (CARB, 1997). Beginning in January 1992 in California, the use of lead additives in on-road motor vehicle fuel was banned, and the amount of lead as a trace contaminant in fuel was restricted to a maximum of 0.05 g/gal (13 mg/L) (CARB, 1997). Thus the contribution of lead from vehicles has certainly fallen from its value in 1989. The contribution of lead from resuspended road dust and soil dust is unknown, although it is expected to decrease over time.

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### REFERENCES


### TABLE 1

<table>
<thead>
<tr>
<th>Inputs to SOCAB atmosphere (kg/day)</th>
<th>Outputs from SOCAB atmosphere (kg/day)</th>
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<tbody>
<tr>
<td><strong>Stationary sources</strong></td>
<td><strong>Near deposition</strong> 330 ± 110</td>
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<tr>
<td>Combustion of leaded gasoline</td>
<td>Far deposition 50 ± 30</td>
</tr>
<tr>
<td>Combustion of unleaded gasoline</td>
<td>Removal by wind 200 ± 110</td>
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<tr>
<td>Road dust</td>
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<tr>
<td>Total inputs</td>
<td>Total outputs 580 ± 160</td>
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*The stationary source emissions have been truncated from 34 to 30 kg/day when computing the sum of inputs in the mass balance.


