

Lead Isotopes as Age Sensitive, Genetic Markers in Hydrocarbons:

3. Leaded Gasoline, 1923-1990 (ALAS Model)

By

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Abstract

Anthropogenic Lead ArchaeoStratigraphy (ALAS Model) utilizes measured lead isotope ratios of documented gasoline releases as preserved in a variety of matrices (product, soils, water) to accurately estimate the year of the release. ALAS is unique, in that it is the only model for which historic data, i.e. U.S. lead production figures, are available that allow the nature of the calibration curve to be modeled and calculated for time intervals where calibration samples are scarce (pre-1960). Independent modeling of the data also allows one to evaluate the assumption that lead isotope ratios (e.g. $^{206}\text{Pb}/^{207}\text{Pb}$) of gasoline additives, such as tetraethyllead, closely followed those of average annual U.S. industrial lead. By integrating U.S. lead production figures with lead isotope ratios of domestic, foreign, and recycled sources, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of average annual U.S. industrial have been calculated from the year lead additives were first introduced, 1923, through 1990, which, for practical purposes, marks the end of the leaded gasoline era. The calculated $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are in excellent agreement with those of ALAS Model calibration samples between 1923 and 1990 ($R^2 = 0.945$). The results indicate that the production of alkylleads by firms such as Ethyl and DuPont relied upon lead purchased from that available on the U.S. market rather than sources that were non-representative of that market. In addition to the ALAS Model's utility in estimating the year of gasoline releases, temporal fluctuations and trends observed in the model between 1923 and 1990 provide a series of chronostratigraphic markers, which can be related to variations in U.S. industrial lead sources and, in some instances, historic events during the 20th Century.

INTRODUCTION

Although the combustion and accidental release of gasoline containing alkylleads (e.g. tetraethyllead; TEL) have resulted in lead pollution on both continental and local scales, gasoline-derived lead preserved in the environment has potential to be used as both a chronometer and stratigraphic marker of the 20th Century during the years when leaded gasolines were prevalent (1923 to ~ 1990). Previous work by Hurst (2000) demonstrated that systematic increases in the lead isotopic composition (e.g. $^{206}\text{Pb}/^{207}\text{Pb}$) of gasoline after 1965 could be calibrated, and the resultant calibration curve, termed the ALAS Model (Anthropogenic Lead ArchaeoStratigraphy), used to estimate the age of episodic and multiple gasoline releases.

Prior to the ALAS Model, methods employed to estimate the age of a gasoline release relied upon degradation rates of alkylbenzenes (Odermatt, 1994; Kaplan et al., 1997) and/or utilizing knowledge of time intervals when certain additive formulations were blended with gasoline (Gibbs, 1990, 1993; Bruce and Schmidt, 1994; Stout et al. 1998). Although these methods were convenient, because the gasoline constituents used to estimate the age of a release were routinely analyzed in the course of environmental remediation, critical reviews of these methodologies indicate the accuracy and age resolution is often insufficient (Morrison 2000a, 2000b). By comparison, age resolution of the ALAS Model ranges from ± 1 to 2.5 years for releases which occurred between 1965 and 1990 (Hurst 1996, 2000).

The objective of this paper is the extension the ALAS Model to 1923, the year alkylleads were first introduced as antiknock compounds to motor fuel (Robert, 1984). Ideally, this would be accomplished in the same manner the ALAS Model was

developed, by analyzing samples of well-dated gasoline releases or actual gasoline samples produced between 1923 and 1965. Although acquisition of such samples is difficult, five have been identified and analyzed for this purpose.

To fill in the gaps where calibration samples are not available, a second approach is employed involving the calculation of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the ALAS Model by assuming gasoline lead isotope ratios follow those of the annual average U.S. industrial lead isotopic signature. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the latter can be modeled by integrating published lead production data (U.S. Bureau of Mines Yearbooks, 1920–1992) with lead isotope ratios of ore sources published in the literature (Doe, 1970; Doe and Deleveaux, 1972; Stacey and Kramers, 1975; Faure, 1986). If $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of calculated U.S. industrial lead are in accord with those observed in ALAS Model calibration samples, i.e. leaded gasoline, it implies that major producers of TEL purchased lead from the average annual U.S. market and that the calculated values are representative of the ALAS Model, allowing the calibration to be accurately extended back in time.

Statistically, there are ~125 data points defining the ALAS Model calibration curve, which for the sake of brevity and due to their restricted $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, are averaged for each year data exist and compared to the calculated value for that year. The maximum age resolution of the ALAS Model is one year, hence attempts to evaluate shorter term fluctuations would not be meaningful. The ALAS Model is unique, being the only method of estimating the age of a gasoline release for which published, historic data exist from which the nature of the calibration curve can be modeled.

LEAD ISOTOPIC EVOLUTION OF ORES

There are four naturally occurring, stable isotopes of lead (Pb), three of which are radiogenic, i.e. their abundances increase over time due to the radioactive decay of either uranium (U) or thorium (Th) isotopes. The three radiogenic Pb isotopes, their radioactive parent nuclides, and half-lives ($t_{1/2}$) given in billions of years (Ga) are as follows:

^{208}Pb - ^{232}Th ($t_{1/2} = 14.01$ Ga); ^{207}Pb - ^{235}U ($t_{1/2} = 0.7038$ Ga); and ^{206}Pb - ^{238}U ($t_{1/2} = 4.468$ Ga; Faure, 1986). The fourth isotope of lead, ^{204}Pb , is nonradiogenic, having no radioactive parent nuclide. Although either ^{204}Pb or ^{206}Pb can be used as a reference isotope, i.e. analytical results reported as $^{206}\text{Pb}/^{204}\text{Pb}$ and/or $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, most environmental studies utilize the latter ratio for comparisons. Despite the long half-lives of U and Th isotopes, high crustal U/Pb and Th/Pb ratios have resulted in increases of $\sim 30\%$ in $^{206}\text{Pb}/^{207}\text{Pb}$ over 4.6 Ga of Earth history (Stacey and Kramers, 1975).

The common ore of lead used in the production of alkyllead is galena (PbS), which contains trace quantities of uranium and thorium relative to $\sim 865,000$ ppm Pb. As a result, once galena is formed during a mineralization event in the crust, its lead isotopic evolution ceases because U and Th concentrations are virtually zero. Hence, galenas which are geologically older, generally have lower, less radiogenic, lead isotope ratios. One exception, however, are ores derived from crustal sources enriched in U and Th, such as the Mississippi Valley type ores discussed below.

Major sources of lead used in the production of alkylleads, such as tetraethyllead, include ores from Australia, Canada, South Africa, Peru, Chile, Mexico, and the former Yugoslavia; domestic sources include lead deposits found in Idaho, Colorado, Utah, Arizona, California, and the Mississippi Valley (U.S. Bureau of Mines Yearbooks, 1920-

1992). Geologic ages of these ore deposits are diverse, ranging from the early Precambrian Era (~ 2.5-3.5 Ga) to the early Tertiary Period of the Cenozoic Era (30-65 Ma; million years; Doe, 1970; Faure, 1986). The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the early Precambrian-age galenas from Australia, Canada, South Africa, and Idaho range from 1.00 to 1.15 while those of Tertiary-age galenas from Peru, Chile, Mexico, and Yugoslavia average ~1.20 (Chow et al., 1975; Doe, 1970).

The Mississippi Valley Type (MVT) lead deposits are hosted in Paleozoic (245-570 Ma) carbonate rocks and are referred to as "anomalous leads" (Doe, 1970; Doe and Deleveaux, 1972). Lead isotope ratios of these ores are extremely radiogenic given their geologic age, with $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of some ores exceeding 1.30 (average \approx 1.28). The systematic, increased reliance of the United States lead industry on lead from MVT sources, was proposed as the reason for the observed increases in gasoline lead isotope ratios beginning circa 1968 as first observed in southern California marine sediments (Ng and Patterson, 1982) and corroborated by the ALAS Model (Hurst, 1996, 2000).

ANTHROPOGENIC LEAD ISOTOPIC RATIOS AND THE ALAS MODEL

Temporal variations in anthropogenic lead isotope ratios are controlled by changes in the sources of lead emitted into the environment. Documented, regional variations have been correlated to coal-burning (Chow and Earl, 1972) and urbanization of the Great Lakes region, beginning with deforestation and coal combustion circa 1860, ore smelting in 1930, and finally gasoline combustion between 1930 and 1980 (Ritson et al., 1994; Graney et al., 1995). Lead isotopic fluctuations in the anthropogenic component of soils (Erel and Patterson, 1994; Monna et al., 1997), aerosols (U.S.-Canada, Sturges and Barrie, 1987), and polar ice (Boutron et al., 1991, 1994; Rosman et

al., 1994) have been attributed to temporal changes in lead input derived from different industrial sources, each source being identified by their unique lead isotopic fingerprint.

Principles of the ALAS Model

Shirahata et al. (1980) and Ng and Patterson (1982) reported rapid, temporal increases in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the anthropogenic lead component of terrigenous and marine sediment in southern California, which they believed were related to increasing proportions of MVT lead used in gasoline through the 1970's. Their work, however, focused on global lead pollution and refinements in analytical methods required to deal with sub-ppb levels of lead in samples (Patterson and Settle, 1976, 1987), rather than the development of a chronometer to estimate ages of gasoline releases. In conjunction with work by Chow et al. (1975), these investigations identified gasoline combustion as the major source of lead pollution and demonstrated that lead isotope ratios in sediment were conservative, remaining unaltered by biogeochemical processes in soils.

The development of the ALAS Model built upon these previous investigations by acquiring reliable calibration samples, and analyzing them using high precision lead isotopic methods. Sources of samples used to calibrate the ALAS Model include university archives (California Institute of Technology, Oregon State University), petroleum industry research lab collections, operating service stations, and sites of documented gasoline releases in the United States (Hurst, 2000). An early version of the ALAS Model is shown in Figure 1. Only 41 of ~125 calibration points can be resolved at the scale of the diagram. The data are presented using a "delta" notation similar to that employed in light stable isotope analyses (e.g. C, H, O, N, S; Faure, 1986):

$$\delta^{206}\text{Pb}_{\text{ALAS}} = \frac{1000 \left[\frac{^{206}\text{Pb}/^{207}\text{Pb}_{\text{SAMPLE}}}{^{206}\text{Pb}/^{207}\text{Pb}_{\text{STANDARD}}} - \frac{^{206}\text{Pb}/^{207}\text{Pb}_{\text{STANDARD}}}{^{206}\text{Pb}/^{207}\text{Pb}_{\text{STANDARD}}} \right]}{^{206}\text{Pb}/^{207}\text{Pb}_{\text{STANDARD}}}$$

Approximate $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are presented in Figure 1 for reference.

The morphology of the post-1960 ALAS Model curve is controlled by the systematic increase in the use of radiogenic ores from MVT sources, which account for ~40-45% of domestic lead production pre-1960 but increase to ~90% by the late 1980's (Figure 2; U.S. Bureau of Mines Yearbooks, 1920-1992). The introduction of these highly radiogenic ores to alkyllead production is the controlling factor, driving the $\delta^{206}\text{Pb}_{\text{ALAS}}$ value up from -24 in the late 1960's to values of +12 by 1980. The influence of MVT lead is evident when one compares the morphology of the ALAS Calibration Curve in Figure 1 to changes in the percentage of MVT ores as a percentage of U.S. lead between 1960 and 1990 (Figure 2). The similarity is striking, with each curve exhibiting steep slopes between ~1965 to 1980, followed by more moderate slopes through the 1980s.

The lack of scatter in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, apparent in the ALAS Model (Figure 1), and applicability throughout the U. S. are attributed to two factors: a relatively well-mixed domestic lead supply (Ng and Patterson, 1982; Hurst, 2000); and nationwide TEL distribution. Lead on the U.S. market during the 20th Century relied heavily on MVT and recycled sources (Figures 2 and 3). Collectively, these two sources have accounted for ~60-85% of total U.S. industrial lead from 1923 to 1990. As a result, the average lead isotopic composition of lead on the U.S. market has been constrained by the well mixed, rapidly utilized recycled pool (Smith, 1998) and MVT lead whose isotopic range is restricted ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.30 \pm 0.02$; Doe, 1970; Faure, 1986).

The distribution of TEL plays a significant role in the geographic applicability of the ALAS Model. Major alkyllead manufacturers, Ethyl and DuPont, often collaborated,

rather than competed on the production - distribution of alkylleads (Robert, 1984), purchasing lead from a U.S. market controlled by the recycled pool and MVT sources. For more than 50 years, through ~1980, TEL not only accounts for ~10-25% of lead consumption annually in the U.S. (Figure 2; U.S. Bureau of Mines Yearbooks, 1920-1992), but also is rapidly distributed nationwide, explaining the applicability of the ALAS Model throughout the U.S. (Hurst, 2000).

CALCULATED VERSUS CALIBRATED $\delta^{206}\text{Pb}$ OF THE ALAS MODEL

By integrating published U.S. Bureau of Mines lead production figures with lead isotopic ratios of ore deposits, the annual average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of U.S. industrial lead, hereafter R_C , can be calculated using the following relationship:

$$R_C = \Sigma \{ [X_D \Sigma(A_i R_{Di})] + [X_F \Sigma(B_i R_{Fi})] + [X_R R_R] \}$$

As discussed next, variables in the calculation of R_C include the weight fractions of U.S. lead derived from domestic, foreign, and recycled lead (X_D , X_F , and X_R respectively); and weight fractions of lead produced by individual states or foreign nations (A_i and B_i respectively). Average lead isotope ratios of ore deposits, as published in the literature mentioned above, have been used. Once R_C is determined, $\delta^{206}\text{Pb}_{\text{ALAS}}$ (hereafter $\delta^{206}\text{Pb}$) is calculated as discussed earlier.

Model Parameters

Weight Fractions of Domestic, Foreign, and Recycled Lead. Yearly production figures are first used to determine the weight fractions of domestic, foreign, and recycled lead (X_D , X_F , and X_R) which contribute to annual U.S. lead production. Note that recycled lead is classified as “old scrap” in government publications. Variations in these three model parameters are presented in Figure 3. Note that foreign lead, derived

primarily from Canada, Mexico, and South America, rarely exceeds 15% of U.S. lead production; domestic and recycled lead production figures mirror each other, i.e. when domestic ore production drops, it is replaced with recycled lead, and consistently total ~90% of the U.S. lead pool since 1923 when TEL was introduced.

Domestic and foreign contributions can be apportioned further using lead production data from individual states and nations; these weight fractions are referred to as A_i and B_i respectively. States or foreign nations whose lead accounted for $> 1\%$ of U.S. lead production in any given year have been included in the calculation.

Ore Lead Isotope Ratios. As discussed earlier, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of each domestic and foreign lead ore source (R_{Di} and R_{Fi} respectively) have been published, allowing the contribution of each of these components to the average lead isotopic ratio of U.S. industrial lead, including TEL, to be modeled. The lead isotopic composition of the recycled lead component (R_R) requires a knowledge of the time lag of lead recycling as well as the lead isotopic ratio of the recycled lead.

Time lags associated with recycling of lead have been estimated to range from ~5 to 10 years, being a function of the time scale of lead production and the useful lifetime of products (~ 3-10 years), such as batteries, which consume lead (Graney, 1994; Graney et al., 1995; International Lead and Zinc Study Group, 1995; Smith, 1998). The efficiency of lead recycling, $>90\%$, and the expediency with which old scrap lead is recycled subsequent to the end of a product's useful lifetime, ~ 1 year, is dramatic (Smith, 1998). Hence, the 5-10 year lag times assumed in the calculation of R_R discussed next, are a reasonable average range for this model parameter.

In order to assess the effect on R_C by 5 to 10 year lag times, two calculations were performed using the calculated $^{206}\text{Pb}/^{207}\text{Pb}$ of U.S. industrial lead five and ten years prior to the year R_C is being calculated; i.e., when calculating the R_C of U.S. industrial lead in 1975, R_R is assigned the calculated value for $^{206}\text{Pb}/^{207}\text{Pb}$ of U.S. industrial lead as determined for 1970, then for 1965, producing two results for R_C , which take into account lag times of recycling of 5 and 10 years respectively; as will be observed, calculated values of R_C using a 5 versus 10 year lag time, are not significantly different except for the time period between 1980 and 1986.

Uncertainty in R_C and $\delta^{206}\text{Pb}$. Variations in average $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of ore deposits produce average uncertainties in R_C ranging from ± 0.003 (1946 to 1990) to ± 0.005 (1923 to 1945); resulting uncertainties in $\delta^{206}\text{Pb}$ are ± 3 to ± 4 respectively. The subsequent discussions of temporal variations in $\delta^{206}\text{Pb}$ are predicated on observed fluctuations in $\delta^{206}\text{Pb}$ which exceed those of the uncertainties.

U.S. INDUSTRIAL LEAD AND THE ALAS MODEL

Results of the calculations to model the evolution of U.S. industrial lead between 1923 and 1990 are plotted in Figure 4. Relationships between $\delta^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are identical to those presented in Figure 1.

Pre-1960 U.S. Industrial versus ALAS Model $\delta^{206}\text{Pb}$

Prior to 1960, the $\delta^{206}\text{Pb}$ of U.S. industrial lead ranges from ~ -20 to -36 with observed fluctuations being dependent on the annual input of radiogenic MVT lead, which averages $\sim 43\%$ of annual domestic U.S. lead production prior to 1960. The recycled lead component, which increases over this same interval, contributes less

radiogenic old scrap to annual production. Both factors work to maintain less radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and lower values of $\delta^{206}\text{Pb}$ for U.S. industrial lead from 1923 to 1960.

It is possible to subdivide 1923 to 1960 into five time intervals, each defined by statistically distinct mean values for $\delta^{206}\text{Pb}$. The subdivisions are as follows (errors are 95% confidence levels; note that mean $\delta^{206}\text{Pb}$ for 1937-1939 and 1941-1946 are identical):

1923 – 1933	-18 ± 1.5
1934 – 1936	-26 ± 0.8
1937 – 1939	-21 ± 0.8
1940	-36 ± 0.8
1941 – 1946	-21 ± 0.8
1947 – 1960	-30 ± 1.5

The post-1933 period is significant because nationwide distribution and market expansion of TEL commences at this time (Robert, 1984).

There are five calibration samples identified to date which define the ALAS Model curve prior to 1960. Three archived California marine sediments impacted by gasoline lead have ^{210}Pb ages of 1925 ± 3 , 1947 ± 2 , and 1959 ± 1 (Ng and Patterson, 1982); measured $\delta^{206}\text{Pb}$ values for these samples are -19.8 , -23.9 , and -29.7 respectively. The fourth sample, a leaded gasoline, was recovered from an underground storage tank at a service station that operated from 1941 to 1945 (1943 ± 2 ; Oregon Department of Environmental Protection; R. Miller, personal communication); $\delta^{206}\text{Pb}$ for this product was determined to be -21.4 . The fifth datum point was acquired through Professor Emeritus T.J. Chow (1998, personal communication) and is a recalculation of lead

isotope results of 1947 TEL published by Chow et al (1975). Their analysis, as was common in the early 1970s, did not include corrections for instrumental variations and normalization to isotopic standards. Following current protocols, the analysis of the 1947 TEL was corrected, yielding a value for $\delta^{206}\text{Pb}$ of -25.5 . The measured $\delta^{206}\text{Pb}$ values for these five calibration sample are in excellent agreement with those calculated for U.S. industrial lead (Figure 4).

The War Years. The time interval from 1937 to 1954, encompassing U.S. involvement in World War II and the Korean War, reflects changes in the utilization of lead for national defense. During 1940, contributions by less radiogenic ore, both foreign and domestic, increase by 25-50% while MVT sources decline (U.S. Bureau of Mines Yearbooks, 1939-1941). The result is an anomalously low value of $\delta^{206}\text{Pb}$ in 1940 (~ -35) relative to other years where lead ore production is more representative of the times (Figure 4). A portion of lead production records remained confidential in 1940 for national security reasons, leading to the possibility that MVT ores were used by labs developing U.S. thermonuclear capabilities (e.g. Oak Ridge, Tennessee; Los Alamos, New Mexico) and other defense related products. Similar low values of $\delta^{206}\text{Pb}$ during the early 1950s (1951 – 1955), the Korean War years, reflect a drop in domestic production and increased reliance on less radiogenic recycled lead (Figures 2 and 4).

Post-1960 U.S. Industrial versus ALAS Model $\delta^{206}\text{Pb}$

The post-1960 interval is initially marked by a decrease in $\delta^{206}\text{Pb}$ to ~ -40 , which is followed by the steady, rapid increase in $\delta^{206}\text{Pb}$ to values of $\sim +30$ by 1990. The increased reliance on MVT lead, recycling of old scrap lead which becomes more radiogenic as stockpiles accrue higher proportions of MVT lead, and gradual decline in

contributions from foreign sources of lead contribute to the dramatic increase in $\delta^{206}\text{Pb}$ of U.S. industrial lead during this time interval (Figures 2 and 3).

The number of calibration points defining the post-1960 portion of the ALAS Model exceeds 100, hence, for brevity, comparisons with calculated values of $\delta^{206}\text{Pb}$ use average annual values from the ALAS Model. The correlation between $\delta^{206}\text{Pb}$ values of calculated U.S. industrial lead versus those of the ALAS Model from 1960 to 1990 is significant ($R^2 = 0.936$; Figure 4). If the five pre-1960 comparisons are added, the impact on the regression analysis is not statistically different ($R^2 = 0.945$), but their inclusion further supports the conclusion that $\delta^{206}\text{Pb}$ values of the ALAS Model, and therefore leaded gasoline, followed those of average annual U.S. industrial lead (Hurst, 2000). Average annual $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the ALAS Model versus R_C agree to $\leq 0.25\%$, indicating that alkylleads were manufactured from stores of lead that were representative of the average annual U.S. market rather than from non-representative sources as implied by critics of the model (see Morrison 2000a and 2000b).

The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (R_R) of the recycled lead component and choice of 5 versus 10 year lag times influence calculated values of R_C between 1980 and 1986 due to rapidly increasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of U.S. industrial lead after 1970. Prior to 1970, and excluding the observed low values of $\delta^{206}\text{Pb}$ (1940, 1951-1955, 1962), the $\delta^{206}\text{Pb}$ of U.S. industrial lead is relatively uniform, averaging -23 ± 2 , hence, the choice of a 5 versus 10 year lag time in recycling has a negligible impact on R_C because R_R is almost constant.

Between 1980 and 1990, the sharp increase in MVT lead use prevalent through the 1970s has leveled off, but MVT ores now account for $>85\%$ of the total domestic U.S. lead (Figure 2). From 1980 to 1986, the lag time for recycled lead impacts the value

of R_C because lead recycled from the late 1970s is more radiogenic than lead in the early 1970s (5 versus 10 year lag times respectively). As a result, each R_C calculated using a 5-year lag time exceeds that based on a 10-year lag time by 0.5% to 0.8%. However, the different lag times do not degrade the agreement between calculated values of R_C relative to those of the ALAS Model, which average $< 0.3\%$ and $< 0.6\%$ for 5 versus 10 year lag times respectively. Overall, the average $\delta^{206}\text{Pb}$ for U.S. industrial lead between 1980 and 1986 calculated using 5 and 10 year lag times is $+12.2$, in excellent agreement with the average $\delta^{206}\text{Pb}$ of ALAS Model calibration samples ($+12.3$; Figure 4).

Between 1986 and 1990, as the era of leaded gasoline approaches its end, annual $\delta^{206}\text{Pb}$ values of calculated U.S. industrial lead and those of the ALAS Model are virtually identical and increase (Figure 4). As was the case for the pre-1970 recycled lead component, $\delta^{206}\text{Pb}$ is relatively uniform in the early 1980s ($+13 \pm 2$), hence the influence of 5 versus 10-year lag times on R_C between 1986 and 1990 is negligible. The large inputs of radiogenic lead from both the recycled pool and MVT sources cause $\delta^{206}\text{Pb}$ to increase, approaching $\sim +30$ by 1990.

$\delta^{206}\text{Pb}$ Minima. In addition to the observed minima in $\delta^{206}\text{Pb}$ during the war years, 1940 and 1951 – 1955, another occurs in 1962 ($\delta^{206}\text{Pb} \sim -40$). This minimum is documented not only in calculated values of $\delta^{206}\text{Pb}$, but also by ALAS Model calibration samples (Figure 4).

This minimum in 1962 can be linked directly to a workers' strike at the largest lead mine in Missouri. While production of MVT ores ceases for months, production of less radiogenic lead from Idaho increases dramatically to fill market needs (U.S. Bureau of Mines Yearbook, 1962). As is evident in Figure 4, the decrease in $\delta^{206}\text{Pb}$ due to the

influx of less radiogenic lead is immediately apparent. The response of the U.S. lead market to the drop in radiogenic MVT ore production in 1962 is rapid as evidenced by the precipitous decrease in $\delta^{206}\text{Pb}$. This rapid response plus observed concordance between $\delta^{206}\text{Pb}$ of calculated U.S. industrial lead and ALAS Model calibration samples between 1961 and 1963 countermand concerns that alkylleads were occasionally manufactured utilizing large quantities of lead that were non-representative of that available on the U.S. market, thereby increasing the uncertainty and compromising the accuracy of the ALAS Model. Rather, the data support earlier conclusions by Hurst (1996, 2000), that the occasional use of large quantities of lead from sources that were non-representative of the average U.S. market did not occur because they would have either been recorded as major fluctuations in $\delta^{206}\text{Pb}$ as observed in 1962 or led to far more scatter than is observed.

The years in which $\delta^{206}\text{Pb}$ exhibit minima, 1940, 1951-1955, and 1961-1963, coincide with those associated with the development and atmospheric testing of thermonuclear devices; perhaps coincidentally, during the latter two periods, dramatic increases in atmospheric concentrations of radioactive fallout products also occur (e.g. ^3H , tritium, and ^{137}Cs ; Faure, 1986; Geyh and Schleicher, 1990). Although the relationship between lead and thermonuclear devices may be more than coincidental given military applications of lead, temporal variations observed in $\delta^{206}\text{Pb}$ from 1923 to 1990 provide a series of chronostratigraphic markers with each minimum or trend directly relatable to variations in U.S. industrial lead sources, which in turn may be tied to historic events of the 20th Century. Where detailed data permit, the ALAS Model should,

and is being compared to other anthropogenic signals to evaluate the possible existence of international or global archaeostratigraphic markers.

CONCLUSIONS

Annual $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and resultant $\delta^{206}\text{Pb}$ values, calculated from U.S. lead production figures and lead isotope ratios of ores, are in excellent agreement and exhibit significant correlations with those of ALAS Model calibration samples between 1923 and 1990. Thus, on the time scale of one year, the maximum resolution of the ALAS Model and time frame of the comparisons discussed herein, the results indicate that the production of alkylleads by firms such as Ethyl and DuPont relied upon lead acquired from the average U.S. market rather than sources that were non-representative of that market as has been suggested in critical reviews of the ALAS Model. Despite the gradual phasing out of lead additives in gasoline in the mid-1970s (Gibbs, 1990, 1993), a significant fraction of lead production in the U.S. went into the manufacturing of tetraethyllead until ~1980 (U.S. Bureau of Mines Yearbooks, 1920-1992).

Prior to ~1960, $\delta^{206}\text{Pb}$ values of five ALAS Model calibration samples are concordant with those calculated from U.S. lead production figures, both being low and relatively uniform, averaging ~ -23. Major decreases are observed in $\delta^{206}\text{Pb}$ circa 1940 and 1951 - 1955, responding primarily to declining inputs from radiogenic Mississippi Valley Type ores to the U.S. lead market, which may, in turn, be related to the use of lead in military applications.

Subsequent to ~1965, $\delta^{206}\text{Pb}$ values of the ALAS Model begin a steady increase from ~ -40 observed circa 1962 to ~ +30 by 1990 as the era of leaded gasoline approaches its end. During this time interval, $\delta^{206}\text{Pb}$ values of ALAS Model calibration

samples and those calculated from U.S. industrial lead production are significantly correlated ($R^2 = 0.936$) and in excellent agreement; both values increasing due to the systematic, increased reliance upon Mississippi Valley Type ores by the U.S. lead industry. Both calculated and ALAS Model calibration sample values of $\delta^{206}\text{Pb}$ exhibit a prominent decline in 1962, rapidly reflecting the removal of radiogenic lead from the U.S. market due to a workers' strike at the largest lead mine in Missouri that same year. The results of this work countermand suggestions that alkyllead manufacturers utilized lead that was non-representative of that available on the U.S. market, which, if correct, could compromise the accuracy of the ALAS Model. The modeling supports conclusions that the routine use of non-representative lead by Ethyl and DuPont would have resulted in significant lead isotopic variability and scatter in the model, neither of which is observed (Hurst, 1996, 2000).

Fluctuations and trends observed in $\delta^{206}\text{Pb}$ from 1920 to 1990 provide a series of chronostratigraphic markers, which can be related to variations in U.S. industrial lead sources and, in some instances, historic events during the 20th Century. The ALAS Model is being compared to other anthropogenic signals to evaluate the possible existence of international or global archaeostratigraphic markers.

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FIGURE CAPTIONS

Figure 1. ALAS Model Calibration Curve (© Richard W. Hurst, 1997; Hurst, 2000)

Figure 2. U.S. domestic lead since 1960: Percentage derived from Mississippi Valley

Type (MVT) sources; tetraethyllead (TEL) production percentage of U.S. lead.

Figure 3. Variation in contributions from domestic, recycled, and foreign sources to U.S.

lead production since 1923.

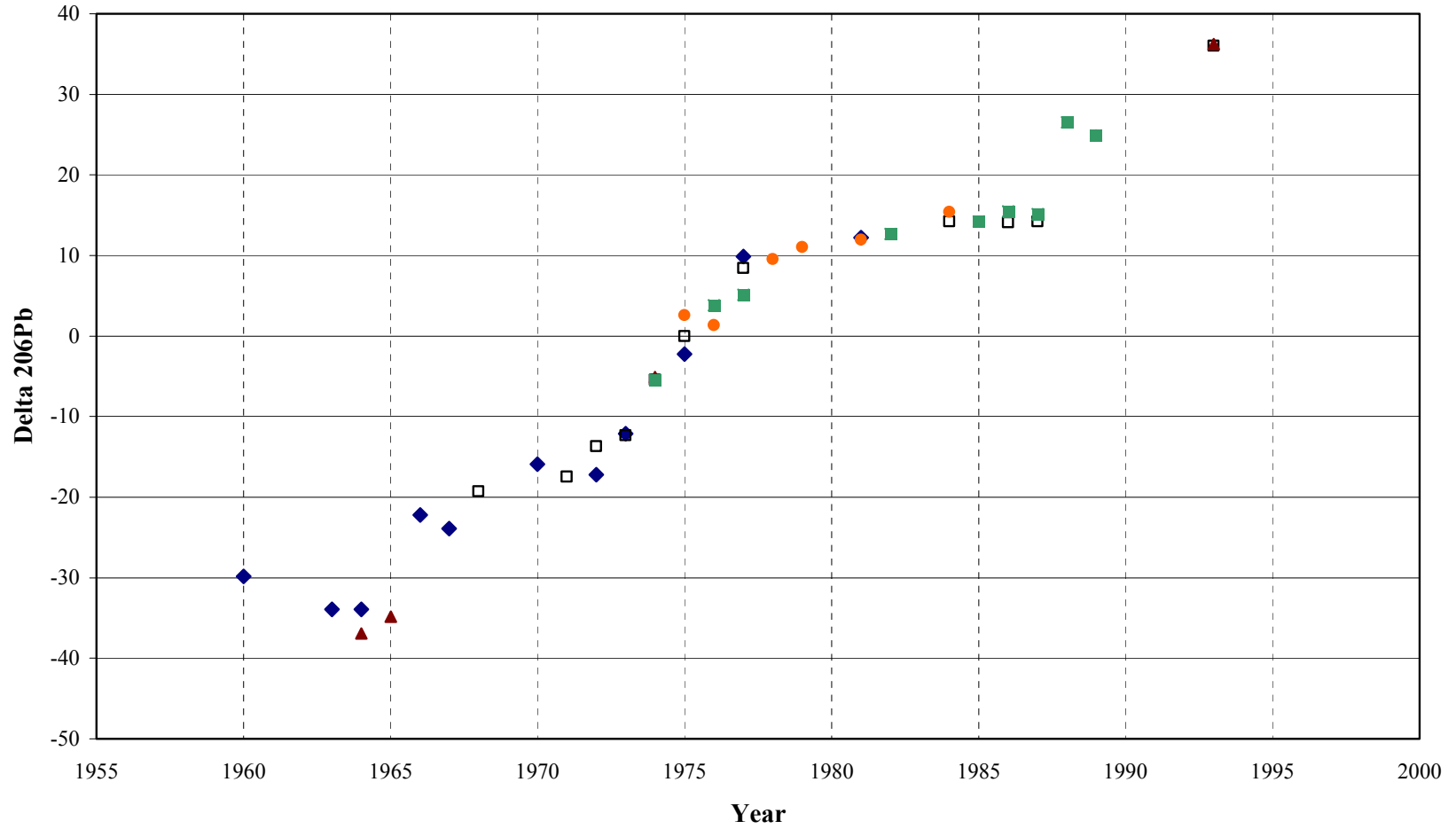
Figure 4. Comparison between measured lead isotopic compositions ($\delta^{206}\text{Pb}$) of ALAS

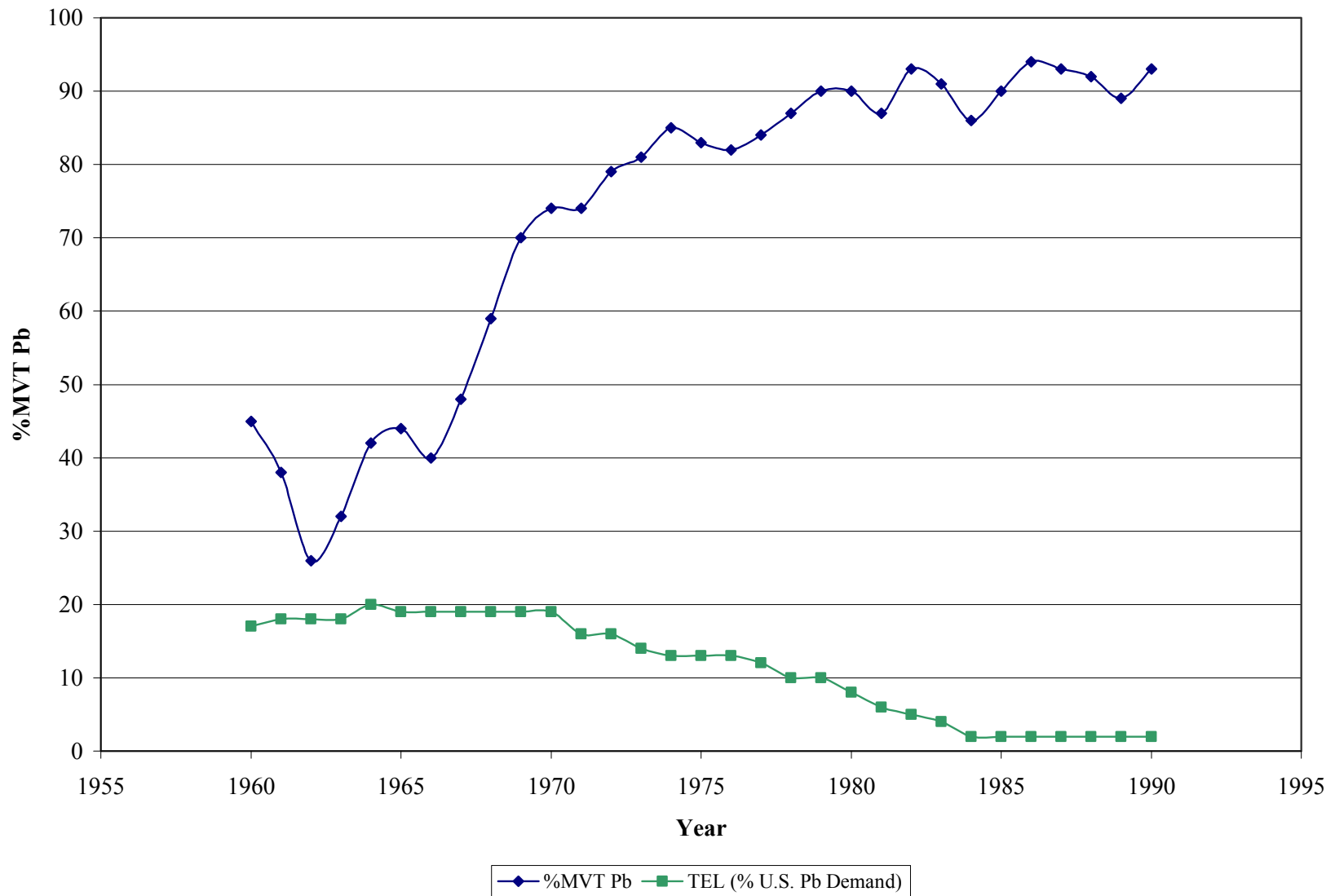
calibration samples and those calculated using U.S. Bureau of Mines annual

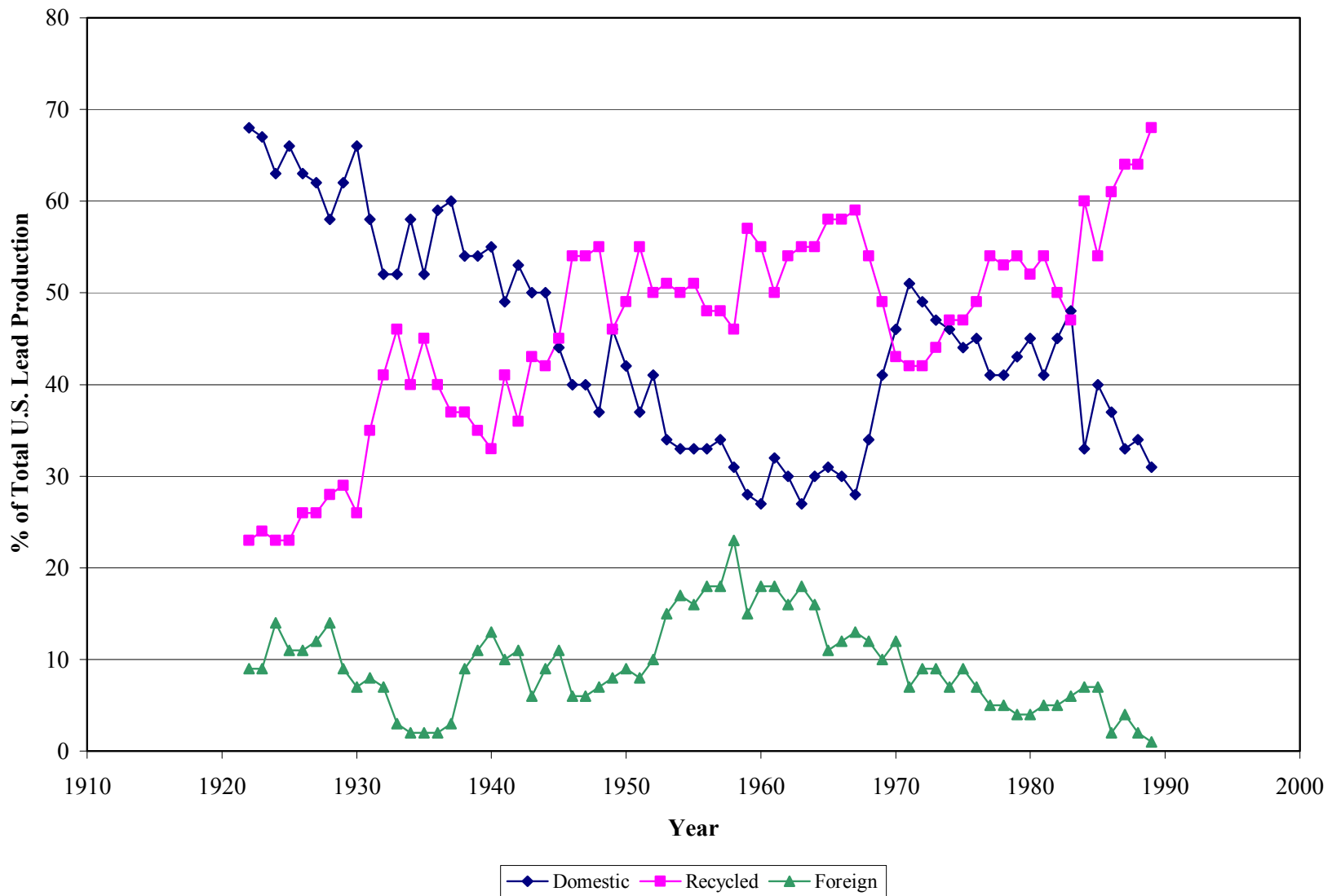
lead production data. For clarity, annual average $\delta^{206}\text{Pb}$ values are plotted

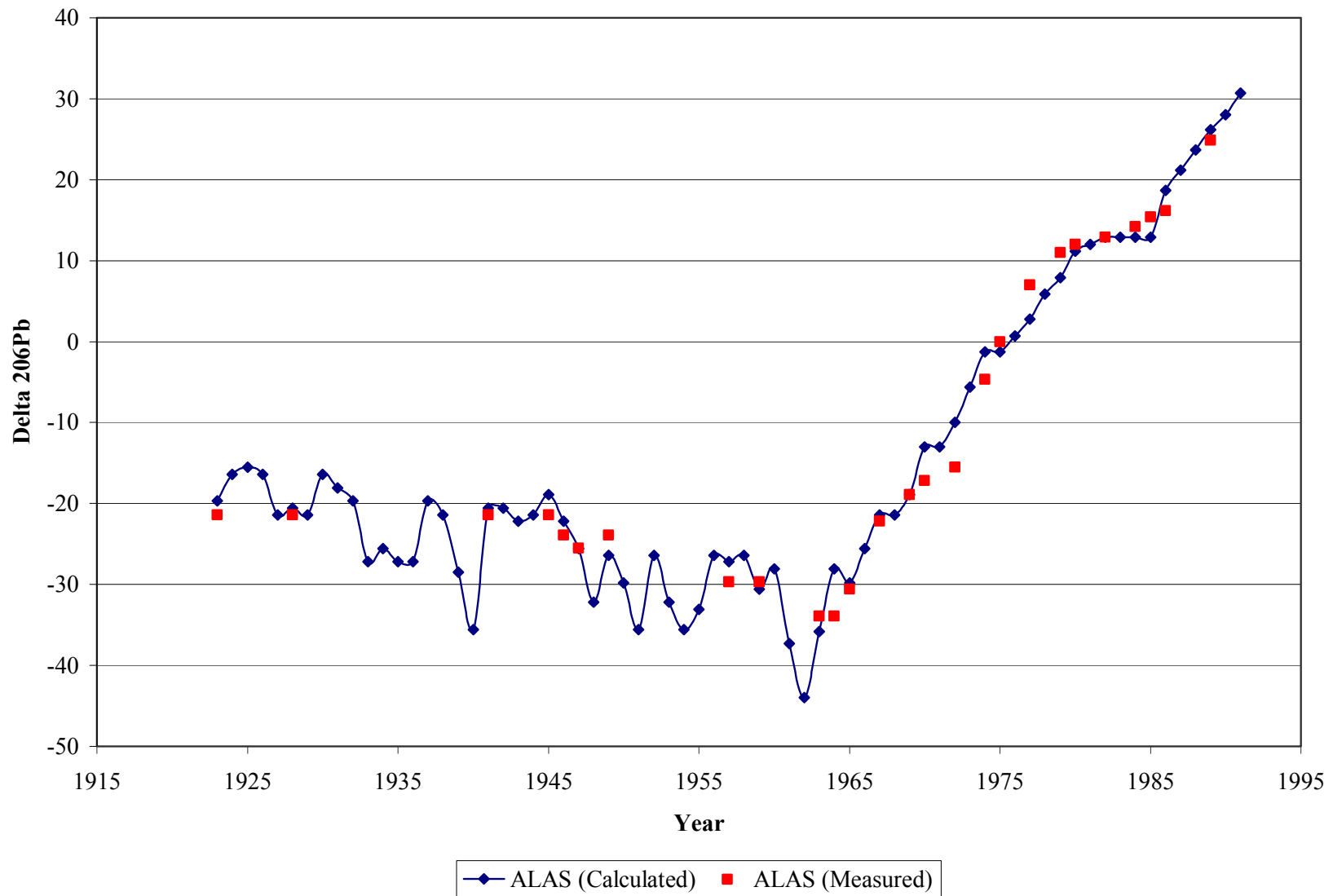
for calibration samples.

ALAS Model (1955-1995)









APPENDIX: ALAS Calibration Samples

<u>Sample Type/Location (Number of Samples)</u>	<u>Year of Product/Release</u>	<u>Chronologic Method; Source</u>
<i>Marine Sediment:</i>		
San Pedro, CA (12)	1945, 1949, 1958, 1960, 1963, 1964, 1966, 1967, 1970, 1972, 1973, 1975	²¹⁰ Pb/Varve Chronology; C. Patterson, CA Inst. Tech.
San Pedro, CA (3)	1977.5, 1981.4, 1990.9	²¹⁰ Pb/Varve Chronology; Huh, OR State Univ.
<i>Dispensed Gasoline (3)</i>		
Ventura County, CA	1983, 1987, 1991	Real Time Collection
San Diego, CA (1)	1965	Real time Collection; T.J. Chow (pers. comm.)
<i>Archived Gasoline:</i>		
Union Oil, CA (2)	1975	Hartley Research Lab, CA
Chevron Oil, CA (3)	1975, 1979, 1984	LaHabra Research Lab, CA
<i>Free Product:</i>		
Torrance, CA (14)	1974, 1976, 1982, 1983, 1986, 1987, 1988	CalEPA, Los Angeles Fire Dept. Records
Santa Ana, CA (3)	1972, 1978	CalEPA Records
Los Angeles, CA (13)	1970, 1971, 1972, 1973, 1974, 1975	Los Angeles Fire Dept. Records
Trenton, NJ (7)	1985, 1991	Site Inventory Records
St. Louis, MO (4)	1974, 1986, 1987, 1988	St. Louis Fire Marshall and Site Inventory Records
Baltimore, MD (3)	1973	¹³⁷ Cs of Impacted Sediment
Chicago, IL (8)	1974, 1975, 1976, 1980	Site Transfer Line Repair Documentation
<i>Gasoline-Impacted Sediment:</i>		
Los Angeles, CA (9)	1970, 1971, 1972, 1973, 1974, 1975	Los Angeles Fire Dept. Records
Simi Valley, CA (7)	1968, 1977, 1986	Dated Aerial Photography; Real Time Collection
Baltimore, MD (2)	1973	¹³⁷ Cs of Impacted Sediment
Tampa Bay, FL (5)	1972, 1988-1990	Site Inventory Records
Chicago, IL (4)	1981, 1982, 1983, 1984	Refinery Pipeline Release Records

Suggested Readings

General Articles (Non-Technical):

Hurst, R.W. (1994). Chemical fingerprinting using lead isotopes. *Calif. Environ. Rept.* **4**, 171-175.

Hurst, R.W. et al. (1996). Lead fingerprints of gasoline contamination. *Environ. Sci. Tech.* **30**, 304A-307A.

Peer-Reviewed Journal Publications and Abstracts:

ALAS Model---

Hurst, R.W. (1996). Age dating of gasoline releases using stable isotopes of lead (ALAS Model) In: *Geochemical Fingerprinting in Environmental Geology*. (Hurst, R.W. and Fisher, J.B.). Amer. Assoc. Petrol. Geol. Short Course #9

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