Using Pb and Sr Isotopes to Assess Asian Aerosol Impacts in Urban and Interior California

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Abstract

We investigated the use of Pb and Sr isotopic measurements of PM2.5 to evaluate the impact of Asian (Chinese) sourced aerosols (including pollutants, and mineral dust) on air quality in California. Aerosols transported across the Pacific can raise local "background" pollutant burdens, limiting the amount of local emissions that can be permitted and still attain State and Federal Air Quality Standards. PM2.5 samples collected at Mt. Tamalpais and Chabot Space and Science Center in the Oakland Hills, archived ARB PM2.5 samples and samples from the Eastern Sierra were analyzed for Pb and Sr isotopes. The Mt. Tamalpais and Chabot samples were also analyzed for elemental composition. The Pb isotopic measurements demonstrated that the collected aerosols contain Pb that was a variable (with time and location) mixture of locally-derived and China-sourced Pb. Likewise, Sr isotopic measurements combined with elemental data show that the aerosols at Mt. Tamalpais contain a variable fraction of Chinese sourced mineral aerosol ("Loess"). These data clearly track Asian sourced transport events and demonstrate the utility of isotopic signatures for portioning the sources of PM2.5, particular elements, and perhaps ozone in California. For example, during the week of 7/21/08 about 45% of the PM2.5 mass at Chabot was sourced in Asia.

Executive Summary

Background

Aerosols from both industrial and natural sources can be lofted into the atmosphere and carried great distances by winds, facilitating the intercontinental communication of soil components, biological material (bacteria, viruses) and pollutant particulates. Far travelled aerosols from Asia (in particular Asis), including mineral dust, pollutant particulates along with any accompanying volatile/gaseous pollutants such as ozone, can all contribute to the pollutant burden in the free troposphere over California. By increasing the local "background" pollutant burden in California, the amount of local emissions that can be permitted and still attain State and Federal Air Quality Standards is reduced. Future growth of emissions in Asia (China) will increase this background contribution, and may well complicate the attainment of air quality standards in California. But the absolute extent of such effects, and their temporal/seasonal nature, in California are not particularly well known.

The focus of the research is the use of the Pb and Sr isotopic compositions of aerosols collected in California as a "return address" for apportioning distal and local sources. Specifically, to quantify the fraction of Pb and Sr in an aerosol sample that originated in Asia (China). The isotopic compositions of Pb and Sr are naturally variable due to radioactive decay processes of their parent isotopes over Earth's history, and provides globally spatially variable "signatures" related to a region's geological history and composition. As this present research and previous research has shown, there is a useful isotopic distinction between Asian and Californian sources of Pb and Sr, with Pb isotopes tracking anthropogenic/industrial sources (the dominant source of Pb to the atmosphere, even with the phase-out of leaded gasoline) and Sr isotopes tracking sources of natural mineral dust. The power of isotopic analysis lies not only in the ability to discern source, but also in the source apportionment of identified endmembers in an intimate aerosol mixture. This allows subtraction of the local component, clarifying the extent and time variation of the far-travelled components, such as PM2.5 and particular elements, as identified by Pb and Sr isotopic analysis.

Methods

We set up two sites for week-long collection periods of PM2.5 aerosols on Teflon filters, Mt. Tamalpais and the Chabot Space and Science Center. Mt. Tamalpais provided a relatively pristine site, above the marine boundary layer and usually, though not always, effected by winds from the west off the Pacific Ocean. The Chabot site is located in the Oakland Hills, east of and typically downwind of the heavily urban areas of San Francisco and Oakland. These two sites are close enough, with similar winds, that sampling at both sites should distinguish the addition of urban aerosols at Chabot to a uniform far travelled aerosol population at both sites. The aerosol samples were analyzed for total mass, Pb and Sr isotopic compositions, and elemental compositions. We also conducted Pb and Sr isotopic analysis of aerosols collected in the Eastern Sierra overlapping in time a portion of the Mt. Tamalpais/Chabot collection campaign. In addition, we analyzed the Pb isotopic

compositions of archived ARB PM2.5 aerosol samples collected in Central California during the springs of 2003, 2004 and 2005.

The total mass of PM2.5 on the Teflon filters was determined by pre- and post-sampling weighing of the filters. The filters were cleaned prior to weighing and deployment in the field. These methods were used for both the Chabot and Mt. Tamalpais filters; however, pre-weighing of filters was not carried out for the ARB samples. Elemental compositions and concentrations of the Chabot and Mt. Tamalpais PM2.5 were determined by XRF (Crocker Lab) and Synchrotron-XRF (S-XRF at the Advanced Light Source, LBNL). The PM2.5 samples were leached from the filters using 6 n HCL, the resulting solutions were put through ion exchange columns to produce Pb and Sr separates for isotopic anlaysis. All sample processing was conducted under clean-room conditions, and high-purity reagents were used. Pb isotopic compositions were measured using a multi-collector magnetic sector ICP mass spectrometer (MC-ICPMS) and Sr isotopic compositions were measured using a thermal ionization multi-collector mass spectrometer (TIMS).

Results

Calculated apparent Pb concentrations in PM2.5 at Chabot and Mt. Tamalpais ranged from from ~20 ppm to over 800 ppm, up to 40 times higher than in average upper continental crust (20 ppm Pb), suggesting the presence of anthropogenic Pb in a majority of the samples. The Pb isotopic analyses of the PM2.5 samples revealed isotopic compositions that on a plot of $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ varied between an array representing California sources and an array representing Asian (mostly Chinese) sources of Pb. Timeseries of the Pb isotopic data for Mt. Tamalpais and Chabot shows that the influence of Asian Pb during 2008 was greatest from March through May. The Pb isotopes are used to calculate the fraction of Asian (Chinese) sourced Pb, which with the total Pb concentration yields the concentration in air of Asian sourced trans-Pacific transported Pb (trans-Pacific Pb, ng/m^3). Sr isotopic compositions of the PM2.5 varied in a similar fashion, and through a relationship between Si/Ca and $^{87}Sr/^{86}Sr$ allowed the identification of Chinese Loess (or desert soil) as an endmember. The concentration in air of trans-Pacific Sr for the Mt. Tamalpais samples could then be calculated. Examination of correlations of isotopically apportioned trans-Pacific Pb and trans-Pacific Sr with concentrations of particular indicative elements, suggests trans-Pacific Pb sourced in Asia is related to coal combustion (trans-Pacific Pb best correlates with K, S, Zn, As), while trans-Pacific Sr is related to natural soil (e.g. Chinese Loess) sources (trans-Pacific Sr best correlates with "soil", Si, Ca, Fe). Timeseries of trans-Pacific Pb, trans-Pacific Sr, calculated "soil" all point to four separate Asian transport events during the March-May 2008 period. In the first three events, the peaks in trans-Pacifc Pb, trans-Pacific Sr and "soil" (and so the arrivals of pollutants and dust) coincide in time, while in the fourth event, the arrivals of maximum Asian Pb and maximum Asian Sr and "soil" were separated by as much as two weeks, reflecting changes in the Asian/Chinese portions of air mass trajectories during that fourth event. Seasonal averages of trans-Pacific Pb (concentration in air, ng/m3) indicate the greastest influence of Asian sources occurred in Spring 2008, with the lowest influence in Summer 2008.

Conclusions

In California (if not western N. America), Pb isotopes are a proxy for Asian sourced pollution, while $^{87}Sr/^{86}Sr$ can serve as a proxy for Asian-sourced mineral dust (Chinese loess and desert soils). The similarity in the records of trans-Pacific Pb between an essentially pristine site (Mt Tamalpais- maximum trans-Pacific Pb = 72% of total Pb) and an urban influenced site (Chabot- maximum of trans-Pacific Pb = 35%) confirms that Pb isotopes can be used to quantify trans-Pacific transported Asian influence at California urban sites. Data from Eastern Sierra demonstrates that the Asian sourced aerosols can be tracked eastward from Mt. Tamalpais by Pb isotopes across the whole of Northern California. High correlations for K, S, Zn, and As with calculated trans-Pacific Pb indicate coal combustion as the source of the anthropogenic Pb. In the case of trans-Pacific Sr, strong correlations with Si, Ca, and Fe support natural soil (e.g. Chinese Loess) as the source of that Sr. Pb and Sr isotopic data can be used to partition the source of PM2.5, particular elements, and perhaps ozone. For example, during the week of 7/21/08 about 45% of the PM2.5 at Chabot in the Oakland Hills, though effected by local urban sources, was sourced in Asia. For Chabot the average percentage of PM2.5 sourced in Asia for the period March through May was ~25%, the season of greatest Asian influence.

Introduction

Aerosols from both industrial and natural sources can be lofted into the atmosphere and carried great distances by winds, facilitating the intercontinental communication of soil components, biological material (bacteria, viruses) and pollutant particulates. Far travelled aerosols from Asia (in particular Asia), including mineral dust, pollutant particulates along with any accompanying volatile/gaseous pollutants such as ozone, can all contribute to the pollutant burden in the free troposphere over California. By increasing the local "background" pollutant burden in California, the amount of local emissions that can be permitted and still attain State and Federal Air Quality Standards is reduced. Future growth of emissions in Asia (China) will increase this background contribution, and may well complicate the attainment of air quality standards in California. But the absolute extent of such effects, and their temporal/seasonal nature, in California are not particularly well known.

The focus of the research reported here is the use of the Pb and Sr isotopic compositions of aerosols collected in California as a "return address" for apportioning distal and local sources. Specifically, to quantify the fraction of Pb and Sr in an aerosol sample that originated in Asia (China). The isotopic compositions of Pb and Sr are naturally variable due to radioactive decay processes of their parent isotopes over Earth's history, and provides globally spatially variable "signatures" related to a region's geological history and composition. As this present research and previous research has shown, there is a useful isotopic distinction between Asian and Californian sources of Pb and Sr. The power of isotopic analysis lies not only in the ability to discern source, but also in the source apportionment of identified endmembers in an intimate aerosol mixture. This allows subtraction of the local component, clarifying the extent and time variation of the far-travelled components, such as PM2.5 and particular elements, as identified by Pb and Sr isotopic analysis.

In the present study we analyzed a time-series of samples that we collected through aerosol (PM2.5) sampling at two Bay Area localities: Mt. Tamalpais, representing a relatively pristine site commonly intercepting air coming in off the Pacific, and at the Chabot Space Sciences Center in the Oakland hills representing a site typically effected by local urban aerosol sources to the west (e.g. Oakland, San Francisco). These aerosol samples, PM2.5 collected on Teflon filters typically for 7 days, were analyzed for PM2.5 mass, elemental composition, Pb and Sr isotopic compositions. The resulting time series of 7-day average samples, allows us to look for seasonal variations, as well as to compare Pb and Sr isotopic records to elemental records and the records of the mass of PM2.5. These comparisons also allows us to seek a relationship between trans-Pacific Pb and PM2.5 at Mt. Tamalpais, which then can be used to evaluate the component of far-traveled (tran-Pacific Asian sourced) PM2.5 in the aerosols collected at Chabot. To investigate the further down-wind behavior of the trans-Pacific Pb isotopic signature we analyzed aerosol samples from the Eastern Sierra (provided by the Great Basin Unified APCD) collected during Spring 2008, correlatable in time to the Mt. Tamalpais and Chabot timeseries. As part of our research we also analyzed archived ARB aerosol PM2.5 samples collected in the northern Central Valley during spring 2003, spring 2004

and spring 2005. As one source of comparison, we analyzed PM2.5 samples collected in the spring of 2002 in Hefei China for Pb isotopic composition.

Background

Lead Isotopes

Lead (Pb) consists of four stable isotopes, ^{204}P, ^{206}Pb, ^{207}Pb and ^{208}Pb in the approximate relative abundances of 1.4%, 24.1%, 22.1% and 52.4% respectively (Faure 1986). However, in detail these relative abundances vary in natural lead, and hence in anthropogenic Pb derived from natural sources, due to radiogenic processes that have occurred over the history of the Earth. Decay of the naturally occurring uranium isotopes ^{235}U and ^{238}U, ultimately produces ^{207}Pb and ^{206}Pb. Decay of ^{232}Th (by far the most abundant isotope of thorium) leads to ^{208}Pb. In contrast, ^{204}Pb is not produced by radioactive decay, and so provides a "benchmark" to gauge the relative abundances of the other Pb isotopes. In mass spectrometry, isotopic data are generated in the form of ratios of the abundances of the isotopes of an element. In the case of Pb this is typically ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb. Two (or three) of these ratios can be plotted against each other, or these ratios can be combined in various ways for alternate graphical presentations of the isotopic data (e.g. ^{207}Pb/^{206}Pb vs. ^{208}Pb/^{206}Pb). The precision of Pb isotopic measurements depends on the method used. For ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios, as used in the research described below, the precision is on the order of ±0.02% or better when measured by multi-collector ICP mass spectrometry (MC-ICPMS) (with Tl doping) or double-spike thermal ionization mass spectrometry (TIMS) (with unspiked and double-spiked runs). Less precision is typically obtained using traditional TIMS (about ± 0.05%) or quadrupole ICP mass spectrometry (±0.1%). Higher precision (i.e. 0.02% or better) is required in many situations to resolve Pb isotopic differences.

The lead content in atmospheric aerosols can be greatly increased by anthropogenic contributions associated with industrial processes (e.g. smelting of ores), combustion of coal and other fuels, waste incineration, and to the use (now greatly reduced) of leaded gasoline. Because the relative concentrations of Pb, U and Th vary in different portions of the Earth, and because Pb has been effectively separated from U and Th as economic deposits at different times of the Earth's history, there is large variation in the isotopic composition of Pb derived from different sources. Different countries and geographic regions use Pb from different sources, and have occasionally switched them as different sources are exploited or become economically favored. This specificity provides the means to use Pb isotopic composition as a fingerprint for tracing sources of Pb in the environment.

Strontium Isotopes

Strontium (Sr) is a naturally occurring trace element, situated just below Ca in the Periodic Table it commonly substitutes for Ca in minerals. Strontium has four stable isotopes, ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr in the relative proportions of 0.56%, 9.86%, 7.00% and 82.58% respectively (Faure 1986). Of these, ^{87}Sr is the only radiogenic isotope, being the daughter of radioactive ^{87}Rb (half-life = 48.8 billion years), one of two isotopes of rubidium (^{85}Rb [72.165%] and ^{87}Rb [27.835%]). The isotopic ratio

that is conventionally measured is $^{87}Sr/^{86}Sr$, and can be measured by mass spectrometric methods typically to a precision of better than ±20 ppm (or ±0.002 %) 2 sigma. In different earth materials, the $^{87}Sr/^{86}Sr$ varies depending on the geochemistry of the material (through the Rb/Sr ratio and correlated chemical signatures) and its geologic history. For example, a geologically old granite will usually have higher $^{87}Sr/^{86}Sr$ than a young granite of the same Rb/Sr ratio, while typically a basalt will have lower $^{87}Sr/^{86}Sr$ than a granite of the same crystallization age. The isotopic variability of Sr gives distinctive "flavors" to rocks (and to materials derived from them) from different geographic regions depending on the local geologic history and geochemistry. In contrast to this variability, the world's oceans today have a uniform isotopic composition of Sr ($^{87}Sr/^{86}Sr$ = 0.70917, though this has varied through geologic time) imparting this characteristic isotopic ratio to sea-spray derived aerosols.

Materials and Methods

Samples for analysis

As an initial test of the Pb isotopic method, and as an interim set while we prepared to collect our own aerosol samples, we analyzed a set of archived PM2.5 samples collected by the California ARB (Fig. 1). The filter samples were selected in consultation with R. A. VanCuren and represented several central California locations collected during the springs of 2003, 2004 and 2005. We also obtained from Duane Ono (Great Basin Valleys Air Pollution Control District) a limited set of aerosol samples from the Eastern Sierra (Fig. 1) covering a portion of spring 2008.

We selected two Bay Area sites for collection of aerosol (PM2.5) samples, the west peak of Mt Tamalpais (37.9239˚N, -122.59966˚W, elevation above sea level: 785m (2574 ft)) and the roof of the Chabot Space and Science Center (37.8186˚N, -122.1806˚W, elevation above sea level: 483m (1584ft)) in the Oakland Hills east of San Francisco and Oakland (Fig. 1). For each site an IPROVE style sampler was used (on extended loan from Stephen Cliff of U.C. Davis). The PM2.5 was collected on a set of three pre-cleaned, pre-weighed 25mm diameter Teflon (Teflo) filters, with an air sampling rate of 22.8 L/min divided equally among three filters. One filter was used for Pb and Sr isotopic analyses, a second for elemental analysis by XRF/S-XRF, and a third was held in reserve for future use. The sampling period at Chabot and Mt. Tamalpais was typically 7 days, with filter change outs at the two sites occurring on the same day within several hours.

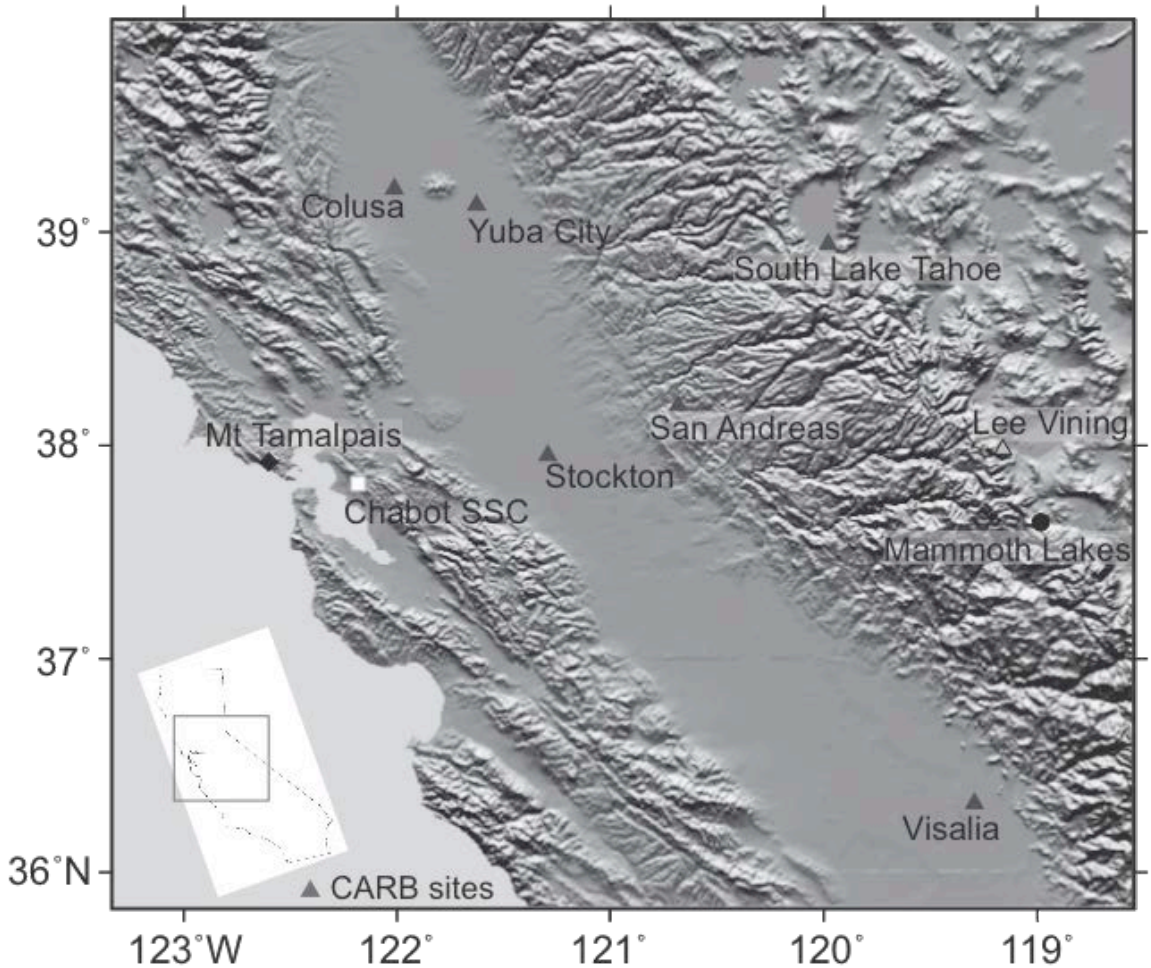

Figure 1. Map showing the locations of long-term sampling sites at Mt. Tamalpais (black diamond) and Chabot Space & Science Center (white square), as well as analyzed CARB sites (grey triangles), and eastern Sierra site at Lee Vining (black outlined triangle) and Mammoth Lakes (black circles).

Analytical Techniques

The elemental compositions of the PM2.5 samples at Mt. Tamalpais and Chabot were conducted by two methods. The first method employed was XRF and was conducted by the Crocker Lab at U.C. Davis using techniques utilized for chemical analysis of IMPROVE samples. The second technique employed was S-XRF (synchrotron XRF) conducted on beamline 10.3.1 at the Advanced Light Source, LBNL. For each filter analyzed, five separate small areas were scanned, and the resulting combined to give a result for the filter in terms of ng/cm2 of filter. Between the overlapping use of these two techniques, data on elemental composition was obtained for Mt. Tamalpais and Chabot filters covering the period from 12/23/07 to 8/16/08.

In order for Pb and Sr isotopic anlyses to be carried out, it was necessary to leach the PM2.5 on the Teflon filters (one per sample set) with 6N HCl in a Teflon vial heated on a hotplate for 3 hours. All filters were pre-cleaned (HF+HNO3) and then pre-weighed using a microbalance (Cahn, model C-31) prior to deployment in the

field, and then weighed again after recovery. All filter pre-cleaning, pre/post weighing, and chemical processing was conducted under clean lab conditions using high-purity reagents. The filter leachates were then chemically processed to separate first Pb and then Sr for isotopic analysis. Pb was separated from the leachates using ion chromatography with small volume columns filled with AG1x8 resin, samples loaded with 0.54 HBr and eluted with 6 N HCl. After Pb separation, the resulting remainder was processed to separate Sr using EiChrom Sr spefic resin on very small volume shrink-fit Teflon columns. The sample was loaded on the resin with 8 N HNO_3 and eluted with 8N HNO_3 and the Sr rinsed off with high purity DI H2O.

Mass spectrometric analyses of the separated Pb and Sr were conducted by multi-collector magnetic sector ICPMS (MC-ICPMS) and thermal ionization mass spectrometry (TIMS) respectively. For isotopic analysis, Pb separates were diluted with 0.3 N HNO3 to 20 ppb, and spiked with thallium with a known $^{203}Tl/^{205}Tl$ ratio. Sample solutions were introduced to the MC-ICPMS (GV Intruments Ltd.) using a desolvation nebulizer (Aridus II, CETAC Technologies) so that a dry sample aerosol is carried to the plasma. The Tl spike added to samples provides data for the correction of the measured Pb isotopic compositions for instrumental mass fractionation. Two Pb isotopic standards, BVO-1 (USGS) and NIST981 were analyzed along with sample unknowns. Tl spiked aliquots of BV0-1 provided the mass fractionation relationship between Tl and Pb isotopes used for correction of the sample unknowns. NIST981 was treated as an unknown and analyzed in the same manner as the sample unknowns and provided for normalization to the standard value. Typical external precision for reported ratios ($^{207}Pb/^{208}Pb$ and $^{206}Pb/^{208}Pb$) is better than ±0.02 % 2s, which is better than conventional TIMS measurements (±~0.05%) and quad-ICPMS measurements (±0.1%). Separated Sr was analyzed for isotopic composition using a Triton (Thermo-Electorn) multi-collector TIMS. Between 5 and 30 ng of Sr was dried down on outgassed Re filaments along with a Ta-Cl emitter solution. A static multi-collector routine was used to measure $^{87}Sr/^{86}Sr$ that was internally corrected for mass fractionation using an $^{86}Sr/^{88}Sr$ ratio of 0.1194. The long-term mean and reproducibility for Sr isotopic standard NIST987 is 0.710248±0.000010 2s (where "s" stands for standard deviation (a.k.a. "σ"), and "2s" is two times the standard deviation).

Data Treatment

The measured Pb isotopic compositions of the analyzed aerosols are evaluated in plots of $^{208}Pb/^{207}Pb$ vs. $^{206}Pb/^{207}Pb$ (e.g. Fig. 2). Data representing local Californian sources of Pb (e.g. Pb from San Francisco Bay water (Steding et al., 2000), Pb from winter samples), fall along a line defined as the "California Array". Samples representing Asia sources, in particular China, (e.g. Bollhöfer and Rosman, 2001; Jones et al. 2000; samples from Hefei, China) fall along a separate "Asia Array". We define a parameter $\Delta^{208}Pb$ to represent the horizontal distance a particular data point is displaced from the California Array toward the Asia Array. For a particular

sample with measured $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$, its $\Delta^{208}Pb$ is given by Equation 1:

$$\Delta^{208}Pb_{smpl} = 1000[(^{208}Pb/^{207}Pb)_{smpl} - (^{208}Pb/^{207}Pb)_{CA}]_{206} \qquad \text{Eq. 1}$$

where the subscript 206 indicates the measured $^{206}Pb/^{207}Pb$ of the sample, which is used to calculate the $(^{208}Pb/^{207}Pb)_{CA}$ the sample should have if it plotted on the California Array. If the calculated $\Delta^{208}Pb_{smpl}$ equals zero, then the sample plots along the California Array, indicating essentially zero influence of Asian sources on the Pb isotopic composition of the sample. Non-zero values of $\Delta^{208}Pb_{smpl}$ indicate Asian influence, increasing with increasing values. We use $\Delta^{208}Pb_{smpl}$ below to provide comparisons to other measured parameters with time. We also use it as a parameter in the calculation of the relative proportions of local and Asian sourced Pb. Equation 2 gives fraction of Asian Pb (F_{Asia}) in a sample:

$$F_{Asia}\ Pb = \Delta^{208}Pb_{smpl}/\Delta^{208}Pb_{Asia} \qquad \text{Eq. 2}$$

where $\Delta^{208}Pb_{smpl}$ and $\Delta^{208}Pb_{Asia}$ are calculated with Eq. 1. The parameter $\Delta^{208}Pb_{Asia}$

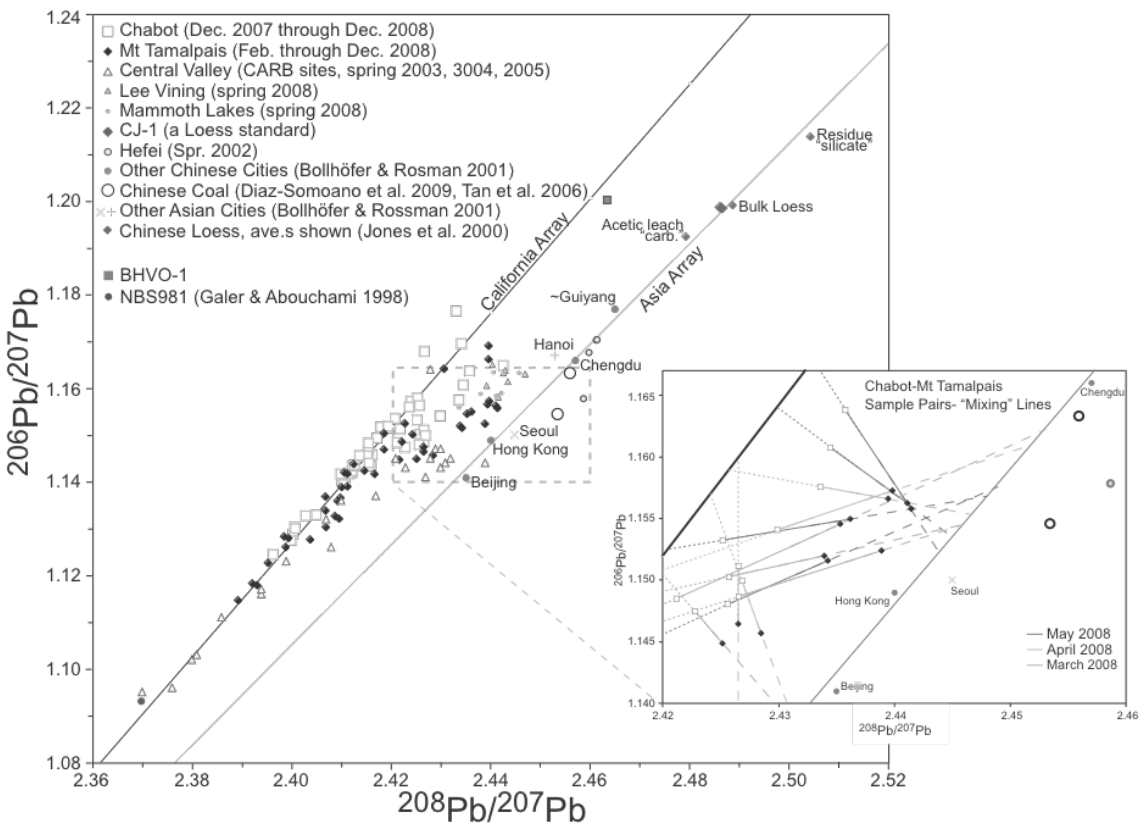

Figure 2. Plot of $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ for samples collected at Mt. Tamalpais, Chabot, the Eastern Sierra and for archived ARB samples from central California. Also shown are the Pb isotopic compositions of samples representative of Asian aerosols. Inset shows an enlargement of the central portion of the figure, illustrating mixing lines for pairs of Chabot-Mt. Tamalpais time-equivalent samples, with extensions defining local California and Asian endmembers.

represents the horizontal offset of the Asian source from the California array. Since the California and Asian arrays are not parallel, this value can change depending on

the observed value of $^{206}Pb/^{207}Pb$ (i.e. the vertical position in Figure 2), though for the range of the analyzed Chabot and Mt. Tamalpais samples the effect is small (at most about 10% on the value of $\Delta^{208}Pb_{Asia}$ and therefore at most ~10% on the calculated value of F_{Asia} Pb). This can be dealt with several different ways. First, where there are contemporaneous samples from Chabot and Mt. Tamalpais, the pairs can be assumed to represent mixing between the local and Asian sources, and so a line passed through them will intercept the Asian array at the composition of the Asian endmember, the proportion of that endmember in the Chabot and Mt. Tamalpais sample represented by their position along that mixing line (e.g. see Figure 2, detail inset). A second method, and the one used in Ewing et al. (2010), is to select a representative value for $\Delta^{208}Pb_{Asia}$. Ewing et al. 2010 used a best-fit line to the Spring Mt. Tamalpais data to find a value of ~24 for $\Delta^{208}Pb_{Asia}$ to use in Eq. 2 for all samples. At the time of preparation of Ewing et al. (2010) we did not have the coal analysis of Diaz-Somoano et al. (2009), which has a higher $\Delta^{208}Pb$. Here for this report a conservative value of 29 (the average value for the Hefei samples and the published coal analyses by Mukai et al. (1993) and Diaz-Somoano et al. (2009)) was used, which gives somewhat lower estimates for trans-Pacific Pb by about 20% (the calculated trans-Pacific scales inversely with $\Delta^{208}Pb_{Asia}$). The main source of relative uncertainties in calculated trans-Pacific Pb concentrations are the uncertainties in the measured Pb loadings of the filters. Two direct techniques were used, whole filter XRF (Crocker Lab, UC Davis) and rastered S-XRF (ALS, LBNL). Though the results from the two techniques are similar, there is a consistent offset between the two data sets. Ewing et al. (2010) took the average value for each filter, and calculated the uncertainty using the standard error of the mean propagated from the uncertainties in the two measurements. The approach used here is to use the correlations between the XRF and S-XRF data sets to fill in date gaps in the XRF (Crocker) data with values interpolated from the SA-XRF (ALS) data, with uncertainties based on the measurement errors. These are the elemental values used in the figures below (Fig.s 3- 6, 9-11). For filters collected after 7/18/08, Pb concentrations based on MC-ICPMS measurement of leachates are used.

Results

Apparent Pb concentrations in the collected PM2.5

The observed Pb concentrations in the collected PM2.5 can provide insights into the broad question of natural vs. anthropogenic sources of the Pb. In Figure 3, we present timeseries for the Chabot and Mt. Tamalpais samples apparent Pb concentrations (in parts per million, ppm) in the collected PM2.5 calculated from the total PM2.5 loading and the measured Pb loading (from S-XRF, XRF, and MC-ICPMS) for each sample. Calculating this value places the amounts of Pb collected into perspective, since they can be compared to the value for average upper continental crust (20 ppm, Taylor and McLennan (1985)) a stand-in for natural soil dust. Any sample that significantly exceeds this value of 20 ppm is likely affected by anthropogenic Pb sources. Overall the two records correspond to each other quite well (with the notable exception of the week of July 4th samples discussed below). Over much of the record, the apparent concentration of Pb greatly exceeds the

average concentration in the upper continental crust (indicated by the dashed line in Fig. 3), by as much as a factor of 40 (enrichment factor = (PM2.5 [Pb] divided by ave. upper Continental Crust). For Spring 2008 the range in apparent Pb enrichment at Chabot and Mt. Tamlpais was from 4 to 40 (only up to 30 at Chabot), while for Summer 2008 (excluding the week of July 4th at Chabot) the range was from 0.2 to 7, with values below 2 (suggesting minimal anthropogenic influence) for the period 6/20 to 8/15 at Mt. Tamalpais. At Chabot for this period (except the week of July 4th when it was 45) Pb enrichment was at minimums for the year but with a higher range (3-7) than at Mt. Tamalpais. One goal of this study is to understand the sources of anthropogenic Pb that has contributed to the apparent excess Pb in the collected aerosols. As shown below, we use Pb isotopes to partition the sources of the Pb into far traveled (Asian) and locally derived components.

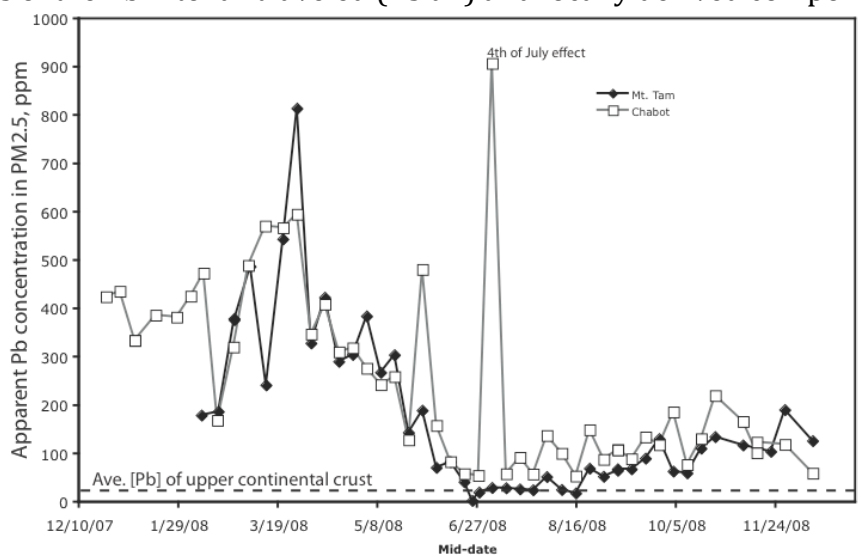

Figure 3. Timeseries of the apparent Pb concentration (ppm) in the collected PM2.5 samples calculated on the basis of the mass of collected PM2.5 and the measured concentration of Pb in the sample (S-XRF, XRF, MC-ICPMS). The horizontal dashed line represents the estimated average concentration of Pb in the upper continental crust (20 ppm, Taylor and McLennan (1985)). Samples falling significantly likely have a significant component of added anthropogenic Pb.

Pb isotope timeseries for Mt. Tamalpais and Chabot

In Fig. 4 we present for the Chabot and Mt. Tamalpais sites timeseries covering 2008 of Pb isotopic composition (shown as Δ^{208}Pb) compared to a timeseries of total Pb concentration in air (ng/m^3). The overall timeseries for total Pb displays a broad high over late winter-mid spring, with declining concentrations from late spring to early summer. A sharp peak in Pb concentration occurs at the sample collected at Chabot the week of July 4th. This is likely due to 4th of July fireworks, and will be discussed further below. Total Pb concentrations remain relatively low for the rest of year with the exception of two minor peaks evident at Chabot in the fall. In general the total Pb concentration in air measured at Chabot is higher than that measured at Mt. Tamalpais for the same sampling period. For Δ^{208}Pb the broad patterns are similar, with higher values (higher Asian influence) from late winter through mid-spring, with declining values from late spring into summer. In contrast to total Pb concentrations, the Δ^{208}Pb value measured at Mt. Tamalpais is typically

higher than at Chabot. Using the Pb isotopic data to calculate F_{Asia} (the fraction of Asian Pb in a sample, see Eq. 1 & 2 above) and multiplying that by the total Pb (in terms of concentration in air, ng/m^3) gives the calculated concentration of Asian (Chinese) sourced trans-Pacific transported Pb displayed as a timeseries in the bottom panel of Fig. 4. This reveals four separate transport events across the Pacific in late winter to spring 2008 as peaks in trans-Pacific Pb. The trans-Pacific Pb timeseries for Chabot and Mt. Tamalpais are essentially coincident between mid-Feburary and early March, and begin to diverge from mid-April with the fourth peak in trans-Pacific centered on May 2nd and evident at Mt. Tamapais suppressed at Chabot. The suppression of this peak at Chabot is apparently due to incursion of the marine boundary layer at Chabot, diluting the trans-Pac Pb signial, as evidenced by high Cl at this time (see elemental data discussion below).

Taking seasonal averages for the calculated trans-Pacific Pb concentration in air for Mt. Tamalpais and Chabot indicates the strongest Asian influence occurred in Spring. For Chabot the average trans-Pacific Pb for Winter 2007-2008 was 0.07 ng/m^3, in Spring 2008 0.34 ng/m^3, Summer 2008 0.01 ng/m^3 and Fall 2008 was 0.00 ng/m^3. At Mt. Tamalpais comparable seasonal averages were observed, with an average trans-Pacific Pb for late Winter 2008 of 0.16 ng/m^3 (note, the average for the same late winter period at Chabot was also 0.16n/m^3), for Spring 2008 of 0.53 ng/m^3, for Summer 2008 of 0.03 ng/m^3, and for Fall 2008 of 0.02 ng/m^3. This seasonal variation is in accord with the observations of VanCuren (2003) and VanCuren and Cahill (2002), based on elemental analyses of IMPROVE network samples, identifying Spring as the period of greatest Asian influence on aerosol samples collected across a wide swatch of the western US (California to Washington).

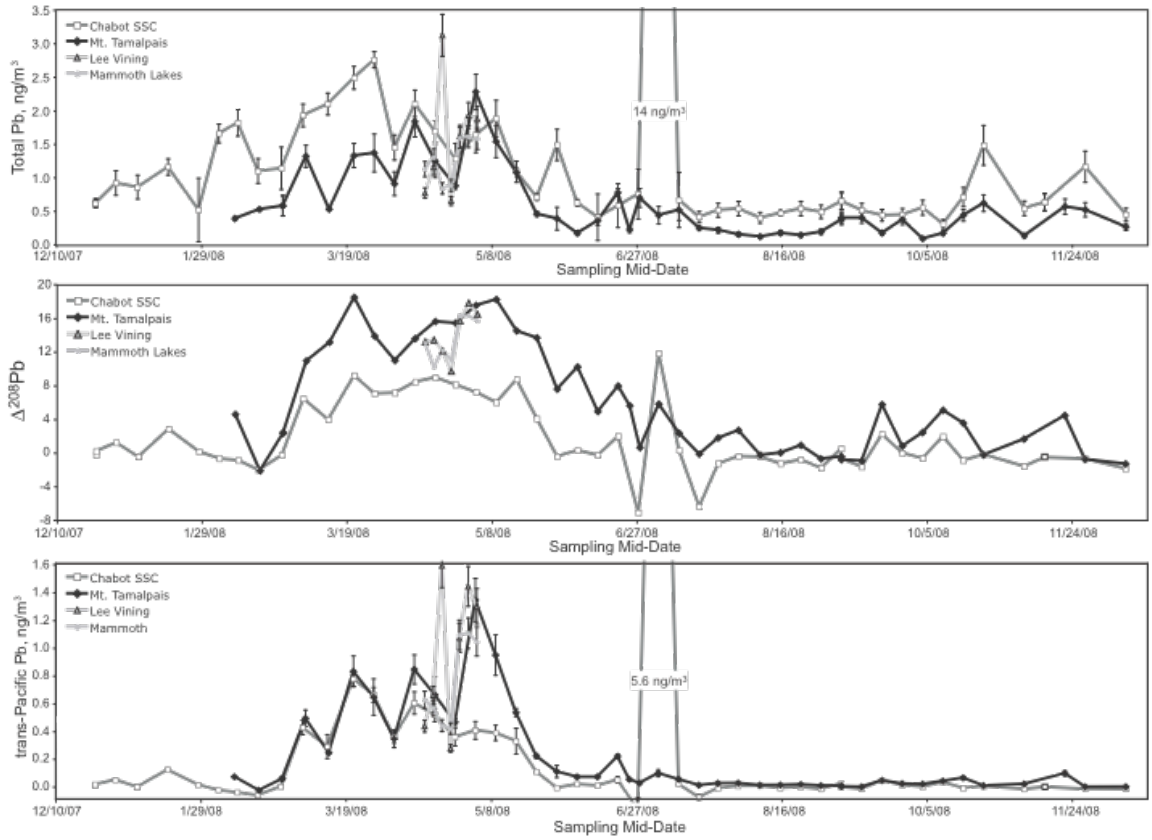

Figure 4. Timeseries for 2008 for Chabot and Mt. Tamalpais aerosol samples. Top-total Pb concentration in air, Middle-Pb isotopic composition as Δ^{208}Pb (see Eq. 1), Bottom- calculated concentration in air of tran-Pacific transported Pb based on Pb isotopic composition and total Pb concentration.

Sr isotope timeseries for Mt. Tamalpais and Chabot

Timeseries for Sr isotopic analyses (^{87}Sr/^{86}Sr) are presented in Figure 5 for Chabot and Mt. Tamalpais aerosol samples. For period Feb-July 2008 the ^{87}Sr/^{86}Sr varies between 0.7084 and 0.7099, roughly mirroring the variation in Δ^{208}Pb, with generally higher (more radiogenic) ^{87}Sr/^{86}Sr observed at Mt. Tamalpais than at Chabot.

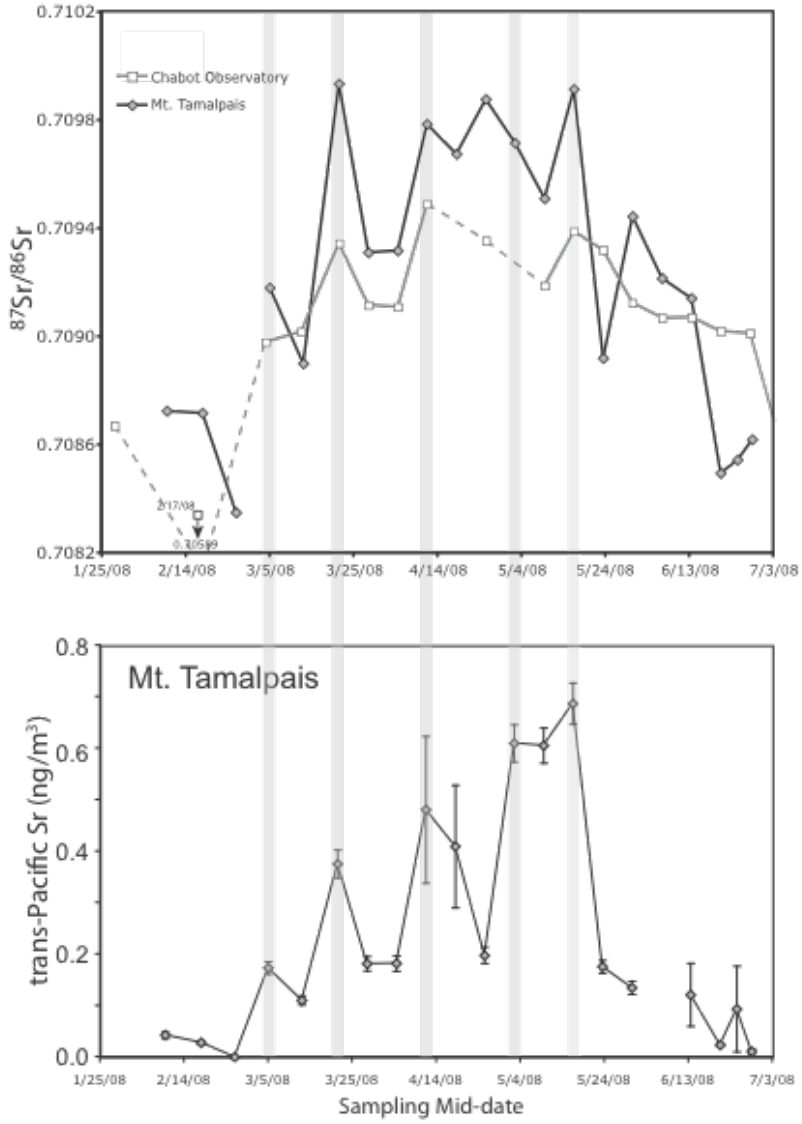

Figure 5. Timeseries for late January to early July 2008 of $^{87}Sr/^{86}Sr$ of Chabot and Mt. Tamalpais aerosol samples (Top) and calculated trans-Pacific transported Sr concentration in air for Mt. Tamalpais (Bottom). Grey bands represent the times of peak trans-Pacific Pb transport seen in Fig. 4.

The relationship seen in Fig. 6 between $^{87}Sr/^{86}Sr$ and Si/Ca ratio for Mt. Tamalpais indicates mixing between a local source with relatively low $^{87}Sr/^{86}Sr$ and low Si/Ca and a second source similar to Chinese Loess with high $^{87}Sr/^{86}Sr$ and low Si/Ca. These observations can be used to estimate the fraction of loess associated Sr in the Mt. Tamalpais aerosol samples through a simple mass balance calculation using Equation 3, assuming the loess endmember soluble Sr has $^{87}Sr/^{86}Sr$ of 0.7109, and the background Sr at Mt. Tamalpais has an $^{87}Sr/^{86}Sr$ of 070835 (Fig. 5).

$$\text{Fraction Loess Sr} = \left(\frac{\left(\frac{^{87}Sr}{^{86}Sr}\right)_{smpl} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{bkg}}{\left(\frac{^{87}Sr}{^{86}Sr}\right)_{Loess} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{bkg}} \right) \qquad \text{Eq. 3}$$

The estimated fraction of Loess Sr and the measured Sr concentration (in air, ng/m^3) for a sample can then be multiplied together to yield the trans-Pacific transported Sr concentration in air (Fig. 4 bottom panel).

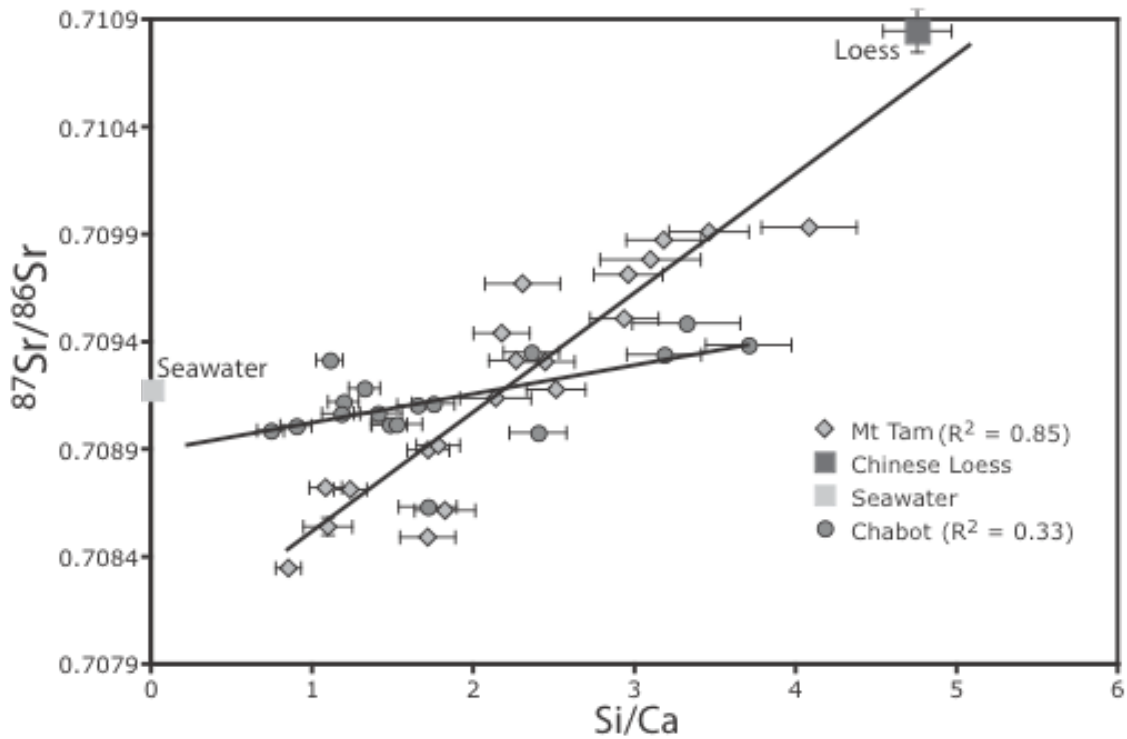

Figure 6. $^{87}Sr/^{86}Sr$ vs. Si/Ca ratio for Mt. Tamalpais samples (diamonds), Chabot samples (circles), seawater (light grey square) and leached Chinese loess (dark grey square). For Mt. Tamalpais, the data are well correlated, allowing calculation of the proportion of Loess Sr (trans-Pacific Sr) in those samples. For Chabot samples, the additional influence of seawater-derived aerosols can be seen.

The resulting timeseries can be compared to the time series of trans-Pacific Pb. In Fig. 4, grey vertical bands highlight the times of peak trans-Pacific Pb transport. The first three peaks in trans-Pacific Pb transport coincide with peaks in trans-Pacific Sr transport. The fourth transport event is more complicated, with the peak in trans-Pacific Pb occurring about two weeks prior to the peak in trans-Pacific Sr (see below and Fig. 10).

Archived ARB Samples from Central California

We analyzed for Pb isotopic composition sets of ARB PM2.5 filters (24 hour collection period, every third day) from several central California city sites collected during the springs of 2003, 2004 and 2005. The results of the isotopic analyses are

plotted in Fig. 2 (large open triangles), and timeseries of the calculated trans-Pacific Pb concentration in air are presented, as well as the percentage of trans Pacific Pb of the total Pb, in Fig. 7. Each spring period includes samples indicating both little or no Asian influence and significant influence. For each spring, the available data suggest consistent temporal and geographic variation patterns in trans-Pacific Pb and its proportion of total Pb. The most complete transport event was captured by the data for spring 2004. The peak was recorded on April 27, 2004 in the sample from San Andreas (Sierra foothills) where 7.6 ng/m3 trans-Pacific Pb was measured, representing over 95% of the total Pb leached from the filter. Other sites on that day saw less trans-Pacific Pb, Stockton (due west but at lower elevation) 5 ng/m3 (or 65% tran-Pacific Pb) and essentially zero trans-Pacific Pb at Yuba City (to the north). At other times, the north-south and elevation variability can be quite small. The 4/21/04 and 5/3/04 24 hour samples from San Andreas and Visalia, record for those dates very similar amounts of trans-Pacific Pb and proportions of trans-Pacific Pb. Likewise, the three samples collected on 4/22/05 at Colusa, Yuba City, and San Andreas record virtually identical trans-Pacific Pb air concentrations (0.5 ng/m3) and proportions of total Pb (10%). These relatively small values and their agreement suggest the high sensitivity of our Pb isotopic method for apportionment, even in urban affected areas.

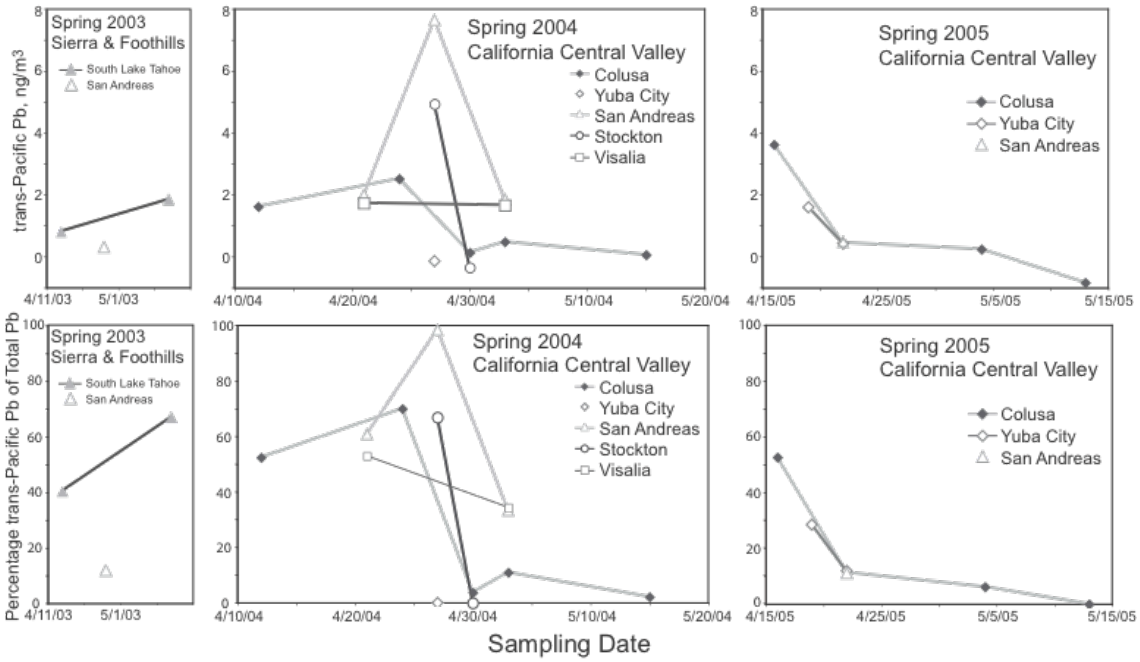

Figure 7. Timeseries for ARB samples collected in central California during the springs of 2003, 2004 and 2005, top row- trans-Pacific Pb concentrations in air (ng/m^3) and bottom row- percentage of the trans-Pacific Pb of the total Pb from the sample.

Eastern Sierra Aerosol Samples (Spr. 2008)

Pb isotopic data for aerosol 24-hour PM2.5 samples collected at Lee Vining and Mammoth Lakes in the Eastern Sierra are presented in Fig. 2, as well as in Fig. 4. These samples were collected during a portion of spring 2008 covering the period of increased trans-Pacific Pb transport observed at Mt. Tamalpais and Chabot. Each of

these Lee Vining and Mammoth Lakes samples have Pb isotopic compositions indicative of a significant fraction of Asia/China sourced Pb, ranging from 40 to 70% of the Pb leached from the PM2.5. The Δ^{208}Pb values of these samples are intermediate between the values observed at Mt. Tamalpais and Chabot over the same period, and are remarkably consistent (Fig. 4, middle panel). The calculated values of trans-Pacific Pb concentrations also compare well between the Lee Vining, Mammoth Lakes, and Mt. Tamalpais samples, with the exception of the April 21st Lee Vining sample records a much higher Trans-Pac Pb concentration, 1.7 ng/m^3, than the Mammoth sample for that date and higher than the Mt Tamalpais and Chabot samples that include that date. However, the overall agreement in Δ^{208}Pb and calculated trans-Pacific Pb concentrations in air among these sites is remarkable considering the more than 300 km downwind separation between Mt. Tamalpais and the two Eastern Sierra sites. We have also ^{87}Sr/^{86}Sr data for the Lee Vining samples (Fig. 8). Though the data set only covers two weeks, there appears to be less agreement between ^{87}Sr/^{86}Sr measured at Mt. Tamalpais/Chabot and at Lee Vining, four samples falling below the range observed at Mt. Tamalpais/Chabot. Unfortunately we do not have XRF/S-XRF elemental data for these Lee Vining and Mammoth Lakes samples, which would aid in the interpretation of the ^{87}Sr/^{86}Sr data. It is possible, though, that the relatively low ^{87}Sr/^{86}Sr samples are due to sources local to Lee Vining.

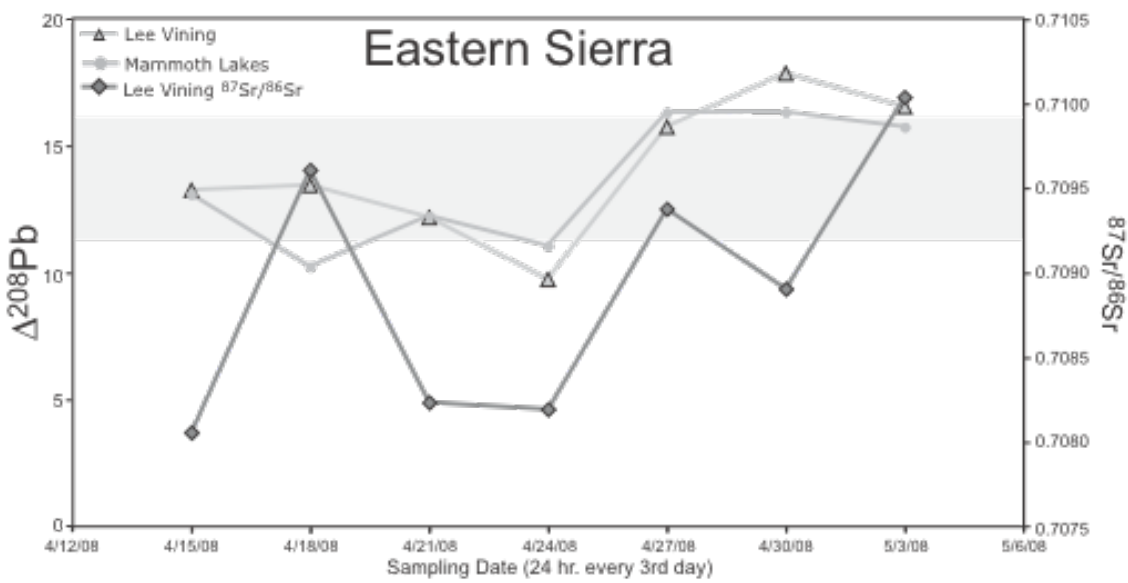

Figure 8. Timeseries for Lee Vining and Mammoth Lakes PM2.5 24-hour samples comparing Δ^{208}Pb and ^{87}Sr/^{86}Sr records. Grey band indicates the range in ^{87}Sr/^{86}Sr observed at Mt. Tamalpais and Chabot during this time period.

Discussion

Records of trans-Pacific Pb and trans-Pacific Sr

Comparison to Bulk Elemental Composition of the PM2.5 Samples

In Fig. 9 we compare the timeseries of trans-Pacific Pb air concentration, calculated from the measured Pb isotopic and concentration data, and selected elemental concentrations from the XRF/S-XRF data. Note, for the elemental values presented in Fig. 9, we have used correlations between the XRF (Crocker Lab) and S-XRF (ALS-LBNL) to calculate elemental values to fill in and normalize the S-XRF data to the XRF data in those portions of the timeseries where only S-XRF was available. In the case of Ewing et al. 2010 (see attached paper), we simply used the average of the XRF and S-XRF data where they overlapped.

The four transport events seen in major peaks in trans-Pacific Pb (Fig. 4 bottom and Fig. 9 top) can also be seen in the timeseries of "soil", K and Ca concentrations in air (Fig. 9) for both Mt. Tamalpais and Chabot. Since the Pb concentrations in the collected aerosols at these peaks is much higher (200 to >400 ppm) than would be expected in natural soils (5-15 ppm), it is likely the additional Pb is of anthropogenic origin. The peaks in "soil" are likely due to natural sources such as lofted desert soils and loess from western China (supported by Sr isotopic data discussed above). Therefore, it appears that the first three transport events involved aerosols with both a natural soil component and an anthropogenic (possibly associated with coal burning, see Fig. 11 and below) component, in roughly consistent proportions. The fourth transport event, between 4/25/08 and 5/23/08 was more protracted and complex than the first three events. This is best illustrated by Figure 10, which compares timeseries for trans-Pacific Pb (top panel), trans-Pacific Sr (middle panel) and "soil" (bottom panel). For the first three transport events, the peaks in trans-Pacific Pb, trans-Pacific Sr and "soil" coincide well in time and relative size. For the fourth transport event, the peak in trans-Pacific Pb occurs ~2 weeks earlier than the peak in "soil" and the peak in trans-Pacific Sr. Moreover, the overall pattern of "soil" concentration matches well the pattern of trans-Pacific Sr during this time period rather than that of trans-Pacific Pb.

As mentioned above, the timeseries of trans-Pacific Pb for Mt. Tamalpais and Chabot correspond very well from late February through late April, but diverge through the first half of May. This divergence may be explained by incursions at Chabot during those sampling periods (e.g. 5/2, 5/9, 5/16) of the marine boundary layer as evidenced by elevated Cl (Fig. 9), and a trend toward seawater $^{87}Sr/^{86}Sr$ and Si/Ca ratios (Fig. 6). The repeated incursions of the marine boundary layer would have reduced the loading of trans-Pacific Pb at Chabot relative to Mt. Tamalpais.

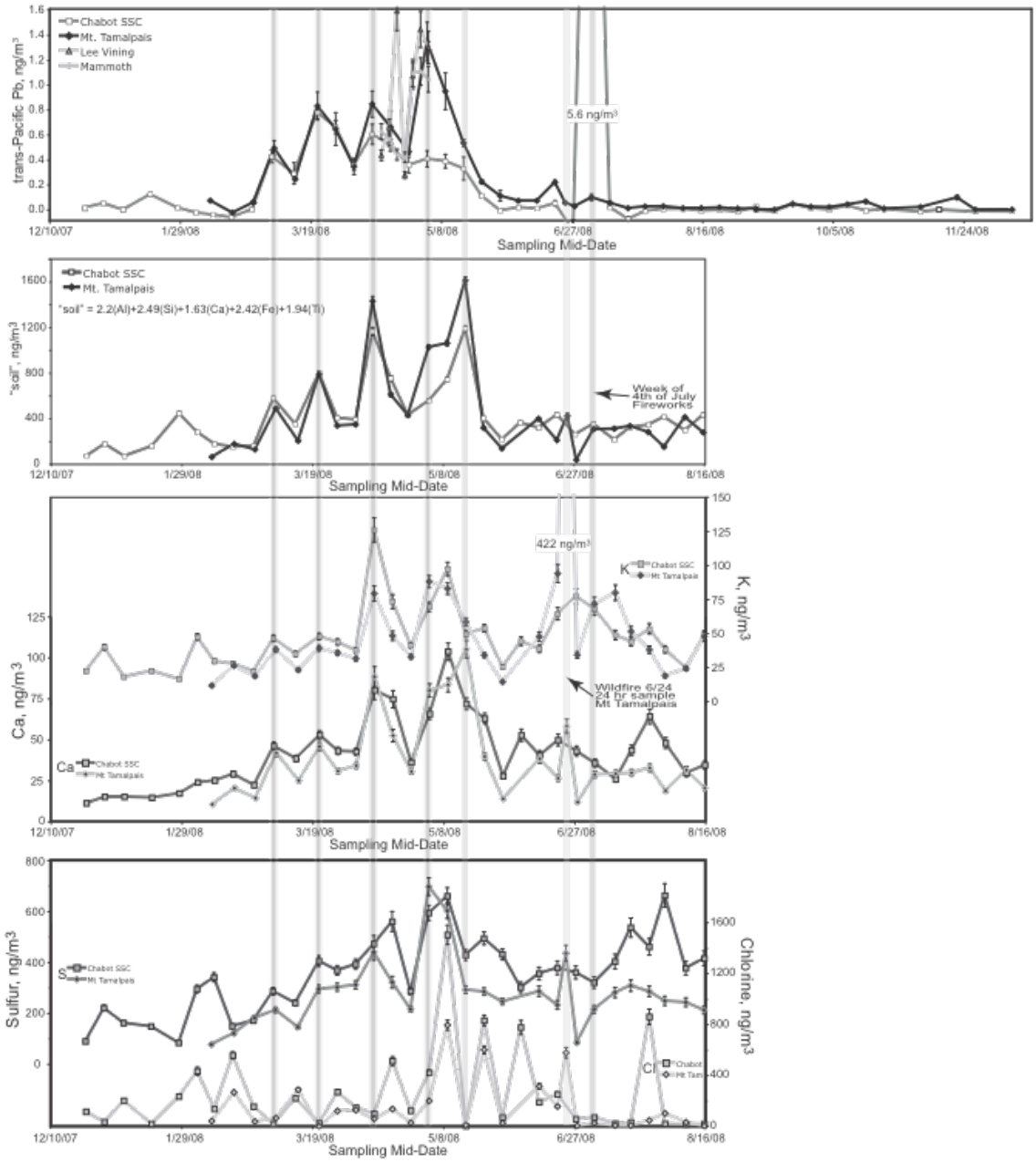

Figure 9. Time series of the elemental composition of the PM2.5 determined by XRF/S-XRF. "Soil" was calculated from the elemental data using the formula: "soil" = 2.2(Al)+2.49(Si)+1.63(Ca)+2.42(Fe)+1.94(Ti). Peaks in "soil", K, Ca & other elements correspond to peaks in trans-Pacific transport as outlined by Pb isotopic signatures of Asian Pb.

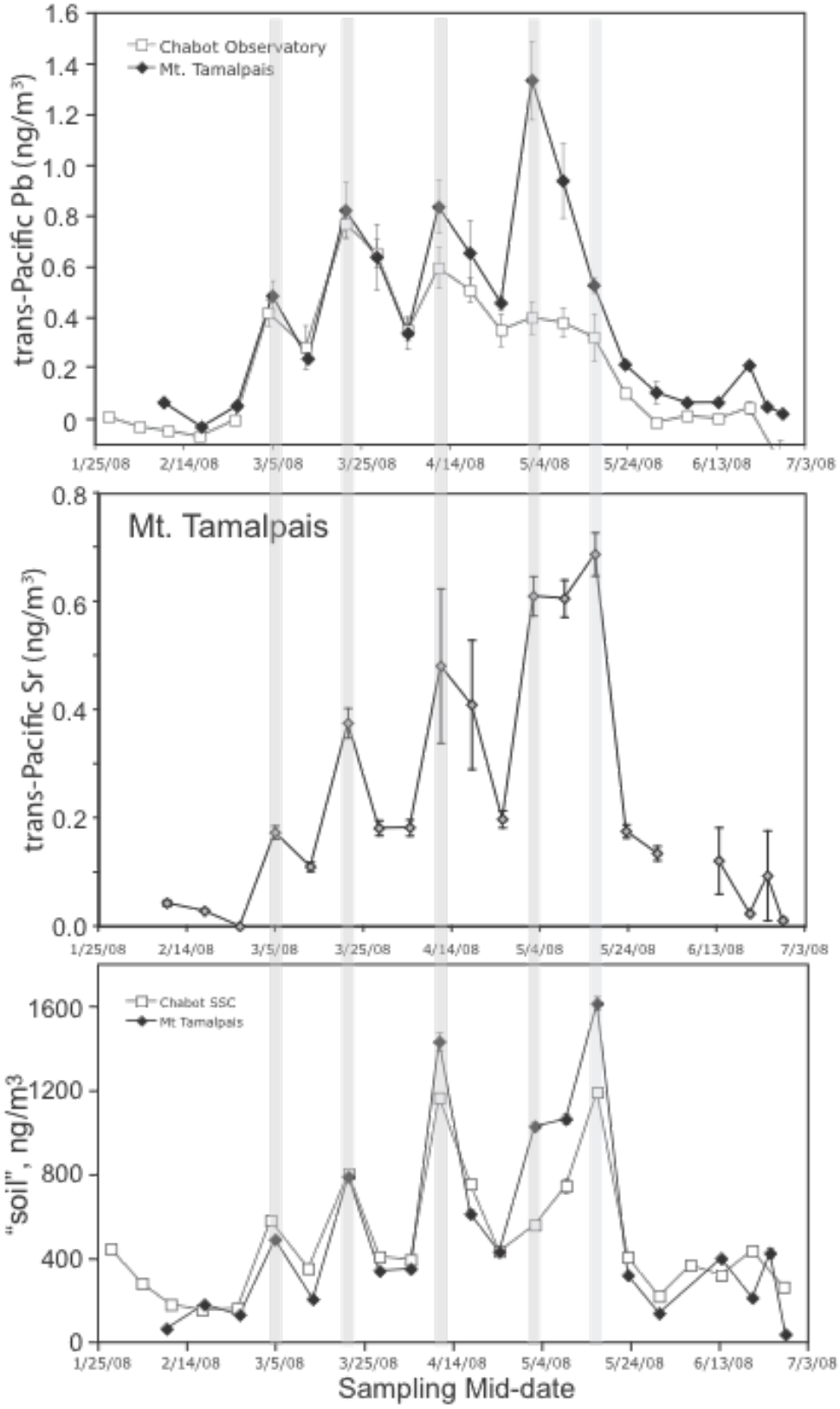

Figure 10. Timeseries comparing trans-Pacific Pb concentration in air (top), to trans-Pacific Sr concentration in air (middle) to "soil" concentration in air based on XRF/S-XRF elemental analyses.

Source Attribution of Selected Elements

The elemental data, Pb and Sr isotopic data (as calculated trans-Pacific Pb and trans-Pacific Sr) can be used to characterize and identify associated sources. The left column of Fig. 11 displays the correlations between trans-Pacific Pb and the concentrations in air of K, S, Zn and As for the Mt. Tamalpais and Chabot sites. For the Mt. Tamalpais data the correlations between trans-Pacific Pb and K, S, Zn and As are quite high (R^2's of 0.78, 0.78, 0.81 and 0.79 respectively). In contrast, the correlations for Chabot are much poorer (R2's of 0.38, 0.32, 0.33 and 0.38 respectively), reflecting the addition of local urban sources for those elements. In all cases the best-fit lines for Chabot lie to the left and parallel to those for Mt. Tamalpais, and have a higher intercept. Typically at Chabot, local sources account for over 50%, but not 100%, of the total collected K, S, Zn and As. The good correlations between the Mt Tam trans-Pacific Pb and K, S, Zn, and As is indicative of anthropogenic sources, and in particular coal burning, for the trans-Pacific Pb.

The right column of Fig. 11 displays the correlations between trans-Pacific Sr and the concentrations in air of "soil", Si, Ca and Fe. For "soil" the correlation with trans-Pacific Sr is much better ($R^2 = 0.87$) than for trans-Pacific Pb (R^2 of 0.52, not shown). Correlations between trans-Pacific Sr and Si, Ca and Fe are also high (R^2's of 0.89, 0.91 and 0.82 respectively), and much better than for those elements with trans-Pacific Pb (R's of 0.55, 0.56 and 0.53 respectively, not shown). Likewise, the correlations between trans-Pacific Sr and those elements that correlated well with trans-Pacific Pb (i.e. K, S, Zn, As) are relatively poor ($R^2 < 0.5$). All together, the correlations between the isotopically apportioned Pb and Sr (as trans-Pacific Pb and Sr) with the elemental data support the idea that $\Delta^{208}Pb$ (i.e. $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$) tracks Asian (Chinese) pollution while $^{87}Sr/^{86}Sr$ tracks Chinese mineral dust (loess and desert soils). This depends on the observed isotopic contrasts between local Northern California sources and Asian (Chinese) sources.

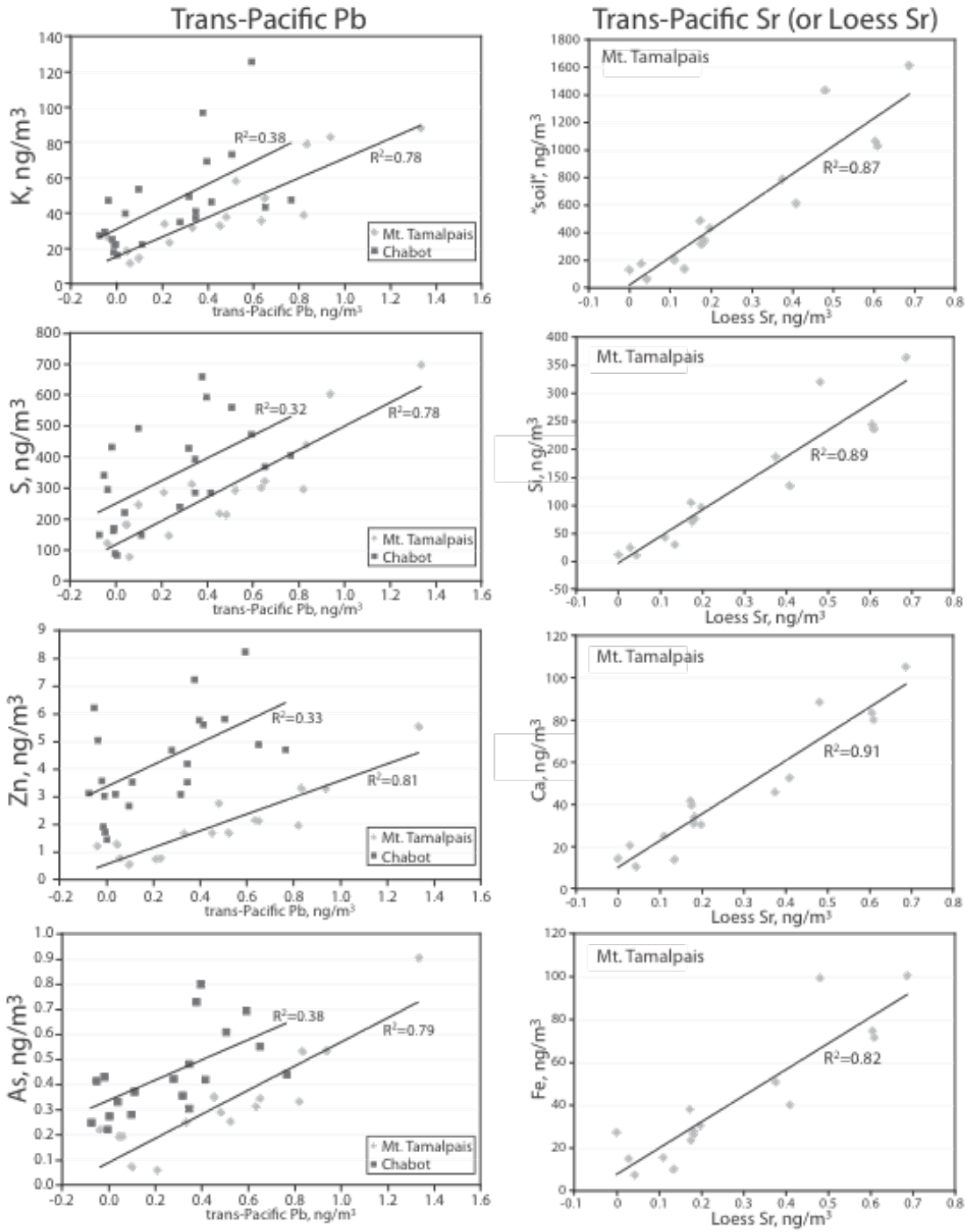

Figure 11. (left hand column) Plots of selected elements (ng/m3 air) vs. trans-Pacific Pb (ng/m3 air). Mt. Tamalpais- grey diamonds. Chabot- squares. (right hand column) Plots of selected elements (ng/m3 air) vs. trans-Pacific Sr for Mt. Tamalpais.

Effects of 4th of July Fireworks and June, 2008 Wildfires

There are two singular local events, 4th of July fireworks and wildfires, that are apparent in both the isotopic and elemental timeseries (Fig. 9). During the third week of June, 2008 a series of wildfires broke out across Northern California started by thunderstorms, with fires to the north and northeast of Mt. Tamalpais. On June 24th, a NASA flyover of Mt. Tamalpais was planned to study a trans-Pacific transport event, with co-ordinated 24-hour sampling by us at Mt. Tamalpais. Due to smoke from the wildfires, the flyover was canceled. However, we did change out filters at Mt. Tamalpais the afternoon of the 23rd, and encountered heavy smoke and elevated temperatures at the site which was obviously within the plume of the distal fires to the N-NE. The filters were again changed on the morning of the 25th, when normal conditions were found. The 24-hour filter representing June 24th was heavily loaded (900 micrograms) compared to typical 7-day samples. Associated with this sample is a very pronounced peak in K concentration (over 400 ng/m^3, higher then any other observed concentration) and smaller local peaks in Ca (55 ng/m^3), S (440 ng/m^3) and Cl (590 ng/m^3). Certainly K and Ca, and possibly S and Cl, are associated in this case with biomass burning during the wildfires. During that time no obvious peak in Pb was observed, however the immediately previous week sample from Mt. Tamalpais did record a Δ^{208}Pb peak and associated peak in trans-Pacific Pb.

The effect of July 4th fireworks displays may be seen in the Chabot sample for the week of July 1-8. That Chabot sample had the highest total Pb we have observed so far, 600 ng Pb collected (yielding an apparent Pb concentration of 908 ppm), and the highest average concentration in air, 7.8 ng/m3, seven times higher than the next highest value. The elemental analysis of this sample also found high concentrations of several other elements, including Cu (14 ng/m^3, ~6 times typical values observed at Chabot) and Zn (50 ng/m^3, 5 to 7 times higher than other Chabot samples). These elements are suggestive of aerosols from fireworks displays, where Cu is used for blue color and Zn for smoke generation. Arsenic concentration was also high at 3ng/m^3, (again 7 times typical concentrations) likely due to the use of copper acetoarsenite, $Cu_3As_2O_3Cu(C_2H_3O_2)_2$ for blue color affects. Lead nitrate ($Pb(NO_3)_2$) or lead chromate (an oxidizer) has also been (and apparently still is) used in fireworks. The Pb isotopic composition of this sample suggests ~70% Asian Pb, consistent with the fact that a high proportion, up to 75%, of fireworks sold in the US in recent years, are manufactured in China. If the high observed loadings of Pb, Cu, Zn etc. are due to 4th of July fireworks, then their actual concentrations in air at Chabot would have been much higher. If a fairly conservative correction factor of 28 (assuming for the seven day sample period, that the fireworks plume affected Chabot for 6 hours. A shorter period would result in a proportionally higher factor), then Pb concentrations in air could have been greater than 200 ng/m^3. Again, if the observed high As concentration is also associated with 4th of July, concentrations in air of As would have been higher than 80 ng/m^3. Back trajectories calculated for the evening/night of July 4th suggests displays at the Berkeley Marina or in San Rafael (Marin Co. Fairgrounds) as possible sources for the plume rather than the San Francisco or Oakland (Jack London Square) displays.

Apportionment of PM2.5 based on trans-Pacific Pb

One of the main goals of this project was to evaluate whether the Pb isotopic compositions of aerosols could be used to partition their associated PM2.5 to different sources; in particular, in order to evaluate the impact of aerosols transported across the Pacific on local California PM2.5 burdens. Fig. 12 shows a series of panels displaying these particular results. The top panel of Fig. 12 shows the correlation between the mass concentration (microgram/m^3) of PM2.5 collected at Mt. Tamalpais during spring 2008 with the air concentration (ng/m^3) of trans-Pacific transported Pb (that is, Pb sourced in Asia) calculated from the Pb isotopic compositions of those samples. The correlation (R^2=0.6) between these to parameters is reasonably good, and the lower intercept indicates that typically 1 to 2 μg/m^3 of PM2.5 at Mt. Tamalpais was sourced locally. The middle panel of Fig. 12 uses the correlation shown in the top panel of Fig. 12 to calculate a times-series of the air concentration of the PM2.5 sourced in Asia for the samples collected at Mt. Tamalpais and more importantly at Chabot Space & Science Center in the Oakland Hillls, a site affected by the urban plume of the East Bay. For Chabot, this was done using the slope (=2.7) of the best-fit line to the data in the top panel of Figure 12 (Mt. Tam. Trans-Pacific Pb vs. Mt. Tam. Total PM2.5), multiplying the calculated value of trans-Pacific Pb for each Chabot sampling period by this slope. This yields an estimate of the trans-Pacific transported PM2.5 at Chabot, assuming the same relationship (i.e. slope) between trans-Pacific Pb and its associated PM2.5 holds for both Chabot and Mt. Tamalpais for the time period under consideration. In the case of Mt. Tamalpais, the trans-Pacific transported PM2.5 shown in the middle panel of Fig. 12 was calculated by subtracting the intercept (=1.8) at zero trans-Pacific Pb from the total observed PM2.5. Finally, for the bottom panel of Fig. 12, the trans-Pacific transported PM2.5 estimated for Chabot was divided by the total observed PM2.5 to give the fraction of trans-Pacific transported PM2.5.

In the bottom panel of Fig. 12, the fraction of the PM2.5 collected at Chabot that was sourced in Asia based on the figures in the middle panel of Fig. 12 are plotted against sampling date. This data analysis suggests that as much as 45% (week of March 21, 2008) of the collected PM2.5 collected at Chabot was sourced in Asia. That was the peak, with the fraction gradually falling off from then through May, with an average value through the spring period March through May of ~25%. Assuming that the relationship between PM2.5 and trans-Pacific Pb observed during 2008 at Mt. Tamalpais is applicable to the peak sample from spring 2004 at San Andreas, the trans-Pacific Pb calculated for that April 27, 2004 sample (7.6 ng/m^3) would imply that an average of ~20 micrograms/m^3 of PM2.5 during that 24 hour period was imported across the Pacific from Asia. Though we don't have the total PM2.5 loading of this particular sample, 20 micrograms/m^3 is a large fraction of the EPA 24 hour standard of 35 micrograms/m^3 and could easily have contributed to pushing that location on that date above the standard.

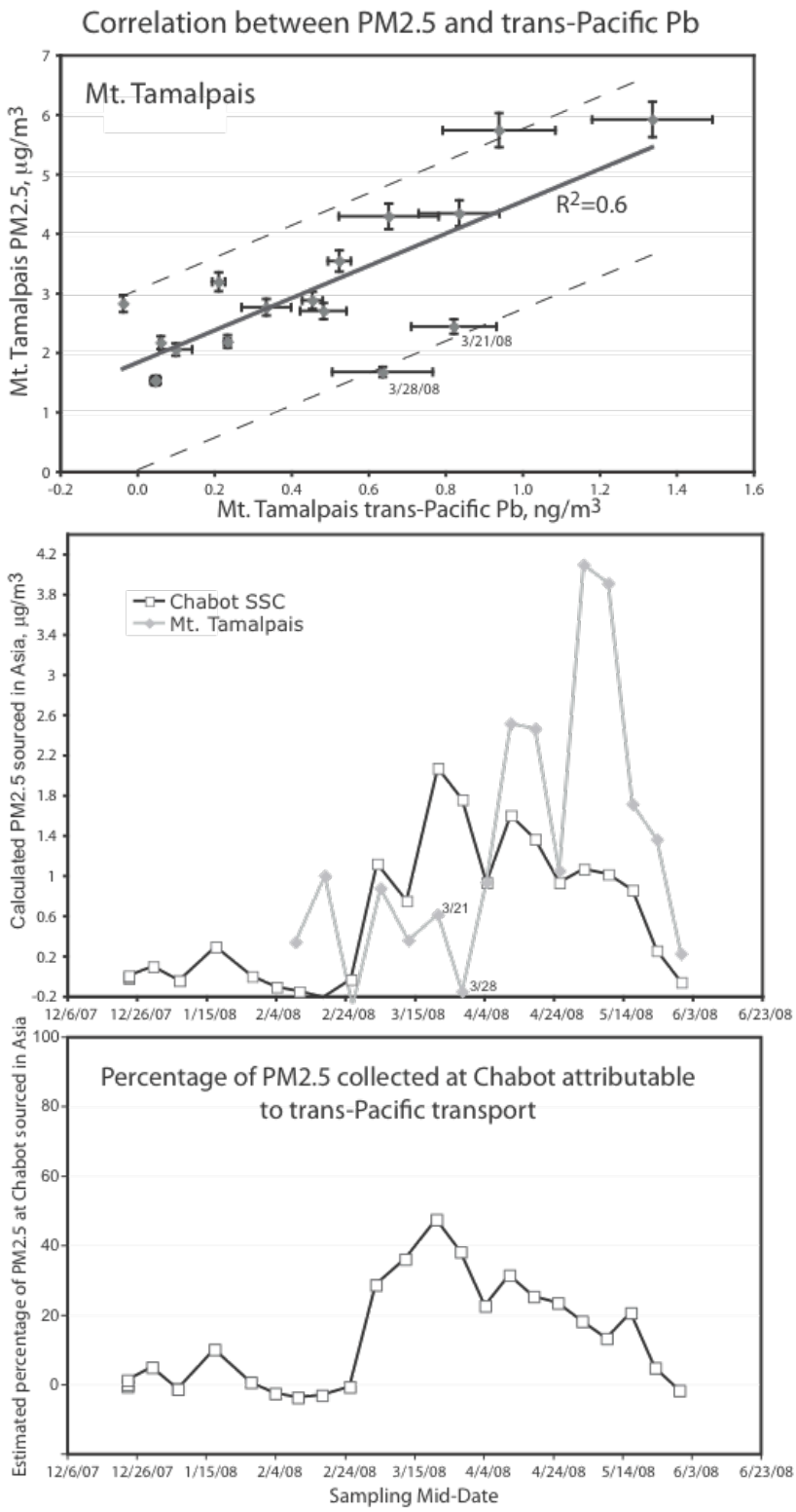

Figure 12. (Top) plot of the observed PM2.5 mass loading against the calculated air concentration of trans-Pacific Pb (based on Pb isotopic analysis) for aerosols collected at Mt. Tamalpais during spring 2008. (Middle) Time series of the calculated mass concentration of PM2.5 sourced in Asia for spring 2008 based on the correlation observed in the top panel. (Bottom) The time-series of the percentage of the PM2.5 collected at Chabot that was sourced in Asia.

A Possible Relationship Between trans-Pacific Pb and Imported Tropospheric Ozone

We have also investigated the source apportionment of ozone using our Pb isotopic data. Fig. 13 shows time series for 2008 of Δ^{208}Pb for Mt. Tamalpais compared to the monthly average ozone measured in San Francisco and ozone measured at Trinidad Head (an essentially pristine coastal site) where the daily data has been binned and averaged to the corresponding sampling periods of the Mt. Tamalpais aerosol samples. Comparing these time series, there's a suggestive correspondence between them, with a seasonal spring peak in ozone coinciding with the spring peak in Δ^{208}Pb (higher values indicate greater Asian influence), followed by a summer minimum in both ozone and Δ^{208}Pb and then a fall rise again in both. (This two-humped pattern in ozone, a hump in spring and a smaller hump in fall, can be seen repeatedly in Bay Area ozone data over at least the past ten years.) In the bottom panel of Fig. 13, Mt Tamalpais Δ^{208}Pb data for 2008 is plotted against the corresponding Trinidad Head ozone data. The correlation between the two data sets is fairly good (R2=0.63) considering that Mt. Tamalpais and Trinidad Head are separated along the coast by over 300 km. This correlation suggests that the local background ozone at Trinidad Head is about 15 to 30 ppbv (i.e. the range for Δ^{208}Pb values of around zero), while trans-Pacific transport adds up to 20-25 ppbv of ozone through some combination of direct transport of ozone and conversion of precursors to ozone during transport. This result is in accord with published analyses of ozone decadal records at Trinidad Head and other west coast localities where the observed increase in ozone along the N. California coast was 10-15 ppbv between 1984 & 2004, a trend of 0.5-0.8 ppbv/yr (Parrish et al. 2009, Cooper et al. 2010). Given the similarity in ozone variability in San Francisco and Trinidad Head, and that it appears based on the correlation with Δ^{208}Pb that up to 20-25 ppbv can reach California from Asia, the indication is that in the spring up to about 50% of the ozone concentration in the inner Bay Area may be imported from across the Pacific.

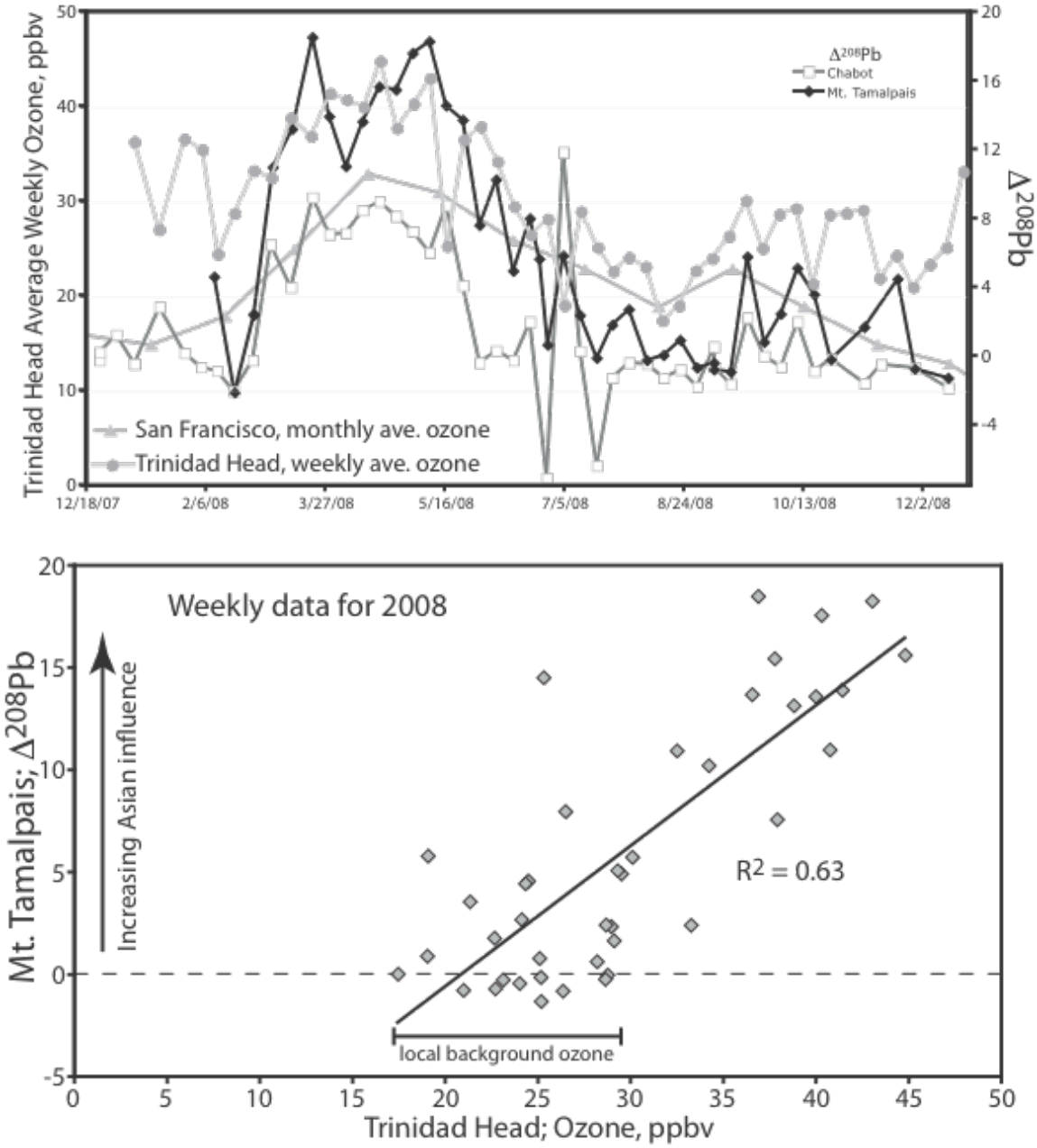

Figure 13. (Top) Comparison of the time-series for Δ208Pb (higher values indicate greater Asian influence) and time-series for ozone concentration in air (ppbv) measured in San Francisco (green, monthly average, data from the BAAQMD) and at Trinidad Head (orange- weekly average to match Mt. Tamalpais sampling periods, data from NOAA Earth System Research Laboratory). **(Bottom)** Mt. Tamalpais aerosol Δ^{208}Pb plotted against ozone measured at Trinidad Head averaged to the same sampling periods. Data covers 2008 as in A. The positive correlation suggests that the local background ozone at Trinidad Head ranges between ~15 to 30 ppbv, with higher values correlated with higher Δ^{208}Pb indicating importation from Asia across the Pacific of as much as ~20 to 25 ppbv ozone (either directly or in part by conversion of ozone precursors during trans-Pacific transport).

Summary and Conclusions

In our study we have investigated the use of Pb and Sr isotopic measurements of aerosols in California as a means to identify and apportion local sources and far-traveled aerosols sourced in Asia (China). We set up two sites for week-long collection periods of PM2.5 aerosols on Teflon filters, Mt. Tamalpais and the Chabot Space and Science Center. Mt. Tamalpais provided a relatively pristine site, above the marine boundary layer and usually, though not always, effected by winds from the west off the Pacific Ocean. The Chabot site is located in the Oakland Hills, east of and typically downwind of the heavily urban areas of San Francisco and Oakland. These two sites are close enough, with similar winds, that sampling at both sites should distinguish the addition of urban aerosols at Chabot to a uniform far travelled aerosol population at both sites. The aerosol samples were analyzed for total mass, Pb and Sr isotopic compositions, and elemental compositions. We also conducted Pb and Sr isotopic analysis of aerosols collected in the Eastern Sierra overlapping in time a portion of the Mt. Tamalpais/Chabot collection campaign. In addition, we analyzed the Pb isotopic compositions of archived ARB PM2.5 aerosol samples collected in Central California during the springs of 2003, 2004 and 2005.

The Pb isotopic analyses of the PM2.5 samples revealed isotopic compositions that on a plot of $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ varied between an array representing California sources and an array representing Asian (mostly Chinese) sources of Pb. Timeseries of the Pb isotopic data (represented by $\Delta^{208}Pb$ values which measure the displacement from the California Pb isotopic array) for Mt. Tamalpais and Chabot shows that the influence of Asian Pb during 2008 was greatest from March through May. The $\Delta^{208}Pb$ values are used to calculate the fraction of Asian (Chinese) sourced Pb, which in turn with the total Pb captured on the PM2.5 filter (and sampled air volume) yields the concentration in air of Asian sourced trans-Pacific transported Pb (trans-Pacific Pb, ng/m^3). Sr isotopic compositions of the PM2.5 varied in a similar fashion, and through a relationship between Si/Ca and $^{87}Sr/^{86}Sr$ allowed the identification of Chinese Loess (or desert soil) as an endmember. From this, the concentration in air of trans-Pacific Sr for the Mt. Tamalpais samples could then be calculated. Timeseries of trans-Pacific Pb, trans-Pacific Sr, calculated "soil" all point to four separate Asian transport events during the March-May 2008 period. In the first three events, the peaks in trans-Pacifc Pb, trans-Pacific Sr and "soil" (and so the arrivals of pollutants and dust) were coincident in time, while in the fourth event, the arrivals of maximum Asian Pb and maximum Asian Sr and "soil" were separated by as much as two weeks, reflecting changes in the Asian/Chinese portions of air mass trajectories during that fourth event.

The temporal patterns in the calculated trans-Pacific Pb records for Mt. Tamalpais and Chabot indicate a strong seasonality in the influence for long-range transport on the PM2.5 aerosols collected at those sites (Fig. 4). Dividing the records into seasons, at Mt. Tamalpais the average trans-Pacific Pb concentrations in air were 0.16 ng/m^3 for late Winter 2008, 0.53 ng/m^3 for Spring 2008, 0.03 ng/m^3 for Summer 2008, and 0.02 ng/m^3 for Fall 2008. Similar results were seen at Chabot, with trans-Pacific Pb concentrations of 0.07 ng/m^3 for Winter 2007-2008 (for comparison to Mt. Tamalpais, the average at Chabot for the late Winter period was

0.16 ng/m^3), 0.34 ng/m^3 for Spring 2008, 0.01 ng/m^3 for Summer 2008 and 0.00 ng/m^3 for Fall 2008. Thus the greatest Asian influence was seen in the Spring of 2008, with much lower influence during the rest of 2008.

The Pb isotopic data (as trans-Pacific Pb or Δ^{208}Pb) and the Sr isotopic data can be used to apportion correlated components (elemental, PM2.5, perhaps ozone) into far traveled (transported from Asia) and local sources. A relationship was found in the 2008 Mt. Tamalpais trans-Pacific Pb and PM2.5 that was used to estimate the percentage of PM2.5 collected at Chabot that was sourced in Asia. The peak proportion was 45% for the week of 3/21/08, and fell over the next 2.5 months back to essentially zero. The average proportion of Asian sourced PM2.5 at Chabot over the spring 2008 period March through May was ~25%. If the Spirng 2008 Mt. Tamalpais relationship between trans-Pacific PM2.5 and trans-Pacific Pb is assumed for a 24-hour sample collected at San Andreas on 4/27/04, perhaps as much as 20 micrograms/m^3 of PM2.5 sourced in Asia (China) was recorded by that sample, 57% of the Federal EPA 24-hour standard. In the case of Pb, the observed concentrations in air of trans-Pacific Pb (<10 ng/m^3) are a very small fraction of the air standard for Pb (150 ng/m^3 EPA). However, on a limited geographic and temporal basis, aerosols sourced in Asia could push sites above PM2.5 air concentration standards. Likewise, ozone sourced in Asia (China), based on an observed relationship between Δ^{208}Pb at Mt. Tamalpais and ozone concentration data from Trinidad Head, may be a major contributor (up to 50%) to springtime surface ozone levels in the inner Bay Area, and may explain much of the observed seasonal variation.

The similarity in the records of trans-Pacific Pb between an essentially pristine site (Mt Tamalpais- maximum trans-Pacific Pb = 72% of total Pb) and an urban influenced site (Chabot- maximum of trans-Pacific Pb = 35%) confirms that Pb isotopes can be used to quantify trans-Pacific transported Asian influence at California urban sites. Results for samples from two Eastern Sierra sites were also similar to Mt. Tamapais/Chabot indicating that the Asian sourced aerosols can be tracked eastward by Pb isotopes across the whole of Northern California. In California (if not western N. America), Pb isotopes are a good proxy for Asian sourced pollution, while ^{87}Sr/^{86}Sr can serve as a proxy for Asian-sourced mineral dust (Chinese loess and desert soils).

In sum, the research presented in this report demonstrates the value of isotopes (here Pb & Sr) for distinguishing between local and distant aerosol sources, and for partitioning associated pollutants. The greatest amount of information can be gleaned when PM2.5 samples are analyzed for Pb and Sr isotopic compositions coupled with elemental (XRF/S-XRF) analysis.

Recommendations for Further Research

Our Research into the Pb and Sr isotopic compositions of aerosols collected in Californis suggest a number of different lines for future research, to verify and extend the use this type of data. Though the results presented above look promising, the relationship between Asian sourced PM2.5 and trans-Pacific Pb needs further investigation and testing. This could be done by analysis of archived ARB samples from selected sites collected during 2008 (these should be available now) to compare to the

2008 Mt. Tamalpais record. Besides investigating the geographic variation of transport of trans-Pacific Pb to inland urban areas, where loading data is available, the fraction of Asian sourced PM2.5 could be estimated.

The relationship between trans-Pacific aerosol transport and trans-Pacific ozone transport could further investigated by co-located (e.g. at Mt. Tamalpais) aerosol sample collection (for Pb and Sr isotopic analysis, and elemental analysis) and ozone concentration monitoring.

The analysis of collected PM2.5 could be extended to include Nd isotopic analysis to the current suite of Pb and Sr isotopic analyses. Though the small amounts of Nd typically collected can present an analytical challenge, Nd isotopes would provide an additional tracer to Sr for Asian/Chinese sourced mineral dust aerosols. Likewise parallel sampling for sulfate for S and O isotopes could provide an additional tracer of anthropogenic pollutants.

Besides pollutant particulates and mineral dust, aerosols can also include biological material such as microbes and fungal spores, that can be carried long distances and still be viable in receptor areas. Metagenomic microbial analysis of aerosol samples correlated with Pb isotopic data sourcing, would allow the investigation of the impact of the transport of microbes from Asia on public health and agriculture in California.

The Pb and Sr isotopic methods illustrated is this report would also allow monitoring future changes in contributions of far-traveled aerosols from Asia (China) to local California pollutant burdens as continued economic development in China drives emission increases. If China develops alternative "Green" renewable sources of energy while slowing or decreasing the building or use of coal fire power plants (or improve their pollution controls), this may also be evident in long-term records tracking aerosol Pb isotopic composition. Likewise, land use changes in China or climate change that detrimentally affects soil stability in Western China and therefore increases mineral aerosol loading across the Pacific should be evident in records of aerosol Sr isotopes. However, to fully interpret long-term changes, the effects of meteorological conditions over the Pacific and in the source areas in China on the efficiency of transport to California receptor areas need to be understood and modeled. To help address these issues, computer modeling and analysis of the temporal relationship between measured trans-Pacific Pb-Sr data and meteorological conditions, including over the Pacific as well as in the source (China/Asia) and receptor (California) regions, needs to be carried out.

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Publications and Abstracts Resulting from this Project

Meeting Abstracts

Ewing, SA; Christensen, JN; Brown, ST; VanCuren, RA; Cliff, SS; and DePaolo, DJ (2008) Pb Isotopes Track Asian Pollution in California. Eos Trans. AGU, 89(53), Fall Meet. Suppl., Abstract H54C-04.

Christensen, JN; Ewing, SA; Brown, ST; VanCuren, RA; Cliff, SS; and DJ DePaolo (2009) A Pb (& Sr) isotopic return address for trans-Pacific transported aerosols. Geochim. Cosmochim. Acta, v.73(13S) p.A223. (Goldschmidt 2009)

DePaolo, DJ; Christensen, JN; Ewing, SA; Cliff, SS; Brown, ST; VanCuren, RA (2009) Isotopic Tracers to Identify Far-traveled Pollutant and Mineral Aerosols in Northern California, *Eos Trans. AGU, 90*(52), Fall Meet. Suppl., A34D-01, (*Invited*)

Christensen, JN; Ewing, SA; Brown, ST; VanCuren, RA; Cliff, SS; and DJ DePaolo (2011) Exploring the Temporal Relationship Between Trans-Pacific Particulate Transport and Ozone Transport to Northern California Using Pb Isotopes. *Abstract A23B-0133 presented at 2011 Fall Meeting, AGU, San Francisco, Calif., 5-9 Dec.*

Published Peer Reviewed Paper

Ewing, SA; Christensen, JN; Brown, ST; VanCuren, RA; Cliff, SS; and DePaolo, DJ (2010) Pb Isotopes as an Indicator of the Asian Contribution to Particulate Air Pollution in Urban California. *Environ. Sci. & Tecnol.*, v.44, pp.8911-8916

Ewing et al. (2010) was published in the Dec. 1st, 2010 issue of Environmental Science and Technology, and is included here as an appendix along with its Supporting Information.