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Pb Isotopes as an Indicator of the Asian Contribution to Particulate Air Pollution in Urban California

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Abstract

During the last two decades, expanding industrial activity in east Asia has led to increased production of airborne pollutants that can be transported to North America. Previous efforts to detect this trans-Pacific pollution have relied upon remote sensing and remote sample locations. We tested whether Pb isotope ratios in airborne particles can be used to directly evaluate the Asian contribution to airborne particles of anthropogenic origin in western North America, using a time series of samples from a pair of sites upwind and downwind of the San Francisco Bay Area. Our results for airborne Pb at these sites indicate a median value of 29% Asian origin, based on mixing relations between distinct regional sample groups. This trans-Pacific Pb is present in small quantities but serves as a tracer for airborne particles within the growing Asian industrial plume. We then applied this analysis to archived samples from urban sites in central California. Taken together, our results suggest that the analysis of Pb isotopes can reveal the distribution of airborne particles affected by Asian industrial pollution at urban sites in northern California. Under suitable circumstances, this analysis can improve understanding of the global transport of pollution, independent of transport models.

1. Introduction

The phaseout of leaded gasoline in North America and Europe starting in the 1970s resulted in a dramatic global decrease in atmospheric Pb deposition by the early 1990s (*1,2*). Yet other industrial sources of atmospheric Pb – in particular, coal combustion– have grown in the last two decades, most dramatically in China (*3-5*), and emissions of combustion products from Asia have increased accordingly (*6,7*). Lead and other

pollutants from Asia, as well as dust, can be transported by winds across the Pacific Ocean to western North America and beyond (*8-19*). The relatively small amount of Asian Pb arriving in North America, and how it is distributed, are poorly known. Yet despite low concentrations, airborne Pb at remote sites has been interpreted as an indicator of the Asian industrial plume (*12*). It is widely suspected that with continued industrial growth in Asia, trans-Pacific pollution will increasingly degrade North American air quality (*12-19*) and contribute to the transformation of global climate resulting from air pollution (*20*). Considerable recent work has documented the persistence of trans-Pacific dust and pollution – particularly in springtime - through observations using remote sensing and adjoint model sensitivity analysis (*10,11,13,16-19*). Here we use Pb isotopes to quantify the Asian Pb increment present in aerosol samples at both a remote location and at urban sites with substantial local pollution. This analysis directly evaluates a component of the Asian pollution reaching North America – independent of modeling or trajectory analysis – and strengthens a new line of evidence for better understanding the processes controlling intercontinental transport of pollutants globally (*20*).

It is well known that the Earth's atmosphere is effective at transporting fine dust particles and other aerosols over long distances. Both natural and anthropogenic Pb have been redistributed by winds throughout human history (*1,2,21-23*). The deserts of Mongolia and China are known to be major sources of wind-blown dust that is distributed over the North Pacific region in particular, and in lesser amounts over most of North America

(*11,16-18,22,24*). Isotopic evidence from North Pacific sediment cores indicates that trans-Pacific transport of Pb-bearing mineral dust from the Chinese loess plateau has occurred for tens of millions of years (*25,26*). By the 1980s, however, industrialization in China had begun to markedly increase Pb concentrations in North Pacific surface waters (*27,28*). Concentrations of Pb in the Mt. Logan ice core in northwest Canada also show a dramatic increase in the last 20 years (*29*). This increase is of particular concern in light of the likely association of anthropogenic Pb with black carbon and hence albedo effects in the arctic (*12,30*), as well as recent evidence that anthropogenic Pb can have a direct role in atmospheric ice nucleation and associated radiative effects (*31*).

Previous research suggests that Pb isotopes provide a useful means for identifying trans-Pacific pollution (*1,2,32,33*). This use of Pb isotopes stems from the fact that the relative proportions of the four stable isotopes of Pb (^{208}Pb, ^{207}Pb, ^{206}Pb, ^{204}Pb) are not constant in nature. The three heaviest isotopes are produced from radioactive decay of U and Th over billions of years, and their proportions vary in rocks and minerals depending on the age of those materials and the relative amounts of U, Th, and Pb they contain. For geologic reasons, only some of which are well understood, the isotopic composition of Pb varies systematically over large regions of the Earth's crust, and in favorable circumstances specific isotopic proportions can be almost unique to certain regions of the continents (*34*). Both Asian mineral dust and other sources of Asian Pb (coal, metal ores) have especially high proportions of ^{208}Pb, the isotope that forms from radioactive decay of Th (*32*).

Combustion processes mobilize airborne particles with Pb isotopic signatures similar to those of the starting material (*2,32*). In East Asia, China is the primary producer and consumer of coal and metal ores (*3-5*). The Pb isotopic distinction between Asian and North American airborne particles was demonstrated by Bollhofer and Rosman in a survey of samples from the northern hemisphere (*32*). They emphasized the "very distinctive isotopic fingerprint" of Chinese airborne particles due to their higher ^{208}Pb (as ^{208}Pb/^{207}Pb vs. ^{206}Pb/^{207}Pb), observed in both Pb ores and coal from China. In a few samples from the west coast of North America in the late 1990s, Bollhofer and Rosman observed increased ^{208}Pb/^{207}Pb and suggested these might reflect trans-Pacific transport of Chinese emissions. This study was designed to test that hypothesis. The distinct Pb isotopic character of Chinese combustion products is a reflection of the use of regional source materials, and offers a potential means of directly detecting trans-Pacific particles in North American air (*32*), independent of modeling or trajectory analysis and without many of the complications inherent in evaluating elemental concentrations.

Here we report Pb isotope ratios and elemental concentrations in airborne particles from a pair of sites selected to distinguish trans-Pacific vs. local urban sources: a coastal site near the San Francisco Bay Area (Mt. Tamalpais) with limited urban influence, and an urban site in the East Bay Area (Chabot Observatory, Oakland, CA) (Figure S1). By sampling from winter through early summer at these two sites, we capture the transition into the season of transport events. We use this sample set to develop a novel approach

for quantifyng the trans-Pacific component in each sample, and then apply this approach to archived samples from other urban communities in northern California.

2. Materials and Methods

2.1. Air sampling. Fine airborne particles (less than 2.5 μm in aerodynamic diameter; PM2.5) were collected at two sites northwest (Mt. Tamalpais; 37°55'23.26"N, 122°35'54.73"W, elev. 772 masl) and east (Chabot Observatory; 37°49'09.82"N, 122°10'53.05"W, elev. 470 masl) of the San Francisco Bay Area (Figure S1), from December 2007 through May 2008. Air samples were collected on pre-cleaned, pre-weighed 25 mm Teflon filters, using samplers similar to those of the Interagency Monitoring for Protected Visual Environments (IMPROVE) program. A cyclone inlet separated PM2.5 particles, and a critical orifice maintained a flow rate of 22.8 L min^{-1}. Flow was divided among three replicate filters. Samples were collected simultaneously at both sites, for approximately one week each. One filter was used for elemental analysis, and a second (and occasionally a third) for Pb isotopic analysis.

Archived samples from inland sites in central California (Figure S1) were provided by the California Air Resources Board for Pb isotope analysis. These samples were collected in 2003-2005 during April and May, the season when Asian dust influence was expected to be high. Fine particles (PM2.5) were collected on 47 mm Teflon filters over 24 hours at a flow rate of 33 L min^{-1}. Three additional samples from Hefei, China were also

analyzed for Pb isotopes; these were PM2.5, collected over 24 hours onto 25 mm Teflon filters with IMPROVE style samplers in 2002.

2.2. Elemental analysis. Elemental concentrations in air samples (Table S1) were determined by two methods. Standard X-ray fluorescence spectroscopy (XRF) of most samples was performed by staff from the IMPROVE program at the University of California, Davis. Samples were also analyzed by synchrotron X-ray fluorescence (S-XRF) using a broad spectrum X-ray beam generated on beam line 10.3.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory (*15*). For S-XRF, five spots on each filter were analyzed and used to quantify uncertainty, whereas in standard XRF, the spot size was essentially the entire filter. Concentrations from the two techniques were comparable, but in some cases the S-XRF uncertainties were substantially greater due to variation among spot analyses. For each filter that was analyzed by both methods, we report the average of the two values and the standard error of the mean, propagated from the two absolute uncertainty values. In many cases the result is that our reported uncertainties exceed those of the concentration obtained by XRF.

2.3. Pb isotopic analysis. Pb isotope ratios were measured in all samples (Table S2) using multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS). This technique allows the Pb isotope ratios to be determined to a 2σ precision of $\pm0.02\%$ and allows for resolution of Asian vs. North American Pb, as further discussed below.

Filter cleaning and weighing was performed in a better than class 10,000 clean laboratory. Pb was leached from filters in pre-cleaned (HF+HNO$_3$) Savillex vials using 6N HCl (Seastar Chemicals Inc., Baseline grade), heated for 3 h. Filters were removed and the Pb in the resulting solutions was purified using standard ion exchange chemistry (AG1-X8 resin, 0.54N HBr, 6N HCl). The Pb solutions were dried, re-dissolved in 2% HNO$_3$, spiked with about 5 ng Tl with a known isotopic composition (^{205}Tl/^{203}Tl = 2.3880), and analyzed by MC-ICPMS (GV Instruments IsoProbe). USGS rock standard BHVO-1 (a Hawaiian basalt) was used to determine the mass fractionation of Pb relative to Tl.

The NBS-981 Pb standard was evaluated as an unknown, with thirty analyses during the data collection period (December 2007 - June 2008). Ratios for unknowns and standards were corrected for mass fractionation using the empirical relationship between Tl and Pb derived from 50 analyses of BHVO-1 (*35-36*). All ratios were corrected using the long term Tl-Pb relationship. Residual fractionation was corrected by normalizing the daily mean values for NBS-981 to those reported in (*37*). Calculated correction factors for each ratio were then applied to unknowns. Analytical uncertainty for NBS-981 was better than 0.01% for all ratios (2σ standard error). Full procedural replicates (two separate filters from the same sampling day) were indistinguishable from one another in ^{207}Pb space.

3. Results and Discussion

3.1. Elemental concentrations at Tamalpais and Chabot. At the Tamalpais and Chabot sites, Pb concentrations in airborne PM2.5 particles averaged 0.193±0.118 0.59 ng Pb μg^{-1} (range = 0.022-0.592 ng Pb μg^{-1}), greatly exceeding expected concentrations for silicate dust (0.010-0.030 ng Pb μg^{-1} for Chinese loess) (*38*). The high mass concentrations suggest that most of the Pb is associated with pollutants rather than mineral dust, although it may occur as secondary coatings on mineral dust particles. The volumetric Pb concentrations were 0.52 to 2.76 ng m^{-3} (Table S1), falling well below the California ambient air quality standard of 1.5 μg m^{-3}. However, these relatively small amounts of airborne Pb can provide an indicator of the source region of airborne particles emitted by industrial combustion processes.

Several episodes of increased volumetric Pb concentration are apparent between February and May at both sites (Figure 2a). These higher Pb concentrations coincide with higher concentrations of Zn, Si, S and Ca, and lower concentrations of Cl (Figure S2, Table S1), suggesting co-occurrence of Pb with both silicate dust and pollution (*12*). The inverse relationship between Cl and Si (Figure S2) reflects local sea salt influence when dust transport is reduced and Si is low (*15*), due to the close proximity of the sample locations to the ocean. Samples with less seasalt (lower Cl) and characterized by elements consistent with Asian derived soil particles and combustion products (increased Si, Pb, Zn, S; *15*) are inferred to derive from long-range transport. It is generally held that lofted soil and anthropogenic aerosols from the Asian source region are mainly transported across the Pacific in the lower free troposphere with limited influence from the western

Pacific marine boundary layer during transport (e.g., *10,17*). The inverse soil/seasalt

relationship reflects the fact that contact of trans-Pacific airmasses with the North Pacific

marine boundary layer would tend to scavenge long-range transported particles.

At Chabot, concentrations of Pb, Zn, S, and Ca are frequently higher than at Tamalpais,

and the dates of maximum concentrations can differ (Figure S2, Table S1). The

Tamalpais concentrations could reflect trans-Pacific transport, but this signal is obscured

at Chabot by local sources. Increased pollution from local sources at Chabot is consistent

with its urban location, and makes it difficult to detect or quantify trans-Pacific influence

from elemental concentrations. We use our Pb isotope analyses to resolve this ambiguity.

3.2. Trans-Pacific influence at Mt. Tamalpais and Chabot Observatory.

The distinction between Chinese urban air samples and wintertime California samples is

shown on a plot of $^{208}Pb/^{207}Pb$ vs. $^{206}Pb/^{207}Pb$ (Figure 1, solid regression lines). The

samples collected in wintertime at Chabot Observatory, which represent the compositions

of local Pb sources, fall on a linear array that is consistent with other data from the San

Francisco Bay region (*39*) (Figure 1) and sites throughout North America (*32*). Data

from Chinese cities and loess fractions (*24,32*) form a linear array that is displaced

toward higher values of $^{208}Pb/^{207}Pb$ (Figure 1). This Chinese array is consistent with less

precise Pb isotope values obtained for air samples and source materials in the region by

quadrupole ICP-MS (*40-43*) (Figure S3) and with our analyses of samples collected at

Hefei, China in 2002 (Figure 1). Between March and May, 2008, the Pb isotopic ratios

of airborne particle samples collected at Tamalpais and Chabot diverge from the regional

array toward the Chinese array, suggesting an increased proportion of trans-Pacific Pb.

Similarly, about half of the springtime PM2.5 samples from central California for the

years 2003 to 2005 diverge, suggesting Asian influence. The Tamalpais samples define a

linear trend between the North American and Chinese arrays, intersecting the Chinese

array at a point close to values for air samples from Chinese cities (Hefei, Xinshao and

Chengdu) and a Shanghai coal sample (*32,41*) (Figure 1).

The range of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios seen in Figure 1 is due to variations in the

U/Pb and Th/Pb ratios of the crustal rocks from which the Pb was originally derived. The

slightly lower slope and higher $^{208}Pb/^{207}Pb$ values in the Chinese array indicate that the

Chinese source rocks have higher Th/U. Because the Chinese samples are characterized

by higher $^{208}Pb/^{207}Pb$ values due to higher Th/U in source rocks, we quantify the

proportion of Chinese Pb in the air samples using the horizontal divergence of the

$^{208}Pb/^{207}Pb$ ratios from the regional California array, which we define as $\Delta^{208}Pb$:

$$\Delta^{208}Pb_{observed} = 1000[^{208}Pb/^{207}Pb_{observed} - {}^{208}Pb/^{207}Pb_{CA}]_{206} \quad (1)$$

where $^{208}Pb/^{207}Pb_{CA}$ is derived from the linear fit to the wintertime samples at Chabot

Observatory, and the observed $^{206}Pb/^{207}Pb$ value. The subscript 206 indicates that the

difference applies to the specific observed value of $^{206}Pb/^{207}Pb$ (i.e., the horizontal offset

from the North American array in Figure 1). This calculation is represented graphically

in Figure S4. The fraction of Pb derived from Asia, F_{Asia} is calculated assuming a

mixture of components from the North American and Asian arrays:

$$F_{Asia} = \frac{\Delta^{208}Pb_{observed}}{\Delta^{208}Pb_{Asia}} \qquad (2)$$

where $\Delta^{208}Pb_{Asia}$ is derived from the horizontal offset between the Chinese and California

arrays at the observed value of $^{206}Pb/^{207}Pb$ (see Figure S4). Due to the difference in

slopes of the two arrays (1.05 ± 0.03 for the Chinese array vs. 1.19 ± 0.07 for the

California array), this offset varies between $\Delta^{208}Pb_{Asia} = 20.4$ and 25.9 over the range of

observed values. At the same time, the linear fit to the Mt. Tamalpais samples ($R^2=0.97$)

suggests that the Chinese endmember for this time series may resemble the Heifei

samples ($^{206}Pb/^{207}Pb=1.169$ and $^{208}Pb/^{207}Pb=2.460$; Figure 1). Our use of the horizontal

intercept with the Chinese array to represent the Asian endmember (Figure S4) would

under or overestimate F_{Asia} by a maximum of 8.5% (average 3.1 ± 2.3%, 1 s.d.) for

samples where the actual endmember falls at the highest or lowest urban datapoint on the

Chinese array (Figure 1, points a and d). Accounting for the uncertainty in slopes of the

regional linear arrays, the average uncertainty in F_{Asia} is 6.2 ± 4.4% (1 s.d.).

The $\Delta^{208}Pb$ values increase between winter and spring at both Mt. Tamapais and Chabot

Observatory, and are higher at Mt. Tamalpais (Figure 2b). Using equation 2, up to 80%

of the Pb in the Tamalpais samples, and up to 37% of the Pb in the Chabot Observatory

samples, reflect trans-Pacific transport (Table S2a,b). The lower Δ^{208}Pb values in the

Chabot samples (Figure 2b) – where there is often more Pb (Figure 2a) – indicate a

higher proportion of locally derived Pb. This is expected from its location closer to and

downwind from urban sources within the San Francisco Bay Area, and from the

elemental data (Table S1). The continuously elevated Δ^{208}Pb values through the

springtime period indicate an ongoing, "background" contribution of trans-Pacific Pb that

is dependent on favorable meteorological conditions rather than dust loading (*12,15*).

3.3. Trans-Pacific influence in central California cities. When we applied our mixing

analysis using the same endmember arrays to the archived central California samples, the

implied fraction of trans-Pacific Pb ranged from 0% to 93%, with 11 of 23 samples

indicating amounts greater than 30%, and every site indicating this degree of influence in

at least one springtime sample (Table S2c). Although the dates and locations vary,

spatial variation in trans-Pacific influence is indicated where dates overlap and the trans-

Pacific component varies (Figure S5a). On April 21, 2004, the proportion of Asian Pb

was 58% at San Andreas in the central Sierra Nevada foothills, but only 2% in the south

central valley city of Visalia; it reached 66% at the north central valley city of Colusa

three days later (April 24). On April 27, the proportion was 93% at San Andreas and

50% in the central valley city of Stockton, but only 13% in Yuba City to the north. Three

days later on April 30, only 9% Asian Pb was detected in a Colusa sample. By May 3,

the proportion of trans-Pacific Pb was still near 30% in Visalia and San Andreas, and

11% in Colusa. Overall this suggests that in this two-week period, an event that was

initially pervasive in the north central valley and foothills on April 21 persisted through April 30 in the foothills and southern locations. This could reflect spatially and temporally varying meteorological conditions affecting the degree of down-mixing to the surface among these sites (*15*). While further analysis of regional endmembers and more extensive sample sets is needed, these data illustrate how Pb isotope analysis of samples from urban sites can potentially provide a measure of the spatial distribution of Asian influence on airborne particles at the regional level.

3.4. Trans-Pacific Pb concentrations. If the F_{Asia} values are multiplied by the amount of Pb in each sample, the concentration of trans-Pacific Pb may be calculated (Figure 2c). Amounts in the weekly Tamalpais and Chabot samples range from 0 to 1.1 ng m^{-3}, with maximum concentrations coinciding at the two sites (Figure 2c). Amounts were comparable in the 24-hour central California samples but ranged higher (0 to 3.6 ng m^{-3}; Figure S5b), possibly because the shorter collection period allowed the peak concentrations to be sampled more accurately (archived samples were selected for likely trans-Pacific character and provide a non-continuous record), or because the earlier events were more intense.

At Mt. Tamalpais and Chabot Observatory, this analysis reveals four distinct episodes of increased trans-Pacific Pb that are similar in magnitude and coincident with increased Si and S concentrations (Figure 2c, Figure 3). This is evident from the Pb isotopic data despite greater addition of local Pb to the Chabot samples (Figure 2a). The similarity of

trans-Pacific Pb concentrations at these two sites is consistent with their proximity to one another, and demonstrates that Pb isotopes can be used to resolve trans-Pacific influence at urban sites. Our results for central California communities suggest spatially variable degrees of trans-Pacific influence at a variety of urban sites, with isotopically variable local Pb (Figure 1, Figure S5).

The relationship of trans-Pacific Pb to total PM2.5 at Tamalpais and Chabot is shown in Figure S6. The linear relationship is stronger at Tamalpais (R^2=0.71) than at Chabot (R^2=0.16), and there is a greater proportion of trans-Pacific Pb at Tamalpais (slope = 0.33±0.06 ng Pb μg^{-1} PM2.5) compared to Chabot (slope = 0.08±0.04 ng Pb μg^{-1} PM2.5), where local sources weaken the linear relationship. These relationships suggest that for individual sites with limited local influence, and where a number of samples are evaluated, Pb isotope ratios can provide an indicator of the total quantity of trans-Pacific particles in a given sample, not just trans-Pacific Pb.

3.5. Influence of local sources. Several aspects of our May results provide clues about the interplay of local sources and reduced trans-Pacific Pb at Chabot late in the springtime period. In general, there is a weak inverse relationship between Si and Cl at both sites between March and May, with peaks in Cl corresponding to low Si and vice versa (Figure 3). Elevated Cl concentrations indicate greater influence of the local marine boundary layer (Figure 3)(*15*), as expected at the onset of summer in the San Francisco Bay Area. The maximum Cl concentrations during the week of May 9 coincide

with peaks in total Pb, Zn, and S at Chabot but not Tamalpais (Figure S2, Figure 3, Table S2), and with lower trans-Pacific Pb at Chabot relative to Tamalpais (Figure 3), implying arrival of trans-Pacific Pb at the Tamalpais site but not at Chabot, where local pollution dominates. High Si at Tamalpais and not Chabot in the May 2 and May 9 samples is consistent with ineffective delivery of trans-Pacific particles to Chabot. Subsequently at both sites, Si concentrations reach their highest level during the week of May 16, accompanied by low Cl, sustained high Δ^{208}Pb values, and decreased total Pb, Zn, and S concentrations (Figure S2, Figure 2b, Figure 3). This suggests that intensified trans-Pacific dust mobilization continued to deliver Asian pollutants to both sites, but in smaller amounts. The reduced entrainment of combustion products in the mineral dust plume could indicate more localized deposition in Asia due to a greater concentration of coarse dust particles, or a strengthened pathway of mineral dust transport that intersected less with combustion sources.

3.6. Implications. The geochemistry of Pb isotopes makes this analytical tool particularly suited to detecting trans-Pacific transport to the west coast of North America. We tested and developed this approach using a time series of aerosol samples at a pair of geographically related sites where local and trans-Pacific components were expected to be of similar character, but vary in their relative influence on sample compositions. We used a novel approach to evaluate mixing proportions when endmembers are not specifically known, but plot on linear arrays. The amount and proportion of Asian Pb indicated by our analysis of Pb isotopic composition was enhanced during the springtime

transport season and corresponded to other particle phase constituents including S and Zn, consistent with previous observations for trans-Pacific pollution. In this geographic context, Pb isotopes allowed us to detect the influence of trans-Pacific aerosols both at remote sites and in urban areas where local sources contribute to observed concentrations. This approach to aerosol source attribution reduces the ambiguity inherent in interpreting elemental concentrations that are the result of atmospheric mixing, and provides an independent constraint for modeling based efforts to ascribe trans-Pacific airborne particles to source areas. It is important to note that a number of gas phase pollutants are also associated with trans-Pacific plumes, including CO, non-methane hydrocarbons and peroxyacetyl nitrate (e.g., 10, *41*), as well as ozone arguably formed by secondary production from Asian pollution (*13-15,18-20,44,45*). Under the right geographic circumstances and in combination with other approaches, analysis of Pb isotopes provides a powerful indicator for improved understanding of intercontinental to global scale transport of dust, black carbon, anthropogenic Pb and associated pollutants that drive climate feedback processes (*15,19,30,31,46-48*).

Literature Cited

(1) Shotyk, W.; Weiss, D.; Appleby, P. G.; Cheburkin, A. K.; Frei, R.; Gloor, M.; Kramers, J. D.; Reese, S.; Van Der Knaap, W. O. History of Atmospheric Lead Deposition Since 12,370 14C yr BP from a Peat Bog, Jura Mountains, Switzerland. *Science* **1998**, *281*, 1635-1640.

(2) Reuer, M. K.; Weiss, D. J. Anthropogenic lead dynamics in the terrestrial and marine

environment. *Phil. Trans. R. Soc. Lond.* **2002**, *360*, 2889-2904.

(3) Akimoto, H.; Ohara, T.; Kurokawa, J.; Horii, N. Verification of energy consumption in China during 1996-2003 by using satellite observational data. *Atmos. Environ.* **2006**, *40*, 7663-7667.

(4) British Petroleum, *Statistical Review of World Energy 2007,* **2008**.

(5) U. S. Geological Survey, *U. S. Geological Survey Minerals Yearbook, vol. I, Metals and Minerals* (U. S. Department of Interior, Washington, D. C.), **2008**.

(6) Ohara, T.; Akimoto, H.; Kurokawa, J.; Horii, N.; Yamaji, K.; Yan, X.; and Hayasaka, T. An Asian emission inventory of anthropogenic emission sources for the period 1980-2020. Atmos. Chem. Phys. **2007**, *7*, 4419-4444.

(7) Richter, A.; Burrows, J. P.; Hendrik, N.; Granier, C.; Niemeier, U. Increase in tropospheric nitrogen dioxide over China observed from space. *Nature* **2004**, *437*, 129-132.

(8) Jaffe, D.; Anderson, T.; Covert, D.; Kotchenruther, R.; Trost, B.; Danielson, J.; Simpson, W.; Berntsen, T.; Karlsodottir, S.; Blake, D.; Harris, J.; Carmichael, G.; Uno, I. Transport of Asian air pollution to North America. *Geophys. Res. Lett.* **1999**, *26*, 711-714.

(9) Wilkening, K. E.; Barrie, L. A., Engle, M. Trans-Pacific air pollution. *Science* **2000**, *290*, 65-67.

(10) Stith, J. L.; Ramanathan, V.; Cooper, W. A.; Roberts, G. C.; DeMott, P. J.; Carmichael, G.; Hatch, C. D.; Adhikary, B.; Twohy, C. H.; Rogers, D. C.; Baumgardner, D.; Prenni, A. J.; Campos, T.; Gao, R.; Anderson, J.; and Feng, Y. An

overview of aircraft observations from the Pacific Dust Experiment campaign. J. Geophys. Res. **2009**, *114*, D05207, doi: 10.1029/2008JD010924.

(11) Uno, I.; Eguchi, K.; Yumimoto, K.; Takemura, T.; Shimizu, A.; Uematsu, M.; Liu, Z.; Wang, Z.; Hara, Y.; Sugimoto, N. Asian dust transported one full circuit around the globe. *Nature Geosci.* **2009**, DOI 10.1038/NGEO583.

(12) VanCuren, R. A. Asian aerosols in North America: Extracting the chemical composition and mass concentration of the Asian continental aerosol plume from long-term aerosol records in the western United States. *J. Geophys. Res.* **2003**, *208*, D20, 4623, doi:10.1029/2003JD003459.

(13) Fiore, A. M.; Jacob, D. J.; Bey, I.; Yantosca, R. M.; Field, B. D.; Fusco, A. C. Background ozone over the United States in summer: Origin, trend and contribution to pollution episodes. *J. Geophys. Res.* **2002**, *107*, D15, 4275, 10.1029/2001JD000982.

(14) Akimoto, H. Global air quality and pollution. *Science* **2003**, *302,* 1716-1719.

(15) VanCuren, R. A.; Cliff, S. S.; Perry, K. D.; Jimenez-Cruz, M. Asian continental aerosol persistence above the marine boundary layer over the eastern North Pacific: Continuous aerosol measurements from Intercontinental Transport and Chemical Transformation 2002 (ITCT 2K2). *J. Geophys. Res.* **2005**, *110,* D09S90.

(16) Fairlie, T. D.; Jacob, D. J.; Park, R. J. The impact of transpacific transport of mineral dust in the United States. *Atmos. Environ.* **2007**, *41*, 1251-1266.

(17) Heald, C. L.; Jacob, D. J.; Park, R. J.; Alexander, B.; Fairlie, T. D.; Yantosca, R. M.; Chu, D. A. Transpacific transport of Asian anthropogenic aerosols and its impact on

surface air quality in the United States, *J. Geophys. Res.* **2006**, 111, D14310, doi:10.1029/2005JD006847.

(18) Goldstein, A. H.; Millet, D. B.; McKay, M.; Jaegle´, L.; Horowitz, L.; Cooper, O.; Hudman, R.; Jacob, D. J.; Oltmans, S.; and Clarke, A. Impact of Asian emissions on observations at Trinidad Head, California, during ITCT 2K2. *J. Geophys. Res.* **2004**, *109*, D23S17, doi:10.1029/2003JD004406.

(19) Cooper, O.R.; Parrish, D. D.; Stohl, A.; Trainer, M.; Ne'de'lec, P.; Thouret, V.; Cammas, J. P.; Oltmans, S. J.; Johnson, B. J.; , Tarasick, D.; Leblanc, T.; McDermid, S.; Jaffe, D.; Gao, R.; Stith, J.; Ryerson, T.; Aikin, K.; Campos, T.; Weinheimer, A.; Avery, M. A. Increasing springtime ozone mixing ratios in the free troposphere over western North America. *Nature* **2010,** 463, 344-348, doi: 10.1038/nature08738

(20) Ramanathan, V.; Feng, Y. Air pollution, greenhouse gases and climate change: Global and regional perspectives. *Atmos. Environ.* **2009**, *43*, 37-50.

(21) Hong, S.; Candelone, J.-P.; Patterson, C. C.; Boutron, C. F. Greenland ice evidence of hemispheric lead pollution two millennia ago by Greek and Roman civilizations. *Science* **1994**, *265,* 1841-1843.

(22) Monastra, V.; Derry, L. A.; Chadwick, O.A. Multiple sources of lead in soils from a Hawaii chronosequence. *Chem. Geol.* **2004**, *204*, 215-231

(23) Shotyk, W.; Zheng, J.; Krachler, M.; Zilanowicz, C.; Koerner, R.; Fisher, D. Predominance of industrial Pb in recent snow (1994-2004) and ice (1842-1996) from Devon Island, Arctic Canada. *Geophys. Res. Lett.* **2005**, *32*, L21824.

(24) Biscaye, P.E.; Grousset, F.E.; Revel, M.; Van der Gaast, S.; Zielinski, G.A.;Vaars, A.; Kukla, G. Asian provenance of glacial dust (stage 2) in the Greenland Ice Sheet

Project 2 ice core, Summit, Greenland. *J. Geophys. Res.* **1997**, *102*, 26765-26781.

(25) Jones, C. E.; Halliday, A. N.; Rea, D. K.; Owen, R. M. Eolian inputs of lead to the

North Pacific. *Geochim. Cosmochim. Acta* **2000**, *64*,1405-1416.

(26) Pettke, T.; Halliday, A. N.; Hall, C. M.; Rea, D. K. Dust production and deposition

in Asia and thenorth Pacific Ocean over the past 21 Myr. *Earth Planet. Sci. Lett.*

2000, *178*, 397-413.

(27) Schaule, B. K.; Patterson, C. C. Lead concentrations in the northeast Pacific:

evidence for global anthropogenic perturbations. *Earth Planet. Sci. Lett.* **1981**, *54*, 97-

116.

(28) Flegal, A. R.; Patterson, C. C. Vertical concentration profiles of lead in the Central

Pacific at 15°N and 20°S. *Earth Planet. Sci. Lett.* **1983**, *64*, 19-32.

(29) Osterberg, E.; Mayewski, P.; Kreutz, K.; Fisher, D.; Handley, M.; Sneed, S.;

Zdanowicz, C.; Zheng, J.; Demuth, M.; Waskiewicz, M.; Bourgeois, J. Ice core

record of rising lead pollution in the North Pacific atmosphere. *Geophys. Res. Lett.*

2008, *35*, L05810.

(30) Ramanathan, V.; Carmichael, G. Global and regional climate changes due to black

carbon. *Nature Geosci.* **2008**, *1*, 221-227.

(31) Cziczo, D. J.; Stetzer, O.; Worringen, A.; Ebert, M.; Weinbruch, S.; Kamphus, M.;

Gallavardin, S. J.; Curtius, J.; Borrmann, S.; Froyd, K. D.; Mohler, O.; Lohmann, U.

Inadvertent climate modification due to anthropogenic lead. *Nature Geosci.* **2009**, *2*,

333-336.

 (32) Bollhofer, A.; Rosman, K. J. R. Isotopic source signatures for atmospheric lead: the

northern hemisphere. *Geochim. Cosmochim. Acta* **2001**, *65*, 1727-1740.

(33) Wu, J.; Rember, R.; Jin, M.; Boyle, E. A.; Flegal, A. R. Isotopic evidence for the
source of lead in the North Pacific abyssal water. *Geochim. Cosmochim. Acta* **2010**,
74, 4629-4638.

(34) Faure, G.; Mensing, T. M. *Isotopes: Principles and Applications*, **2005** (John Wiley
& Sons).

(35) Woodhead, J. A simple method for obtaining highly accurate Pb isotope data by
MC-ICP-MS. *J. Analytical Atomic Spectrometry* **2002**, 1381-1385.

(36) White, W. M.; Albarede, F.; Telouk, P. High-precision analysis of Pb isotope ratios
by multi-collector ICP-MS. *Chemical Geology* **2000**, *167*, 257-270.

(37) Galer, S. J. G. Optimal double and triple spiking for high precision lead isotopic
measurements. *Chemical Geology* **1999**, *157*, 255-274.

(38) Nishikawa, M.; Hao, Q.; Morita, M. Preparation and evaluation of certified reference
materials for Asian mineral dust. *Global Environ. Res.* **2000**, *4*, 103-113.

(39) Steding, D. J.; Dunlap, C. E.; Flegal, A. R. New isotopic evidence for chronic lead
contamination in the San Francisco Bay estuary system: Implications for the
persistence of past industrial lead emissions in the biosphere. *Proc. Nat. Acad. Sci.*
2000, *97*, 11181-11186.

(40) Lee, C. S. L.; Li, X.-D.; Zhang, G.; Li, J.; Ding, A.-J.; Wang, T. Heavy metals and
Pb isotopic composition of aerosols in urgan and suburban areas of Hong Kong and
Guangzhou, South China – evidence of the long-range transport of air contaminants.
Atmos. Environ. **2007**, *41*, 432-447.

(41) Mukai, H.; Furuta, N.; Fujii, T.; Ambe, Y.; Sakamoto, K.; Hashimoto, Y. Characterization of sources of lead in the urban air of asia using stable lead isotopes. *Environ. Sci. Technol.* **1993**, *27*, 1347-1356.

(42) Tan, M. G.; Zhang, G. L.; Li, X. L.; Zhang, Y. X.; Yue, W. S.; Chen, J. M.; Wang, Y. S.; Li, A. G.; Zhang, Y. M.; Shan, Z. C. Comprehensive study of lead pollution in Shanghai by multiple techniques. *Anal. Chem.* **2006**, *78*, 8044-8050.

(43) Wang, W.; Liu, X.; Zhao, L.; Guo, D.; Tian, X.; Adams, F. Effectiveness of leaded petrol phase-out in Tianjin, china based on the aerosol lead concentration and isotope abundance ratio. *Sci. Tot. Environ.* **2006**, *364*, 175-187.

(44) Jaffe, D.; McKendry, I.; Anderson, T.; Price, H. Six 'new' episodes of trans-Pacific transport of air pollutants. *Atmos. Environ.* **2003**, *37*, 391-404.

(45) Zhang, L., Jacob, D. J., Kopacz, M., Henze, D. K., Singh, K., and Jaffe, D. A. Intercontinental source attribution of ozone pollution at western U.S. sites using an adjoint method. *Geophys. Res. Lett.* **2009**, *36*, L11810, doi:10.1029/2009GL037950.

(46) Tollefson, J. Climate's smoky spectre. *Nature* **2009**, *460*, 29-32.

(47) Ramanathan, V.; Ramana, M. V.; Roberts, G.; Kim, D.; Corrigan, C.; Chung, C.; Winker, D. Warming trends in Asia amplified by brown cloud solar absorption. *Nature* **2007**, *448*, 575-578.

(48) Saikawa, E.; Naik, V.; Horowitz, L. W.; Liu, J.; Mauzerall, D. L. Present and potential future contributions of sulfate, black and organic carbon aerosols from China to global air quality, premature mortality and radiative forcing. *Atmos. Environ.* **2009**, *43*, 2814-2822.

Acknowledgments

Supporting Information

Figs. S1-S5; Tables S1, S2

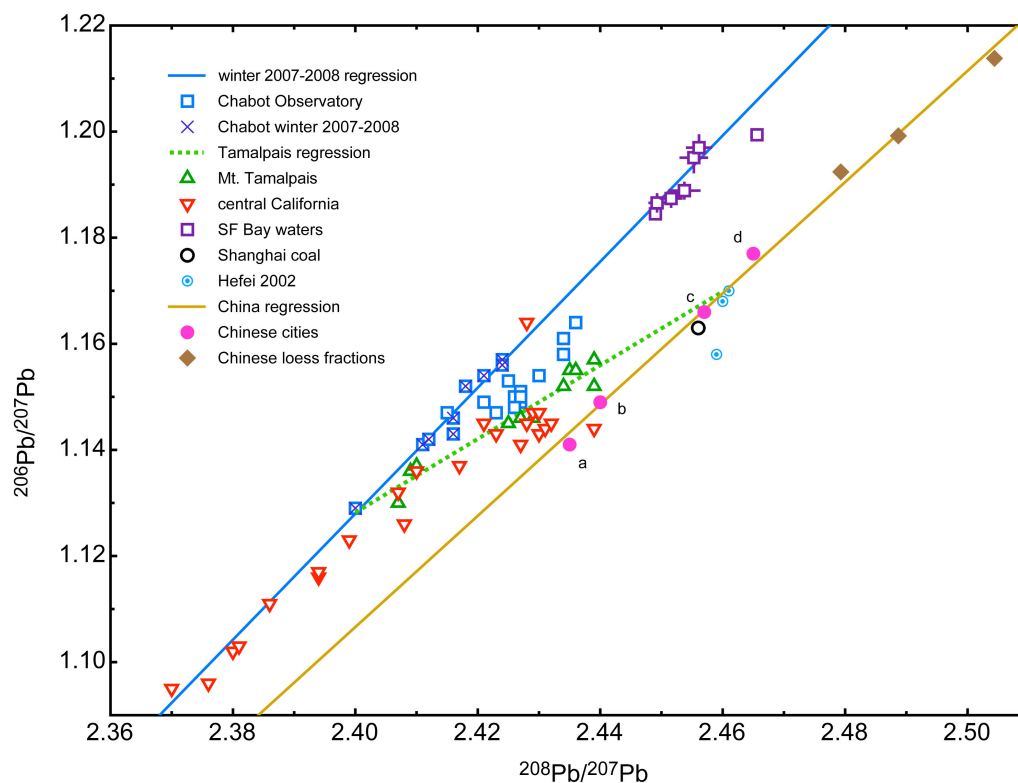FIGURE 1. $^{208}Pb/^{207}Pb$ vs. $^{206}Pb/^{207}Pb$ in airborne particles at sites in California and Hefei, China (this study), and in San Francisco bay waters (*38*), Shanghai coal (*41*), Chinese cities (*32*), and Chinese loess fractions (*25*). Lower case letters indicate Chinese cities (*32*): (a) Beijing, (b) Hong Kong, (c) Chengdu, (d) Xinshao. Linear regression lines are shown in blue for wintertime Chabot samples (slope = 1.19±0.03), light brown for Chinese cities and loess (slope = 1.05±0.05) and dotted green for Mt. Tamalpais (slope = 0.69±0.01).
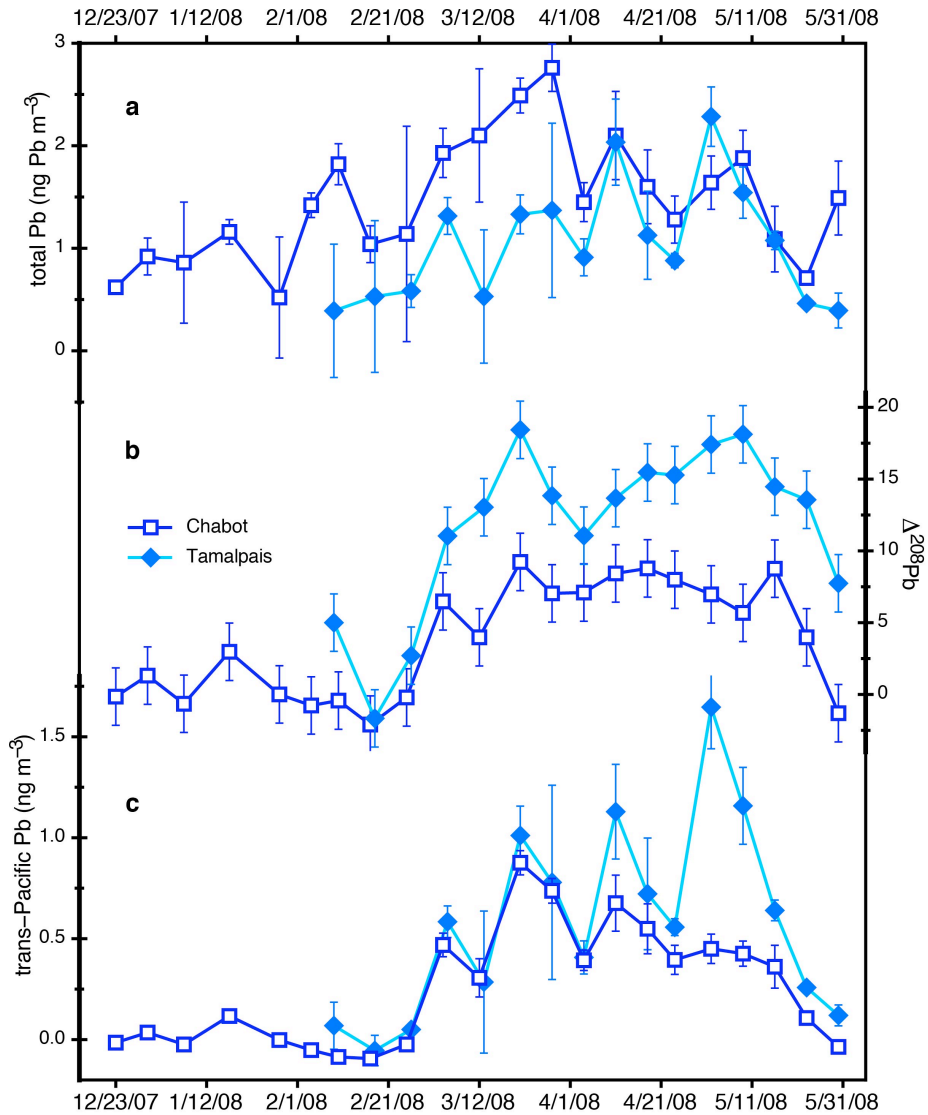
FIGURE 2. Time series of Pb in fine airborne particles (PM2.5) at Mt. Tamalpais (solid diamonds) and Chabot Observatory (open squares), winter-spring 2008: (a) total Pb; (b) Δ^{208}Pb; and (c) trans-Pacific Pb. Error bars indicate one standard error for two separate analyses by XRF and S-XRF. Each symbol represents a weekly sample placed at the middle date for that week. Uncertainty in Δ^{208}Pb values is 1.3±0.9‰ (6.2±4.4%), shown in (b) as 2‰. Trans-Pacific Pb is more dominant at Tamalpais, but Pb isotope analysis shows that

amounts are similar at the two sites, despite greater local pollution at Chabot.
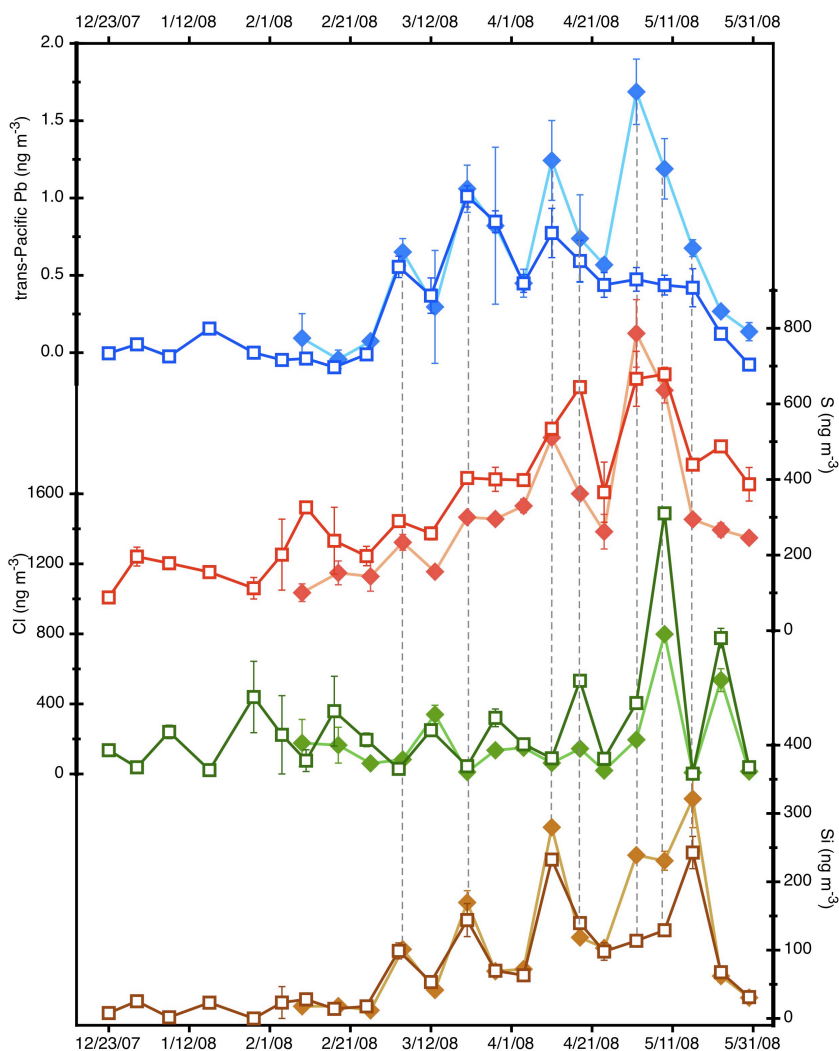
FIGURE 3. Time series of trans-Pacific Pb, total S, total Cl and total Si in weekly PM2.5 samples at Mt. Tamalpais (solid diamonds) and Chabot Observatory (open squares). Error bars indicate one standard error for two separate analyses by XRF and S-XRF. Elevated Si during the weeks of March 5, March 21, April 11, and May 2 mark dust transport events in which trans-Pacific Pb and S also peaked. A final dust event during the week of May 16 was accompanied by less trans-Pacific pollution. Elevated Cl concentrations during the weeks of April 18 and May 9 mark local marine influence and coincide with elevated local S and reduced trans-Pacific Pb at Chabot.