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Unraveling the sources of ground level ozone in the Intermountain Western United States using Pb isotopes

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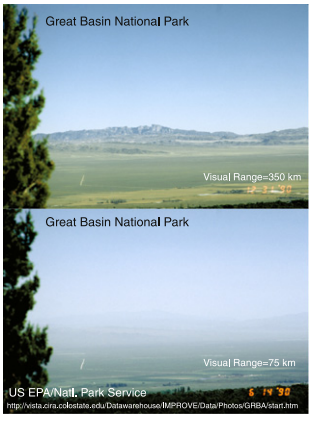
HIGHLIGHTS

- Ozone can significantly impact human and ecosystem health and climate.
- Pb isotopes and back-trajectory analysis were used to distinguish sources of O_3.
- Baseline concentrations in the Western US are ~54 ppbv.
- During discrete Asia events O_3 increased by 5 ± 5.5 ppbv and during S CA events by 15 ± 2 ppbv.
- Data indicate that Asian ozone inputs will exceed other sources by 2015–2020.

GRAPHICAL ABSTRACT



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ABSTRACT

Ozone as an atmospheric pollutant is largely produced by anthropogenic precursors and can significantly impact human and ecosystem health, and climate. The U.S. Environmental Protection Agency has recently proposed lowering the ozone standard from 75 ppbv (MDA8 = Maximum Daily 8-Hour Average) to between 65 and 70 ppbv. This will result in remote areas of the Intermountain West that includes many U.S. National Parks being out of compliance, despite a lack of significant local sources. We used Pb isotope fingerprinting and back-trajectory analysis to distinguish sources of imported ozone to Great Basin National Park in eastern Nevada. During discrete Chinese Pb events (>1.1 ng/m^3 & >80% Asian Pb) trans-Pacific transported ozone was 5 ± 5.5 ppbv above 19 year averages for those dates. In contrast, concentrations during regional transport from the Los Angeles and Las Vegas areas were 15 ± 2 ppbv above the long-term averages, and those characterized by high-altitude transport 3 days prior to sampling were 19 ± 4 ppbv above. However, over the study period the contribution of trans-Pacific transported ozone increased at a rate of 0.8 ± 0.3 ppbv/year, suggesting that Asian inputs will exceed regional and high altitude sources by 2015–2020. All of these sources will impact regulatory compliance with a new ozone standard, given increasing global background.

1. Introduction

In the troposphere, the layer below the stratosphere that extends to the Earth's surface, ozone (O_3) is a secondary air pollutant generated by

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reactions between oxides of nitrogen (NOx) and volatile organic compounds (VOCs), derived from combustion, industry, agriculture, and natural processes (United Nations Economic Commision, 2010). This reaction chemistry is complex and can be affected by the relative concentrations of NOx compounds versus VOCs (Finlayson-Pitts and Pitts (1999)). As a significant atmospheric pollutant of concern, O_3 has been shown to reduce lung function, contribute to premature death, exacerbate asthma, damage crops and ecosystems, and deteriorate materials, as well as contribute to climate change (Kolb et al., 2010).

In the United States, O_3 is regulated using a National Ambient Air Quality Standard (NAAQS) as part of the Clean Air Act. Review of the NAAQS is required by the Clean Air Act (Sec 109(d)) every 5 years. In March 2008 the primary and secondary 8-hour standards were set at 75 ppbv, down from the original standard of 120 ppbv. The U.S. Environmental Protection Agency recently has proposed lowering the current standards to between 65 and 70 ppbv. An area is out of compliance if the three-year mean of the fourth highest maximum daily 8-hour average (MDA8) exceeds this value. This method for establishing a standard is of concern for it does not consider the long-term exposure of humans and ecosystems, and chronic level effects (Gustin et al., 2015). Additionally, in order to develop an appropriate standard the contribution due to emissions that are controllable within the United States must be known.

Much of the Intermountain Western United States is rural and home to remote forested ecosystems occurring at high elevations. This area also hosts many of the National Parks. Recent data analyses indicate that Great Basin National Park and other rural regions of the west will exceed a lowered ozone standard (Jaffe, 2011). An additional concern is the primary standard, set for human health, is likely not adequate for protection of vegetation (Miller, 2011). Exposure to ozone has the potential to exacerbate other climate-change driven effects on forest viability by increasing susceptibility to drought and thermal stresses (Ainsworth et al., 2012).

Exceedance of the MDA8 ozone standard may be due to local conditions and sources, but also may be due to regional or long-range transport of ozone and its precursors (e.g., (Ambrose et al., 2011)), or intrusions of naturally occurring stratospheric ozone (Ambrose et al., 2011; Langford and Reid, 1998; Langford et al., 2009, 2012). High ozone may also be produced from precursors generated in forest fires (Jaffe and Wigder, 2012). For the Western United States, recent modeling of long-range transport suggests Asia may at times be an important source of ozone and its precursors (e.g., (Lin et al., 2012a)). Re-analysis of historical ozone data from globally distributed sites suggests that mid-19th century seasonally averaged ozone levels were on the order of ~5–15 ppbv (e.g., Volz and Kley, 1988; Marenco et al., 1994; Pavelin et al., 1999), 3 to 4 times lower than levels in the remote Western US in recent decades (e.g., Jaffe, 2011; Parrish et al., 2012) reflecting increased hemispheric background. Therefore, there is a need to develop data-based tools to evaluate the relative importance of various sources as contributors to ozone concentrations and events that exceed the standard in the rural Intermountain West.

For this work we hypothesized that the isotopic composition of lead (Pb) associated with discrete ozone events recorded in the past could be applied to evaluate the sources of ozone or its precursors. Lead is emitted as a co-pollutant with ozone precursors in industrial and urban plumes and transported as fine aerosols. In the case of China from 2001 to 2009 an average of 6×10^9 g of Pb was emitted per year to the atmosphere, with an increasing fraction associated with coal combustion that currently is the principal aerosol source followed by nonferrous ore smelting (Li et al., 2012). The advantage of using isotopic tracking of Pb is that it is not affected by the aerosol concentration or Pb concentration in air, and the isotopic signature of the source will not be altered as it is transported. As such, this method can be used to fingerprint the source. Previous studies have shown that aerosol-associated Pb in Chinese urban centers (Bollhöfer and Rosman, 2001, 2002; Ewing et al., 2010), Chinese sourced coal (Tan et al., 2006; Díaz-Somoano et al., 2009), and Chinese Loess (e.g., Jones et al., 2000; Ewing et al., 2010) have an isotopic composition distinct from sources in Western North America (Bollhöfer and Rosman, 2001, 2002; Ewing et al., 2010) (Fig. 2A). Ewing et al. (2010) demonstrated that the Pb isotopic composition of a mixed-source aerosol can be used to apportion and quantify the amount of Pb coming from local California sources versus sources in Asia (China). Further, they demonstrated a distinct seasonality of the intensity of Pb transport across the Pacific from Asia with peaks in spring, consistent with other long-term observations of trans-Pacific transport (e.g., VanCuren, 2003; Jaffe et al., 2003a; Reidmiller et al., 2009). Here we use the Pb isotopic composition to derive indices (the air concentration of trans-Pacific transported Pb = Trans-Pac Pb ng/m^3 and the percentage of the collected Pb sourced in Asia) to evaluate the influence of different sources on ozone measured at Great Basin National Park (GBNP), a remote site with no local ozone sources in eastern Nevada. We combine our Pb isotopic measurements of aerosols with back-trajectory analyses as a tool to help distinguish regional transport from major urban centers (Los Angeles and Las Vegas), long-range transport from Asia, and high altitude transport. The latter could potentially be influenced by stratospheric exchange or simply represent global dispersal of a pollutant in the upper troposphere.

2. Sample selection and categorization into groups

We conducted a retrospective study of PM2.5 aerosol filter samples collected by the Interagency Monitoring of Protected Visual Environments (IMPROVE) network at a site in GBNP where co-located hourly ozone data were also collected (Supporting Fig. S1). At this site, particulates <2.5 μm (PM2.5) have been collected on 25 mm Teflon filters for 24-hour periods twice a week since 1996. To provide a basis of comparison of ozone levels for dates where significant Asian influence is identified through isotopic analysis of the collected Pb we categorized our selected sample dates into 6 groups whose definitions are given below. The over arching requirement for our selected filters was that the Pb concentrations reported by the IMPROVE network (http://views.cira.colostate.edu/fed/) be above >0.0005 μg/m^3 or ~17 ng of Pb per filter (n = 710), the minimum needed for Pb isotopic analysis. From among that set we selected filters for dates when the Maximum Daily Average 8 hour (MDA8) ozone was greater than 70 ppb (n = 97), and we used Hybrid Single Particle Langrangian Integrated Trajectory (HYSPLIT) back trajectory analyses covering the 3 days prior to sample dates to identify samples potentially effected by high altitude transport or by transport from Los Angeles and/or Las Vegas (also see discussion below of sample groupings). Other filters were selected as background samples (see below). Based on these criteria, we requested from the IMPROVE Network and the National Park Service, retrieval of archived filters with the characteristics given in Supporting Table S2 which were divided into 6 categorized groups. Group 1 (n = 20) represents sampling dates with >1.4 ng/m^3 of Pb in air; Group 2 (n = 4) represents dates with MDA8 O_3 ≥ 70 ppbv but with unclear source areas based on the 3-day back trajectories; Group 3 (n = 6) represents dates with MDA8 O_3 ≥ 70 ppbv and back trajectories indicating high altitude transport (>3 km) the last three days prior to the collection dates; Group 4 (n = 6) represents dates with MDA8 O_3 ≥ 70 ppbv and back trajectories through the Los Angeles and/or Las Vegas areas; Group 5 (n = 1) is a sampling date affected by local fires; and Group 6 (n = 10) represents "background" sampling dates with moderate O_3 (MDA8 34 to 65 ppbv) and moderate Pb (<1 ng/m^3). Supporting Fig. S2 displays the record of MDA8 ozone for GBNP over the entire period and shows the dates for our selected PM2.5 samples. Similarly, Fig. 1B shows the record of total Pb loading at GBNP and the dates of the selected samples.

3. Methods

Filters were retrieved from the archive at U.C. Davis where they were re-analyzed by X-ray fluorescence (XRF) for elemental composition

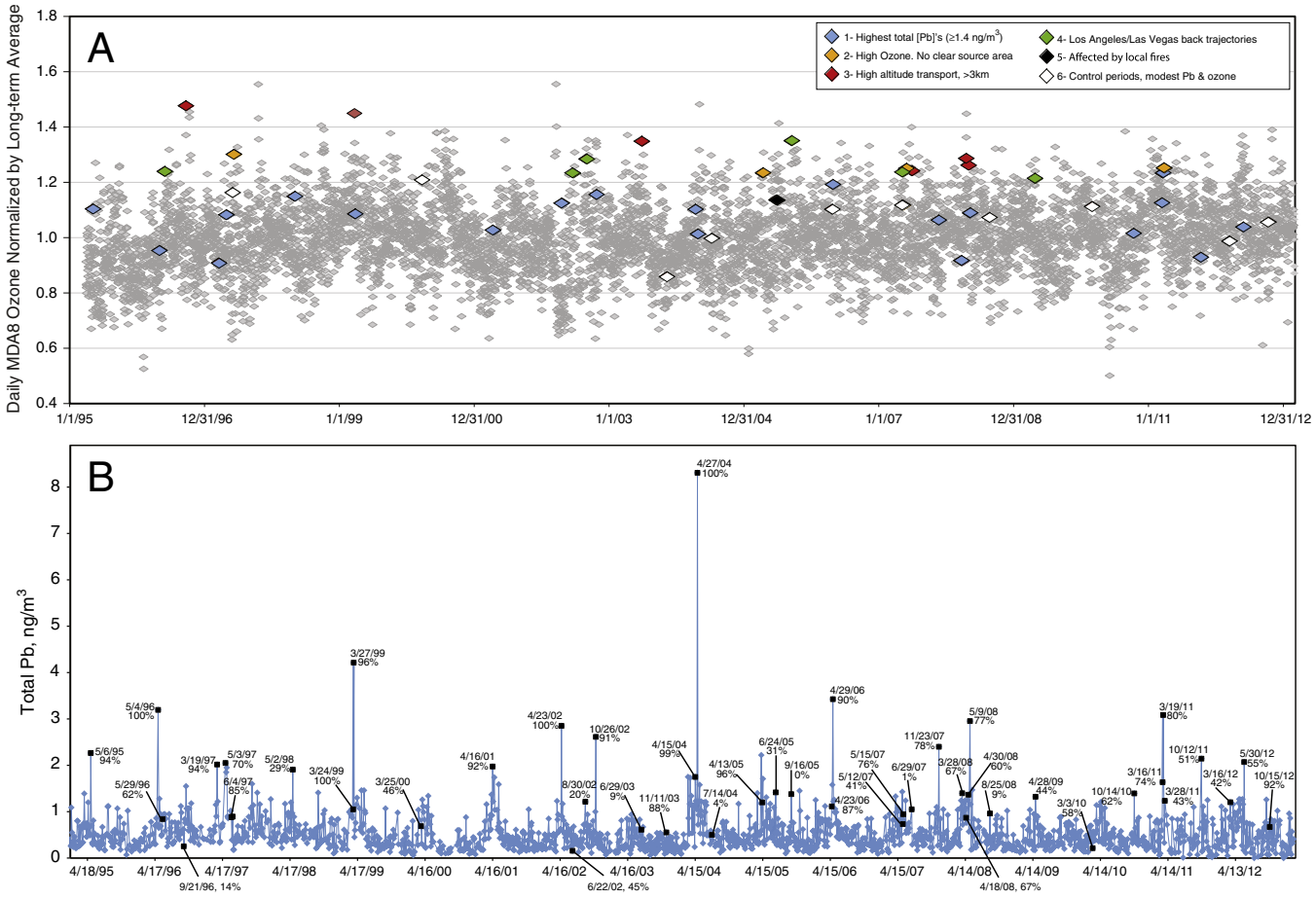

Fig. 1. In A the daily MDA8 ozone at GBNP normalized by the long-term (1995–2013) average MDA8 of each calendar date. The average normalized value is 1.00. Colored diamonds show the dates of analyzed PM2.5 24 hour samples. See text for descriptions of the categories. In B the record of Pb concentration in air for GBNP (data from http://views.cira.colostate.edu/fed/) showing sample dates for filters used in this study. Numbers adjacent to dates are the percentage of the total Pb sourced in Asia (China) calculated based on Pb isotopic analysis. The time series shown in A and B are aligned in time.

including Pb (Supporting Table S1) at the Crocker Nuclear Laboratory at U.C. Davis using a PANalytical Epsilon 5 XRF instrument (see Supporting Fig. S3 for a comparison of the original and new Pb analyses). PM2.5 mass loadings were determined by the IMPROVE program by weighing filters before and after deployment prior to the original XRF analyses.

Following XRF analysis, the filter samples were sent to Lawrence Berkeley National Laboratory (LBNL) for Pb isotopic analysis. Lead was chemically separated from acid leachates of the filters, spiked with ^{203}Tl-^{205}Tl for instrumental mass fractionation correction and analyzed on a multi-collector ICPMS (IsoProbe) (for more details see SI and (Ewing et al., 2010)). Analytical uncertainties of the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios are less than ±0.05‰ (2σ).

Back trajectory and residence time calculations for the sampling dates were conducted using the NOAA-HYSPLIT v. 4 model (Draxler and Hess, 1997) and input meteorological data from the National Centers for Environmental Prediction (NCEP) Global Reanalysis Data set with resolution in the horizontal of 2.5° in latitude and longitude, in the vertical of 17 pressure levels, and temporal of 6 h. (see SI for details). These analyses were conducted out to 12 days prior to samples dates, longer than the 3 day back trajectories used in sample selection and categorization.

In order to remove seasonality from the MDA8 ozone data collected at GBNP by the Clean Air Status and Trends NETwork (CASTNET), we used the long-term (1995 to 2013) means for each calendar date (cf. Jaffe, 2011) to normalize each individual MDA8 ozone value, yielding a data set with a mean of 1 (ave. MDA8 = 49.6 ppbv). For example, the MDA8 ozone value for November 2nd, 2002 was normalized (divided) by the mean of the MDA8 ozone values for every November 2nd from 1995 to 2013.

4. Results

The time series for normalized MDA8 ozone is shown in Fig. 1A, compared to the record of Pb concentration air (Fig. 1B) and compared to the MDA8 ozone time series in Supporting Fig. S2. The average MDA8 ozone over 1992–2013 was 49.6 ppbv (±9 ppbv), at the upper range of the North American background value calculated in models (with North American emissions turned off). Fiore et al. (2014) reported seasonal average maximum MDA8 values of 40–50 ppbv for the spring and for the summer a range of 25 to 40 ppbv based on global models (GEOs-Chem and GFDL AM3). In the GBNP data set, only 3% of dates had MDA8 ozone below 35 ppbv, while 5.5% of dates had MDA8 ozone above 65 ppbv (average of 69.7 ppbv). This illustrates the utility of observational data to verify models. Here we are providing data to test model results for the effect of long-range transport on ozone concentrations in the Intermountain West using GBNP as an exemplar.

The results of Pb isotopic analyses of the PM2.5 samples are provided in Supporting Table S1 and displayed in Fig. 2. Most GBNP samples fall between an array representing California (Western U.S.) PM2.5 sources and an array representing Asian, specifically Chinese, sources (arrays from Ewing et al. (2010)). PM2.5 samples collected by Ewing et al. (2010) in spring 2008 at Mt. Tamalpais and Chabot (Oakland, CA) fall in a similar region in Fig. 2, as do data from filters collected in Central California during the springs of 2003, 2004 and 2005. Some GBNP

samples fall along or just to the right of the Asian array indicating that those samples essentially consist entirely of Asian (Chinese) sourced Pb, while a few fall along the California array. Eleven of the group 1 (high Pb) samples fall near the Asian array, along with 1 sample from group 3 (high altitude (HA)), and four samples from group 6 (control samples). The fraction of the total Pb sourced in Asia (F_{Asia}Pb) can be calculated based on the isotopic composition of the sample (see SI and (Ewing et al., 2010)). The F_{Asia}Pb value for each sample can then be used to calculate the average concentration in air (ng/m^3) during the 24-hour sampling period of Pb sourced in Asia and transported across the Pacific; we call this parameter Trans-Pac Pb with units of ng/m^3 (SI Table 1).

The calculated Trans-Pac Pb in our GBNP (elevation 2060 msl) samples ranges from 0 to 8.3 ng/m^3. For comparison, the highest 7-day average Trans-Pac Pb observed at Mt. Tamalpais (elevation 772 msl) in 2008 (centered on 5/2/08) was 1.7 ng/m^3 (Ewing et al., 2010). Nearly all samples have total Pb concentrations in the collected aerosols significantly greater than the average concentration in upper continental crust (20 ppm (Taylor and McLennan, 1985), shown as a dashed line in Supporting Fig. S4), a stand-in for natural soil dust. This indicates that most GBNP samples were affected by anthropogenic sources of Pb. The total concentration of Pb in the aerosols shows some tendency to increase with the % of Asian Pb suggesting that higher Pb concentrations are due in part to Asian (Chinese) aerosol pollutant sources (Supporting Fig. S4). For samples with greater than 80% of the Pb sourced in Asia, there are strong correlations between Trans-Pac Pb and S and Zn (Fig. 3) suggesting that a large fraction of the Asian sourced Pb is due to a combination of coal combustion and the smelting of nonferrous ore. It is noteworthy that the 4/16/2001 sample coincided with the notorious Asian 2001 dust cloud (Jaffe et al., 2003b); and the 4/27/2004 sample was contemporaneous with observations of an Asian polluted air mass affecting the Mt Bachelor Observatory (Weiss-Penzias et al., 2006).

In Fig. 4A we compare the Trans-Pac Pb concentration of samples to the residence time of HYSPLIT back trajectories in the Asian box (for definition see Supporting Table S3), expressed as a percentage of the total transport time of 288 h, of air arriving at GBNP during each sampling period. Samples with the highest Trans-Pac Pb concentrations (and higher total Pb) tend to have higher Asian box transit residence times, while samples with low Trans-Pac Pb concentrations (<0.75 ng/m^3) tend to have low Asian box transit residence times. Sample dates in Group 3 have lower Trans-Pac Pb (average 0.43 ng/m^3) compared to the Group 1 sampling dates with high Pb loadings for a similar range of Asian box transit residence times. In Fig. 4B the residence time in the Asian box is compared to the residence time in the high altitude box (for definition see Supporting Table S3) and both are expressed as a percentage of the total transport time of 288 h. Sample dates with larger

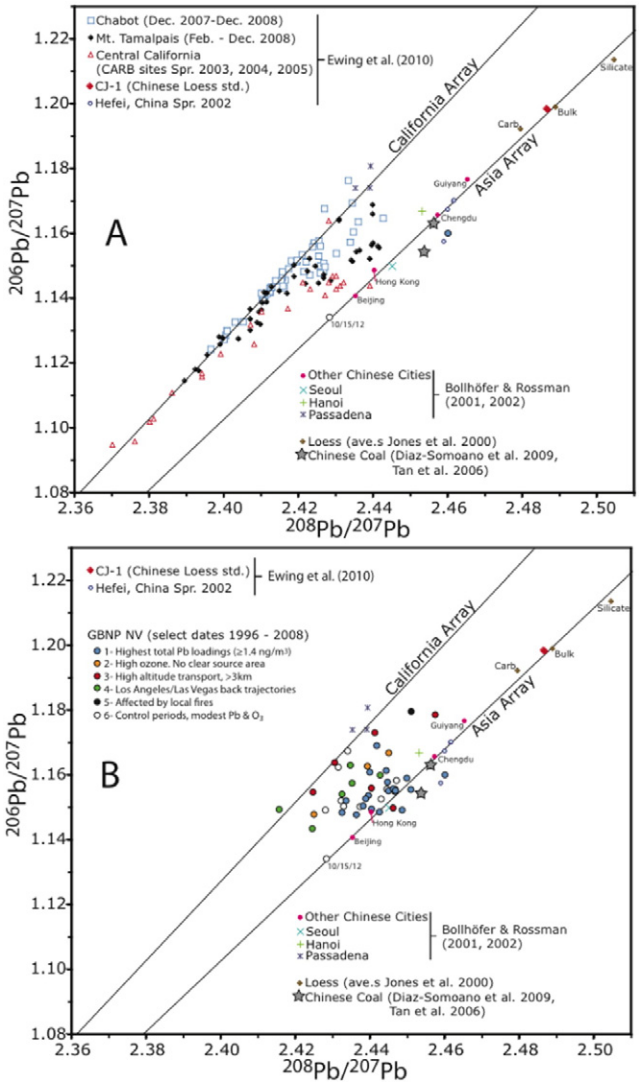

Fig. 2. Plots of ^{206}Pb/^{207}Pb vs. ^{208}Pb/^{207}Pb. In A, are shown data for samples collected at Mt. Tamalpais, Chabot Science Center (Oakland, CA), and for archived ARB samples from central California from Ewing et al. (2010). Also shown (in A and B) are the Pb isotopic compositions of samples representative of Asian aerosols (Bollhöfer and Rosman, 2001, 2002), Chinese coal (Tan et al., 2006; Díaz-Somoano et al, 2009), Chinese Loess (Jones et al., 2000; Ewing et al., 2010), and Hefei, China (Ewing et al., 2010). In B are shown data for selected IMPROVE samples taken in Great Basin National Park, NV between 1996 and 2012 and analyzed for this paper.

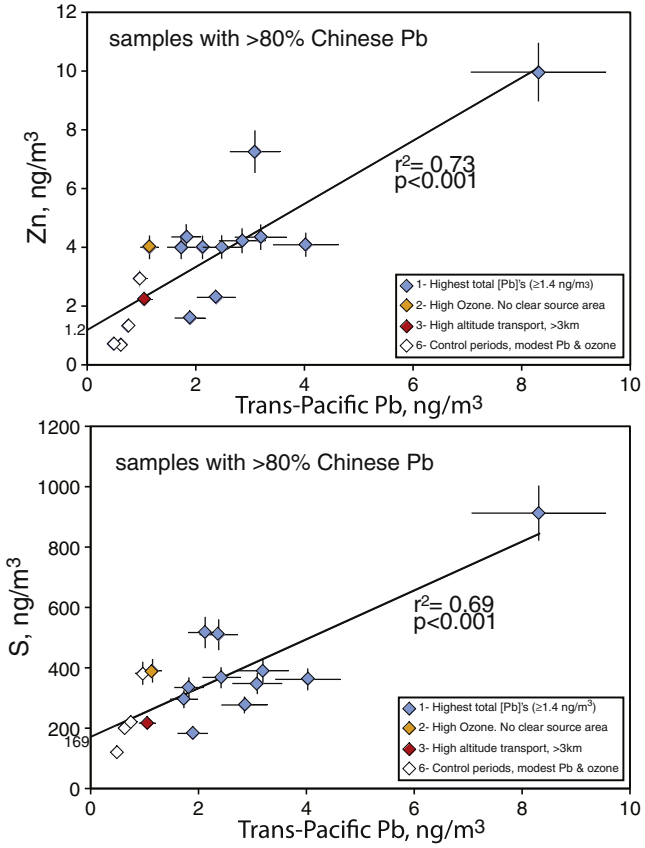

Fig. 3. Top panel, Trans-Pac Pb (ng/m^3) for the samples with >80% of the Pb sourced in Asia (China) versus total S, ng/m^3. Bottom panel, Trans-Pac Pb (ng/m^3) for the samples with >80% of the Pb sourced in Asia (China) against total Zn, ng/m^3. These correlations suggest that coal combustion in China is a significant contributor to Trans-Pacific Pb in the Western US.

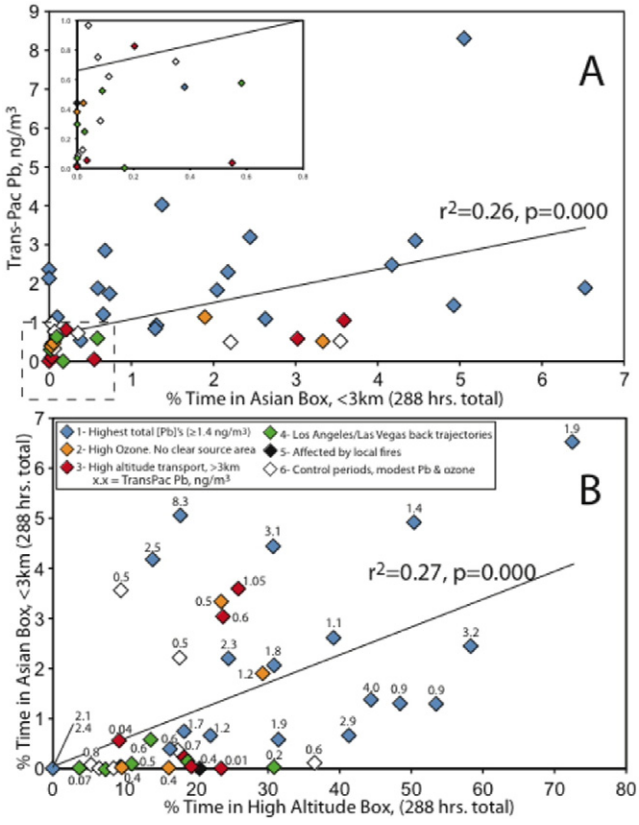

Fig. 4. A. Trans-Pacific Pb concentration in air (ng/m^3) vs. the percentage of the transport time spent in an Asian box (20–50°N, 100–140°E; encompassing eastern China, eastern Mongolia, the Korean peninsula and western Japan; altitude below 3 km). B. Percentage of the total transport time (288 h.) spent in the Asian box against the percentage of the total transport time (288 h.) spent in the high altitude box. Numbers by data points are values of Trans-Pac Pb in ng/m^3.

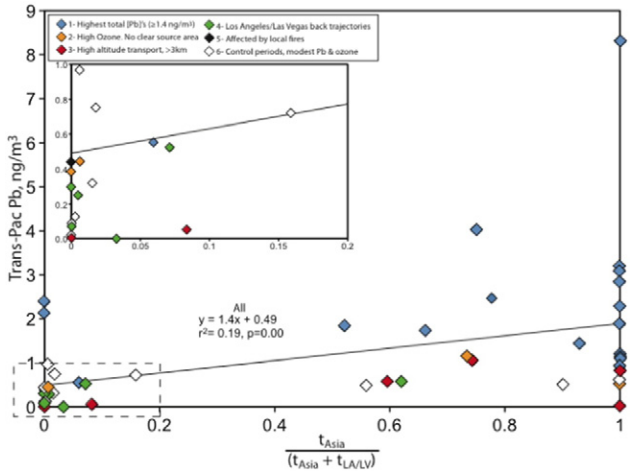

Fig. 5. Trans-Pacific Pb concentration in air (ng/m^3) vs. the fraction transit residence time for the Asian box relative to the total transit residence times for the Asian and Los Angeles/Las Vegas boxes.

percentages of time in both the Asian and the HA boxes tend to have greater levels of Trans-Pac Pb (numbers by data points). This is consistent with the greater efficiency of transport from Asia of aerosols at high altitudes (>3 km) (Task Force on Hemispheric Transport of Air Pollution, 2011). These observations are emphasized in Fig. 5, where samples with the lowest fraction of residence time in the Asian box compared to residence time in the Los Angeles/Las Vegas boxes have the lowest Trans-Pacific Pb.

5. Discussion and conclusions

Comparing Trans-Pac Pb to the normalized MDA8 ozone provides constraints on the influence of Asian sourced pollutants on ozone concentrations at GBNP. In Fig. 6, the normalized MDA8 ozone for our sample dates are plotted against the air concentration of Trans-Pac Pb. The data can be divided into two groups based on Trans-Pac Pb concentration in air: samples with less than 1.1 ng/m^3 and those with Trans-Pac Pb greater than 1.1 ng/m^3. For this latter group, the average normalized MDA8 ozone is 1.09 ± 0.09 (or 54.1 ± 4.5 ppbv), suggesting that this is the average net effect of trans-Pacific transport on background ozone levels at GBNP because air coming into Nevada has been shown to be affected by the free troposphere (Huang and Gustin, 2012; Weiss-Penzias et al., 2009) and the state in general is limited in ozone precursors (VanCuren and Gustin, 2015-in this issue). In contrast, samples with <1.1 ng/m^3 of Trans-Pac Pb cover a range of normalized MDA8 ozone from 0.86 to 1.45. This group can be further subdivided based on back-trajectory characterization. Group 4 sample dates with back-trajectories through the Los Angeles/Las Vegas regions have an average normalized MDA8 ozone of 1.26 ± 0.05 (or 62.5 ± 2.5 ppbv), significantly greater than 1.0 indicating as expected enhancement of ozone levels relative to the long-term normalized average. Group 4 sample dates involving high altitude transport (>3 km) during the last three days prior to sampling have an average normalized MDA8 ozone of 1.34 ± 0.10 (or 66.5 ± 5.0 ppbv), also significantly higher than 1.0, indicating ozone enhancement. Sample dates that were chosen as controls have an average normalized MDA8 ozone of 1.07 ± 0.10, indistinguishable from the sample dates with significant Asian influence based on the concentration in air of Trans-Pac Pb (>1.1 ng/m^3).

In Fig. 7, the normalized MDA8 ozone for each sample date is plotted against the fraction of time spent by air parcels in the Asian box relative to the Los Angeles/Las Vegas box (cf. Fig. 4). As in Fig. 5, sample dates with $t_{Asia}/(t_{Asia} + t_{LA/LV})$ ratios of 1, had back-trajectories that passed through the Asian box but not through the Los Angeles/Las Vegas box, while sample dates with $t_{Asia} / (t_{Asia} + t_{LA/LV})$ ratios of 0 had back-trajectories that did not pass through the Asia box. Sample dates, excluding Group 6 control samples, that have $t_{Asia} / (t_{Asia} + t_{LA/LV})$ ratios between 0 and 0.1 have an average normalized MDA8 ozone of 1.23 ± 0.09 (61 ± 4.5 ppbv), while sample dates with $t_{Asia} / (t_{Asia} + t_{LA/LV})$ ratios between 0.9 and 1 have a lower average normalized MDA8 ozone of 1.09 ± 0.15 (54 ± 7 ppbv). If sample dates with less than 1.0 ng/m^3 of Trans-Pac Pb are excluded in the latter analyses, the average normalized MDA8 (1.05 ± 0.10 [52 ± 5 ppbv]) is lower and better resolved from the average for sample dates with ratios of 0 to 0.1. Alternately, all Group 1 dates with $t_{Asia} / (t_{Asia} + t_{LA/LV}) = 1$ have an average normalized MDA8 of 1.03 ± 0.09 (51 ± 2.5 ppbv). Again, the indication is that the sample dates experiencing the greatest influence of Asian urban/industrial sources have

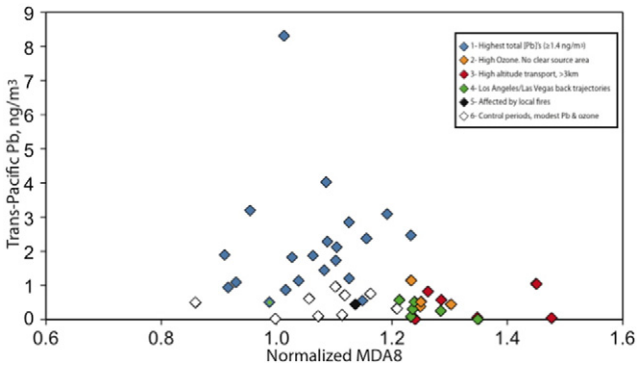

Fig. 6. Trans-Pacific Pb (ng/m^3) versus MDA8 ozone normalized by the long-term averages of daily MDA8 over the period 1995–2013.

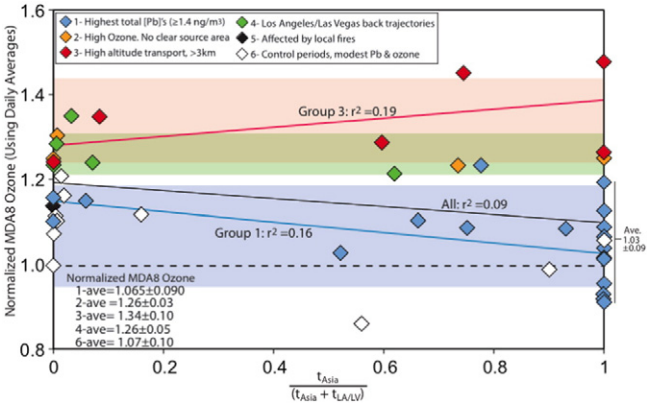

Fig. 7. Normalized MDA8 ozone plotted against the fraction of transit residence times for the Asian box relative to the total transit residence times for the Asian and Los Angeles/Las Vegas boxes. The pink band represents the average ± 1 s of normalized MDA8 for the Group 3 samples (high altitude transport), the green band represents the average ± 1 s for the Group 4 samples (Los Angeles/Las Vegas), and the blue band represents the average ± 1 s for the Group 1 samples (high Pb loadings).

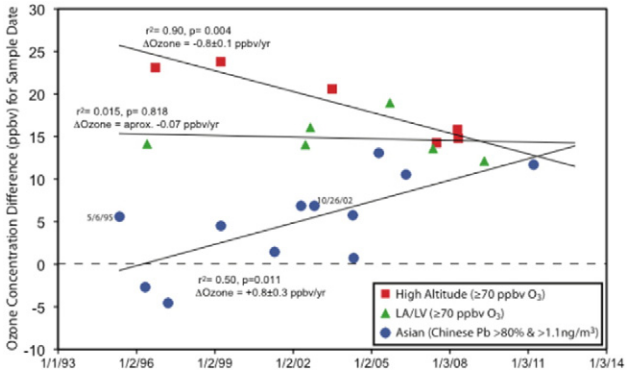

Fig. 8. The difference between the MDA8 ozone concentration for a sample date and the long-term (1995–2013) average for that calendar date plotted against sample date. Shown are samples for dates dominated by high altitude transport (squares, Group 3), transport from the Los Angeles/Las Vegas areas (triangles, Group 4) and dates with clear Asian influence based on having TransPac Pb > 1.1 ng/m3 and >80% of the collected Pb having an Asian origin (circles). Best fit lines to each of the categories gives the average rate of decrease (negative slopes) or increase (positive slopes) of the effect of each category on GBNP ozone over the period (1996–2012) covered by this study. The horizontal dashed line represents a zero difference between the MDA8 ozone for the sample date and the long-term average for the calendar date.

moderate normalized ozone concentrations within 5% of the long-term normalized average at GBNP.

The above analysis, based on Pb isotope quantification of Trans-Pacific Pb and back trajectories, allows us to calculate and compare the individual contributions from the major sources considered (strong Chinese influence, Los Angeles/Las Vegas trajectories, and high-altitude trajectories) to baseline ozone values at GBNP. The average difference between the long term average MDA8 ozone for each calendar date and the MDA8 ozone for the sampling day for the days with identified Chinese Pb >1.1 ng/m^3 and >80% of total Pb is 5 ± 5.5 ppbv above the 15-year average (54 ppbv for those dates). In contrast, sample dates characterized by regional transport events from the Los Angeles and Las Vegas areas were 15 ± 2 ppbv above the long-term average (54 ppbv for those dates), and those characterized by high-altitude transport for the three days prior to sampling were 19 ± 4 ppbv above (53 ppbv for those dates). These results can be compared to estimates from modeling of ozone transport to the Western US. Lin et al. (2012a) used a global chemistry-climate model to examine the effect of ozone transport across the Pacific from Asia on ozone levels in the Southwestern US. In their model for strong Asian episodes, a contribution of 8 to 15 ppbv ozone was derived for days when ozone exceeded 60 ppbv, which is within the uncertainties of our value, 5 ± 5.5 ppbv, based on observation. For stratospheric intrusion as an ozone source, (Lin et al., 2012b) estimate through modeling that the contribution is 15 to 25 ppbv for MDA8 ozone events in the range of 60 to 70 ppbv and 17 to 40 ppbv for events in the range 70 to 85 ppbv. Though we did not explicitly consider stratospheric intrusion as an ozone source, our average increase attributable to high altitude transport events, 19 ± 4 ppbv (range 71–79 ppbv, average 74 ppbv), and the increase attributable to Los Angeles/Las Vegas [15 ± 2 ppbv (range 70–74 ppbv, average 73 ppbv)] are quite similar to the Lin et al. (2012b) results indicating similar impacts for all three of these sources.

Now that we have calculated the average impacts over the study period of Chinese sources, Los Angeles/Las Vegas sources, and high-altitude transport on surface ozone at GBNP; next we examine these data with time. Plotted in Fig. 8 is the difference in MDA8 from the long-term average for that calendar date against the sampling date. The late high-altitude group shows a decrease with time (1995–2008) at a rate of −0.8 ± 0.1 ppbv/year (perhaps consistent with decreasing Northern Hemisphere stratospheric exchange over recent decades found through modeling (e.g., Hsu and Prather, 2009)), while the Los Angeles/Las Vegas group shows little change (−0.07 ppbv/year). In contrast, the contribution of long-range transport from Asia/China appears to have grown with time over the same period. Using sampling dates (n = 12 dates) where both the TransPac Pb concentration was >1.1 ng/m3 and >80% of the total Pb was Asian in origin, the increase has been at a rate of +0.8 ± 0.3 ppbv/year for an Asian/Chinese source attribution (Fig. 8). An alternative criteria of $t_{Asia} / (t_{Asia} + t_{LA/LV}) = 1$ (no time in the LA/LV box) and, as before, TransPac Pb >1.1 ng/m3 (n = 7 dates) yields a similar rate of +0.75 ± 0.35 ppbv/year. These rates are very similar to measured rates of ozone increase in East Asia (Beijing, China; Hong Kong; Taiwan) ranging from +0.6 to +1.4 ppbv/year over a contemporaneous period (Chou et al., 2006; Ding et al., 2008; Wang et al., 2009; Lin et al., 2010; Li et al., 2010). Our rate of increase in the ozone contribution of Asian/Chinese sources is also consistent with the value, +0.84 ppbv/year, for the increase (over 1995-1998) in spring-time ozone in the Western US derived from ozone data by Cooper et al. (2010). Projecting the rates derived from Fig. 8 into the future suggests that the contribution of Asian sources to ozone at GBNP will likely exceed contributions due to high altitude transport and from the Los Angeles/Las Vegas urban areas by the end of the decade, potentially increasing the frequency of MDA8 ozone exceedance events particularly under a lowered regulatory standard.

Roles of the authors

J.N. Christensen was responsible for the isotope analyses, interpretation and data synthesis, P. Weiss-Penzias performed the trajectory analyses, Rebekka Fine aggregated and processed the ozone data, C. McDade and K. Trzepla conducted the XRF analyses, S.T. Brown assisted in sample analysis, and M. Gustin conceived the idea for this project and coordinated the IMPROVE filter and data analyses. JNC, MSG and PW-P were responsible for writing the m.s.

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Appendix A. Supplementary data

Supplementary material to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.04.054.

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