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Sources of Atmospheric Lead in and Around an Indian Megacity.

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Abstract: Lead (Pb) is a toxic metal whose global anthropogenic fluxes are an order of magnitude higher than natural fluxes. Among all the environmental compartments, the atmosphere is the major initial recipient of Pb. To minimize the exposure to this toxic metal, it is important to determine the potential sources of atmospheric Pb. This study uses a multiproxy approach, Pb isotopes in conjunction with metal composition of aerosols to determine the possible sources of anthropogenic Pb in the atmosphere, in and around an Indian megacity, Kolkata. In Asia, India is the second largest atmospheric Pb emitter, after China through coal combustion. Indian automobile and high temperature metallurgy industries are growing rapidly and Pb emissions from India can be traced as far south as in Chagos Island in the Indian Ocean. This study investigates the anthropogenic sources of atmospheric Pb in eastern India at three locations along a 150 Km N-S stretch. The locations have very different environmental settings; a pristine river island, a megacity, and an industrial town. Pb isotope and metal compositions indicate different sources of atmospheric Pb for the three locations: gasoline exhaust from road and riverine traffic in the island, emissions from the high temperature metallurgy industry in the industrial town and long-range transport of coal combustion and industrial emissions for the megacity. The Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb} = 1.1155\text{--}1.1681$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.3905\text{--}2.4494$) measured in this study have a wider range and are mostly higher than previously measured in Indian aerosols. Pb isotope compositions of two end members, Indian coal and road dust are also measured. This study shows that post leaded gasoline phase-out, the atmospheric Pb emissions in India are dominated by Indian coal combustion and ore processing.

Keywords: Lead isotopes, metals, aerosols, Indian coal, road dust.

1. Introduction

Rapid urbanization coupled with high population growth led to constant increase in demand for energy in major developing countries in Asia (Shahbaz et al., 2015). With renewable energy still in its nascence, these countries are heavily dependent on non-renewable energy resources (Gabriel 2016, Tripathi et al., 2016), which have contributed significantly to air pollution (Guttikunda and Jawahar 2014). Previous studies showed evidence of air pollution from industrial emissions impacting not only within national borders but also across neighbouring countries (Murano et al., 2000; Oh et al., 2015). A recent study (Gu and Yim 2016) estimated that transboundary air pollution from China leads to 22% premature mortalities in Taiwan caused by outdoor air pollution.

Lead (Pb) is one of the major toxic air pollutants that is primarily released by smelting, industrial uses, coal combustion and burning of leaded and un leaded gasoline (Nriagu 1990, Pacyna et al. 2009). Most developing countries such as China and India, have seen a marked increase in Pb emissions since the 1950s due to an order of magnitude increase in coal combustion and rise in number of vehicles (Hao et al., 2008; Lee et al., 2014; Sen et al., 2016). Pb pollution results in grave repercussions as high blood lead level (BLL) causing neurological impairment in children (Gao et al., 2001; Zheng et al., 2008) and increases the risks of cardiovascular diseases and cancer in adults (Menke et al., 2006). After the phase-out of leaded gasoline in developing countries, Pb contribution from coal increased significantly (Jaramillo et al., 2007; Wang et al., 2016). Due to ever increasing coal combustion, industrial and vehicular emissions, Pb concentrations of Asian aerosols measured in the last decade were generally an order of magnitude higher than those from elsewhere (Bollhöfer and Rosman, 2000, 2001).

Pb has an atmospheric lifetime of 5-10 days (Sturges and Barrie 1987) and can travel long distances crossing international boundaries. For instance, anthropogenic Pb from coal combustion and Pb-ore extraction in southwest China and South Asia were transported and enriched in soil and mosses high up on the Tibetan plateau (Bing et al., 2014). Corals from around Singapore sourced Pb from leaded gasoline and South China

ores (Chen et al., 2015). Corals from Chagos Archipelago sourced Pb from Indian emissions (Lee et al., 2014). Relatively high concentrations of Pb in the northern and central Indian Ocean have been attributed to late phase-out of leaded gasoline and rapid economic development in India, China, and some other south Asian countries (Boyle et al., 2014).

Pb sources in the environment can be identified using Pb isotopic compositions (Komárek et al., 2008). Pb exists as four naturally occurring stable isotopes, ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb . Except for ^{204}Pb which is non-radiogenic, the other three stable isotopes are result from radioactive decay of uranium and thorium (^{238}U , ^{235}U , ^{232}Th). Typically, Pb isotopic compositions are expressed as ratios. For example, old Pb ores exhibit lower $^{206}\text{Pb}/^{207}\text{Pb}$ as compared to young Pb ores (Gulson et al., 1981). Pb is a heavy metal with low relative atomic weight differences between the isotopes. This results in minimal mass-dependant Pb isotope fractionation in natural physical, chemical, and biological processes (Doe, 1970; Flegal and Smith, 1995; O’Nions et al., 1998). Pb isotopes do not fractionate during industrial and environmental processes and can preserve the source signature even after degradation, processing, and transportation. Thus Pb isotopes provide an excellent ‘fingerprinting’ tool for identifying Pb sources (Flegal and Smith, 1995; Cheng and Hu, 2010).

Interpreting Pb-isotope alone can be complex because there are multiple anthropogenic sources and their Pb end members are either not well defined, or overlap in the isotope space (Mukai et al., 1993). Thus, a combined approach using both Pb-isotopes and metal concentrations can be useful to delineate Pb origins such as those carried out in China (Lee et al., 2007; Hao et al., 2008; Bing et al., 2014; Zhao et al., 2015), Japan (Takeda et al., 2000), Middle East (Erel et al., 1997), US, (Graney et al., 1995; Véron and Church 1997) and Europe (Cloquet et al., 2015).

India is the second largest Pb emitter in Asia after China (Lee et al., 2014). To date, very limited work on Indian aerosol Pb isotope exists (Bollhöfer and Rosman, 2001; Kumar et al., 2016; Sen et al., 2016). The three previous studies were carried out in western and northern India. This study analyses Pb isotopic and elemental composition of aerosols collected from three locations with different environmental settings in eastern India. The aim of this study is to understand atmospheric Pb sources in three different environmental backgrounds. Additionally, Indian coal and road dust from each of the three locations are measured. This study aims to investigate the spatial variability of Pb sources in aerosols.

2. Materials and Method

2.1 Sampling: Aerosol samples were collected from three locations in West Bengal, India (Figure 1) during the monsoon season (August and September 2016). All the three sites are located in the Gangetic Delta on a ~150 Km N-S transect along the banks of River Hooghly, a major distributary of River Ganges. The southernmost location is Sagar Island, a 224 square Km island formed at the confluence of River Hooghly with the Bay of Bengal on the continental shelf. The next location is about 100 Km north of Sagar Island in the megacity of Kolkata. Kolkata, the capital of West Bengal is the only megacity (population greater than 10 million) in eastern India and the financial hub of the region. The third location is Bandel, an industrial town, approximately 50 Km north of Kolkata. Bandel is home to a coal fired thermal power plant and numerous medium and small scale industries including automobile manufacturing, iron and steel, chemical, rubber, textile etc. The three locations represent three different environments, from a pristine island to a megacity to an industrial town. The sampling locations are selected along a south to north transect on the path of the strong South West monsoon winds blowing from the Bay of Bengal. The monsoon season was selected for sampling as the winds from the Bay of Bengal are likely to have little anthropogenic Pb picked up from point sources in contrast to the winter northerly winds that sweep over northern India before blowing over the study area in south Bengal. Sampling details including dates, GPS coordinates, temperature, relative humidity, and rainfall are reported in Table S1 in Supplementary section. A portable low volume particulate sampler pump (Deployable Particulate Sampler from Leland Legacy) with a pumping efficiency of 10 L/min was used to collect PM_{10} (particulate matter 10 micrometres or less in aerodynamic diameter). Details about the performance of the inertial impactor (d_{50}), efficiency curve sharpness of the sampler, and particle loss can be found at https://www.skinc.com/catalog/pdf/instructions/Modular_Impactors_Poster.pdf. The PM_{10} was collected on 47 mm PTFE filters. The filters were extensively acid washed in concentrated ultrapure HCl-ethanol mixture (3:7 by volume) to remove possible organo-lead contamination followed by dilute ultrapure HNO_3 wash as

described in Bollhöfer et al. (1999). After rinsing the filters with Milli-Q water, they were air dried under a HEPA filter fitted clean bench. Before the filters were brought to the field, the dry filters had been weighed and packed in Millipore petri dishes with a cover. The petri dishes were prewashed in 2% HNO₃ to prevent any contamination.

In Sagar Island and Bandel, the pump was placed on the first-floor roof top of buildings, at a heights of ~6 m above ground level (AGL). In Kolkata, the pump was placed on the roof top of a five-storied building (~ 22 m AGL). During each sampling, the pump was run for ~24 hours. A total of 15 samples and three blanks were collected. Post collection the filters were immediately sealed in the Petri dishes and stored in a refrigerator at ~4°C. Road dust samples were also collected from each location on weighing papers using brushes and were immediately transferred into prewashed Ziploc bags. Three field blanks were collected by placing the Teflon filter in the filter cartridge without turning on the pump and the filter was removed after ~5 minutes, approximately the time taken to change sample filters. The blank filters were treated in the same way as the sample filters and brought back to the laboratory for chemical analysis. Coal samples were also collected from three collieries in eastern and central India. The sampling details are reported in Table S1.

2.2 Metal Analysis: The filters were brought back to the Earth Observatory of Singapore where all the chemical analyses were performed in a class 100 clean chemistry lab. The filters were first cut into halves using a ceramic scissor. The scissor was washed with Milli-Q water and methanol after each use. Halves of the filters were used for Pb isotope analysis and the other halves were used for determination of metal concentrations. The dust samples were dried at 50°C in an oven overnight. Subsequently they were ground to homogenize using an agate mortar and pestle. As this study investigates anthropogenic lead sources in aerosol, hydrofluoric (HF) acid digestion was not used. Hence, Pb contained in silicate structure (in aeolian dust) was not extracted. Instead, strong acid leaching was used to liberate all metals that are environmentally available.

The coal samples were dry ashed in a muffle furnace at 300 °C for 1 hour and 500 °C for 2 hours following the methods described in Diaz-Somoano et al. (2007). Approximately 100 mg of coal ash samples were dissolved in 6 ml of HNO₃ and 0.1 ml of HF in a closed cap Teflon vial on a hot plate at 120 °C for 12 hours (Diaz-Somoano et al., 2007, 2009). Digested samples were then evaporated to dryness and re-dissolved in 3 ml HNO₃. Half of the solutions were diluted for Pb concentration analysis and the rest were used for Pb isotope analysis.

To validate the hot plate digestion method, two coal ash samples were dissolved in a Milestone microwave system (ETOS EZ, Italy) using the same HF-HNO₃ mixture. Using the microwave radiation (Power 1200 W) temperature was ramped to 180°C in 30 minutes and the temperature was held for 15 minutes. The vessels were opened several hours after cooling down to the room temperature. Half of the solution was used for Pb isotope analysis and the remaining was diluted for Pb concentration measurement. Pb concentrations and isotope ratios obtained by dissolution of coal ash by two different methods, hot plate digestion and microwave digestion, are given in Table S2 in Supplementary section. The maximum difference in Pb concentration between the two methods was 8% which was less than the analytical uncertainty (~10%) of the instrument. Similarly the maximum difference of 0.07% was observed in the ²⁰⁶Pb/²⁰⁷Pb ratio obtained from the two methods.

Metal concentration analyses were performed at the Central Environmental Science and Engineering Laboratory (CESEL), at the School of Civil and Environmental Engineering at Nanyang Technological University. For metal concentration analysis, halves of the filters (including the blank filters) were leached in closed capped Teflon beakers on a hot plate in HNO₃-H₂O₂ mixture following the Environmental Protection Agency (EPA) method 3050B (Edgell, 1996; Sen et al., 2016). Similar chemical extraction procedure was applied to ~100 mg of dust samples as well. This strong acid digestion method liberates all the metals adhering to the particulate matter. The extracts were then diluted with ultrapure water to a final concentration of ~10 ppm TDS (total dissolved solids), and transferred to ICP sample vials. One ppb of Indium was added as internal standard. Instrumental drift was corrected by a combination of internal and external drift correction using Indium as the internal standard and external calibration from the bracketing standard. The filter leachates, dust, and coal ash solutions were run at high dilutions (~10ppm TDS) to minimize any potential matrix effects between leachates and bracketing standards (Das et al., 2013). Measurements were performed on a Perkin Elmer Elan-DRC-e Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) equipped with a dynamic reaction cell that uses methane gas to minimize interferences. The instrument was tuned using the Perkin Elmer SMART Tune Solution with 10 ug/L (Ba, Be, Ce, Co, In, Mg, Pb, Rh & U) in 1% HNO₃. Oxides monitored by Ce/CeO ratio were kept below 3%. Concentrations were calculated using NIST Buffalo River Sediment Standard and a multi element standard solution from High Purity Standards diluted to the concentration range of the samples.

Averages of the filter blanks that ranged from 1.3 - 6% of the average signal intensity of the samples were subtracted from the final concentrations. To check the chemical extraction efficiency and analytical precession, NIST SRM 1648a (urban particulate matter standard) was also analysed. Like the filters, the standard was leached with concentrated HNO₃-H₂O₂ mixture following (EPA) method 3050B. The extract was then evaporated to dryness and re-dissolved in 2% HNO₃ and run at 10 ppm TDS to match with the filter extracts. Recoveries for all metals were found to be > 90%.

2.3 Pb isotope analysis: For Pb isotope analyses, halves of the filters and ~50 mg of dust samples were leached in 0.4 N HBr for 2 hours at 100°C in PFA beakers following the methods in Sen et al. (2016). The leached solutions were transferred to another Teflon beaker and dried at 90 °C under a HEPA filter. Pb was separated from the sample matrix by passing the solution through an ion exchange column (Eichrom AG-1X8 chloride form, 200-400 mesh). The sample solutions were loaded on the column in 1.1 N HBr and extracted using hydrobromic and hydrochloric mixed acid (HBr-HCl) (Reuer et al., 2003).

Pb isotope ratio analyses were performed on a Neptune MC-ICP-MS (Thermo-Fisher, Germany) at the Earth Observatory of Singapore, Nanyang Technological University. Thallium (Tl) was added as an internal standard and a ²⁰³Tl/²⁰⁵Tl ratio of 0.418911 was used to correct for instrumental mass fractionation (White et al., 2000). The samples were measured at similar Pb/Tl ratios as the standards to avoid any analytical bias. ²⁰²Hg signal was used to correct the isobaric interference of ²⁰⁴Pb by ²⁰⁴Hg. The isotope ratios of NBS-981 Pb standard measured during the analytical sessions were ²⁰⁶Pb/²⁰⁴Pb = 16.9317 ± 0.0036, ²⁰⁷Pb/²⁰⁴Pb = 15.4859 ± 0.0049, ²⁰⁸Pb/²⁰⁴Pb = 36.6830 ± 0.0102, ²⁰⁶Pb/²⁰⁷Pb = 1.0934 ± 0.0002, ²⁰⁸Pb/²⁰⁷Pb = 2.3688 ± 0.0002 (2 standard deviations, n = 15) (Table 1). Post measurement, correction was applied to the measured Pb isotope ratios of the samples by normalizing the data to NBS 981 values measured during the same day with the true value as reported in Baker et al., 2004 (Chen et al., 2016). The internal precision of the Pb-isotope ratios were always found to be better than the external reproducibility of the standards.

Chemical procedures identical to the samples (HBr leaching followed by column chemistry) were also applied on the blank filters and the total procedural blank measured was ~75 pg. This is insignificant compared to the Pb extracted from the aerosol (~46 ng Pb extracted from the lowest concentration sample) which is <0.2% of the Pb signal from the processed sample which had the lowest Pb concentration. Therefore, no blank correction was applied to the Pb isotope compositions.

3. Results and Discussions

The Pb concentrations and isotope ratios of the aerosol, road dust, coal samples, and procedural blank filters are reported in Table 1. Metal concentrations of the aerosols are reported in Table 2. This study uses the Pb isotope ratios, Pb concentrations, metals, and the meteorological parameters (Table S1) to characterize the sources of anthropogenic Pb. Though atmospheric residence time of Pb is 5-10 days (Sturges and Barrie 1987), during monsoon, the residence time decreases due to frequent washout of the atmosphere (Chandra et al., 2014). Hence 24 hours and 72 hours air mass back trajectories at 6 hour intervals at an elevation of 100 m AGL are constructed for the sampling period using HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) data from the U.S. National Oceanic and Atmospheric Administration's (NOAA) website (Draxler and Rolph, 2003) (Figure S1).

3.1 Isotopic Composition of Anthropogenic Lead: The three major anthropogenic sources of atmospheric Pb are 1) vehicle exhausts, 2) coal combustion, and 3) high temperature industrial processes. India phased out leaded gasoline in 2000 (UNEP, 2007). Since then atmospheric Pb from vehicle exhaust has reduced significantly (Lee et al., 2014). However, Pb from vehicle exhaust can still contribute significantly to atmospheric Pb for two reasons. Firstly, historic Pb once emitted due to extensive use of leaded gasoline can stay in the environment and recirculate back to the atmosphere. Secondly, unleaded gasoline and diesel still contain trace amounts of Pb that are emitted by vehicle exhaust (Pulles et al., 2012 and references therein). The large fleet of vehicles on the roads of urban metropolis magnify the Pb emissions to the atmosphere (Gioia et al., 2010). The Pb in the tetraethyl lead added to gasoline in the last century to improve fuel economy was primarily sourced from two Pb ore deposits, Broken Hill type deposit in Australia and Mississippi Valley type deposit in USA (Bollhöfer and Rosman, 2000). Both the Pb ore deposits have distinct ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb signatures (Bollhöfer and Rosman, 2001) (Figure 2). Hence, Pb isotopic signature in leaded gasoline plots on or close to the mixing line between Broken Hill and Mississippi Valley type deposits (Erel et al., 1997; Monna et al., 1997; Hansmann and Köppel, 2000; Geagea et al., 2008; Sen et al., 2016). Leaded gasoline previously reported have

narrow range of $^{206}\text{Pb}/^{207}\text{Pb}$ (1.0862-1.1254) and $^{208}\text{Pb}/^{207}\text{Pb}$ (2.3594-2.3915) ratios. India banned leaded gasoline in 2000. Hence for the present study leaded gasoline exhaust is not considered a major source of atmospheric Pb. Exhaust from vehicles using unleaded gasoline and diesel can have a wide range of $^{206}\text{Pb}/^{207}\text{Pb}$ (1.1080 -1.1894) and $^{208}\text{Pb}/^{207}\text{Pb}$ (2.3733 - 2.4517) ratios (Erel et al., 1997; Chen et al., 2006; Geagea et al., 2008; Gioia et al., 2017) and varies based on geographic location. On average, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ are higher in unleaded gasoline, diesel oil and present-day vehicle exhaust as compared to leaded gasoline exhaust (Figure 2). The present study did not measure any gasoline or diesel. In absence of the local gasoline data we assume the available literature data (Figure 2) as relevant to the present study. In addition to vehicular exhaust, re suspended road dust can be a major source of atmospheric Pb. Road dusts are a combination of crustal dust mixed with road surface abrasion, vehicular emissions, tyre and brake wear (Gioia, 2017, 2010). We measured road dust from three locations to understand whether local re suspended road dust can be a source of atmospheric Pb.

Since the phase-out of leaded gasoline, coal combustion has become the largest contributor of atmospheric Pb in developing countries like India and China (Lelieveld et al., 2001; Ramanathan et al., 2001; Lee et al., 2014). Present day coal-based power generation in India releases approximately 3300 tonnes of Pb per year, and emissions from this source are comparable to those from leaded gasoline exhausts in India in 1990s (Lee et al., 2014). Though there has been many studies on the Pb isotopic composition of Chinese coal (Mukai et al., 1993; Zheng et al., 2004; Diaz-Somoano et al., 2009; Cheng and Hu, 2010), data on Indian coal were absent till very recently (Das et al. 2016). This study measured Pb isotopic composition of Indian coal from three coal fields, the details of which are documented in the supplementary section (Table S1). $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios in Indian coal measured in this study and from a recent publication (Das et al., 2016) have a small range and are similar to those in Australian coal, but the values are slightly higher than Indonesian and Chinese coal (Diaz-Somoano et al., 2009). India imported coals from Australia (69%) and Indonesia (10%) from 1988 to 2000 (COMTRADE, 2009, <http://comtrade.un.org/db/default.aspx>). Hence the bulk coal combustion emissions from India will be far from unique and the coal isotopic signatures will be a mixture of those from India, Australia and Indonesia in relative proportions.

High temperature metallurgy, smelting, mining, waste incineration also release significant quantity of anthropogenic Pb to the atmosphere which has a Pb isotope signature similar to that in Pb ores. Indian ore deposits have $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios range of 1.0356-1.1138 and 2.3110-2.3961 respectively (Deb et al., 1989; Sangster et al., 2000), overlapping with those of the Broken Hill type ore deposits and leaded gasoline emissions. Hence it is somewhat difficult to differentiate between Pb from leaded gasoline and industrial emissions solely based on Pb isotope ratios. Under such circumstances, elemental concentrations play an important discerning role in determining atmospheric Pb sources.

3.2 Sources of Anthropogenic Pb in the aerosols: The Pb concentrations in the aerosols range from 7.4 to 395 ng/m³ (Table 1). Overall, the Pb concentrations increase along the N-S transect from south to north. Among all the samples, the Sagar Island aerosols have the lowest average Pb concentrations (9.5±3 ng/m³, 1SD) followed by Kolkata (48.5±17 ng/m³, 1SD). The highest Pb concentrations are measured in Bandel (226±190 ng/m³, 1SD) which also shows the largest variation in concentration range (from 31 to 395 ng/m³). The Pb concentrations measured in this study are within the ranges of previously reported values in India (Tripathi, 1994; Ghosh et al., 2014; Sen et al., 2016), but much lower than those reported from Delhi (Kumar et al., 2016) and those of the USEPA chronic exposure limit of 1500 ng/m³. The Pb isotopes measured from the three locations have a wide range of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios from 1.1155-1.1681 and 2.3905-2.4494, respectively. However, the ratios do not systematically increase or decrease along the N-S transect as observed in Pb concentrations. These ratios have a wider range and are mostly higher than previously measured in Indian aerosols ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios from 1.1187-1.1370 and 2.3952-2.4134, respectively) in Ahmedabad (Bollhöfer and Rosman, 2001), Kanpur (Sen et al., 2016) and Delhi (Kumar et al., 2016).

3.2.1 Sagar Island: The back trajectories show two prominent wind directions in the Sagar Island during the sampling period. During the first two days of sampling (7th and 8th Sept., 2016), the wind was blowing from over the Indian landmass (Figure S1) before reaching Sagar Island. For the next two days of sampling (9th and 10th Sept., 2016), the predominant wind direction was due south from the Bay of Bengal. Though the Pb concentrations and isotopes do not show much variation during the sampling period, the Cr concentrations are one order of magnitude higher for the first two days of sampling. This is probably due to the long-range transport of Cr from Sukinda in Orissa, the largest open cast chromite ore mine in the world (Figure S1).

In the triple isotope plot (Figure 2), the Pb isotope ratios in Sagar Island aerosols vary from 1.1231-1.1398 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.3973-2.4119 for $^{208}\text{Pb}/^{207}\text{Pb}$. The road dust in Sagar has a higher $^{206}\text{Pb}/^{207}\text{Pb}$ (1.1751-1.1786) and $^{208}\text{Pb}/^{207}\text{Pb}$ (2.4500-2.4512) ratio as compared to the aerosol and is closer to the average bulk continental crustal composition as estimated by previous workers (Alle`gre and Lewin, 1989; Rudnick and Goldstein, 1990). Hence road dust possibly is not the dominant source of atmospheric Pb for this location. The Sagar aerosols plot in the field of unleaded gasoline and diesel exhaust. Ni and V that are released mainly from oil combustion (Paycna and Paycna, 2001) correlate strongly ($r = 0.98$) with each other and also with Pb ($r = 0.78$ and 0.81 , respectively) (Table S3). Further, Sagar aerosols are characterized by a higher V/Pb (0.63-1.1) ratios as compared to aerosols from Kolkata (0.04-0.11) and Bandel (0.03-0.12) (Figure 3). Typically vehicle exhaust have V/Pb ratios ≤ 1 as compared to coal combustion emissions ($\text{V/Pb} > 1$) and industrial emissions ($\text{V/Pb} \ll 1$) (Sen et al., 2016; Kumar et al., 2016). V/Pb and Ni/Pb ratios of Sagar aerosols (Figure 3) plot close to average Delhi aerosols collected during a Middle Eastern dust storm event observed over Delhi (Kumar et al., 2016). Elemental composition of the dust storm aerosols were influenced by Middle Eastern crude oil composition. Sagar Island is a pristine location without any major industries. The probable source of local anthropogenic Pb pollution are the gasoline and diesel exhaust from the road and riverine traffic.

3.2.2 Kolkata: A megacity can have complex Pb emissions sources. Traffic can be a major source. In addition, there are numerous medium and small scale industries in and around Kolkata that can contribute towards atmospheric Pb emissions.

Pb concentrations during the sampling period do not show much variation (25-80 ng/m³). However, the Pb isotopes show a large range of $^{206}\text{Pb}/^{207}\text{Pb}$ (1.1192-1.1681) and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios (2.3947-2.4494) with a bimodal distribution. Three samples (A11, A12, A13) have $^{206}\text{Pb}/^{207}\text{Pb}$ ratios between 1.1192 and 1.1247, whereas the remaining 4 samples (A9, A10, A14 and A15) have $^{206}\text{Pb}/^{207}\text{Pb}$ ratios between 1.1515 and 1.1681 (Figure 2). In the triple isotope plot, the Kolkata aerosol samples plot in two clusters along a mixing line between Indian ore and coal, and plots away from the gasoline mixing line. Assuming the bulk coal emissions to be a mixture of 69% Australian coal, 21% Indian coal, and 10% Indonesian coal (COMTRADE, 2009, <http://comtrade.un.org/db/default.aspx>), the Pb isotopic compositions of bulk coal emissions in India are estimated to be $^{206}\text{Pb}/^{207}\text{Pb} = 1.2040$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4882$. Using a simple binary mixing model, Kolkata aerosol samples with high Pb isotopes (A9, A10, A14 and A15) can be explained by 59-72% mixing of coal combustion emissions with 28-41 % Pb emissions from high temperature metallurgy. The low Pb isotope group (A11, A12, A13) has a larger influence of Pb ore (62-67%). The street dust measured in this study ($^{206}\text{Pb}/^{207}\text{Pb} = 1.1320 - 1.1334$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4097 - 2.4143$) and a previous study (Das et al., 2016, average $^{206}\text{Pb}/^{207}\text{Pb} = 1.1378$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4121$) show similar isotopic composition, and both plot in between the low and the high ratios of $^{206}\text{Pb}/^{207}\text{Pb}$. The low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios overlap with the Indian ore field. The high ratios overlap with the diesel and unleaded gasoline exhaust field and plot closer to the Indian coal. Hence, it is hard to determine the relative influence of each source by only using the Pb concentrations and isotope ratios. Other parameters such as wind directions and metal concentration profiles are applied to understand the source(s) of Pb.

The 24-hour and 72- hour back trajectories show two distinct wind directions during the sampling periods; one blowing along the east coast of India and the other along the Myanmar and Bangladesh coasts. Lower $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are observed when wind was blowing from the Bangladesh side. For the low ratio group, Pb correlates strongly with Cd ($r = 0.74$), Cu ($r = 0.90$), Ni ($r = 1$) and moderately with As ($r = 0.36$) (Table S4). High temperature non-ferrous metallurgy releases volatile metal pollutants such as Cd, Cu, Zn and Pb (Pacyna, 1987). Moderately strong correlation of Pb with V ($r = 0.68$) coupled with low V/Pb ratios (0.04 to 0.11) (Figure 3) also indicate industrial emissions as the primary source of Pb. Hence it is inferred that the low $^{206}\text{Pb}/^{207}\text{Pb}$ ratio samples have a large contribution from industrial source.

Higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are measured when wind was blowing along the east coast of India (Figure S1). Couple of hundred miles inland from the east coast, there are several large coal fired power plants, Vindhyachal Thermal Power Station in Madhya Pradesh, Talcher Super Thermal Power Station in Odisha, Sipat Thermal Power Plant in Chhattisgarh, to name a few. Numerous industries and steel plants (viz. Vizag) exist along the coast as well. Hence long range transport along the east coast of India is likely to bring Pb isotopic signature of coal combustion and industrial emissions. The Pb isotopes also plot along the mixing line between Indian coal and ore. Pb does not show strong correlation with any of the measured elements except Cr (Table S5). V and Ni does not correlate with each other ($r = 0.08$). Pb shows weak correlation with V ($r = 0.47$) and Ni ($r = -0.48$)

indicating different sources of origin. Hence V/Pb and Ni/Pb ratios could not be used conclusively to understand the plausible sources of Pb. This is probably because Pb in these aerosols has a mixed source, coal combustion and industrial emissions that underwent long range transport.

3.2.3 Bandel: Bandel is located about 50 Km north of Kolkata on the banks of River Hooghly. Out of the three locations, highest concentrations of Pb, Zn, Cd, V and As are measured in Bandel. The wide range of concentrations of Pb and other metals in Bandel is probably due to rainfall wash out effect (Chandra et al., 2014). A rainfall amount of 75 mm was recorded during collection of the first two samples (A5 and A6), which led to lower concentrations of Pb and other metals like Zn, Cr, and Cd. In spite of the large variation in Pb concentrations, the Pb isotopic compositions show very little variation, for example, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios range from 1.1155-1.1240 and 2.3905-2.3949, respectively. In the triple isotope plot (Figure 2) the Bandel aerosol overlaps the field of Indian ore. Strong correlation of Pb and As ($r = 0.81$) indicates coal combustion as an important source as well (Table S6). Pb also correlates strongly with Cd ($r = 0.86$), Zn ($r = 0.98$), Cu ($r = 0.91$) and V ($r = 0.79$) (Table S6) indicating high temperature metallurgy as a second and probably a dominant source. This assumption is also supported by the very low V/Pb ratio (0.03-0.12). Coal combustion would lead to V/Pb ratio > 1 (Figure 3), as coal is enriched in V in ppm levels (Sen et al., 2016; Kumar et al., 2016). Street dust from Bandel have slightly higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (1.1334-1.1393), similar to Kolkata street dust. Typically, in pristine setting road dust are crustal dust. But in a polluted setting it is a mixture of crustal dust with vehicular and industrial emission. $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in bulk continental crust ranges from 1.163 – 1.192 (Alle`gre and Lewin, 1989; Rudnick and Goldstein, 1990) and average upper continental crust (UCC) is 1.205 (Millot et al., 2004). Neither Bandel nor Kolkata street dust plot close to the range for bulk continental crust or UCC composition as they are mixtures of crustal dust with vehicular and industrial emission. Bandel has a Thermal Power Plant (TPP) with a rated capacity of 530 MW. Besides the TPP, Bandel has numerous medium and small scale industries including chemical, iron and steel, foundries, rubber, textile, high temperature metallurgy to name a few (<http://www.hooghly.gov.in/industscal.htm>). Hence the Pb source of Bandel aerosols is dominated by high temperature metallurgy.

3.3 Pb isotopes in Indian Aerosol: The first ever Pb isotope measurement in Indian aerosol was done by Bollhöfer and Rosman [2001]. The samples were collected in 1995 from Ahmedabad, Gujarat, 5 years before India phased out leaded gasoline. Average Pb isotopes measured in the aerosols were 1.137 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.407 for $^{208}\text{Pb}/^{207}\text{Pb}$ and plots in between the mixing lines for leaded gasoline and Indian coal and ore (Figure 2). In comparison, aerosol Pb collected from Kanpur (Sen et al., 2016), Delhi (Kumar et al., 2016) and this study plots closer to the mixing line between Indian coal and ore. This is probably because aerosol Pb collected in 1995 still had a significant portion coming from leaded gasoline. In Kanpur aerosols, industrial emission was the primary source ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios from 1.1187-1.1353 and 2.3951-2.4105, respectively) (Sen et al., 2016). Pb isotopes of the Bandel aerosols are over all similar to those observed in Kanpur. However, two samples (A7 and A8) have lower radiogenic Pb compared to Kanpur aerosols. Incidentally A7 (383 ng/m³) and A8 (395 ng/m³) have the highest Pb concentrations among all the aerosols collected in this study, a similar observation reported in Kanpur. The least radiogenic Pb aerosol in Kanpur had the highest Pb concentrations (912 ng/m³). This implies strong influence of Pb ore or high temperature metallurgy as the major source. Aerosol Pb collected from Delhi in 2012 had a more complex source, Middle Eastern dust storm with more radiogenic Pb ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios from 1.1230-1.1331 and 2.4018-2.4134, respectively) as compared to New Delhi aerosols ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios from 1.1212-1.1270 and 2.3991-2.4045, respectively). The dust storm aerosol Pb was interpreted to have originated from fossil fuel combustion in Middle East based on Ni, V concentrations, elemental ratios and Pb isotope ratios. The Sagar aerosols show a similar range for Pb isotopes as those collected from Delhi during Middle Eastern dust storm. Based on strong correlation between Ni and V and their ratios (Figure 3) we interpreted the atmospheric Pb source to be local fossil fuel combustion in Sagar Island. Pb isotopes of Kolkata aerosol plots in two clusters. While the less radiogenic Pb isotope ratios are similar to Kanpur or Delhi aerosols the other group with high radiogenic Pb isotope ratios are first of its kind reported in Indian aerosol. Possibly these samples are showing strong influence of coal combustion.

4. Conclusions

This study investigates the spatial distribution of Pb isotopes in aerosols from in and around a megacity in eastern India. Two major end members of anthropogenic Pb pollution, Indian coal and road dust as proxy for present-day vehicle emission are also measured. Road dust contains an integration of anthropogenic Pb

emission from vehicles for years and is also mixed with crustal dust. Aerosols are collected from three locations with diverse environmental setting within a 150 Km stretch. The results based on Pb isotopes in conjunction with metals show that Pb sources in the atmosphere are dynamic, varying significantly even over short distances. Pb source is likely a combination of local point sources and long range transport. In the river island, the Pb sources are primarily exhaust from road and riverine traffic. In the industrial town, the Pb emissions are dominated by high temperature metallurgy. In the megacity, Pb sources are most complex. Consecutive seven days of sampling show two distinct clusters of Pb isotope ratios with little variation in Pb concentrations. Air mass back trajectories during the sampling period revealed that the ratios are closely related to the air mass movement from two distinct directions, from the Bay of Bengal along Indian east coast and along Bangladesh–Myanmar coast. Wind blowing along Indian east coast carries aerosols that have higher Pb isotope ratios than previously reported in Indian aerosols. This possibly indicates a larger input of coal-derived Pb than the other locations studies so far. To better understand the anthropogenic Pb sources in the atmosphere, study in underway on temporal variability of atmospheric Pb, transboundary pollution and Pb isotopic signature of present-day vehicle exhaust.

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Table 1. Pb concentration and Pb isotope composition of aerosols (A1-A15), street dust (SD) and coal (C1-C5) samples.

Sample No	Location	$^{206}\text{Pb}/^{204}\text{Pb}$	2se	$^{207}\text{Pb}/^{204}\text{Pb}$	2se	$^{208}\text{Pb}/^{204}\text{Pb}$	2se	$^{206}\text{Pb}/^{207}\text{Pb}$	2se	$^{208}\text{Pb}/^{207}\text{Pb}$	2se	Pb conc
ng/m ³												
A1	Sagar	17.7390	0.0010	15.5942	0.0010	37.5963	0.0035	1.1375	0.00001	2.4109	0.00004	13.8
A2	Sagar	17.7817	0.0010	15.6011	0.0013	37.6273	0.0041	1.1398	0.00002	2.4119	0.00006	8.7
A3	Sagar	17.7014	0.0013	15.6132	0.0014	37.6135	0.0036	1.1337	0.00002	2.4091	0.00005	7.4
A4	Sagar	17.4698	0.0012	15.5549	0.0014	37.2910	0.0044	1.1231	0.00002	2.3973	0.00006	7.9
A5	Bandel	17.4227	0.0018	15.5016	0.0021	37.1262	0.0067	1.1240	0.00004	2.3949	0.00009	95
A6	Bandel	17.4395	0.0011	15.5401	0.0013	37.2099	0.0041	1.1223	0.00002	2.3946	0.00004	31
A7	Bandel	17.3727	0.0010	15.5573	0.0012	37.2292	0.0041	1.1167	0.00002	2.3930	0.00006	383
A8	Bandel	17.3380	0.0012	15.5423	0.0016	37.1532	0.0054	1.1155	0.00003	2.3905	0.00008	395
A9	Kolkata	18.0478	0.0011	15.5271	0.0012	37.9263	0.0039	1.1624	0.00002	2.4426	0.00005	42
A10	Kolkata	18.1383	0.0010	15.5280	0.0012	38.0346	0.0041	1.1681	0.00002	2.4494	0.00005	55
A11	Kolkata	17.5397	0.0013	15.5944	0.0015	37.4376	0.0047	1.1247	0.00003	2.4006	0.00006	25
A12	Kolkata	17.4198	0.0011	15.5650	0.0013	37.3041	0.0042	1.1192	0.00002	2.3967	0.00006	80
A13	Kolkata	17.3960	0.0012	15.5323	0.0016	37.1943	0.0053	1.1200	0.00003	2.3946	0.00008	52
A14	Kolkata	17.9223	0.0012	15.5645	0.0014	37.8648	0.0049	1.1515	0.00002	2.4328	0.00007	51
A15	Kolkata	18.1347	0.0012	15.5724	0.0013	38.1380	0.0041	1.1645	0.00002	2.4491	0.00005	36
in ppm												
SD	Sagar	18.4128	0.0012	15.6686	0.0014	38.3868	0.0048	1.1751	0.00002	2.4500	0.00006	3.8
SD	Kolkata	17.6648	0.0014	15.6050	0.0017	37.6023	0.0059	1.1320	0.00003	2.4097	0.00009	42
SD	Bandel	17.6644	0.0012	15.5848	0.0015	37.5691	0.0051	1.1334	0.00002	2.4107	0.00007	32
in ppm												
C1	Coal	18.9187	0.0015	15.7298	0.0018	39.3100	0.0061	1.2027	0.00003	2.4990	0.00008	22
C2	Coal	19.0398	0.0013	15.7384	0.0012	39.3291	0.0042	1.2097	0.00002	2.4989	0.00005	20
C3	Coal	19.0016	0.0011	15.7279	0.0012	39.2475	0.0044	1.2082	0.00002	2.4954	0.00006	32
C4	Coal	19.2233	0.0019	15.7825	0.0022	39.4460	0.0079	1.2180	0.00003	2.4993	0.00010	144
C5	Coal	18.9218	0.0011	15.6830	0.0013	38.8782	0.0045	1.2065	0.00002	2.4790	0.00006	39
		$^{206}\text{Pb}/^{204}\text{Pb}$	2SD	$^{207}\text{Pb}/^{204}\text{Pb}$	2SD	$^{208}\text{Pb}/^{204}\text{Pb}$	2SD	$^{206}\text{Pb}/^{207}\text{Pb}$	2SD	$^{208}\text{Pb}/^{207}\text{Pb}$	2SD	
NBS 981 (True Value)		16.93736						1.0933	0.0004	2.3704	0.0012	
NIST 981 (n =15)		16.93167	0.0036	15.48585	0.0049	36.6830	0.0143	1.0934	0.0002	2.3688	0.0002	
Filter Blank (n=3)		17.5956	1.1617	15.2198	0.3916	36.8837	1.1878	1.1540	0.0447	2.4208	0.0110	

Table 2. Metal concentrations of aerosols in ng/m³.

	Pb	Th	U	V	Cr	Ni	Zn	Al	Cu	Cd	Fe	As
A1	13.8	0.15	0.08	10.59	229	3.94	31.9	492	6.21	0.54	824	4.43
A2	8.7	0.08	0.06	5.52	150	2.65	17.8	317	3.13	0.31	446	0.53
A3	7.4	0.13	0.07	7.86	9.47	3.29	17.0	581	3.51	0.22	757	2.24
A4	7.9	0.10	0.06	5.96	3.24	2.50	20.1	426	5.26	0.22	485	7.19
A5	95.2	0.17	0.08	11.34	3.62	4.76	154.1	1516	5.58	1.53	840	6.05
A6	30.8	0.03	0.02	2.50	3.58	1.82	15.1	324	6.27	0.69	311	1.07
A7	382.5	0.19	0.10	12.88	6.61	2.84	406.4	706	7.47	8.31	810	7.59
A8	395.1	0.35	0.17	29.03	8.14	2.98	391.4	790	7.97	4.26	1001	7.03
A9	42.1	0.05	0.03	3.14	3.34	1.31	20.5	290	5.34	0.48	361	1.41
A10	54.9	0.02	0.03	3.16	44.79	1.62	18.2	336	4.69	0.33	237	<DL
A11	24.6	0.05	0.04	2.81	5.77	1.89	110.6	266	7.49	0.65	431	0.55
A12	79.8	0.09	0.05	3.41	6.37	2.42	33.6	420	103.03	1.13	569	1.58
A13	51.6	0.12	0.05	3.65	5.54	2.16	21.5	394	13.91	0.50	736	3.32
A14	50.7	0.11	0.07	4.04	5.90	2.18	29.6	440	15.47	0.80	704	2.24
A15	35.8	0.04	0.03	3.04	6.17	2.84	26.5	471	9.58	0.29	397	3.10

1 FIGURES

2

3 *Figure 1. Map showing the sampling locations. Chromite mine at Sukinda is plotted for*
4 *reference.*

Figure 2. $^{208}\text{Pb}/^{207}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ of Indian aerosols (this study and previous study), in comparison to the possible anthropogenic end members. Open squares are street dust samples. The mixing line between Pb ores from the Broken Hill type deposit in Australia and Mississippi Valley type Pb deposit in USA is shown as the brown line (Leaded Gasoline Mixing Line). Theoretical mixing line between Indian ore and Indian coal is drawn in black. References: coal (Indian coal-this study and Das et al., 2016; Australian and Indonesian coal - Díaz-Somoano et al., 2009); unleaded gasoline and diesel exhaust (Erel et al., 1997; Geagea et al., 2008; Gioia et al., 2017); Australian and USA ore (Sangster et al., 2000); Indian ore (Deb et al., 1989); Indian Aerosol Literature (Bollhöfer and Rosman 2001; Kumar et al., 2016; Sen et al., 2016).

Figure 3. V/Pb versus Ni/Pb plot of Sagar, Kolkata and Bandel aerosols (this study). Delhi aerosols collected during a Middle Eastern dust storm event, the winter months (Kumar et al., 2016), and the ratios for coal from different countries are plotted for comparison (Xu et al., 2003).

Supplementary Section.

Table S1. Sampling details for the aerosol and coal samples.

AEROSOL SAMPLES								
Filter Number	Location	GPS Co-ordinate	Sampling Date	Pump Run Time ((in minutes)	Average Temp. (in degree C)	Average Relative Humidity (in %)	Rainfall (in mm)	PM₁₀ conc (in ug/m³)
A1	Sagar Island		7/9/2016	1440	29	88	0	49
A2	Sagar Island	21.38.328 N	8/9/2016	1440	30	83	0	42
A3	Sagar Island	88.04.465 E	9/9/2016	1440	31	84	2	49
A4	Sagar Island		10/9/2016	1280	28	77	0	39
A5	Bandel		21/8/2016	1440	26	91	71	49
A6	Bandel	22.54.996 N	22/8/2016	1440	26	94	4	42
A7	Bandel	88.23.257 E	23/8/2016	1440	29	84	13	56
A8	Bandel		24/8/2016	1440	30	81	9	62
A9	Kolkata		18/9/2016	1654	30	82	1	30
A10	Kolkata		19/9/2016	1287	30	78	0	31
A11	Kolkata	22.31.647 N	21/9/2016	1402	30	80	0.9	36
A12	Kolkata	88.21.780 E	22/9/2016	1440	30	86	12	30
A13	Kolkata		15/9/2016	1440	30	76	0	90
A14	Kolkata		16/9/2016	1440	31	82	4	83
A15	Kolkata		17/9/2016	1482	31	87	34	40

COAL SAMPLES				
Sample Number	Age	GPS Co-ordinate	Basin	Location
C1	Lower Permian	22° 12' 17.65"N 78° 27' 28.59"E	Satpura Coal Basin	Narmada River Valley Coal Field, Madhya Pradesh
C2	Lower Permian	22° 14' 23.49"N 78° 56' 58.28"E	Satpura Coal Basin	Narmada River Valley Coal Field, Madhya Pradesh
C3	Lower Permian	23° 46' 28.92"N 86° 22' 36.81"E	Jharia Coal Basin	Damodar River Valley Coal Field, Jharkhand
C4	Lower Permian	23° 43' 44.51"N 86° 26' 23.23"E	Jharia Coal Basin	Damodar River Valley Coal Field, Jharkhand
C5	Upper Permian	23° 43' 50.26"N 86° 16' 22.62"E	Mahuda Coal Basin	Jharia Coal Field, Jharkhand

Table S2. Comparison between hot plate dissolution and microwave dissolution of coal ash.

Sample No,	Dissolution Method	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	Pb conc (ppm)
C4	Hot plate dissolution of ash	19.2233	15.7825	39.4460	1.2180	2.4993	144
C4	Microwave digestion	19.2109	15.7685	39.3989	1.2183	2.4986	156
C2	Hot plate dissolution of ash	19.0398	15.7384	39.3291	1.2097	2.4989	20
C2	Microwave digestion	19.0412	15.7499	39.3699	1.2089	2.4997	20.8

Table S3. Pearson's Correlation Coefficients (r) between different elements in Sagar aerosol.

	Pb	Th	U	V	Cr	Ni	Zn	Al	Cu	Cd	Fe	As
Pb	1.00											
Th	0.60	1.00										
U	0.80	0.83	1.00									
V	0.81	0.95	0.91	1.00								
Cr	0.88	0.28	0.71	0.54	1.00							
Ni	0.78	0.94	0.97	0.98	0.58	1.00						
Zn	0.97	0.65	0.72	0.84	0.74	0.76	1.00					
Al	0.05	0.83	0.45	0.62	-0.29	0.61	0.16	1.00				
Cu	0.72	0.52	0.35	0.64	0.35	0.49	0.87	0.22	1.00			
Cd	0.99	0.54	0.82	0.77	0.93	0.76	0.92	-0.02	0.62	1.00		
Fe	0.56	0.99	0.86	0.94	0.29	0.95	0.59	0.83	0.42	0.53	1.00	
As	0.12	0.14	-0.27	0.13	-0.28	-0.06	0.35	0.19	0.77	-0.02	0.02	1.00

Table S4. Pearson's Correlation Coefficients (r) between different elements in Kolkata aerosol with low Pb isotope ratios (sample numbers A11, A12, A13).

	Pb	Th	U	V	Cr	Ni	Zn	Al	Cu	Cd	Fe	As
Pb	1.00											
Th	0.56	1.00										
U	0.85	0.92	1.00									
V	0.68	0.99	0.97	1.00								
Cr	0.72	-0.17	0.24	-0.02	1.00							
Ni	1.00	0.59	0.86	0.70	0.69	1.00						
Zn	-0.79	-0.95	-0.99	-0.99	-0.13	-0.81	1.00					
Al	0.93	0.83	0.98	0.90	0.40	0.94	-0.96	1.00				
Cu	0.90	0.15	0.53	0.30	0.95	0.89	-0.44	0.67	1.00			
Cd	0.74	-0.14	0.27	0.01	1.00	0.71	-0.16	0.43	0.96	1.00		
Fe	0.44	0.99	0.85	0.96	-0.31	0.47	-0.90	0.74	0.01	-0.29	1.00	
As	0.36	0.97	0.80	0.93	-0.40	0.39	-0.86	0.68	-0.08	-0.37	1.00	1.00

Table S5. Pearson's Correlation Coefficients (r) between different elements in Kolkata aerosol with high Pb isotope ratios (sample numbers A9, A10, A14, A15).

	Pb	Th	U	V	Cr	Ni	Zn	Al	Cu	Cd	Fe	As
Pb	1.00											
Th	0.15	1.00										
U	0.34	0.96	1.00									
V	0.47	0.93	0.99	1.00								
Cr	0.70	-0.57	-0.35	-0.24	1.00							
Ni	-0.48	0.15	0.22	0.08	-0.31	1.00						
Zn	-0.27	0.78	0.78	0.67	-0.65	0.72	1.00					
Al	-0.31	0.36	0.46	0.33	-0.31	0.97	0.84	1.00				
Cu	0.01	0.88	0.92	0.84	-0.51	0.58	0.96	0.76	1.00			
Cd	0.34	0.97	0.93	0.95	-0.43	-0.09	0.61	0.15	0.76	1.00		
Fe	0.04	0.98	0.95	0.90	-0.60	0.35	0.90	0.55	0.96	0.90	1.00	
As	-0.43	-0.18	0.01	-0.11	0.90	1.00	0.64	0.93	0.41	-0.38	0.08	1.00

Table S6. Pearson's Correlation Coefficients (r) between different elements in Bandel aerosol.

	Pb	Th	U	V	Cr	Ni	Zn	Al	Cu	Cd	Fe	As
Pb	1.00											
Th	0.83	1.00										
U	0.85	1.00	1.00									
V	0.79	0.99	0.99	1.00								
Cr	0.96	0.87	0.90	0.87	1.00							
Ni	-0.04	0.32	0.24	0.22	-0.15	1.00						
Zn	0.98	0.84	0.85	0.78	0.91	0.12	1.00					
Al	-0.06	0.31	0.24	0.21	-0.17	1.00	0.10	1.00				
Cu	0.91	0.70	0.75	0.72	0.96	-0.41	0.82	-0.43	1.00			
Cd	0.86	0.48	0.49	0.38	0.71	-0.08	0.88	-0.11	0.71	1.00		
Fe	0.74	0.93	0.90	0.86	0.69	0.61	0.82	0.60	0.47	0.50	1.00	
As	0.81	0.82	0.79	0.71	0.68	0.54	0.90	0.52	0.50	0.74	0.94	1.00

Figure S1. 24 hour and 72 hour air mass back trajectories in the sampling location during the sampling period. $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are given in the boxes, colour coded with the back trajectory paths.