

Lead isotopic fingerprinting of aerosols to characterize the sources of atmospheric lead in an industrial city of India



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ABSTRACT

Anthropogenic Pb in the environment is primarily sourced from combustion of fossil fuel and high-temperature industries such as smelters. Identifying the sources and pathways of anthropogenic Pb in the environment is important because Pb toxicity is known to have adverse effects on human health. Pb pollution sources for America, Europe, and China are well documented. However, sources of atmospheric Pb are unknown in India, particularly after leaded gasoline was phased out in 2000. India has a developing economy with a rapidly emerging automobile and high temperature industry, and anthropogenic Pb emission is expected to rise in the next decade. In this study, we report on the Pb-isotope compositions and trace metal ratios of airborne particulates collected in Kanpur, a large city in northern part of India. The study shows that the PM₁₀ aerosols had elevated concentration of Cd, Pb, Zn, As, and Cu in the Kanpur area, however their concentrations are well below the United States Environmental Protection Agency chronic exposure limit. Lead isotopic and trace metal data reveal industrial emission as the plausible source of anthropogenic Pb in the atmosphere in Kanpur. However, Pb isotopic compositions of potential source end-members are required to fully evaluate Pb contamination in India over time. This is the first study that characterizes the isotopic composition of atmospheric Pb in an Indian city after leaded gasoline was phased out by 2000.

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1. Introduction

The anthropogenic flux of lead (Pb) in the surface environment (4309 ± 72 Gg/yr) is almost an order of magnitude higher than its corresponding natural flux (Sen and Peucker-Ehrenbrink, 2012). Such large input of human induced Pb into the environment has significantly altered the global cycle of Pb, and therefore anthropogenic lead signature can be observed everywhere (Wolff and Suttie, 1994; Bollhöfer and Rosman, 2000, 2001; Lee et al., 2011). Because Pb is a toxic metal with adverse effect on human health (Needleman, 2004), it is important to identify the sources and pathways of Pb in the atmosphere.

Anthropogenic Pb in the environment is primarily sourced from gasoline combustion and high temperature industries like smelters, mining, and coal combustion (Pacyna et al., 2009). Anthropogenic

Pb in the last century was primarily sourced from combustion of leaded gasoline. For example in 1971, 83% of the Pb emission from fossil fuel burning in India was attributed to combustion of leaded gasoline (Lee et al., 2014). However leaded gasoline was phased out from most of the countries by 2000 (UNEP, 2007), and as a result, Pb emissions from gasoline combustion have significantly decreased (Lee et al., 2014). In contrast, Pb emissions from coal combustion have increased by an order of magnitude for developing countries like India and China (Lee et al., 2014), which are also some of the largest consumers of coal. A substantial body of published information already exists on the magnitude and sources of Pb pollution in North America (Sturges and Barrie, 1987; Graney et al., 1995; Bollhöfer and Rosman, 2001; Gross et al., 2012), Europe (Monna et al., 1997; Vile et al., 1999; Bollhöfer and Rosman, 2001; Novák et al., 2002), and China (Wong and Li, 2004; Chen et al., 2005; Lee et al., 2007; Cheng and Hu, 2010). However, only few studies have investigated the sources of atmospheric Pb in India, despite a rapidly emerging high-temperature and automobile industry in and around India (Fig. 1) that are likely sources of anthropogenic Pb

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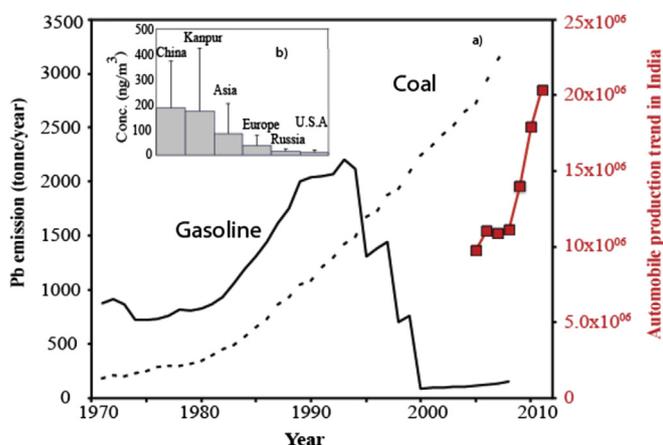


Fig. 1. (a) Historical Pb emission from coal and gasoline combustion (left y-axis) for India (Lee et al., 2014), and automobile production trends for India (right y-axis). Automobile includes passenger vehicles, commercial vehicles, three wheelers and two wheelers (Sen, 2013). (b) The inset bar diagram shows the average Pb concentration in airborne particulate matters from various places (Bollhöfer and Rosman, 2001).

(Sen, 2013).

The sources of Pb in the environment can be traced by using the Pb isotopic compositions (Komárek et al., 2008). Lead has four naturally occurring stable isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb). The isotopes ^{206}Pb , ^{207}Pb , ^{208}Pb are radiogenic daughters of radioactive parent isotopes ^{238}U , ^{235}U and ^{232}Th , respectively; ^{204}Pb is stable and not produced by radioactive decay. The Pb-isotope compositions of terrestrial materials record the time-integrated fractionation of the uranium/lead (U/Pb) and thorium/lead (Th/Pb) ratios in the sources. Due to the extremely long half-life of the parent isotopes (700 Ma for ^{235}U to 14 Ga for ^{232}Th) the Pb-isotope compositions of different terrestrial materials remain practically constant for the time interval associated with anthropogenic processes. Moreover, there has been no evidence for biological or physiochemical fractionation of Pb isotopes. As such, the Pb isotope composition of aerosols can be used to trace their origin from various terrestrial sources and therefore is used over the last few decades for Pb source apportionment (e.g., Sturges and Barrie, 1987; Bollhöfer and Rosman, 2000, 2001; Komárek et al., 2008; Lee et al., 2014).

A difficulty in using Pb-isotopes as source tracers arise when the Pb isotope compositions of potential source end-members (terrestrial or anthropogenic) are not well defined, or overlap, or the anthropogenic Pb is derived from multiple sources over a period of time (Cheng and Hu, 2010). For example, coal from various regions (with different isotopic composition) is often blended according to industry requirements leading to a wide range in Pb-isotope composition of the combustible coal. Also, fossil fuels are internationally traded (United Nations Statistics Division, <http://comtrade.un.org/db/default.aspx>). India imported almost 135 million tons of coal in 2012–2013 (Government of India; Ministry of statistics and programme implementation, <http://www.mospi.gov.in>), therefore the geochemical characteristics of Indian-combusted coal may be far from unique. In such cases, a single proxy approach in tracing anthropogenic inputs of Pb could be challenging, and multi proxies may be more useful for Pb source apportionment studies. Here, we report chemical data on the combined trace element concentrations such as cadmium (Cd), arsenic (As), zinc (Zn), copper (Cu), vanadium (V), cesium (Cs), rare earth elements (REE) etc. and Pb isotope ratios of airborne particulates collected in Kanpur, India. The main objective of the study is to provide constrains on the sources of atmospheric Pb in an Indian

industrial city.

2. Materials and methods

Aerosols were collected using a high volume (1000 L/min) atmospheric aerosol sampler (Envirotech PM₁₀ sampler, model number: APM 460 DXNL) in March 2013. The sampler was placed on roof of a 15 m tall building in the Indian Institute of Technology Kanpur campus (latitude: 26°30′47.69″ N; longitude: 80°13′56.39″ E). The sampling site was ~16 Km northwest of the Kanpur City, one of the largest industrialized centers in the state of Uttar Pradesh, India. The site is located ~5 Km north of a coal fired thermal power plant (Panki Thermal Power Plant) and a kilometer west of National Highway (NH-91). The sampler was operated for ~9 h each day. Samples were collected between 9:00 AM to 6:00 PM (Indian Standard Time) and approximately 530 m³ of air per sample was pumped through each 20 cm × 25 cm quartz fiber Whatman™ filter. Eleven samples were collected, and the dates of sample collection are reported in Table 1. It is noteworthy to mention that these samples only represent the daytime conditions, and not daily levels. After collection, the aerosol-laden filters were powdered using a preconditioned ceramic shatter box at Woods Hole Oceanographic Institution, USA. The powdered quartz fiber filters, including blank filters were used for trace metal concentrations and Pb isotope analyses.

Metal concentrations and Pb isotope analyses were performed at the Center for Elemental Mass Spectrometry, Department of Earth and Ocean Sciences, University of South Carolina. For metal concentration determinations, the filters were leached in single use pre-cleaned polypropylene vials in a temperature controlled acid resistant digestion block using HNO₃ and H₂O₂ mixtures following the Environmental Protection Agency (EPA) protocol 3050B (Edgell, 1996). This method liberates the strongly bound metals from the silicate particulates. As our study is focused on determining the concentrations of the anthropogenically derived metals, hydrofluoric acid digestion was avoided so as not to attack the filter or the silicate fraction (presumably aeolian dust) adhered on the filter, which would otherwise dilute the adsorbed metals signal, and would impose a rock-type metal and Pb-isotope signature to the signal. A gravimetrically determined aliquot of the digest was diluted, spiked with 2 ppb In and run for trace element concentrations. Three blank filters were processed, along with the samples, to quantify the total procedural blanks for the trace metals.

The concentrations were determined on a THERMO ELEMENT 2 Magnetic Sector ICPMS following established techniques in this lab for environmental samples (Das et al., 2013; Moskalski et al., 2013). Different mass resolution modes were used to optimize separation of measured isotopes from interfering polyatomic species (e.g. ^{75}As from $^{40}\text{Ar}^{35}\text{Cl}$) and improve detection limits. Concentrations were determined using an United States Geological Survey external rock standard BHVO-2, using the recommended concentrations reported in GEOREM (Jochum et al., 2005; <http://georem.mpch-mainz.gwdg.de/>) and a multi-element standard solution (High Purity Standards) diluted to the appropriate concentrations, depending on the signal range of the analyzed isotopes of each element in the samples. The final concentrations were blank – corrected using the average blank filter concentrations. Average blank corrections were less than 2% for Cd, Cs, Pb, As, less than 6% for V, Zn, and 14% for Cu. Blank corrections for aluminium (Al) and REE concentrations were in the order of 20–50%, consistent with the fact that those elements dominantly reside in the silicate minerals that were not quantitatively dissolved in our method. Blank-corrected concentrations were converted to mass/m³ of each element (ng/m³).

For the Pb isotope analyses, a portion of the filter was leached

Table 1
Trace element concentrations (ng/m³) leached out from PM₁₀ aerosols.

Sample no. day/month/year	01/03/13	07/03/13	08/03/13	12/03/13	12/03/13*	13/03/13	14/03/13	15/03/13	16/03/13	19/03/13	21/03/13
Volume of air samples (m ³)	528	528	528	534	534	528	545	545	545	534	528
Cd	4.58	4.29	3.50	1.71	1.81	6.97	6.41	2.18	0.82	9.09	1.37
Pb	96.0	192.2	63.8	75.1	79.2	249.9	911.9	79.6	41.6	83.5	76.6
As	2.86	6.94	8.19	2.94	3.48	10.66	4.88	2.85	1.35	7.09	2.60
Zn	183.3	436.8	198.4	123.4	136.9	363.1	380.3	221.2	195.3	118.7	119.6
Cu	25.29	42.14	13.28	12.30	21.51	34.17	60.41	47.02	69.36	10.72	17.33
V	3.99	5.85	3.87	3.46	3.80	5.90	6.36	4.42	2.25	3.93	3.34
Cs	0.18	0.18	0.16	0.21	0.21	0.35	0.30	0.28	0.12	0.20	0.15
Rb	2.09	2.81	2.29	3.28	3.25	6.20	4.36	4.30	1.72	2.19	1.99
Th	0.23	0.15	0.15	0.24	0.32	0.37	0.48	0.39	0.13	0.19	0.20
Al	1961	1542	367	939	1107	1527	1921	3292	930	2200	955
La	0.55	0.37	0.18	0.45	0.54	1.19	1.22	0.93	0.29	0.53	0.41
Ce	1.09	0.70	0.38	0.99	1.17	2.27	2.34	1.93	0.57	1.05	0.92
Pr	0.12	0.07	0.04	0.11	0.13	0.26	0.27	0.22	0.06	0.11	0.10
Nd	0.44	0.25	0.16	0.44	0.48	0.90	0.98	0.81	0.21	0.39	0.39
Sm	0.11	0.07	0.05	0.11	0.12	0.17	0.22	0.18	0.05	0.09	0.09
Eu	0.02	0.01	0.01	0.02	0.03	0.04	0.04	0.04	0.01	0.03	0.02
Gd	0.11	0.06	0.05	0.12	0.12	0.20	0.23	0.20	0.06	0.11	0.11
Dy	0.07	0.04	0.03	0.07	0.09	0.11	0.15	0.11	0.03	0.06	0.05
Ho	0.01	0.01	0.01	0.01	0.02	0.02	0.03	0.02	0.01	0.01	0.01
Er	0.04	0.02	0.02	0.03	0.04	0.06	0.07	0.06	0.02	0.03	0.02
Tm	0.004	0.003	0.002	0.004	0.006	0.008	0.01	0.008	0.003	0.005	0.003
Yb	0.03	0.02	0.01	0.03	0.03	0.05	0.06	0.05	0.02	0.03	0.02
Lu	0.005	0.003	0.002	0.005	0.005	0.007	0.010	0.006	0.002	0.004	0.003

* Duplicate analysis.

with 0.4 N Hydrobromic (HBr) acid at 100 °C for 2 h in Perfluoroalkoxy alkane (PFA) beakers. The solution was collected and dried in clean PFA beakers in a double High-Efficiency Particulate Arrestance (HEPA) filtered airflow box. Lead was extracted using hydrobromic and nitric (HBr–HNO₃) mixed acids in anion resin (Manhes et al., 1978; Bizimis et al., 2013). Three unused quartz fiber filters treated identical to the unknowns were processed to assess the entire Pb procedural blank. Pb isotope ratios were determined on a THERMO Neptune Multi Collector-Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) with the thallium (Tl) addition method (White et al., 2000), using $^{203}\text{Tl}/^{205}\text{Tl} = 0.418911$ to correct for instrumental mass fractionation. The NBS-981 Pb standard was determined at $^{206}\text{Pb}/^{204}\text{Pb} = 16.936 \pm 0.0019$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4901 \pm 0.0011$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.696 \pm 0.0036$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.16672 \pm 0.00005$, $^{207}\text{Pb}/^{206}\text{Pb} = 0.91461 \pm 0.00004$ (2 standard deviations, n = 12). These values are within the error associated to those reported for NBS-981 (Todd et al., 1996), so no additional correction was applied to the data. The samples were run at the same Pb/Tl ratios as the standards and at similar beam intensities to avoid any analytical bias. The internal precision of the

Pb-isotope ratios is always better than the external reproducibility of the standards. The Pb isotope composition of a full procedural duplicate sample filter (Table 2, sample 12/3/13) was reproduced at the same level as the NBS-981 standard. The total Pb signal in each of the three unused quartz fiber filters treated identical to the unknowns was ~1% of the Pb signal from the processed sample. Therefore, no blank correction was applied to the Pb isotope compositions.

3. Results and discussion

3.1. Trace element and Pb isotope systematics

The analyzed metal concentrations are given in Table 1. The Pb concentration in the airborne particulates generally varies between 42 and 250 ng/m³, with only one sample with very high (912 ng/m³) Pb concentration. These concentrations are well below the United States Environmental Protection Agency (USEPA) chronic exposure limit (1500 ng/m³) and similar to previously reported values in India (Tripathi, 1994; Ghosh et al., 2014). The ambient Pb

Table 2
Pb isotope compositions.

Sample no.	$^{206}\text{Pb}/^{204}\text{Pb}$	2se	$^{207}\text{Pb}/^{204}\text{Pb}$	2se	$^{208}\text{Pb}/^{204}\text{Pb}$	2se	$^{208}\text{Pb}/^{206}\text{Pb}$	2se	$^{207}\text{Pb}/^{206}\text{Pb}$	2se
01/03/13	17.5645	0.0004	15.5786	0.0005	37.4514	0.0014	2.13224	0.00004	0.88694	0.00001
07/03/13	17.6093	0.0005	15.5713	0.0006	37.4959	0.0014	2.12933	0.00004	0.88427	0.00001
08/03/13	17.6639	0.0006	15.5877	0.0007	37.5630	0.0019	2.12657	0.00005	0.88247	0.00001
12/03/13	17.6043	0.0005	15.5835	0.0006	37.4897	0.0017	2.12958	0.00004	0.88522	0.00001
12/03/13*	17.5997	0.0006	15.5825	0.0006	37.4839	0.0016	2.12980	0.00004	0.88539	0.00001
13/03/13	17.5255	0.0004	15.5804	0.0004	37.4158	0.0013	2.13496	0.00004	0.88902	0.00001
14/03/13	17.4228	0.0004	15.5745	0.0005	37.3031	0.0015	2.14106	0.00005	0.89391	0.00001
15/03/13	17.6222	0.0006	15.5851	0.0006	37.5031	0.0019	2.12816	0.00004	0.88440	0.00001
16/03/13	17.7019	0.0005	15.5908	0.0005	37.5801	0.0014	2.12296	0.00003	0.88075	0.00001
19/03/13	17.6504	0.0006	15.5844	0.0007	37.5668	0.0019	2.12839	0.00004	0.88295	0.00001
21/03/13	17.6115	0.0008	15.5841	0.0007	37.5481	0.0019	2.13201	0.00003	0.88488	0.00001
	$^{206}\text{Pb}/^{204}\text{Pb}$	2stdev	$^{207}\text{Pb}/^{204}\text{Pb}$	2stdev	$^{208}\text{Pb}/^{204}\text{Pb}$	2stdev	$^{208}\text{Pb}/^{206}\text{Pb}$	2stdev	$^{207}\text{Pb}/^{206}\text{Pb}$	2stdev
Av. Filter Blank (n = 3)	18.16	0.05	15.591	0.005	37.81	0.08	2.0827	0.0019	0.8587	0.0020
NIST – 981 (n = 12)	16.9360	0.0019	15.4901	0.0011	36.696	0.004	2.16672	0.00005	0.91461	0.00004

*Duplicate analysis. 2se is the internal precision of each analyses as: $2se = 2 \times \text{standard deviation}/\sqrt{(n)}$, where n = number of scans, typically 35.

concentration in Kanpur is similar to other Asian countries (Fig. 1) such as Pakistan, Vietnam and UAE, but much higher than North America and European cities (Bollhöfer and Rosman, 2001). The other heavy metals vary by factor of 10 or less, e.g. Cd = 0.8–9.1 ng/m³, As = 1.3–10.7 ng/m³, Zn = 118.7–436.8 ng/m³, Cu = 10.7–69.4 ng/m³, and all are below the USEPA chronic exposure limits (e.g., Cd = 10 ng/m³, As = 15 ng/m³) and Occupational Safety and Health Administration's (OSHA) permissible exposure limits (e.g., Zn = 5000 ug/m³ and Cu = 1000 ug/m³). Although not shown here, lead concentration in the aerosols generally correlates positively with Cd, As, Zn and Cu, but no correlation with the Rare Earth Element (REE) and Al is observed. Similarly, the REE show less than one order of magnitude variability and highly correlate with each other ($R^2 > 0.9$). The trace element systematics did not show any relationship with the air mass back trajectories, which indicates that heavy metal chemistry of airborne particulate matters can only be explained by admixing different proportions of natural and anthropogenic sources.

Trace element systematics can be used to delineate natural versus anthropogenic sources. For example, the average Pb/Cu ratio of natural aeolian dust composition is 1.77 (Lawrence and Neff, 2009), while the aerosols in Kanpur have much higher Pb/Cu ratios (Pb/Cu = 5.4 ± 3.7 ; $n = 11$, 1 S.D.). To a first order, this implies a non-aeolian dust origin for Pb, which in turn is attributed to anthropogenic sources. Other trace element ratios can also be used to differentiate between natural and anthropogenic signatures. As the chemical composition of aeolian dust in the vicinity of Kanpur is not known, we used the average chemical composition of upper continental crust (McLennan, 2001) as a proxy for aeolian dust composition because dust is derived from soil, which is a weathered product of upper continental crust. As the chemical composition of soil is within a factor of 2–3 of the average upper continental crust (Schütz and Rahn, 1982), the assumption is justified. Using the average upper continental crust as a chemical proxy for natural aeolian dust composition, it is observed that all ratios involving the heavy metals (Pb, Cu, Cd, Zn, As, and V) are very different than the upper continental crustal signature. For example, the average Cd/Zn and As/V ratios of aeolian dust composition are 0.001 and 0.015 respectively (McLennan, 2001), whereas the aerosols in Kanpur have much higher Cd/Zn and As/V ratios (Cd/Zn = 0.004–0.08, As/V = 0.6–2.11). This suggests a strong anthropogenic origin for As and Cd as well. In contrast, all REE ratios in the aerosols are similar to the upper continental crust composition. For example, the Sm/Nd ratio of aeolian dust is around 0.17 (McLennan, 2001), whereas the Sm/Nd ratio of Kanpur aerosols varies in the range 0.19–0.33. Therefore the REEs primarily have a crustal (natural) origin. The positive correlations of Al with REEs ($R^2 > 0.5$, not shown), and the lack of correlation of Al, or REE with heavy metals further support the findings that the heavy metals are primarily sourced from anthropogenic sources, whereas the REEs have a crustal origin.

To demonstrate the extent to which the aerosols were influenced with natural vs. anthropogenic contributions, enrichment factors (EF) were calculated with respect to natural sources represented by the Al concentration of upper continental crust. Fig. 2 shows that Cd, Pb, As, Zn, and Cu concentrations in the filters are 10–1000 times enriched relative to concentrations expected if these metals were solely derived from continental crustal material, in this case leaching of aeolian dust from the filters. This strongly suggests a dominant contribution of the heavy metals from anthropogenic sources in the Kanpur aerosols. In turn, the EF values of the REEs are very close to the crustal signature, consistent with a dominant origin from aeolian dust. These enrichments of Cd, As, Zn and Cu in urban dusts can be derived from traffic sources such as vehicle exhaust particles, tire wire particles, and break lining wire

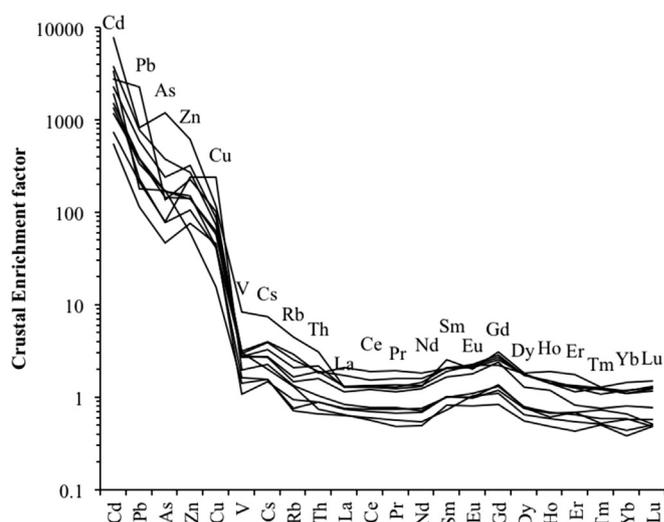


Fig. 2. Natural vs. anthropogenic sources. The enrichment factors (EF) were calculated with respect to natural sources represented by the Al concentration of upper continental crust (McLennan, 2001). $EF_X = (X/Al)_{\text{aerosols}} / (X/Al)_{\text{crust}}$, where X/Al is the ratio of element X to Al. Elements that have approximately crustal X/Al ratios in the filters will have approximately EF=1. These elements should be primarily sourced from the upper continental crust. In contrast, elements with high EF (here taken as EF > 10) are decoupled from the upper continental crust due to anthropogenic contributions to the filtered particulates. The figure shows that Cd, Pb, As, Zn and Cu are dominated by anthropogenic sources.

particles, as well as industrial sources like metallurgical industries, auto repair shops, and fossil fueled power plants (Wei and Yang, 2010).

Pb-isotope ratios are reported on Table 2. The $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ vary narrowly between 0.881–0.894 and 2.123–2.141 respectively, and are highly correlated with each other ($R^2 > 0.95$, not shown). This suggests small variance in the sources of Pb during the sampling period. The highly linear correlation further implies that Pb is source from two dominant endmembers (i.e. the line is interpreted as binary mixing). Fig. 3 shows that the Pb isotopic compositions of the Kanpur aerosols overlap with other aerosol measurements, particularly from Europe and some Asian countries,

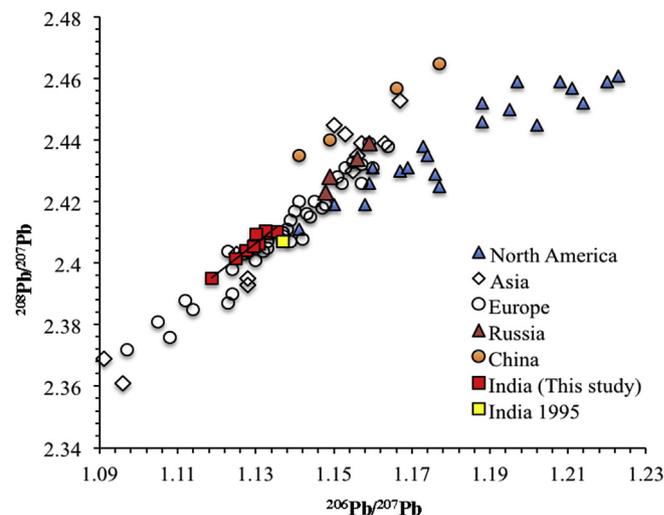


Fig. 3. Triple isotope plot for the Pb in Kanpur (India) and the aerosols collected from northern hemisphere (Bollhöfer and Rosman, 2001). Pb isotopic composition of aerosols collected in 1995 from Ahmedabad (India) shows slightly higher $^{208}\text{Pb}/^{206}\text{Pb}$ value compared to the Kanpur aerosols.

but very different than China and North America. This difference in Pb isotopic compositions could be attributed to contributions from different anthropogenic source(s) or by an admixture of different proportions of anthropogenic sources to a natural source. The $^{207}\text{Pb}/^{206}\text{Pb}$ ratios of an eroding continental crust ranges between 0.808 and 0.857 (Millot et al., 2004). As the Kanpur samples have significantly more radiogenic ^{207}Pb ($^{207}\text{Pb}/^{206}\text{Pb} = 0.880\text{--}0.887$, Table 2), it indicates that Pb is not dominantly sourced from eroding crustal materials (e.g. aeolian dust), consistent with the trace element concentration inferences above.

3.2. Sources of anthropogenic Pb

Pb isotope ratios ($^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$) can be used in Pb source identification (Chow and Johnstone, 1965; Mukai et al., 1993; Rosman et al., 1994; Planchon et al., 2003; Inoue and Tanimizu, 2008; Lee et al., 2011). The major anthropogenic sources of Pb are (I) vehicle exhausts; (II) coal combustion products; and (III) industrial emissions (Lee et al., 2014). The anthropogenic end-members show a large variation (Fig. 4) in the Pb isotope systematics (Chow and Johnstone, 1965; Chiaradia et al., 1997; Erel et al., 1997; Monna et al., 1997; Farmer et al., 1999; Veron et al., 1999; Hansmann and Köppel, 2000; Sangster et al., 2000; Novák et al., 2002; Rabinowitz, 2002; Ettler et al., 2004; Rabinowitz, 2005; Cloquet et al., 2006; Geagea et al., 2008; Díaz-Somoano et al., 2009). For example, vehicle exhausts have $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ranging between 0.862–0.935 and 2.095–2.198 respectively (Erel et al., 1997; Hansmann and Köppel, 2000; Geagea et al., 2008). Atmospheric lead pollution was attributed to vehicle exhausts primarily because of the combustion of leaded gasoline. In order to understand the Pb isotopic composition of leaded gasoline, it is important to understand the source of lead in gasoline products. Lead was used as an additive in the gasoline, and therefore its compositional range can be predicted (Bollhöfer and Rosman, 2000). Lead was added in the form of alkyl-Pb, which is supplied

by Associated Octel and Ethyl Corporation, the two major suppliers of alkyl-Pb in the world (Bollhöfer and Rosman, 2001). They use Pb ores from the Broken Hill type deposit in Australia and Mississippi Valley type Pb deposit in USA, and both have distinct $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ signatures (Fig. 4). The Pb isotopic composition of Indian aerosols from this study plot close to the Broken Hill and Mississippi Valley type ore deposits mixing line, as well as overlaps with the Pb isotopic composition of leaded gasoline (Fig. 4) suggesting that combustion of leaded gasoline can be a dominant source of Pb in Kanpur. While leaded gasoline was phased out from India in 2000 (Singh and Singh, 2006), countries around India such as Afghanistan, Iran and Myanmar still use leaded gasoline products. Since the residence time of Pb aerosols in the atmosphere is around ~5–10 days (Sturges and Barrie, 1987), anthropogenic Pb could be readily dispersed from countries that use leaded gasoline. To understand the extent of transboundary pollution, air mass trajectories were computed 12 h back in time at 6 h intervals at an elevation (height above ground level-AGL) of 15 m, 500 m and 1000 m during the sampling period using the HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) data from the U.S. National Oceanic and Atmospheric Administration's (NOAA) website (Draxler and Rolph, 2003). The archived data file GDAS1 was used for computations. The air mass back trajectory models clearly reveal that the air masses are coming mostly from northwestern part of India (Supplementary Fig. S1), and therefore Pb is not a transboundary pollutant. It is also possible that the Pb emitted from leaded gasoline has remained in the local environment, and the observed Pb signature can be attributed to recirculation of historical source (Morton-Bermea et al., 2011; Flegal et al., 2010). For example, it has been shown that although the use of leaded gasoline was banned in Mexico since 1997, recent Pb pollution source in Mexico can still be traced back to the historical use of Pb in gasoline (Morton-Bermea et al., 2011). Since automobile emission was a predominant source of lead pollution before leaded gasoline was phased out from India in 2000 (Tripathi, 1994), re-suspension of historic Pb sourced from leaded gasoline could be the source of anthropogenic Pb in Kanpur air. As the Pb isotopic composition of Indian leaded gasoline used prior to 2000 is unknown, additional proxies are required to fully investigate the role of vehicle emission as Pb polluting source.

Another important Pb pollution source is coal combustion. Fig. 4 also plot the Pb isotopic composition of coal from different parts of the world (Monna et al., 1997; Farmer et al., 1999; Novák et al., 2002; Díaz-Somoano et al., 2009). Coals show a wide range in Pb isotope ratios that generally fall below the Broken Hill–Mississippi Valley type Pb deposits mixing line (Fig. 4). The isotopic composition of Pb in Kanpur aerosols is different than the Pb isotopic composition of the coal or even coal fly ash. The average $^{207}\text{Pb}/^{206}\text{Pb}$ for coal is 0.837 ± 0.023 ($n = 86$, 2.SD) (Monna et al., 1997; Farmer et al., 1999; Novák et al., 2002; Díaz-Somoano et al., 2009) lower than the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios of the Kanpur aerosols ($^{207}\text{Pb}/^{206}\text{Pb} = 0.885 \pm 0.007$; $n = 11$, 2.SD). Therefore Pb isotopic data of coals around the world indicates that contributions from coal are unlikely the major source of atmospheric Pb in Kanpur, the caveat being that Pb isotope composition of Indian coals are not currently available to further evaluate this idea.

Indian ore deposits have $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ranging between 0.898–0.966 and 2.152–2.232 respectively (Sangster et al., 2000), very similar to the Australian ore deposits. As the only source of industrial Pb is ore deposits, it is expected that the isotopic signature of industrial Pb from mining, smelter and waste incineration would have an isotopic signature similar to that of ore deposits. The Pb isotopic composition of Indian aerosol plots close to that of the Indian ore deposits, with slightly more radiogenic ^{208}Pb and ^{206}Pb . The Pb isotope data seem to rule out coal

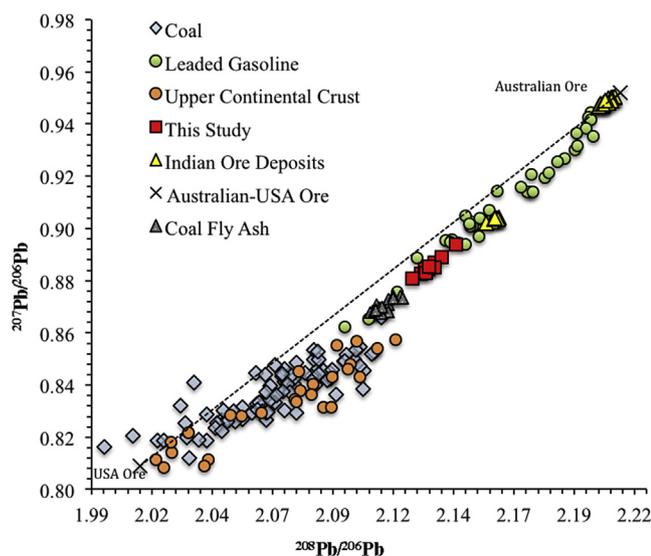


Fig. 4. $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ of Indian aerosols in comparison to literature values for natural and anthropogenic end members. References: coal (Farmer et al., 1999; Novák et al., 2002; Díaz-Somoano et al., 2009); leaded gasoline (Chow and Johnstone, 1965; Erel et al., 1997; Monna et al., 1997; Hansmann and Köppel, 2000; Geagea et al., 2008); fly ash (Hansmann and Köppel, 2000; Geagea et al., 2008); Australian and USA ore (Sangster et al., 2000); Indian ore (Deb et al., 1989); and continental crust (Millot et al., 2004). 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 dashed line.

combustion products as a major source of Pb, however, the data was unable to differentiate between leaded gasoline and industrial emission sources since their isotopic compositions have overlapping ranges, as well as these source end-members in India are not well constrained.

In order to understand the source of atmospheric Pb, we further investigated trace metal systematics, since anthropogenic end-members should have distinct trace metal signatures. For example, roasting and smelting of ores in non-ferrous metal smelters releases more volatile metal pollutants such as Cd, Cu, Zn, and Pb, whereas coal combustion primarily releases Pb and As (Pacyna, 1987). Fig. 5 shows that coal combustion products and vehicle exhausts in and around Kanpur are characterized by a higher Cu/Pb ratio compared to the aerosols (<0.5), whereas non-coal burning industrial effluents and emissions around the study area have trace metal characteristics similar to the aerosols (e.g., Rawat et al., 2009; Gowd et al., 2010). This is also supported by other trace metal ratios. For example, coal is usually enriched ($\mu\text{g/g}$ level) in V and V/Pb ratio of coal is always >1, whereas vehicle exhaust has a V/Pb ratio always <1, and non-coal burning industrial effluents such as tanneries have V/Pb ratio <<1 (Gowd et al., 2010). The aerosols collected in Kanpur have very low V/Pb ratios (0.01–0.06), which indicates that the geochemical signature of the Kanpur aerosols could be sourced from non-coal burning industries.

4. Conclusions

The Pb, Cd, As, Zn and Cu concentrations are significantly enriched (10–1000 times) in the Kanpur aerosols when compared to the average upper continental crust, although their concentrations are below the USEPA chronic exposure limits. The study demonstrates that Pb source apportionment based only on Pb isotopes could be challenging, and trace metal ratios can be combined with Pb isotopes as additional source tracers. Combination of Pb isotope and trace metal data shows that the major plausible source of anthropogenic Pb in Kanpur aerosols is from industrial emissions. However, in order to fully investigate the applicability of Pb isotopes in tracing Pb pollution sources in India, a larger dataset including Pb isotopic composition of each potential end-members is needed to track and evaluate Pb apportionment in India over time. This is the first study that characterizes the isotopic

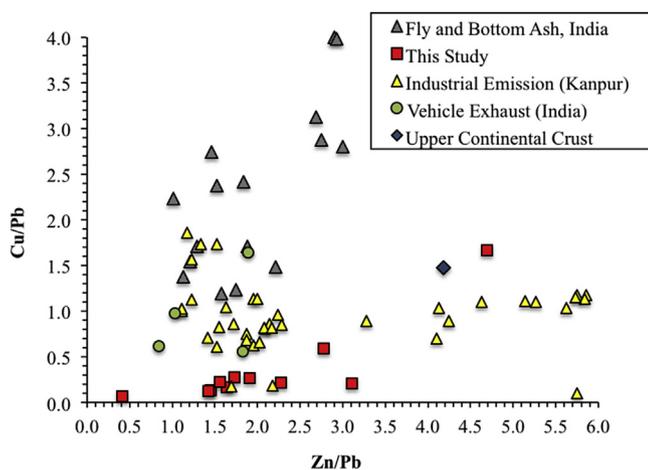


Fig. 5. Zn/Pb versus Cu/Pb ratios of Kanpur aerosols (this study) in comparison to literature values for natural and anthropogenic end members. References: industrial emission (Rawat et al., 2009; Gowd et al., 2010); fly ash bottom ash (Reddy et al., 2005; Sarkar et al., 2006; Sushil and Batra, 2006); vehicle exhausts (Banerji, 2003); and upper continental crust (McLennan, 2001).

composition of atmospheric Pb in an Indian city after leaded gasoline was phased out by 2000, and the study provides the baseline and a framework for tracing Pb pollution sources in India using the isotopic composition of Pb.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2016.01.005>.

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