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# ISOTOPES AS TRACERS OF SOURCES OF LEAD AND STRONTIUM IN AEROSOLS (TSP & PM<sub>2.5</sub>) IN BEIJING

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## ABSTRACT

Even after its being phased out in gasoline in the late 90's, lead (Pb) is still present at relatively high levels in the atmosphere of Beijing, China ( $0.10\text{-}0.18 \mu\text{g}\cdot\text{m}^{-3}$ ). Its origin is subject to debate as several distinct sources may contribute to the observed pollution levels. This study proposes to constrain the origin(s) of Pb and strontium (Sr) in aerosols, by coupling both Pb and Sr isotope systematics. The characterisation of the main pollution sources (road traffic, smelters, metal refining plants, coal combustion, cement factories, and soil erosion) shows that they can unambiguously be discriminated by the multi-isotope approach ( $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ ). The study of total suspended particulates (TSP) and fine particles ( $\text{PM}_{2.5}$ ) from Beijing and its vicinity indicates that both size fractions are controlled by the same sources. Lead isotopes indicate that metal refining plants are the major source of atmospheric lead, followed by thermal power stations and other coal combustion processes. The role of this latter source is confirmed by the study of strontium isotopes. Occasionally, emissions from cement plants and/or input from soil alteration are isotopically detectable.

**Keywords:** *Air pollution, Lead isotopes, Strontium isotopes, Aerosol sources*

## INTRODUCTION

High concentrations of fine particles are found in the air of big cities, which can be up to  $300 \mu\text{g}\cdot\text{m}^{-3}$  for  $\text{PM}_{10}$  particles (Particulate Matter with a diameter  $<10 \mu\text{m}$ ; Seinfeld and Pandis, 1997). As fine atmospheric particles (e.g.  $\text{PM}_{2.5}$ ) have a damaging effect on public health (e.g. Kappos *et al.*, 2004), they have recently become a cause of major concern. Isotope compositions have proved to be reliable tracers of the origin of aerosols in the atmosphere, including urban air (e.g. Sturges et Barrie, 1989; Monna *et al.*, 1997). Natural variations of selected isotope compositions (e.g. carbon ( $\delta^{13}\text{C}$ ), nitrogen ( $\delta^{15}\text{N}$ )) and isotope ratios (e.g.  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{206}\text{Pb}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ) can provide clearer evidence for anthropogenic input compared to concentrations data alone, as the different anthropogenic sources, whether point-source or of regional scale, commonly show distinct characteristic isotope compositions compared to those found in natural sediments (e.g., Hamelin *et al.*, 1990; Monna *et al.*, 1997). The signatures of “heavy” isotope may ultimately be related to the isotope geochemistry of the ore deposit from which the industrial element was produced (Sangster *et al.*, 2000). In the case of Pb air pollution, impact studies were supported, since the 1980s (e.g. Mukai *et al.*, 1993), by the well defined isotopic composition of automobile emissions, the major source of lead in the ambient air (Nriagu, 1990). However, since 1975 in the US, the mid-1980s in Europe and 2000 in China, legislative measures have passed to reduce and eventually eliminate Pb in gasoline. As a consequence of the phasing-out of Pb, the abundance of Pb in troposphere has decreased world-wide, but Pb remains essentially anthropogenic in atmospheric aerosols (e.g. Widory, 2006). Mukai *et al.* (2001) coupled sulphur and Pb isotopes to characterise the atmosphere of several Chinese urban sites. Lead isotope ratios suggested that coal combustion considerably contributed to atmospheric Pb in some cities in China. At the same time, influences by the emission of Chinese lead ores were also observed in northern Chinese

cities. Seasonal variations of Pb isotope ratios indicated the existence of a certain amount of industrial sources other than coal combustion (Mukai *et al.*, 2001).

Studies of atmospheric aerosols using Sr isotopes have mainly been carried out for the soluble components of aerosols in rainwater (Herut *et al.*, 1993; Nakano and Tanaka, 1997). However, Sr is a soil constituent element, and water-soluble Sr is only a part of the total Sr content of an aerosol. Kanayama *et al.* (2002) studied  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios coupled with both major and trace elements chemistry to track the contribution of long-range-transported Asian dust (Kosa) on the overall atmosphere of Japan. Recently, Xu and Han (2009) monitored the monthly  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of rainwater in Beijing over a period of one year to estimate the inputs of sea salt ( $^{87}\text{Sr}/^{86}\text{Sr}=0.70917$ ; Dia *et al.*, 1992) and terrestrial elements, as well as anthropogenic emissions.

The city of Beijing in general, and particularly during the preparation for the 2008 Olympics, has been trying hard to improve the air quality. Leaded gasoline in the city has been phased-out since 1998, but even if a slight decrease in its atmospheric concentrations has been observed, the levels remain critically high ( $0.10\text{-}0.18\ \mu\text{g}\cdot\text{m}^{-3}$  in 2005-2006). Industrial emissions, particularly from the non-ferrous industry as well as coal-combustion are the usual suspected vectors of pollution (Xiao *et al.*, 2008; Li *et al.*, 2008), but so far the classical chemical methods for assessing Pb levels have proven limited in their ability to determine the respective sources' contributions.

The present study assesses the use of coupling both lead ( $^{206}\text{Pb}/^{204}\text{Pb}$ ) and strontium ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) isotope systematics to help determine the origin of aerosols (TSP and  $\text{PM}_{2.5}$ ) in the atmosphere of Beijing (China). Potential sources of pollution in the atmosphere of Beijing, such as cement factories, coal combustion and Pb refining, were first chemically and isotopically characterized. Then, through the isotope characterisation of ambient aerosols, the major sources of pollution were identified and, when possible, their respective contributions to particulate-matter contents appraised.

## **MATERIALS AND METHODS**

The major sources of aerosol pollution in the atmosphere of Beijing, analysed during this study, include: coal combustion (4 samples), cement factories (3 samples) and smelters (1 sample). Chemical and isotope characteristics from road traffic were taken from the literature (Chen *et al.*, 2005; Widory *et al.*, 2007b). Wind transport of aerosols from surrounding deserts and non-polluted rural areas were also taken into account (2 standardised loess and 3 soils from different locations in China were sampled and analysed). A total of 63 samples of ambient  $\text{PM}_{2.5}$  were collected at the Sino-Japan Friendship Centre for Environmental Protection in Beijing, BMCEM, located on the North 4<sup>th</sup> ring (Figure 1), every 6 days, from September 2005 to September 2006. In parallel, 23 samples of ambient TSP were collected, from September 2005 to September 2006, at various locations around Beijing (Figure 1): 1) Changping (50 km north of Beijing, at the foot of the Jundu Mountains), 2) Downtown Beijing and 3) Liangxiang (31 km southwest of Beijing). These 23 TSP samples were part of a larger 166 sample set, described elsewhere (see Li *et al.*, 2008 and Xiao *et al.*, 2008), and claimed to represent the influence of either heavy pollution or Asian dust events. At the different sites, collection

of particles was made on quartz filters (QMA). PM<sub>2.5</sub> were sampled during runs of 24 hours at a constant flow of 1 m<sup>3</sup> h<sup>-1</sup>, using a low volume sampler, while TSP samples were collected using a high volume sampler (runs of 24 hours).

In the laboratory (in a class-10 000 clean room with class-100 laminar flow hood), samples (filters in the case of PM<sub>2.5</sub> and TSP, and solids and particles in the case of the different inputs end-members) were leached with Supra-pure hydrobromic acid (HBr). The efficiency of Pb (& Sr) complexation by HBr is generally better than 90 %, confirming that the major part of these elements is contained in the labile fraction (e.g. Widory, 2004b and 2006). Pb & Sr concentrations were measured with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS; precision 5%). Blank measurements made on quartz sampling filters yielded relatively low Pb and Sr contents (3.9±0.7 and 0.7±0.05 ng, respectively), compared to those obtained from ambient air samples and pollution sources (lower by at least a factor 15).

Pb-isotope measurements were measured on a Neptune Multiple Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS; Thermo-Finnigan). The procedure, described in White *et al.* (2000), was slightly modified in order to certify some key features of the instrument's double-focusing system (Motellica-Heno *et al.*, 2003). Due to the physical principles of this machine, a rather high mass fractionation is observed (~0.7%/amu). Use of thallium (Tl), an element of similar mass, as an internal standard (Longrich *et al.*, 1987) provides an opportunity for correction of mass dependency of the instrumental bias. Despite the fact that the fractionation coefficients are not strictly identical for Tl and Pb, the ratio of these coefficients remains constant for a given analytical session (White *et al.*, 2000). Furthermore, Tl normalisation seems to reduce a potential matrix effect. In addition, sample-standard bracketing was applied to control potential random instability of the instrument as a whole, resulting in the following sequence: Blank – NIST 981 – Cleaning solution HNO<sub>3</sub>, 3% – Blank – Sample – Cleaning solution HNO<sub>3</sub>, 3% – Blank – etc. The blank level obtained is very low (<1 mV on <sup>208</sup>Pb) and is subtracted from the next sample in the sequence. For this environmental study, samples were diluted to 50 to 100 ppb of Pb in solution, and 20 to 30 ng of Tl were added to 1 ml of solution. Baselines were measured at mass 100 at the beginning and end of each analysing sequence. A correction for <sup>204</sup>Hg used a <sup>202</sup>Hg measurement, applying a <sup>202</sup>Hg/<sup>204</sup>Hg ratio of 4.35. For routine analyses following this procedure, avoiding any chemical lead purification, the uncertainty level was 0.01% for <sup>208</sup>Pb/<sup>206</sup>Pb and <sup>207</sup>Pb/<sup>206</sup>Pb, and 0.1% for <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb.

Chemical purification of Sr (~3 µg) was performed, on the HBr leachate, using an ion-exchange column (Sr-spec) before mass analysis according to a method adapted from Pin and Bassin (1992), with a total blank of less than 1 ng for the entire chemical procedure. After chemical separation, around 150 ng of Sr was loaded onto a tungsten filament with tantalum activator and analysed on a MAT 262 Thermo-Ionisation Mass Spectrometer (TIMS; Finnigan). The <sup>87</sup>Sr/<sup>86</sup>Sr ratios were normalised to a <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.1194. An average internal precision of ±10 ppm (2σ) was obtained and the reproducibility of the <sup>87</sup>Sr/<sup>86</sup>Sr measurements was tested through repeated analyses of the

NBS987 international standard, for which a mean value of  $0.710243 \pm 0.000022$  ( $2\sigma$ ;  $n=13$ ) was obtained during the period of analysis.

## RESULTS AND DISCUSSION

### Characterization of potential end-members

Both Pb and Sr concentrations from pollution sources display large fluctuations (Table 1), among which several trends appear. The highest Pb concentrations are measured in the samples from the Pb refining plants ( $95 \pm 4$  %), while the lowest correspond to emissions from the cement factories ( $21 \pm 8$  ppm). Emissions from smelters (3.83 %;  $n=1$ ; this value is similar to concentrations obtained by Banic *et al.*, 2006), and to a lesser extent from coal combustion ( $109 \pm 7$  ppm; similar to the values reported by Block and Dams, 1975, on samples from thermal power stations) present intermediate Pb concentrations. Strontium, on the other hand, was found to be under the detection limit (i.e.  $10^{-1}$  ppm) in samples from the lead refining plants, in low concentrations in the smelters (5 ppm;  $n=1$ ), and yield comparable concentrations in both the emissions from coal combustion ( $517 \pm 15$  ppm) and from the cement factories ( $513 \pm 15$  ppm). Their corresponding isotope ratios show that while aerosols from coal combustion and cement factories have similar ranges of  $^{206}\text{Pb}/^{204}\text{Pb}$ , 17.873-18.326 (average of  $18.09 \pm 0.25$ ) and 17.729-18.365 (average of  $18.05 \pm 0.32$ ), respectively, the smelter yields aerosols with a significantly lower ratio ( $^{206}\text{Pb}/^{204}\text{Pb}=16.380$ ;  $n=1$ ). The Sr isotopes display a large range of variations, allowing a clear discrimination of the different emitters. Coal combustion yields the aerosols with the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $0.70924 \pm 0.00028$ ), and the smelters the most radiogenic value ( $0.712064 \pm 0.00028$ ). The cement factories produce particles with intermediate  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $0.71029 \pm 0.00029$ ). The isotope characteristics of emissions from road traffic were taken from the literature. The phasing-out of leaded gasoline started in 1997 in China (Chen *et al.*, 2005). The use of leaded gasoline was first banned in Beijing in 1997, and then in Shanghai, Guangzhou, Tianjin and other big cities (Sun *et al.*, 2006). Chen *et al.* (2005) report Pb concentrations (77 to 399 ppm) and  $^{207}\text{Pb}/^{206}\text{Pb}$  (0.862 to 0.879) in unleaded vehicle exhausts. However, the authors were not able to measure the  $^{204}\text{Pb}$  content, using their particular ICP-MS technique.

The “natural” sources of aerosols measured in this study include loess and soils collected at various locations in China (Table 1). Slight variations are observed in both their Pb and Sr concentrations, from 24 to 41 ppm (average of  $32 \pm 7$  ppm) and 242 to 333 ppm (average of  $286 \pm 36$  ppm), respectively. No clear chemical discrimination is apparent between the loess and the soils. Their corresponding  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios form a somehow compact range, from 18.312 to 18.693, with an average of  $18.459 \pm 0.17$ . This is consistent with the values of  $18.671 \pm 0.006$  reported for soils by Jones *et al.* (2000).  $^{87}\text{Sr}/^{86}\text{Sr}$ , in loess and soils, range from 0.7118 to 0.7148 (average of  $0.7136 \pm 0.0012$ ), similar to previous studies. Zhang *et al.* (1995) reported  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.7111–0.7154 from rivers around the Taklimakan Desert in northwest China, similar to those measured at both the Huanghe river

(Yellow River; 0.7111; Palmer and Edmond, 1989), and the Central Loess Plateau (0.7111; Yokoo *et al.* 2004).

## Characterisation of ambient air samples

While certainly not representative of its overall budget in Beijing, data for TSP concentrations in the air (Figure 2), measured at the three sampling sites (Changping, Downtown Beijing and Liangxiang), mostly exceed the 24-hours average range guidelines of 150-230  $\mu\text{g}\cdot\text{m}^{-3}$ , proposed by the World Health Organisation (WHO). These guidelines are for combined exposure to both sulphur dioxide and TSP). At the selected sites, the concentrations also exceed the Class 2 China air quality standards (300  $\mu\text{g}\cdot\text{m}^{-3}$ ), and occasionally also the class 3 standards (500  $\mu\text{g}\cdot\text{m}^{-3}$ ). The concentrations exceeding this latest threshold correspond to the spring Asian dust events. The  $\text{PM}_{2.5}$  concentrations in the air measured at the downtown Beijing site exceeds the 24-hour mean recommended value (WHO, 2005) of 25  $\mu\text{g}\cdot\text{m}^{-3}$ , which also corresponds to the European target for 2015 (2008/50/CE). The highest concentrations of  $\text{PM}_{2.5}$  (as high as 636  $\mu\text{g}\cdot\text{m}^{-3}$ ) were measured in May 2006, at about the same period as the highest TSP concentrations, which would be consistent with the influence of the regional Asian dust events. Still, it clearly demonstrates the need for continued efforts for a better air quality management (including identification of the corresponding pollution sources).

Lead contents (Figure 3A) vary between 70 and 2940 ppm (average of  $1364\pm 620$  ppm) in  $\text{PM}_{2.5}$ , and between 32 and 2188 ppm (average of  $920\pm 638$  ppm) in TSP. These values are significantly greater than those reported in some other megacities around the world, such as Paris (e.g. Widory *et al.*, 2004a; Widory, 2006). Except for samples taken on the 3<sup>rd</sup> of January (both  $\text{PM}_{2.5}$  and TSP), the  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios (Figure 3B) do not show any significant variations with time, with an average value of  $18.0\pm 0.1$  ( $17.98\pm 0.09$  for  $\text{PM}_{2.5}$  and  $17.99\pm 0.1$  for TSP). This could be indicative of either i) a sole source of contamination through the year, or more likely ii) a constant mixing of different sources. If we compare the Pb isotope ratios with those reported in Table 1, they fall into the range of emissions from coal combustion, lead refining plants and cement factories. The  $\text{PM}_{2.5}$  and TSP samples taken on the 3<sup>rd</sup> of January yield  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios that are closer to those measured in the emissions from the smelter. Strontium, on the other hand, is in significantly greater abundance in the coarser mode (Figure 4A), with an average concentration of  $215\pm 196$  ppm (variations from 90 to 958 ppm). In  $\text{PM}_{2.5}$ , the Sr concentrations fluctuate from 11 to 185 ppm, with an average of  $90\pm 49$  ppm. This pattern is similar to what has been previously observed in other cities (e.g. Widory *et al.*, 2007b). The corresponding  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (Figure 4B) vary from 0.7086 to 0.7107 (average of  $0.7097\pm 0.0005$ ) in the TSP, and from 0.7092 to 0.7101 (average of  $0.7097\pm 0.0003$ ) in the  $\text{PM}_{2.5}$ . This overlap between the ranges found in both size fractions may argue for similar sources, but the isotope disparity clearly indicates at least two distinct sources. The comparison with results from Table 1 shows that emissions from both coal combustion and cement factories have similar  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios compared to those measured in the aerosols. Still, for the lowest Sr isotope ratios measured (close to 0.7086), the input from another

unidentified source is required (see below). Variations of Sr and Pb concentrations in both TSP and PM<sub>2.5</sub> seem to be roughly linear (with opposite slopes for PM<sub>2.5</sub> and TSP, negative and positive, respectively; Figure 5). While at low Pb concentrations the trends for TSP and PM<sub>2.5</sub> merge, perhaps indicating a single origin for both size fractions in the atmosphere, at high Pb concentrations, at least two distinct sources seem to be required. At high Pb concentrations, the source of PM<sub>2.5</sub> is characterised by a high Pb content coupled with a relatively low Sr content (<100 ppm), while the source of TSP is characterised by high Pb and Sr concentrations. This conclusion is in agreement with the fact that PM<sub>2.5</sub> samples are expected to be mainly influenced by activities such as lead refining, while the coarser TSP fraction incorporates inputs from activities such as coal combustion or emissions from cement plants (Zhang *et al.*, 2007). Two TSP samples taken on the 28<sup>th</sup> of January 2006 plot outside these trends (one is from downtown Beijing, while the other is from Changping, suburb of Beijing). They coincide with the Chinese New Year's Eve festivities, which would explain the high Sr concentrations measured (>600 ppm), as Sr is commonly used as a colouring compound in fireworks. Even though Pb has been phased-out in Beijing since 1997, it is still present (in low quantities) in the unleaded gasoline burnt today in the city, and thus may represent a potential source of contamination (Wang *et al.*, 2003). Figure 6A compares the <sup>207</sup>Pb/<sup>206</sup>Pb measured in both TSP and PM<sub>2.5</sub> with those characterising the different sources of particles in the air (including ranges of road traffic emissions measured by Chen *et al.*, 2005). For the majority of samples, results confirm that, road traffic is no longer a major source of atmospheric Pb, which was expected following its phasing-out in gasoline. Only two samples, taken consecutively, one TSP sample taken in Changping (01/05/2006) and one PM<sub>2.5</sub> sample (01/04/2006) show isotope characteristics compatible with the input of aerosols from either road traffic or smelters. The dual isotope approach (<sup>208</sup>Pb/<sup>204</sup>Pb vs. <sup>206</sup>Pb/<sup>204</sup>Pb; Figure 6B) shows that all Pb isotope ratios measured in the ambient air samples (both TSP and PM<sub>2.5</sub>) plot within the ranges obtained on aerosols from the main pollution sources noted above (Table 1), indicating that no other pollution source is required for explaining our aerosols sample set. Still, the use of the sole Pb isotopes is not sufficient for precisely tracing the origin of these elements in the aerosols (both TSP and PM<sub>2.5</sub>). Figure 6C plots the more discriminating <sup>206</sup>Pb/<sup>204</sup>Pb ratio versus the reciprocal of Pb concentrations in the samples. Two distinct emitters appear to play a major role in the observed Pb pollution levels: i) Pb refining plants (to which most of the aerosols samples are closely associated), and to a lesser extent ii) the Jingneng coal-fired power station, located southeast of Beijing. Two samples taken on the 28<sup>th</sup> of January 2006, both TSP (downtown Beijing and Changping sites) and PM<sub>2.5</sub> (Beijing site) display the most radiogenic <sup>206</sup>Pb/<sup>204</sup>Pb ratios (Figure 6C). Their date of sampling and Sr contents (>600 ppm) may corroborate the influence of fireworks residues, used during the New Year's Eve festivities. This is consistent with conclusions drawn from Figure 5, but this has yet to be confirmed by measurements, as to our knowledge no studies have ever reported Pb-isotope ratios for lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>), used in fireworks and other pyrotechnics. As discussed above, samples taken on the 4<sup>th</sup> (PM<sub>2.5</sub>) and 5<sup>th</sup> (TSP Changping) of January may indicate an input from road traffic (Figure 6A), or more probably, the influence of smelter emissions due to their relatively high Pb concentrations (1145 and 621 ppm, respectively). Finally, one TSP sample taken in Changping (22<sup>nd</sup> of April) suggests that emissions from cement plants are the corresponding source of



pollution. Figure 7 shows that most samples in both size fractions plot within the range of  $^{87}\text{Sr}/^{86}\text{Sr}$  from the analysed end-members (Table 1), and are consistent with a mixing between 1) a major end-member, emissions from coal combustion, and 2) “secondary” contributors, such as cement plants and smelters. Four  $\text{PM}_{2.5}$  samples (4<sup>th</sup> of March, 21<sup>st</sup> of June, 1<sup>st</sup> and 19<sup>th</sup> of September), as well as two TSP samples from the Changping and downtown Beijing sites (both taken on the 28<sup>th</sup> of January) plot on a binary mixing line ( $r^2=0.97$ ; Figure 7) that yields a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.7086 and a Sr concentration of at least 103 ppm for its corresponding source. This Sr isotope ratio is significantly lower than the range measured on potential end-members (Table 1), and could correspond to i) emissions from coal combustion, assuming that the samples measured during this study do not reflect the total  $^{87}\text{Sr}/^{86}\text{Sr}$  natural variability of coal combustion, or ii) an input from carbonaceous alteration, brought by wind from outside the city, which is consistent with the  $^{87}\text{Sr}/^{86}\text{Sr}$  variations of marine carbonates from 0.7080 to 0.7090, reported by Derry *et al.*, 1994, during the early Cambrian stage, or, 3) residues from fireworks, as deduced from Figures 5 and 6B. This latter source would explain the TSP samples, but hardly fits with the  $\text{PM}_{2.5}$  samples that were taken at different periods in the year (May, June and September).

The equation of mixing for a  $k$  component system for isotope ratios  $I$  can be expressed in the following way (Douglas and Schilling, 2000):

$$I = \frac{\sum_{i=1}^k z_i n_i I_i}{\sum_{i=1}^k z_i n_i}$$

With  $\sum_{i=1}^k z_i = 1$  and  $0 \leq z_i \leq 1$ , and where  $I$  is the isotope ratio in the mixture,  $I_i$  the isotope ratio in each end-member component,  $z_i$  the mass fraction of component 1, 2, 3, ..., and  $n_i$  the relative enrichment of element  $I$  in component 1, 2, 3, ..., relative to component  $k$  (i.e.  $n_i = c_i/c_k$ ; where  $c$  is the concentration of element  $I$ ). From our data set, and considering the average concentrations and isotope ratios for each major pollution source (refining plants, coal burning and smelter; from Table 1), it is possible to estimate their respective contributions for each ambient air samples. Results indicate that for most of the aerosols, the Pb contribution from the smelter is negligible (<2%), while coal burning usually represents less than 20%. Results show that most of the atmospheric Pb, both TSP and  $\text{PM}_{2.5}$ , in Beijing comes from refining plants. Nevertheless, as discussed above, 2 distinct samples seem to identify a non negligible contribution from the smelter. The calculation for the TSP sample taken on the 5<sup>th</sup> of January gives an amount of about 10% of its Pb from the smelter. In the case of the  $\text{PM}_{2.5}$  sample taken on the 4<sup>th</sup> of January, the contribution of the smelter is around 4%. From most of the samples plotting on the mixing line between the refining plants and the Jingneng coal-fired power station (Figure 6C), the contribution of this latter source is, of at least ~70%. Calculation with the Sr isotopes confirms that this element is mainly dominated, in the atmosphere of Beijing, by coal combustion. Results give a contribution of the smelter  $\approx 10\%$ .

Combining the two isotope systematics ( $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ ) yields even more constraints on the source of atmospheric particles in the atmosphere of Beijing. Results (Figure 8) confirm the great impact of emissions from coal combustion, as well as from the cement plants. The sample plotting outside this trend, taken on the 5<sup>th</sup> of January, has a significant lower  $^{206}\text{Pb}/^{204}\text{Pb}$  coupled with a relatively low  $^{87}\text{Sr}/^{86}\text{Sr}$ , which could indicate the potential influence of road traffic.

## CONCLUSIONS

China, and particularly its megacities such as Shanghai or Beijing, is working towards improving air quality, especially regarding airborne particulate matter. Measures have already been taken, including the phasing-out of Pb in gasoline (the major vector of atmospheric lead until the end of the 90's). However, critically high concentrations of this toxic element are observed. We studied here the possibility of using Pb isotope systematics coupled with Sr isotopes systematics, to help decipher the origin of these elements (and ultimately the origin(s) of both  $\text{PM}_{2.5}$  and TSP) in the atmosphere of Beijing and its vicinity. Results lead to the following conclusions:

1. Pb and Sr concentrations in the different size fractions are relatively high (up to 2500 and 1000 ppm, respectively). When compared, Pb and Sr concentrations show that while at low Pb concentrations a common source, or a constant mixing of aerosols from multiple sources, seems possible, at higher Pb concentrations at least two distinct sources, one for the  $\text{PM}_{2.5}$  and another for the TSP, are implicated. We cannot uniquely identify these sources at this point. For two particular samples taken during the festivities of the Chinese New Year's Eve, residues from fireworks appear to have impacted the levels of TSP and  $\text{PM}_{2.5}$  observed.
2. Lead isotopes ( $^{206}\text{Pb}/^{204}\text{Pb}$ ) identify emissions from metal, lead-related, refining plants as the major emitter of this element in Beijing's atmosphere, followed by coal-fired power stations (such as the Jingneng station). As expected after the phasing-out of Pb in gasoline, the influence of road traffic has drastically decreased, but still the data indicate that it may contribute to the concentrations measured for (only) two samples (one TSP and one  $\text{PM}_{2.5}$ ) out of the total set. It is more likely that these two samples reflect the input of smelter emissions. The samples yielding the highest  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios may present the characteristics of fireworks, a suggestion that is reinforced by both the date of sampling and the relatively high Sr contents of these samples. Cement plants are occasionally isotopically identified, while erosion of soils seems to have a slight influence in the overall Pb atmospheric budget.
3. Strontium isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) indicate that this element in the atmosphere of Beijing is mainly controlled by coal combustion and to a lesser extent by cement plants and/or smelters. For a few number of samples (both TSP and  $\text{PM}_{2.5}$ ), either road traffic, or carbonaceous particles brought into the city by windy mid- to long-range transport, or fireworks may explain the observed  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios.

4. Coupling the Pb and Sr isotope systematics gives deeper insight into the sources responsible for the levels of those elements in the aerosols measured. Results confirm the major role played by coal combustion and, to a lesser extent, cement plants.

While the study of Pb and Sr concentrations may have hinted at a correlation between the source(s) involved and the size fraction of the aerosols (i.e. each size fraction being influenced by a specific pollution source), the use of the multi-isotope approach shows that TSP and PM<sub>2.5</sub> are both derived from the same source of contamination.

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Table 1. Characteristics of the sources of aerosols in the atmosphere of Beijing.

Sample	Remarks	Pb (ppm)	<sup>207</sup> Pb/ <sup>206</sup> Pb	<sup>206</sup> Pb/ <sup>204</sup> Pb	Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr
<b><i>Terrigenous inputs</i></b>						
S-CJ-1	Chinese loess	29	0.8340	18.693	295	0.714524
S-CJ-2	Simulated Chinese loess	40	0.8389	18.390	242	0.714797
S-ELHT	Soil collected at Erlianhoat	41	0.8466	18.300	261	0.711784
S-SZWQ	Soil collected at Siziwangi	24	0.8526	18.321	300	0.713303
S-BYZE	Soil collected at Bayinzhuoer	28	0.8774	18.578	333	0.713653
<b><i>Coal combustion</i></b>						
CC-JN-A	Beijing Jingneng thermal power Co. Ltd (Shijingshan	112	0.8662	17.873	530	0.709470
CC-JN-B	Beijing Jingneng thermal power Co. Ltd (Shijingshan	103	0.8658	17.879	510	0.709492
CC-JG	Jiangong thermal power station	118	0.8501	18.326	500	0.709033
CC-BY	Beiyuan thermal power station (Shandong Sheng	104	0.8510	18.290	530	0.708970
<b><i>Smelter</i></b>						
M1 - HNXW	Sludge from a Pb smelting factory in Xiuwu county	38 300	0.9425	16.380	5	0.712064
<b><i>Cement factories</i></b>						
Diamond	Heibei Yanxin Construction Material Co. Ltd	14	0.8479	18.365	530	0.710380
Lafaji	Beijing Shunfa Co. Ltd	20	0.8611	18.064	510	0.709963
Tangshan	Tangshan Yutian County Cement Factory	30	0.8757	17.729	500	0.710528
<b><i>Lead refining plants</i></b>						
P1 - SFDJ	End-product, high purity, production of Pb batteries	997 700	0.8647	18.040	<i>udl</i>	-
P2 - SFHJ	End-product, high purity, production of Pb batteries	940 600	0.8682	17.970	<i>udl</i>	-
P3 - HDDJ	End-product, high purity, production of Pb batteries	994 300	0.8672	17.989	<i>udl</i>	-
M2 - NKR	Raw material, high purity, from North Korea	900 700	0.8651	18.039	<i>udl</i>	-
M3 - TJBD	Raw material, high purity, from Tianjan (Baodi county)	921 100	0.8676	17.982	<i>udl</i>	-
M4 - HBBD	Raw material, high purity, from Baoding (Hebei	771 400	0.8682	17.969	<i>udl</i>	-

*udl*: under detection limit (10<sup>-1</sup> ppm).

4

## FIGURE CAPTIONS

5 Figure 1: Location map of the different sampling sites in Beijing and its vicinity: TSP (A:  
6 Changping; B: Downton Beijing; C: Liangxiang) and PM<sub>2.5</sub> (D: BMCEM on the North 4<sup>th</sup>  
7 ring).

8

9 Figure 2: Atmospheric TSP and PM<sub>2.5</sub> concentrations. European, WHO's recommendations  
10 and China air quality standards are reported.

11

12 Figure 3: Lead characteristics of TSP and PM<sub>2.5</sub> during the period of sampling. A) Variations  
13 of Pb concentrations in the particles. B) Variations of the <sup>206</sup>Pb/<sup>204</sup>Pb ratio.

14

15 Figure 4: Strontium characteristics of TSP and PM<sub>2.5</sub> during the period of sampling. A)  
16 Variations of Sr concentrations in the particles. B) Variations of the <sup>87</sup>Sr/<sup>86</sup>Sr ratio.

17

18 Figure 5: Pb & Sr concentrations in the TSP and PM<sub>2.5</sub>.

19

20 Figure 6: Isotope tracking of sources of atmospheric Pb (TSP and PM<sub>2.5</sub>) in the atmosphere of  
21 Beijing and its vicinity. A) <sup>207</sup>Pb/<sup>206</sup>Pb ratios, used to provide consistency with previous  
22 studies, vs. 1/Pb. B) <sup>208</sup>Pb/<sup>204</sup>Pb vs. <sup>206</sup>Pb/<sup>204</sup>Pb ratios. C) <sup>206</sup>Pb/<sup>204</sup>Pb ratios vs. 1/Pb. Binary  
23 mixing relationships are modelled. In a Pb isotope ratio versus 1/Pb diagram, binary mixing is  
24 described by a straight line).

25

26 Figure 7: Isotope tracking of sources of atmospheric strontium (TSP and PM<sub>2.5</sub>) in the  
27 atmosphere of Beijing and its vicinity. A) <sup>87</sup>Sr/<sup>86</sup>Sr vs. Sr concentrations. B) Binary mixing  
28 relationships are modelled. In a <sup>87</sup>Sr/<sup>86</sup>Sr ratios versus 1/Sr diagram, binary mixing is  
29 described by a straight line. Characteristics of road traffic emissions of particles are also  
30 reported (adapted from Widory *et al.*, 2007b). Note that the X-axis is under a logarithmic  
31 scale.

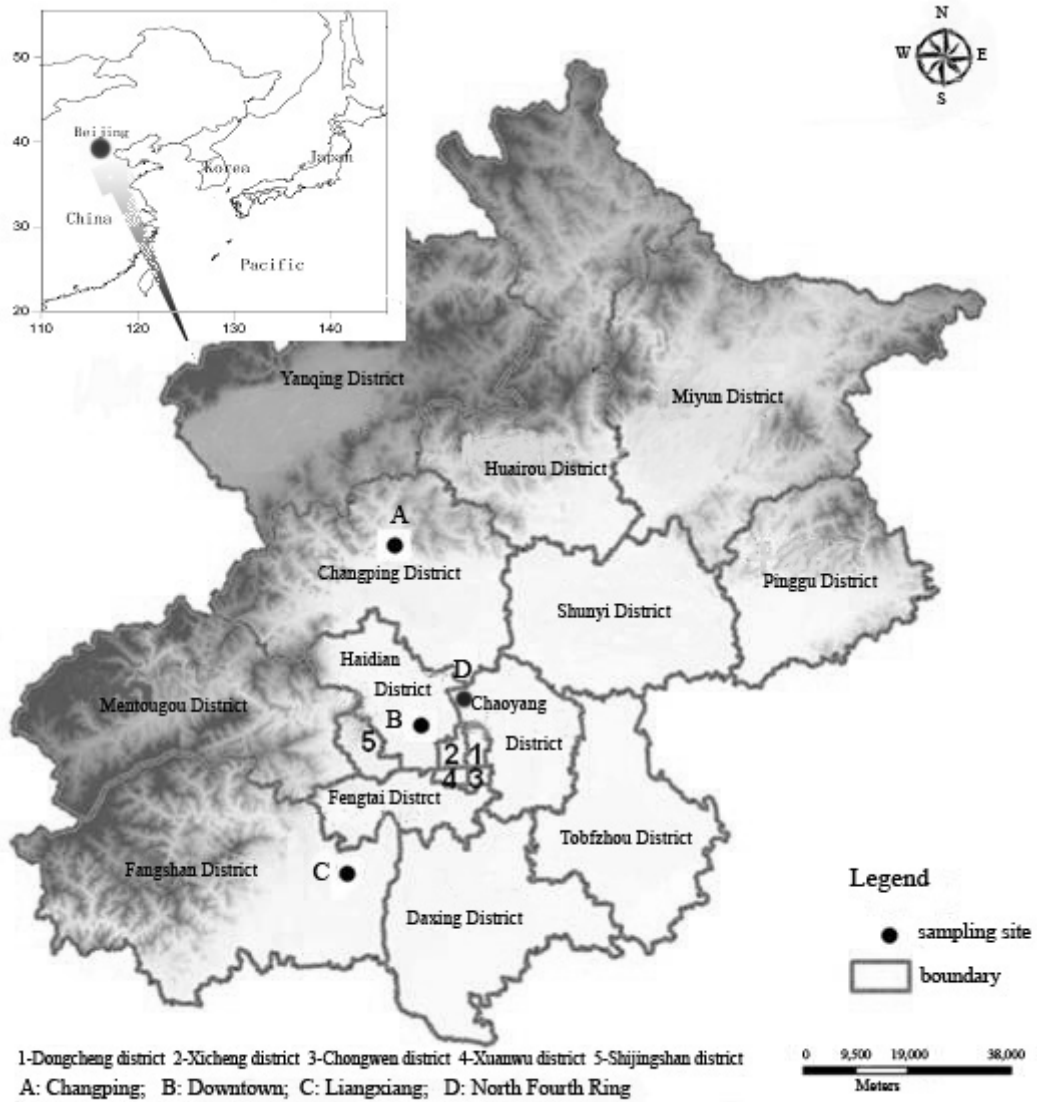
32

33 Figure 8: The multi-isotope approach. Coupling both <sup>206</sup>Pb/<sup>204</sup>Pb and <sup>87</sup>Sr/<sup>86</sup>Sr ratios brings  
34 more constrains on the origin of TSP and PM<sub>2.5</sub> in the atmosphere of Beijing and its vicinity.  
35 Isotope characteristics of samples from Geagea *et al.* (2008) are also reported.



36  
37  
38

FIGURE 1

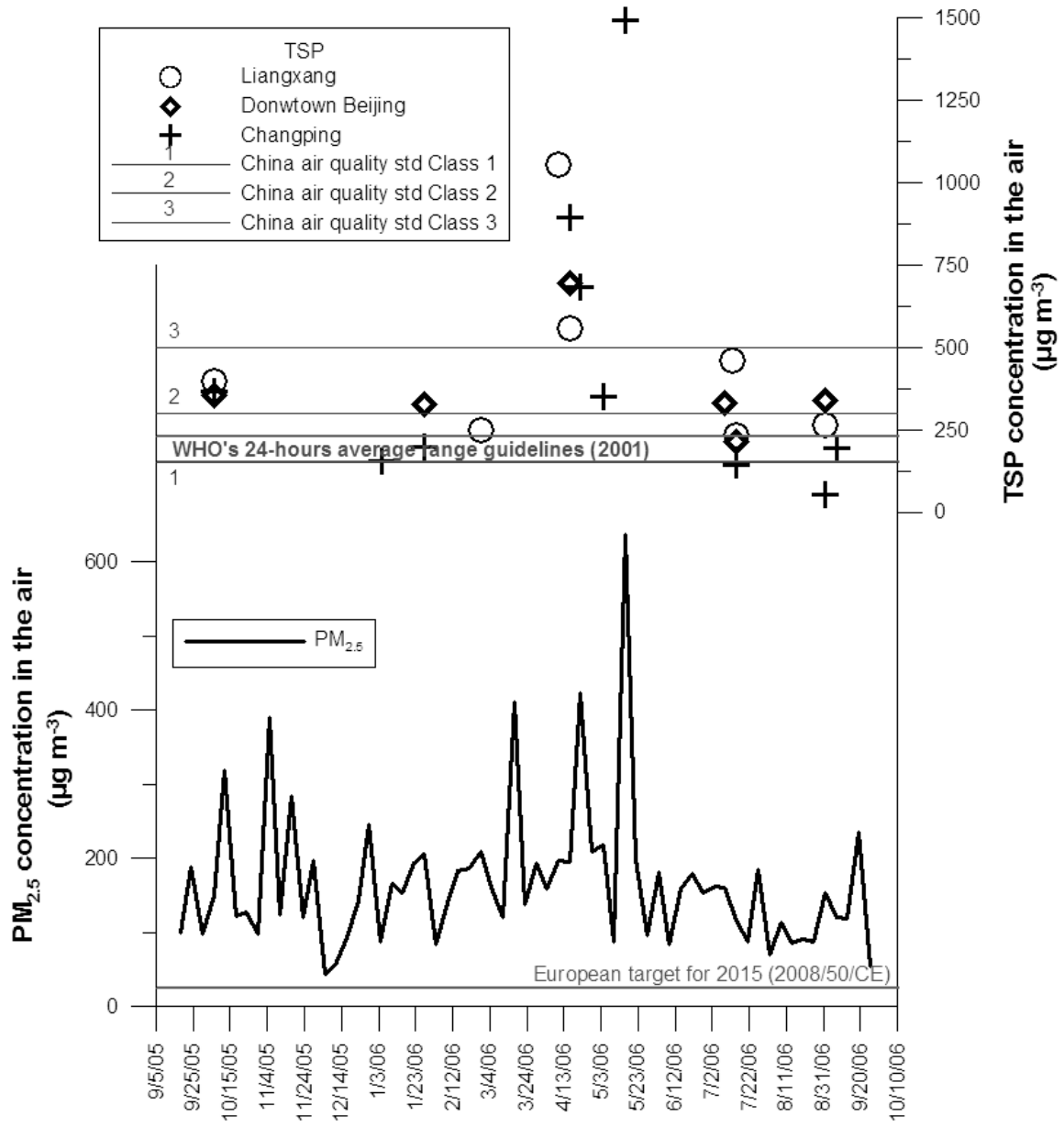


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FIGURE 2

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FIGURE 3

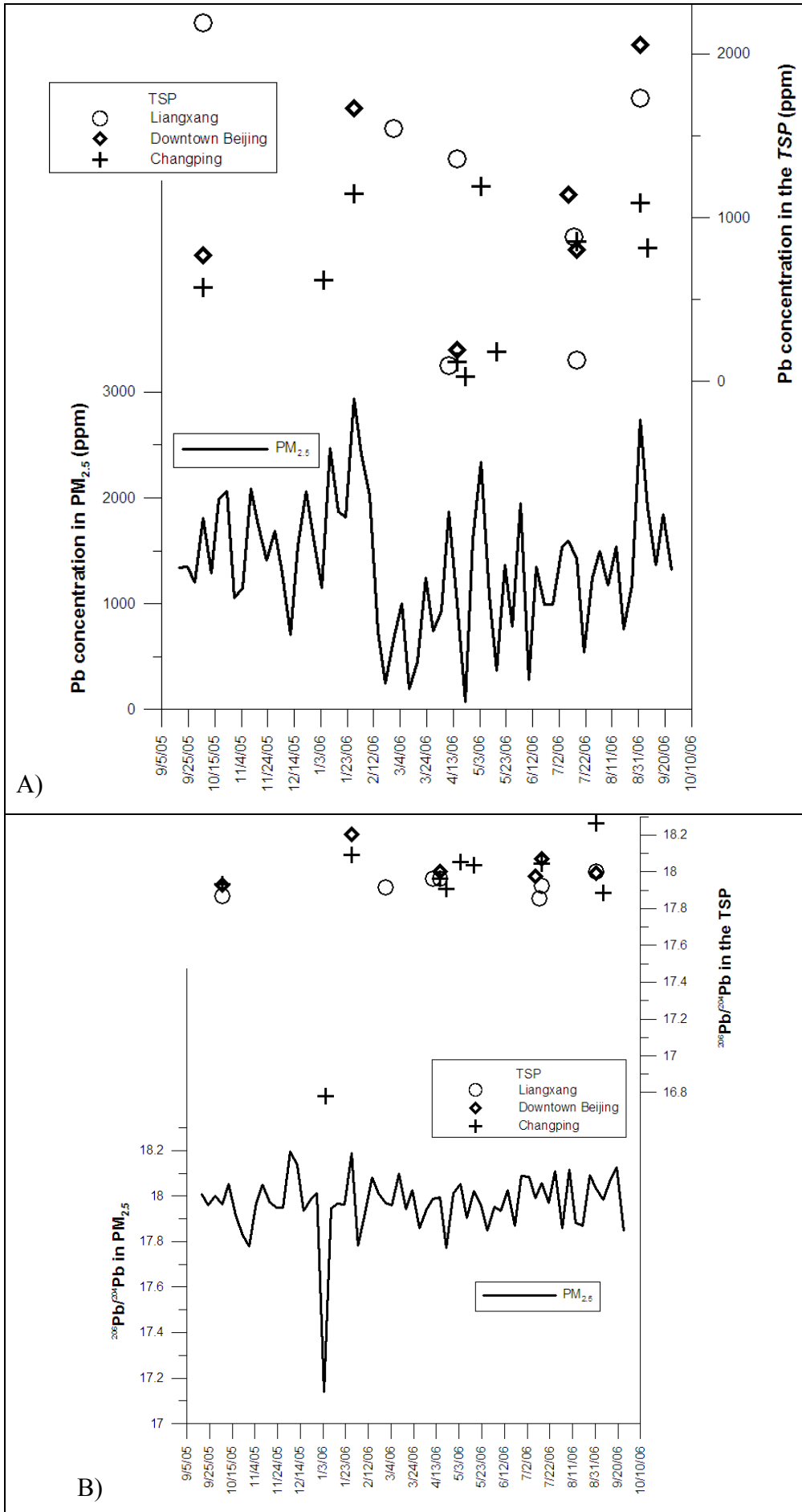


FIGURE 4

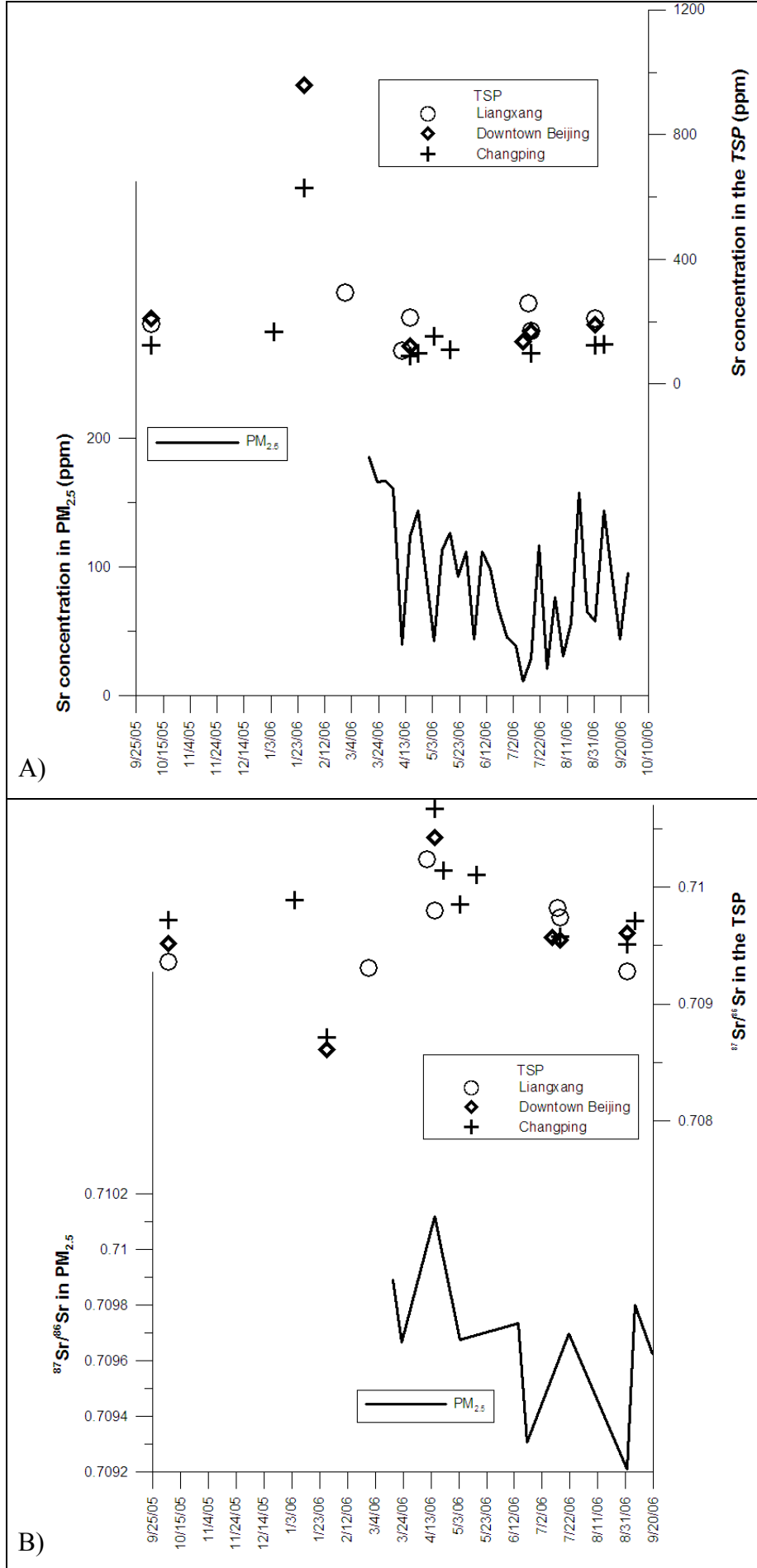


FIGURE 5

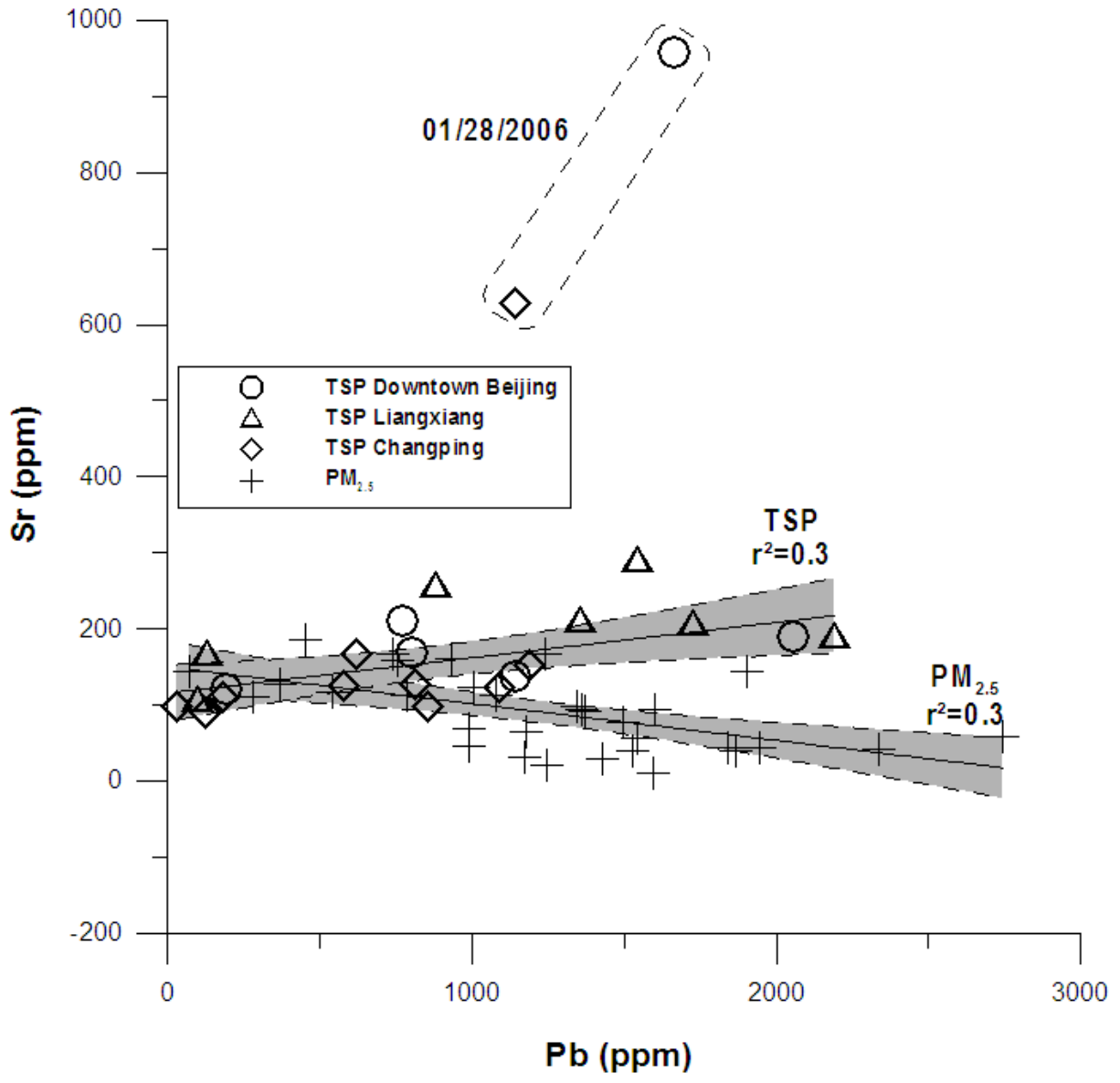


FIGURE 6

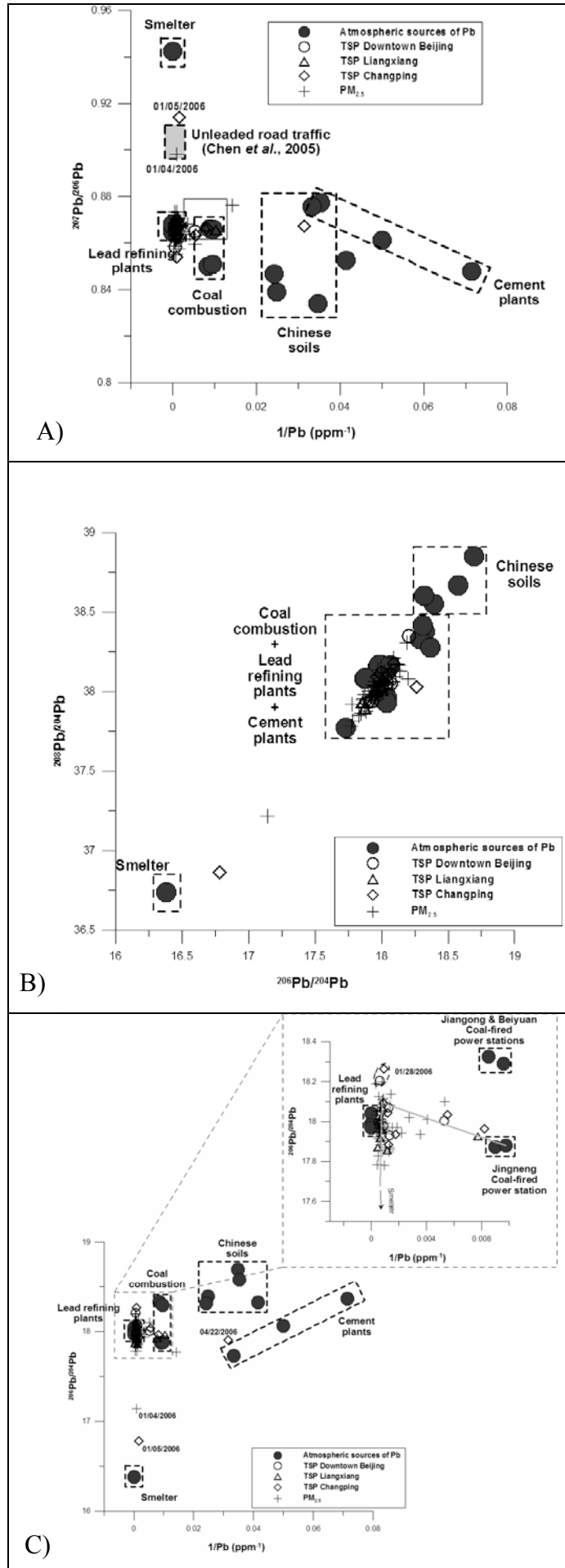


FIGURE 7

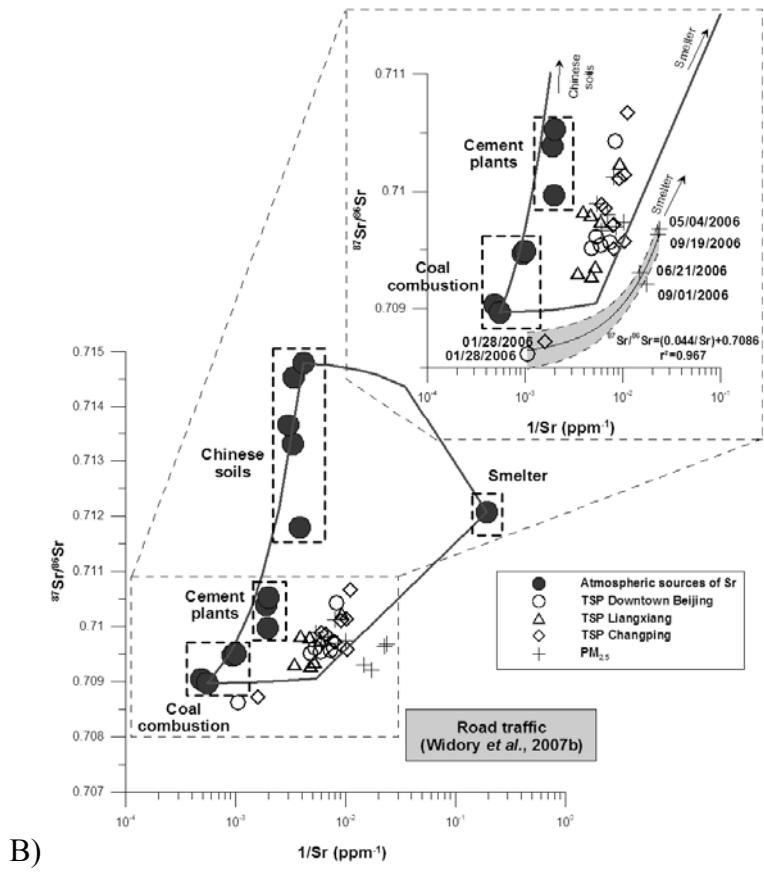
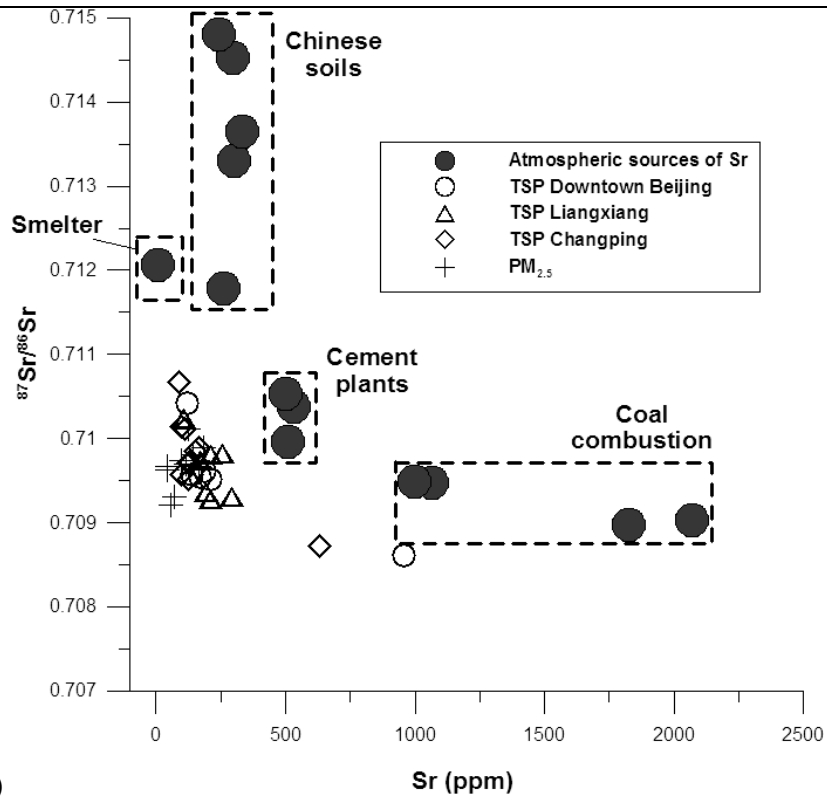


FIGURE 8

