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Spatial–temporal variations, sources, and transport of airborne inhalable metals (PM_{10}) in urban and rural areas of northern China

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Abstract

Atmospheric particle pollution is a serious environmental issue in China, especially the northern regions. Ambient air loadings (ng m^{-3}), pollution sources and apportionment, and transport pathways of trace (Cd, Co, Cu, Ni, Pb, V, and Zn) and major (Al, Ca, Fe, and Mg) metals associated with inhalable particulate matters (PM_{10} aerosols) were characterized in urban, rural village, and rural field areas of seven cities (from inland in the west to the coast in the east: Wuwei, Yinchuan, Taiyuan, Beijing, Dezhou, Yantai, and Dalian) across northern China by taking one 72 h sample each site within a month for a whole year (April 2010 to March 2011). Ambient PM_{10} pollution in northern China is especially significant in the cold season (October–March) due to the combustion of coal for heating and dust storms in the winter and spring. Owing to variations in emission intensity and meteorological conditions, there is a trend of decrease in PM_{10} levels in cities from west to east. Both air PM_{10} and the associated metal loadings for urban and rural areas were comparable, showing that the current pattern of regional pollution in China differs from the decreasing urban–rural-background transect that is usual in other parts of the world. The average metal levels are Zn (276 ng m^{-3}) ≫ Pb (93.7) ≫ Cu (54.9) ≫ Ni (9.37) > V (8.34) ≫ Cd (2.84) > Co (1.76). Judging from concentrations (mg kg^{-1}), enrichment factors (EFs), a multivariate statistical analysis (principal component analysis, PCA), and a receptor model (absolute principal component scores-multiple linear regression analysis, APCS-MLR), the airborne trace metals (Zn, Pb, Cu, and Cd) in northern China were mainly anthropogenic, and mostly attributable to coal combustion and vehicle emissions with additional industrial sources. However, the Co was mostly of crustal origin, and the V and Ni were mainly from soil/dust in the western region and mostly from the petrochemical industry/oil combustion in the east. The accumulation of typical "urban metals" (Pb, Zn, Cd, and Cu) showed a trend of increase from west to east, indicating their higher anthropogenic contribution in eastern cities. The winter northwestern monsoon and westerly jet stream were the dominant

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forces in the long-range transport of airborne PM metals in northern China, with potentially global implications.

1 Introduction

Suspended particulate matter (PM) is an important constituent of the atmosphere and contribute substantially to air pollution, and has a critical impact both on natural geochemical processes and on human health (Nguyen et al., 2013; Pope and Dockery, 2013; Silva et al., 2013; Turoczi et al., 2012). Epidemiological studies have indicated that elevated concentrations of inhalable particles with an aerodynamic diameter of less than 10 µm (PM_{10}) are associated with increased respiratory problems, mortality, and morbidity, especially in children and elderly people (Humbert et al., 2011; Strak et al., 2012). There is broad acceptance that ambient air PM is an important pollutant in a typical urban environment (Filippelli et al., 2012; Marshall, 2013), that it is generated from a wide range of sources (Calvo et al., 2013), and that it may be composed of numerous hazardous components, such as toxic trace metals, which play an important role in the development of pulmonary and cardiovascular diseases (Chen and Lippmann, 2009; Lee et al., 2007a; Moreno et al., 2011). Furthermore, some toxic metals, such as cadmium (Cd), cobalt (Co), nickel (Ni), lead (Pb), and vanadium (V), which can be found in PM, are also carcinogenic (WHO, 2012). The inhalation of airborne trace metals can therefore have a long-term and serious impact on human health. Although all of these metals are typically present in elevated concentrations in the urban ambient air, very few of them are clearly regulated through proper legislation on air PM pollution (Table 1). The effective control of air pollution requires detailed knowledge of the distribution of ambient inhalable PM, as well as of its chemical components, emission sources, transport pathways, and so on.

The level and composition of urban PM strongly depend on the characteristics of the city (sources and intensity of pollution, etc.), its geographical location, and meteorological conditions (Dall'Osto et al., 2013). The PM levels in the urban areas of

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most megacities are higher than in their near suburban and rural areas (Mutlu and Lee, 2012). Air pollutants generated in urban environments can also travel to rural and remote areas (Li et al., 2010; Moreno et al., 2011). Natural (e.g., crustal minerals originating from wind-eroded bare soils or transported from arid areas by episodic dust storms), road traffic (e.g., exhaust from vehicles and non-exhaust emissions from mechanical abrasion, such as brake-, tyre-, and road-wear by re-suspension), and industrial emissions (fossil fuel combustion and industrial metallurgical processes) are the principal sources of trace metal-bearing aerosols (Calvo et al., 2013; Han et al., 2006; Pant and Harrison, 2013). Naturally derived trace metals are usually distributed in $PM_{10-2.5}$, and those of anthropogenic origin are mainly in $PM_{2.5}$ (Lee and Hieu, 2011; Luo et al., 2011). Their characteristics and concentration levels also vary with spatial and temporal factors (Dall'Osto et al., 2013; Moreno et al., 2011). Thus, the different site- and time-specific sources of pollutants, and the mixing of particles of different origin pose a real challenge to the assessment of overall atmospheric pollution and source apportionment (Nguyen et al., 2013; Wang et al., 2005). In order to identify the various sources of aerosol metals and to better understand their transport and deposition, it is necessary to investigate patterns relating to airborne metals both at local and regional scales.

Globally, $PM_{2.5}$-related mortality is widespread in populated regions, principally in East Asia and India, but also in Southeast Asia, Europe, and Russia (Silva et al., 2013). Atmospheric PM pollution is a particularly serious environmental issue in China (Chen et al., 2013; Zhang et al., 2012). The rapid industrialization, urbanization, and associated increase in energy demand during the last three decades have led to elevated amounts of PM and its associated pollutants in many regions, and resulted in profound deterioration of regional air quality (Cheng et al., 2013; Luo et al., 2012). China recently released a new ambient air quality standard of 70 $\mu g\,m^{-3}$ (CMEP, 2012), lower than the previous threshold value of PM_{10} but still much higher than the values of the WHO (20 $\mu g\,m^{-3}$) and EU (40 $\mu g\,m^{-3}$). Data on the long-term and nationwide ambient levels and risks of airborne trace metals are still limited. Although the PM and trace

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metals in some major cities of China have been investigated in previous studies, the main focus has been on levels of airborne metals in one city or in one type of site. Very few studies have been conducted on spatial or temporal variations in a large city (Shi et al., 2012) or in city clusters (Zhao et al., 2013). Furthermore, owing to China's large territory and population, and the rapidly growing economy, its environmental problems have important implications for the global environment. One significant implication is the transport and outflow of polluted aerosols to other regions (Lee et al., 2007b). In East Asia, China is the primary producer and consumer of coal and metal ores; thus, the possible trans-Pacific transport of Chinese emissions is also a significant issue in North America (Ewing et al., 2010; Gallon et al., 2011). Because numerous sources of PM are abundant in northern China (Li et al., 2011), the region has some of the worst air pollution in the world (Cheng et al., 2013). However, both the long-term loadings/concentrations of PM associated trace metals and the long-range transport of metal contaminants through air in the region have not been well characterized. Therefore, it is of vital importance to investigate temporal patterns of airborne metals, and to identify the potential sources of metal containing PM both in urban and rural areas of typical cities across northern China.

In this study, we analyzed both the airborne loadings ($ng\,m^{-3}$) and concentrations ($mg\,kg^{-1}$) of trace metals and Pb isotopic compositions in PM_{10} samples from a total of 18 sites (three types for each city: urban, rural village, and rural field) situated in seven cities across northern China. The sampling was conducted from west to east for a one-year period from 2010 to 2011. The primary objectives were: (1) to characterize spatial (both local and regional) and temporal patterns and variations in the levels of ambient airborne metals, the major sources of contribution, and the long-range transport mechanisms; and (2) to analyze the local, regional, and global implications of this PM pollution in northern China.

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2 Materials and methods

2.1 Sample collection

Air samples were collected at seven urban, five rural village, and six rural field sites of seven cities across northern China (nC) from west to east that might be influenced by the East Asian winter and summer monsoons, the Indian summer monsoon, and the westerly jet stream. These cities were: Wuwei (WW), Yinchuan (YC), Taiyuan (TY), Beijing (BJ), Dezhou (DZ), Yantai (YT), and Dalian (DL) (Fig. 1; Wang et al., 2012). The urban sites were located in the downtown area of big cities, the rural sites were in villages with at least 100 households, and the rural field sites were at least 200 m away from the nearest village. Both PM_{10} and gaseous phase samples were collected using a medium volume (200–400 L min^{-1}) cascade impactor (PM10-PUF-300, Guangzhou, China), with PM_{10} being sampled using glass-fiber filters (GFF, 200 × 150 mm^2, baked under 450 °C for 12 h). The GFFs were equilibrated in a desiccator (25 °C) for 24 h and weighed both before and after sampling. One 72 h sample was taken in every month from April 2010 to March 2011 at each site (12 months: April to September is the warm season, October to March is the cold season).

2.2 Sample analysis

The PM_{10} samples were analyzed for concentrations of major elements (Al, Ca, Fe, and Mg) and trace metals (Cd, Co, Cu, Ni, Pb, V, and Zn), and for Pb isotopic composition (Lee et al., 2007a). The PM_{10} samples (GFFs) were digested by being immersed in concentrated HNO_3-$HClO_4$ acids heated using heating block and finally dissolved in 5 % (v/v) high-purity HNO_3. Procedural blanks, sample replicates, and standard reference materials (NIST SRM 1648, urban PM) were randomly inserted for quality control. The metal concentrations were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Perkin Elmer Optima 3300DV). The elemental concentrations of the blanks were < 1 % of the mean analyte concentration for all metals,

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and the precision (relative standard deviations, RSD) of the control standards and replicates were generally lower than 5 %. The recovery rate (%) was 58, 104, 106, 111, 100, 96, 87, 90, 101, 95, and 108, for Al, Ca, Cd, Co, Cu, Fe, Mg, Ni, Pb, V, and Zn, respectively.

For source identification (Luo et al., 2011) and long-range air transport analysis, the Pb isotopic analysis was conducted using ICP-Mass Spectrometry (ICP-MS, Perkin Elmer Sciex Elan 6100 DRC^{plus}) for 70 selected samples (34 urban, 18 rural village, and 18 rural field) collected from June 2010 to March 2011. The solutions were diluted to a Pb concentration of about 25 $\mu g\,L^{-1}$ to optimize the analytical performance of the instrument. The analytical parameters were set at 250 sweeps per reading and 10 readings per sample solution. Procedural blanks and standard reference materials (NIST SRM 981, common Pb) were used for quality control. The analysis was repeated when the differences between the measured and certified values of the standard reference materials exceeded 0.5 %. The Pb counts of the blanks were < 0.5 % of the samples, and the RSD of the Pb isotopic ratios of the 10 replicates was typically < 0.5 %. The average measured ratios of $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ for SRM were 0.06461 ± 0.00013, 1.0936 ± 0.0019, and 2.3707 ± 0.0041, and in good agreement with the certified standard values (0.06455, 1.0933, and 2.3704, respectively).

2.3 Enrichment factors (EF)

Enrichment factor (EF) can be utilized to differentiate the metals originating from human activities and those from natural sources, and to assess the degree of anthropogenic influence (Tanner et al., 2008). The EF of each metal (M, $mg\,kg^{-1}$) relative to the mean composition of the earth's crust composition using Fe as the reference metal for terrigenous material was calculated by: $EF = [M/Fe]_{PM}/[M/Fe]_{crust}$. EFs close to 1 pointed to a crustal origin, while those greater than 10 were considered to have an anthropogenic source.

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2.4 Long-range air mass transportation by trajectory calculation and clustering

Generally, the qualitative identification of air pollutant transport pathways can be conducted through air trajectory clustering by grouping similar trajectories in terms of air mass movement. Backward air trajectories arriving at the aerosol sampling sites were calculated using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT, Version 4) model (http://ready.arl.noaa.gov/HYSPLIT.php). Because the synoptic atmospheric conditions at three locations in the same city were quite similar, back trajectories ending at these seven cities were calculated for urban location. Four 120 h backward trajectories (Lee et al., 2007a) were computed daily (local time: 02:00, 08:00, 14:00, 20:00) for the whole sampling year at an elevation of 500 m a.g.l. (above ground level). Then, cluster analysis (Rozwadowska et al., 2010) was used to classify trajectory groups for the total trajectories of each city in each season.

2.5 Multivariate statistical analysis

The statistical analysis was performed using PASW Statistics 18 (IBM SPSS software) and plotted by Origin 8 (OriginLab Corporation). The values represented in the box plot summarizing data distribution included the 1st, 5th and 25th percentiles, the median, the mean, and the 75th, 95th and 99th percentiles. Relationships between various variables were determined by the Pearson correlation coefficients (r). Principal component analysis (PCA) was conducted for source identification using factor extraction with eigenvalues > 1 after varimax rotation.

For source apportionment of airborne metals, the receptor model (absolute principal component scores-multiple linear regression analysis, APCS-MLR, Thurston et al., 2011) was used to estimate the source contributions of each metal. The APCS method enabled categories of the major sources of air pollution to be identified along with the quantitative contributions of pollutant species to each source group. In this study, stepwise MLR was applied using airborne metal concentrations (mg kg^{-1}) as dependent variables and absolute factor scores (obtained from PCA) as independent variables.

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The resultant regression coefficients were then employed to convert the absolute factor scores to produce estimates of each PC source contribution (Harrison et al., 1996).

3 Results and discussion

3.1 PM_{10} mass concentrations

The annual mean PM_{10} level at urban and rural areas of the seven cities was 160 $\mu g\,m^{-3}$ for northern China (Table 1), twice the CMEP standard (70 $\mu g\,m^{-3}$) and eight times the WHO guideline (20 $\mu g\,m^{-3}$). This value was much higher than the values observed in European countries, but lower than those in some developing Asian countries, such as Pakistan (von Schneidemesser et al., 2010) and India (Kulshrestha et al., 2009). The annual average PM_{10} concentration of 113 key cities in China was 88 $\mu g\,m^{-3}$ in 2010, indicating significant PM contamination in northern China (Chen et al., 2013; Cheng et al., 2013). The PM_{10} levels in all cities and areas were lower in the warm season than in the cold season, with highest value recorded in March (Fig. 2). The average PM_{10} concentrations in the cold season for the urban, rural village, and field areas (217, 235, 163 $\mu g\,m^{-3}$, respectively) of the seven sampled cities were all much higher than those in the warm season (123, 132, 93.5 $\mu g\,m^{-3}$). Similar patterns were also found in previous studies, such as of Mongolia (Nishikawa et al., 2011), and Beijing (Sun et al., 2004) between the warm and cold seasons.

For overall PM levels in northern China, the trend was generally in the order of urban > rural village > rural field in each city in summer (July–September), December and March, while in other months the trend was rural village > urban > rural field (Fig. 2b). The data clearly showed the regional pollution pattern rather than the usual trend of decrease for the urban–rural-background transect found in other places (Juda-Rezler et al., 2011). The regional results followed a trend of decreasing levels of PM_{10} from west to east for these locations in northern China, especially from Wuwei to Taiyuan in northwestern China and from Beijing to Dalian in northeastern China in the warm

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season, and from Wuwei to Yinchuan, and from Taiyuan to Dalian in the cold season, with the highest levels in Wuwei (Fig. 2a).

The spatial (local/regional) and seasonal variations of PM_{10} (Fig. 2) suggest different input sources and their relative contributions. An inventory of emissions developed from energy consumption and emission factors showed that the industrial burning of coal (such as in cement and iron/steel manufacturing) plus coal-fired power plants and biomass combustion in the residential sector were the largest sources of primary $PM_{2.5}$ emissions (Cao et al., 2012; Zhang et al., 2012). Meanwhile, it is believed that traffic emissions are now the main source in urban areas due to the rapidly increasing number of motor vehicles in cities (Zhao et al., 2013). At present, coal is still the primary fuel in most areas of northern China. It is widely used for industrial processes and daily life, and more coal is combusted for heating in the winter (Chen et al., 2013). The high PM_{10} in rural village areas of some cities indicates significant local emissions from the combustion of household solid fuel (e.g., coal, and biomass) for cooking and heating. The lack of precipitation, unfavorable diffusion conditions, and/or increased intensity of emissions in winter of northern China make it the most polluted season of the year. Lower PM_{10} concentrations were observed in eastern coastal cities (Dalian and Yantai), while the dust storms originating from the deserts of Xinjiang or Inner Mongolia can cause significant PM_{10} contamination in the western region (e.g., Wuwei and Yinchuan) in spring (Fig. 1). The strong winds in spring also blow dust from roads and construction sites in inland cities.

3.2 Loadings (ng m^{-3}) and spatial–temporal variations of ambient trace metals

Table 1 shows the average loadings of PM_{10} associated trace metals in different land use areas of the seven cities. The overall level of ambient air metals is Zn (276) $\gg$ Pb (93.7) $\gg$ Cu (54.9) $\gg$ Ni (9.37) > V (8.34) $\gg$ Cd (2.84) > Co (1.76 ng m^{-3}). In comparison with the currently available worldwide guidelines and threshold values of Cd (5), Ni (20), Pb (500), and V (1000 ng m^{-3}) in PM_{10} (WHO, EU, UK, USEPA, CMEP; Table 1),

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it can be seen that the levels of Cd (Dezhou) and Ni (Taiyuan, Wuwei, and Yinchuan) in some cities and areas exceeded the guidelines (Fig. 3).

Differences in trace metal loadings among the sampling sites (cities, areas) in the warm and cold seasons are illustrated in Figs. 3 and S1 in the Supplement. The levels of most metals were higher in the cold season than in the warm season, similar to the PM_{10} pattern, and mainly due to the role of PM_{10} mass loadings. Spatially, unlike with the PM_{10} levels there was no clear trend in trace metal levels among the studied cities, since in the western cities, Co, V, and Ni were high, while Pb, Zn, and Cd were low. The remarkable role played by PM_{10} concentrations in levels of airborne metals was similar to that observed in most other studies (Cheung et al., 2011; Srimuruganandam and Nagendra, 2011). Again, there were some exceptions for trace metals in different areas (Ho et al., 2003) and seasons (Contini et al., 2010; Moreno et al., 2011; Sun et al., 2004), implying that the role of particle sources on chemical components. Furthermore, compared with past monitoring data (2001–2003) for Beijing (Okuda et al., 2004), the levels of all ambient air metals decreased significantly in the current study, an indication of the environmental benefits of changes in energy consumption and industry structures, such as the gradual replacement of coal with natural gas and electricity in urban areas.

3.3 Sources of the airborne metals at different sites, areas, and cities, and the transportation of PM across northern China

As anthropogenic tracers, airborne metals are generated mainly by traffic exhaust (gasoline: Ce, La, Pt, Ba, Sb, V, Cu, Mn, and Sr; diesel: Ba, Cd, Zn, Sb, and V) and abrasion emissions (Zn, Pb, Ni, Ba, Cu, and Sb), the combustion of coal (Al, Sc, Se, Co, As, Ti, Th, Pb, and Sb), the burning of oil (V, Ni, Mn, Fe, Cr, and As), and metallurgical processes and industry (Cr, Ni, Mo, Cu, As, Mn, Fe, Zn, W, Rb, Sb, Pb, and Al) (Calvo et al., 2013; Luo et al., 2011; Pant and Harrison, 2013). As crustal or geological tracers, airborne metals (Si, Al, K, Na, Ca, Fe, Ba, Sr, Rb, and Li) come from re-suspended soil/dust. Fine particles derived from coal combustion (soot or fly ash) usually contain

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more Pb, Cu, Zn, As, and Cd than vehicle exhaust (Marmur et al., 2005). An important industry in China, nonferrous metal smelters are also important sources of atmospheric anthropogenic metals (Zhu et al., 2010). Urban street dust and fine soil fractions are enriched with anthropogenic trace elements such as Pb which, if re-suspended, can make a notable contribution to the inhalable trace metal load of urban aerosols (Luo et al., 2011; Mielke et al., 2010). Furthermore, episodic dust storms and volcanic eruptions may lead to the deposition of mineral matter thousands of kilometers away from their source regions (Grobety et al., 2010).

3.3.1 Trace metal concentrations (mg kg^{-1}) in PM_{10}

With regard to particle compositions, the average concentrations of metals associated with PM_{10} in different sampling sites of northern China are illustrated in Figs. 4 and S2. Spatially, the concentrations of Cd, Pb, and Zn in urban sites showed a trend of increase from west to east (Fig. 4), indicating a higher input from natural sources in western cities (high PM_{10} loadings) or a higher input from trace metal-enriched anthropogenic sources in eastern cities (low PM_{10} loadings). However, the differences in trace metals among the urban, rural village, and field sites were relatively small, reflecting the regional pollution characteristics in all of the sampled cities (Figs. 4 and S2 in the Supplement). In contrast to air metal loadings (ng m^{-3}), for northern China as a whole the average concentrations (mg kg^{-1}) of most trace metals in PM_{10} in the cold season were lower than in the warm season (Figs. 4 and S2), probably due to the presence of dust storms. However, in urban areas, concentrations of Pb, Zn, and Cu were still higher in the cold season due to the burning of coal. It is a fact that the main source of aerosols in China is anthropogenic (Khan et al., 2010). Coal for generating electricity (> 75 % from coal-fired power stations) and for domestic cooking and heating accounts for approximately 70 % of the national energy budget (Cao et al., 2012), and when it is burned, large amounts of metals are emitted due to a "concentration effect" (Zhu et al., 2010).

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3.3.2 EFs

For the whole of northern China, a similar order was observed for the EFs of metals in urban, rural village and field areas, namely: Cd (544) ≫ Pb (169) > Zn (113) ≫ Cu (17) ≫ Ni (2.6) > V (1.7) > Co (1.5); Cd (567) ≫ Pb (182) ≫ Zn (98) ≫ Cu (16) ≫ Ni (2.6) > V (1.6) > Co (1.5); and Cd (640) ≫ Pb (205) ≫ Zn (114) ≫ Cu (46) ≫ Ni (3.0) > V (2.0) > Co (1.5), respectively. The high EFs of Cd, Pb, Zn, and Cu ("urban metals") pointed to anthropogenic sources for these metals, while human activities contributed less to the presence of Co, V, and Ni. Similar to the metal concentration patterns, the average EFs for most trace metals were lower in the cold season due to natural dust storms, with the exception of Pb and Cu in urban areas due to their intensive anthropogenic input from coal combustion (Fig. S3 in the Supplement).

3.3.3 Source identification by PCA and source apportionment by APCS-MLR

For northern China, the relationships among metals are illuminated by correlation analysis (CA) (Table S1) and PCA (Table 2). In the warm season, three factors explain 75.2 % of the variations, namely: Al, Mg, Fe, Ca, and Co in PC1, with a 41.8 % variance attributed to crustal sources (re-suspended soil or dust); Cd, Zn and Pb in PC2 with a 23.1 % variance attributed to coal combustion and traffic sources; and V and Ni in PC3, with a 10.3 % variance attributed to the petrochemical industry and oil combustion (Khan et al., 2010). However, in the cold season, V and Ni are also in PC1 and attributed to crustal sources. These findings corroborate the concentration ($mg\,kg^{-1}$) patterns and the low EF values for V and Ni (cold < warm) but high EFs for Cd, Pb, and Zn (cold > warm, especially in urban areas), pointing to the presence of V and Ni as being more natural in the cold season than in the warm season due to sandstorms in the spring. There should be an additional anthropogenic source for Cu, such as the mining or smelting industries.

For the comparison among different cities, the PCA results for the city groups of Wuwei-Yinchuan-Taiyuan (western), Beijing-Dezhou (central), and Yantai-Dalian (east-

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ern coastal) (Fig. 1) are shown in Table S2 in the Supplement. There were two PCs (crustal: Al, Mg, V, Co, Fe, Ca, and Ni; coal combustion and traffic: Pb, Cd, Zn, and Cu) for the western group, and three PCs for both the central (Cu and Ni: metallurgical industry) and eastern (V and Ni: petrochemical industry, oil combustion) groups, indicating more complicated mixture of sources from west to east. Then, the quantitative APCS-MLR results of the source contribution (%) for each metal in different regions are shown in Table 3. In the western city group, dust/soil accounted for 81–109 % of the major metals (Ca, Fe, Mg, and Al) and 65–100 % of the trace metals (Ni, Co, and V), while coal combustion and traffic were responsible for 73–95 % of typical "urban metals" (Pb, Cd, Zn, and Cu). As for the central city group, Cu and 43 % of Ni were attributed to the metallurgical industry, while 65 % of Ni and 40 % of V were from mixed sources. In the eastern city group, crustal sources accounted for 35–50 % of trace metals (Ni, Co, and Cd), coal combustion and traffic for 58 % of Fe and 31 % of Co, and the petrochemical industry and oil combustion for 39 % of Ni and 56 % of V. These results demonstrate that the largest contributions to airborne "urban metals" (Cd, Cu, Pb, and Zn) in northern China were from coal combustion and traffic sources, whereas the most important contributor of Co, major metals (Al, Ca, Mg, and Fe), western V and Ni was soil/dust, while eastern V and Ni came mainly from oil combustion and industry. From west to east, the crustal contribution decreased, and the sources of all metals became more diverse with the possible long-range transport of both nearby regional pollutants (such as Cd from the central region to the east, Table 3, Fig. 3) and more distantly sourced pollutants (such as Ni from western sandstorms).

3.3.4 Pb isotopic characterization and source apportionment

Detailed Pb isotopic signatures of PM_{10} from selected sampling sites are plotted in Figs. 5 and S4 and listed in Table S3 in the Supplement. Major potential end-members for airborne Pb and their chemical and isotopic characteristics from the literature are also given in Fig. 5a and Table S3. Dust re-suspension and wind transport from surrounding deserts and non-polluted areas were considered natural sources (Widory

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et al., 2010), in this case the loess and soils from northern China and nearby regions. These had a low Pb concentration (14.1–39.3 mg kg^{-1}) and high isotopic ratios (^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb). Possible anthropogenic sources include coal combustion, vehicle exhaust, cement factories, and smelters (Cheng and Hu, 2010). The aerosol data for northern China is located along the Chinese lead line (Pb ore and coal, Fig. 5a), suggesting mainly native sources, but the total trend shifts slightly downward from the lead growth curve, which is a common tendency for Chinese Pb, and is likely influenced by the Th-rich continental crust in China (Mukai et al., 2001).

Large variations in PM_{10} Pb isotope ratios were obvious both for sampling sites and seasons (Figs. 5 and S4 in the Supplement), especially in Yinchuan and Wuwei in northwestern China. Dalian and Dezhou had higher ^{206}Pb/^{207}Pb, and Dezhou and Taiyuan had higher ^{208}Pb/^{207}Pb than other cities. They matched the Chinese coal scale or fell between the coal and Pb free petrol exhaust, and thus were mainly contributed by coal combustion mixed with traffic sources (Fig. 5a). The airborne Pb concentrations (137–1740 mg kg^{-1}) mainly falling within the coal combustion level (1788 mg kg^{-1}) and Pb free vehicle exhaust level (238 mg kg^{-1}) confirmed the results (Fig. 5b, Table S3). Temporally, the overall mean values for both ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb were higher in the warm season than in the cold season, corroborating the view that the trends of Pb concentration (mg kg^{-1}) and EF (higher in the cold season) are mainly due to coal combustion. After the phase-out of leaded gasoline in China from 1997, the major source of airborne Pb in China is coal combustion rather than vehicle exhaust. Yinchuan and Wuwei in northwestern China had low Pb isotopic ratios (Figs. 5a and S4 in the Supplement), especially which were lowest in their rural areas during the cold season, with low Pb concentrations (< 500 mg kg^{-1}), suggesting possible Pb tailing re-suspension input there (Pb ore isotopic ratios are much lower in northern than in southern China). The mixed and indistinguishable Pb isotopic ratios of different cities across northern China and the seasonal variations also imply the long-range atmospheric transport of metals.

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3.3.5 Long-range airborne transport of metals

Due to meteorological conditions and sources, the air pollution situation can vary according to season (Moreno et al., 2011). Since metal pollution in northern China is more significant in the cold season, an air-mass trajectory analysis was conducted to investigate the effects of possible long-range transport. In total, 728 five-day backward airflow trajectories were calculated using the HYSPLIT Model for each city in the cold season, and then classified into three to six groups by clustering (Fig. S5 in the Supplement). For the air mass directions arriving at eastern coastal and central cities in northern China, an average of 74–80 % were from the northwest and 13–26 % were from the north, while for western cities, all were from the northwest. Based on the synoptic atmospheric and climate conditions together with the trajectory analysis, the winter northwestern monsoon and the westerly jet stream were deemed to have the most substantial impact on the long-range transport of airborne metals in northern China (Fig. 1). Such results are also supported by the Pb isotopic model analysis. In summer, the composition of the air in northern China cities is less affected by long-range transport, especially from the west; thus, the values can represent the local background air. Alternatively, the aerosol Pb isotopic ratio in the warm season can be regarded as a characteristic value representing local aerosols of anthropogenic origin. Thus, the relative contribution of airborne Pb through long-range transport in the cold season could be estimated (Hsu et al., 2006). A two component end-member mixing model (Kusunoki et al., 2012) was adopted to compute the Pb isotopic characteristic values (R, $^{206}Pb/^{207}Pb$ or $^{208}Pb/^{207}Pb$) for long-range sources in the cold season ($R_{\text{cold source}}$), using the equation:

$$R_{\text{cold source}} = (C_{\text{cold}} \cdot R_{\text{cold}} - C_{\text{warm local}} \cdot R_{\text{warm local}})/(C_{\text{cold}} - C_{\text{warm local}})$$

where C is the Pb concentration (mg kg^{-1}) in PM samples. The results of the predicted long-range source $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ values in the cold season for the urban areas of these seven cities are shown in Fig. 6. There was some evidence of Pb

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transport from Beijing/Taiyuan/Wuwei to Dezhou, and from Taiyuan/Dezhou to Dalian, indicating air transport from west to east and some contribution from the north. On a decreasing scale from Yinchuan to Beijing, Taiyuan, and Yantai, there may be a significant contribution from sandstorms in the cold season, reflecting long-range transport from west to east in northern China in Asian dust episodes. Since the Taklamakan Desert and the Qaidam Basin in northwestern China and the Badain Jaran Desert and Tengger Desert of northern China are some of the largest sources of global atmospheric dust and, along with the deserts of Mongolia, contribute 70 % of total Asian emissions (Ferrat et al., 2012), the long-range transport of natural dust from the northern/northwestern deserts and loess deposits is an important contributor to Chinese urban air pollution. However, the relatively clean eastern coastal cities were less influenced by long-range sandstorms due to the effects of distance and particle size, but more affected by nearby regional anthropogenic air pollution from the north and west in the cold season.

4 Conclusions

The combined air pollution from coal combustion and traffic emission in China is significantly different from most developed countries' situation. Atmospheric PM_{10} pollution in northern China is serious, and shows a regional pollution pattern for urban–rural areas. Owing to the large land area, variations in emission sources (mainly anthropogenic) and meteorological conditions among different cities lead to distinguished spatial models. Furthermore, intensive coal combustion for heating and natural dust storms in the winter and spring of northern China result in specifically seasonal patterns. Thereby, the winter northwestern monsoon and westerly jet stream dominate the long-range transport of PMs and associated pollutants in northern China, and also has potentially global implications. Although trace metals are minor components in atmospheric PMs, their pollution levels and chemical compositions are not always consistent with the overall bulk PMs. Thus, both human health risk assessment and air quality guidelines

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for PM pollution control should consider and incorporate these key pollutants. More detailed and precise source investigations for urban ambient aerosols and associated trace metals are needed in future research.

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Table 1. Average annual loadings of particles (PM_{10}, $\mu g\,m^{-3}$) and associated trace metals ($ng\,m^{-3}$) in the ambient air of different land use areas of seven northern Chinese cities from April 2010 to March 2011 compared with the ambient air quality guideline values worldwide. The bold values stand for those higher than the guideline.

City	Site	PM_{10}	Cd	Co	Cu	Ni	Pb	V	Zn
WW	U	**361**	2.96	3.76	64.7	16.8	92.3	14.6	210
WW	R	**354**	2.08	3.74	78.7	14.5	68.3	14.8	260
WW	B	**196**	1.94	2.50	48.4	10.5	65.1	9.70	258
YC	U	**119**	2.24	1.58	28.7	7.26	91.2	5.69	475
YC	R	**156**	1.46	2.33	13.6	10.6	46.4	8.57	102
YC	B	**148**	1.98	1.77	15.0	7.50	69.0	6.47	157
TY	U	**226**	3.51	2.42	75.1	19.7	165	9.82	359
TY	R	**183**	2.54	1.56	39.4	10.5	88.5	6.55	167
TY	B	**143**	3.37	1.23	246	9.50	121	4.89	236
BJ	U	**193**	3.70	2.39	88.1	7.88	145	8.78	411
DZ	U	**140**	**5.16**	1.17	27.0	7.27	116	7.94	470
DZ	R	**115**	4.01	0.97	25.3	5.48	111	5.27	356
DZ	B	**134**	4.41	1.39	68.8	9.28	120	6.47	416
YT	U	**103**	2.79	1.27	61.4	8.74	109	11.3	323
YT	R	**107**	2.64	1.06	25.5	6.93	91.0	8.75	219
YT	B	**95.3**	2.63	1.16	35.4	8.33	98.4	10.9	255
DL	U	68.1	2.09	0.94	24.3	5.93	61.5	5.84	202
DL	B	46.6	1.83	0.58	29.2	3.98	47.4	5.14	118
CMEP, 2012	Secondary	70					500		
WHO, 2000	Guideline	20	5				500	1000	
USEPA, 2012	Primary/secondary	150					150		
EU, 2008	Target value	40	5			20	500		
UK, 2010	Limit value	40					500		
UK, 2010	Target value		5			20			

Notes: WW – Wuwei, YC – Yinchuan, TY – Taiyuan, BJ – Beijing, DZ – Dezhou, YT – Yantai, DL – Dalian; U – urban, R – rural village, B – rural field.

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Table 2. PCA rotated component matrix for concentrations (mg kg^{-1}) of trace metals and major elements in the air particulates (PM_{10}) of the warm (N = 105) and cold (N = 105) seasons of seven northern Chinese cities. Factor loading values ≥ 0.50 are in bold.

	Warm			Cold	
	PC1	PC2	PC3	PC1	PC2
Al	**0.967**	−0.038	0.094	**0.979**	−0.051
Ca	**0.791**	0.214	0.211	**0.909**	0.212
Cd	0.094	**0.850**	0.129	0.101	**0.751**
Co	**0.907**	−0.048	0.185	**0.967**	0.64
Cu	0.068	0.372	−0.181	0.108	**0.511**
Fe	**0.832**	0.024	0.062	**0.949**	0.135
Mg	**0.946**	−0.029	0.162	**0.969**	0.024
Ni	0.342	0.186	***0.793***	***0.793***	0.183
Pb	−0.010	**0.840**	0.351	0.017	**0.930**
V	0.174	0.045	***0.916***	***0.874***	0.177
Zn	−0.120	**0.842**	0.085	0.081	**0.840**
Eigenvalue (> 1)	4.60	2.54	1.13	6.19	2.32
% of Variance	41.8	23.1	10.3	56.2	21.1
Cumulative %	41.8	64.9	75.2	56.2	77.4
Main sources	Crustal (Soil/dust)	Coal combustion/ Traffic	Oil combustion/ Industry	Sandstorm	Coal combustion/ Traffic

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Table 3. Contribution (%) of each PC source for each metal in different city groups by stepwise MLR applied to absolute principle component scores after Table S2[a]. The bold values stand for the main sources contribute for each metal.

	WW-YC-TY (n = 105)				BJ-DZ (n = 47)					YT-DL (n = 58)				
	Crustal	Coal combustion/ Traffic	*UIS*[b]	R^2	Crustal	Coal combustion/ Traffic	*Metallurgical industry*	*UIS*	R^2	Crustal/ *Long-range*	Coal combustion/ Traffic	*Petrochemical industry, oil combustion*	*UIS*	R^2
Al	**109**	−6.1		0.99	**86**		14	1.8	0.91	**75**	14	9.1		0.99
Ca	**81**	27		0.96	**77**	24			0.99	**94**		15		0.95
Cd	30	**77**		0.94		**175**	−54		0.85	***50***	**65**			0.91
Co	***91***		10	0.95	***79***		23		0.99	***45***	***31***	9.3	15	0.71
Cu		**295**		0.31			***118***		0.88		**101**	20		0.80
Fe	**94**		7.8	0.92	**88**		17		0.99	31	***58***	−8.6	23	0.64
Mg	**99**		2.4	0.94	**95**		7.4		0.99	**75**	13	11		0.99
Ni	***65***	32	11	0.56			*43*	***65***	0.50	***35***	21	***39***	4.4	0.86
Pb		**73**	40	0.88		**64**	12	27	0.83		**99**		8.5	0.61
V	***100***		0.6	0.93	***49***	16		***40***	0.50	20		***56***	21	0.90
Zn		**109**	5.3	0.54		**85**	18	0.3	0.82		**79**	−6.3	30	0.78

[a] Values are presented as the percentage (%) of the concentration (mg kg^{-1}) attributed to each source, R^2 is the square of the coefficient of multiple correlation.
[b] Unidentified sources.

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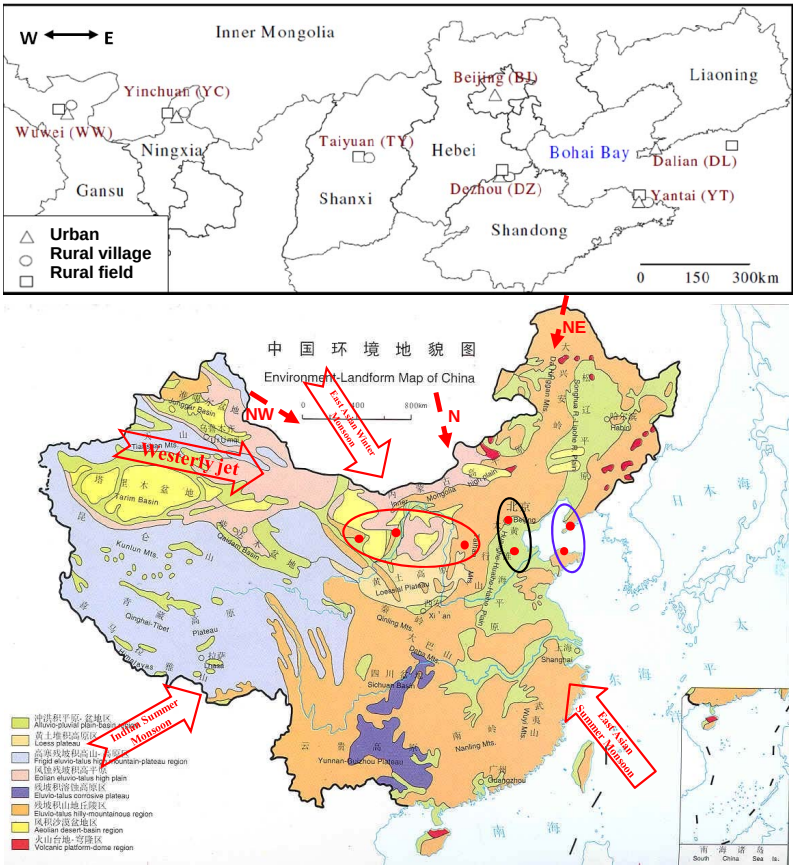

Figure 1. Sampling sites in different areas (seven urban, five rural village, six rural field) of seven cities in northern China (nC, from west to east). The approximate wind directions associated with the East Asian winter and summer monsoons, the Indian summer monsoon, and the westerly jet stream.

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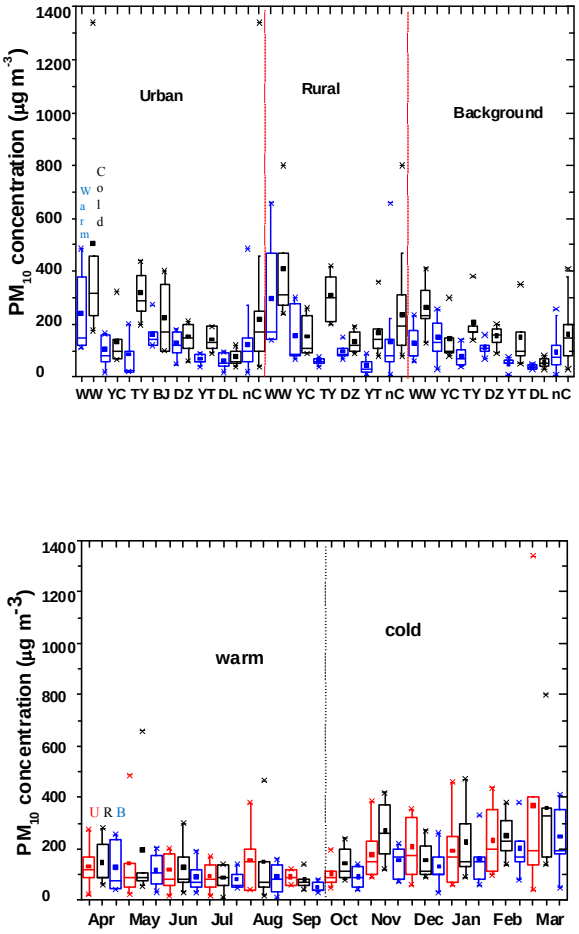

Figure 2. Concentrations and temporal variations (warm and cold seasons) of PM_{10} ($\mu g\,m^{-3}$) in different areas (U – urban, R – rural village, B – rural field background) of seven cities in northern China (nC, from west to east).

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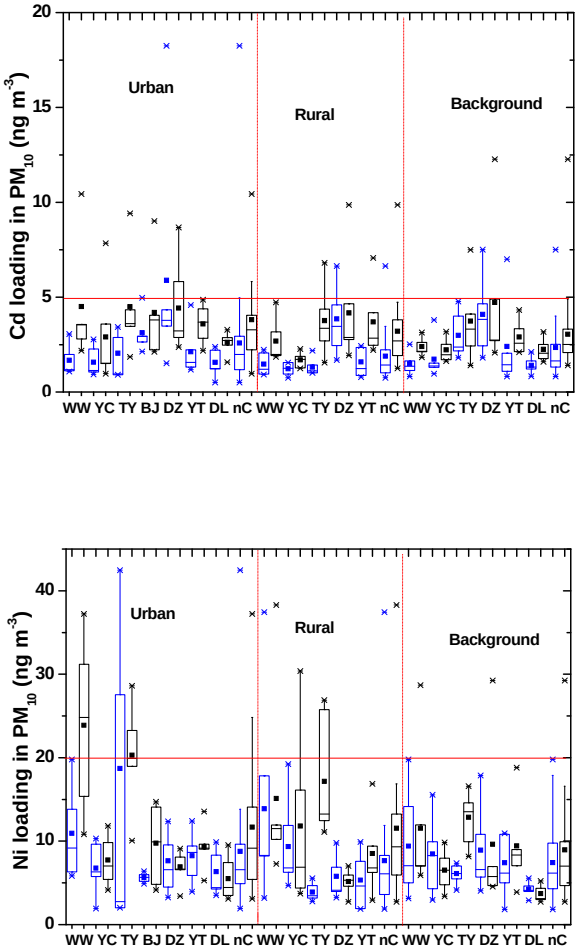

Figure 3. Trace metal loadings (ng m^{-3}) in the warm and cold seasonal PM_{10} of different areas of seven northern Chinese cities (nC, from west to east).

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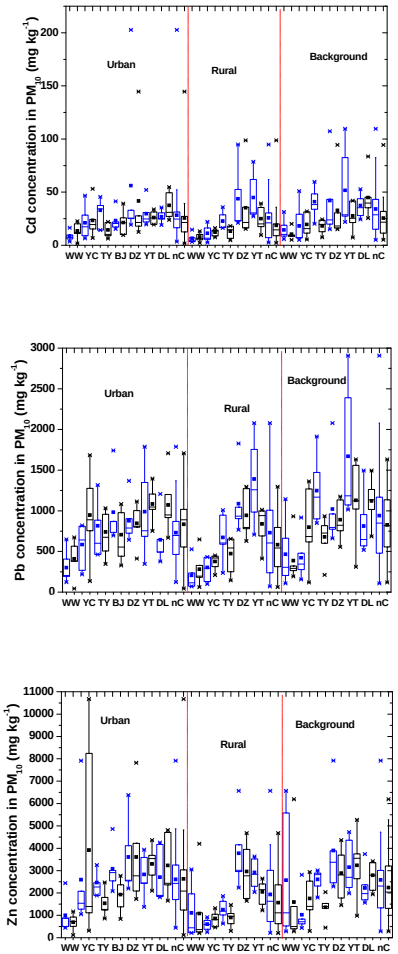

Figure 4. Trace metal concentrations (mg kg^{-1}) in the warm and cold seasonal PM_{10} of different areas in seven cities in northern China (nC, from west to east).

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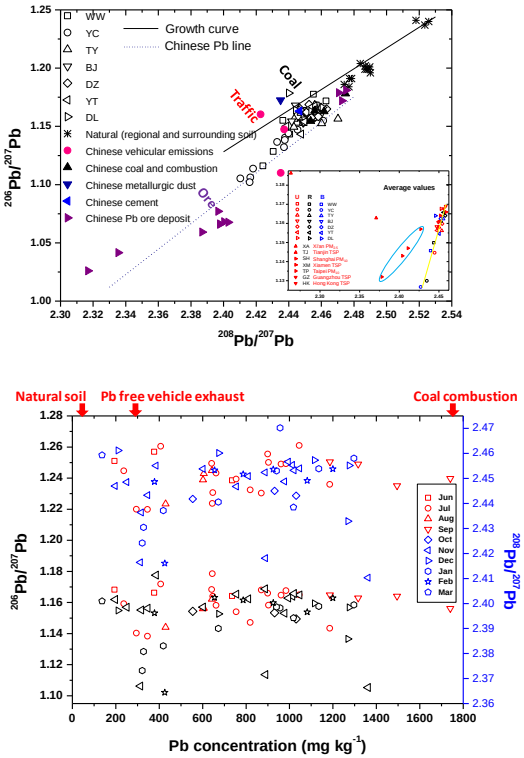

Figure 5. $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ for 70 selected aerosol (PM_{10}) samples collected in different areas (U-Urban, R-Rural village, B-Rural field) and months of seven cities in northern China from June 2010 to March 2011compared with natural background and potential anthropogenic sources; and compared with other Chinese cities using data drawn from the literature. The lead growth curve was based on Cumming and Richards (1975). The dotted Chinese lead line was drawn using data on major Pb ore deposits and coal in China from references listed in Table S3 in the Supplement.

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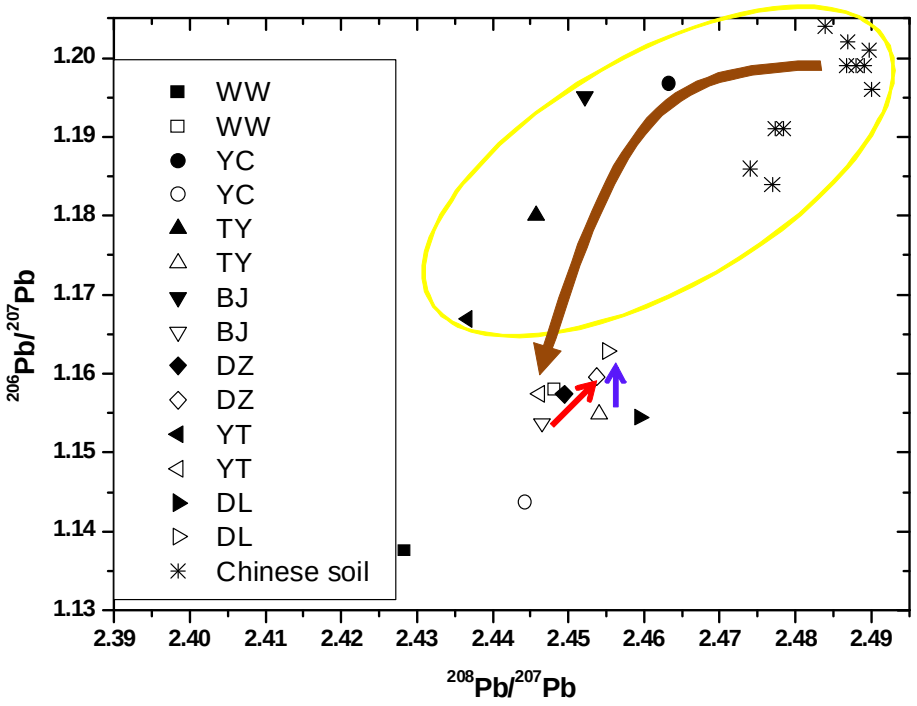

Figure 6. Long-range Pb source for urban airborne Pb in the cold season using the warm season as the local background (anthropogenic) source. The solid icons are the Pb source values predicted by the two-component end-member model compared with surrounding Chinese soil values (Table S3), and the hollow icons are the monitored cold urban sample values in each city. The predicted values close to the soil values and other city sample values imply the possible long-range source contribution, indicated using arrows.

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