Heavy metals and Pb isotopic composition of aerosols in urban and suburban areas of Hong Kong and Guangzhou, South China – evidence of the long-range transport of air contaminants

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Abstract

Rapid urbanization and industrialization in South China has placed great strain on the environment and on human health. In the present study, the total suspended particulate matter (TSP) in the urban and suburban areas of Hong Kong and Guangzhou, the two largest urban centres in South China, was sampled from December 2003 to January 2005. The samples were analysed for the concentrations of major elements (Al, Fe, Mg and Mn) and trace metals (Cd, Cr, Cu, Pb, V and Zn), and for Pb isotopic composition. Elevated concentrations of metals, especially Cd, Pb, V and Zn, were observed in the urban and suburban areas of Guangzhou, showing significant atmospheric trace element pollution. Distinct seasonal patterns were observed in the heavy metal concentrations of aerosols in Hong Kong, with higher metal concentrations during the winter monsoon period, and lower concentrations during summertime. The seasonal variations in the metal concentrations of the aerosols in Guangzhou were less distinct, suggesting the dominance of local sources of pollution around the city. The Pb isotopic composition in the aerosols of Hong Kong had higher $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in winter, showing the influence of the northern inland areas of China and the Pearl River Delta (PRD) region, and lower $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in summer, indicating the influence of Pb from the South Asian region and from marine sources. The back trajectory analysis showed that the enrichment of heavy metals in Hong Kong and Guangzhou was closely associated with the air mass from the north and northeast that originated from northern China, reflecting the long-range transport of heavy metal contaminants from the northern inland areas of China to the South China coast.

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Keywords: Aerosols; Heavy metals; Pb isotopes; Trajectories; South China

1. Introduction

Atmospheric particulate pollution has imposed a great burden on the terrestrial environment on a regional scale and even in a global context (Lelieveld et al., 2002; Venkataraman et al., 2005). Particulate matters are solid and liquid particles that are suspended in the air. Epidemiological studies have indicated that elevated concentrations of fine-particulate matters are associated with increased mortality and morbidity, especially in children and elderly people (Dockery and Pope, 1994; Pope et al., 1995; Schwartz et al., 1996). The rapid economic development that has taken place in China during recent years has led to severe deterioration of the local environment. Owing to China's large territory and population, the country's environmental problems have important implications for the global environment (Liu and Diamond, 2005). Past studies have demonstrated that aerosol and other pollutants can be transported from the Asian region to other countries (Jaffe et al., 1999). The Pearl River Delta (PRD) region is situated in the southern part of China, in which mega cities, such as Hong Kong and Guangzhou, and a number of recently established urban centres are located. It is one of the most developed areas in China. The rapid industrialization and urbanization of the PRD have caused elevated amounts of particulate matter and its components to be present in the region (Cao et al., 2004; Cheung et al., 2005; Lee et al., 2006). The result is the severe degradation of air quality in the South China region.

Heavy metals are non-degradable, and can accumulate in the human body system, causing damage to a person's nervous system and internal organs. They also act as confounding factors of cardiovascular diseases, reproductive impairments and cancer (Nriagu, 1988; Raghunath et al., 1999; Waisberg et al., 2003). Metals in the ambient air can catalyze the oxidative stress in the body cells, eliciting inflammatory injuries in the airway and lungs (Ghio et al., 1999; Nel, 2005). The inhalation of airborne trace metals can therefore have a long-term and serious impact on human health. Previous studies have investigated the characterization of chemical species in particulate matter in urban and rural areas of Hong Kong (Lam et al., 1997; Ho et al., 2003), the Pearl River Delta (PRD) region (Bergin et al., 2004) and several major cities in Asia (Cohen et al., 2004). However, these studies mainly focused on the chemical characterization of particulate

matter and on identifying the sources of particulate matter and its major components (carbonaceous species, major ions and mineral dust). Only a limited number of studies have been conducted on atmospheric heavy metal pollution in South China. The long-range transport through air of metal contaminants among the various Asian regions has not been well illustrated. Moreover, the long-term heavy metal concentrations of particulate matter in South China have not been well characterized. Although there have been some investigations into the atmospheric Pb isotopic composition of particulate matter in China (Mukai, et al., 1993; Bollhöfer and Rosman, 2001; Zhu et al., 2001), the information available on the Pb isotopic composition of particulate matter and its long-term variations in South China is still very limited. For these reasons, the present study was conducted, with the main objectives being: 1) to assess the annual average heavy metal concentration of aerosols in urban and suburban coastal areas of the Pearl River Delta (PRD) region in South China; 2) to evaluate the temporal variations of the Pb isotopic composition and the sources of atmospheric Pb in the PRD region using the Pb isotopic composition analysis; 3) to study the effect of the long-range atmospheric transport of heavy metal contaminants in the region using a back trajectory analysis.

2. Materials and Methods

2.1 The study area

The present study was conducted in urban and suburban areas of Hong Kong and Guangzhou, South China (Figure 1). Hong Kong is a highly urbanized metropolitan area situated at the southeastern tip of China. With a total area of only 1104 km^2 and a population of about 6.9 million, Hong Kong has one of the highest population densities in the world (6420 per km^2). Hong Kong's service industry has boomed in the past two decades, becoming a major economic contributor to the territory's economy. Key services sub-sectors include the wholesale, retail and import/export trades, and restaurants and hotels (Information Services Department, 2005). The manufacturing industry underwent a major restructuring during the 1980s and early 1990s, with most land- and labour-intensive processes have been relocated to mainland China and other countries in the region. Guangzhou is a major industrial and economic centre in South China. With a total area of 7434 km^2 and a population over 10 million, it is the largest city in South China.

Major industries in the city include automobile manufacturing, electronic and communication equipment manufacturing and petrochemical industries. Other sectors such as the fine chemical industry and the logistics industry have been expanding rapidly in the past few decades.

2.2 Sampling programme

Sampling of total suspended particulates (TSP) was conducted at two urban sites, at the Hong Kong Polytechnic University, Hong Kong (PU) and Sun Yet-sen (Zhongshan) University, Guangzhou (ZU); and at two suburban sites, at Hok Tsui (Cape D'Aguilar), Hong Kong (HT), and Baiyun Mountain, Guangzhou (BY) (Figure 1). The samples were taken on a bi-weekly basis over a one-year period, from December 2003 to January 2005. They were collected on a pre-heated (4 hr at 450°C) quartz microfibre filter (Whatman QM-A, 20.3×25.4 cm) using a high-volume sampler (of the Anderson type) at a flow rate of 0.217 - 0.228 m^3 min^{-1}. A sampling period of 24 hr was adopted. A total of 93 samples were collected at the four monitoring stations. The filters were then wrapped in aluminium foil and stored in polyethylene bags at 4°C.

2.3 Heavy metal analysis

The TSP samples (quartz filters) were digested using concentrated acids (Wong et al., 2003). One quarter of the filter was cut using stainless steel scissors and placed in acid-cleaned Pyrex test tubes. Subsequently, 14 ml of concentrated high-purity HNO_3 and 3.5 ml of concentrated $HClO_4$ were added, in which the filters were fully submerged. Procedural blanks and sample replicates were randomly inserted for quality control. The mixtures were then gently shaken using a vortex and then heated progressively to 190 °C in an aluminium heating block for 24 hr, until completely dry. Twelve ml of 5% (v/v) high-purity HNO_3 were added after initial acid digestion. The test tubes were then heated at 70 °C for 1 hr. After cooling, the solutions were decanted into acid-cleaned polyethylene tubes before being analysed.

The elemental concentrations of aerosols were determined using Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES, Perkin Elmer Optima 3300DV). Blanks, quality control standards, and standard reference materials (NIST SRM 1648, urban particulate matter) were inserted during the analytical measurement to detect contamination and drift. The

elemental concentrations of the blanks were <1% of the mean analyte concentration for all metals, and the precision (RSD) of the control standards and replicates were generally lower than 5%. The recovery rates for the heavy metals and major elements in the standard reference material (NIST SRM 1648) ranged from 88% to 96%. The recovery rate for Al was around 52% due to the presence of aluminosilicate minerals.

2.4 Pb isotopic composition analysis

The Pb isotopic composition analysis was conducted using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS, Perkin Elmer Sciex Elan 6100 DRC^{plus}). The solutions were diluted to a Pb concentration of about 25 μg l^{-1} using 5% high-purity HNO_3 to optimize the analytical performance of the machine. The analytical parameters were set as 250 sweeps per reading and 10 readings per sample solution. Procedural blanks and standard reference materials (NIST SRM 981, common lead) 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 precision (% RSD) of the Pb isotopic ratios of the ten replicates was typically <0.5%. The average measured Pb ratios of $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ (0.0644±0.0003, 1.0925±0.0024 and 2.3696±0.0029, respectively) were in good agreement with the certified standard values (0.0646, 1.0933 and 2.3704, respectively).

2.5 Statistical analysis

The results were summarized into a multi-elemental database using Excel®. As the data was not normally distributed (as shown in the large deviations from the normal distribution values in the Q-Q plots), the Kruskal-Wallis test (a non-parametric test) was employed to investigate on the differences in metal concentrations using SPSS 12.0 statistical software.

2.6 Back trajectory calculation

To investigate the sources of heavy metals, air mass backward trajectories were calculated using the HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory, Version

4.7), a comprehensive modelling system developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (Draxler and Rolph, 2003). Because the synoptic atmospheric conditions at two locations in the same city (i.e. the PU and HT sites in Hong Kong, and the ZU and BY sites in Guangzhou) were quite similar, seven-day back trajectories ending at Hong Kong and Guangzhou at 0600 UTC, i.e. 14:00 local time for all sampling dates, were calculated. For the classification of air masses, these trajectories ended at the height of 500 m AGL (above ground level), a level of about half the height of the mean daytime planet boundary layer (PBL), to represent general transport conditions in the PBL. Trajectories ending at different levels, i.e. 100 m, 500 m and 1000 m AGL were also calculated for detailed episode studies.

3. Results and discussion

3.1 Heavy metal concentrations

The annual mean elemental concentrations of Al, Cd, Cr, Cu, Fe, Mg, Mn, Pb, V and Zn of the aerosol samples collected at the four sites (PU, HT, ZU and BY) are summarized in Table 1. The average concentrations of most heavy metals in the urban and suburban areas of Guangzhou were higher than those in Hong Kong, indicating significant atmospheric trace metal pollution in Guangzhou. Since BY is located at the suburbs of Guangzhou city, the elevated concentrations of trace elements at the BY site showed that the atmospheric trace metal pollution in Guangzhou was affecting wider areas away from the urban centre. In particular, the mean concentrations of Cd, Pb, V and Zn of aerosols in the urban area of Guangzhou were much higher than those in the urban area of Hong Kong, which were about 4.9-fold, 4.8-fold, 3.1-fold and 4.0-fold higher. The mean trace element concentrations of aerosols (TSP) in the present study were compared with those in the urban areas of other major cities of the world (see Table 2). In comparison with Beijing (Okuda et al., 2004) and Taichung (Fang et al., 2003), Guangzhou had higher mean concentrations of V and Zn, while the mean Pb concentration was higher in Beijing and Taichung. On the other hand, the mean concentrations of heavy metals, including Cr, Cu, Pb, V and Zn, in Guangzhou were higher than those in Hong Kong (the present study), Tokyo (Var et al., 2000) and Ho Chi Minh City (Hien et al., 2001).

3.2 Temporal variations in heavy metal concentrations

The trace elemental concentrations of aerosols measured at the four monitoring sites (PU, HT, ZU and BY) over the one-year period are plotted as a time-series in Figure 2a-d. Distinguished seasonal patterns were found in the heavy metal concentrations of aerosols at PU and HT (Figure 2a-b). The concentrations of most elements, Cd, Cu, Pb, V and Zn, during the winter seasons (Dec 2003 – early Feb 2004 and Oct 2004 – Jan 2005) were significantly higher than at other times. The heavy metal concentrations of aerosols were relatively low during the spring to summer season (Mar 2004 – July 2004). This kind of seasonal pattern, with lower concentrations of heavy metals in summer, is similar to those of other airborne primary pollutants in this region (Lam et al., 2001; Wang et al., 2003). Considering the subtropical climate with strong solar radiation but many clouds in these coastal regions, the seasonal change in the height of planet boundary layer might be relative small. Therefore, the long-range transport due to Asian monsoon could be the most dominated effects to the seasonal variations in heavy metals at these sites (see further discussion in Section 3.5).

In Figure 2c-d, the concentrations of Cd, Cr, Cu, Pb and V at ZU and BY exhibited less temporal variability. However, the Zn concentration at ZU and BY peaked during the winter season (Jan 2004 – Feb 2004). Relatively low trace metal concentrations were observed in April 2004 at both the urban and suburban sites of Guangzhou. The concentrations of most heavy metals remained high throughout the year, suggesting that the sources of atmospheric heavy metal pollution in Guangzhou were probably local, such as from industrial and vehicular emissions within the city.

3.3 Temporal variations in Pb isotopic composition of aerosols

Lead has four stable isotopes, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. The last three Pb isotopes (^{206}Pb, ^{207}Pb and ^{208}Pb) are radiogenic, and are the end-members of the radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively. Depending on the age and initial U and Th content of the source rock, each Pb ore has its own characteristic Pb isotopic composition. Because the isotopic composition of the Pb from each source is different, the Pb isotopic ratios of aerosols reflect the mixing of

naturally derived Pb with the anthropogenic Pb from other sources, and can be used to identify the different origins of Pb in the atmosphere. As discussed earlier, elevated metal concentrations were observed during the winter period (Dec 2003 – Feb 2004 and Oct 2004 – Jan 2005) and low metal concentrations in the summer time (Mar 2004 – July 2004). The average Pb isotopic compositions of aerosols during the winter and summer periods and the annual average values from each site are shown in Table 3. The annual average Pb isotopic compositions ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios) of aerosols at PU (1.161±0.008 and 2.451±0.012) and HT (1.161±0.013 and 2.449±0.015) were found to be lower than those measured at ZU (1.168±0.005 and 2.456±0.006) and BY (1.169±0.05 and 2.459±0.005). The time-series of the $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ ratios at the four sites are illustrated in Figure 3a-d. As seen from the figures, the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios at PU and HT exhibited clear seasonal pattern during the annual cycle, with relatively higher $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios during the winter seasons (Dec 2003 – Feb 2004 and Oct 2004 – Jan 2005), and lower Pb isotopic ratios in the summer (Mar 2004 – July 2004) (see Figure 3a-b). The seasonal variability in the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios was observed to be more pronounced in the suburban areas (HT), due to the less influences from local pollution sources. However, a drastic increase in Pb isotope ratios occurred at the end of May and early June at PU and HT. Back trajectories analysis showed that the air masses came from the east (on 24th May) and northeast (on 7th June) regions (classified as CT and CI in Figure 6a, respectively), which were different from the most common trajectory pattern in summer, i.e. from the ocean in the south. The increase in Pb isotopic ratios hence showed the impact of long-range transport of pollutants to the coastal areas of Hong Kong. The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of Guangzhou aerosols were less varied during the annual cycle (Figure 3c-d), showing that the Pb may mainly come from relatively homogenous sources (e.g. local emissions). In general, both the results of the Pb isotopic composition and heavy metal concentrations showed strong seasonal variations at the two sampling sites (PU and HT) in Hong Kong.

3.4 Sources of Pb in aerosols

Table 4 shows the Pb isotopic compositions of natural and anthropogenic sources in the PRD region. To elucidate the sources of atmospheric Pb during different seasons, the Pb isotopic

compositions of the aerosols collected at the study sites (PU, HT, ZU and BY) at different periods of the annual cycle were compared with known natural and anthropogenic sources in the PRD region (see Figure 4).

3.4.1 Winter season

During the winter seasons, from December 2003 to February 2004, and in the following year from November 2004 to January 2005, the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios were relatively higher compared to other sampling times (see Figure 4). The Pb isotopic ratios of the winter aerosols were found to closely resemble those of the Pb ore and from industrial sources in the PRD region, probably reflecting the significant inputs of Pb from industrial emissions and the use of Pb from local ore (e.g. the Fankou Pb ore) in the region. The Pb isotopic ratios of the aerosols were also closely related to those of the vehicular emissions and the road dust in the PRD region, showing the influence of traffic sources. Although leaded petrol has been phased out in Hong Kong since 1999 and all over China since 2000, Pb can be emitted into the atmosphere from the wind-blown dust and soil particles which are known to be highly contaminated with Pb in Hong Kong due to the historical uses of Pb (Duzgoren-Aydin et al., 2004; Lee et al., 2006). Other possible local sources of Pb include the fly ash emissions from the coal fired power stations in Hong Kong, however, no Pb isotopic composition data was available for comparison. As most industrial activities in Hong Kong have been relocated to mainland China, the resemblance of the winter aerosols of Hong Kong to those of the PRD industrial sources is strong evidence of cross-border pollution from the PRD region to the coastal area of Hong Kong. Polluted air masses from the northern inland areas of China and the PRD region can be brought to the downwind areas of Hong Kong through the winter monsoon air flow. In summary, the Pb isotopic ratios of aerosols were less varied during the winter period (see Figure 4), showing that regional emissions from China Mainland, particularly the PRD region were the dominant pollution sources in the study region. The Pb inputs in the air were due to the mixing of anthropogenic Pb from various sources, including local Pb ore, industrial and vehicular emissions, and other sources.

3.4.2 Summer season

From March 2004 to August 2004, the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of some of the aerosols were lower, and were close to or the same as those of South Asian aerosols from Ho Chi Minh City, Vietnam (1.155, 2.430); Bangkok, Thailand (1.127, 2.404); Kuala Lumpur, Malaysia (1.141, 2.410) and Jakarta, Indonesia (1.131, 2.395) (Bollhöfer and Rosman, 2000) (see Figure 4). During the spring and summer seasons, the prevailing winds in the PRD region were the oceanic winds from the south. Figure 5a-b shows the back trajectory of the air mass on two typical days during which lower $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios were observed at all of the sites (11^{th} – 12^{th} May 2004 and 7^{th} July 2004) (see Figure 3a-d). The trajectory on 12^{th} May 2004 showed that the air mass originated from the Philippines travelling north-westerly, which eventually reached the coastal areas of South China region. On the other hand, the air mass on 7^{th} July 2004 originated from the Indian Ocean, and moved in a north-easterly direction, passing through the South Asian countries, such as Vietnam and Malaysia, to the coastal areas of South China region. Furthermore, the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios were observed to be lower when the air masses had originated from the sea (air trajectories not shown), possibly due to the dilution/mixing effect of the marine air mass. Particles that originated from South Asian countries and marine sources may be transported to the coastal areas of South China, causing a change in the Pb isotopic composition of the aerosols. As discussed earlier, the seasonal variations in the Pb isotopic ratios of aerosols in Guangzhou were less significant than those in Hong Kong, due to the dominance of local sources of pollution. The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of some of the aerosols there remained high ($^{206}Pb/^{207}Pb$, 1.165; $^{208}Pb/^{207}Pb$, 2.460), even during the summer season (see Figure 4).

3.5 Back trajectory analysis

3.5.1 Air masses classification

Figures 6a-b presents the plots of the seven-day back trajectories ending at Hong Kong and Guangzhou during the measurement period (Dec 2003 – Jan 2005). In general, three categories of air masses can be identified during the annual cycle, 1) CI – air masses coming from the north or northeast that originated from the continental inland areas of northern China, Mongolia, Central Asia and Siberia and reaching the South China region through the inland areas of China; 2) CT – air masses from the north or northeast that originated from continental inland areas of the northern

China, reaching the South China region through the Southeast China coast; 3) SS – air masses coming from the south, southwest, or east that originated mostly from the sea, including the South China Sea, the Indian Ocean and the Pacific Ocean. The characteristics of the long-range transport pattern of the air masses arriving at the South China region exhibited a clear seasonal pattern throughout the annual cycle. From December 2003 to March 2004, the whole South China region was generally dominated by the air masses CI and CT, due to the Asian winter monsoon. Since early April 2004, the region had begun to be influenced by the marine air masses SS, although sometimes the continental air masses occasionally affected the study sites. At the end of the annual cycle, from mid August 2004 to January 2005, the air masses CI and CT were again dominant.

3.5.2 Metal concentrations in different air masses

The mean concentrations of major and trace elements in the three categories of air masses are shown in Table 5. In Hong Kong, the CI Category had the highest concentrations of heavy metals, including Cd, Cr, Cu, Mn, Pb, V and Zn, which were 2.85, 16.5, 68.7, 57.1, 75.7, 16.6 and 362 ng m^{-3}, respectively. In Guangzhou, the CT Category contained the highest concentrations of heavy metals, including Cd, Cr, Cu, Mn, Pb, V and Zn, which were 10.9, 24.0, 106, 94.5, 396, 58.3 and 1560 ng m^{-3}, respectively. Elevated concentrations of heavy metals were also found in Guangzhou under the CT Category (see Table 5). The results showed that significant amounts of heavy metals were transported from the northern inland areas and the PRD region to the coastal areas of South China. On the contrary, the cleaner marine air mass contained the lowest concentrations of heavy metal during the SS period. It should be noted that despite similar meteorological conditions at Hong Kong and Guangzhou, the heavy metal concentrations in Guangzhou aerosols were much higher than those in Hong Kong, suggesting that local emissions play an important role in heavy metal pollution in Guangzhou, apart from the influence of the long-range transport of pollutants from the northern region.

To further examine differences in the mean elemental concentrations (Al, Cd, Cr, Cu, Fe, Mg, Mn, Pb, V and Zn) of the different air masses, the Kruskal-Wallis test was performed. In Hong Kong, the mean concentrations of elements such as Al, Cd, Pb and Zn ($P<0.01$) and Cu, Fe, Mg and Mn ($P<0.05$) were found to be statistically different under different air masses. CI contained the

highest mean concentrations of Al, Cd, Cu, Fe, Mn, Pb and Zn, and CT contained the highest mean concentrations of Mg. The significant enrichment of metals, especially Al, Cd, Pb and Zn, in the aerosols of Hong Kong under CI and CT clearly indicated the long-range transport of metal pollutants by the air mass originating from northern inland areas (including the PRD region) to the downwind areas of Hong Kong. Other metals, such as Cr and V exhibited no significant variability ($P > 0.05$).

In Guangzhou, the mean concentrations of Cd, Cu, Mn and Pb ($P < 0.01$) and Cr, Fe and Zn ($P < 0.05$) were statistically different under different air masses. The highest mean concentrations of Cd, Cr, Cu, Fe, Mn, Pb and Zn were found in CT. The significant enrichment of these metals, particularly Cd, Cu, Mn and Pb, observed in the aerosols of Guangzhou under CT could be partly attributed to the long-range transport of pollutants by the air mass originating from northern China, which passed through the South China coast to Guangzhou. However, as discussed earlier, local emissions in Guangzhou also contributed significantly to the heavy metal pollution in the region, as revealed by the lack of seasonal variations in the heavy metal concentrations and the Pb isotopic composition. Previous studies have suggested that aerosol sources in and around Guangzhou are responsible for a significant fraction of the fine particulate matter in the PRD area (Bergin et al., 2004). There was no significant difference in the mean concentrations of other metals, such as Al, Mg and V ($P > 0.05$).

3.5.3 Episodic days of metallic pollutants

As discussed earlier, the heavy metal concentrations in aerosols were less varied in Guangzhou. However, several episodic days were observed at PU and HT (Hong Kong) during the one-year sampling period (see Figure 2a-b). Most of the episodic days were found during the winter monsoon period, although some occasional occurrences were also observed during summertime. The seven-day backward trajectories during the episodic days ending at three heights (i.e. 100 m, 500 m and 1000 m) over the sites are shown in Figure 7.

Elevated heavy metal concentrations were observed on 31st December 2003 at both PU and HT (see Fig 2a-b), when the northerly winds prevailed during the winter monsoon period. On the

episodic day, the concentrations of Cd, Cu, Mn, Pb, V and Zn at PU were notably high, at 7.72, 90.0, 176, 267, 32.0 and 824 ng m^{-3}, respectively; and those measured at HT reached 4.88, 65.4, 90.4, 172, 17.1 and 590 ng m^{-3}, respectively. Figure 7a shows that the high-speed air mass originated from Siberia, and travelled southwards along the China coast. Subsequently, the air masses passed through areas near Guangzhou before reaching Hong Kong via northerly winds. One trajectory showed that the higher-altitude air mass passed through southern areas of Taiwan before it reaching Hong Kong. Industrial and vehicular emissions in northern inland areas of China and the PRD region could contribute to the enrichment of heavy metals in the downwind areas of Hong Kong through the long-range transport of air pollutants. Similar phenomena were also observed on the 19th October 2004 and 3rd January 2005, when elevated heavy metal concentrations were found at PU and HT (see Figure 2a-b). The trajectories showed that the air mass originated from Eurasia, and travelled southwards through continental inland areas of China to the coastal area of Hong Kong (see Figure 7b-c). On the 24th August 2004, elevated heavy metal concentrations were observed at PU and HT (see Figure 2a-b) during the summertime. Figure 7d shows that the air mass originated from the east coast of China, near Shandong province, and travelled southwards to the coastal areas of Hong Kong. The air mass passed through northern inland areas and the PRD region at a moderate speed, which resulted in the transport of pollutants to the downwind areas of Hong Kong. Nevertheless, the metal concentrations during this summer episode were relatively lower than those measured during the winter monsoon period (see Figure 2a-b).

4. Conclusions

Elevated concentrations of trace metals were found in the urban and suburban aerosols of Guangzhou, especially Cd, Pb, V and Zn, showing significant atmospheric trace metal pollution. Distinct seasonal trends were found in the heavy metal concentrations of aerosols in Hong Kong, with higher concentrations of metal during the winter monsoon period, and lower concentrations during the summertime, while no clear seasonal variability was observed in the metal concentrations of aerosols in Guangzhou. The Pb isotopic composition in the aerosols of Hong Kong had higher $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in winter, showing the influence of pollution

sources in the northern inland areas of China and the PRD region, and lower $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in summer, reflecting the influence of Pb from the South Asia region and from marine sources. The back trajectory analysis showed that high concentrations of heavy metals in Hong Kong and Guangzhou were significantly associated with the air mass from the north and northeast that originated from northern China, reflecting the long-range air transport of metal contaminants from northern inland areas to the South China coast. Nevertheless, local emissions also constituted a significant part of the atmospheric heavy metal pollution in Guangzhou, as indicated by the lack of clear seasonal variations in the atmospheric metal concentrations and Pb isotopic composition throughout the year.

Acknowledgements

This work was supported by the Research Grants Council (RGC) of the Hong Kong SAR Government (PolyU 5147/03), and the Natural Science Foundation of China (NSFC) (Nos. 40590391 and 40473041). We thank Dr S. C. Zou of Sun Yet-sen (Zhongshan) University, and Dr G. Q. Liu, Mr X. Liu and other members of the Guangzhou Institute of Geochemistry, CAS, for their help with the sampling programme of the present study.

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Table 1. The mean concentrations of major and trace elements of TSP in urban, suburban and suburban areas of Hong Kong and Guangzhou, South China, during a one-year period

($ng\ m^{-3}$)	Poly U (PU) urban n = 25	Hok Tsui (HT) suburban n = 26	Zhongshan U (ZU) urban n = 22	Baiyun Mt. (BY) suburban n = 23
	Mean ± S.D.			
Al	1470±1800	891±632	3390±2500	2810±1780
Cd	1.61±1.86	2.53±1.65	7.85±7.40	5.73±3.81
Cr	15.3±11.8	12.4±7.75	20.9±13.9	16.9±7.08
Cu	70.8±88.2	30.8±16.6	82.3±67.7	65.2±30.6
Fe	1480±2190	599±385	2860±1750	2090±1460
Mg	546±322	1110±645	638±389	794±1330
Mn	48.3±47.5	30.7±24.0	84.7±47.6	65.4±41.1
Pb	56.5±65.0	53.5±43.1	269±238	219±133
V	14.3±16.4	11.9±7.92	44.8±41.5	28.1±20.6
Zn	298±214	241±143	1190±1470	899±1020

Table 2. The annual mean trace elemental concentrations of TSP in Hong Kong, Guangzhou and other major cities in the world

Location	(ng m^{-3})	Cd	Cr	Cu	Pb	V	Zn	Reference
Hong Kong – PU (n=26)	Urban	1.61	15.3	70.8	56.5	14.3	298	Present study
Hong Kong – HT (n=26)	Suburban	2.53	12.4	30.8	53.5	11.9	241	Present study
Guangzhou – ZU (n=22)	Urban	7.85	20.9	82.3	269	44.8	1190	Present study
Guangzhou – BY (n=19)	Suburban	5.73	16.9	65.2	219	28.1	899	Present study
China								
Beijing (n=618-728)	Urban	6.8	19	110	430	13	770	Okuda et al. (2004)
Japan								
Tokyo (n=23)[a]	Urban	-	6.09	30.2	124.7	8.90	298.7	Var et al. (2000)
Vietnam								
Ho Chi Minh City (n=61)	Urban	-	8.63	1.28	146	7.3	203	Hien et al. (2001)
Taiwan								
Taichung (n=43)	Urban	8.5	29.3	198.6	573.6	-	395.3	Fang et al. (2003)

[a] Long-term average concentration (23 yr) based on the annual average concentration.

Table 3. The Pb isotopic compositions of aerosols at urban and suburban areas of Hong Kong and Guangzhou

			$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	Pb (ng m^{-3})
PU		Range	0.06313-0.06495	1.1463-1.1791	2.4290-2.4695	
urban	winter[a]	Mean	0.06363	1.1631	2.4579	94.0
	(n=11)	S.D.	0.00026	0.0058	0.0081	82.6
	summer[b]	Mean	0.06410	1.1549	2.4390	24.0
	(n=10)	S.D.	0.00044	0.0068	0.0087	19.7
	annual	Mean	0.06386	1.1611	2.4506	56.5
	(n=25)	S.D.	0.00039	0.0084	0.0123	65.0
		95% C.I.[c]	0.06370-0.06402	1.1576-1.1645	2.4455-2.4557	
HT		Range	0.06306-0.06520	1.1255-1.1819	2.4065-2.4707	
suburban	winter[a]	Mean	0.06390	1.1636	2.4566	80.1
	(n=12)	S.D.	0.00049	0.0059	0.0068	37.5
	summer[b]	Mean	0.06408	1.1516	2.4360	23.6
	(n=10)	S.D.	0.00046	0.0141	0.0156	28.1
	annual	Mean	0.06396	1.1606	2.4491	53.5
	(n=26)	S.D.	0.00045	0.0125	0.0149	43.1
		95% C.I.[c]	0.06378-0.06414	1.1556-1.1656	2.4431-2.4551	
ZU		Range	0.06309-0.06395	1.1551-1.1750	2.4446-2.4679	
urban	winter[a]	Mean	0.06378	1.1690	2.4598	393
	(n=8)	S.D.	0.00021	0.0044	0.0065	336
	summer[b]	Mean	0.06360	1.1661	2.4519	147
	(n=10)	S.D.	0.00027	0.0054	0.0041	92
	annual	Mean	0.06366	1.1677	2.4561	269
	(n=22)	S.D.	0.00024	0.0047	0.0062	238
		95% C.I.[c]	0.06356-0.06377	1.1656-1.1698	2.4533-2.4588	
BY		Range	0.06320-0.06403	1.1545-1.1783	2.4487-2.4695	
suburban	winter[a]	Mean	0.06374	1.1698	2.4627	280
	(n=9)	S.D.	0.00025	0.0033	0.0047	148
	summer[b]	Mean	0.06369	1.1677	2.4549	167
	(n=10)	S.D.	0.00019	0.0069	0.0037	123
	annual	Mean	0.06367	1.1690	2.4586	219
	(n=23)	S.D.	0.00022	0.0050	0.0054	133
		95% C.I.[c]	0.06358-0.06377	1.1668-1.1711	2.4563-2.4610	

[a] Dec 2003 – Feb 2004 and Oct 2004 – Jan 2005 (high metal concentrations observed in this study)
[b] Mar 2004 – July 2004 (low metal concentrations observed in this study)
[c] 95% confidence interval for annual means

Table 4. The Pb isotopic compositions of natural and anthropogenic sources in the PRD region

	No. of samples	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	References
Natural sources				
Granite in eastern Cathaysia	102	1.1834	2.4680	Zhu (1998)
Granite in the PRD	6	1.1842	2.4824	Zhu (1998)
Volcanic rocks in Foshan	8	1.1993	2.4965	Zhu et al. (1989)
Uncontaminated soils in the PRD	2	1.1952	2.4815	Zhu et al. (2001)
Country park soils in Hong Kong	11	1.1996	2.4953	Lee et al. (2006)
Anthropogenic sources				
Foshan Pb-Zn deposit	26	1.1716	2.4725	Zhu (1998)
Foshan aerosols (hardware factory)				Zhu et al. (2001)
- April 1994	1	1.1622	2.4569	
- October 1994	1	1.1650	2.4630	
Foshan aerosols (plastic factory)				Zhu et al. (2001)
- April 1994	1	1.1552	2.4569	
- October 1994	1	1.1664	2.4646	
Automobile exhaust in the PRD	3	1.1604	2.4228	Zhu et al. (2001)
Hong Kong road dust				Duzgoren-Aydin et al. (2004)
- HKU car park	3	1.1514	2.4318	
- High Street	3	1.1574	2.4456	
- Mongkok	3	1.1550	2.4427	

Table 5. The mean concentrations of TSP at Hong Kong (PU and HT) and Guangzhou under different air masses

($ng\ m^{-3}$)	Air mass	n		Al	Cd	Cr	Cu	Fe	Mg	Mn	Pb	V	Zn
Hong Kong	CI	24	Mean	1490	2.85	16.5	68.7	1450	828	57.1	75.7	16.6	362
(PU & HT)			S.D.	1780	2.26	11.4	90.6	2250	586	48.1	67.4	16.4	194
	CT	16	Mean	1170	1.76	10.1	29.8	787	1070	26.4	54.0	9.94	205
			S.D.	854	0.76	6.21	11.4	425	667	16.0	27.1	6.84	83.6
	SS	11	Mean	484	0.87	13.5	40.6	470	515	19.4	11.2	9.88	159
			S.D.	243	0.65	9.73	26.7	315	213	8.01	9.90	7.80	168
Guangzhou	CI	23	Mean	3200	7.58	20.1	78.5	2550	606	86.0	263	30.0	1190
(ZU & BY)			S.D.	2060	4.17	13.1	41.0	1690	391	42.5	134	30.5	1160
	CT	9	Mean	4210	10.9	24.0	106	3400	778	94.5	396	58.3	1560
			S.D.	2860	9.23	7.64	83.1	1970	391	52.9	291	47.4	1970
	SS	13	Mean	2140	2.45	13.1	42.1	1690	875	41.4	103	32.1	431
			S.D.	1410	1.89	5.81	19.5	828	1750	22.4	65.3	19.8	288

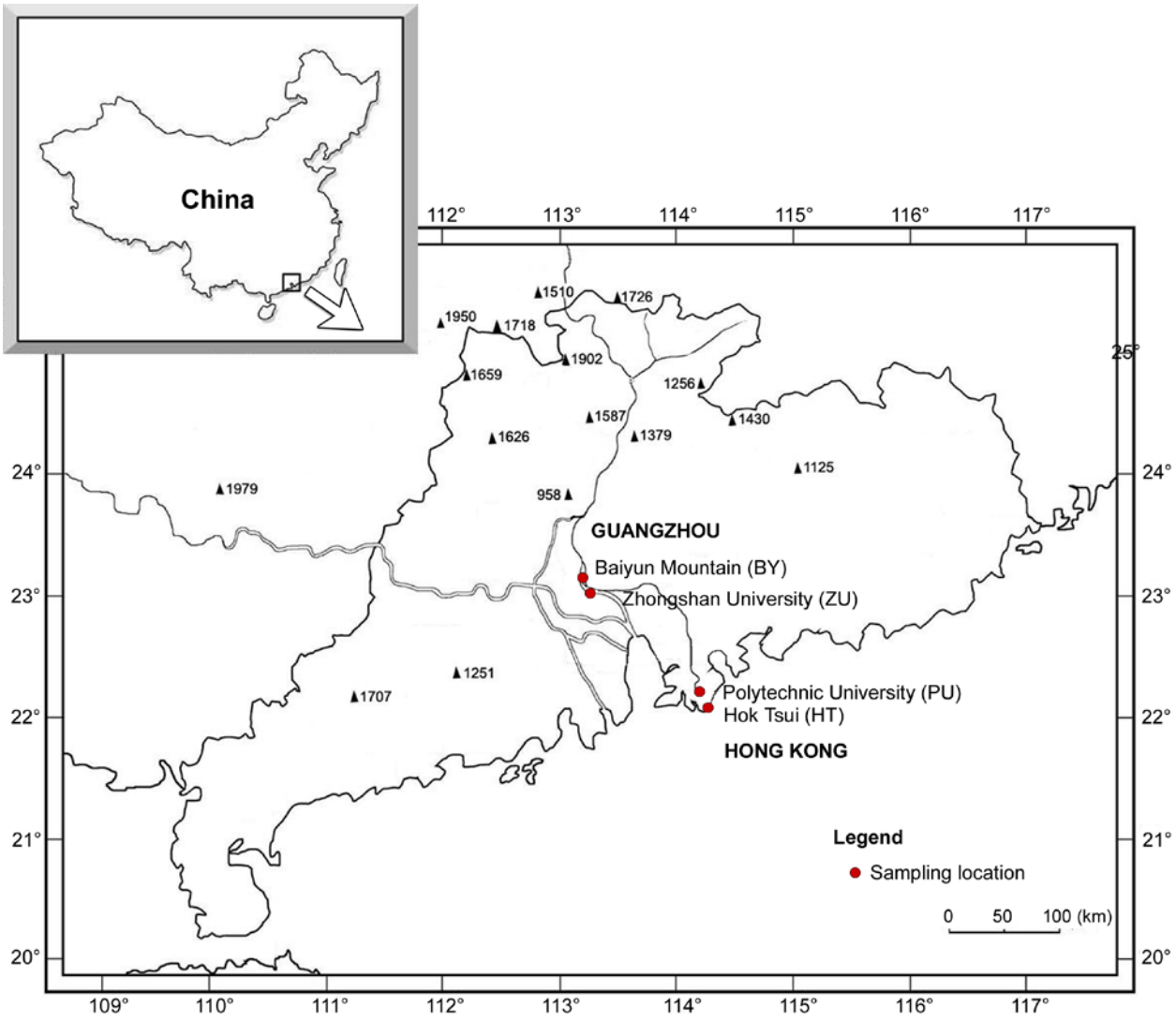

Figure 1. Sampling locations

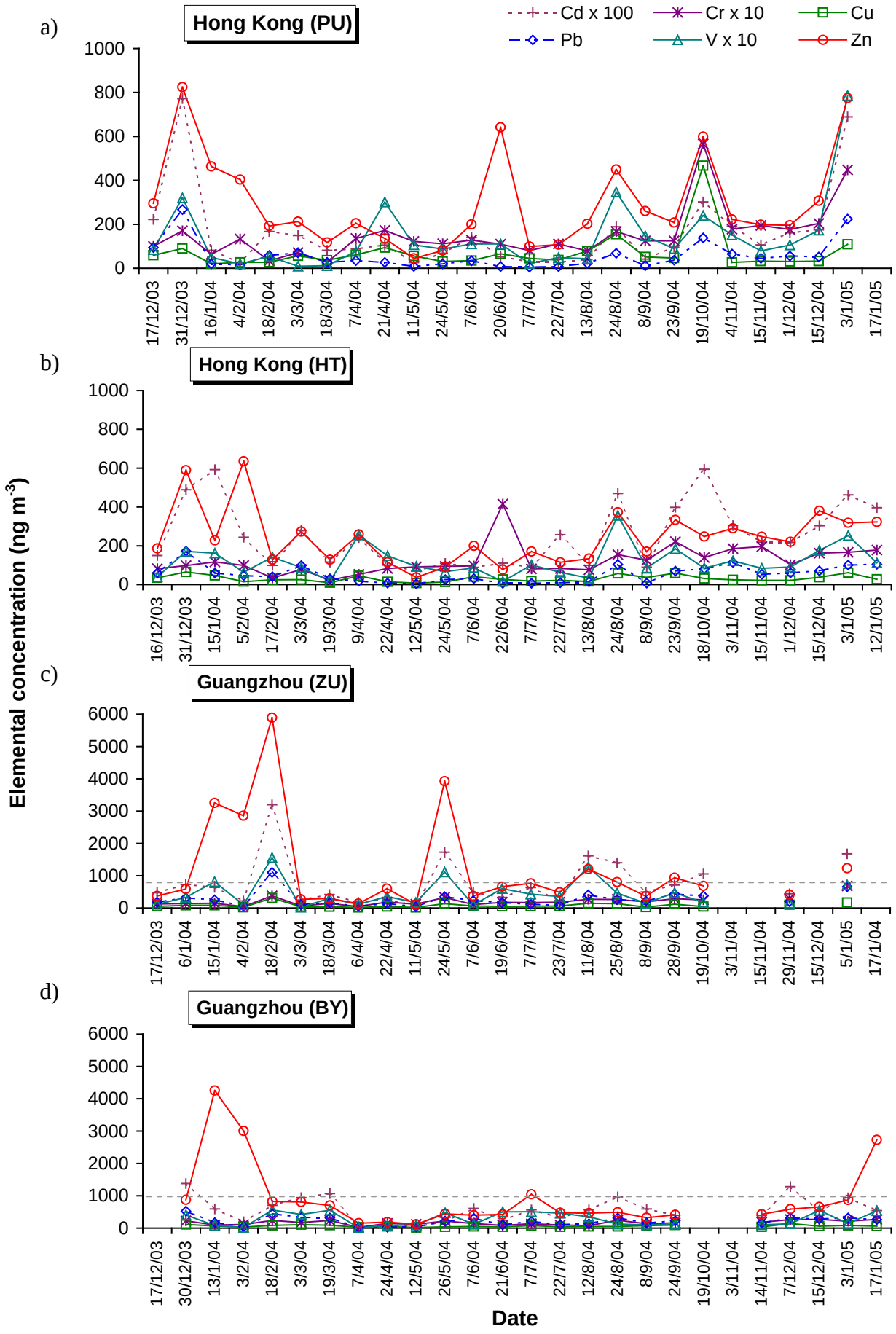

Figure 2. Trace elemental concentrations of particulate matter (TSP) in urban and suburban areas of Hong Kong and Guangzhou, South China

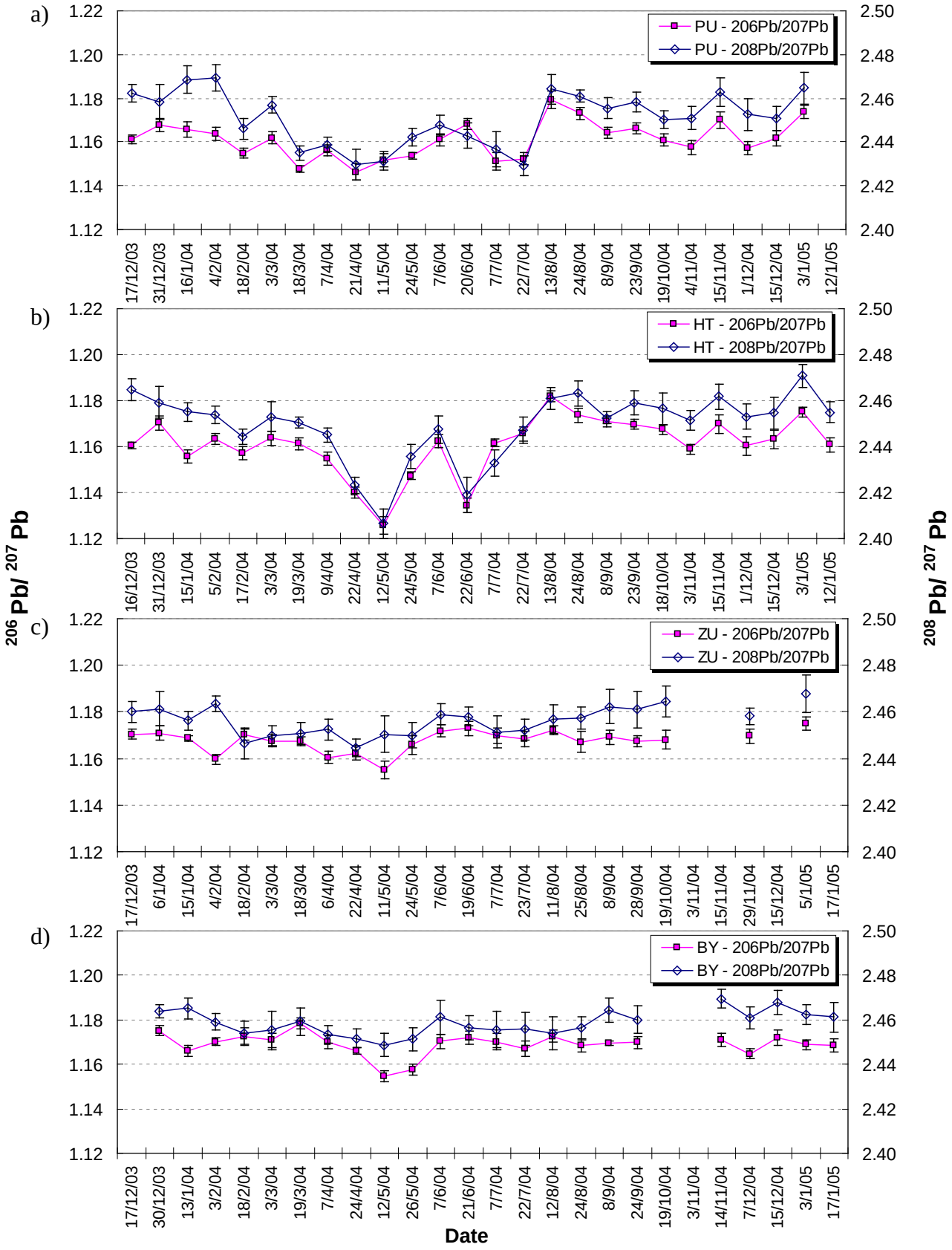

Figure 3. Comparison of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in urban and suburban aerosols of Hong Kong and Guangzhou during the period December 2003 – January 2005

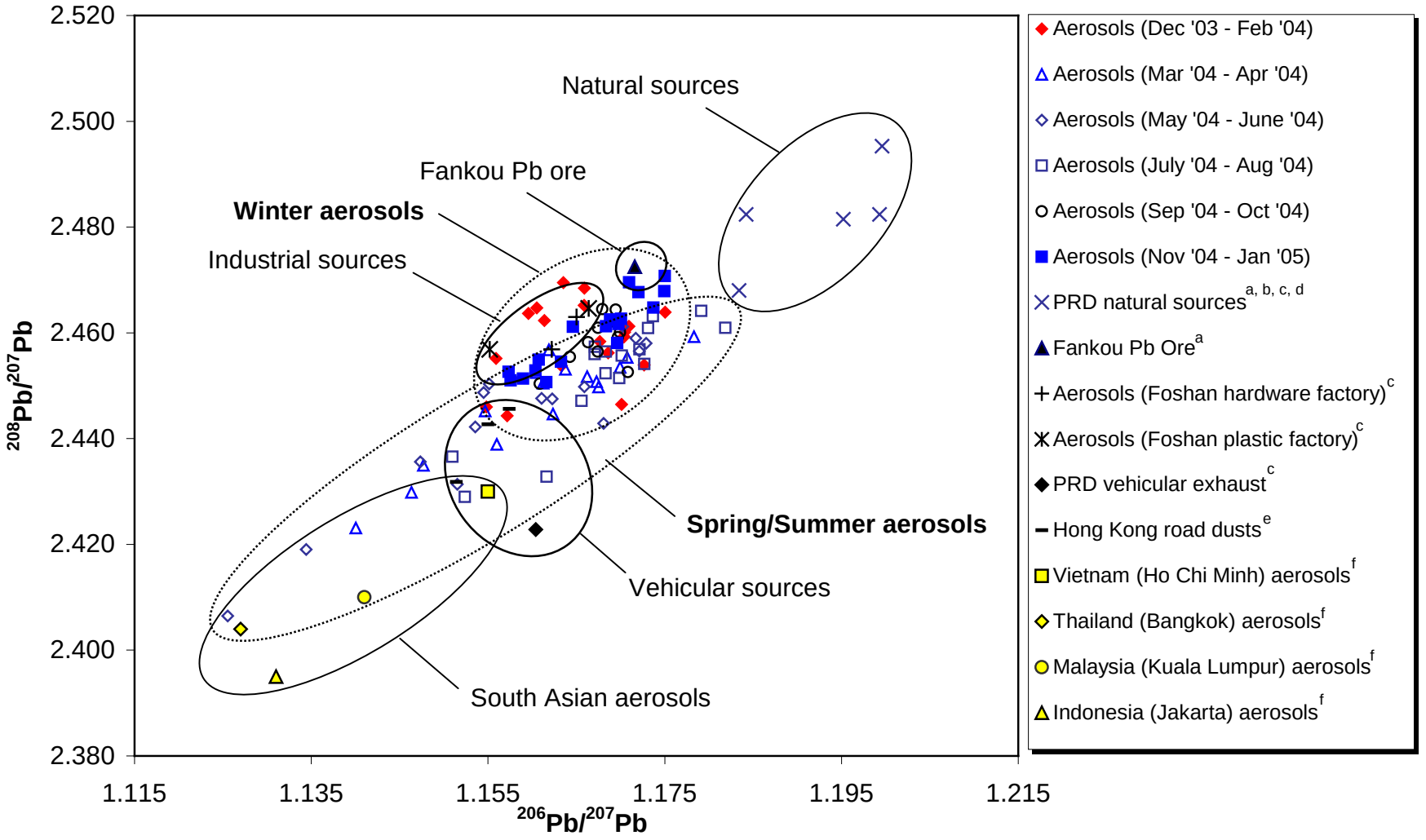

Figure 4. Comparison of the Pb isotopic ratios of winter and spring/summer aerosols in the PRD region (PU, HT, ZU and BY) and other environmental samples ([a] Zhu et al., 1989; [b] Zhu, 1998; [c] Zhu et al., 2001; [d] Lee et al., 2006; [e] Duzgoren-Aydin et al., 2004; [f] Bollhöfer and Rosman, 2000)

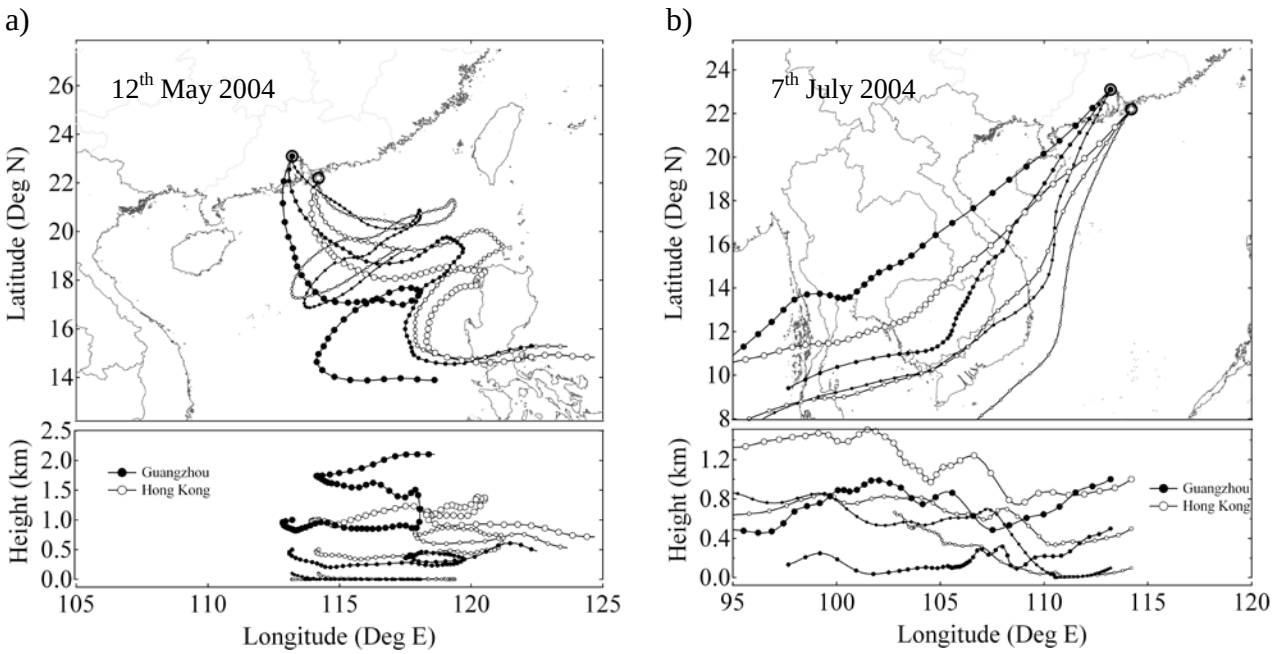

Figure 5. Back trajectory plots on the days with low Pb isotopic ratios

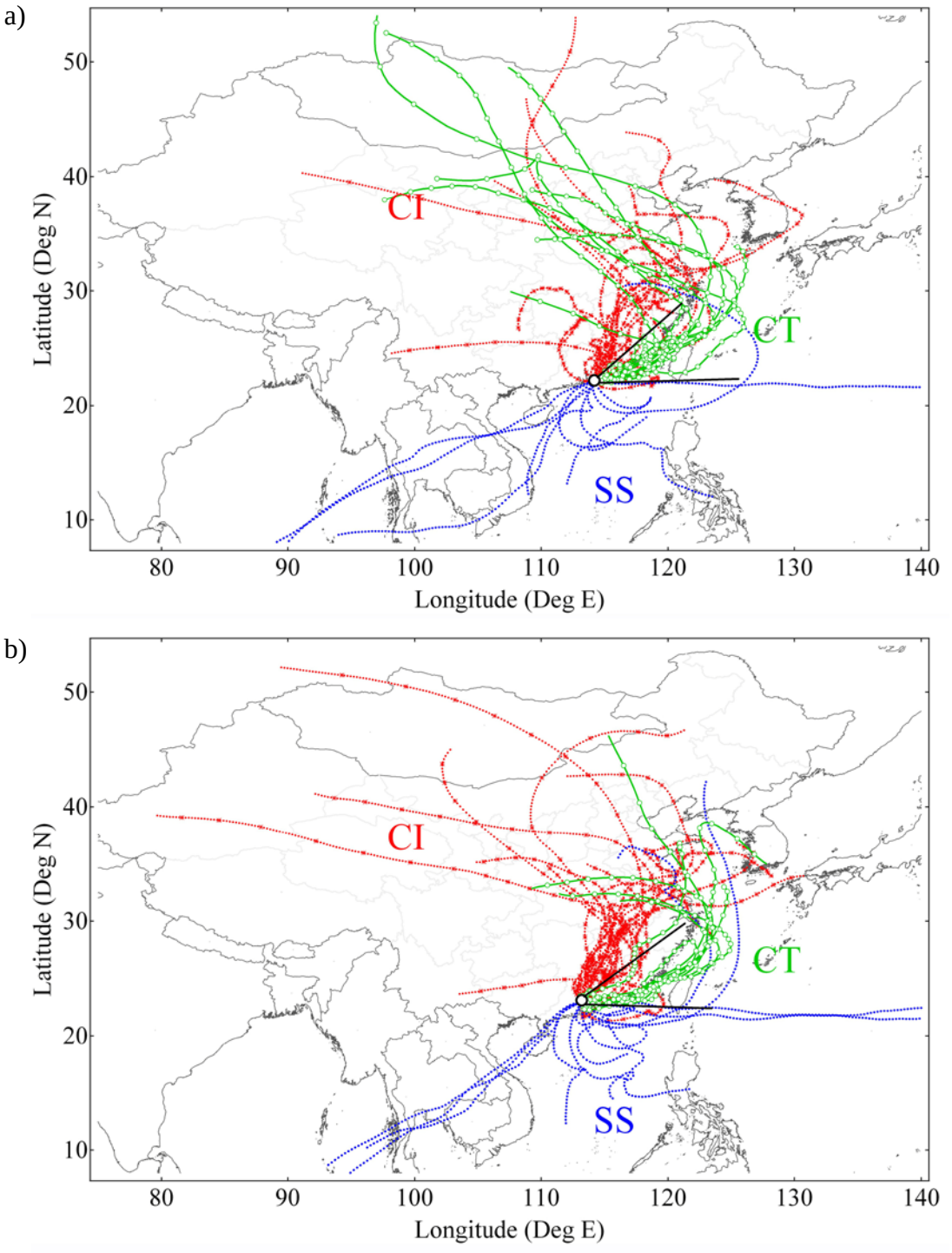

Figure 6. The back trajectories of air masses in a) Hong Kong and b) Guangzhou. Air mass categories: CI – continental inland areas; CT – coastal areas; SS – marine sources

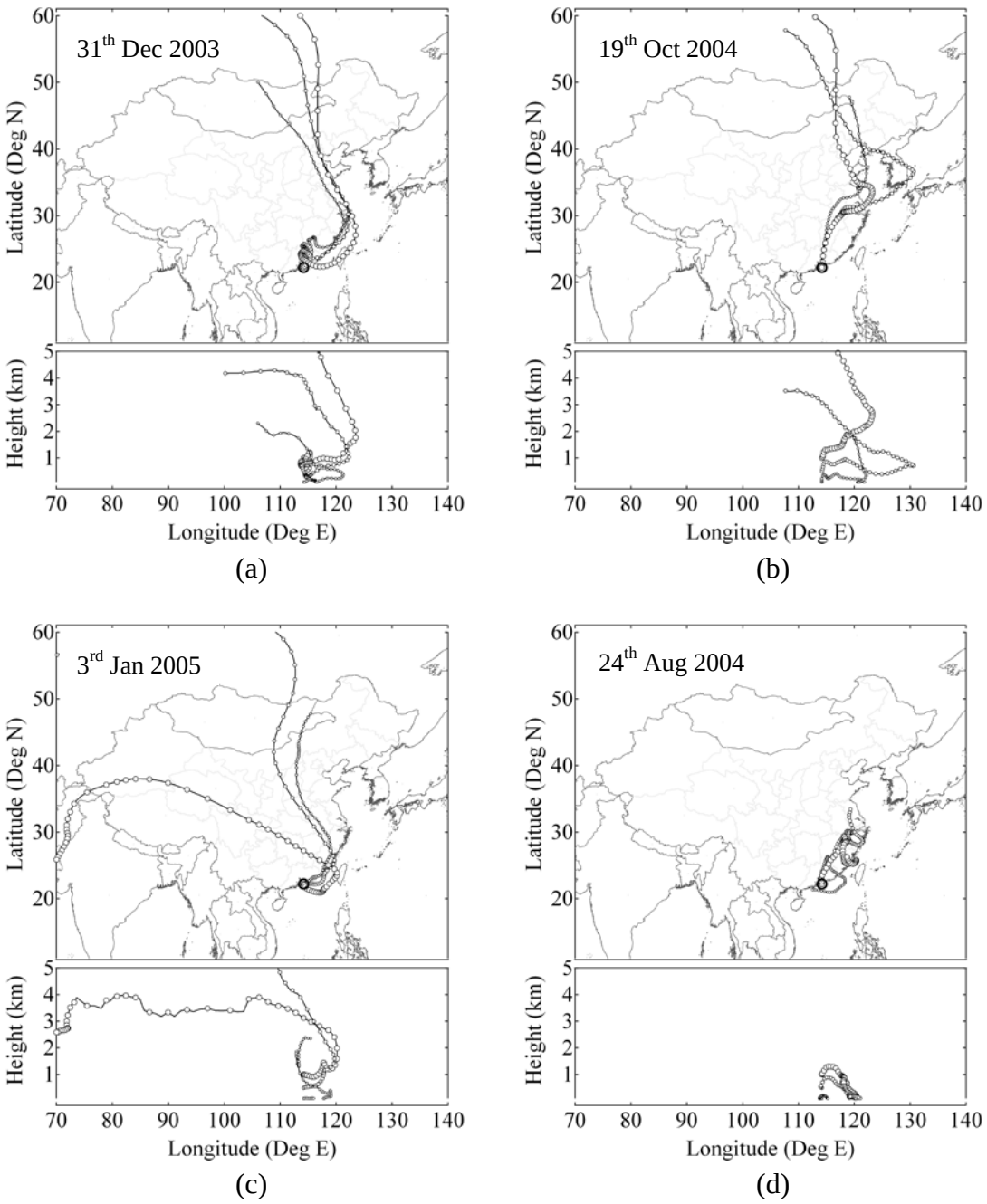

Figure 7. Back trajectory plots (with increasing marker sizes to represent levels at 100 m, 500m and 1000 m, respectively) on the episodic days with elevated heavy metal concentrations