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Atmospheric Environment 40 (2006) 5393–5404
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

Lead isotope ratios in ambient aerosols from Taipei, Taiwan: Identifying long-range transport of airborne Pb from the Yangtze Delta

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Received 20 October 2005; accepted 21 April 2006

Abstract

A total of 142 sets of PM_{10} and $PM_{2.5}$ aerosol particles collected from Taipei during a period from April 2003 to February 2004 were determined for atmospheric Pb concentrations. Among these samples, 77 sets of samples representing four seasons were selected for measuring Pb isotopic compositions to determine the relative contributions of various pollution sources. Results reveal an evident seasonality of high winter and low summer Pb concentrations, resembling those observed in Shanghai, China as well as many East Asian countries. Together with synoptic atmospheric conditions analysis, the seasonal pattern is attributable to the impact of long-range transport of Pb-rich anthropogenic aerosols from the Chinese pollution outflows in the northeast monsoon and to the effective removal by wet deposition in summer. Results of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotope ratios show a minimum in summer, thereafter increasing progressively to fall to winter and reaching a maximum in spring. The summer values are similar to that of tunnel particles for $^{206}Pb/^{207}Pb$ ratio but dissimilar to that of tunnel particles for $^{208}Pb/^{207}Pb$ ratio. Here summer aerosols may represent a local pollution-influenced case, and tunnel particles represent a vehicle exhaust source for atmospheric Pb. Therefore apart from vehicle emissions of Pb for Taipei aerosols, other sources such as incineration, metalliferous industry and coal combustion of fire power plants need to be taken into account. The winter and spring Pb isotope ratios are quite comparable with those measured in China, especially Shanghai in the Yangtze Delta. Again this demonstrates northern Taiwan has already been affected by continental pollution of long-range transport during the northeast monsoon season beginning in early fall and ending in late spring. By employing a two end-member mixing model based on the assumption that the summer case represents the local source end-member, the relative contributions of long-range transport for anthropogenic Pb have been estimated to be 40% in fall, 50% in winter, and 75–85% in spring.

Keywords: Lead isotope composition; Source apportionment; Asian pollution outflow; Cross-boundary transport; Shanghai

1. Introduction

Lead has adverse health effects, especially with respect to the damage to the nervous systems of

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doi:10.1016/j.atmosenv.2006.05.003

fetuses and young children, resulting in lowered IQ and learning problems. Usually, one of the major sources of Pb exposure is air pollution. Lead air pollution abruptly became severe until leaded gasoline was used since 1920s (Nriagu, 1996), of which the principal lead compound of leaded gasoline is tetraethyl lead ($Pb(C_2H_5)_4$). As a result of utilization of leaded gasoline together with other various emission sources like mining, smelting, waste incineration and coal combustion, atmospheric Pb was fast, greatly built up. It is not only harmful to public health but also to the biota in both terrestrial and aquatic ecosystems. Through long-range transport airborne Pb has also enhanced the Pb concentrations globally in surface oceans and other aquatic environments and altered the biogeochemical cycle of Pb in these environmental systems (Patterson and Settle, 1987). This has been well demonstrated by high time-resolution Pb analysis of a variety of environmental archives such as marine sediments (Marcantonio et al., 2002), lake sediments (Renberg et al., 1994), coal (Shen and Boyle, 1987), ice cores (Planchon et al., 2003), peat bog (Shotyk et al., 1998) and moss (Rosman et al., 1998). A lot of efforts have been made for reducing Pb in air. Fortunately, the gradual introduction of unleaded gasoline has greatly reduced atmospheric Pb concentrations generally to a value much lower than $100\,ng\,m^{-3}$ in most of developed countries since 1970s (Nriagu, 1989; Var et al., 2000).

Unleaded gasoline was officially introduced in Taiwan in 1993. In 2000, the lead content in gasoline has been reduced even to a low level of $0.026\,g\,l^{-1}$. As a consequence, atmospheric Pb in Taipei has already sharply declined from higher than $500\,ng\,m^{-3}$ in 1991 (Mao and Chen, 1996) to the present level with an annual mean of $34\,ng\,m^{-3}$ in 2002 (Hsu et al., 2005). Nevertheless, Hsu et al. (2005) observed a maximal concentration in winter ($62\,ng\,m^{-3}$) when the northeast monsoon wind prevails higher than those in the rest of seasons by a factor of one to two, attributable to the long-range transport of Chinese pollution outflows. This seasonal pattern is comparably consistent with that measured in Shanghai based on a 10-year long-term database (Chen et al., 2005). In Shanghai, at present extraordinarily high Pb concentrations with a mean value of $500\,ng\,m^{-3}$ are still occurring in winter although leaded gasoline was banned in Beijing and Shanghai during 1997 and extended to the entire nation in 2000 (Zheng et al., 2004). The major pollution source of airborne Pb was suggested to be from coal combustion rather than from vehicle emission that accounted for less than 30% of the total airborne Pb loadings in Shanghai according to Pb isotopic compositions (Zheng et al., 2004; Chen et al., 2005). It was also verified that airborne Pb of Chinese pollution outflows can be carried toward other East Asian countries and areas through long-range transport (Mukai et al., 1994; Fang et al., 1999; Kim and Song, 1997; Var et al., 2000; Hsu et al., 2005). Moreover, heavy Pb air pollution in China has resulted in high Pb concentration in its neighboring East China Sea with the highest Pb in seawater among the world oceans (Lin et al., 2000).

In order to qualitatively and quantitatively characterize the temporal variation and assess the relative contribution of atmospheric Pb from long-range transport in northern Taiwan more efforts are merited, that will make air quality managements more feasible and practical. Nonetheless, atmospheric Pb concentration alone cannot be used to achieve these goals because the mixing process of multiple components and preferential removal of specific Pb-associated particles during transport will become more difficult in identifying the likely sources. A specific fingerprint for Pb-like isotopic compositions may be effective for source apportionments (Sturges and Barrie, 1987; Mukai et al., 1994; Monna et al., 1997; Flament et al., 2002). Isotopic compositions of these human-made Pb sources are related to the isotope geochemistry of ore deposits. Temporal and geographic variability in the isotopic compositions of Pb can provide more convincing evidence for source apportionment as different anthropogenic Pb sources often exhibit their own characteristic Pb isotope ratios (Mukai et al., 1994; Bollhofer and Rosman, 2001). Lead isotope ratios can thus be a reliable tool for identifying anthropogenic Pb sources (source regions). Moreover, this technique has been extensively applied in various environmental samples since Pb isotope ratio measurements were feasible by using ICP-MS (Becker and Dietze, 2000).

Like a fingerprint or gene, the ratios of Pb isotopes are useful for tracing sources of pollution and the movement of air masses (Bollhofer and Rosman, 2001). Based upon the characterizations of Pb isotope ratios of airborne particulate samples collected from Oki Island located in the Sea of Japan, Mukai et al. (1994) identified the Pb source of long-range transport from China, Russia, South Korea and Japan. Bollhofer and Rosman (2001) recently carried out a global measurement for

atmospheric Pb isotope ratios. Geographic variations in Pb isotope ratios of aerosols have been demonstrated by a $^{208}Pb/^{207}Pb$ versus $^{206}Pb/^{207}Pb$ plot. By using the isotopic data, long-range transport of Pb pollution from China and Russia has been detected in the western United States and parts of Europe.

It will be expected that considerable quantities of air pollutants will continuously be delivered toward the downwind countries and regions as the Chinese mainland is in rapid developments of industrialization and urbanization. In order to precisely assess the impact of long-range transport of Asian continental pollution outflows on local air quality, long-term measurements with respect to seasonality and annual (even interannual and decadal) variations as well as the applications of effective techniques are urgently required. Ambient aerosol samples (PM_{10} and $PM_{2.5}$) collected in metropolitan Taipei from early 2003 to early 2004 were determined for Pb concentrations and Pb isotopic compositions. Coupled with our previous study, a 2-year seasonality was established in the study. Based on the results of Pb isotope ratios together with air-mass trajectory analysis, the relative contributions of long-range transport of airborne Pb were computed using a two-endmember mixing model. This study is the first systematic investigation on the isotopic compositions of atmospheric Pb in Taiwan.

2. Materials and methods

2.1. Sampling

A total of 142 sets of PM_{10} and $PM_{2.5}$ aerosol samples were collected from metropolitan Taipei in the time period from April 2003 to February 2004 and determined for Pb concentrations. A total of 77 sets of PM_{10} and $PM_{2.5}$ aerosol samples (52 sets collected during the period from April 2003 to February 2004 and another 25 sets collected in March 2003) were determined for Pb isotopes. Details of sampling time for the samples used for analyzing Pb isotope ratios are given in Table 1. The sampling site was located at the Central Weather Bureau (CWB) in metropolitan Taipei, Taiwan. The Partisol® Model 2300 speciation sampler (Rupprecht & Patashnick Co. Inc., Albany, NY, USA) was employed to simultaneously collect PM_{10} and $PM_{2.5}$ ambient aerosol particles. An active volumetric flow control system was used to maintain the volumetric flow rate at a constant rate of $16.7\,l\,min^{-1}$. The samplers were set on the rooftop of the CWB building approximately 25 m above the ground level. The medium used for aerosol filtration was polytetrafluoroethylene (PTFE) membrane filters (PallGelman, 1.0 μm pore size and 47 mm in diameter with a PE ring). Sampling was carried out in the last week of each month; besides, additional sampling was made when dust events were forecasted by the Environmental Protection Administration (EPA) of Taiwan. Samples were collected at 12-h intervals. Details relevant to the sampling information and strategy can be found elsewhere (Hsu et al., 2004, 2005). Although unleaded gasoline has been completely available, unleaded gasoline still contains low levels of Pb; the lead content in gasoline is approximately $0.026\,g\,l^{-1}$. To evaluate the contribution of vehicle emissions, four tunnel particle samples were collected from the tiling wall of three main tunnels (Xin-Hai, Zi-Qiang and Ba-Du) in Taipei.

Table 1
Collection periods and sample numbers (in unit of set) of aerosol samples (PM_{10} and $PM_{2.5}$) collected from Taipei, Taiwan during four seasons for Pb isotopic analysis

Sample category	Collection period	Sample number
Spring	3/7–3/14/2003 (excluding 0307D, 0310D and 0314N) 3/25–3/31/2003 (excluding 0328N and 0331D)	25
Summer	7/28–8/3/2003	14
Fall	11/24/–11/30/2003	10
Winter	2/6–2/19/2004	28

Samples are identified by a sampling time code in the month (mm), day (dd), and daytime/nighttime (D/N) format; e.g., 0307D denotes March 7 daytime.

2.2. Chemical analysis

Aerosol-laden PTFE filters were completely dissolved in an acid mixture, i.e. 5 ml HNO_3, 5 ml HF, and 0.5 ml $HClO_4$ (all ultrapure grade from J.T. Baker) in Teflon beakers. The digestion solution was diluted with Milli-Q water to 20 ml (in 2% HNO_3). The acid digestion was also used for tunnel particle samples. Lead concentrations were determined using a quadrupole-based inductively coupled plasma mass spectrophotometer (ICP-MS, Elan 6100, Perkin Elmer™ SCIEX, USA). Indium was added to the digests as an internal standard

($10\,\mu g\,l^{-1}$). The detection limit for Pb was $0.2\,ng\,m^{-3}$. Calibration was achieved using a multi-element standard prepared from stock standard (Merck) made up in a 2% HNO_3 solution. The quality assurance and quality control (QA/QC) of analyses were validated by analyzing the standard reference material (NIST SRM 1648, urban particulate matter from National Institute of Standards and Technology, USA). The recovered value for the target element fell within 3% of certified values ($n = 5$). Blanks were used to assess reagents, methods, standards, instruments, and calibrations. The details on the digestion method and ICP-MS analysis have been described elsewhere (Hsu et al., 2004, 2005).

In the recent decade, various aspects of studies on lead isotope ratios in geological, environmental and biological samples utilizing the quadrupole-based ICP-MS have been well documented (Becker and Dietze, 2000, and references therein). Those studies have verified the instrumentation having sufficient precision and accuracy of meeting the research requirements. Lead isotopic determinations were performed by the quadrupole-based ICP-MS; this analysis run was separated from the concentration measurement. The intensities of ^{206}Pb, ^{207}Pb, and ^{208}Pb were measured in the peak hop mode with short settling times, 100 ms dwell times, and total measurement times of 75 s. The relative standard deviation (RSD) in the measurements of Pb isotope ratios ($^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$) at the $5\,\mu g\,l^{-1}$ level was about 0.5%. An isotopic standard reference material, NIST SRM 981 (common lead isotope) was analyzed at a regular interval of $n = 5$ in each batch for data quality control, i.e., calibration and monitoring the instrument drift and mass bias. The ratio correction factors obtained were typically in the range 0.995–1.005 for both ratios. Modest improvements to the precision can be achieved by increasing analysis time if necessary. The optimization of the quadrupole-based ICP-MS instruments, the nature of noise sources, and strategies to enhance precision and accuracy have been dealt with by a number of authors (Monna et al., 2000).

3. Results and discussion

3.1. Concentrations of airborne Pb and its temporal variations

Atmospheric concentrations of particulate Pb measured in ambient PM_{10} and $PM_{2.5}$ aerosols in Taipei from April 2003 to February 2004 range

Table 2
Data summary for atmospheric Pb concentrations in Taipei PM_{10} aerosols during a period from April 2003 to February 2004

	Range (Mean $\pm 1\sigma$)	Collection period	Sample type	Sample number
Taipei, Taiwan[b]	ND[a]-404 (27 $\pm$ 61)	April 2003–February 2004 (nearly a year)	PM_{10}	142
Taipei, Taiwan[c]	ND-207 (34)	March 2002–March 2003 (over a year)	PM_{10}	186
Hong Kong, China[d]	~85	November 2000–February (Winter)	PM_{10}	—
Shanghai, China[e]	167–854 (515)	Late 2001-Early 2002 (Winter)	PM_{10}	—
Beijing, China[f]	~150[g]	June –July 2002 (Summer)	PM_{10}	65
	~440[g]	December 2002 (Winter)	PM_{10}	56
Tokyo, Japan[h]	(64.4)	1995–2000 (Five years)	PM_{11}	—
Seoul, Korea[i]	39–401 (200 $\pm$ 97)	December 2002	PM_{10}	17

For comparison, other results measured in several selected East Asian countries and areas are also given.
[a]Below the detection limit ($0.2\,ng\,m^{-3}$).
[b]This work.
[c]Our previous study, refer to Hsu et al. (2005).
[d]Ho et al. (2003).
[e]Zheng et al. (2004).
[f]Sun et al. (2004).
[g]Calculated from the published data in the cited references.
[h]Zheng et al. (2004) and references therein.
[i]Mishra et al. (2004).

from under detection limit ($<0.2\,ng\,m^{-3}$) to $404\,ng\,m^{-3}$ with a geometric mean of $27\,ng\,m^{-3}$, as summarized in Table 2. The arithmetic mean and median were also calculated to be 50 and $29\,ng\,m^{-3}$, respectively. The two values of the geometric mean and the median are close, reflecting that the data set of Pb is a log-normal distribution. The values of Pb concentrations are very consistent with our previous results conducted at the same site in Taipei from March 2002 to March 2003 (Hsu et al., 2005). For comparison, data on atmospheric Pb concentrations from the East Asian mega-cities were compiled in Table 2. From the viewpoint of public health, the Pb concentrations are at low levels following the standard guideline of exposure risk except few days. Compared to those data obtained from Taipei about 10 years ago (Mao and Chen, 1996), airborne Pb concentrations have declined greatly from an annual mean of higher than $100\,ng\,m^{-3}$ to the present level of around $30\,ng\,m^{-3}$ owing to the gradual phase-out of leaded gasoline over Taiwan since 1993. Compiling the present data with our previous data, a 2-year seasonality (i.e., 2002 and 2003) can be established, as illustrated in Fig. 1. Obviously, the seasonality of airborne Pb in 2002 is similar to that in 2003, commonly showing a winter maximum and a spring/summer minimum. This temporal pattern is very similar to that observed in Shanghai (Chen et al., 2005) as well as other Chinese coastal cities (Zhang and Friedlander, 2000; Dan et al., 2004). Also, it resembles those observed in the surrounding countries and areas such as Korea (Kim and Song, 1997), Japan (Var et al., 2000) and Hong Kong (Ho et al., 2003).

Based on the synoptic atmospheric conditions together with the air-mass back trajectory analysis, numerous studies have documented that during the northeastern monsoon seasons massive quantities of air pollutants are carried to northern Taiwan (Hsu et al., 2004, 2005; Lin et al., 2005). Wang (2005) made a 9-year (1994–2002) long-term air-mass back trajectory analysis, definitely demonstrating that the air parcel usually passes over the Changjiang Delta (or Shanghai City) where is now the most urbanized and industrialized area in mainland China (Hsu et al., 2004). For example, two cases happened on 29 November 2003 and 6 February 2004 when atmospheric Pb concentrations reached 276 and $132\,ng\,m^{-3}$, respectively. By using not only backward but also forward air mass trajectory analysis (Fig. 2), it is clear that air masses can quickly move from Shanghai (or Yangtze Delta) to northern

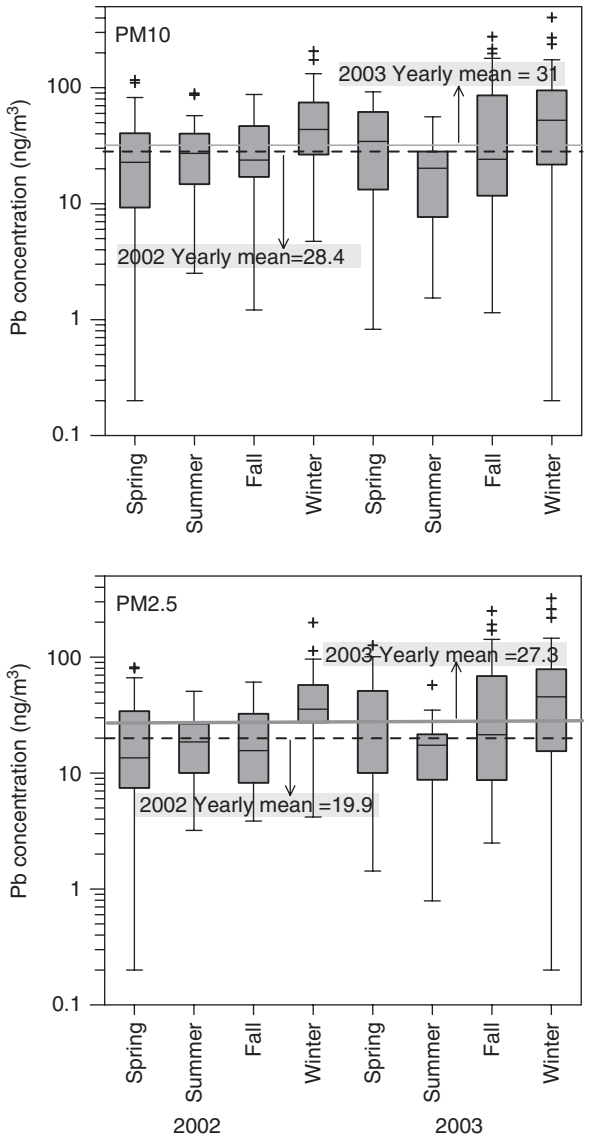

Fig. 1. Seasonal variations in atmospheric Pb concentrations in Taipei ambient PM_{10} (upper panel) and $PM_{2.5}$ (lower panel) aerosols during a 2-year period from March 2002 to February 2004, of which data for the first year were taken from our previous study (Hsu et al., 2005).

Taiwan approximately in 1 day. The air parcels are capable of bringing a large amount of Pb-bound anthropogenic aerosols to northern Taiwan. Chen et al. (2005) found a permanent winter maximum for airborne Pb in the recent decade, and the present wintertime concentrations are still up to $500\,ng\,m^{-3}$, reflecting that Pb air pollution is continuously severe. Therefore, along with seasonal differences in emission strength the seasonality can be attributable to two other causes: cross-boundary transport

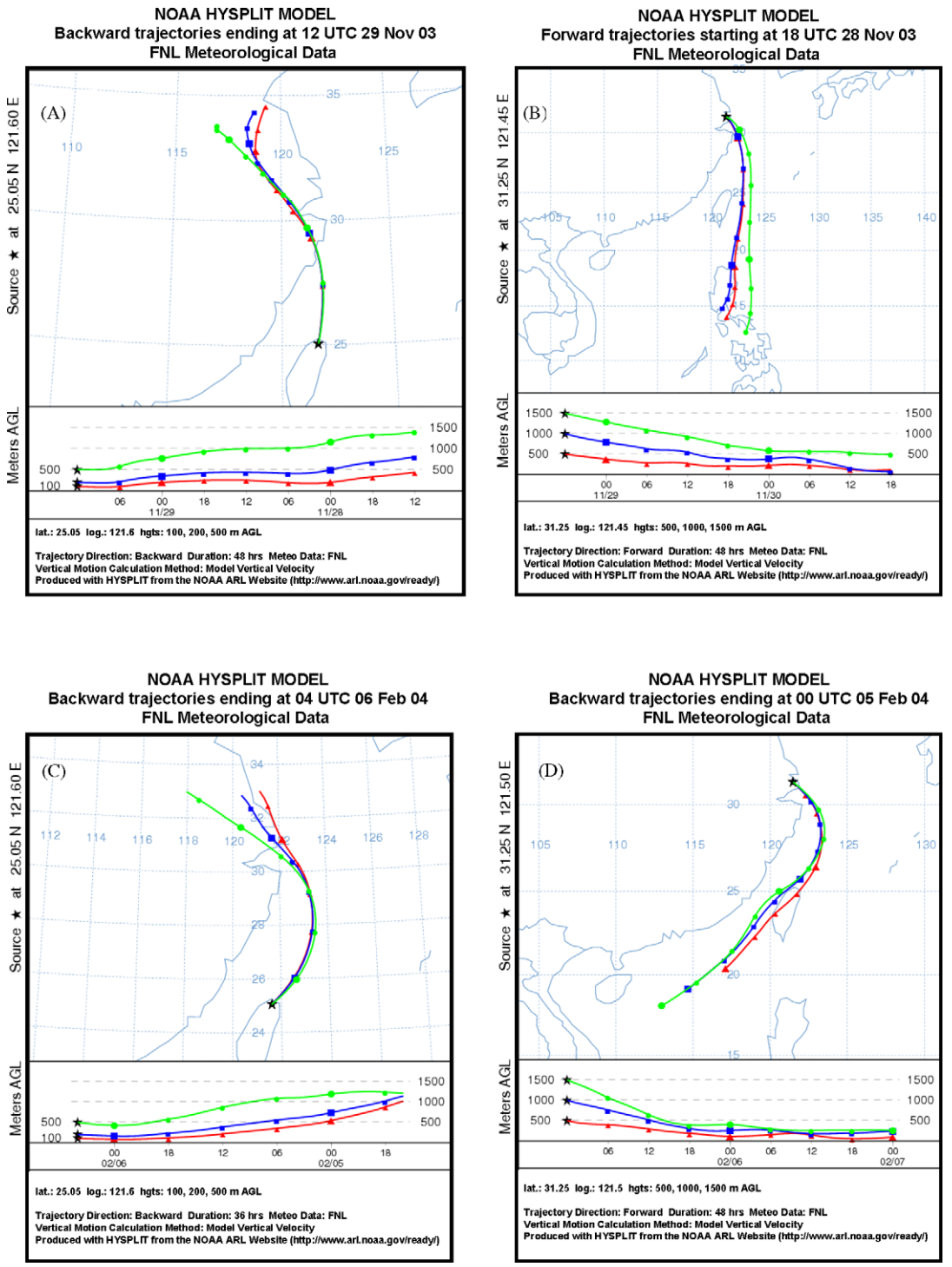

Fig. 2. Backward (from Taipei, Taiwan) and forward (from Shanghai, China) air mass trajectory analysis for 2 days: November 29 (November 28 for forward analysis) 2003 (upper panel) and February 6 (February 5 for forward analysis) 2004 (lower panel); both were carried out by using the HYSPLIT Model, NOAA.

of anthropogenic aerosols in the northeast monsoon seasons, and the effective removal by frequent rain in the summer monsoon season.

3.2. Characteristics of Pb isotope ratios for identifying Pb sources in Taipei aerosols

Results of Pb isotope ratios for Taipei ambient aerosols are summarized in Table 3. Fig. 3 displays the scatter plots of $^{208}Pb/^{207}Pb$ (x-axis) versus $^{206}Pb/^{207}Pb$ (y-axis) for PM_{10} and $PM_{2.5}$ aerosols. Overall, $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ isotope ratios of all samples fell within a moderate range from 2.35 to 2.45 and from 1.12 to 1.17 (with two exceptions), respectively. There are almost no differences between PM_{10} and $PM_{2.5}$ aerosols (Fig. 3); it is not surprising as fine mode aerosol particles dominate Pb partitions (Fig. 1), resulting in Pb isotope ratios in PM_{10} aerosols resembling those in $PM_{2.5}$ aerosols. Note that in Fig. 3 Pb isotope ratios for four months (seasons) seem to be differentiable although they look like clustering together; seasonal variations will hence be considered below. Also shown in Fig. 3, there are two characteristic isotope ratios in Chinese and Australian aerosol particles identified by Bollhofer and Rosman (2001). According to reports by Council for Economic Planning and Development, Taiwan, the main import country of lead ores for Taiwan demands has changed from Australia to mainland China in this recent decade. To evaluate the possible sources, represented areas of airborne Pb isotope ratios from the two countries were therefore indicated in the plots. Overall, most of our isotopic data certainly fell within the two areas. Nonetheless, we cannot make a definite conclusion regarding the relative contributions until robust evidence can be provided.

As depicted in Figs. 4 and 5, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios vary evidently among 4 months (also representing four seasons) similarly for PM_{10} (Fig. 4) and $PM_{2.5}$ (Fig. 5) samples. The seasonality is obvious, showing an increasing trend from summer to fall to winter to spring. Also shown in these plots are the ratios of tunnel particles collected from two principal traffic tunnels in downtown Taipei, which are assumed to represent the local vehicle emission source. As illustrated in Figs. 4 and 5, the $^{206}Pb/^{207}Pb$ ratios (1.131) of tunnel particles are very close to the summer mean ratio (1.132) of ambient aerosols, while the $^{208}Pb/^{207}Pb$ ratio (2.405) of tunnel particles are moderately higher than the summer ratios. The summer is a very clean season,

Table 3
Data summary of mean Pb isotope ratios in Taipei PM10 aerosols for four seasons. Literature data from other Asian countries and areas are also listed for comparison

	Taipei, Taiwan[a]				Shanghai, China[b]	Beijing, China[c]		Hong Kong, China[d]		Jeju-do, Korea[e]	Oki Islands, Japan[f]
	Summer	Fall	Winter	Spring		Summer	Winter	Summer[g]	Winter[g]		
$^{206}Pb/^{207}Pb$	1.132 (0.018)	1.143 (0.008)	1.147 (0.008)	1.157 (0.008)	1.1617 (0.0024)	1.159	1.148	1.161–1.167	1.168–1.177	1.139–1.157	1.149 (0.016)[h]
$^{208}Pb/^{207}Pb$	2.378 (0.018)	2.404 (0.011)	2.411 (0.014)	2.427 (0.013)	2.4454 (0.0109)	2.441	2.444	2.453–2.461	2.454–2.472	2.403–2.485	2.436 (0.068)[h]

[a]This work.
[b]Recalculated from Zheng et al. (2004).
[c]Recalculated from Mukai et al. (2001).
[d]Wong et al. (2003).
[e]Recalculated from Oh et al. (2004).
[f]Recalculated from Mukai et al. (1994).
[g]Atmospheric deposition.
[h]Calculated from data published in Mukai et al. (1994).

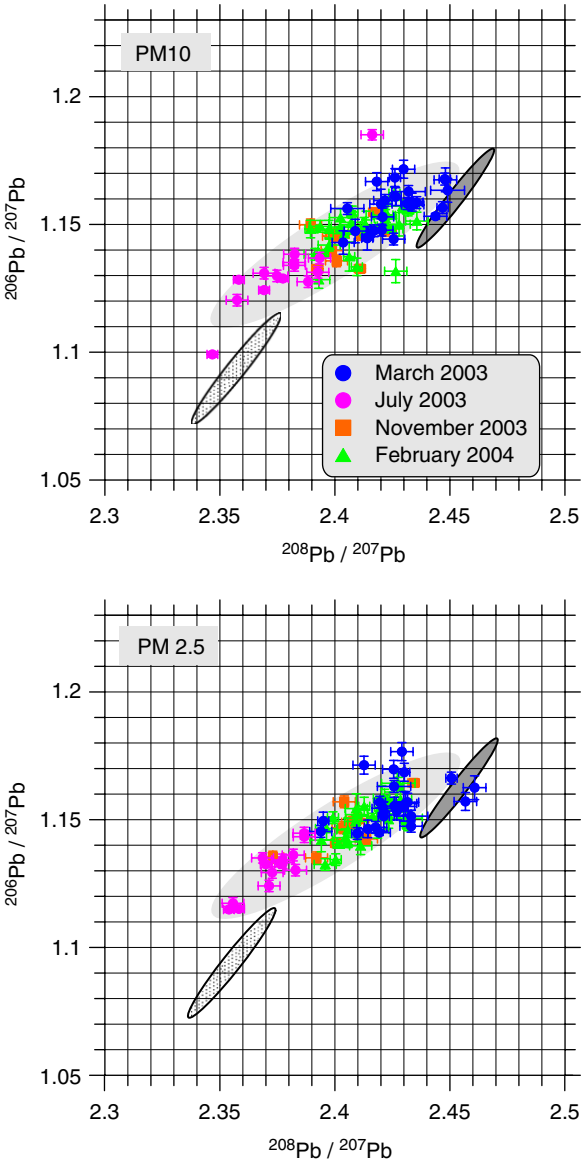

Fig. 3. Scatter plots of $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ for PM_{10} (upper panel) and $PM_{2.5}$ (lower panel) aerosol particles taken from 4 months (seasons) in Taipei. A light-grayed ellipse area represents data points for a general pattern of $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$. The dark-grayed area indicates the characteristic isotope ratios for the Chinese aerosols and the dotted area for the Australian aerosols; refer to Bollhofer and Rosman (2001) for details. The reason of showing the data area for China and Australia is that they are the major exporting countries of Pb ores to Taiwan.

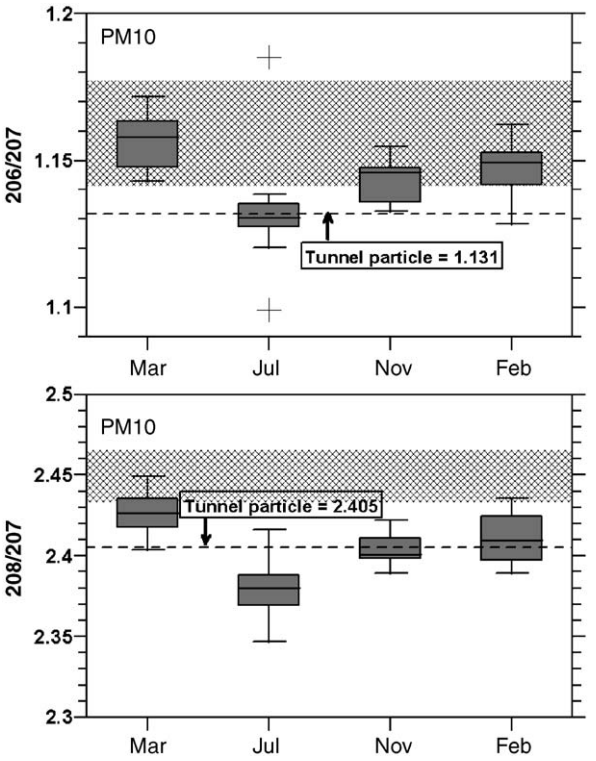

Fig. 4. Seasonal (individual month representing each season) variations in $^{206}Pb/^{207}Pb$ (upper panel) and $^{208}Pb/^{207}Pb$ (lower panel) isotope ratios in Taipei PM_{10} aerosol particles. Also indicated by a dashed line in the plots is the average value of tunnel particles. Additionally, the range of Pb isotope ratios in atmospheric particles from China reported by Bollhofer and Rosman (2001) is marked by a cross square area.

suggestive to be conclusively affected by local pollution emissions, at least without significant long-range transported pollutants from mainland China (Wang, 2005). Therefore, this indicates that apart from vehicle emissions there are additional Pb sources such as incineration, metalliferous industry and coal combustion of fire power plants in summer (Hsu et al., 2005); the isotopic signatures of other local sources need to be determined for identifying more sources. In view of other seasons when the northeastern monsoon prevails approximately starting in late September, both $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios progressively increase to the maximal peak in spring (Figs. 4 and 5), corresponding to the increased impact of long-range transport at that time. Thereby, the impact can reach a maximum in spring.

Chen et al. (2005) pointed out that lead air pollution continued over Shanghai after the phase-out of leaded gasoline in 1995. On the basis of nearly 10-year long-term measurements, the seasonal pattern always showed a winter maximum. At present, the average winter concentrations are still as high as 500 ng m^{-3} although they have declined substantially from several μg m^{-3}. According to the

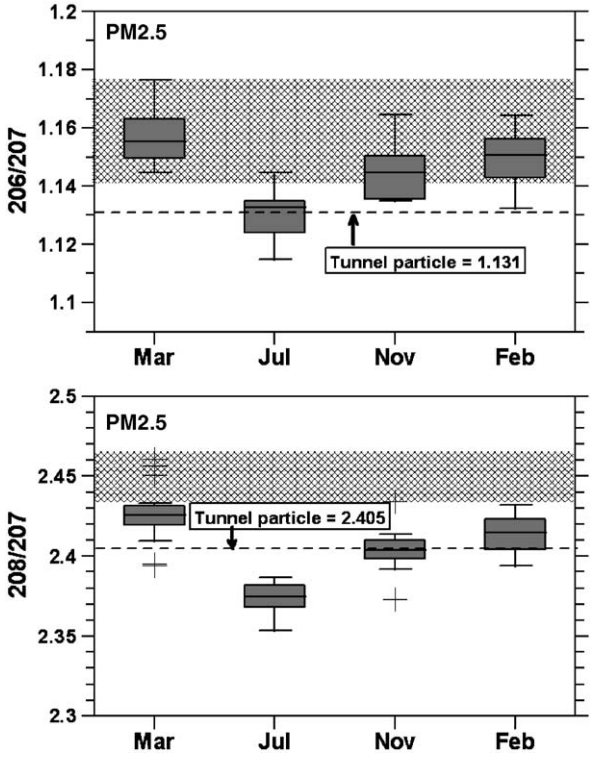

Fig. 5. As in Fig. 4, but for $PM_{2.5}$ aerosol particles.

Pb isotopic compositions of total suspended particles (TSP) in air, Chen et al. (2005) suggested that stationary pollution emission was always a dominant source in Shanghai and that the primary components was believed to be contributed by vast combustion of lead-containing coal utilized mainly by industrial activities recently. These authors further assessed the contribution from leaded gasoline being only 27.5%. Likewise, Zheng et al. (2004) analyzed Pb isotope ratios in Shanghai PM_{10} aerosols, and reported characteristic Pb isotope ratios in PM_{10} aerosols to be 0.8608 ± 0.0018 for $^{207}Pb/^{206}Pb$ ratios and 2.105 ± 0.005 for $^{208}Pb/^{206}Pb$ ratios, that can be converted to 1.162 for $^{206}Pb/^{207}Pb$ and 2.445 for $^{208}Pb/^{207}Pb$. They evaluated the contribution of Pb from vehicle exhausts to be around 20%, somewhat lower than the estimate (27%) by Chen et al. (2005). Zheng et al. (2004) demonstrated that the major emission sources of atmospheric Pb included metallurgic dust, coal combustion and cement. Based on single aerosol particle analyses using a nuclear microprobe, Wang et al. (2000) suggested the cement industry, coal combustion, oil combustion, metallurgic dust and automobile exhaust responsible for lead pollution in Shanghai air.

For comparison, isotopic data for atmospheric Pb from East Asian countries and areas are also summarized in Table 3. Comparing our Pb isotope ratios with those measured in China, the spring $^{206}Pb/^{207}Pb$ ratio (1.157 ± 0.008) is rather comparable to that (1.162) measured in Shanghai PM_{10} aerosols as mentioned above (Zheng et al., 2004, Fig. 6). Furthermore, Chen et al. (2005) observed that the $^{206}Pb/^{207}Pb$ ratio in Shanghai aerosols has switched from 1.147 ± 0.002 before 1995 to the current characteristic value of 1.162 ± 0.002, responding to the phase-out of leaded gasoline in Shanghai in 1995. Compared with the ratios of 1.141–1.177 for $^{206}Pb/^{207}Pb$ and 2.435–2.465 for $^{208}Pb/^{207}Pb$ measured in China (Bollhofer and Rosman, 2001), most data of our northeastern monsoon samples fall within their ranges although some data points fall at the lower end of characteristic ratio ranges, as indicated by the dotted area in Fig. 3. This illustrates that the springtime values are closer to those of China aerosols (Figs. 4 and 5). The present result of similarity in Pb isotopes, together with statistical results of long-term airmass trajectories given by Wang (2005), reveals the domination of long-range transport of Chinese Pb pollution principally from the Yangtze Delta in spring.

Now a question may be raised as to why Pb concentrations have not reached a spring maximum (but showed a spring minimum, Fig. 2) to correspond to the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ maxima in spring (Fig. 4). Along with high emissions from coal combustion in winter, two other processes may be responsible for the seasonality. First, frequent rain associated with frontal systems often occurring around the offshore area of northern Taiwan in the spring (on average, 15 rainy days per month or more in spring) can remove a majority of airborne Pb particles and/or Pb-bounded aerosol particles regardless of local and long-range transported origins. Moreover, another important process is the preferential deposition of coarse particles due to gravitational settling like dust aerosol, which seems to be a crucial host particle of atmospheric Pb from the Chinese continental pollution outbreak (Hsu et al., 2005).

3.3. Estimating the relative contribution from long-range transport

In summer air compositions of Taiwan are seldom affected by long-range transport from

China. Therefore the summertime air can represent the local background air (Wang, 2005). Alternatively, the summertime aerosol Pb isotope ratios can be regarded as a characteristic ratio of representing local aerosols of anthropogenic origin. It thus allowed the probable assessment of the relative contribution for airborne Pb through long-range transport in respective seasons other than summer. We adopted a two end-member mixing model to compute the contribution using the following equation (Flament et al., 2002):

$$R_{obs} = R_{lp}X_{lp} + R_{lrt}(1 - X_{lp}), \quad (1)$$

where R_{obs} is the observed isotope ratio in the northeast monsoon season (i.e., fall, winter and spring) other than summer, R_{lp} is the characteristic ratio of local aerosols represented by the summertime value, R_{1rt} is the characteristic ratio of long-range transported Pb-bound aerosols represented by the mean value of Shanghai aerosols, X_{lp} is the relative contribution through local pollution, and $(1-X_{lp})$ is the relative contribution through long-range transport. Then we separately calculated the contributions by using the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotopic data. All the parameters used in the calculations are given in Table 4. Here the representative values of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotope ratios for the local Pb pollution are the summertime data (i.e., 1.132 and 2.378, respectively, Tables 3 and 4) while for the long-range transport of aerosol Pb are the Shanghai PM_{10} data (i.e., 1.1617 and 2.4454, Table 4) that were calculated from isotopic data reported by Zheng et al. (2004). The result is that the seasonal contributions of long-range transport of airborne Pb vary from 38% (39%) in fall to 52% (49%) in winter to 84% (73%) in spring when using the $^{206}Pb/^{207}Pb$ ($^{208}Pb/^{207}Pb$) isotopic data. The relative contributions based on the $^{206}Pb/^{207}Pb$ or $^{208}Pb/^{207}Pb$ isotopic data seem to be quite consistent, implying that the impact of long-range transport of air pollutants from developing China, especially the Yangtze Delta, is very substantial.

The estimated contributions of long-range transport ranging from 38% to 84% in the northeastern monsoon is very consistent with our previous study that Cd/Pb ratios in Taipei aerosols were low (0.018) in the Asian dust episodes, reflecting long-range transport, whereas high (0.030) in summer, reflecting local pollution (Hsu, et al., 2005). In the northeast monsoon other than Asian dust periods there is a moderate Cd/Pb ratio of 0.024. Likewise, by employing a two end-member mixing model, it thus allows us to make a rough estimation of the long-range transport of anthropogenic metals in the monsoon, the value being 50% for Pb. In addition, the estimations of long-range transport contributions for airborne Pb in the northeast monsoon in Taipei are somewhat consistent with those for various pollutant species such as PM_{10} aerosol and CO in northern Taiwan (Lin et al., 2005).

4. Summary

This is the first report dealing with atmospheric Pb isotopic signatures to evaluate the impact of long-range transport from China. A 2-year long-term measurement result of atmospheric Pb shows an evident seasonality of high winter and low summer/spring concentrations, demonstrating that long-range southward transport of air pollutants from the China continental outflows greatly enhanced atmospheric concentrations of anthropogenic metals such as Pb in winter. Differentiating anthropogenic Pb from various sources can be achieved by Pb isotopic signatures. Low $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios were observed in summer

Table 4
Estimated relative contributions (%) from local pollution and long-range transport for airborne Pb in the northeast monsoon season (including spring, fall and winter) in Taipei

	Long-range transport		Local pollution	
	$^{206}Pb/^{207}Pb$ (1.1617)	$^{208}Pb/^{207}Pb$ (2.4454)	$^{206}Pb/^{207}Pb$ (1.132)	$^{208}Pb/^{207}Pb$ (2.378)
Spring	84	73	16	27
Fall	38	39	62	61
Winter	52	49	48	51

Also given in the parentheses are the characteristic values of $^{206}Pb/^{207}Pb$ or $^{208}Pb/^{207}Pb$ isotope ratios used for representing the two sources to calculate the contribution. Refer to the text for details.

aerosols, followed by an increase from fall to winter and a maximum in spring; the isotope ratios gradually become similar to those detected in Shanghai (Yangtze Delta), China. Together with backward and forward air-mass trajectory analysis, it reveals an increased impact of long-range transport with varying northeast monsoon seasons. A two end-member mixing model was adopted to assess the relative contributions of long-range transport of airborne Pb. Results show an increased contribution from nearly 40% in fall to 85% in spring, certainly demonstrating the substantial influence of the Chinese pollution outbreak on Taiwan local air quality.

Because of the present fast development of industry in China it can be expected that the air pollution in China will become more severe in the future years. Consequently, it can further be predicted that the impact of long-range transport of air pollutants will be continued. Obviously, this needs to be taken care of when implementing the air quality management for Taiwanese governments.

Acknowledgments

We thank Mr. T.K. Chen and Mr. C.H. Liu for their help with sampling. Thanks are also extended to Profs. C.A. Huh, C.H. Wang, F.K. Shiah and S.J. Kao for their helpful comments and suggestions. Special thanks go to the Climate Monitoring and Diagnostics Laboratory of the National Oceanic and Administration (USA) for providing air mass back trajectories. This work was supported by the theme research project of Academia Sinica (Project number: 33, 2002) and Environmental Protection Administration grants EPA-91-FA11-03-A062 to S. C. L.

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