Atmospheric deposition of heavy metals in the Pearl River Delta, China

C.S.C. Wong[1], X.D. Li[1]*, G. Zhang[2], S.H. Qi[2] and X.Z. Peng[2]

[1]Environmental Engineering Unit, Department of Civil and Structural Engineering,
The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong
[2]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry,
Chinese Academy of Sciences, Guangzhou, 510640, China

Abstract - Rapid urban and industrial development in China in the last few decades has provoked some serious environmental concerns. As one of the regions with the fastest economic development in China, the Pearl River Delta (PRD) is particularly susceptible to environmental degradation. Atmospheric emissions represent a major pathway of anthropogenic inputs of heavy metals into the surface environment. Samples of atmospheric deposits were collected at urban, suburban and rural locations in the PRD (including Hong Kong) using bulk deposition samplers in the summer and winter seasons of 2001-2002. The samples were analyzed for heavy metal concentrations and Pb isotopic compositions. According to the analytical results, atmospheric deposition of Cr, Cu, Pb and Zn in the PRD (6.43 ± 3.19, 18.6 ± 7.88, 12.7 ± 6.72 and 104 ± 36.4 $mg/m^2/yr$, respectively) was significantly elevated compared with other regions, e.g. the Great Lakes region in North America and the North Sea in Europe. It was also found that atmospheric deposition of Cu, Cr and Zn was generally higher in the summer than that in the winter, which could be caused by the washout effect of the rainy season in the subtropical region. The Pb isotopic composition of the air deposits ($^{206}Pb/^{207}Pb$ 1.161 - 1.177) indicated that atmospheric inputs of Pb derived mainly from anthropogenic sources, e.g. vehicular exhaust and Pb ore in the PRD. However, the distribution of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of some atmospheric deposits in the summer season suggested that atmospheric Pb at some locations of the PRD could be attributed to other anthropogenic source(s).

Key word index: Atmospheric deposition; heavy metals; Pb isotopes; Pearl River Delta; China.

1. INTRODUCTION

Air pollution is a major environmental concern in China (Florig, 1997). Atmospheric emissions of gaseous and particulate pollutants have caused profound environmental and health implications in recent years. Furthermore, excessive inputs of heavy metals and other pollutants into the surface environment as a consequence of atmospheric deposition can impose a long-term burden on biogeochemical cycling in the ecosystem (Nriagu, 1988; Nriagu and Pacyna, 1988; Kelly *et al.*, 1996). It is thus imperative to understand the atmospheric deposition of heavy metals on the surface environment.

The moss technique developed by Rühling and Tyler (1968, 1970 & 1971) has been widely used in many parts of the world to estimate atmospheric heavy metal deposition, especially in forest lands (Kubin and Lippo, 1996; Berg and Steinnes, 1997, Wolterbeek, 2002). This technique, however, poses some limitations in urbanized or contaminated areas where environmental conditions do not normally encourage the proliferation of indigenous moss. Alternatively, direct collection of atmospheric

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[*] Corresponding author, E-mail address: cexdli@polyu.edu.hk; Fax: (852) 2334-6389; Tel: (852) 2766-

deposition using various sampling devices offers a more practical approach to monitor atmospheric heavy metal deposition. Some of the commonly used sampling devices include low-volume air samplers, high-volume air samplers and passive bulk deposition samplers (Monna *et al*., 1999; Dye *et al*., 2000; Matschullat *et al*., 2000). In comparison with the low- and high-volume air samplers that actively draw and filter air samples to collect atmospheric particulates, the bulk deposition samplers can be considered as a passive sampling device where the deposition of heavy metals and other pollutants is solely governed by the ambient environment. The use of this passive sampling method can therefore provide valuable information on the influences of atmospheric inputs of heavy metals on the surface environment.

In addition to the quantitative analysis of heavy metals, the use of stable Pb isotopes can also strengthen the understanding of input patterns and sources of atmospheric Pb. This analytical tool has been widely applied in different ecosystems, including soils (Hansmann and Köppel, 2000; Wong *et al*., 2002), sediments (Farmer *et al*., 1996; Munksgaard *et al*., 1998; Li *et al*., 2001), biological organisms (Gelinas and Schmit, 1997; Farmer *et al*., 2002), and aerosols (Bollhöfer and Rosman, 2000 & 2001; Flament *et al*., 2002). Furthermore, the isotopic signatures of major Pb sources in North America, Europe and Asia have also been characterized (Sturges and Barrie, 1987; Zhu, 1995; Bacon *et al*., 1996; Farmer *et al*., 1996; Mukai *et al*., 2001).

The Pearl River Delta (PRD) is located in the southern part of Guangdong Province, China (see Fig. 1). The summer season (May – October) in the PRD is usually wet and hot, while the weather in winter (November - April) is relatively dry and cool. Since the implementation of economic reforms in 1978, the PRD has experienced rapid economic growth and significant urban and industrial development. Today, the PRD has a total population of 22.6 million and covers an area of 41,700 km^2. Major cities established within the PRD include Guangzhou, Shenzhen, Dongguang, Foshan, Jiangmen, Zhuhai, Zhongshan, and Huizhou, of which Guangzhou is the largest light industrial base in China. Hong Kong is situated in the southeast part of the PRD. Intense human activities in this region have caused a mounting pressure on its environmental quality.

Information on atmospheric deposition of heavy metals and its Pb isotopic composition in the PRD is very limited. Hence, the primary objective of the present study was to determine atmospheric deposition of heavy metals and its Pb isotopic composition in the PRD, and to study possible seasonal variations of the air deposition flux. Based upon these results, the study also attempted to examine elemental associations in atmospheric deposition and to elucidate the potential sources of heavy metal contaminants in the region.

2. METHODS AND MATERIALS

A total of 28 air deposit samples were collected at 14 urban, suburban and rural locations within the PRD, including Hong Kong, using simple cone-shaped samplers over two 3-month periods from July to September 2001 and December 2001 to April in 2002. These samplers were purposely placed at locations away from known local sources of heavy metals, e.g. major motorways and large factories. The 14 sampling locations are depicted in Fig. 1, and descriptions of the sampling locations, including elevation and sampling duration, are briefly summarized in Table 1. The cone-shaped samplers, with a cross-sectional sampling area of 0.049 m^2, were lined with Whatman EPM 2000 Silicate

Microfibre filters and exposed to the ambient environment over a period of 84-99 days, except for GZ02 (~32 days). Deposits collected on the filters were then covered with a layer of medical-use cotton gauze on each side to avoid loss of loose particles and for ease of handling. The filters were then wrapped in aluminum foil and stored in polyethylene bags at 4^{o}C.

One quarter of the filters, along with the gauze, was carefully cut using a pair of stainless steel scissors and digested in strong inorganic acids according to USEPA (1999), with some modifications. Briefly, the filters with the gauze were carefully placed in acid-cleaned Pyrex test tubes. 20.0 ml of 70% high-purity HNO_3 and 5.0 ml of 65% $HClO_4$ were added, in which the filters were completely submerged. The use of $HClO_4$ instead of hydrochloric acid (HCl) as suggested in the USEPA method was to minimize potential spectral interferences with Pb isotopic analysis by Inductively Coupled Plasma - Mass Spectrometer (ICP-MS). The mixtures were gently shaken using a vortex, and heated progressively to 190^{o}C in an aluminum heating block for 24 hours to near dryness. After the test tubes were cool, 20.0 ml of high-purity 5% (v/v) HNO_3 were added. The solutions were thoroughly mixed using a vortex and then heated at 70^{o}C for 1 hr. After cooling, the solutions were decanted into acid-cleaned polyethylene tubes for storage. With respect to quality control, procedural blanks with and without filters, each representing 25% of the sample population, were randomly inserted in the analytical programme.

Determination of the elemental concentrations of the solutions was achieved by Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES; *Perkin Elmer Optima DV3300*), while Pb isotopic composition of the solutions was determined by ICP-MS (*Perkin Elmer Sciex Elan 6100 DRC*^{plus}) after dilution using 5% high-purity HNO_3. The concentrations of Ca, Cd, Co, Cu, Cr, Fe, Mg, Mn, Ni, Pb, V and Zn were measured by ICP-AES after calibration using Perkin Elmer high-purity standard in 5% high-purity HNO_3. The elemental concentrations of the procedural blanks were generally < 5% of the mean analyte concentrations for all metals. Blanks (5% high-purity HNO_3) and quality control standards were measured at every 10 samples to detect contamination and drift. Three replicates of each of the digested solutions were measured, and precision was generally lower than 2.0% and 4.0% for trace and major elements, respectively.

For Pb isotopic composition analysis of the solutions, an international standard reference material (the SRM 981 Common Pb Isotopic Standard) from the National Institute of Standards and Technology (NIST) was used for calibration and analytical control. The instrumental parameters of the ICP-MS were set as 150 sweeps per reading and 10 replicates per sample solution. Pb counts of the procedural blanks were generally <1% of the samples. The precision (% RSD) of the Pb isotopic ratios was typically <0.5%. The certified $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of NIST SRM 981 were 0.0646, 1.0933, and 2.3704, respectively, which was in good agreement with the measured values of 0.065, 1.095, and 2.371, respectively.

It is recognized that the results of the air deposit samples in the present study reflect the atmospheric deposition of heavy metals during the summer and winter seasons in the PRD. Nonetheless, for ease of comparison, daily (summer and winter) and annual atmospheric heavy metal deposition rates were calculated based on the current data. To calculate the daily atmospheric deposition of heavy metals per unit area ($\mu g/m^2/day$) in each season, the measured heavy metal concentration of the solution, [HM] in $\mu g/L$, was divided by the number of sampling days, D in day, exposed to the ambient environment and cross-sectional sampling area of the sampler, A in m^2, and multiplied by 4 to account for the whole filter, as well as by the solution dilution factor, DF. Therefore, the daily metal deposition ($\mu g/m^2$/day) = [HM] ÷ D ÷ A × 4 × DF. In order to estimate the annual atmospheric inputs, the daily deposition rates in the summer (May – October) and winter (November – April) were multiplied by the number of days in each of the seasons. The obtained seasonal atmospheric deposition rates were then summed up to estimate the annual atmospheric deposition of heavy metals.

An attempt was made to investigate the potential elemental associations among heavy metals and major elements in the deposits by principal component analysis (PCA). The annual atmospheric deposition of heavy metals and major elements was used as input data, and a rotation method Varimax with Kaiser normalization was used. The statistical computation of the principal components (PCs) was achieved using SPSS 10.

3. RESULTS AND DISCUSSION

Annual atmospheric deposition of heavy metals (Cd, Co, Cr, Cu, Ni, Pb, V & Zn) and some major elements (Ca, Fe, Mg & Mn) at the 14 sampling locations in the PRD is presented in Table 2. The deposition of Cr, Cu, Pb and Zn in the region is depicted in Fig. 2. The results showed that atmospheric deposition of Cr ranged from 3.68 mg/m^2/yr at ZQ01 to 16.2 mg/m^2/yr at GZ01. As shown in Table 2, atmospheric Cr deposition declined from GZ01 to FS02 and FS01 (7.95 and 8.36 mg/m^2/yr). Atmospheric Cu and Ni deposition at ZH01 and HK01 (Cu 40.9 and 27.6 mg/m^2/yr; Ni 34.3 and 15.1 mg/m^2/yr, respectively) were among the highest, while atmospheric inputs of Cu and Ni at other sampling locations were usually <20.0 and <10.0 mg/m^2/yr, respectively. Within the PRD, atmospheric Pb deposition varied from 2.87 mg/m^2/yr at HK01 to 25.4 mg/m^2/yr at GZ02. In addition to GZ02, atmospheric Pb deposition exceeding 20.0 mg/m^2/yr was also found at FS01 and FS02 (20.3 and 20.5 mg/m^2/yr, respectively). Atmospheric Zn deposition varied from 57.7 mg/m^2/yr at JM01 to 164 mg/m^2/yr at ZH01, and annual atmospheric Zn deposition exceeding 150 mg/m^2/yr was also detected at ZQ01 and DG01. In general, the annual atmospheric deposition of heavy metals showed large variations among the different sampling locations, suggesting that emissions of the metals could vary significantly with the PRD region. It was also observed that atmospheric deposition of Cu, Ni and Zn at ZH01 tended to be significantly elevated as compared to the other locations, indicating the influences of possible sources of heavy metals in the vicinity of this sampling site.

A comparison was made with data from the Great Lakes in North America and the North Sea in Europe, where concentrations of urban and industrial development were established. Annual atmospheric deposition of Cu, Cr, Pb and Zn in the Great Lakes, other regions in the United States, and the North Sea is shown in Table 3. The current results showed that mean atmospheric deposition of Cu, Cr and Zn in the PRD was significantly elevated compared with those reported in North American and Europe. The mean atmospheric Pb loading in the PRD was also very high when compared with that of the Great Lakes (1993-1994) and the North Sea (1992-1994) (Sweet *et al.*, 1998; Injuk *et al.*, 1998). However, it was comparable to annual atmospheric Pb deposition in N.W. Indiana (1975-1980) and W. Pennsylvania (1975-1980) when leaded petrol was still in use in the United States. The prominent differences in atmospheric heavy metal deposition between the PRD and the various regions in North America and Europe indicated that aerial emissions of Cu, Cr, Pb and Zn in the PRD were serious, provoking concerns over the potential long-term environmental and health implications of excessive atmospheric deposition of heavy metals on the surface environment.

In order to examine potential seasonal variations, atmospheric deposition (μg/m^2/day) of Cr, Cu, Pb and Zn in the summer and winter seasons were calculated on a daily basis. As shown in Table 4, atmospheric deposition of Cr, Cu and Zn, exhibited statistically significant seasonal differences, where atmospheric fluxes of these metals tended to be higher in the summer than in the winter. This pattern was similar to the results of heavy metal seasonal deposition in the North Sea and the Lake Erie (Injuk *et al*., 1998; Sweet *et al*., 1998). The seasonal variations could be caused by the washout effects of frequent rainfall events during the summer in the subtropical region. The majority of annual precipitation usually falls between April and September in the PRD. The use of cone-shaped samplers as a passive sampling mode was designed to collect particulates by gravity, therefore favouring the entrapment of large particulates. However, during the summer season when rainfall event is frequent, fine particulates attached to rain droplets can also be collected in the samplers, and the clouds could also gather contaminants from wider area and greater height than the sampling locations (Sweet *et al*., 1998). These factors could lead to an increase in atmospheric deposition of heavy metals in the summer season. The lack of a seasonal tendency in Pb deposition as compared to the elevated deposition of Cu, Cr and Zn in the summer could be attributed to the differences in origin and/or particle size of emission sources between Pb and other heavy metals (Sweet *et al*., 1998).

In order to further investigate the potential implications of elevated deposition of atmospheric heavy metals, attempts were made to estimate surface soil enrichment in the region using the calculated annual atmospheric deposition of heavy metals. Distribution of heavy metals in agricultural and undisturbed soils in the PRD was recently studied by Wong *et al*. (2002). The mean Cu, Pb and Zn concentrations of the undisturbed soils (0-5 cm) were approximately 15, 30 and 45 mg/kg, respectively. It was assumed that atmospheric deposition was the sole source of heavy metal input to the soils, and that the metals were retained in the surface soils. Assuming a soil density of 1300 kg/m^3 and that the deposition rate remained unchanged over a 20-year period, it was calculated that Pb concentration of the undisturbed soils would increase by 13% from 30 mg/kg to 33.9 mg/kg over a period of 20 years. In the worst case scenario, where Pb atmospheric deposition of 25.4 mg/m^2/yr was measured, a 26% increase of soil Pb concentration was predicted. Using the same assumptions, it was calculated that atmospheric Cu input of 18.6 and 40.9 mg/m^2/yr could lead to an increase of Cu concentrations of the soils by ~38% and ~84%, respectively, over a period of 20 years. Zn concentrations of the surface soils would also increase from 45 to 77 mg/kg if the atmospheric input over 20 years was 104 mg/m^2/yr. In the worst case scenario, where atmospheric Zn input was 164 mg/m^2/yr, Zn concentration of the soils might reach 95.5 mg/kg, representing a significant increase of 112% in the concentration of undisturbed soils. These estimates showed that the elevated atmospheric deposition of heavy metals could cause potential long-term concern over heavy metal enrichment in surface soils and potential health concerns in the PRD region.

In order to gain further understanding of potential sources of atmospheric Pb in the PRD, the Pb isotopic composition of the deposits was analyzed. As shown in Table 5, the ^{204}Pb/^{207}Pb, ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of the deposits ranged between 0.064 – 0.065, 1.161 – 1.177, and 2.366 – 2.501, respectively. The Pb isotopic composition of geological materials and some anthropogenic Pb sources in the PRD have been reported (Zhu, 1995 & 1998; Zhu *et al.*, 1989 & 2001). The ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of Pb derived from natural geological materials, e.g. granite and volcanic rocks, and anthropogenic sources, e.g. automobile exhaust and Fankou Pb-Zn deposit, are summarized in Table 6. The ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of aerosols collected previously in the PRD and other Chinese cities are presented in Table 7. In general, the Pb isotopic composition of the air deposits showed that the ^{206}Pb/^{207}Pb ratios of the deposits (1.161-1.177) were generally lower than those of the naturally derived Pb (1.18-1.20) and comparable to those of the anthropogenic Pb sources, such as traffic and Pb ore in the PRD. A comparison with the previously published Pb isotopic ratios of the aerosols in other Chinese cities and the PRD (see Table 7) showed that the Pb isotopic ratios of the air deposits of the present study were not only comparable with those measured in the same region, but also in close agreement with those found in other cities in China. These results may reflect the influences of rapid industrial and urban development in the Chinese cities in the last two decades.

The relationship between the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of the atmospheric deposits in the PRD is depicted in Fig. 3. In addition, the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of known Pb sources in the PRD, such as vehicular exhaust and Pb-Zn ore deposit, and the ratios of aerosols in other Chinese cities are also plotted in Fig. 3. In general, the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of the air deposits collected in the summer were in a wider range than those of the deposits collected in the winter. Nonetheless, the ratios of most air deposits fell within the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of the known natural and anthropogenic sources in the PRD (see Fig. 3), indicating aerial inputs of Pb from both the natural geological materials and anthropogenic Pb sources within the PRD. The Pb isotopic composition of the air deposits collected in the northwestern area of the PRD (FS01, FS02, GZ01 & QY01) in the summer showed different signatures from the current known Pb sources in the PRD, reflecting possible contribution of Pb from other new sources at these locations. Further studies will be required to trace the anthropogenic Pb input sources in these areas.

The rotated component matrixes of the principal component analysis (PCA) of the atmospheric deposition of heavy metals and major elements are presented in Table 8. In the PCA of the annual deposition of heavy metals, the first three PCs accounted for 81.4% of the total variance. As shown in Table 8, major elements, including Ca, Fe, Mg and Mn, and some heavy metals, such as Co and V, were strongly dominated by PC1. The strong association among Ca, Fe, Mg, Mn, Co and V may suggest that PC1 be strongly governed by the influences of natural geological materials. Cu, Ni and Zn, commonly regarded as typical heavy metal contaminants released from industrial processes were dominated by PC2. The significant associations among these heavy metals might reflect the impacts of anthropogenic activities on the atmospheric deposition of Cu, Ni and Zn in the region. The unique association of Cr with PC3 suggested a governing geochemical factor on the atmospheric deposition of Cr. Atmospheric deposition of Cd and Pb was neither significantly associated with other metals nor strongly dominated by one of the three PCs (Table 8). The moderate association of Cd and Pb with PC1 and PC2 probably indicated that atmospheric deposition of Cd and Pb in the PRD could be governed by more than one factor. This phenomenon was similar to the weak association of Pb with other heavy metals and major elements found in the agricultural and undisturbed soils, and estuary sediments of the PRD (Li *et al.*, 2000; Wong *et al.*, 2002).

4. CONCLUSIONS

The present study showed that atmospheric deposition of heavy metals (Cu, Cr, Pb and Zn) in the PRD was significantly elevated in comparison with the reported data from North America and Europe, reflecting strong anthropogenic inputs as a consequence of rapid industrial and urban development in the region. The current heavy metal input rate from atmospheric deposition may have significant effects on the surface environment of the PRD. The ^{206}Pb/^{207}Pb ratios of atmospheric Pb in the PRD also showed the influences of anthropogenic sources within the region. The distribution of the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of some atmospheric deposits implied that, in addition to automobile emission and Pb ore, elevated deposition of atmospheric Pb could be attributed to other Pb sources in the region.

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Table 1. Sampling locations of atmospheric deposition samples in the Pearl River Delta

Sample ID	Location	Elevation (m)	Sampling duration (day)	
			Summer	Winter
DG01	Southwestern Dongguan	530	87	91
FS01	Countryside in Shunde City	10	84	88
FS02	Countryside in Naihai City	10	84	88
GZ01	Northeastern suburban Guangzhou	534	86	81
GZ02	Northern urban Guangzhou	110	32	33
GZ03	Southern suburban Guangzhou	295	85	86
JM01	Western margin of Pearl River Delta	280	84	88
QY01	Northern suburban Qingyuan	609	84	87
QY02	Qingyuan mountain region	802	84	97
ZH01	South Hengqing Island, Zhuhai	30	85	96
ZQ01	Zhaoqing	500	84	85
ZS01	Southeastern Zhongshan	530	85	96
HK01	Cape D’Aguilar, Hong Kong	10	92	87
HK02	Tai Mo Shan, New Territories, Hong Kong	900	92	99

Table 2. Annual atmospheric deposition of major and trace metals (mg/m^2/yr) in the Pearl River Delta

Sample ID	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	V	Zn
DG01	86.5	0.04	0.16	4.85	16.4	464	55.7	6.23	7.04	8.73	2.30	154
FS01	327	0.15	0.34	7.95	21.5	923	125	14.0	6.98	20.3	4.10	86.2
FS02	145	0.11	0.28	8.36	14.6	838	116	12.2	5.56	20.5	5.61	61.2
GZ01	113	0.11	0.22	16.2	14.5	571	72.4	9.00	10.3	12.9	1.95	107
GZ02	288	0.06	0.21	5.26	16.6	721	82.4	12.0	4.13	25.4	2.09	85.4
GZ03	146	0.04	0.12	4.02	14.3	438	49.5	7.29	3.21	7.45	1.56	61.9
JM01	96.4	0.04	0.16	4.57	13.6	569	96.0	8.62	3.27	9.23	2.34	57.7
QY01	202	0.14	0.14	4.22	13.4	773	74.1	8.87	3.05	18.5	1.86	89.8
QY02	82.4	0.08	0.07	6.65	14.7	362	53.9	4.62	4.83	9.50	0.81	72.7
ZH01	181	0.01	0.25	5.48	40.9	340	64.2	8.88	34.3	4.16	1.31	164
ZQ01	92.3	0.04	0.08	3.68	10.7	339	43.2	5.39	2.24	17.8	1.12	156
ZS01	336	0.04	0.16	4.83	24.1	485	71.7	8.76	6.90	10.0	2.22	123
HK01	93.5	0.02	0.15	7.58	27.6	311	55.8	7.37	15.1	2.89	0.56	107
HK02	209	0.07	0.32	6.32	17.4	633	94.3	12.4	9.95	10.6	1.48	127
Mean (n=12)	171	0.07	0.19	6.43	18.6	555	75.3	8.98	8.35	12.7	2.09	104
S.D.	89.9	0.04	0.08	3.19	7.88	199	24.9	2.80	8.26	6.72	1.32	36.4

Table 3. Comparison of atmospheric deposition of heavy metals (mg/m^2/yr) between the PRD and other regions

Location	Cu	Cr	Pb	Zn
Lake Superior (1993-1994)[a]	3.10	0.22	1.50	8.80
Lake Michigan (1993-1994)[a]	1.90	0.20	1.60	6.00
Lake Erie (1993-1994)[a]	4.20	1.10	1.80	17.0
NW Indiana (1975-1980)[b]	9.00	3.20	60.0	100
W. Penna. (1975-1980)[c]	-	2.80	10.0	4.10
L. Erie (1975)[d]	2.60	-	4.20	30.0
North Sea (1993-1994)[e]	1.24	2.43	3.52	6.50
PRD (the present study)	18.6 ± 7.88	6.43 ± 3.19	12.7 ± 6.72	104 ± 36.4

[a] Sweet *et al*., 1998
[b] Cole *et al*., 1990
[c] Schell, 1986
[d] Kuntz, 1978
e Injuk *et al*., 1998

Table 4 Daily atmospheric deposition of heavy metals (μg/m^2/day) during summer and winter in the Pearl River Delta

	Cu		Cr		Pb		Zn	
Sample ID	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
DG01	83.0	6.25	21.9	4.57	31.1	16.6	656	184
FS01	65.2	52.6	28.2	15.3	55.3	55.7	264	208
FS02	37.7	42.4	27.6	18.2	54.0	58.6	175	161
GZ01	68.0	11.3	80.5	7.78	53.0	17.6	534	45.2
GZ02	48.3	42.6	11.6	17.2	55.5	84.1	199	269
GZ03	61.6	16.6	14.0	7.97	20.7	20.1	232	106
JM01	42.8	31.6	13.1	11.9	27.0	23.6	159	157
QY01	44.1	29.3	12.2	10.9	47.1	54.4	267	225
QY02	51.4	29.2	14.1	22.4	27.5	24.5	262	135
ZH01	195	28.1	21.1	8.80	16.7	5.97	629	264
ZQ01	26.9	31.9	12.8	7.34	73.9	22.9	401	454
ZS01	112	19.9	14.2	12.2	25.2	29.7	490	180
HK01	123	27.6	34.0	7.27	7.25	8.61	368	218
HK02	65.7	29.5	27.9	6.59	42.6	15.4	373	320

Table 5. Pb isotopic ratios of atmospheric deposits in the Pearl River Delta

Sample ID		$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
DG01	Summer	0.064	1.164	2.427
	Winter	0.064	1.170	2.448
FS01	Summer	0.066	1.166	2.366
	Winter	0.064	1.169	2.446
FS02	Summer	0.066	1.167	2.378
	Winter	0.064	1.167	2.432
GZ01	Summer	0.065	1.164	2.374
	Winter	0.064	1.168	2.450
GZ02	Summer	0.065	1.177	2.445
	Winter	0.064	1.176	2.467
GZ03	Summer	0.064	1.177	2.471
	Winter	0.064	1.169	2.446
JM01	Summer	0.064	1.166	2.435
	Winter	0.064	1.173	2.439
QY01	Summer	0.065	1.165	2.400
	Winter	0.064	1.171	2.455
QY02	Summer	0.065	1.175	2.456
	Winter	0.064	1.171	2.433
ZH01	Summer	0.064	1.166	2.472
	Winter	0.064	1.172	2.468
ZQ01	Summer	0.064	1.175	2.501
	Winter	0.064	1.175	2.472
ZS01	Summer	0.064	1.162	2.429
	Winter	0.064	1.171	2.459
HK01	Summer	0.064	1.167	2.461
	Winter	0.064	1.168	2.472
HK02	Summer	0.064	1.161	2.453
	Winter	0.064	1.177	2.454

Table 6. Isotopic composition of Pb derived from natural and anthropogenic sources in the Pearl River Delta

	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Natural sources:		
Granite in the eastern Cathaysia[a]	1.1834	2.4680
Granite in the Pearl River Delta[a]	1.1842	2.4824
Volcanic rocks in Foshan[b]	1.1993	2.4965
Uncontaminated soils[c]	1.1952	2.4815
Anthropogenic sources:		
Fankou Pb-Zn deposits[a]	1.1716	2.4725
Automobile exhausts in the Pearl River Delta[c]	1.1604	2.4228

[a] Zhu (1998)
[b] Zhu *et al*. (1989)
[c] Zhu *et al*. (2001)

Table 7. Pb isotopic ratios of aerosols collected in various Chinese cities and the PRD

Sampling sites		$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Harbin[a]	Summer	1.148	2.436
	Winter	1.172	2.460
Changchun[a]	Summer	1.145	2.441
	Winter	1.166	2.463
Dalian[a]	Summer	1.138	2.441
	Winter	1.135	2.441
Shanghai[a]	Summer	1.159	2.450
	Winter	1.156	2.449
Nanjing[a]	Summer	1.166	2.460
	Winter	1.161	2.460
Guiyang[a]	Summer	1.189	2.465
	Winter	1.185	2.461
Foshan hardware factory, PRD[b]	Apr. 1994	1.162	2.457
	Oct. 1994	1.165	2.463
Plastic factory, PRD[b]	Apr. 1994	1.155	2.457
	Oct. 1994	1.166	2.465
Tongji primary school, PRD[b]	Apr. 1994	1.155	2.457
	Oct. 1994	1.166	2.474
Environmental bureau, PRD[b]	Apr. 1994	1.160	2.462
	Oct. 1994	1.170	2.469
Atmospheric deposits, PRD	Summer 2001	1.161 – 1.177	2.366 – 2.501
	Winter 2001	1.167 – 1.177	2.432 – 2.472

[a] The values were calculated using $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios reported by Mukai *et al*. (2001).

[b] Zhu *et al*. (2001)

Table 8. The rotated component matrixes of annual atmospheric deposition of heavy metals and major elements in the Pearl River Delta

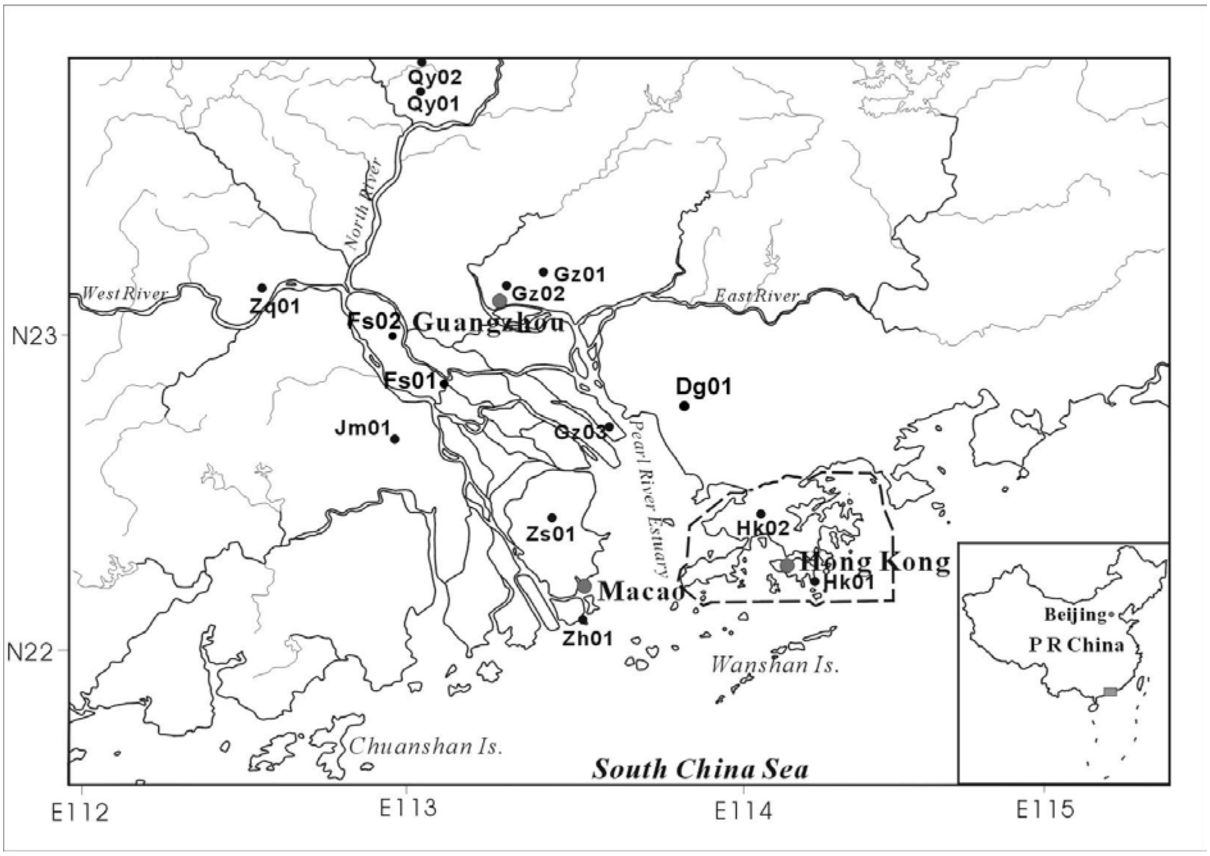
Element	PC1	PC2	PC3
Ca	0.752	0.123	-0.432
Cd	0.568	-0.547	0.347
Co	0.863	0.308	0.268
Cr	0.168	0.016	0.904
Cu	0.134	0.937	-0.044
Fe	0.877	-0.432	0.085
Mg	0.904	-0.160	0.195
Mn	0.963	0.036	0.069
Ni	0.024	0.943	0.194
Pb	0.592	-0.590	-0.149
V	0.746	-0.304	0.183
Zn	-0.215	0.642	-0.187

List of Figure Captions:

Fig. 1. Sampling locations of atmospheric deposits in the Pearl River Delta.

Fig. 2. Annual atmospheric deposition of Cr, Cu, Pb and Zn in the Pearl River Delta.

Fig. 3. The relationship between ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of atmospheric deposits in the Pearl River Delta.



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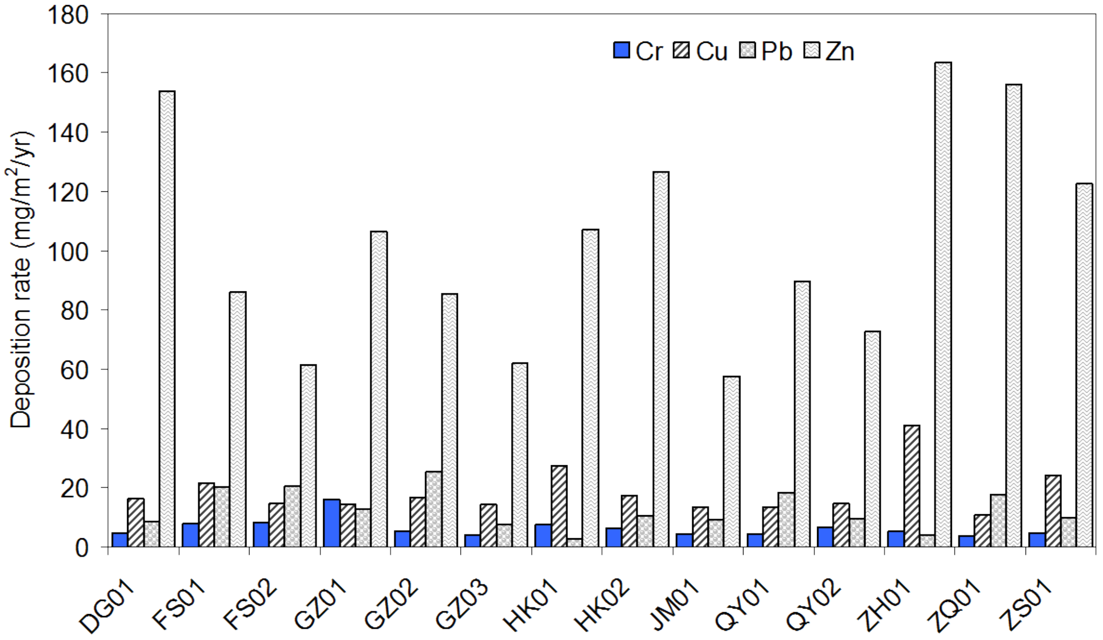

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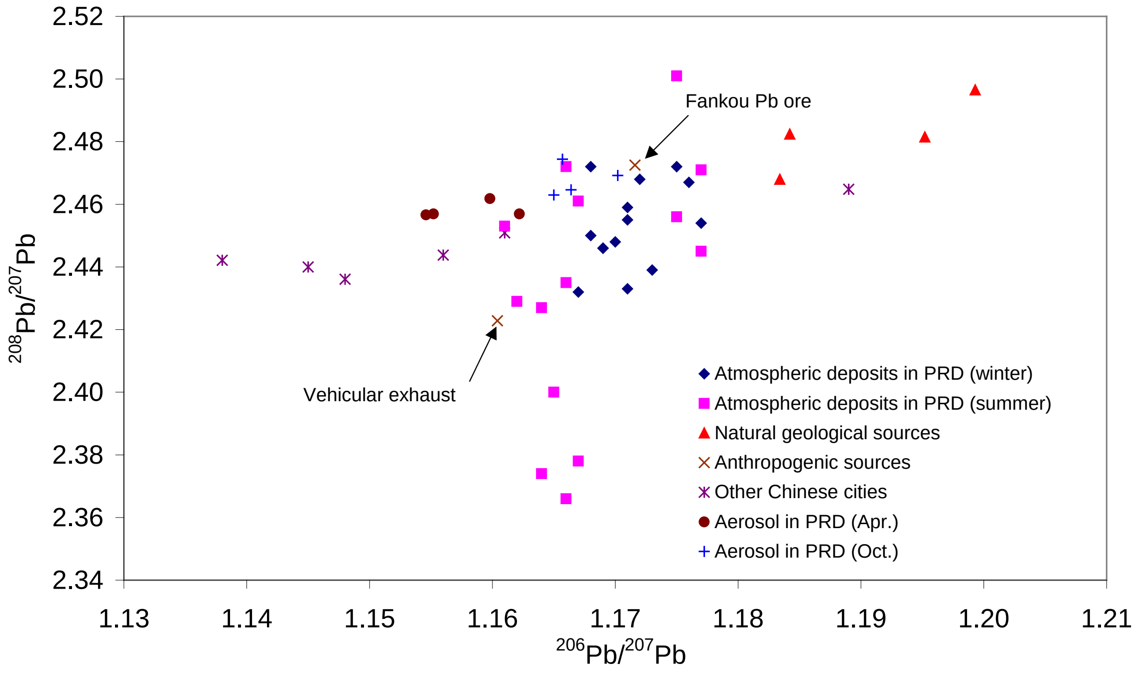

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