The Hong Kong Polytechnic University
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STUDY OF ATMOSPHERIC TRACE METALS IN PARTICULATE MATTER, DRY AND WET DEPOSITIONS, AND MOSSES IN THE PEARL RIVER DELTA REGION

By

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A thesis submitted in partial fulfilment of the requirements for the degree of

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CERTIFICATE OF ORIGINALITY

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LEE SIU LAN

Abstract of thesis entitled
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The study of trace metals in the atmosphere is important due to the critical effects of trace metals on human health and the geochemical balance of the ecosystems. Trace metals in particulate matter are important phases in the air environment, which can be transported and deposited to places far away from their sources in the terrestrial environment. In the past few decades, China has undergone drastic economic development, leading to the rapid industrialisation and urbanisation in many parts of the country. The Pearl River Delta region (PRD) is the most important economic zone in South China region, and in recent years, it has been susceptible to severe atmospheric pollution from rapid industrial development and urbanisation process in the region, imposing mounting pressure to the regional environmental quality.

The objective of this study was to investigate the current level of atmospheric trace metal pollution in urban and rural areas of the Pearl River Region over one year period of measurement, which would provide insights to the sources and temporal and spatial distributions of trace metals in the air of the PRD region. The research project also examined the transport of particulate trace metals and their pathways of deposition (by dry and wet depositions) in the PRD region, which is important in strategic environmental planning and pollution control. The potential use of mosses in bio-monitoring of air quality in the PRD region was also evaluated. A few moss species were identified to be used in monitoring of atmospheric trace metal pollution in subtropical areas.

This study focused on an integrated study of trace metals in particulate matter, dry and wet depositions and mosses in the PRD region. Sampling of aerosols, and dry and wet depositions was conducted over one-year period from Dec 2003 – Jan 2005, and mosses during Jan 2003 in the Nanling Mountains, and May 2004 in Dinghu Mountain. Moreover, $PM_{2.5}$ samples collected from Guangzhou area of the PRD region in an annual sampling campaign during May 2005 – May 2006. The samples were analysed for the concentrations of major

elements (Al, Fe, Mg and Mn) and trace metals (Cd, Co, Cr, Cu, Ni, Pb, V and Zn), and for Pb isotopic composition. The dataset collected in various urban and rural areas in the PRD region provided comprehensive information of the atmospheric trace metal pollution both locally and in a regional context.

High concentrations of trace 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. The high $PM_{2.5}$/TSP ratios of trace metals such as Cd, Cu, Ni, Pb and V in urban areas of Guangzhou showed that the metals were predominately associated with finer fractions, and relatively low ratios were depicted for Co, Cr and Zn, probably reflecting greater influences from natural sources.

Elevated dry and wet deposition fluxes were found in the urban and rural areas of the inland PRD area (near Guangzhou), showing severe atmospheric pollution in the region, especially for Cd, Pb and Zn. Distinguished temporal variation were observed in the dry and wet depositions for trace elements in the urban and rural areas, but those in suburban areas was less distinct. Higher dry deposition flux of Zn was found in the urban areas during the winter season, probably due to the influx of pollutants to the PRD region due to the winter monsoon system and the relatively dry condition in the winter time. The wet deposition fluxes of Co, Cu and Zn in the urban areas were observed to be higher in summer, attributed to a greater scavenging effect by rain. The mode of deposition was found to vary for different elements. Aluminium, Fe and Cr were found to be mainly deposited as dry depositions, and Cd, Co, Cu, Mg, Mn and Zn were primarily deposited as

wet depositions, during both the winter and summer seasons. The predominant pathway for Pb and V was dry deposition during winter and wet deposition during the summer season. The Pb isotopic ratios of most dry and wet deposits, during both the winter and summer seasons, were found to be similar to the anthropogenic sources in the PRD region, such as the Pb ore, industrial and vehicular emissions. The input of Pb could be originated from various anthropogenic sources in the PRD region. Some of the dry deposits in the coastal areas were found to have Pb isotopic composition similar to the Vietnam aerosols, showing that the long range transport of pollutants during the summer season from South Asian countries may have significant effect on the atmospheric dry depositions in the coastal PRD area.

The suitability of the moss *Hypnum plumaeforme* as a new biomonitor of atmospheric trace element pollution in southern China was also evaluated. The results showed that the moss had a good capacity to absorb and retain heavy metals such as Cd, Co, Cu, Cr, Pb, V and Zn. The northern part of the Nanling mountain range was found to have more trace elements than the southern range, possibly reflecting the long range transport of pollutants from northern China. The elemental concentrations of the mosses in the northern range were found to be well correlated with elevations. The concentrations of heavy metals decreased as elevations increased, and became relatively constant above 1100 m a.s.l. The Pb isotopic compositions indicated that atmospheric inputs of Pb in mosses were mainly derived from anthropogenic sources, including vehicular emissions and Pb used in local industries. A comparative study was conducted on the metal uptakes of different moss species, including *Hypnum plumaeforme, Leucobryum chlorophyllosum, Pogonatum contorium, Thuidium tamariscinum and Bazzania tridens*. The results showed that the moss species, *Hypnum plumaeforme* and *Thuidium tamariscinum* were suitable to be used as biomonitors of trace metals in the South China region, as they were found to have higher uptakes of most trace metals compared with other species, which has great potential use in the future monitoring of atmospheric trace metal pollution in the South China region and other subtropical areas.

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Chapter 1 - Introduction

Trace metals in the atmosphere have raised great concerns for their long-term ecological and health effects which are often less ubiquitous but highly toxic. In the past few decades, due to the rapid urbanisation and industrialisation in many parts of the world, large quantities of trace metals have been emitted from various sources to the atmosphere, such as smelting of metallic ores, industrial fabrication and commercial applications of metals, as well as burning of fossil fuels (Nriagu and Pacyna, 1988). Trace metals are non-biodegradable, and can accumulate in human body system, causing damage to the 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). Excessive inputs of metals into the environment also result in the perturbations of biogechemical cycles of trace elements in the environment (Galloway *et al*., 1982).

Particulate matter in the atmosphere has residence time varying between days and weeks (Seinfeld and Pandis, 1998). Trace metals adsorbed on ambient particles, especially the fine particulate matter, can be carried high into the atmosphere to large distances and influence the atmospheric concentrations in locations far away from their initial sources. Eventually, the trace metals will ultimately exit the atmosphere through two natural processes: the dry and wet depositions, affecting large parts of the hydrological and terrestrial environment (Seinfeld and Pandis, 1998).

1.1 Background

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 land area and population, the country's environmental problems have important implications for the global environment (Liu and Diamond, 2005). Past studies have demonstrated that particulate matter 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 industrialisation and urbanisation 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 one of the examples of the severe degradation of air quality in the South China region.

Previous studies have investigated the characterisation of chemical species in particulate matter in urban and rural areas of Hong Kong (Lam *et al*., 1997; Ho *et al*., 2003), the PRD region (Bergin *et al*., 2004) and several major cities in Asia (Cohen *et al*., 2004). However, these studies mainly focused on the chemical characterisation of particulate matter and on identifying the sources of particulate matter and its major components (carbonaceous species, major ions and mineral dust). The studies on atmospheric trace metal pollution in South China are scarce.

Past studies have indicated that the atmospheric deposition in Hong Kong had higher concentrations of trace metals during several occasions of low rainfall amount, small rainfall intensity and low wind speed, coinciding with more acidic

rainwater (pH values down to 3.6) (Tanner and Wong, 2000). However, the studies on the atmospheric deposition of trace metals in the South China region are still limited (Tanner and Wong, 2000; Wong *et al*., 2003; Zheng *et al*., 2005). Moreover, few studies have been made on the spatial and temporal variations of trace metals in dry and wet depositions in the region, which are vital in understanding the levels of trace metal pollution and the long-term environmental implications in the South China region.

Although the technique of moss monitoring has been well adopted in Europe and North America (Percy, 1982; Markert *et al*., 1996; Zechmeister, 1998; Rühling and Steinnes, 1998; Aceto *et al*., 2003), limited studies were found in the literature to use mosses as biomonitors for atmospheric deposition in China. Most of the studies focus on the atmospheric deposition of mercury (Xiao *et al*., 1998; Tan *et al*., 2000; Liu *et al*., 2003), and the application in other trace metals is scarce (Bi *et al*., 2006). Moreover, very few attempts have been made to use mosses as biomonitors of trace metals in the South China region.

For a comprehensive understanding of the trace metal pollution status in the fast developing South China region, there is a need for an integrated study of trace metals in particulate matter and dry and wet depositions in the region. The present study provides insights to the characteristics, transport pathway, and geochemical fate of trace metals in the South China region. The present study of trace metals in several moss species commonly found in the region also explores the potential use of mosses for monitoring ambient air quality in the South China region and other subtropical areas. Furthermore, the present study would be valuable in the formulation of future air quality management and pollution control by providing

useful information on geochemical composition of trace metals in particulate matter, depositions and mosses in the rapidly developing areas of the South China region.

1.2 Objectives

The present research includes an integrated study of heavy metal contaminants in the air, which encompasses particulate matter, dry and wet depositions and mosses in the PRD region. The objectives of the study are:

1) to elucidate the transport pathways of heavy metals by studying the aerosols and meteorological conditions in the PRD region;
2) to evaluate the heavy metal concentrations in dry and wet depositions and aerosols in rural and urban PRD region;
3) to study the temporal and spatial variations of dry and wet depositions and their seasonal patterns;
4) to identify the source of the metal pollutants using Pb isotopic composition analysis; and
5) to assess the suitability of *Hypnum plumaeforme* and other moss species which are commonly found in the region, for monitoring ambient air quality in a subtropical area.

1.3 Scope of work

This thesis focuses on heavy metal contamination in the PRD region. The study includes total suspended particulate matter (TSP), fine particulate matter ($PM_{2.5}$), dry and wet depositions and mosses in the region. The laboratory programme includes analyses of trace metal concentrations, Pb isotopic composition and

carbonaceous species of the samples. Back trajectory and statistical methods were also used for data interpretations.

1.4 Organisation of the thesis

This thesis is divided into eight chapters. The present chapter covers the background, objectives, and scope of the research project. A detailed literature review is given in Chapter Two, which presents the scientific background in trace metal contamination in the environment, in particular with respect to atmospheric pollution. In addition, a general review of potential health and environmental implications of trace metal contamination, the current status of research on trace metal contamination in particulate matter, dry and wet depositions and mosses, as well as information on the assessment of trace metal contamination and analytical approaches adopted in the present study are given. Chapter Three includes a detailed description of methods and materials used during the course of the study. The results and discussion are presented in Chapter Four, Chapter Five, Chapter Six, and Chapter Seven. Chapter Four focuses on heavy metal contamination of particulate matter in the PRD region. Chapter Five includes the study on heavy metal contamination of dry and wet depositions in the PRD region. Chapter Six discussed heavy metal contamination of mosses in the PRD region and the Nanling Mountains. Chapter Seven includes an integrated study on the relationships of trace metals in particulate matter, dry and wet depositions and mosses, and the implications to regional environmental quality of the PRD region. Finally, a general conclusion is presented in Chapter Eight which reviews and highlights the major findings and contributions in this study. Moreover, recommendations and future study areas are also given in this chapter.

Chapter 2 - Literature Review

2.1 Trace metals

Trace metals refer to elements that occur in natural and perturbed systems in small amounts and that, when present in sufficient concentrations, are toxic to living organisms. The terms “heavy metals” were synonymous with trace metals, and usually designates to elements having densities greater than 5.0 (Adriano, 1986). In the present work, trace elements being included in the study are: cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn). To investigate the possible elemental associations among trace and major elements, major elements, including aluminum (Al), iron (Fe), magnesium (Mg), and manganese (Mn) are also included in the study.

2.2 Essential trace elements and toxic metals

Some trace elements, including B, Cu, Co, Fe, Mn, Mo and Zn are essential for the nutrition of higher plants. Copper, Co, Fe, Mn, Mo, Zn, Cr, F, Ni, Se, Sn and V are also essential elements for animal nutrition (Adriano, 1986; Kabata-Pendias and Pendias, 1992). These trace elements are micro- or macro- nutrients that are essential to maintain a good health status in humans and other organisms. Table 2-1 categorises elements that must be ingested regularly by human for the various body organs to function optimally. There are ranges of concentrations of bioavailable, yet potentially toxic, essential metals/metalloids that are needed in micro-quantities by critical organs and for biochemical process. Where there is an excess or a deficiency in the diet of one or more than one of these elements over time, an organism can develop an abnormal condition, disease, or even die (Siegel, 2002).

However, trace metals such as Pb, Cd and Hg are classified as toxic elements which have potential toxic effects to human health once ingested or inhaled at relatively low concentrations. These elements are non-essential and have no adverse impact on human health when missing from a diet. Other potentially toxic and non-essential heavy metals are shown in Table 2-1 (Underwood, 1977; Passwater, 1983; Siegel, 2002).

Table 2-1: Essential micronutrients and macronutrients and non-essential heavy metals

	Heavy metals
Essential heavy metal micronutrients[a] (a few mg or μg per day):	As, Co, Cr, Cu, Fe, Mn, Mo, Se, V, Zn
Non-essential heavy metals[a,c]:	Be, Cd, Hg, Ni, Pb, Sb, Sn, Ti
Macronutrients[b] (~ 100 mg or more per day):	Ca, Cl, Mg, P, K, Na, S
Other essential micronutrients[b]:	F, I, Si

Note: [a] Data compiled from Mertz, 1981; Fergusson, 1990; Merian, 1991
[b] Data from Crounse *et al*., 1983
[c] Ni and Sn may be essential micronutrients (Crounse *et al*., 1983)

2.3 Toxicity of trace metals

As discussed earlier, some heavy metals are essential to maintain the good health in organisms, while others have potentially toxic properties at relatively low concentrations. Nevertheless, all heavy metals are considered to be toxic if ingested or inhaled at sufficiently high levels and for long enough periods. This has been recognised by Bertrand, who formulated such dose dependence into Bertrand's Law. Other researchers have also expanded this concept of dose dependence and presented the dose response in the form of a curve (Underwood, 1977). Hence, all heavy metals exhibit certain toxic properties depending on the

dosage of intake. The present study focuses on heavy metals, such as Cd, Co, Cr, Cu, Ni, Pb, V and Zn, among which Cd and Pb are well known as the toxic elements, while others are essential to plants and animals. The potential toxicity of some of these essential elements and the toxic elements will be discussed in the following sections. The information on toxicity of individual trace metals included in the present study was mainly obtained from the two references (WHO, 1996; Reilly, 2004).

Cadmium (Cd)

Cadmium is classified as toxic elements. The adverse effects of Cd to health are greatest through the inhalation of Cd from occupational sources which results directly in lung damage. The effects of less acute exposure to dietary or environmental sources usually reflect the toxic action of a high body burden on the kidney and possibly the skeleton. Cadmium retention in body tissues is related to the formation of cadmium-metallothionein, a cadmium-protein complex of low molecular weight. The synthesis of metallothionein is induced by the essential metals copper and zinc in liver and kidney, but also by Cd, which may replace these metals or share the protein with them. Cadmium can cause damages to kidneys and skeletons. The effects of Cd on the kidney take the form of renal tubular dysfunction and subsequent pathological changes. Severe cadmium nephropathy may cause renal calculi and excessive urinary loss of calcium in the human body, which results in associated skeletal changes due to calcium loss. Moreover, inhalation of Cd causes irritation and possibly an acute inflammatory reaction of the lungs. Long-term exposure produces chronic bronchitis and increased susceptibility to infections, bronchiectasis and emphysema. Cadmium is also a potential human carcinogen. It has been classified as carcinogenic to

humans (Group 1) by the International Agency for Research on Cancer (IARC 1993) based on sufficient evidence for carcinogenicity in both human and animal studies. The maximum tolerable weekly intake of Cd recommended by the Joint FAO/WHO Expert Committee on Food Additives is 7 μg of Cd/kg of body weight (ATSDR, 1999a; WHO, 1996).

Lead (Pb)

Lead is another toxic metal which has been well-studied due to it adverse effects on human health. The toxic effects of Pb involve several organs and are the consequence of a variety of biochemical defects. The nervous system of infants and children is particularly sensitive to lead toxicity. Adults exposed occupationally or accidentally to excessively high levels exhibit peripheral neuropathology and/or chronic nephropathy. However, the critical or most sensitive effect for adults in the general population may be the development of hypertension. Acute lead toxicity leads to anaemia. The shortened life span of the red blood cell is probably the consequence of the increased mechanical fragility of the cell membrane. Lead also has toxicological effects on kidney, the reversible renal tubular dysfunction, and irreversible chronic interstitial nephropathy characterised by vascular sclerosis, tubular cell atrophy, interstitial fibrosis and glomerular sclerosis. Epidemiological studies also indicate an association between an elevated body burden of Pb and increased blood pressure in adults. Moreover, Pb is classified as a category 2B carcinogen by the International Agency for Research on Cancer. The evidence of carcinogenicity of Pb is adequate in animals but inadequate in humans. The Joint FAO/WHO Expert Committee on Food Additives provisionally recommends that the weekly intake of Pb should not

exceed 25 μg/kg of body weight per week for adults, children and infants (WHO, 1996; ATSDR, 1999b).

Cobalt (Co)

Cobalt is an essential trace element which occurs in animals, including human, in minute amounts. It is an integral part of vitamin B12 or cobalamin. However, excessive intake of Co was responsible for an epidemic of cardiac failure. It has been shown that the Co alone was not responsible for the epidemic and that two other factors, a high alcohol intake and a dietary deficiency of protein and/or thiamin, played a part. When cobalt salts have been used in the treatment of certain refractory anaemias, excessive dosage of Co was found to produce serious toxic effects, including goiter, hypothyroidism and heart failure (Reilly, 2004).

Chromium (Cr)

Chromium is an essential element that potentiates insulin action and thus influences carbohydrate, lipid and protein metabolism. Trivalent chromium has such a low toxicity that deleterious effects of excessive intake of this form of Cr do not really occur. Hexavalent chromium is much more toxic than the trivalent form, and an oral administration of 50 μg/g diet has been found to induce growth depression together with liver and kidney damage in experimental animals (WHO, 1996; Reilly, 2004).

Copper (Cu)

Copper is a widely distributed essential element in biological tissues, where it occurs largely in the form of organic complexes, many of which are metalloproteins and function as enzymes. Acute copper poisoning is rare and

usually results from contamination of food or beverages by copper containers or from the accidental or deliberate ingestion of large quantities (in grams) of copper salts. Symptoms of acute copper poisoning include salivation, epigastric pain, nausea, vomiting and diarrhea, all of which are probably due to the irritant effect of Cu on the gastrointestinal mucosa. In addition, copper poisoning may be accompanied by severe intravascular haemolysis and jaundice, hepatic necrosis and tubular failure, vascular collapse and death (WHO, 1996; Reilly, 2004).

Nickel (Ni)

Nickel has been recognised as an essential nutrient for farm and experimental animals. However, its essentiality for humans is still a matter of controversy. No clear biochemical function for the element has as yet been identified in humans although there is evidence that it serves as a cofactor or structural component of several metalloenzymes similar to certain nickel-containing enzymes that have been identified in plants and microorganisms. These include urease, hydrogenase and carbon monoxide dehydrogenase. Serum concentrations above 1.0 μg of Ni/litre probably indicate a chronically excessive intake of Ni. An intake of a large dose of Ni (between 8 and 50%) in drinking water after an overnight fast in humans can result in marked hypernickelaemia (WHO, 1996; Reilly, 2004).

Vanadium (V)

Vanadium is a trace element which is probably essential, as there is growing evidence in the essentiality of V to animals, including humans. Vanadium may play a role in the regulation of Na^+/K^+-exchanging ATPase, phosphoryl-transfer enzymes, adenylate cyclase and protein kinases. The role of the vanadyl ion as an enzyme cofactor, and its roles in hormone, glucose, lipid, bone and tooth

metabolism have also been recognised. No specific biochemical function, however, has yet been identified for V in higher animals. Vanadium is a relatively toxic element. A variety of signs of vanadium toxicity exist because they vary both with species and with dosage. Pentavalent vanadium is the most toxic and the toxicity of vanadium compounds usually increases with valency. Some of the more consistent signs include depressed growth, elevated organ vanadium, diarrhea, depressed food intake and death. Signs of excessive vanadium intake in humans include gastrointestinal disturbances and green tongue (WHO, 1996; Reilly, 2004).

Zinc (Zn)

Zinc is an essential element which has an important role in many fundamental activities of life. It is an essential component of the catalytic site of a large number of enzymes. It also participates in the synthesis and degradation of carbohydrates, lipids, proteins and nucleic acids. Moreover, Zn plays an essential role in polynucleotide transcription and translation and thus in the processes of genetic expression. Acute zinc poisoning can be resulted in high intakes of Zn. Symptoms of acute zinc poisoning include nausea, vomiting, diarrhea, fever and lethargy and have been observed typically, after ingestion of 4-8 g of Zn. There is evidence that a high intake of Zn may, in some cases, have a negative effect on immune function. Anaemia, growth retardation, copper deficiency and immunosuppression have also been reported to occur as a result of excessive intake of Zn by children and adults. Such adverse effects point to the need for caution when large zinc supplements are taken for prolonged periods of time (WHO, 1996; Reilly, 2004)

2.4 Sources of trace metals in the atmosphere

The release of trace metals in the atmosphere comes from a wide spectrum of sources, which can be of natural or anthropogenic origins.

2.4.1 Natural sources of trace metals

Trace metals can be naturally emitted into the atmosphere from the windblown dusts and soil particles, forest fires, volcanic emissions, vegetation, seasalt sprays and others. The worldwide emissions of several trace metals from natural sources are summarised in Table 2-2. Eroded soil particles attribute to ~60 - 80% of Cu, Pb, Ni and Zn, and volcanic emissions account for ~60% of Cd from natural sources. Vegetative exudates are an important source of metals which accounts for nearly 20% of Zn from natural sources. Forest fires and seasalt sprays represent only minor sources of trace metals in the atmosphere, accounting for <10% of the natural emissions (Nriagu, 1979).

Table 2-2: Worldwide emissions of trace metals from natural sources

Source	Global production ($x10^9$ kg/yr)	Worldwide annual emissions ($x10^6$ kg) Cd	Cu	Ni	Pb	Zn
Windblow dusts	500 (6-1100)	0.1 (0.001-0.22)	12 (0.14-26)	20 (0.24-44)	16 (0.19-35)	25 (0.30-55)
Forest fires	36 (2-200)	0.012 (0.001-0.07)	0.3 (0.025-1.7)	0.6 (0.05-3.3)	0.5 (0.04-2.8)	2.1 (0.18-12)
Volcanogenic particles	10 (6.5-150)	0.52 (0.3-7.8)	3.6 (2.3-54)	3.8 (2.4-56)	6.4 (4.2-96)	7.0 (4.6-105)
Vegetation	75 (75-1000)	0.2 (0.2-2.7)	2.5 (2.5-33)	1.6 (1.6-21)	1.6 (1.6-21)	9.4 (9.4-125)
Seasalt sprays	1000 (300-2000)	~0.001	0.08 (0.02-0.2)	0.04 (0.01-0.08)	0.02 (0.01-0.05)	0.01 (0.004-0.02)
Total		0.83	18.5	26.0	24.5	43.5

[Source: Nriagu, 1979]

In the PRD region, some studies have been made on the metal concentrations in the rural sites away from major pollution sources (Lam *et al*., 1997; Zheng and Fang, 2000; Ho *et al*., 2003; Cohen *et al*., 2004). Lam *et al*. (1997) has studied the metal concentrations and other constituents in the fine and coarse particles and the total suspended particulate matter in a coastal site in Hong Kong, Hok Tsui (Cape D'Aguilar) for a one-year period. Zheng and Fang (2000) also presented the trace metal concentrations in TSP at a rural site at the south-eastern tip of Hong Kong over a one-year period. These measurements can be considered as the background concentrations of trace metals in the South China region. Table 2-3 summarises the information about some background metal concentrations of particulate matter in the South China region.

Table 2-3: Background trace metal concentrations at rural areas of Hong Kong, South China

(ng/m^3)	Co	Cr	Cu	Ni	Pb	V	Zn	Reference
TSP (n = 63)	0.60	12.95	1.78	1.17	6.76	1.56	108.02	Lam *et al*. (1997)
PM_{10} (n = 57)	0.69	18.53	1.80	1.31	7.26	1.38	116.06	Lam *et al*. (1997)
TSP (n = 111-120)	-	-	-	-	40.73	4.04	70.08	Cheng *et al*. (2000)
PM_{10} (n = ~23)	-	4.97	15.33	8.27	62.75	4.70	130	Ho *et al*. (2003)
$PM_{2.5}$ (n = ~23)	-	4.19	9.71	6.33	60.13	4.36	120	Ho *et al*. (2003)

Note: The symbol "-" denotes no data is available

2.4.2 Anthropogenic sources of trace metals

The major anthropogenic sources of trace metals in the atmosphere include smelting of metallic ores, industrial fabrication and commercial applications of metals, as well as burning of fossil fuels. Table 2-4 shows the worldwide emissions of trace elements, including Cd, Cr, Cu, Mn, Ni, Pb, V and Zn to the atmosphere. Combustion of hard coal, lignites and brown coal in electric power plants is a very significant source for Cr and Mn. Combustion of oil is an important source of V and Ni. Moreover, the non-ferrous metal industry accounts for the largest fraction of Pb (in addition to gasoline production), Cd, Cu and Zn emitted. Iron and steel industry is a primary source of Cr and Mn (Nriagu and Pacyna, 1988).

Due to the rapid urbanisation and industrialisation in the South China region, especially the PRD, trace metals together with other pollutants are continuously emitted to the atmosphere. Relatively few studies, however, have been made on the trace metals in the particulate matter, and those deposited on the terrestrial surfaces (dry and wet depositions). Some data of trace metals are available in some studies on the characterisation of chemical species in particulate matter in Hong Kong (Lam *et al*., 1997; Ho *et al*., 2003), PRD region (Bergin *et al*., 2004) and several major cities in Asia (Cohen *et al*., 2004), to identify the sources of particulate matter and its chemical composition. Previous studies have revealed that combustion is a dominant source of particulate matter in the PRD region (Zheng and Fang, 2000). Other major sources of particulate matter in the PRD region include biomass burning, industrial and vehicular emissions (Lam *et al*., 1997; Cheng *et al*., 2000; Ho *et al*., 2003; Louie *et al*., 2005). Moreover, it has been shown that the aerosols in Asia have different source composition from those

of Europe and North America, since more coal and vegetation are burnt in Asia (Chameides *et al*., 1999).

Table 2-4: Worldwide emissions of trace elements to the atmosphere in 1983

Source category	(10^3 kg/yr)	Cd	Cu	Ni	Pb	Zn
Coal combustion	- electric utilities	77-387	930-3100	1395-9300	775-4650	1085-7750
	- industry and domestic	99-495	1390-4950	1980-14850	990-9900	1485-11880
Oil combustion	- electric utilities	23-174	348-2320	3840-14500	232-1740	174-1280
	- industry and domestic	18-72	179-1070	7160-28640	716-2150	358-2506
Pyronmetallurgical non-ferrous metal production	- mining	0.6-3	160-800	800	1700-3400	310-620
	- Pb production	39-195	234-312	331	11700-31200	195-468
	- Cu-Ni production	1700-3400	14450-30600	7650	11050-22100	4250-8500
	- Zn-Cd production	920-4600	230-690		5520-11500	46000-82800
Secondary non-ferrous metal production		2.3-3.6	55-165		90-1440	270-1440
Steel and iron mfg.		28-284	142-2840	36-7100	1065-14200	7100-31950
Refuse incineration	- municipal	56-1400	980-1960	98-420	1400-2800	2800-8400
	- sewage sludge	3-36	30-180	30-180	240-300	150-450
Phosphate fertilizers		68-274	137-685	137-685	55-274	1370-6850
Cement production		8.9-534		89-890	18-14240	1780-17800
						1200-6000
Wood combustion		60-180	600-1200	600-1800	1200-3000	
Mobile sources					248030	
Miscellaneous					3900-5100	1724-4783
Total, emissions		3100-12040	19860-50870	24150-87150	288700-376000	70250-193500

[Source: Nriagu and Pacyna, 1988]

2.5 Trace metal contamination in particulate matter

2.5.1 Particulate matter

Atmospheric particulate matter refers to solid or liquid particles, often smaller than 100 μm in diameter, suspended in the air. Very small particles include carbon black, silver iodide, combustion nuclei, and sea-salt nuclei. Larger particles include cement dust, windblown soil dust, foundry dust and pulverized coal. Liquid particulate matter includes raindrops, fog and sulphuric acid mist. Particulate matter in the atmosphere may therefore be inorganic and organic, and sometimes includes biological matter, such as fungal spores and pollen (Manahan, 2005). The chemical composition of particulate matter also varies with size. The very small particles tend to be acidic and often originate from atmospheric gas-to-particle conversion, such as from the conversion of sulphur dioxide gases to sulphuric acid. Larger particles tend to consist of materials generated mechanically, such as by grinding of limestone, and have a greater tendency to be basic (Manahan, 2005).

2.5.2 Health effects of particulate matter

Epidemiological studies have found that elevated fine particulate matter concentrations ($PM_{2.5}$) are associated with increased mortality and morbidity in the general population, especially among children and the elderly (Dockery *et al*., 1993; Pope *et al*., 1995; Pope, 1996; Schwartz *et al*., 1996). No such correlation was observed with the concentrations of the PM_{10} particulate fraction. There is evidence that inhaled particles can penetrate into the lung where they interact with pulmonary cells and may lead to a chain of inflammatory and systemic reactions (Lippmann *et al*., 2003; Pradhan *et al*., 2005). Recent studies have also revealed that particulate matter causes DNA damages to body cells and potentially lead to

cancer (Soares *et al*., 2003; Upadhyay *et al*., 2003). Epidemiological studies in human and animals have shown that inhalation of particles elicits proinflammatory effects, cytokine production, and enhancement of allergic responses in the upper and lower airways (Nel *et al*., 1998; Ghio and Devlin, 2001). Particulate matter has been found to be associated to the inflammation in the airway through the generation of reactive oxygen species and oxidative stress (Gurgueira *et al*., 2002; Tao *et al*., 2003; Nel, 2005). PM constituents including pro-oxidative organic hydrocarbons (such as polycyclic aromatic hydrocarbons and quinines) and transition metals (such as Cu, V, Cr, Ni, Co and Fe) were found to play a role in the production of reactive oxygen species (Silbajoris *et al*., 2000; Li *et al*., 2003).

2.6 Trace metal contamination in dry and wet depositions

Atmospheric deposition refers to the removal of pollutants from air to soil, water and other surface environment. Toxic pollutants, such as heavy metals, can enter the surface water, soil and vegetation through atmospheric deposition. There are three main processes in atmospheric deposition, which are dry deposition, wet deposition and air-water exchange (The Delta Institute, 2000). In this study, we only focus on the heavy metal contamination in the dry and wet depositions.

2.6.1 Dry deposition

Dry deposition is conventionally defined as the direct transport of particles and the contaminants associated with them onto the surface environment. Generally, the amount of contaminants depends on their concentrations in the air mass; however, the relationship is complex and dependent on physical parameters including wind speed, the area of the receiving surface and whether the surface is water or land, and the properties of the contaminants, such as reactivity and the size of the

particle with which they are associated (The Delta Institute, 2000). Dry deposition can be calculated based on both modelled estimates from airborne particle concentrations, and dry deposition velocity (which is a function of particle size), such as the dry deposition models of Sehmel (1973), Slinn and Slinn (1980), and Noll and Fang (1989), although direct measurements by aerodynamically designed surrogate surfaces (Holsen *et al*., 1992; Zufall *et al*., 1998) and automatic dry deposition samplers (Shahin *et al*., 2000) are also well-adopted. However, there is still no universally agreed method to directly measure or calculate dry deposition.

2.6.2 Wet deposition

Wet deposition is defined as the incorporation of both gases and particles into all types of precipitation: rain, fog or snow. Pollutants are removed from the atmosphere by wet deposition through three main mechanisms: 1) small particles can serve as cloud condensation nuclei and become entrapped in raindrops; 2) particles can be incorporated into falling raindrops by a variety of mechanisms depending on their size, referred to as particle scavenging; 3) gaseous pollutants can be dissolved into cloud droplets and falling rain or snow. Trace metals can become associated with rain either by being dissolved in the raindrop or by being incorporated as particles (The Delta Institute, 2000). Wet deposition is conventionally collected using a precipitation collector. The wet deposition flux is subsequently calculated using the concentration of pollutants measured in precipitation samples and the precipitation amount recorded for each collection period. In some studies, during which extensive rainfall collection is not feasible, the wet deposition flux can be estimated from air concentrations using previously determined relationships between air and rain chemistry (Schmidt and Andren, 1984).

2.6.3 Environmental impacts of atmospheric deposition of trace metals

Metal transfer through the atmosphere is vital to the biogeochemical cycling of these elements. Due to the dynamic nature of the atmosphere, metals can be deposited in areas remote from their origins. The rate of emissions has been low historically because of the low volatility of most metals. However, with the advent of high-temperature processes (smelting and fossil-fuel combustion), the rate of emission for some metals has substantially increased, and hence resulted in the increase in the metal concentrations in the atmosphere and in atmospheric deposition (Galloway *et al*., 1982).

Past studies have revealed that atmospheric depositions of metals have adverse impacts to the terrestrial environment. The effects of atmospheric depositions of heavy metals on the surface environment, including vegetation, soils and water bodies, are discussed in the following.

2.6.3.1 Vegetation

Vegetation is an important sink for airborne materials originating from natural and anthropogenic sources. Due to the reactivity of its large surface area, the foliage of vegetative canopies serves as a very effective receptor for airborne substances. Foliage also provides a surface of interaction for particulate substances that may range from the biologically toxic to those essential for life processes (Hosker *et al*., 1982). Excess of trace elements in soils, even among the essential micronutrients, could result in phytotoxicity. For an instance, Cd was associated with yield decrements in crops, such as beans, turnips, corn, lettuce, tomato and barley etc. (Bingham and Page, 1975). Pb toxicity in plants was manifested as stunted growth, which is more pronounced in roots than in shoots (Khan and Frankland, 1983).

Moreover, plants can accumulate trace elements in or on their tissues and enter the food chain when they were ingested as food. They, hence, act as intermediate reservoirs through which trace elements from soils and partly from waters and air were transferred to man and animals (Kabata-Pendias and Pendias, 1992).

2.6.3.2 Soils

Trace metals can enter the surface soils through atmospheric deposition. The persistence of contaminants in soil is much longer than in other compartments of the biosphere, and contamination of soil by heavy metals appears to be virtually permanent. Metals accumulated in soils are depleted very slowly by leaching, plant uptake, erosion, or deflation (Kabata-Pendias and Pendias, 1992). The first half-life of heavy metals, as calculated by Iimura *et al*. (1977) for soils in lysimetric conditions, are 13 to 1100 years for Cd, 310 to 1500 years for Cu, and 740 to 5900 years for Pb. Trace elements introduced to the soils can geochemically exist in various forms: (1) dissolved in soil solution, (2) held onto exchange sites of organic solids or inorganic constituents, (3) occluded or fixed into soil minerals, (4) precipitated with other compounds in soils, (5) incorporated into biological material. The first two forms are mobile and phytoavailable, and can be readily absorbed by plants. These metals eventually enter the food chain and have adverse effects on human health. Moreover, soil also acts as a natural buffer controlling the transport of chemical elements and substances to the atmosphere, hydrosphere, and biota. Hence, excessive inputs of metals to the surface environment can disturb the ecological and agricultural functions of soils (Kabata-Pendias and Pendias, 1992).

2.6.3.3 Water bodies

Atmospheric deposition is well recognised as significant source of terrestrial and anthropogenic derived compounds from their sources to the aquatic environment, including freshwater (Pirrone and Keeler, 1996; Paode *et al*., 1998; Shahin *et al*., 2000; Motelay-massei *et al*., 2005) and marine systems (Ottley and Harrison, 1991; Injuk *et al*., 1998; Gaiero *et al*., 2003). Heavy metals are known to have lethal and sublethal effects on aquatic biota, such as increase in mortality and malformations, decrease in growth rate (vonWesternhagen *et al*., 1988; Luckenbach *et al*., 2001; Hansen *et al*., 2002). A wide range of studies have demonstrated that the toxicity of heavy metals, including Cd, Cr, Cu, Pb, Ni, V and Zn, are associated with the increase in mortality and reduced growth in freshwater and marine fish as well as aquatic invertebrates, such as crustaceans, molluscs, annelids, rotifers and insects (Mance, 1987).

Moreover, heavy metals such as Cd, Zn and Mn were found to be associated with incidence of infectious diseases and alter the immune systems in fish (O'Neill 1981; Ghanmi *et al*., 1989). Past studies have also shown that chronic exposure to Cd at sublethal concentration disturb the ionoregulation and oxygen-carrying capacity of fish, possibly indicating alterations in membrane integrity and fluidity (Majewski and Giles, 1981; Giles, 1984; Palace *et al*., 1993). Chronic exposure of fish to Pb produces characteristic responses of blackfinning and spinal curvature (lordoscoliosis), the latter is neural in origin rather than actual physical deformity. These effects are initially reversible but severe blackfinning develops into irreversible rotting of the fins (Hodson *et al*., 1982).

2.7 Biomonitoring of atmospheric trace metals using moss

2.7.1 Biomonitor

A biomonitor is an organism (or a part of an organism or a community of organisms) that contains information on the quantitative aspects of the quality of the environment. The term biomonitor is used differently from bioindicator in which the latter refers to an organism (or part of an organism or a community of organisms) that contains information on the quality of the environment. A biomonitor often is a bioindicator as well, but a bioindicator does not necessarily meet the requirements for a biomonitor (Markert *et al*., 2003).

2.7.2 Moss as a biomonitor for trace metals in the air

Mosses have been well studied as tools for the biomonitoring of atmospheric pollution. Unlike higher plants, mosses have no root system or cuticle layer; hence, mineral adsorption occurs over their entire surface (Rühling and Tyler, 1968). Mineral uptakes from soil play a minor role and the adsorption of heavy metal is mainly derived from atmospheric flux on the surfaces of the moss. Mosses also grow in large carpets on the ground and have more surface to intercept particulate deposition (Manning and Feder, 1980). Past studies have demonstrated there was a strong correlation between the annual sum of precipitation and heavy metal concentrations in the mosses (Grodzinska, 1978). Therefore, mosses form excellent biomonitors for trace elements in the air.

2.7.3 Mechanisms of metal uptakes in moss

Metals suspended in air reach the moss surface via physical processes of sedimentation, impaction and diffusion, or via air particulate deposited in precipitation (Taylor and Witherspoon, 1972; Wallin, 1976; Onianwa, 2001).

Uptake by the moss occurs by ion exchange and complex formation. Exchange and chelation of metals in mosses is made possible by the chemical constituents of the moss structure which consists of a variety of organic functional groups capable of chelate formation and exchange of ions (Onianwa, 2001). The organic functional groups responsible for ion exchange in Sphagnum mosses are the uronic acids, which are formed during the synthesis of new cell wall materials (Richardson, 1981). Other organic groups which have been involved in the ion exchange in various species of mosses include carbohydrates, fatty acids, aliphatic hydrocarbons, alcohols, ketones, flavonoids, terpenes (Siegfried, 1980; Reitz, 1995), and hydroxybenzenes (Wilson *et al*., 1989).

2.7.3.1 Ion exchange of metals

The exchange of metal ions in solution has been demonstrated in many species of mosses. Past studies have shown that the moss tissues of Sphagnum and other mosses were easily saturated with high concentrations of hydrogen ions and lighter metals which were also readily displaced by heavier metals with greater exchange potentials, as would be the case in synthetic ion exchange resins (Andre and Pijarowski, 1977; Crist *et al*., 1996). Cation binding capacity in Sphagnum moss is high and was calculated to be about 900-1500 μmol/g (Richardson *et al*., 1981). Ion exchange of other moss species such as *Hylocomium splendens* (Rühling and Tyler, 1970), *Rhacopilopsis trinitensis, Stereoplyllum virens* and *Thuidium gratum* (Onianwa *et al*., 1986) have been studied, among many others.

2.7.3.2 Chelation of metals

The uptake of metals by chelate formation depends on the stability of the bound metals to displacement by other metals. In *Hylocomium splendens*, the retention of

the metals was in the order Cu ~ Pb > Ni > Co > Zn > Mn (Rühling and Tyler, 1970), while in the species studied by Onianwa *et al*. (1986), the order was Cu > Pb > Cd. Electron microscope studies have shown that the sorbed metal may be held either in the extracellular region outside of the cytoplasm, bound to the cell wall, or actually held within the nucleus of the leaf cells (Onianwa, 2001). Brown and Bates (1972) and Skaar *et al*. (1973) noticed that lead was only bound to the extracellular regions in the mosses, while Czarnowska and Rejment-Grochowska (1974), Gullvag *et al*. (1974), Ophus and Gullvag (1974) and Buck and Brown (1978) noticed electron dense inclusions of lead within the nuclei of mosses studied. The differences in the observations have been attributed to species variations. The metals sorbed are strongly held within the moss tissue to withstand desorption under field conditions is not in doubt (Onianwa, 2001). Mosses were found to be able to retain sorbed heavy metals under various leaching conditions using extractants such as EDTA, acetic acid, dilute mineral acid, calcium, magnesium, sodium and potassium ions, etc. (Rühling and Tyler, 1970; Onianwa *et al*., 1986). However, in the mosses *Rhacopilopsis trinitensis*, *Stereophyllum virens* and *Thuidium gratum*, equilibration with nitric acid leached out significant fraction of Cd, Pb and Cu from the moss tissue. This implied that in areas where significant acidity in rainfall occurs, some of the metals sorbed by the moss may be released in contact with wet precipitation (Onianwa *et al*., 1986).

2.8 Researches on atmospheric trace metals

2.8.1 Review on studies of trace metals in particulate matter

Particulate matter with aerodynamic diameters of less than 10 μm (PM_{10}), especially the finer particle fraction of less than 2.5 μm ($PM_{2.5}$), has been found to be associated with urban health problems such as increases in mortality. It causes amenity problems such as visibility degradation and affects the climate forcing. Hence, many research efforts have been made in the past to characterise the chemical species (including trace metals) in particulate matter (Macias *et al*., 1981; Barbiaux *et al*., 1991; Chow *et al*., 1993; Chow *et al*., 1996; Chan *et al*., 1997; Janssen *et al*., 1997). Past researches have analysed the elemental composition of particulate matter, and estimated the contributions of various sources to the PM mass and heavy metal concentrations using receptor-oriented source apportionment models. The most widely used models include the chemical mass balance (CMB), principal component analysis (PCA)/absolute principal component scores (APCS) and positive matrix factorization (PMF) (Thurston and Spengler, 1985; Hien *et al*., 2001; Arditsoglou *et al*., 2005; Park and Kim, 2005).

In particular, due to the acute toxicity of trace metals, various researches have also been initiated to investigate the sources of trace metals in the air, which may have natural or anthropogenic origins (Nriagu, 1979; Chow *et al*., 1993; Fang *et al*., 2005). The distribution of trace elements in different sizes of particulate matter has been studied (Horvath *et al*., 1996; Brewer and Belzer, 2001; Wang *et al*., 2005; Herner *et al*., 2006). This is vital in understanding the effects of particulate matter on human health, and also controls the extent to which metals may be dispersed via atmospheric transport and hence is prerequisite for the determination of rates of

deposition of metals to Earth's surface (Allen *et al*., 2001). Moreover, some studies have been made on the speciation of volatile and particulate metals (Pavageau *et al*., 2004).

In China, research efforts have been made on the characterization of the chemical species, including trace metals, in particulate matter (Zhang *et al*., 2001; Ho *et al*., 2003; Shi *et al*., 2003; Louie *et al*., 2005). Several studies have been made using the receptor models in the source contributions of heavy metals in particulate matter in China (Lei *et al*., 2004; Okuda *et al*., 2004). However, there are only a few studies on the trace metals in particulate matter in South China region. Most of the studies on aerosols in the region focus on the aerosol characterization (Lam *et al*., 1997; Cheng *et al*., 2000; Ho *et al*., 2003; Bergin *et al*., 2004; Cohen *et al*., 2004) and other major species, including carbonaceous species, major ions and mineral dust (Zheng and Fang, 2000; Cao *et al*., 2004). Past studies have also been made on the long-range transport of aerosols (Fang *et al*., 1999; Louie *et al*., 2005). Some data on the trace metal concentrations were available mainly as part of the aerosol characterization studies. Table 2-5 summarises the information on the trace metal concentrations in urban and rural areas in the South China region.

In the past study, Lam *et al*. (1997) has calculated the enrichment factors for trace elements as an indication of anthropogenic activities, and found that the enrichment factor values of PM_{10} are in general higher than those for TSP. Toxic elements As, Pb, Se and Zn are more enriched in the PM_{10} fraction. Ho *et al*. (2003) has shown that sulphate, organic matter and elemental carbon are the major constituents in particles especially in $PM_{2.5}$ collected at the urban areas of Hong Kong. The major constituents of PM_{10} in relatively rural areas of Hong Kong are

sea salt and sulphate. It has been shown that the chemical components with relation to anthropogenic sources such as V, Pb and Zn were observed to accumulate in the fine fraction. Cohen *et al*. (2004) have studied the aerosol characteristics in several Asian sites located in rural areas of Hong Kong in China, Cheju Island in South Korea and Sado Island in Japan and found that Hong Kong had a significantly higher $PM_{2.5}$ mass than the two other rural sites. Soil has been identified as a significant component in the $PM_{2.5}$ in these sites with $PM_{2.5}$ soil concentrations up to 35% of the fine mass due to the impact of significant fine soil events during the study period. Moreover, heavy metals such as Cr, Cu Zn and Pb were found to be associated with automobiles and industry and had the highest median values and extreme events at the Hong Kong site. Similarly, Ni and V were also highest at the Hong Kong site and were probably associated with diesel and heavy oil burning for power generation and shipping. Elements such as black carbon, sulphur, Pb and Zn. were found to have low coarse and high fine fraction, showing they are mainly associated with the fine particles.

On aspects of long-range transport of heavy metals to South China region, Fang *et al*. (1999) has provided evidence of the long-range transport of mineral dusts from northern China to the coastal areas of Hong Kong. Trace elements including Ca, Ni, Co, and V in aerosols (TSP) were found to have enrichment factor values (calculated using Fe as a reference element for crustal material) approaching unity during the episodic events, inferring that crust was the dominant source of these elements. Bergin *et al*. (2004) has demonstrated that strong sources of $PM_{2.5}$ were within the Guangdong region, in the vicinity of Guangzhou and transported to the downwind areas of Shenzhen and Zhongshan during the north-northeasterly flow conditions. Louie *et al*. (2005) has shown the impact of Asian dusts in the aerosols

in Hong Kong during spring season. Consistently high $PM_{2.5}$ carbonaceous material and trace metals were found during the winter period, probably influenced by $PM_{2.5}$ source regions in south-eastern China and western Taiwan.

Table 2-5: Trace metal concentrations in urban areas of South China region

(ng/m^3)		n	Co	Cr	Cu	Ni	Pb	V	Zn	Reference
Urban areas										
Hung Hom	PM_{10}	-	-	6.85	35.38	8.62	98.74	5.15	340	Ho *et al*. (2003)
	$PM_{2.5}$	-	-	2.43	17.32	5.34	76.86	4.46	290	Ho *et al*. (2003)
Kwun Tong	PM_{10}	-	-	5.75	63.53	9.58	100.52	4.46	460	Ho *et al*. (2003)
	$PM_{2.5}$	-	-	4.51	36.78	6.00	91.62	3.84	380	Ho *et al*. (2003)
Rural areas										
Hok Tsui	TSP	63	0.60	12.95	1.78	1.17	6.76	1.56	108.02	Lam *et al*. (1997)
	PM_{10}	57	0.69	18.53	1.80	1.31	7.26	1.38	116.06	Lam *et al*. (1997)
Hok Tsui	TSP	111-120	-	-	-	-	40.73	4.04	70.08	Cheng *et al*. (2000)
Hok Tsui	PM_{10}	-	-	4.97	15.33	8.27	62.75	4.70	130	Ho *et al*. (2003)
	$PM_{2.5}$	-	-	4.19	9.71	6.33	60.13	4.36	120	Ho *et al*. (2003)

Note: The symbol "-" denotes no data is available

2.8.2 Review on studies of trace metals in dry and wet depositions

Many large-scale research projects which have been carried out on the atmospheric deposition of air pollutants in recent years were associated with the Integrated Atmospheric Deposition Network (IADN) which was initiated in 1988 by Canada and the United States to monitor and assess the air toxics deposition to the Great Lakes, including organic pollutants and trace metals (As, Cd, Pb and Se) (Hillery *et al*., 1998; Sweet *et al*., 1998). Large-scale schemes, such as the EUROTRACT and EMEP, were also initiated in the European countries to investigate trends in emissions, atmospheric concentration and deposition of sulphur, ozone, persistent organic component and heavy metals (Hg, Cd and Pb) in Europe. Various studies have also been carried out to measure the atmospheric dry and wet depositions of heavy metals in urban and rural areas (Takeda *et al*., 2000; Azimi *et al*., 2003; Fang *et al*., 2004), the long range transport and deposition of heavy metals (Yi *et al*., 2001; Han *et al*., 2004), and the verification of model calculations with the measured deposition flux (Holsen *et al*., 1992; Golomb *et al*., 1997; Injuk *et al*., 1998).

Several co-operative programmes have also been initiated within the East Asian region, such as the EANET which was set up in 1998 and entered into regular monitoring phase since 2001, with 12 participating countries from Asia, to study the acidic deposition in East Asia (detailed information is available at http://www.eanet.cc). Many other research works have also been carried out by Asian countries, such as Japan, Korea and China, to assess the long-range transport and deposition pathway of sulphate, nitrate and other major ions in Asia by direct measurements (Xu and Carmichael, 1999; Fujita *et al*., 2000; Nakamura

et al., 2005) and using models (Park and Cho, 1998; Terada *et al*., 2002; Kim *et al*., 2003; Han *et al*., 2006). However, relatively few studies were available on the atmospheric deposition of trace metals in Asia (Takeda *et al*., 2000; Azimi *et al*., 2003; Fang *et al*., 2004).

In China, many studies have been focused on the acidic deposition, such as sulphur and nitrogen deposition, due to their potential damage to plants, water, soils and buildings (Zhao *et al*., 1988; Xiao and Liu, 2002; Sorimachi *et al*., 2003; Kim *et al*., 2004; Ta *et al*., 2005; Utiyama *et al*., 2005; Vogt *et al*., 2006). Previous studies on the atmospheric deposition of trace metals in China are rare (Zhang *et al*., 1993), and only limited studies have been made on the dry deposition of mercury (Fang *et al*., 2001). Similarly, many studies have been carried out to investigate the depositions of ionic species in dry and wet deposition in South China region, especially in the coastal areas of Hong Kong (Sequeira and Lung, 1995; Sequeira and Lai, 1998; Tanner, 1999a, 1999b; Tanner and Fai, 2000; Tanner *et al*., 2001; Wai *et al*., 2005). However, there have been limited studies on the atmospheric deposition of trace metals in South China region (Tanner and Wong, 2000; Wong *et al*., 2003; Zheng *et al*., 2005).

Wong *et al*. (2003) has compared the atmospheric depositions of heavy metals in the PRD region with those in the Great Lakes in North America and the North Sea in Europe (see Table 2-6). The mean atmospheric deposition of Cu, Cr and Zn in the PRD was significantly elevated compared with those reported in North America 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), but comparable to atmospheric Pb deposition in N.W. Indiana

(1975 - 1980) and W. Pennsylvania (1975 - 1980) due to the use of leaded petrol during the 1980s in the U.S. The study showed the severe aerial depositions of Cu, Cr, Pb and Zn in the PRD region. Zheng *et al*. (2005) have investigated the dry and wet deposition of trace metals in Hong Kong, and have compared the dry deposition fluxes obtained by direct (by measurement) and indirect methods (by modeling). It has been shown that marine elements (Na, Mg and Sr) exhibited the highest deposition velocities (from 1.0 ± 0.2 cm/s for Sr to 1.2 ± 0.2 cm/s for Na), followed by crustal elements (Fe, Ti, Ba, and Mn) (ranged from 0.7 m/s for Mn and Ba to 1.0 m/s for Fe and Ti), and pollution elements (V, Sb, Pb and Zn) which are known to be enriched in fine particles had the lowest deposition velocities (from 0.2 to 0.4 cm/s). In general, the pollution elements showed lower deposition velocities relative to elements in the coarse fraction. The comparison of dry and wet deposition fluxes showed that these elements were deposited dominantly by wet scavenging process (93% for V, 86% for K, 81% for Sb, and 75% for Pb). In addition to the low dry deposition velocities of submicrometer particles, the abundant rainfall in Hong Kong also contributed to higher wet fluxes of metal contaminants.

Table 2-6: Atmospheric deposition of heavy metals (mg/m^2/yr) in PRD and other regions

	Mean				
Location	Cu	Cr	Pb	Zn	Reference
PRD region (2001-2002)	18.6	6.43	12.7	104	Wong *et al*. (2003)
Lake Superior (1993-1994)	3.10	0.22	1.50	8.80	Sweet *et al*. (1998)
Lake Michigan (1993-1994)	1.90	0.20	1.60	6.00	Sweet *et al*. (1998)
Lake Erie (1993-1994)	4.20	1.10	1.80	17.0	Sweet *et al*. (1998)
NW Indiana (1975-1980)	9.00	3.20	60.0	100	Cole *et al*. (1990)
W. Penn. (1975-1980)	-	2.80	10.0	4.10	Schell (1986)
L. Erie (1975)	2.60	-	4.20	30.0	Kuntz (1978)
North Sea (1993-1994)	1.24	2.43	3.52	6.50	Injuk *et al*. (1998)

2.8.3 Review on studies of trace metals in mosses

The technique of moss biomonitoring has been widely used in Europe (Rühling and Tyler, 1968, 1970; Markert *et al*., 1996; Zechmeister, 1998; Rühling and Steinnes, 1998; Aceto *et al*., 2003) and North America (Groet, 1976; Barclay-Estrup and Rinne, 1979; Percy, 1982) in the past few decades. The types of species recommended for use in European moss surveys include *Hylocomium splenders* and *Pleurozium schreberi* (Ross, 1990). Other moss species such as *Hypnum cupressiforme* and *Scleropodium purum* are more widespread and commonly used in southern Europe (Bargagli *et al*., 1995). In a large-scale sampling, the use of more than a single species is necessary. An interspecies study showed that the moss *Hypnum cupressiforme* accumulated 50% - 125% more Al, Co, Mo, Ni, Pb and Zn, as compared to other species such as *Pleurozium schreberi* as *Hypnum cupressiforme* grow in denser mats (Sucharová and Suchara, 1998). Similar results were obtained for elements such as Zn in the study by Galsomiés (2003), whereas Rühling and Tyler (1968) showed that *Hypnum cupressiforme* contained only slightly more Pb than *Pleurozium schreberi*.

However, relatively few attempts were found in the literature to use mosses as biomonitors for air pollution in China, despite their wide application in other countries. Moreover, most of these studies were on the atmospheric deposition of mercury (Xiao *et al*., 1998; Tan *et al*., 2000; Liu *et al*., 2003), only few were on other trace metals, such as cadmium (Bi *et al*., 2006). The moss species used include *Thulium Symbiforium*, *Aulacomnium Androggnum* and *Hypnum Revolutum*. The use of moss technique to evaluate the atmospheric deposition of heavy metals in South China region was also scarce.

2.9 Trace metal pollution monitoring and assessment

2.9.1 Measurement of trace and major elements using ICP-AES and ICP-MS

Many analytical techniques are applicable for the determination of heavy metals, such as inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence (XRF), and atomic absorption spectrometry (AAS). In the present study, the ICP-AES and ICP-MS were used for the analysis of major and trace elements in the particulate matter, dry and wet deposition and moss samples. ICP-AES was able to detect elemental concentrations at the levels around ppm, and it is sufficient for most of the samples in this study and was used whenever applicable. Alternatively, ICP-MS was used to determine samples with very low limits of detection (<10 ppt).

The ICP method is a multi-element analytical technique which involves the use of inductively coupled argon plasma as a source of energy for the atomization, ionisation and excitation of the sample. ICP-AES has the capability of determining a wide-range of concentrations, from trace levels to major components. Moreover, it enables simultaneous determination of a large number of elements in a relatively short time (Thompson and Walsh, 1989). For the ICP-MS system, it is equipped with a quadrupole mass analyzer. The detection limit obtained by ICP-MS is sufficient for ultratrace elemental and isotopic determination, and the technique has a dynamic range of three to four orders of magnitude (Greenfield and Foulkes, 1999).

2.9.2 Acid digestion

Samples which consist of solid material need to be brought into solution forms prior to the analysis. Decomposition and dissolution of the samples can be achieved by the use of strong acids or the fusion method. Acid digestion methods were generally adopted in many geochemical analyses of soil, sediment, plant and particulate matter samples, which use a concentrated acid or a mixture of concentrated acids, such as hydrofluoric acid (HF), suphuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3), perchloric acid ($HClO_4$) and/or aqua-aqui. The treatment with strong acids is to dissolve the inorganic elements that are attached to particle surface and/or entrapped in crystal structure of the material and to transform the solid material into solution, which can be readily analysed using conventional analytical equipment (Hossner, 1996).

In this study, we have adopted the digestion method using a mixture of nitric and perchloric acids. This method of digestion is quite effective, and it has been reported that it is able to solubilise many of the elements of interest, such as Cu, Pb, Zn, Cd, Co, Ni and Mn. However, it is not effective in the decomposition of resistant minerals, so that elements such as Sn, Cr, W and Be are not solubilised (Thompson and Walsh, 1989). Silicates and other crystal structures cannot be decomposed using this method, and HF has to be used. The use of $HClO_4$ is also preferred over other strong acids, such as H_2SO_4 which may cause chemical interference to the spectrometric analysis due to the formation of insoluble sulphates. Perchlorates, with the notable exception of the potassium salt, are freely soluble. The addition of HNO_3 is to facilitate the dissolution of the sample and to prevent explosive reactions of organic materials with $HClO_4$ (Thompson and Walsh, 1989; Hossner, 1996).

2.9.3 Pb isotopic analysis

The measurement of isotope ratios has been proven to be useful and powerful tools in environmental geochemistry to identify the origins of environmental pollutants or geological materials. Various isotopes have wide applications in environmental studies, including the use of Os ratios in geochronology (Lichte *et al*., 1986; Masuda *et al*., 1986; Peucker-Ehrenbrink *et al*., 1995; Suzuki *et al*., 1996), Sr and B isotopic ratios for tracing the origins of pollutants in groundwater and spring water (Basu *et al*., 2001; Swarzenski *et al*., 2001; Pennisi *et al*., 2006), and Pb isotopic ratios to identify the sources of Pb inputs in sediments, soils, atmospheric depositions and aerosols (Farmer *et al*., 1996; Bollhöfer and Rosman, 2000, 2001; Wong *et al*., 2003; Bacon *et al*., 2005).

Analysis of Pb isotopic composition is one of the most commonly used methods to trace the sources of Pb in the environment. In the present study, this technique has been adopted to evaluate the origins of Pb in aerosols, dry and wet depositions and mosses. 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 environment.

The Pb isotopic composition of various ores and rocks in South China has been extensively studied by Zhu (1995, 1998) and Zhu *et al*. (1989), who has shown that

both Th-derived (^{208}Pb) and U-derived (^{206}Pb and ^{207}Pb) isotopes are enriched in crust and mantle. In the PRD region, the natural background Pb isotopic composition of granite were around 1.1834 and 2.4680 for ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb, respectively (Zhu, 1998). Similar isotopic signatures were found in uncontaminated soils in the PRD, which were 1.1952 and 2.4815 for ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb, respectively (Zhu *et al*., 2001). Table 2-7 shows the Pb isotopic ratios of Pb ore bodies in various parts of the world, including those in the PRD. The anthropogenic Pb from the mining ores generally had lower Pb isotopic ratios than those of the background geogenic sources. By comparing the Pb isotopic signatures of the environmental samples with those of natural background materials and various sources of Pb (i.e. coal burning, vehicular and industrial emissions), the origins of the Pb contamination can be traced.

Previous studies have also demonstrated that the decrease in the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios in soils and dusts in the PRD region were associated with the enrichment of anthropogenic Pb from sources such as vehicular and industrial emissions (Wong *et al*., 2003; Li *et al*., 2004; Duzgoren-Aydin *et al*., 2004; Lee *et al*., 2006). However, in general, only limited studies were available on the Pb isotopic data of atmospheric Pb in the PRD region (Zhu *et al*., 2001; Wong *et al*., 2003).

Table 2-7: The $^{206}Pb/^{207}Pb$ ratio of major Pb ore bodies in various parts of the world

Major Pb ores	$^{206}Pb/^{207}Pb$
Fankou, Guangdong, China (PRD)[a]	1.172
Missouri, USA[b]	1.385
Idaho, USA[b]	1.052
Altay, Kazakhstan, Russia[b]	1.131
Broken Hill, Australia[b]	1.037
British Columbia, Canada[b]	1.064
New Brunswick, Canada[b]	1.160
Ontario, Canada[b]	0.920
Cerro de Pasco, Peru[b]	1.200
Trepca, Yugoslavia[b]	1.195
Durango, Mexico[b]	1.192

[Source: [a] Zhu, 1998; [b] Vanhaecke *et al*., 1999]

2.9.4 Statistical analyses

Bivariate and multivariate statistics have important applications in many environmental studies. Various statistical techniques can be used to analyse the observed data and chemical measurements in environmental monitoring studies of the air and water quality, risk assessment, and other problems concerning the environment. These include the use of descriptive statistics, hypothesis testing, analysis of variance, regression analysis and modelling.

The use of statistics in environmental studies is relatively young as compared to the applications in other fields, and it employs several statistical methods that have been developed in other fields of statistics, although increasing use has been made in the context of environmental science (Pentecost, 1999; Millard and Neerchal, 2001). In the present study, several statistical techniques have been employed in the analysis and interpretation of the data, which include Pearson correlation (PC), Principal Component Analysis (PCA), Linear regression, Student's T-test and the Kruskal-Wallis test. A brief introduction of these statistical techniques is given below.

Pearson correlation (PC) – This is also known as the product-moment correlation. The Pearson correlation coefficient is obtained by dividing the covariance by a pooled standard deviation (sx1, sx2). This is done to make the correlation independent of the original scale of the measurements being taken, making it more practicable. The Pearson correlation coefficient (r) takes values in the range -1 to +1, from perfect negative to perfect positive correlation. It is positive when the values of the two variables increase together, and has negative

values when the value of one variable increases and the value of the other variable decreases. The correlation coefficient (r) is symmetric. In the Pearson correlation, which is a parametric test based on a bivariate normal distribution, it is assumed that the sample distributions are normal (Pentecost, 1999).

Linear regression – The most common type of bivariate analysis for quantitative random variables is simple linear regression. In the simple linear regression model one variable, say Y the dependent variable, is assumed to be dependent on the other variable, X, which is called the explanatory variable. The purpose is usually to explain the variation of Y in terms of the variation in the variable X, which is assumed to be linearly related to Y. The least squares method is commonly used to formulate the linear regression function of Y on X. The best fit line is formulated so that the total squared deviation of points from the line is a minimum.

Principal component analysis (PCA) – The analysis is concerned with explaining the variance-covariance structure through a few linear combinations of the original variables. Its general objectives are data reduction and interpretation. In the PCA analysis, larger components, p, which are required to reproduce the total system variability, are reduced to a smaller number of components, k of the principal components, which account for much of the total system variability.

The first principal component is the combination that accounts for the largest amount of variance in the sample. The second principal component accounts for the next largest amount of variance and is uncorrelated with the first. Successive components explain progressively smaller portions of the total sample variance

and all are uncorrelated with each other. In this way, major factors that explained most of the variability of the system can be identified (Johnson and Wichern, 2002; Norušis, 2005).

Student's T-test – This is a statistical procedure used to test hypotheses about two population means. The T-tests are based on the assumption that the sample is from a normal population. If the population distribution is not normal, then the T-tests are approximately valid for large sample size. Practically, $n \geq 30$ is used as a criterion for sufficient sample size. If $n \geq 30$, the approximations by T-tests are generally good and the assumption of normality in the sample distribution is not necessary. However, when $n < 30$, it needs to assume that the data are from a normal distribution in order to use the T-tests.

In the T-test, the null hypothesis is that two population means are equal (H_0: $a = b$). The alternative hypothesis is that the two population means are not equal (H_1: $a \neq b$). There are three different types of T-tests: one-sided test, two-independent samples test, and paired-samples test (Norušis, 2005).

Kruskal-Wallis test – This is a non-parametric test where the assumptions regarding the data are more relaxed and normality of the sample distribution do no need to be assumed. In performing the Kruskal-Wallis test, the samples need only be independent of one another with the measurements at least at ordinary level. For this test the null hypothesis states that the sample populations are identical with respect to their medians. As with other non-parametric tests, ranking is involved and here all samples were first ranked together, with the lowest rank assigned to the lowest value (Conover, 1999; Pentecost, 1999).

2.9.5 Back trajectory analysis

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). The FNL archive meteorological datasets from the National Weather Service's National Centers for Environmental Prediction (NCEP) were used to compute the trajectories, which includes the global meteorological data for both northern and southern hemispheres. The data are on hemispheric 129 by 129 polar stereographic grids with resolution of about 191 km (Stunder, 1997).

Chapter 3 − Methodology

3.1 Characteristics of the study region

A description covering the geographical location and regional characteristics of the PRD region and the Nanling Mountains is given in this section.

3.1.1 Pearl River Delta Region

The PRD region is situated at the southern part of the Guangdong Province, it covers an area of 42,821 km^2 with a population (excluding foreign migrants) of 23.6 million (Guangzhou Statistics Bureau, 2003). The PRD region encompasses major cities, such as Guangzhou, Shenzhen, Zhuhai, Zhongshan, Dongguan, Foshan, Jiangmen, the urban districts of Huizhou and Zhaoqing, and the two special administrative zones of Macao and Hong Kong (Figure 3-1).

Figure 3-1: The Pearl River Delta (PRD) Region

Since the economic reforms in the 1970s, the region has been susceptible to rapid industrial development and urbanisation in the past few decades. Many multinationals and local corporations have established their manufacturing operations in the PRD region due to the low cost of labour and raw materials. The major manufacturing industries in the PRD economic zone includes electronics production, textiles and garment, paper, non-ferrous minerals, coal mining, petroleum and gas extraction.

Most of the goods manufactured in the PRD are destined for export. In 2002, exports from the PRD reached $113 billion, representing 35% of China's total export (Guangdong Statistical Yearbook, 2003; National Bureau of Statistics, P.R. China, 2004). Table 1 shows the economic statistics of the PRD cities in 2001. The gross output value of industry in the PRD economic zone in 2001 was $188 billion, of which $82 billion, or 44%, was destined for export. The greatest export values were produced in Shenzhen ($38 billion), Guangzhou ($12 billion) and Dongguan ($10 billion), and exports accounted for 88%, 31% and 79% of total industrial production in these three cities. Emissions from industrial, traffic and human activities has accounted for mounting pressures on the environmental quality in the region, which have attracted great public concerns. There is an acute need for better pollution control strategy in the PRD region, to protect the health of industrial workers and the general population in the region.

Table 3-1: Regional Economic Data for the PRD economic zone in 2001

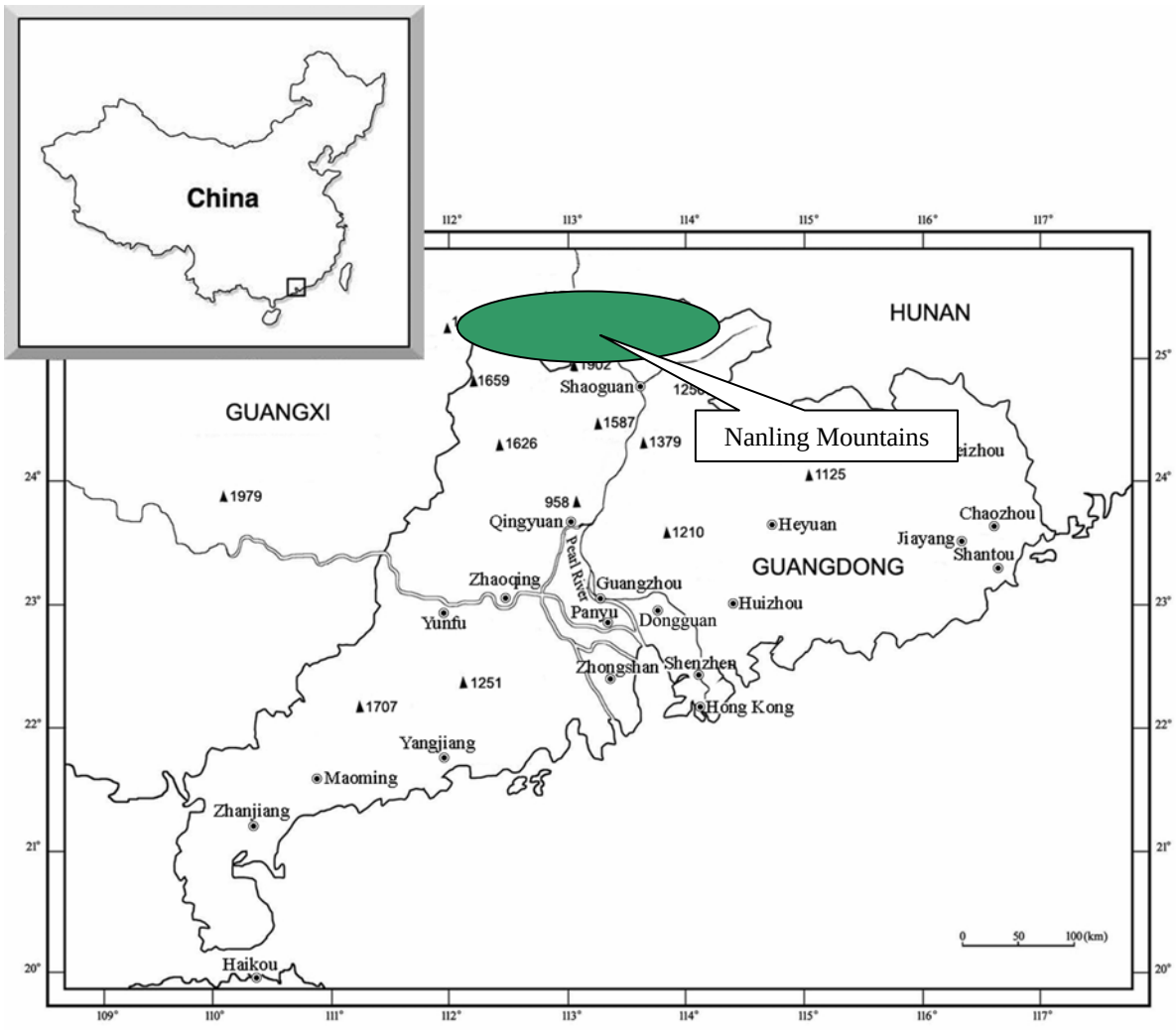
cities	gross output value of industry ($100 million U.S.)	gross output value of industry (100 million yuan)	total value of exports ($100 million U.S.)	total value of exports (100 million yuan)	ratio of exports/total
Guangzhou	380	3142	116	962	0.31
Shenzhen	424	3508	375	3102	0.88
Zhuhai	115	950	38	314	0.33
Huizhou	150	1242	49	406	0.33
Dongguan	132	1091	104	864	0.79
Zhongshan	127	1047	47	361	0.34
Jiangmen	180	1487	26	213	0.14
Foshan	302	2499	64	526	0.21
Zhaoqing	75	621	8	63	0.10
PRD economic zone total	1883	15586	823	6811	0.44
Guangdong total			954	7898	

Note: Values extracted from Streets *et al*. (2006)

3.1.2 Nanling Mountains

The Nanling mountain range is located in southern China and straddles from west to east across the borders of Guangxi, Guangdong, Hunan and Jiangxi provinces for more than 1,000 km. The mountain range is an important boundary in south China between the temperate continent in the north and subtropical regions in the southeast coast. The area is the key pathway for the long-range transport of air pollutants from northern China to the PRD region, particularly during the dry winter monsoon period. To the south of the Nanling range lies the Pearl River Delta (PRD) region of Guangdong Province (Figure 3-2).

Figure 3-2: Locations of the Nanling Mountains



3.2 Sample collection methods

3.2.1 Overview of the sampling programme

In order to investigate the atmospheric trace metals in the air and those deposited on the terrestrial environment, a sampling programme has been conducted for one-year period, from December 2003 to January 2005, to collect TSP and atmospheric depositions (both dry and wet depositions) at various locations in the PRD region. Table 3-2 shows the details of the sampling programme. Fine particulate matter ($PM_{2.5}$) was also collected in urban areas of Guangzhou over a one-year period, from May 2005 to May 2006, to further elucidate the heavy metal concentrations in finer particles.

Moss samples (*Hypnum plumaeforme*) and aerosol samples were also collected during a period between November 2002 and January 2003 in the Nanling Mountains and the PRD region, to study the potential use of the mosses for monitoring ambient air quality in a subtropical area, such as the South China region. Sampling of other moss species, including *Leucobryum chlorophyllosum*, *Pogonatum contorium*, *Thuidium tamariscinum* and *Bazzania tridens*, was carried out during May 2004 in the Dinghu Mountain for the intercomparison in the heavy metal uptakes in several moss species commonly found in the PRD region. An overview of the sampling programme of the mosses in the Nanling Mountains and the PRD region, and the Dinghu Mountain is shown in Tables 3-3. Moreover, some aerosols samples were also collected in the Nanling Mountains and the PRD region to study the relationship of trace metals in mosses and aerosols, and the overview of the sampling programme is shown in Table 3-4.

Table 3-2: Overview of the sampling programme for aerosols and dry and wet depositions in the PRD region over a one-year period

	PRD cities	ID	Site location	Site characteristics	Sampling frequency
Aerosols	Guangzhou	ZU	Sun Yet-sen (Zhongshan) University	urban city	bi-weekly - TSP and weekly - $PM_{2.5}$
	Guangzhou	BY	Baiyun Mountain	suburban mountain top	bi-weekly - TSP
	Hong Kong	PU	Hong Kong Polytechnic University	urban city	bi-weekly - TSP
	Hong Kong	HT	Hok Tsui	suburban coast	bi-weekly - TSP
Dry and wet depositions	Qingyuan	QY	Qingyuan	rural mountain top	bi-monthly
	Jiangmen	JM	Jiangmen	rural mountain top	bi-monthly
	Zhongshan	ZS	Zhongshan	rural mountain top	bi-monthly
	Shenzhen	WT	Wutong Mt	rural mountain top	bi-monthly
	Shenzhen	YM	Yangmeihang	rural mountain top	bi-monthly
	Hong Kong	TM	Tai Mo Mt.	rural mountain top	bi-monthly
	Hong Kong	HT	Hok Tsui	suburban coast	bi-weekly and bi-monthly
	Hong Kong	TO	Tai O	suburban coast	bi-monthly
	Hong Kong	HH	Haihawan	suburban coast	bi-monthly
	Foshan	NH	Nanhai	urban town	bi-monthly
	Foshan	SD	Shunde	urban town	bi-monthly
	Guangzhou	BY	Baiyun Mt	suburban mountain top	bi-weekly and bi-monthly
	Guangzhou	DH	Guangzhou Institute of Geochemistry	urban city	bi-monthly
	Guangzhou	ZU-1	Sun Yet-sen (Zhongshan) University	urban city	bi-weekly and bi-monthly
	Guangzhou	ZU-2	Sun Yet-sen (Zhongshan) University	urban city	bi-monthly
	Hong Kong	PU	Hong Kong Polytechnic University	urban city	bi-weekly and bi-monthly

Table 3-3: Overview of the sampling of mosses in the Nanling Mountains (Jan 2003) and the Dinghu Mountain (May 2004)

	ID	Site location	Site characteristics	Species
Mosses	NL	Nanling Mountains (northern part)	rural mountain	*Hypnum plumaeforme*
	MS	Nanling Mountains (southern part)	rural mountain	*Hypnum plumaeforme*
	DH-a	Dinghu Mountain	rural areas	*Hypnum plumaeforme*
	DH-b	Dinghu Mountain	rural areas	*Leucobryum chlorophyllosum*
	DH-c	Dinghu Mountain	rural areas	*Pogonatum contorium*
	DH-d	Dinghu Mountain	rural areas	*Thuidium tamariscinum*
	DH-e	Dinghu Mountain	rural areas	*Bazzania tridens*

Table 3-4: Overview of the sampling of TSP in the Nanling Mountains and the PRD region (Nov 2002-Jan 2003)

	ID	Site location	Site characteristics	Sampling frequency
Aerosols	YTH	Nanling Mountains (northern part)	rural mountain	2 aerosol samples – TSP
	QY	Nanling Mountains (southern part)	rural mountain	2 aerosol samples – TSP
	GZ	Guangzhou Institute of Geochemistry, Guangzhou	urban areas	4 aerosol samples – TSP
	ZS	Wuguishan, Zhongshan	suburban areas	4 aerosol samples – TSP

3.2.2 Sampling methods

The sampling methods for aerosols, dry and wet depositions and mosses are discussed in details in the following sections.

3.2.2.1 Aerosols in the Pearl River Delta Region

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 3-3). The samples were taken on a bi-weekly basis over a one-year period, from December 2003 to January 2005. Fine particulate matter ($PM_{2.5}$) was also collected at the ZU site on a weekly basis over a one-year period, from May 2005 to May 2006.

The samples 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 (see Figure 3-4). 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.

Figure 3-3: Sampling locations of aerosols in the PRD region

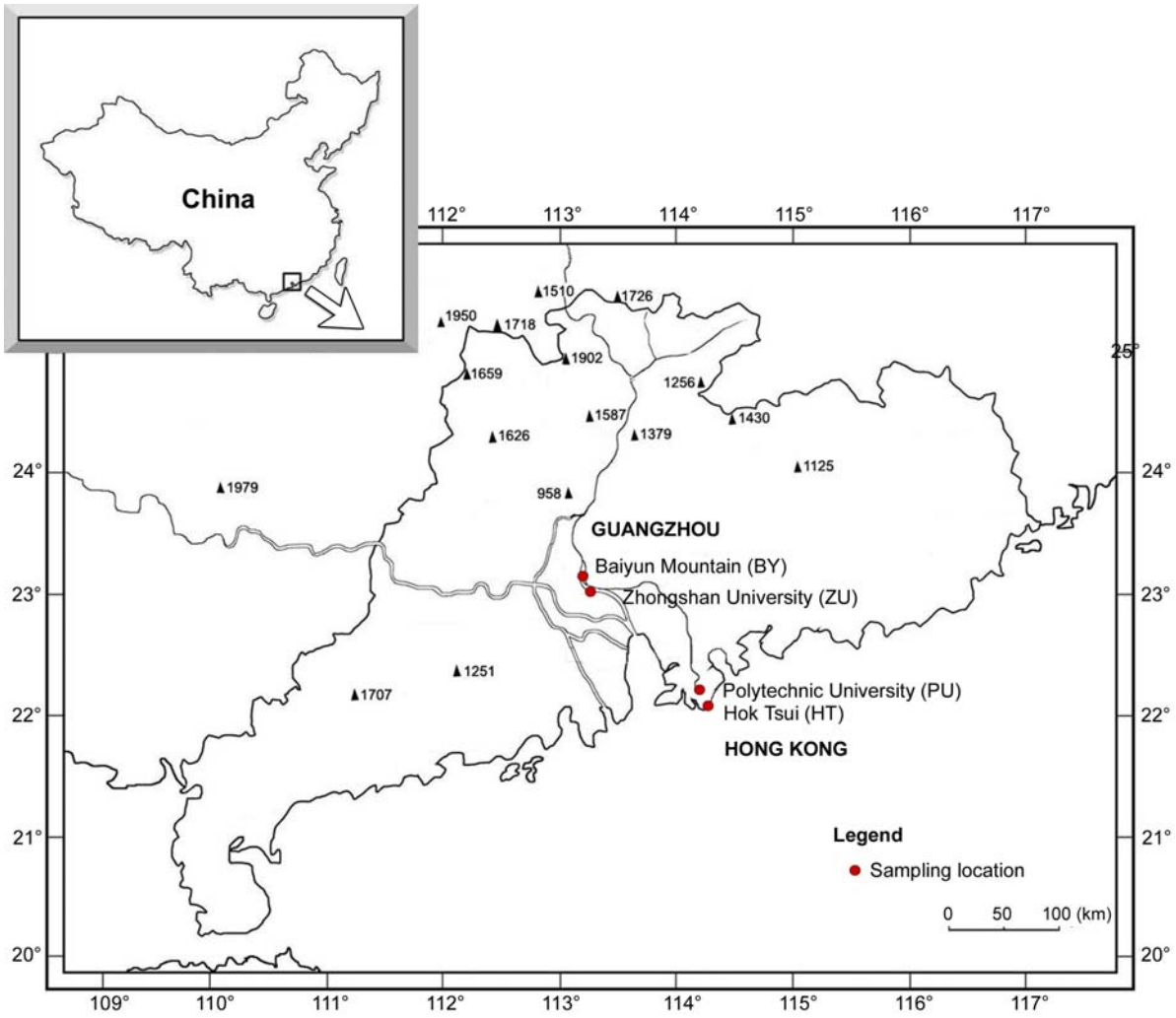
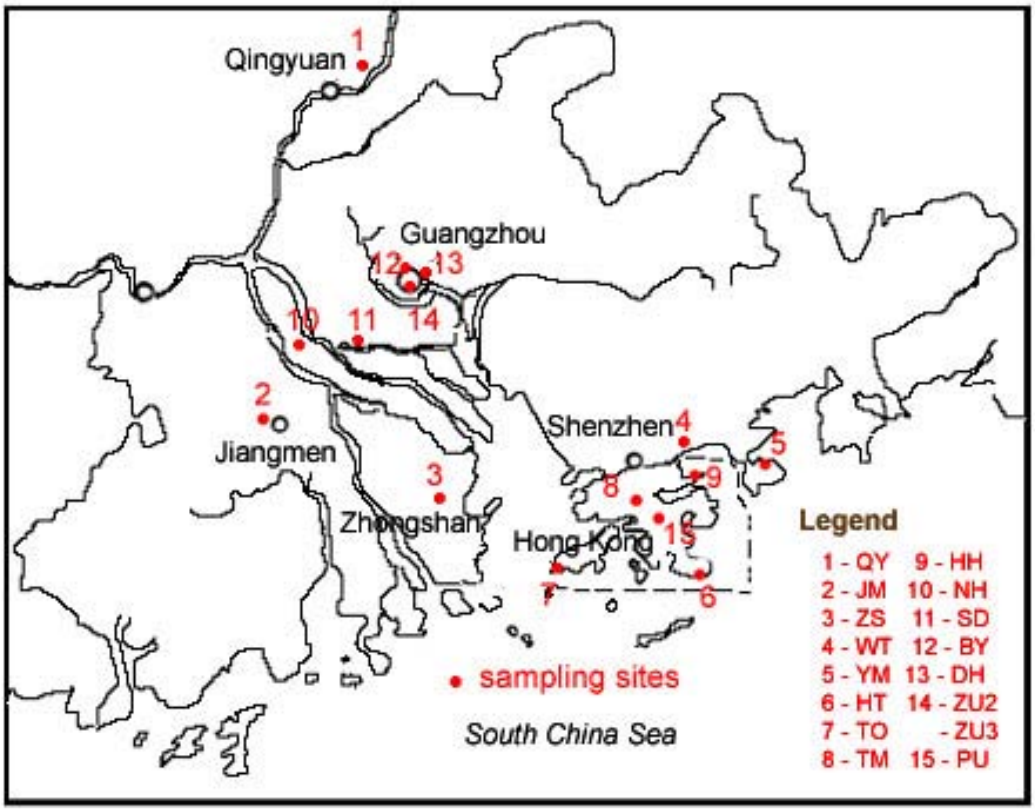


Figure 3-4: High-volume TSP sampler (Anderson type)

3.2.2.2 Dry and wet depositions in the Pearl River Delta Region

Dry and wet deposits were collected simultaneously at a two-month interval from December 2003 to January 2005 at 16 urban, suburban and rural sites within the PRD region (see Figure 3-5), and a total of 112 dry deposits and 77 wet deposits were collected within the one year cycle. No wet deposits samples were collected during October 2004 to January 2005, due to the low amount of rainfall.

Figure 3-5: Sampling locations of dry and wet depositions in the PRD region



A cone-shaped sampler, with a cross-sectional sampling area of 0.049 m^2, and a polystyrene bottle, housed in a wooden box at the bottom of the cone structure, were used in the sampling of dry and wet deposition (see Figure 3-6). The sampler was lined with Whatman Silicate Microfibre filters and two layers of medical-use cotton gauze (top and bottom of the filters), to increase the integrity of the silicate filter. Dry deposits were collected on the filter, while precipitation passing through the filter was collected in the pre-cleaned polystyrene bottle. The bottle containing the wet deposition was sealed with a cap. The dry and wet deposition samples were transported to the clean laboratory.

Figure 3-6: Dry and wet deposition sampler

There is still no standardized method for sampling and analyzing dry and wet deposition fluxes. In general, dry deposition can be collected using (a) bucket, (b) surface plate, and (c) water vessel (Shannigrahi *et al*., 2005), and wet deposition can be collected using (a) bucket and (b) the automatic wet deposition sampler (Mangoni *et al.,* 1998). Dry and wet deposition can also be collected simultaneously using an automatic dry and wet deposition sampler (Sakata *et al.*, 2006). In the present study, sampling was conducted at both urban and rural areas of the PRD region. The sampling programme covers 16 strategic locations over the PRD region and at certain locations, sampling was conducted at the mountain top and coastal sites where electricity is not available and automatic samplers can not be used. Hence, the current sampler device has the advantages of providing a simple and convenient method to estimate the dry and wet deposition of trace metals, especially at the remote areas. However, some of the soluble fraction of trace metals in dry deposition was washed down and collected in the bottle during a rain event, resulted in the underestimation of trace metals in the dry deposition. Past studies have shown that insoluble fraction of dry deposition was predominant over soluble one (Morselli *et al.,* 2003). Cadmium and Zn were two of the most soluble metals in dry deposition, which accounted for 33% of the total Cd dry flux and 25% of the total Zn dry flux, respectively. Hence, it can be estimated that the dry deposition flux of trace metals were underestimated by about 20 – 30%.

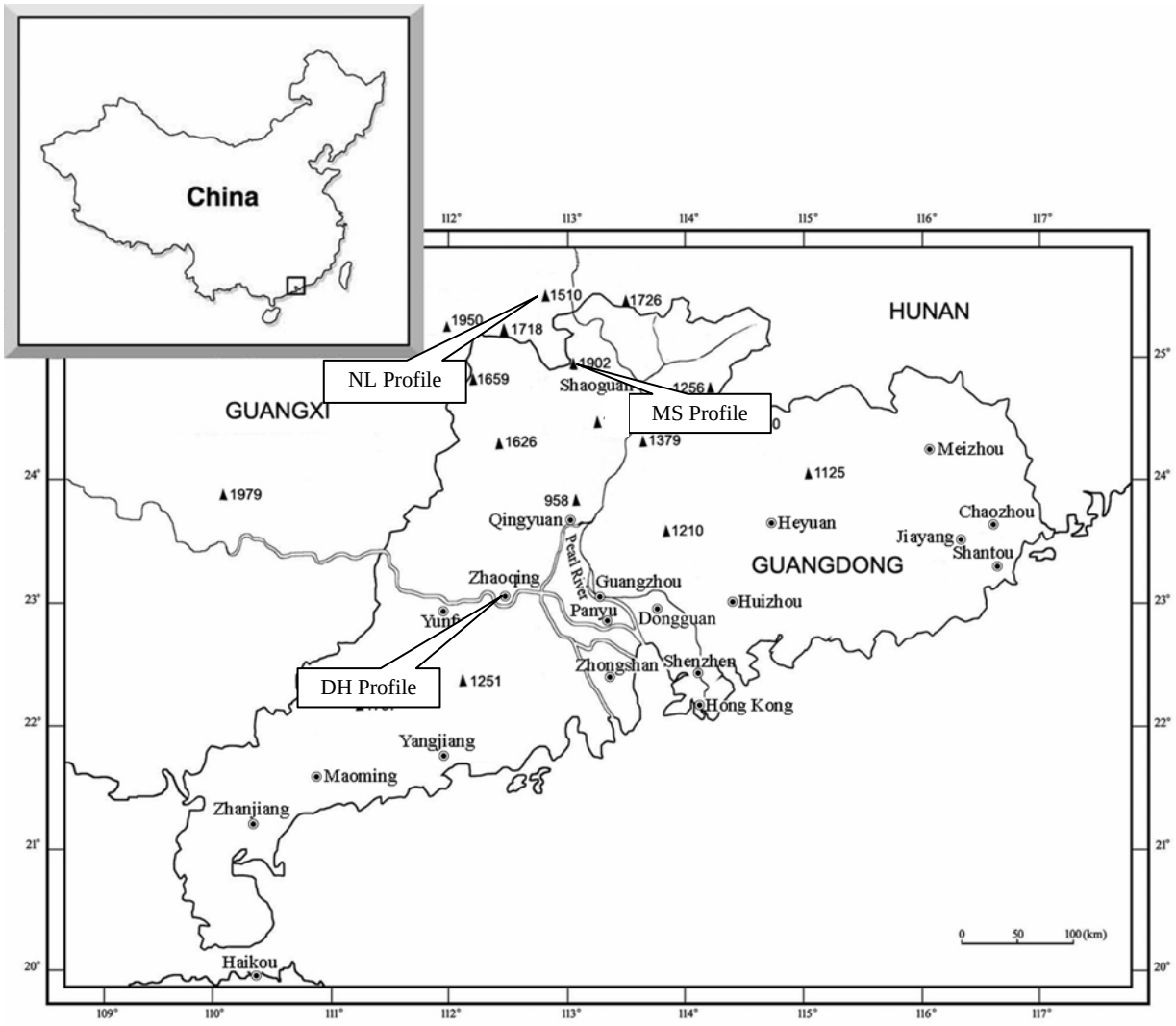
3.2.2.3 Mosses and aerosols in the Nanling Mountains, the Dinghu Mountain, and the PRD region

The moss *Hypnum plumaeforme* was collected at two sampling areas, the upper northern part of the Nanling Mountains, the NL series; and the lower southern part of the mountain range, the MS series, in January 2003 (Figure 3-7). Eight moss sampling sites were chosen in each area at various altitudes to study the topographical effect of metal concentrations in moss. Other moss species were also sampled in the Dinghu Mountain, the DH series, in May 2004 to assess the ability of metal uptakes by different moss species commonly found in the region (see Figure 3-7). These include *Hypnum plumaeforme*, *Leucobryum chlorophyllosum*, *Pogonatum contorium*, *Thuidium tamariscinum* and *Bazzania tridens*. The mosses were picked up with a plastic shovel and stored in polyethylene bags.

A total of 12 aerosol samples were also collected in the Nanling Mountains, and in Guangzhou and Zhongshan of the PRD during the winter season (November 2002 – January 2003) (Figure 3-7). Two aerosol samples were collected at each location in the north (YTH series; at 1450 m a.s.l.) and south (QY series; at 802 m a.s.l.) of the Nanling Mountains. The Guangzhou aerosols were collected at the roof top of a building in the urban centre of Guangzhou (~50 m a.s.l.). The Zhongshan aerosols were sampled on a small mountain (~500 m a.s.l.), in a suburban area of Zhongshan city. The aerosols at Nanling, Guangzhou and Zhongshan, located at the northern, central and southern part of the PRD, represented the general atmospheric condition of the region.

A high-volume sampler (Anderson-type) was deployed in the sampling sites to collect aerosol samples. The samplers were operated at a flow rate of 0.465 m^3/min to collect the total aerosols on 20.3 x 25.4 cm glass fibre filters. A sampling duration of 12 h was adopted. The filters were then wrapped in aluminium foil and stored in polyethylene bags.

Figure 3-7: Sampling locations of mosses and aerosols in the Nanling Mountains (NL and MS), Dinghu Mountain (DH) and the PRD region



3.3 Sample preparation

The descriptions of sample preparation and laboratory analyses are given in this section. All the glass-ware and plastic-ware used for the chemical analysis of trace and major elements were soaked in 10% high purity HNO_3 for 24 hr before use. All the acid-treated test tubes and apparatus were rinsed thoroughly with distilled and de-ionised water (DDIW) before use.

3.3.1 Aerosol and dry deposition sample preparation

The aerosols and dry deposits collected on the filters were wrapped in an aluminium foil in situ and subsequently stored in polyethylene bags at 4 °C. For the aerosols samples, one quarter of the filter was cut using stainless steel scissors and placed in acid-cleaned Pyrex test tubes. Similarly, the filter collecting dry deposition was cut into half using stainless steel scissors and placed in the test tubes.

3.3.2 Wet deposition sample preparation

The wet deposition samples were stored in tightly capped bottles at 4 °C. The wet deposition samples were acidified by adding 2.0 ml of 20% (v/v) high-purity HNO_3 to 8.0 ml of the sample prior to analysis.

3.3.3 Moss sample preparation

The green part of the moss 1-3 cm from the top was separated and thoroughly washed with tap water first, and then with DIW, until no soil particles adhered on the surfaces. The samples were dried in an oven at 60 °C for 3 days, and were subsequently ground in an agate pot until fine particles (< 200 μm) were obtained. The samples were stored in polyethylene bags in a dessicator.

3.4 Analytical methods

3.4.1 Determination of trace and major element concentrations

The aerosol, dry deposition, and moss samples were digested using concentrated acids (Wong *et al*., 2003). No digestion is needed for the wet deposition sample, since it is already in soluble form. Approximately 0.350 g of the moss samples was weighted and placed into the test tubes. Subsequently, concentrated high-purity HNO_3 and concentrated high-purity $HClO_4$ were added to the samples in the proportion of 4:1 (v/v). The volume of HNO_3 and $HClO_4$ added depends on the area of the filter paper and the weight of the samples. The mixture of concentrated acids was added until the filters were fully submerged for the complete digestion. Table 3-5 shows the volume of acids used in the present study.

For quality control, procedural blanks and sample replicates were randomly inserted. The mixtures were then gently shaken using a vortex and then heated progressively to 190 ºC in an aluminium heating block for 24 h, until completely dry. The temperature settings for the heating are shown in Table 3-6. Twelve ml of 5% (v/v) high-purity HNO_3 were added to the aerosol samples after initial acid digestion. Ten ml of 5% (v/v) high-purity HNO_3 were added to the dry deposition and moss samples. The test tubes were then heated at 70 ºC for 1 hr. Upon cooling, the solutions were decanted into acid-cleaned polyethylene tubes.

Table 3-5: Volume of concentrated HNO_3 and $HClO_4$ used in the strong acid digestion

Samples	Concentrated HNO_3 (ml)	Concentrated $HClO_4$ (ml)
Aerosols (TSP)	14.0	3.5
Aerosols ($PM_{2.5}$)	12.0	3.0
Dry depositions	8.0	2.0
Mosses	12.0	3.0

Table 3-6: The temperature settings for the heating in the acid digestion

Temperature (ºC)	Duration (hr)
50	1
90	2
125	2
150	2.5
175	1
190	3

After the aerosol, dry deposition and moss samples have been fully digested using concentrated acids, and the wet deposition samples have been acidified, they were ready for analysis. The elemental concentrations of the aerosol, dry and wet deposition and moss samples were determined using Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES, Perkin Elmer Optima 3300DV). Blanks, replicates, quality control standards, and standard reference materials from the National Institute of Standards and Technology (NIST SRM) were inserted during the analytical measurement to detect contamination and drift.

Since the matrices of the samples were not the same, different types of standard reference materials were used in the analysis of aerosols, dry depositions and

mosses. Standard reference material, NIST SRM 1648-urban particulate matter, was incorporated in the analysis of aerosols and dry depositions. 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. In the analysis of moss samples, standard reference material, NIST SRM 1515-apple leaves, was used. The recovery rates for the heavy metals and some major elements in the standard reference material (NIST SRM 1515) ranged from 86 to 115%. However, no standard reference material was available for the analysis of wet depositions. The elemental concentrations of the blanks in all the trace metal analyses 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%.

3.4.2 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 using 5% high-purity HNO_3 to optimise the analytical performance of the machine. The analytical parameters were set as 250 sweeps per reading and 10 replicates per sample solution. Procedural blanks and an international standard reference material (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 $^{208}Pb/^{207}Pb$ of the SRM 981 are shown in Table 3-7.

The measured ratios were in good agreement with the certified standard values (0.0646, 1.0933 and 2.3704, respectively).

Table 3-7: The average measured Pb ratios of $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ of the SRM 981 for the analysis of aerosols, dry and wet depositions, and mosses

	Aerosols (TSP) n=31	Aerosols ($PM_{2.5}$) n=5	Dry depositions n=15	Wet depositions n=14	Nanling mosses n=13
$^{204}Pb/^{207}Pb$	0.0644±0.0003	0.0646±0.0001	0.0645±0.0003	0.0645±0.0003	0.0647±0.0001
$^{206}Pb/^{207}Pb$	1.0925±0.0024	1.0933±0.0008	1.0933±0.0023	1.0923±0.0017	1.0936±0.0014
$^{208}Pb/^{207}Pb$	2.3693±0.0034	2.3696±0.0025	2.3711±0.0035	2.3691±0.0046	2.3674±0.0052

3.4.3 Statistical analyses

The analytical results were compiled to form a multi-elemental database using Microsoft Excel®. Statistical methods, including Pearson correlation (PC), Principal component analysis (PCA), Linear regression, Student's T-test, Kruskal-Wallis test were performed using SPSS®12.0 for the data analysis and interpretation.

3.4.4 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 a.g.l. (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, 500 and 1000 m a.g.l. were also calculated for detailed episode studies.

3.4.5 Organic and elemental carbon analysis

The samples were analysed by an OC/EC analyzer (Thermal/Optical Carbon Analyser Model 2001). The IMPROVE thermal/optical reflectance (TOR) protocol described by Chow and Watson (2002) and Cao *et al*. (2003) was used for carbon analysis. A 0.526-cm^2 punch of a sampled quartz filter was heated at various temperatures in helium atmosphere to evolve OC and in 2% oxygen atmosphere to evolve EC. The carbon evolved at each temperature is oxidized to carbon dioxide and then reduced to methane, with a flame ionization detector for quantification.

3.4.6 Health hazard index and relative exposure level

Trace metals have long-term implications on human health. As discussed earlier, inhalation of trace metals are associated with the production of oxidative stress and lung injury (Ghio and Devlin, 2001; Silbajoris *et al*., 2000). In the present study, the risks associated with the inhalation of trace metals were assessed using the hazard index (HI). The hazard index is defined as a measure of the relative significance of the exposure to a chemical, and it has been commonly used in

risk assessment of the health impacts of chemicals through different pathways, such as oral, dermal and inhalation. The HI is calculated by dividing the exposure level by the reference exposure level (REL) (Gratt, 1996; OEHHA, 2003). To assess the long-term health impact of trace metals through the inhalation pathway, the chronic inhalation REL was used in the present study.

For a single compound, the HI was calculated by the following equation (OEHHA, 2003):

$$HI_{single} = \frac{\text{Annual Average Concentration } (\mu g/m^3)}{\text{Chronic Reference Exposure Level } (\mu g/m^3)} \qquad \text{(Eq. 3-1)}$$

The risk assessment methodology for a single compound does not reflect the potential synergistic effect on exposure to a mixture of chemicals. To investigate on the potential health implications due to the exposure of various chemical compounds, the HI for chemical mixtures was calculated (USEPA, 1987; OEHHA, 2003). In the present study, the HI for a mixture of chemicals was denoted as HI_{mix}, which was defined as follows:

$$HI_{mix} = \frac{EL_1}{REL_1} + \frac{EL_2}{REL_2} + \ldots + \frac{EL_i}{REL_i} \qquad \text{(Eq. 3-2)}$$

where E_i = exposure level to the i^{th} toxicant and REL_i = reference exposure level

Similar to Eq. 3-1, the annual average concentration was used as the exposure level in the above calculation. In Eq. 3-2, assumption of dose addition has been made.

The calculated HI (both HI_{single} and HI_{mix}) was compared with the value 1.0. An HI of 1.0 or less indicates that adverse health effects are not expected to occur. As the HI increases above 1.0, the probability of human health effects increases by an undefined amount. However, it should be noted that a HI above 1.0 is not necessarily indicative of health impacts due to the application of uncertainty factors in deriving the RELs (OEHHA, 2003).

Chapter 4 − Heavy Metals in Particulate Matter of Hong Kong and Guangzhou, South China

The major objectives of the aerosol study are: (1) to assess the annual average heavy metal concentrations 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; (4) to investigate the distribution of trace metals in coarse and fine fractions of the particulate matter. The study is useful in understanding the trace metal contamination in particulate matter in South China region. It also clearly demonstrates the long-range transport of trace metals from the inland areas to the coastal South China, which is valuable for strategic environmental management of cross-border pollution in the region.

4.1 Trace metal concentrations in total suspended particulate matter (TSP)

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 4-1. 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 4-2). 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).

Table 4-1: The mean concentrations of major and trace elements of TSP in urban 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 4-2: 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)

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

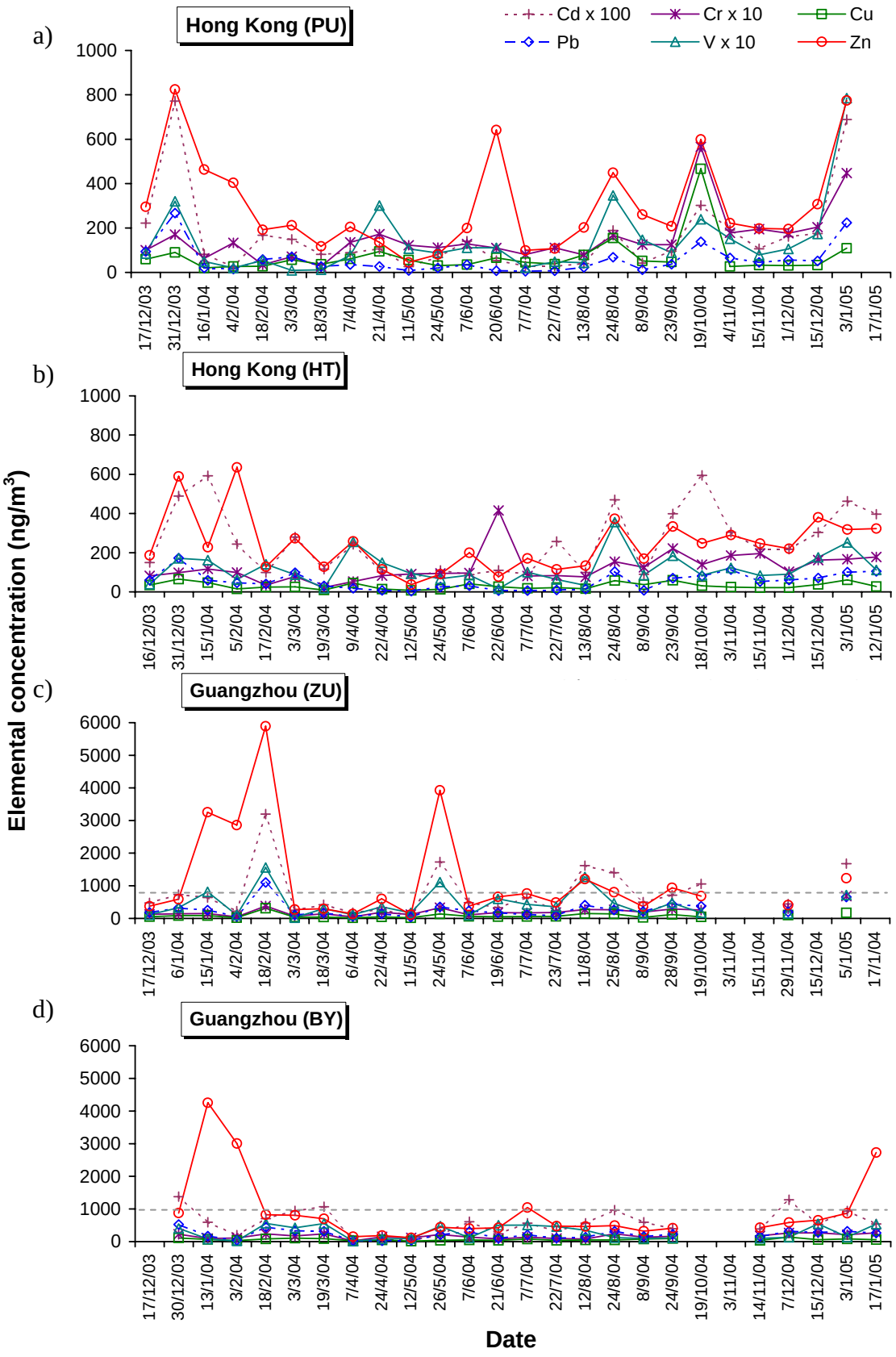
4.2 Temporal variations in heavy metal concentrations of TSP

The trace element 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 4-1a-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 4.5).

In Figure 4-1c-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.

Figure 4-1: Trace elemental concentrations of particulate matter (TSP) in urban and suburban areas of Hong Kong and Guangzhou, South China



4.3 Temporal variations in Pb isotopic composition of aerosols of TSP

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 4-3. 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 $^{208}Pb/^{207}Pb$ ratios at the four sites are illustrated in Figure 4-2a-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 Pb isotopic 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 4-2a-b). During the summer/autumn period (Aug 2004 – Sep 2004), the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios were relatively high (Figure 4-2a-b). The back trajectory plots showed that the air masses were originated from the northern regions. The high Pb isotopic ratios observed during the summer/autumn period could probably indicate the impact of long-range transport of pollutants from the northern inland areas due to the change in the synoptic wind pattern in the South China region.

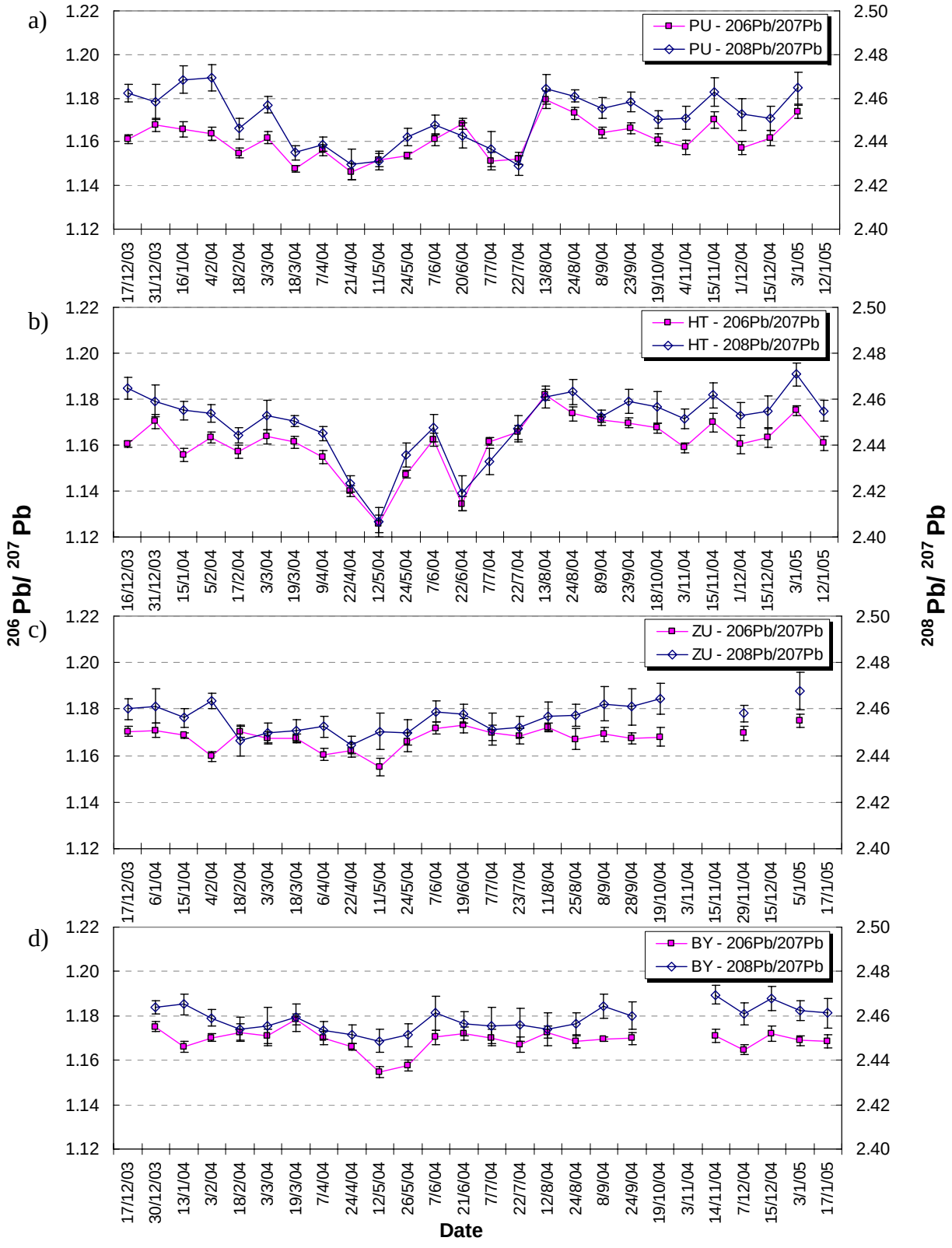
Furthermore, the seasonal variability in the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios was observed to be more pronounced in the suburban areas (HT), due to the less

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 4-2c-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.

Table 4-3: 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	

Figure 4-2: 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



4.4 Sources of Pb in aerosols (TSP)

Table 4-4 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).

4.4.1 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 4-3). 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. Moreover, the Pb isotopic ratios of the winter aerosols were close to those in Shanghai and Beijing collected during winter season. This could reflect the possible inputs of Pb from eastern and northern China by long-range transport during the winter monsoon period. Other studies also showed that polluted air masses from the northwest-central or southwest China and the PRD region can be transported to the downwind areas of South China through the winter monsoon air flow (Wang *et al.*, 2003; Chan *et al.*, 2004).

In summary, the Pb isotopic ratios of aerosols were less varied during the winter period (see Figure 4-3), 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.

4.4.2 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) and Taiwan aerosols (Hsu *et al.*, 2006) (see Figure 4-3). During the spring and summer seasons, the prevailing winds in the PRD region were the oceanic winds from the south. Figure 4-4a-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 4-2a-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, Taiwan 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).

Table 4-4: 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				
Fankou 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
- HKU car park	3	1.1514	2.4318	*et al*. (2004)
- High Street	3	1.1574	2.4456	
- Mongkok	3	1.1550	2.4427	

Figure 4-3: **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; [g] Zheng et al., 2004 (winter data only); [h] Mukai et al., 2001; [i] Hsu et al., 2006)**

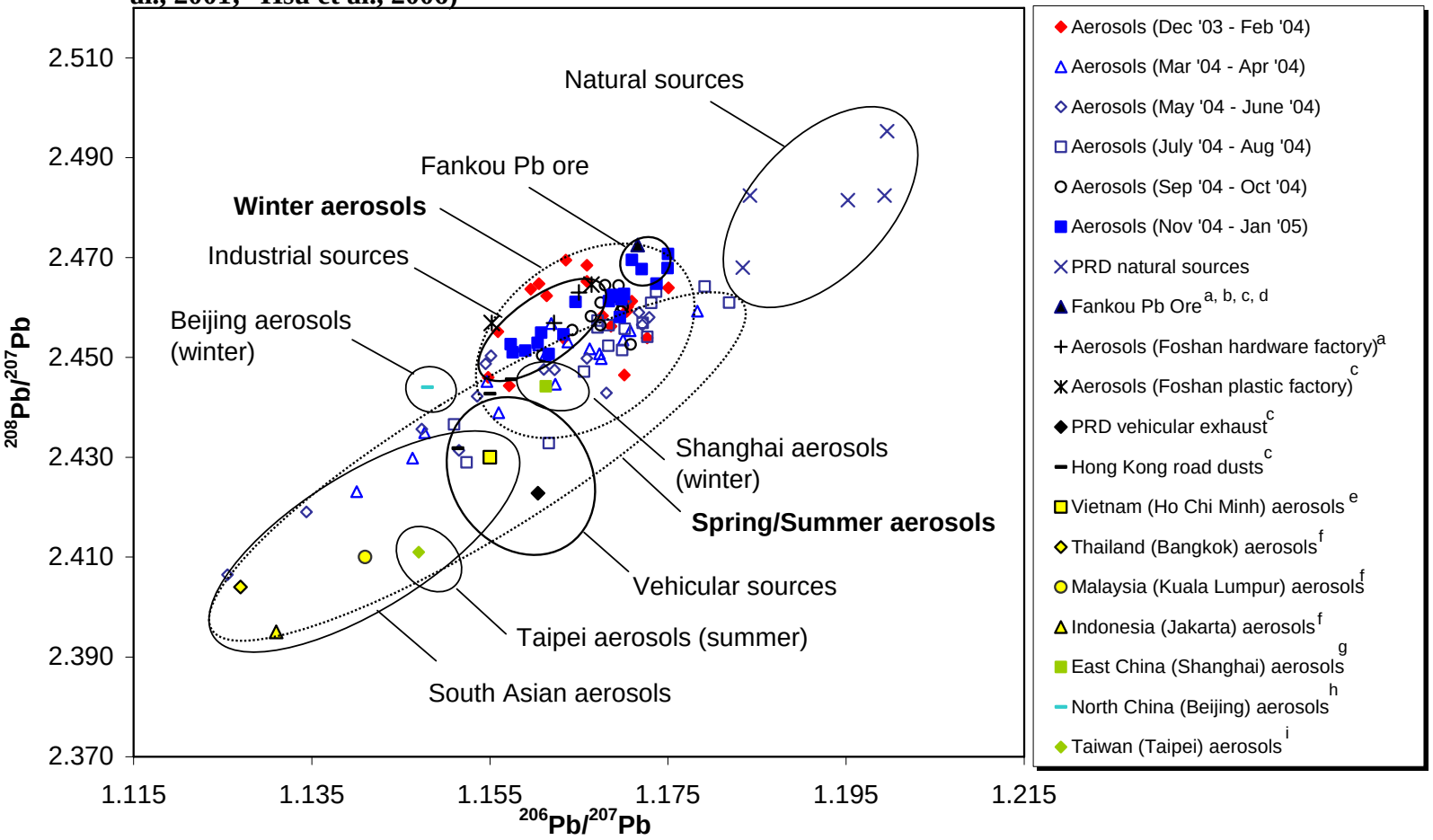
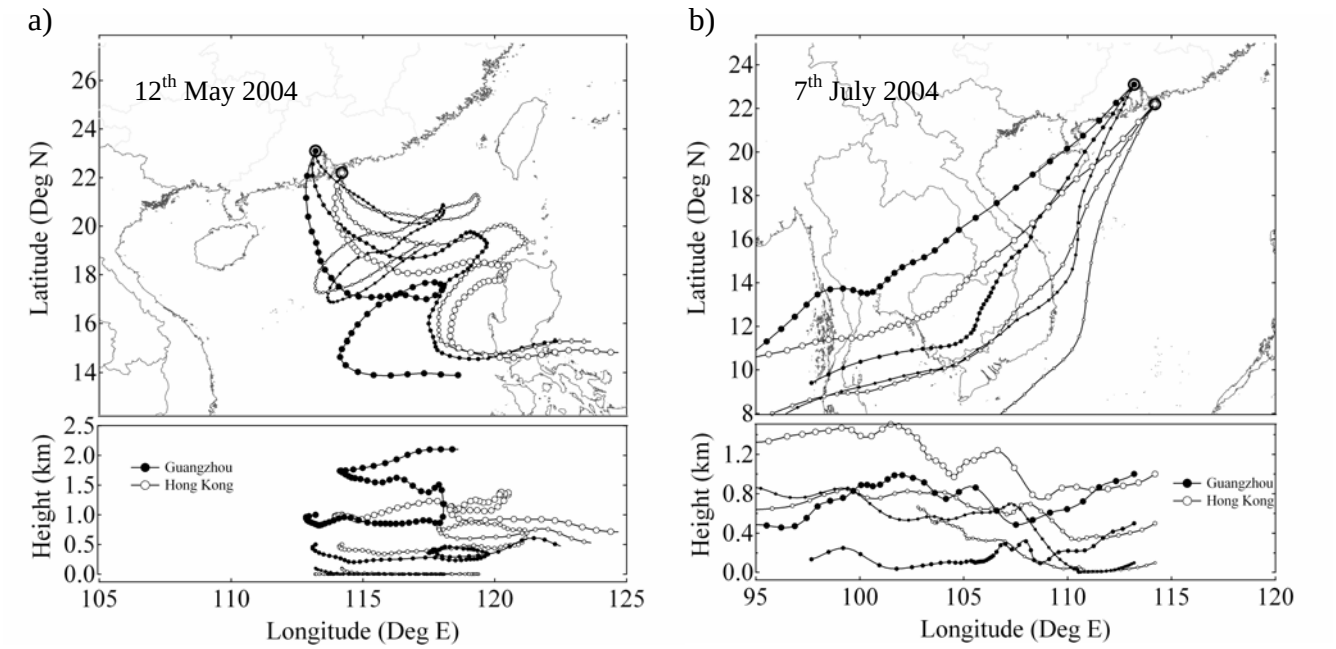


Figure 4-4: Back trajectory plots on the days with low Pb isotopic ratios

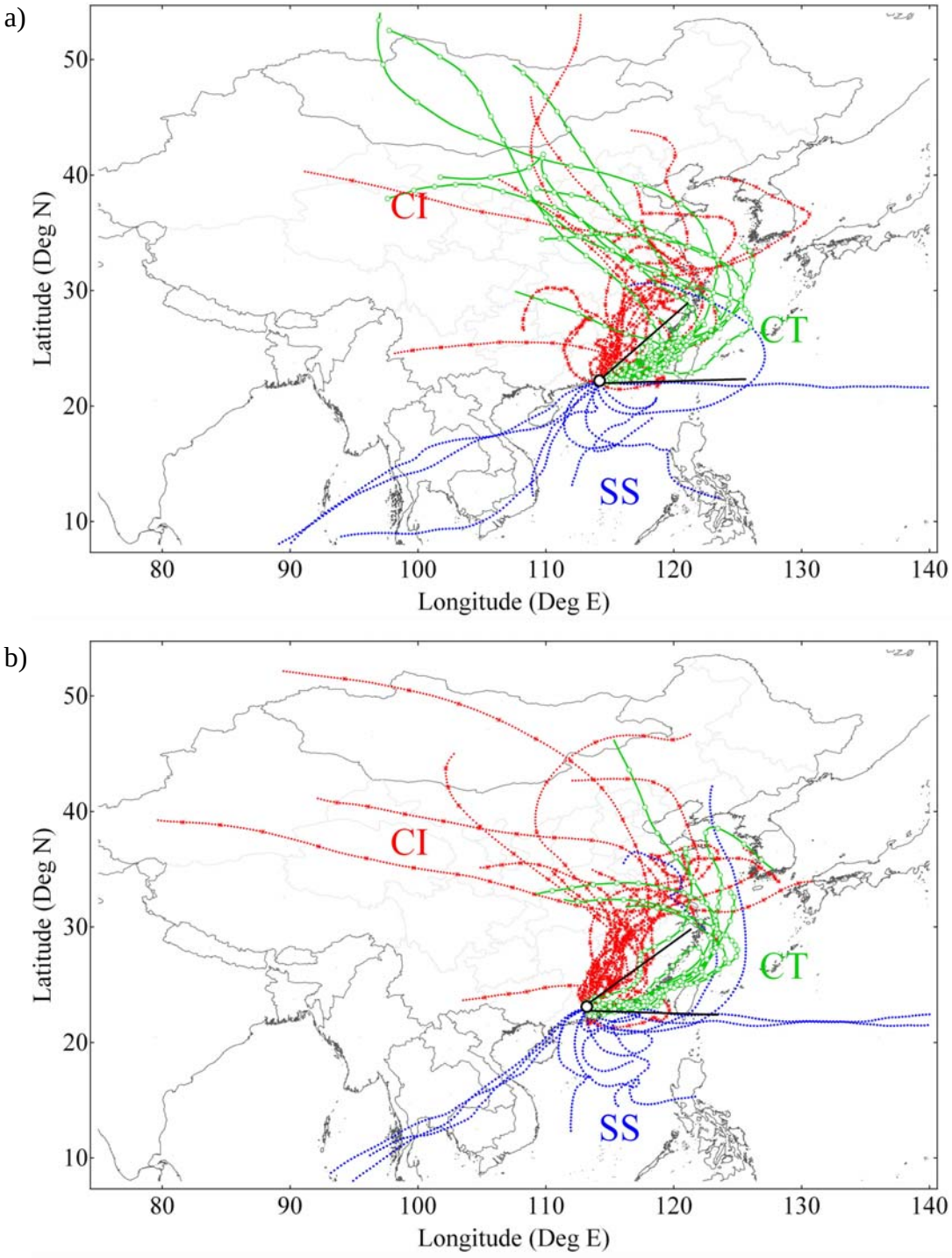


4.5 Back trajectory analysis

4.5.1 Air masses classification

Figures 4-5a-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.

Figure 4-5: 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.



4.5.2 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 4-5. 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 (Table 4-5). 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.

Table 4-5: 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

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 concentration 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 ($P>0.05$).

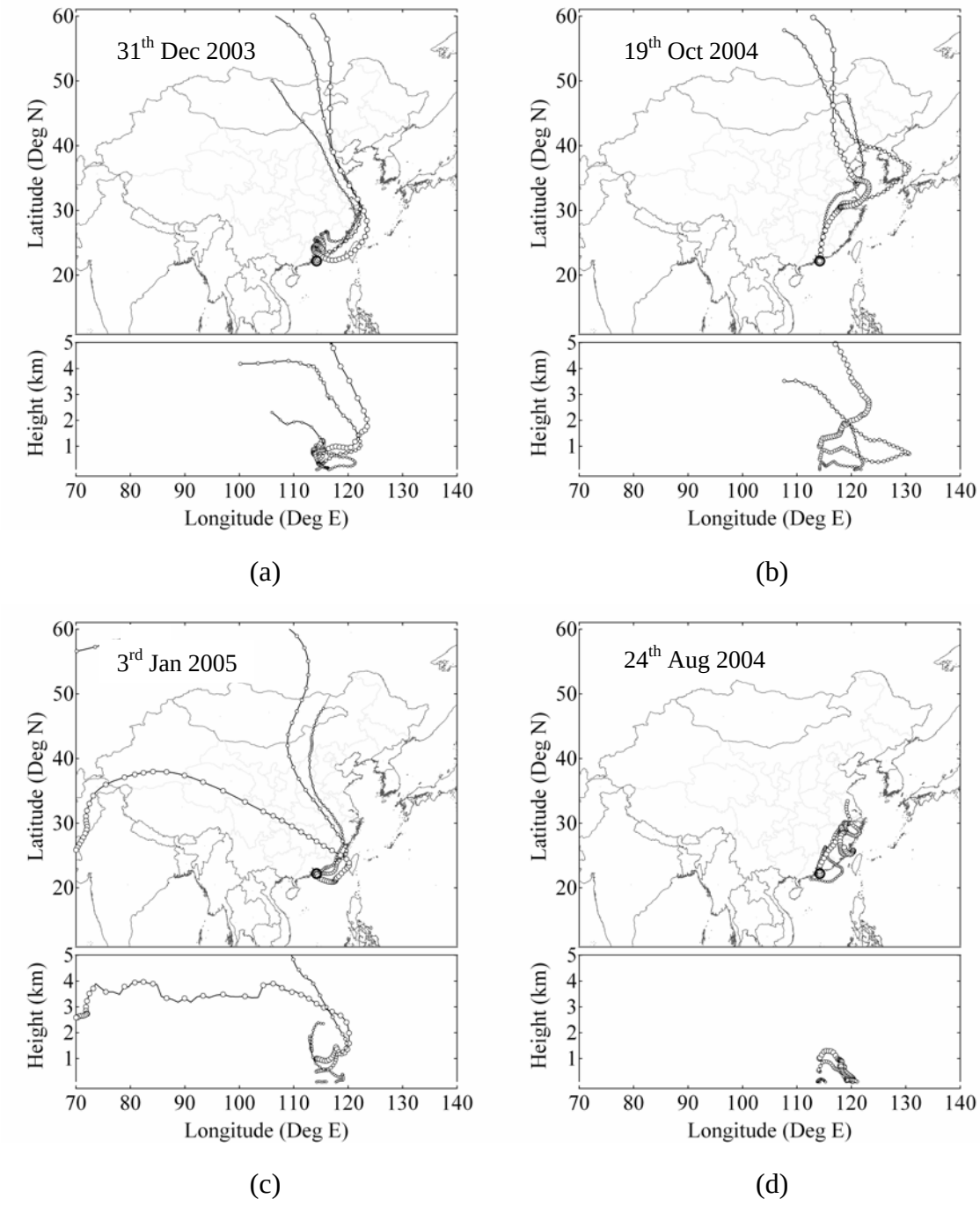
In Guangzhou, the mean concentrations of Cd, Cu, Mn and Pb ($P<0.01$) and Cr, Fe and Zn ($P<0.05$) were statistically different under different air masses. The highest mean concentrations of Cd, Cr, Cu, Fe, Mn, Pb and Zn were found in CT. The significant enrichment of these metals, particularly Cd, Cu, 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 ($P>0.05$).

4.5.3 Episode 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 4-1a-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, 500 and 1000 m) over the sites are shown in Figure 4-6.

Figure 4-6: Back trajectory plots (with increasing marker sizes to represent levels at 100, 500 and 1000 m, respectively) on the episodic days with elevated heavy metal concentrations



Elevated heavy metal concentrations were observed on 31st December 2003 at both PU and HT (see Fig 4-1a-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 4-6a 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 4-1a-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 4-6b-c). On the 24th August 2004, elevated heavy metal concentrations were observed at PU and HT (see Figure 4-1a-b) during the summertime. Figure 4-6d 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 4-1a-b).

4.6 Heavy metal concentrations in $PM_{2.5}$

To further elucidate the distribution of metals in different particle size, $PM_{2.5}$ samples were collected at the urban site, the Sun Yet-sen (Zhongshan) University, Guangzhou (ZU), which is at the same location as the previous sampling (see Figure 3-3 in Chapter 3). A total of 58 samples were collected on a weekly basis over one year period from May 2005 to May 2006. The annual mean elemental concentrations of Al, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn $PM_{2.5}$ in urban areas of Guangzhou are summarised in Table 4-6. The annual average trace metal concentrations of $PM_{2.5}$ in urban areas of Guangzhou were compared to other major cities in the world (see Table 4-7). The $PM_{2.5}$ in Guangzhou had the highest mean concentrations of Pb, V and Zn than the urban areas in the European and North America (Chow *et al*., 1993; Gao *et al*., 2002; Rodríguez *et al*., 2004; Hueglin *et al*., 2005; Zereini *et al*., 2005). The concentration of Ni were higher than most of the urban cities, and was comparable to an urban site, Bakersfield in California, the United States (Chow *et al*., 1993). This shows the severity of the trace metal pollution in the urban areas of Guangzhou, which has significant implication on human health and the environment.

Table 4-6: The annual mean concentrations of major and trace elements in $PM_{2.5}$ in urban areas of Guangzhou

(ng/m^3)	Al	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	V	Zn
Mean	520	5.01	0.44	2.78	71.8	447	128	23.6	12.5	196	28.9	477
S.D.	627	3.50	0.39	2.55	58.8	475	119	15.4	8.26	105	23.1	266

Table 4-7: Comparison of the annual average trace metal concentrations of $PM_{2.5}$ in urban areas of Guangzhou and other major cities in the world

(ng/m^3)	n	Cd	Co	Cr	Cu	Ni	Pb	V	Zn	Reference
China										
Guangzhou (2005-2006)		5.01	0.44	2.78	71.8	12.5	196	28.9	477	Present study
Taiwan										
Taichung	23	4.3	-	33.5	11.5	11.8	283.1	-	177.8	Fang *et al*. (2003)
Germany										
Frankfurt (main street) (2001-2002)	60	0.3	0.8	16.3	101.5	7.3	32.6	3.2	105.6	Zereini *et al*. (2005)
Spain										
Barcelona (L'HO) (1999-2000)	63	-	-	6	49	6	120	9	162	Rodríguez *et al*. (2004)
Switzerland										
Bern (1998-1999)	79	0.21	-	-	8.7	1.3	30	1.6	-	Hueglin *et al*. (2005)
Zurich-Kaserne (1998-1999)	79	0.31	-	-	6.1	3.1	21	1.1	-	Hueglin *et al*. (2005)
USA										
New York – New Brunswick (urban) (1998-1999)	62	0.15		1.4	7.3	4.0	6.6	3.6	18	Gao *et al*. (2002)
New York – Sandy Hook (coastal/urban) (1998-1999)	59	0.14		1.3	4.7	4.0	4.9	5.4	16	Gao *et al*. (2002)
California – Stockton (1988-1989)	35	-	-	5.2	140	4.2	41	4.5	110	Chow *et al*. (1993)
California – Fresno (1988-1989)	35	-	-	1.6	69	2.3	51	3.4	69	Chow *et al*. (1993)
California – Bakersfield (1988-1989)	33	-	-	5.6	140	15	43	9.7	110	Chow *et al*. (1993)

4.7 Elemental associations in $PM_{2.5}$

The Principal Component Analysis (PCA) was carried out to further investigate on the elemental associations among trace and major elements of the $PM_{2.5}$ samples. Elements that are strongly associated may share similar geochemical properties and/or originated from common sources. The results of the PCA are presented in Table 4-8. The first principal component (PC1) explained 57% of the total variance, while the second component (PC2) accounted for 13% of the variance. The third (PC3) and forth (PC4) components accounted for 10% and 7% of the total variance, respectively.

In the Guangzhou fine particulate matter, elements such as Cd, Cu, Mn, Pb and Zn were closely associated in the first component (PC1). This may indicate the influence of anthropogenic inputs of these elements into the particulate matter in Guangzhou. Trace metals, such as Cd and Zn, have natural associations in rock minerals. Moreover, Cd is also a by-product of lead and zinc production as shown by the close association in fine particulate matter. The second principal component (PC2) included geogenic elements such as Al, Fe and Mg, which may depict the association of these elements originated from the parental rock materials. Nickel, V and Co were found to be closely associated in the third principal component (PC3), suggesting they may be originated from the same source. Nickel and vanadium are markers for residual oil combustion (Chow and Watson, 2002). The close association between Ni and V evidenced that oil combustion could be the source of these elements. Since the first principal component accounted for most of the variability (over 50%) in the data. Hence, anthropogenic activities were shown to be the dominant source of the fine

particulate matter in Guangzhou, while natural sources also contribute significantly, particularly to the geogenic elements such as Al, Fe and Mg in the $PM_{2.5}$.

The elemental association in TSP was also analysed using the PCA method and the results are shown in Table 4-9. Trace elements, such as Cd, Cr, Cu and Pb, were found to be closely associated with the major elements such as Al, Fe, Mg and Mn in PC1, probably indicated the influence from the natural crustal materials. Similarly, PC2 generally depicted the elemental associations between heavy metals such as Ni, V and Zn with major elements such as Al, which may reflect the influence of some anthropogenic sources. Co was univocally isolated in PC3. As TSP contained a greater fraction of coarse particles, heavy metals were found to strongly associate with the geogenic elements, suggesting the natural soil materials also significantly contributed to the heavy metals in the TSP of Guangzhou.

Table 4-8: The matrix of principal component analysis loadings of trace and major elements in $PM_{2.5}$ of Guangzhou

	Principal Component			
(n=58)	PC1	PC2	PC3	PC4
eigenvalue, λ	6.9	1.6	1.2	0.8
Al	0.303	<u>0.811</u>	0.310	0.284
Cd	<u>0.862</u>	0.101	0.272	0.065
Co	0.333	0.567	<u>0.610</u>	0.346
Cr	0.179	0.159	-0.005	<u>0.910</u>
Cu	<u>0.811</u>	0.255	-0.057	0.205
Fe	0.370	<u>0.702</u>	0.305	0.403
Mg	0.151	<u>0.932</u>	-0.008	-0.006
Mn	<u>0.646</u>	0.377	0.416	0.283
Ni	0.137	0.209	<u>0.951</u>	0.013
Pb	<u>0.738</u>	0.532	0.217	-0.055
V	0.254	0.044	<u>0.932</u>	-0.019
Zn	<u>0.776</u>	0.153	0.399	0.224

Note: Numbers underlined are the dominant elements in different PCs

Table 4-9: The matrix of principal component analysis loadings of trace and major elements in TSP of Guangzhou

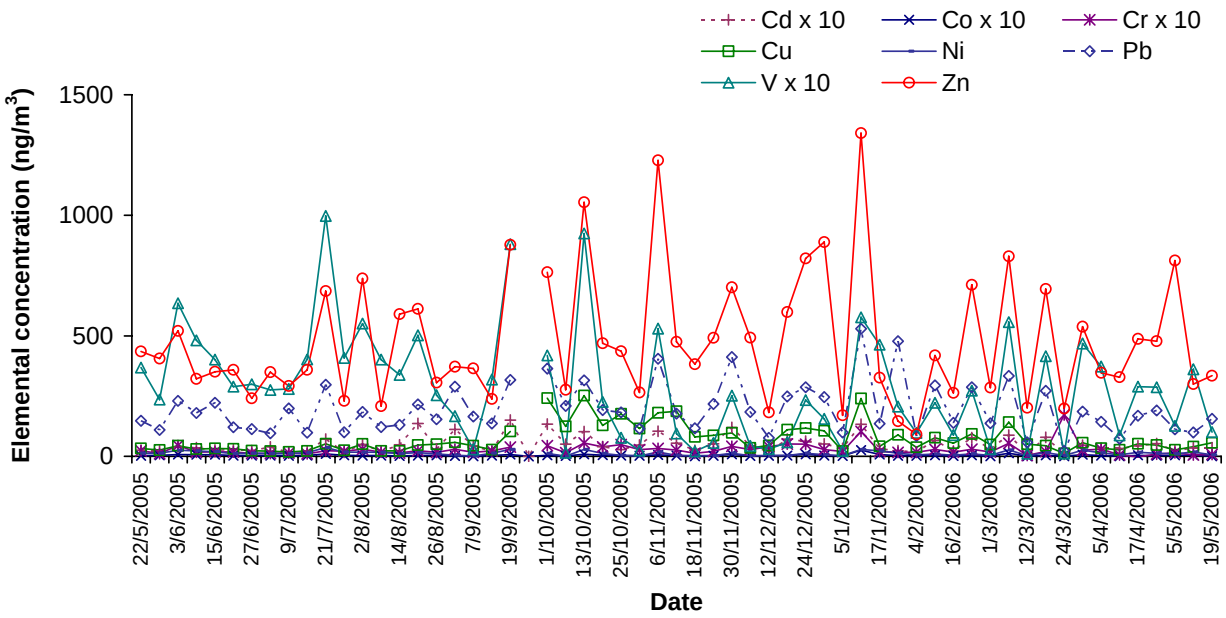
	Principal Component		
(n=22)	PC1	PC2	PC3
eigenvalue, λ	8.7	1.5	0.6
Al	<u>0.689</u>	<u>0.662</u>	0.241
Cd	<u>0.740</u>	0.575	0.056
Co	0.229	0.003	<u>0.960</u>
Cr	<u>0.811</u>	0.102	0.465
Cu	<u>0.788</u>	0.537	0.0.54
Fe	<u>0.847</u>	0.412	0.246
Mg	<u>0.850</u>	0.340	0.273
Mn	<u>0.679</u>	0.452	0.297
Ni	0.282	<u>0.900</u>	-0.080
Pb	<u>0.869</u>	0.432	0.026
V	0.482	<u>0.814</u>	0.046
Zn	0.278	<u>0.876</u>	0.125

Note: Numbers underlined are the dominant elements in different PCs

4.8 Temporal variations in heavy metal concentrations

Guangzhou is located at the coastal areas of South China, and hence influenced by the Asian monsoon system which brings the northeast winds during winter period and the southwest wind during the summer period. However, as discussed earlier, the seasonal variations in heavy metals concentrations of TSP in Guangzhou was not distinguished due to the predominance of local emission sources. In contrast, some seasonal trends were observed in most of the heavy metals in the $PM_{2.5}$ (see Figure 4-7). Figure 4-7 shows the plot of the time-series of Cd, Co, Cr, Cu, Ni, Pb, V and Zn over the annual cycle. The concentrations of trace metals such as Cd, Cu, Pb and Zn were found to be higher during Sep 2005 – Feb 2006 which was during the wintertime, and lower during May 2005 – Aug 2005 and Mar 2006 – May 2006, which were the summer seasons (Figure 4-7). The concentrations of Ni and V were observed to be highly varied, and those of Co and Cr remained at low values throughout the annual cycle. No distinct seasonal trend was observed in the concentrations of Ni, V, Co and Cr.

Figure 4-7: Trace elemental concentrations of fine particulate matter ($PM_{2.5}$) in urban areas of Guangzhou, South China



4.9 Enrichment factor

The enrichment factor is used to evaluate the enrichment of trace elements in aerosols with respect to the background crust materials. Due to its natural abundance in crustal materials, Fe is used as a reference material in the calculations of the enrichment factors. The enrichment factors (EF) are calculated as follows:

$$EF = [E/Ref]_{air}/[E/Ref]_{upper\ crust}$$

where E is the targeting element, Ref refers to the reference material; and $[E/Ref]_{air}$ and $[E/Ref]_{crust}$ refer to the concentration ratios of element E to Fe in $PM_{2.5}$ and in the upper crust, respectively. The elemental concentrations of the upper crust materials used in the calculation were cited from Wedepohl (1995).

Table 4-10 shows the enrichment factors for major elements including Al, Fe, Mg, Mn and Cd, Co, Cr, Cu, Ni, Pb, V and Zn. A graph is also plotted to compare the enrichment ratios of the elements (see Figure 4-8). The EF close to unity suggests that the element is dominantly from crustal materials or the anthropogenic sources contribute only a minor fraction. As shown in Figure 4-8, elements such as Cd, Cu, Ni, Pb, V and Zn has very high EFs, ranging between 46 for Ni to 3400 for Cd. These elements were highly enriched in $PM_{2.5}$ as compared to the continental crustal materials and strongly suggested that they were originated from some anthropogenic sources, such as vehicular and industrial emissions. On the other hand, major elements such as Al, Mg and Mn and trace metals such as Co, Cr probably had a natural origin, such as the crustal materials.

Figure 4-8: Enrichment factors of major and trace elements in $PM_{2.5}$ of Guangzhou

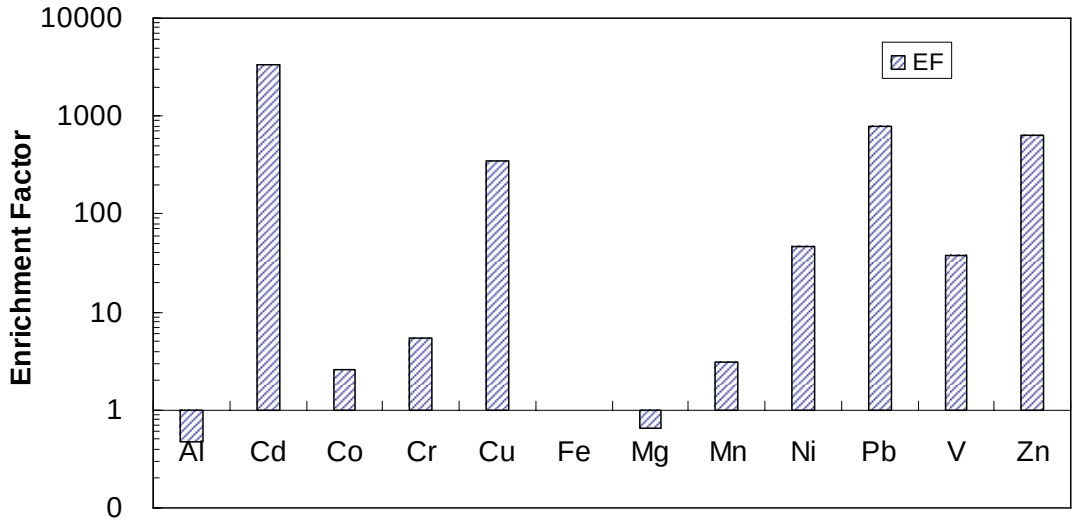


Table 4-10: Enrichment factors of major and trace elements in $PM_{2.5}$ of Guangzhou (relative to Fe)

	Al	Cd	Co	Cr	Cu	Mg	Mn	Ni	Pb	V	Zn
EF	0.47	3390	2.62	5.49	350	0.66	3.09	46.3	797	37.6	634

4.10 Ratios of metal concentrations in $PM_{2.5}$/TSP

The annual average trace metal concentrations in $PM_{2.5}$ in Guangzhou, South China, were compared with those in TSP collected previously at the same location (ZU). The average concentration ratios between trace metals in $PM_{2.5}$/TSP were shown in Table 4-11. The results showed that trace elements, including Cd, Cu, Ni, Pb and V, were highly enriched in the $PM_{2.5}$ fraction. These elements were probably originated from anthropogenic sources since they were associated with fine particulate matter (< 2.5 μm). The results were compared with the average concentration ratios of $PM_{2.5}/PM_{10}$ in the urban areas of Hong

Kong, which is located in the south of Guangzhou (Ho *et al*., 2003). Similarly, the trace metals, such as Ni, Pb and V in the urban areas of Hong Kong were found to be highly enriched in the finer fraction. However, lower $PM_{2.5}$/TSP ratios were observed for Zn in Guangzhou as compared to those in Hong Kong. As discussed earlier, the Zn concentrations in Guangzhou aerosols (TSP) were relatively high compared with urban areas in the other major cities in the world, such as Hong Kong, Tokyo, Ho Chi Minh City and Taichung and were comparable to Beijing. The low $PM_{2.5}$/TSP ratios of Zn and the high Zn concentrations in both $PM_{2.5}$ and TSP in urban Guangzhou suggested that a large fraction of the Zn were associated with larger particles (> 2.5 μm).

Table 4-11: Average concentration ratios of trace metals in $PM_{2.5}$/TSP in urban areas of Guangzhou and $PM_{2.5}/PM_{10}$ in urban areas of Hong Kong

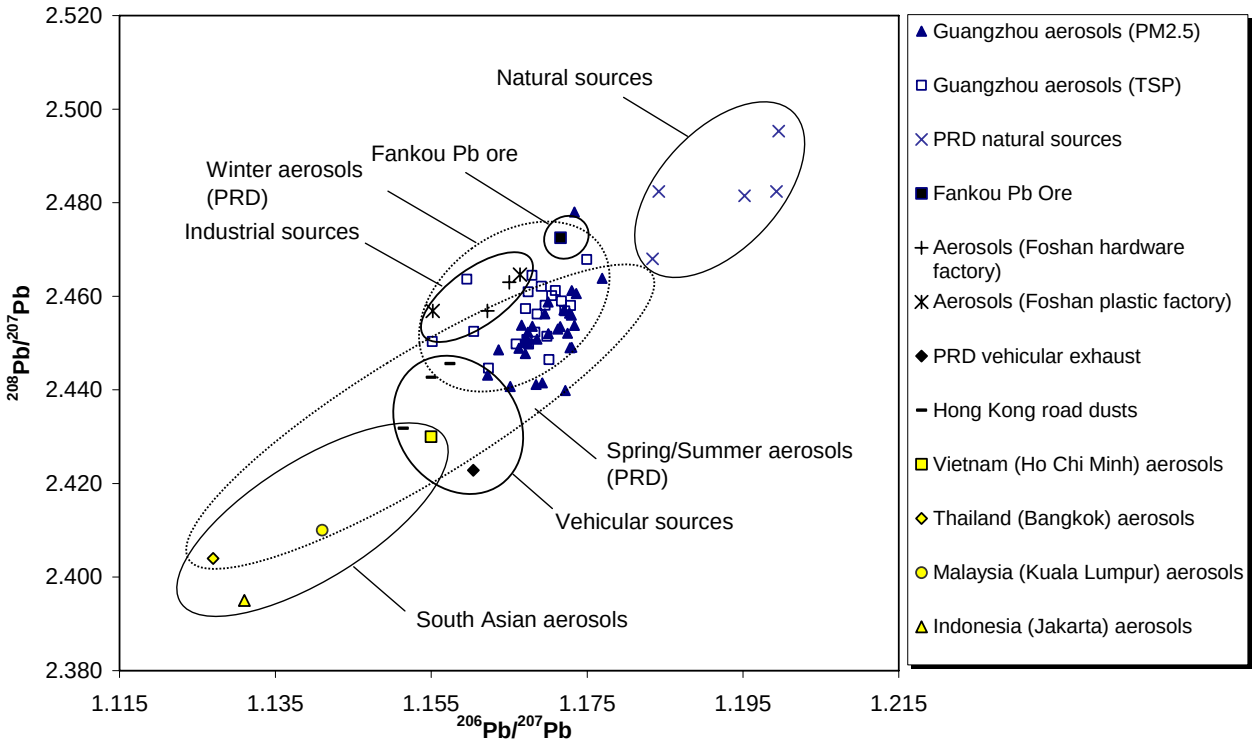
(%)	Al	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	V	Zn
$PM_{2.5}$/TSP[a,b] (Guangzhou)	15.4	63.8	10.8	13.3	87.2	15.6	20.1	27.8	68.0	72.8	64.4	40.1
$PM_{2.5}/PM_{10}$[c] (HK-PolyU)	26	-	-	36	49	30	31	43	62	78	87	83
$PM_{2.5}/PM_{10}$[c] (HK-KT)	55	-	-	78	58	61	51	76	63	91	86	83

Note: [a] Numbers underlined are the elements dominating in $PM_{2.5}$ fraction
[b] the present study
[c] Ho *et al*. (2003)

4.11 Pb isotopic composition of $PM_{2.5}$ in Guangzhou

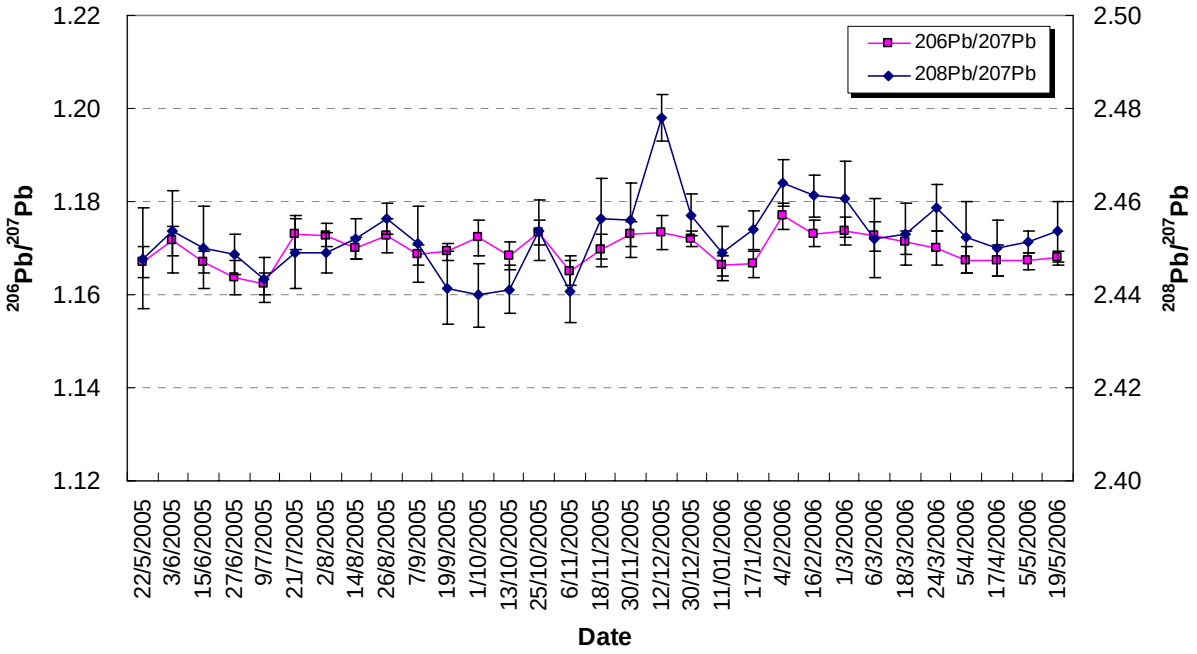
The annual average concentrations of $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios $PM_{2.5}$ at ZU were 0.0640, 1.1699 and 2.4524, respectively. The Pb isotopic ratios of $PM_{2.5}$ in Guangzhou were compared with those of TSP in Guangzhou, the aerosols in the PRD region (from the present study - see Section 4.4), as well as the natural and anthropogenic sources in the PRD region (see Figure 4-9). The Pb isotopic compositions of $PM_{2.5}$ in Guangzhou were found to be closely resembled to those of Pb ore and from industrial sources in the PRD region (see Figure 4-9). Similar to the TSP, the Pb inputs to the fine particulate matter were attributed to the use of Pb from local ore (e.g. the Fankou Pb ore) in the region.

Figure 4-9: Comparison of Pb isotopic ratios in urban fine particulate matter ($PM_{2.5}$) of Guangzhou during the period May 2005 – May 2006



The temporal variations in the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of $PM_{2.5}$ at ZU are shown in Figure 4-10. The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios exhibited less temporal variability. This implied that the Pb inputs in the aerosols may come from similar sources. However, as discussed earlier, the concentrations of trace metals such as Cd, Cu, Pb and Zn exhibited some seasonal variability, with higher metal concentrations during winter time (Sep 2005 – Feb 2006), and lower values during the summer period (May 2005 – Aug 2005 and Mar 2006 – May 2006). This showed that the high metal concentrations were probably attribute to greater emissions of the trace elements during the winter time compared to the summer season, but came from similar source (e.g. local emissions) as reflected by the similar Pb isotopic signature. Guangzhou was located in the inland areas of South China and the seasonal change in the height boundary layer is relatively significant. The enrichment of the trace metals in the $PM_{2.5}$ observed during wintertime in Guangzhou may be attributed to the relatively low boundary layer during winter period causing poor dispersion of metal pollutants.

Figure 4-10: The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of fine particulate matter ($PM_{2.5}$) in urban areas of Guangzhou, South China



4.12 Carbonaceous species in TSP

The organic carbon (OC) and elemental carbon (EC) in the TSP samples collected at urban and suburban areas of Hong Kong (PU and HT) and Guangzhou (ZU and BY) were also analysed. The carbonaceous species provides further information on the sources of the aerosols.

4.12.1 OC and EC concentrations

Table 4-12 shows the results of the OC and EC measurements for the TSP in urban and suburban areas of Hong Kong (PU and HT) and Guangzhou (ZU and BY) over one-year period. EC has a chemical structure similar to impure graphite, which originates primarily from direct emissions of particles, predominantly during combustion. In contrast, OC can be originated from primary anthropogenic sources and/or produced from chemical reactions in the atmosphere (Cao *et al.*, 2004). The annual average concentrations of OC and EC

at PU were 10.4 and 4.71 μg/m^3, respectively, and those at HT were 6.96 and 2.04 μg/m^3, respectively. In comparison with Hong Kong, Guangzhou were found to have higher concentrations of the carbonaceous species, with the annual average concentrations of OC and EC of 25.8 and 11.6 μg/m^3, respectively at ZU, 17.2 and 7.96 μg/m^3, respectively at BY. The high carbonaceous concentrations observed in both the urban and suburban areas suggested the severe atmospheric pollution in Guangzhou city and its surrounding areas, probably due to the high traffic flows and industrial emissions.

Table 4-12: The annual average concentrations of OC and EC in urban and suburban areas of Hong Kong and Guangzhou

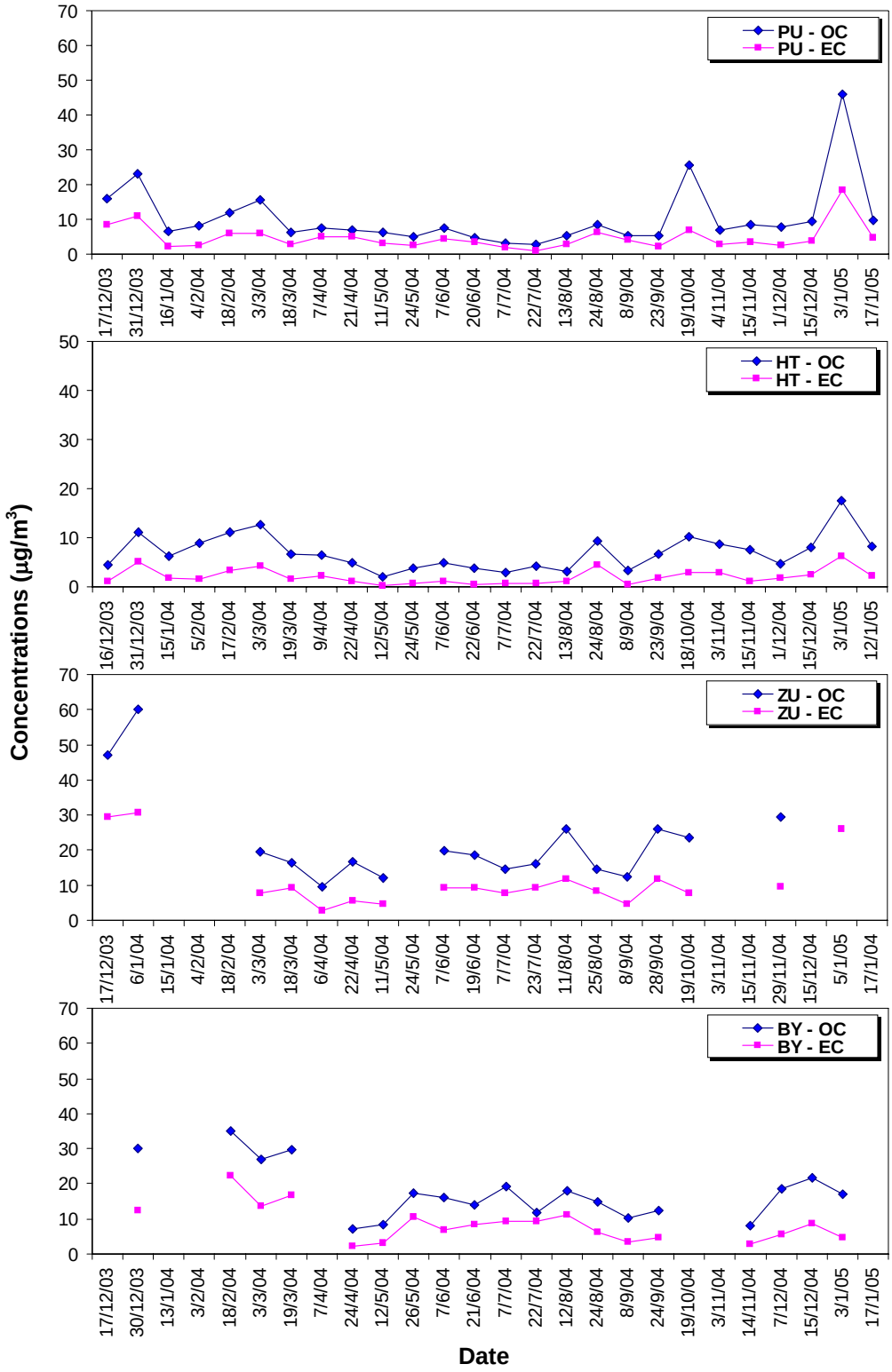
		OC (μg/m^3)	EC (μg/m^3)	OC/EC
Hong Kong	PU (n=26)	10.4±9.11	4.71±3.56	2.20±0.62
	HT (n=26)	6.96±3.59	2.04±1.56	4.49±2.10
	Average (n=52)	8.66±7.07	3.37±3.04	3.35±1.92
Guangzhou	ZU (n=18)	25.8±18.9	11.4±8.32	2.37±0.58
	BY (n=19)	17.7±7.96	8.50±5.19	2.37±0.69
	Average (n=37)	21.6±14.7	9.93±6.96	2.37±0.63

4.12.2 Temporal variations in OC and EC concentrations

Figure 4-11 shows the temporal variations in OC and EC concentrations at the four sites over the 1-year period. More distinct seasonal variations were observed in the OC and EC concentrations at PU and HT. Similar to the results for the heavy metal concentrations measured at the same locations, the carbonaceous species at PU and HT had higher values during the winter time and lower values

during the summer seasons. The enrichments of OC and EC during winter period were attributed to the long-range transport of air pollutants from the northern inland areas of China (including PRD). In contrast, the OC and EC concentrations at ZU and BY exhibited less variability and remained high throughout the year (see Figure 4-11). This indicated that the OC and EC in urban and suburban areas of Guangzhou may be dominated by local sources.

Figure 4-11: OC and EC concentrations of particulate matter (TSP) in urban and suburban areas of Hong Kong and Guangzhou, South China



4.12.3 Relationship between OC and EC

The origin of carbonaceous particulate matter can be estimated based on the relationship between OC and EC. The OC/EC ratio exceeding 2.0 has been used to identify secondary organic aerosols (Chow *et al*., 1993b, 1996). Table 4-12 shows that HT was found to have the highest average OC/EC ratio (4.49). The OC/EC ratios at PU, ZU and BY were relatively low, which were 2.20, 2.37 and 2.37, respectively. The significantly high OC/EC ratio observed at HT (>2.0), strongly suggested that a large fraction of the organic carbon at HT came from secondary sources. As indicated earlier, HT was located at a coastal area which is subjected to the influence of long-range transport of pollutants from northern regions of China (including PRD) during the winter time. This gave further evidence that the atmospheric particulate matter reaching HT may originate from distant sources.

Previous study has shown that low OC/EC ratios were depicted in $PM_{2.5}$ (1.7) and PM_{10} (1.8) at PU (Cao *et al*., 2003). Since PU is located adjacent to a major road leading to a cross-harbour tunnel, direct vehicular emission of primary OC and EC accounts for the major compositions in the ambient $PM_{2.5}$ and PM_{10}. Cao *et al*. (2003) also reported that the OC/EC ratios in Guangzhou were relatively higher, which were 2.1-2.9 for $PM_{2.5}$ and 2.4-2.9 for PM_{10} at several sites in Guangzhou, showing that there was relatively higher secondary organic carbon (SOC). In the present study, the relatively lower OC/EC ratios observed at PU, ZU and BY could reflect the greater influence of primary OC and EC emissions from direct vehicular exhaust and other urban sources. Nevertheless, the annual average OC/EC ratios at PU, ZU and BY exceed 2.0, which may indicate the

influences of some secondary sources.

Figure 4-12a-d shows the regression lines plotted for the OC and EC concentrations at the four sites. Generally good correlations were observed between OC and EC at all the four sites (R^2>0.80). This shows that the OC and EC in the urban and suburban areas of Hong Kong and Guangzhou originated from similar sources. The scatter plots show that the OC and EC concentrations at ZU and BY (R^2=0.8097, R^2=0.8119, respectively) were less linearly correlated compared to those at PU and HT (R^2=0.8823, R^2=0.8476, respectively) (see Figure 4-12c-d). This suggested that the OC and EC at ZU and BY might have more varied sources. As discussed earlier (in Section 4.5), the aerosols at HT were strongly influenced by the long-range transport of pollutants from northern inland areas (including PRD). Hence, the high OC/EC ratio and correlation between OC and EC at HT suggested that the carbonaceous species may be originated from some distant sources in northern China and the PRD region, and transported to the downwind areas of Hong Kong. The sources of OC and EC at PU may be due to the influence of both fresh vehicular exhaust and regional pollution as indicated by the relatively low OC/EC ratio but good correlation between OC and EC. The relatively low correlation between OC and EC at ZU and BY indicated the presence of other sources.

Furthermore, the time series the OC/EC ratios at PU, HT, ZU and BY are depicted in Figure 4-13. There was no distinguished pattern in the temporal variations of the OC/EC ratios at PU, ZU and BY. At HT, the OC/EC ratios were relatively high compared at the other sites, especially during May 2005 – July 2005. This period was during summer time and the southerly winds prevailed. As

discussed earlier, the air mass reaching the coastal areas of Hong Kong was originated from the sea. The high OC/EC ratios showed the presence of secondary organic aerosols. Atmospheric formations of secondary organic compounds were dominant sources of OC in HT during the summer time. Although the OC/EC ratios were lower during the winter season, but they generally >2.0 showing that the significant amount of secondary organic compounds were present. HT was located at the southern part of the major urban centre of Hong Kong Island and Kowloon. The relatively lower ratios during the winter period could attribute to the influence of some anthropogenic emissions of primary OC and EC from the urban centres (at the northern part of HT), which was transported to the southern coast by the northerly winds. There was less variability in the OC/EC ratios at ZU and BY. The OC/EC ratios at ZU and BY exceeded 2.0 occasionally, depicting that the carbonaceous particulate matter was originated from secondary sources.

Figure 4-12: Relationship between OC and EC concentrations in particulate matter (TSP) in urban and suburban areas of Hong Kong and Guangzhou

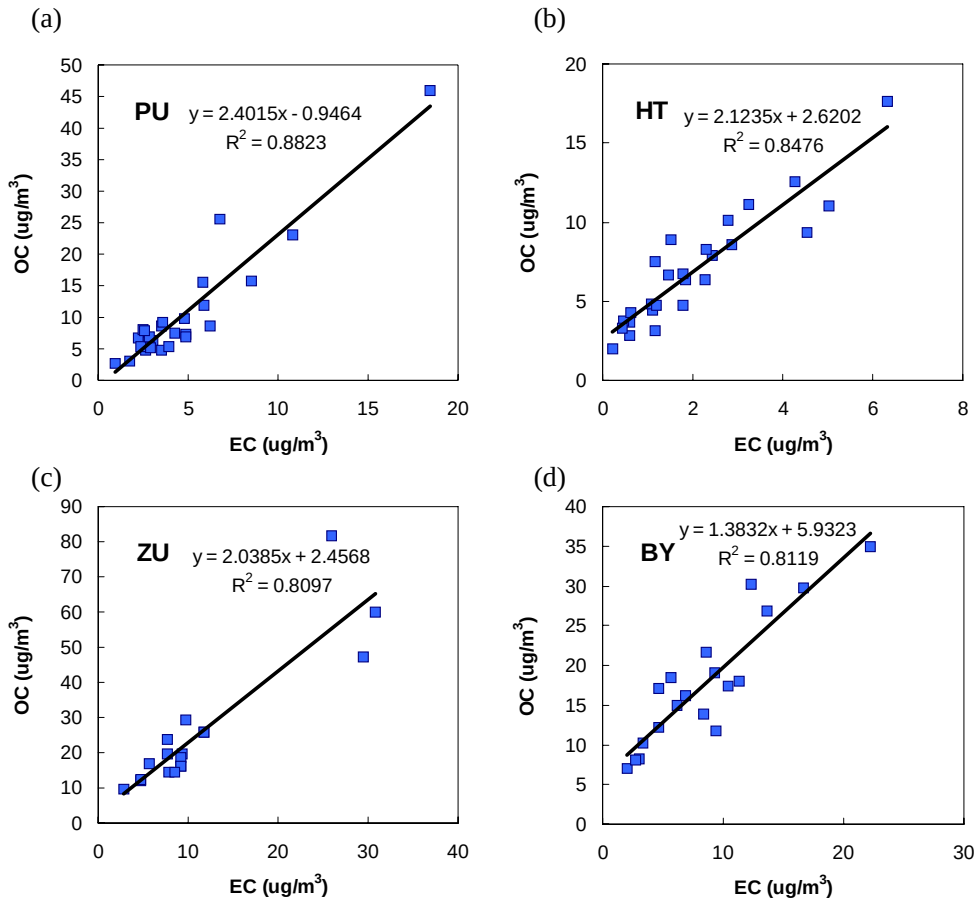
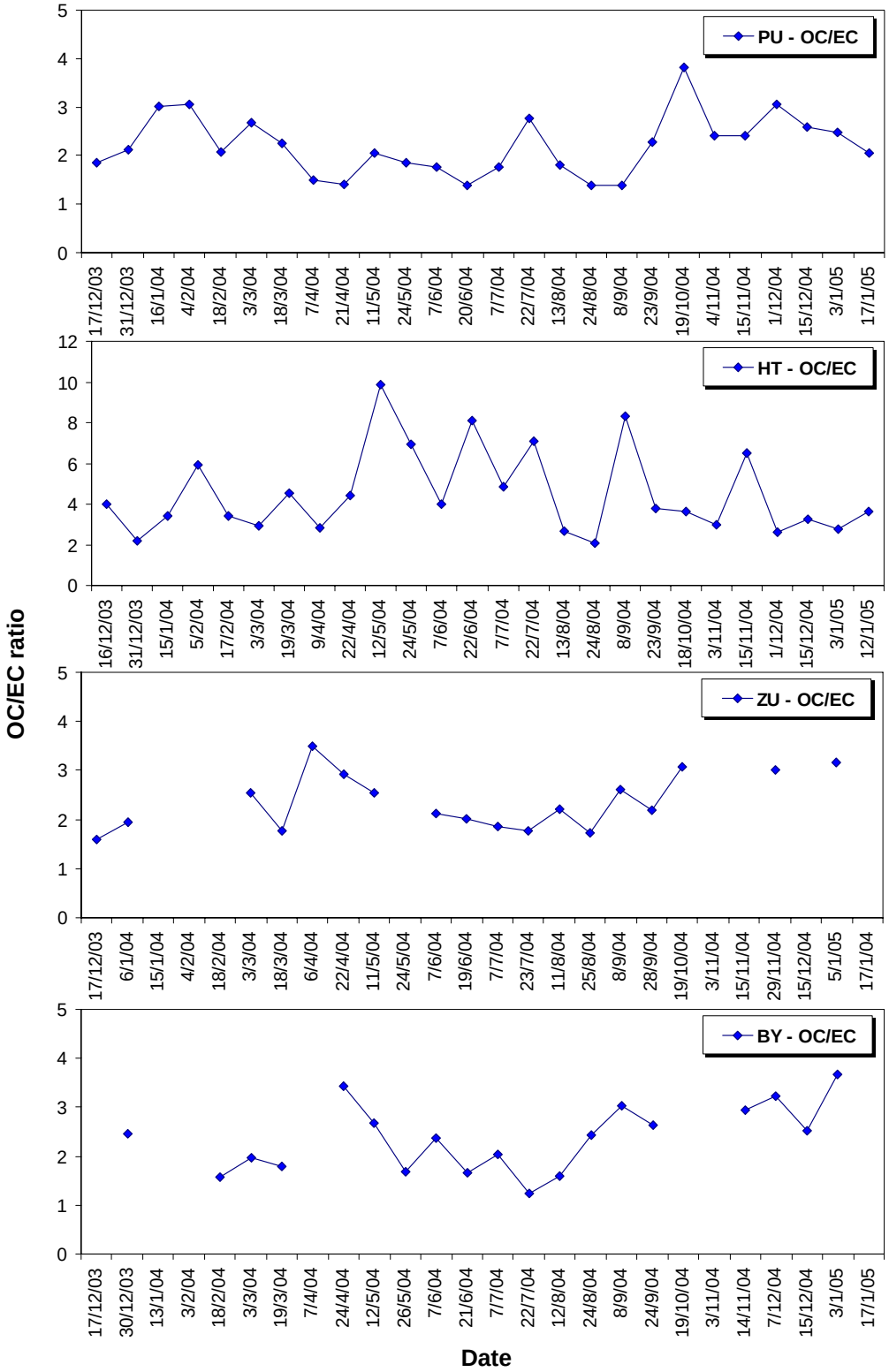


Figure 4-13: The temporal variation in OC/EC ratios in urban and suburban particulate matter (TSP) of Hong Kong and Guangzhou



4.13 Summary

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 trace metals during the winter monsoon period, and lower metal 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.

Chapter 5 − Atmospheric dry and wet depositions of trace metals in the Pearl River Delta region, South China

The major objectives of the present study are (1) to evaluate the spatial and temporal variation of atmospheric trace metal depositions in the PRD region, (2) to elucidate the major pathways of metal contaminants, and (3) to study the potential sources of atmospheric trace metal deposits using Pb isotopic composition.

5.1 Annual mean deposition flux

5.1.1 Dry deposition flux

The dry deposition fluxes of heavy metals were calculated by dividing the measured mass of heavy metals by the sampling area and duration. The annual mean dry deposition fluxes of Al, Cd, Co, Cr, Cu, Fe, Mg, Mn, Pb, V and Zn at the 16 sampling sites and the overall annual mean dry deposition fluxes in the PRD are summarised in Table 5-1. To compare the mean dry deposition fluxes of elements in the urban, suburban and rural areas, the Student T-test (Independent samples) was performed by assuming equal variance at a 95% confidence level. The results from T-test are shown in Table 5-2. The mean deposition fluxes of Cd, Cu, Fe, Pb, V and Zn in urban and suburban areas were found to be statistically different ($P<0.01$) from that in rural areas. Moreover, the deposition flux of Al in urban area were significantly different ($P<0.05$) from that in rural areas, but no significant difference was found between the dry deposition fluxes of most elements in the urban and suburban areas, except Mn ($P<0.05$) (Table 5-2). Dry deposition fluxes of heavy metals, including Cd, Cu, Pb, V and Zn in

the urban and suburban areas were higher than that in rural areas (Table 5-1). This showed the dominance of these elements in the dry depositions in urban and suburban areas, most probably originated from anthropogenic sources.

Table 5-1: Annual average dry elemental fluxes (mg/m^2/year) at the 16 sites and the total average in the PRD region

Location	Site condition	n	Al	Cd	Co	Cr	Cu	Fe	Mg	Mn	Pb	V	Zn
QY	rural	7	413	0.06	0.17	6.12	2.58	501	45.3	5.90	6.81	1.31	12.6
JM	rural	7	1516	0.07	0.29	7.01	4.38	967	140	11.9	6.08	4.01	17.8
ZS	rural	7	1972	0.09	0.46	10.34	5.10	1172	119	15.2	10.5	3.00	23.3
WT	rural	7	359	0.03	0.21	5.62	1.06	275	50.0	5.09	1.68	0.57	6.02
TM	rural	7	512	0.03	0.31	3.32	1.63	265	39.4	4.34	1.96	0.53	3.92
YM	rural	7	118	0.01	0.17	4.65	1.11	111	21.4	2.90	0.66	0.19	2.45
HT	rural	7	260	0.03	0.97	27.1	2.93	391	354	26.1	0.78	0.41	3.44
TO	rural	7	425	0.04	0.23	8.04	2.62	389	43.9	6.84	2.60	0.75	8.10
HH	rural	7	178	0.02	0.16	6.09	0.85	194	37.5	4.37	0.97	0.38	3.17
NH	suburban	7	1048	0.09	0.29	7.33	5.41	681	74.8	9.42	7.91	2.42	16.0
SD	suburban	7	1159	0.11	0.48	11.8	10.4	966	107	11.1	15.0	3.80	27.2
BY	suburban	7	742	0.08	0.33	6.46	3.74	768	60.4	8.30	8.09	2.22	32.2
DH	urban	7	1339	0.15	0.67	8.01	8.05	1107	102	14.9	15.4	3.07	32.6
ZU2	urban	7	1027	0.12	0.44	10.1	7.91	1041	98.7	13.0	13.8	2.85	33.2
ZU3	urban	7	1065	0.12	0.63	10.0	8.88	1153	107	14.8	14.6	3.51	37.2
PU	urban	7	644	0.05	0.37	7.81	4.39	563	64.8	7.99	4.02	0.93	19.0
PRD	(16 sites)												
Overall	Mean	112	799	0.07	0.39	8.74	4.44	659	91.5	10.1	6.93	1.87	17.4
Rural	Mean	63	639	0.04	0.33	8.70	2.47	474	94.4	9.19	3.56	1.24	8.98
Suburban	Mean	21	983	0.09	0.37	8.54	6.51	805	80.7	9.59	10.3	2.81	25.1
Urban	Mean	28	1019	0.11	0.53	8.98	7.31	966	93.0	12.7	12.0	2.59	30.5

Table 5-2: Comparison between dry deposition fluxes of major and trace elements in urban, suburban and rural areas

	Urban vs Rural			Suburban vs Rural			Urban vs Suburban		
Dry deposition	Degree of freedom	T-value	Sig.	Degree of freedom	T-value	Sig.	Degree of freedom	T-value	Sig.
Al	89	2.201	0.030*	82	1.720	0.089	47	0.266	0.792
Cd	89	3.717	0.000**	82	4.863	0.000**	47	1.268	0.211
Co	89	1.605	0.112	82	0.266	0.791	47	1.811	0.077
Cr	89	0.135	0.893	82	-0.066	0.948	47	0.243	0.809
Cu	89	6.923	0.000**	82	5.349	0.000**	47	0.636	0.528
Fe	89	4.702	0.000**	82	2.966	0.004**	47	1.369	0.177
Mg	89	-0.030	0.976	82	-0.249	0.804	47	1.141	0.259
Mn	89	1.189	0.237	82	0.122	0.904	47	2.329	0.024*
Pb	89	6.274	0.000**	82	5.432	0.000**	47	0.760	0.451
V	89	3.533	0.001**	82	3.708	0.000**	47	-0.503	0.617
Zn	89	6.529	0.000**	82	4.963	0.000**	47	1.016	0.315

*P<0.05

**P<0.01

5.1.2 Wet deposition flux

Similarly, the wet deposition fluxes were obtained by dividing the measured mass of the elements by the area of the sampling area and duration. The annual mean wet deposition fluxes at the 16 sites and the overall annual mean wet deposition fluxes in the PRD region are shown in Table 5-3. The results of the T-test are tabulated in Table 5-4. The mean wet depositions fluxes of Al, Cd, Pb and Zn in urban and suburban areas were found to be statistically different ($P<0.01$) from that in rural areas. The wet deposition fluxes of heavy metals, including Cd, Pb and Zn, in urban and suburban areas were higher than that in rural areas, indicating the dominance of these elements in urban and suburban areas (Table 5-4). The mean wet depositions fluxes of Cu and V in suburban areas were significantly different ($P<0.01$) from rural areas, but no significant difference was depicted between the fluxes of these elements in urban and rural areas. The mean wet deposition fluxes of Cu and V in suburban areas were found to be higher than that in rural areas (Table 5-3). The results depicted that there were high enrichments of Cu and V in the wet deposition fluxes in suburban areas.

Table 5-3: Annual average wet elemental fluxes (mg/m^2/year) at the 16 sites and the total average in the PRD region

Location	Site condition	n	Rainfall (mm)	Al	Cd	Co	Cr	Cu	Fe	Mg	Mn	Pb	V	Zn
R-QY	rural	5	208	177	1.11	2.10	3.27	13.6	107	367	102	11.7	2.97	271
R-JM	rural	5	218	81	0.48	0.85	2.22	8.92	85.9	224	50.8	3.94	3.27	126
R-ZS	rural	5	214	146	0.73	1.61	6.35	12.9	168	220	51.1	16.8	1.01	138
R-WT	rural	5	191	55	0.37	1.86	3.79	10.5	140	172	32.9	3.91	0.54	47.2
R-TM	rural	5	185	58	0.36	2.41	7.20	7.55	91.2	276	47.3	4.09	0.95	52.6
R-YM	rural	5	198	32	0.14	1.49	1.09	6.67	64.2	191	27.6	1.52	0.47	85.1
R-HT	rural	5	181	29	0.15	3.72	14.0	14.0	301	1015	128	1.11	0.26	43.4
R-TO	rural	5	174	31	0.24	1.66	1.69	4.38	246	382	61.1	1.50	0.75	158
R-HH	rural	5	204	34	0.23	1.56	4.23	10.2	150	197	53.8	2.95	0.48	53.9
R-NH	suburban	5	205	158	0.84	1.53	2.51	13.9	140	268	69.9	7.67	4.62	211
R-SD	suburban	5	224	176	0.88	1.83	2.06	23.2	163	204	41.4	14.5	2.96	235
R-BY	suburban	5	243	242	1.14	1.26	3.78	20.6	145	339	61.7	24.4	3.26	1540
R-DH	urban	4	344	170	0.80	1.91	1.47	14.6	54.7	297	64.2	10.1	2.54	237
R-ZU2	urban	5	248	199	1.06	1.34	4.02	20.6	94.6	270	71.5	24.1	2.08	184
R-ZU3	urban	3	381	248	1.44	1.59	2.35	27.7	70.7	317	68.8	30.3	3.12	275
R-PU2	urban	5	244	71	0.29	1.19	8.67	6.55	43.8	199	43.4	4.55	0.49	227
PRD	(16 sites)													
Overall	Mean	77	223	115	0.62	1.75	4.38	13.1	132	308	60.7	9.68	1.82	242
Rural	Mean	45	197	71.5	0.42	1.92	4.87	9.86	150	338	61.6	5.28	1.19	108
Suburban	Mean	15	224	192	0.95	1.54	2.78	19.2	149	270	57.7	15.5	3.61	662
Urban	Mean	17	293	163	0.84	1.47	4.49	16.3	66.1	264	61.0	16.1	1.90	225

Table 5-4: Comparison between wet deposition fluxes of major and trace elements in urban, suburban and rural areas

	Urban vs Rural			Suburban vs Rural			Urban vs Suburban		
Wet deposition	Degree of freedom	T-value	Sig.	Degree of freedom	T-value	Sig.	Degree of freedom	T-value	Sig.
Al	60	3.339	0.001**	58	5.067	0.000**	30	-0.611	0.546
Cd	60	3.011	0.004**	58	4.396	0.000**	30	-0.536	0.596
Co	60	-0.840	0.404	58	-0.691	0.492	30	-0.167	0.868
Cr	60	-0.201	0.841	58	-1.238	0.221	30	0.945	0.352
Cu	60	2.315	0.024*	58	4.238	0.000**	30	-0.644	0.524
Fe	60	-1.944	0.057	58	-0.026	0.979	30	-1.888	0.069
Mg	60	-0.905	0.369	58	-0.785	0.436	30	-0.150	0.882
Mn	60	-0.040	0.968	58	-0.279	0.781	30	0.218	0.829
Pb	60	3.361	0.001**	58	3.455	0.001**	30	0.108	0.915
V	60	1.378	0.173	58	4.493	0.000**	30	-2.291	0.029*
Zn	60	3.326	0.002**	58	3.574	0.001**	30	-1.712	0.097

*P<0.05

**P<0.01

5.2 Concentrations of metals in wet deposition

The wet deposition flux shows the total amount of element deposited over an area in a certain period of time, which depends on the total amount of rainfall. To evaluate the amount of heavy metals per unit volume of rainwater, the concentration of rainwater were considered. The concentrations of wet depositions during the winter (Dec 2003 – Feb 2004) and summer (June 2004 – Aug 2004) seasons are shown in Table 5-5. The mean concentrations of Cd, Co, Cr, Cu, and Zn were found to be higher during the winter season. The mean concentration of Pb was found to be higher during the summer season, and that of V was about the same during the winter and summer seasons. The seasonal variation depicted in the mean concentrations of most heavy metals could be attributed to a lower amount of rainfall during the winter time (mean bi-monthly rainfall of 52.6 mm), than that during the summer period (mean bi-monthly rainfall of 348 mm). Due to the low amount of rainfall, the dilution effect during the winter time was minimum, and hence the heavy metals scavenged from the atmosphere were more concentrated.

Table 5-5: The concentrations of wet depositions (mg/l) of major and trace elements during the summer and winter seasons

		Al	Cd	Co	Cr	Cu	Fe	Mg	Mn	Pb	V	Zn
Winter season	Urban (n=4)	75.9	0.58	2.40	32.9	13.8	109	849	104	0.67	2.80	114
	Suburban (n=3)	334	1.18	7.98	3.50	41.0	627	700	222	2.48	3.22	428
	Rural (n=4)	208	1.37	11.0	12.0	41.3	599	1373	221	4.29	1.55	320
	Mean (n=16)	216	1.22	9.13	13.2	37.3	535	1154	205	3.38	2.09	314
Summer season	Urban (n=4)	80.5	0.59	0.34	0.87	7.46	13.0	106	20.6	9.55	1.79	96.1
	Suburban (n=3)	123	0.52	0.43	0.98	11.1	16.7	134	29.7	10.4	2.27	635
	Rural (n=4)	34.3	0.24	0.27	2.86	3.48	17.8	142	22.8	4.43	0.80	61.0
	Mean (n=16)	62.5	0.38	0.32	2.01	5.90	16.4	132	23.6	6.84	1.32	177

5.3 Elemental associations

The results of the principal component analysis of the dry and wet depositions fluxes of metals are presented in Table 5-6. In general, the elemental associations between the dry and wet deposition fluxes of heavy metals were similar. Trace elements such as, Cd, Pb, V and Zn were found to be closely associated with rock-forming elements such as Al and Fe in the first principal component (PC1), showing the influences from both anthropogenic and natural sources. Cobalt was associated with major elements such as Fe, Mg and Mn in the second principal component (PC2), depicting the input from natural sources. Chromium was univocally identified in the third principal component (PC3), and was not associated with the crustal elements such as Al and Fe, and anthropogenic elements such as Cd, Pb and Zn. In particular, high dry and wet deposition fluxes were observed in the coastal site of HT, in southern part of the PRD region (see Table 5-1 and 5-3), showing that the input of chromium was probably related to both the natural bedrock materials and marine sources, such as the sea salts.

Table 5-6: The loadings of principal component matrices of dry deposition fluxes and wet deposition fluxes

	Dry deposition				Wet deposition		
	PC1	PC2	PC2		PC1	PC2	PC2
Al	0.838	0.080	0.121	Al	0.930	0.178	0.046
Cd	0.875	0.218	-0.187	Cd	0.921	-0.093	-0.086
Co	0.165	0.948	0.064	Co	-0.024	0.863	0.227
Cr	0.071	0.073	0.950	Cr	-0.004	0.304	0.800
Cu	0.843	0.322	-0.003	Cu	0.799	0.402	0.228
Fe	0.919	0.115	0.287	Fe	0.020	0.687	0.467
Mg	0.026	0.969	-0.015	Mg	-0.039	0.824	-0.088
Mn	0.253	0.947	0.063	Mn	0.228	0.822	0.308
Pb	0.916	0.059	0.062	Pb	0.902	-0.168	0.171
V	0.864	0.026	0.197	V	0.643	-0.055	-0.412
Zn	0.812	0.143	-0.201	Zn	0.644	-0.062	-0.079

Note: Numbers underlined are the dominant elements in different PCs

5.4 Spatial variations in dry and wet deposition fluxes

The annual mean dry and wet deposition fluxes of heavy metals at the 16 locations within the PRD region are shown in Figure 5-1 and 5-2. As seen from the figures, the urban areas generally had higher dry and wet deposition fluxes of heavy metals than the rural areas, especially those located in the eastern part of the PRD coast, such as WT, TM, YM, TO and HH. To provide some insights of the overall spatial distribution of atmospheric metal depositions in the region, several sites were selected to be discussed in details. The first sector consists of Qingyuan (QY), which is located at the rural area on the northern border of the PRD region, to assess the regional pollution in the northern PRD region. The second sector includes the urban areas of Guangzhou, including the Guangzhou Institute of Geochemistry of Guangzhou (DH) and Zhongshan University (ZU), to investigate on the urban pollution in the region, and the suburban areas of Guangzhou, the Baiyun Mt., which is an appropriate site to study the sub-regional pollution near Guangzhou areas. The third sector consists of Jiangmen (JM) and Zhongshan (ZS), which were rural sites located at the western inland areas of the PRD region, to ascribe the regional pollution in the western PRD region. The forth sector consists of urban areas of Hong Kong, including the HK Polytechnic University (PU), which was located at the southern part of PRD region, to illustrate the urban pollution at the coastal PRD region. The fifth sector includes the rural areas at the southern part of the PRD, Hok Tsui (HT), Tai O (TO) and Haihawan (HH) of Hong Kong and Yangmeihang (YM) of Shenzhen, to study the regional pollution in the coastal PRD region.

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Figure 5-1: Annual mean dry deposition fluxes (mg/m^2/year) of heavy metals in the PRD region

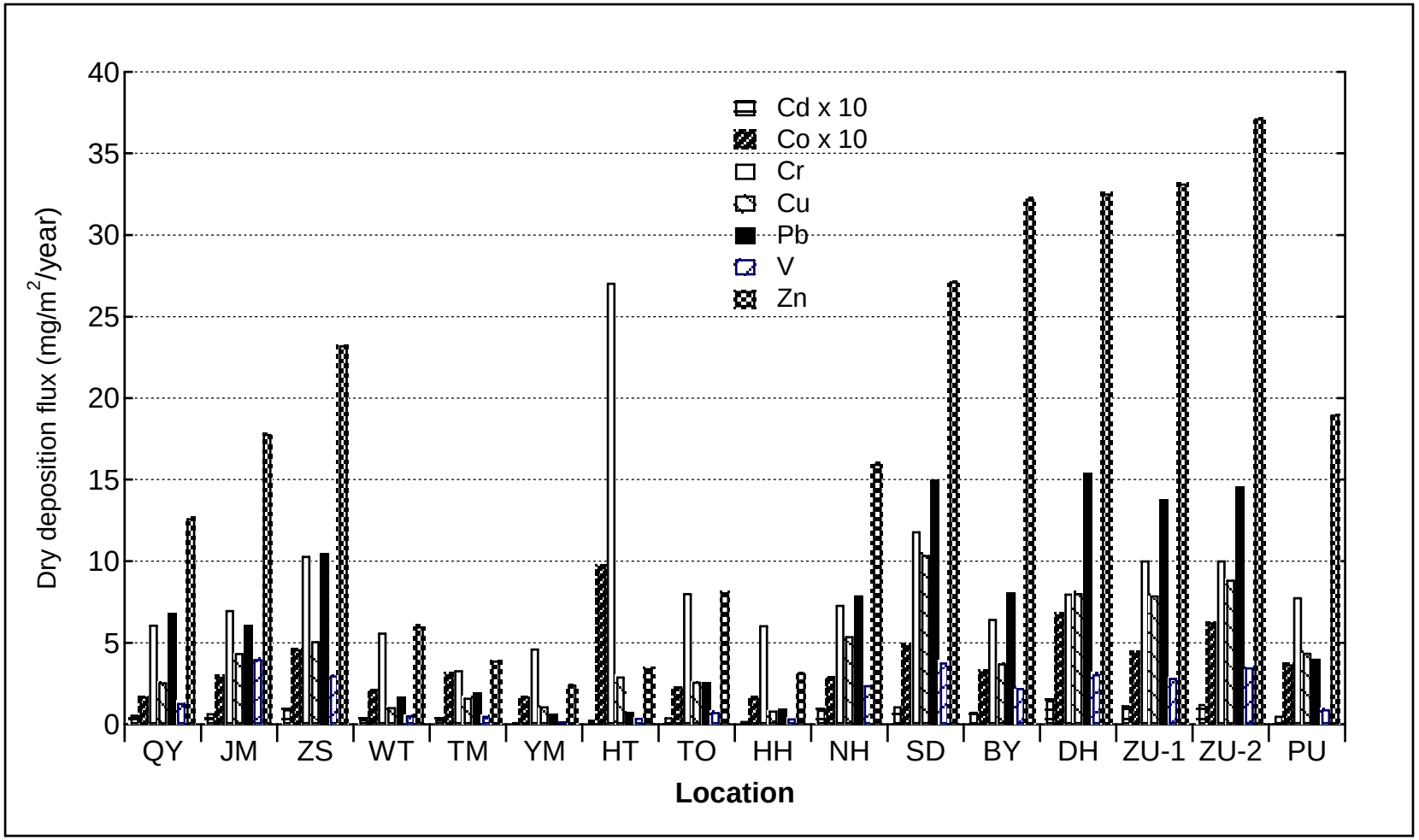
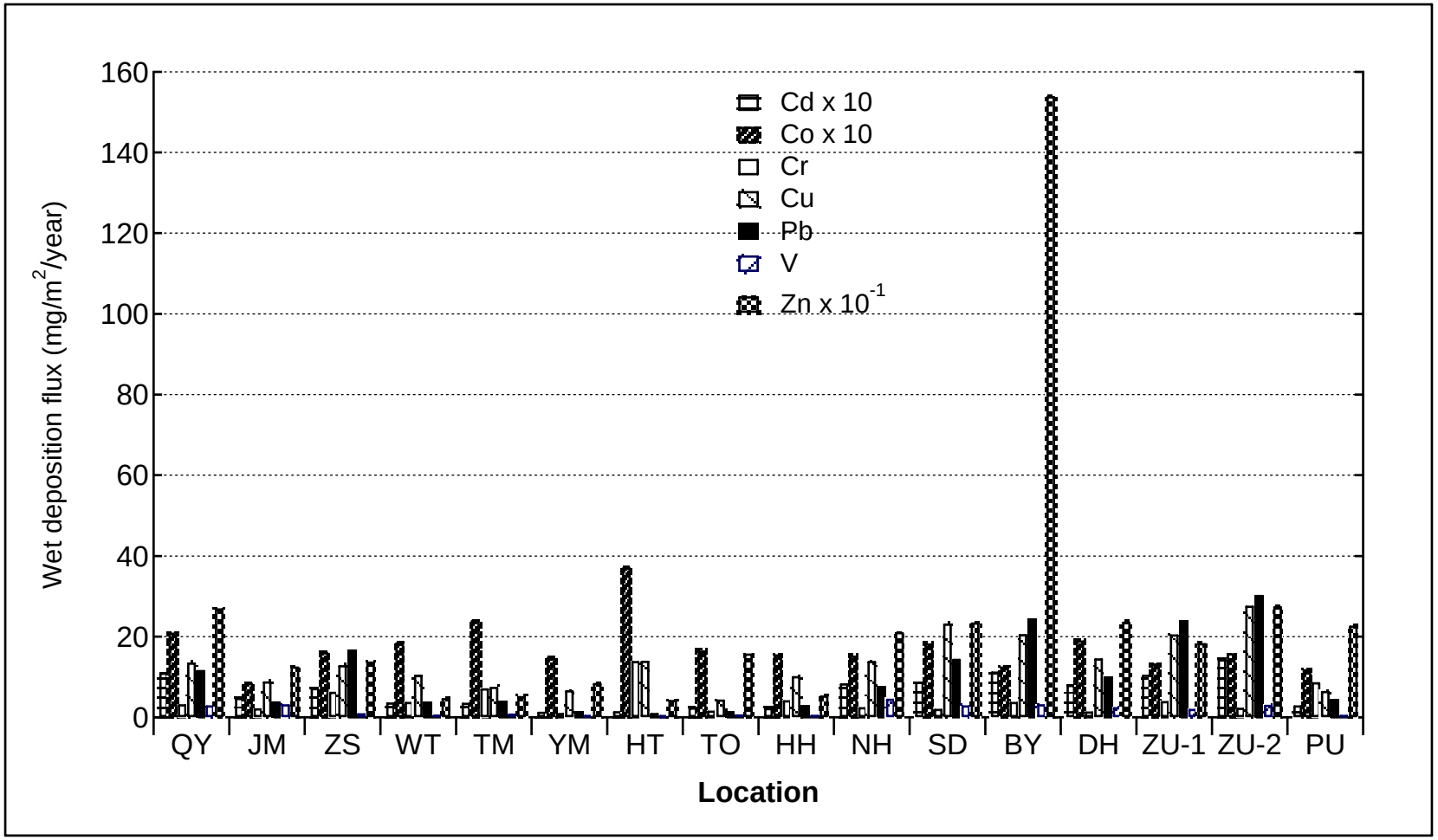


Figure 5-2: Annual mean wet deposition fluxes (mg/m^2/year) of heavy metals in the PRD region



5.4.1 Zone one (rural areas of the northern PRD region)

The dry deposition fluxes of Cd, Pb, V and Zn at QY were close to the annual average of the PRD region, which were 0.06, 6.81, 1.31 and 12.6 mg/m^2/year, respectively (Table 5-1). The wet deposition fluxes of Cd, Co, Pb, V and Zn exceeded the annual mean values of the PRD region, which were 1.11, 2.10, 11.7, 2.97 and 271 mg/m^2/year, respectively, showing a substantial deposition of these elements in the area through the scavenging of rain (Table 5-3). Since there was minimum urban anthropogenic influence at the remote areas of QY, the results showed that there were significant atmospheric depositions of heavy metals such as Cd, Co, Cu, Pb, V and Zn in the northern PRD region, probably due to the regional pollution from the surrounding urban centres. The predominant mode of metal deposition was from wet deposition.

5.4.2 Zone two (urban and suburban areas of inland PRD region)

In general, the sites DH, ZU-1 and ZU-2 had the highest dry deposition fluxes of Cd, Pb and Zn within the PRD region, which were 0.15, 15.4 and 37.2 mg/m^2/year, receptively, about 2.14-, 2.22- and 2.14- fold higher than the annual mean values of the PRD region (Table 5-1). The dry deposition fluxes of Cd, Co, Cu, Pb, V and Zn at the three urban sites were all higher than the annual mean values, and that of Cr was close to the annual mean value. The three urban sites also had the highest wet deposition fluxes of Cd, Cu, and Pb within the PRD region, which were 1.44, 27.7 and 30.3 mg/m^2/year, respectively, about 2.32-, 2.11- and 3.13- fold of the annual mean values of the PRD region (Table 5-3). The wet deposition fluxes of Cd, Cu, Pb, V and Zn were generally higher than the annual mean values, and that of Co and Cr were close to the annual mean

values. Guangzhou has been known to be the biggest urban centre in southern China, which was subjected to severe atmospheric pollution (Wong *et al*., 2003; Lee *et al*., 2005). The elevated dry and wet heavy metal depositions in the inland urban areas of the PRD region, may come from various anthropogenic sources, such as industrial, traffic, and power plant emissions etc.

On the other hand, the dry deposition fluxes of Cd, Pb, V and Zn at BY exceeded the annual mean values of the PRD region, which were 0.08, 8.09, 2.22, 32.2 mg/m^2/year, respectively (Table 5-1). It has to be noted that the site BY has the highest wet deposition fluxes of Zn, which was 1540 mg/m^2/year, about 6.36-fold of the annual mean value (Table 5-3). The wet deposition fluxes of Cd, Cu, Pb and V were higher than the annual mean values, which were 1.14, 20.6, 24.4 and 3.26 mg/m^2/year, respectively. The suburbs of Guangzhou were generally susceptible to severe dry and wet heavy metal deposition, showing that the atmospheric trace metal deposition pollution in urban areas of Guangzhou was affecting the surrounding areas in a sub-regional scale.

5.4.3 Zone three (rural areas of the western PRD region)

The dry deposition of vanadium at Jiangmen was the highest within the PRD region, which was 4.01 mg/m^2/year, about 2.14- fold of the annual mean values of the PRD region (Table 5-1). The dry deposition fluxes of Cd, Cu, Pb and Zn were 0.07, 4.38, 6.08 and 17.8 mg/m^2/year, respectively, which were close to the annual average values. The wet deposition fluxes of Cd, Co, Cr, Cu, Pb, V and Zn were generally lower than the annual average of the PRD region, which were 0.48, 0.85, 2.22, 8.92, 3.94, 3.27 and 126 mg/m^2/year, respectively (Table 5-3). The enrichment of vanadium at Jiangmen could attribute to the emissions from

oil combustions by cargo vessels travelling in the Pearl River, which was an important means of transportation in the PRD region. In general, the remote area was susceptible to moderate regional atmospheric depositions of heavy metals, mainly through dry deposition.

At Zhongshan, the dry deposition fluxes of Cd, Co, Cr, Cu, Pb, V and Zn were higher than the annual mean values of the PRD region, which were 0.09, 0.46, 10.34, 5.10, 10.5, 3.00 and 23.3 mg/m^2/year, respectively (Table 5-1). On the other hand, the wet deposition fluxes of Cd, Cr and Pb were found to be higher than the annual mean values of the PRD region, which were 0.73, 6.35 and 16.8 mg/m^2/year, respectively (Table 5-3). As depicted in Figure 5-1 and 5-2, relatively high dry and wet depositions of Pb were observed in the rural areas of Zhongshan. This could probably attribute to the influences of local sources, such as emissions from various industrial activities, such as electronic products, food production and furniture in the urban areas of Zhongshan.

In general, the dry and wet depositions of trace metals in the rural areas of Zhongshan were much more significant than that in Jiangmen. This showed that, besides the influences from regional sources, local emission sources played an important role in the atmospheric trace metal depositions in the western part of the PRD region.

5.4.4 Zone four (urban areas of coastal PRD region)

The dry deposition flux of Zn at PU (19.0 mg/m^2/year) exceeded the annual mean of the PRD region, and that of Co and Cu were 0.37 and 4.39 mg/m^2/year, respectively, which were close to the annual mean values (Table 5-1). The wet

deposition flux of Cr (8.67 mg/m^2/year) exceeded the average mean values, and that of Zn (227 mg/m^2/year) was close to the annual mean value (Table 5-3). The earlier result from PCA analysis has shown that the dry deposition fluxes of Cr in the PRD region has a unique source of origin, since it was not associated with the crustal elements, such as Al, Fe, and anthropogenic originated elements, such as Pb and Zn. The atmospheric enrichment of Cr could attribute to some other sources, such as the marine sources, as the site PU was situated at the coastal areas of PRD region subjected to the influence of the sea breeze during the summer season. The atmospheric deposition of Zn may come from anthropogenic sources, such as the emissions from power plants, and from traffic due to the abrasion of tyre materials. In general, the coastal urban area of the PRD region was subjected to moderate atmospheric depositions of heavy metals. The predominant mode of deposition was wet deposition, especially for Zn.

5.4.5 Zone five (rural areas of coastal PRD region)

The dry deposition of Co and Cr at HT were the highest within the PRD region, which were 0.97 and 27.1 mg/m^2/year, respectively (Table 5-1). The wet depositions of Co and Cr at HT were also the highest, which were 3.72 and 14.0 mg/m^2/year, respectively (Table 5-3). Similar to the PU site, which was located at the coastal areas of the PRD region, the elevated dry and wet depositions of Cr at HT could be originated from marine sources. From the PCA results, it can be seen that Co was closely associated with the major elements such as Fe, Mg and Mn. The enrichment of Co in the dry and wet depositions could come from the inputs from the natural bedrock materials. In general, the dry deposition of Cd, Cu, Pb, V and Zn at all the rural coastal sites (YM, HT, TO, HH) were much lower than the annual mean values. The rural areas at the coastal PRD were

relatively clean and have minimum influences from anthropogenic elements such as Cd, Cu, Pb, V and Zn.

5.5 Temporal variations in dry and wet deposition fluxes

The dry and wet deposition fluxes of Cd, Co, Cr, Cu, Pb, V and Zn collected bi-monthly at various locations in the PRD region are shown in Figure 5-3 and 5-4. The Kruskal-Wallis test was employed to compare the means of heavy metal deposition fluxes obtained during different periods of measurement. As discussed earlier, the atmospheric deposition fluxes of most metals are higher in the urban areas as compared to the suburban and rural sites. To account for the different site characteristics, the Kruskal-Wallis test was applied to the dry and wet deposition fluxes in urban, suburban and rural areas separately. The temporal variation in atmospheric depositions in the contaminated urban sites, including DH, ZU-1, ZU-2 and PU, the suburban sites, including NH, SD and BY, and the rural sites, QY, JM, ZS, WT, TM, YM, HT, TO and HH, were discussed in the following sections.

Figure 5-3: Temporal variation of dry deposition of heavy metals (mg/m^2/year) in the PRD region

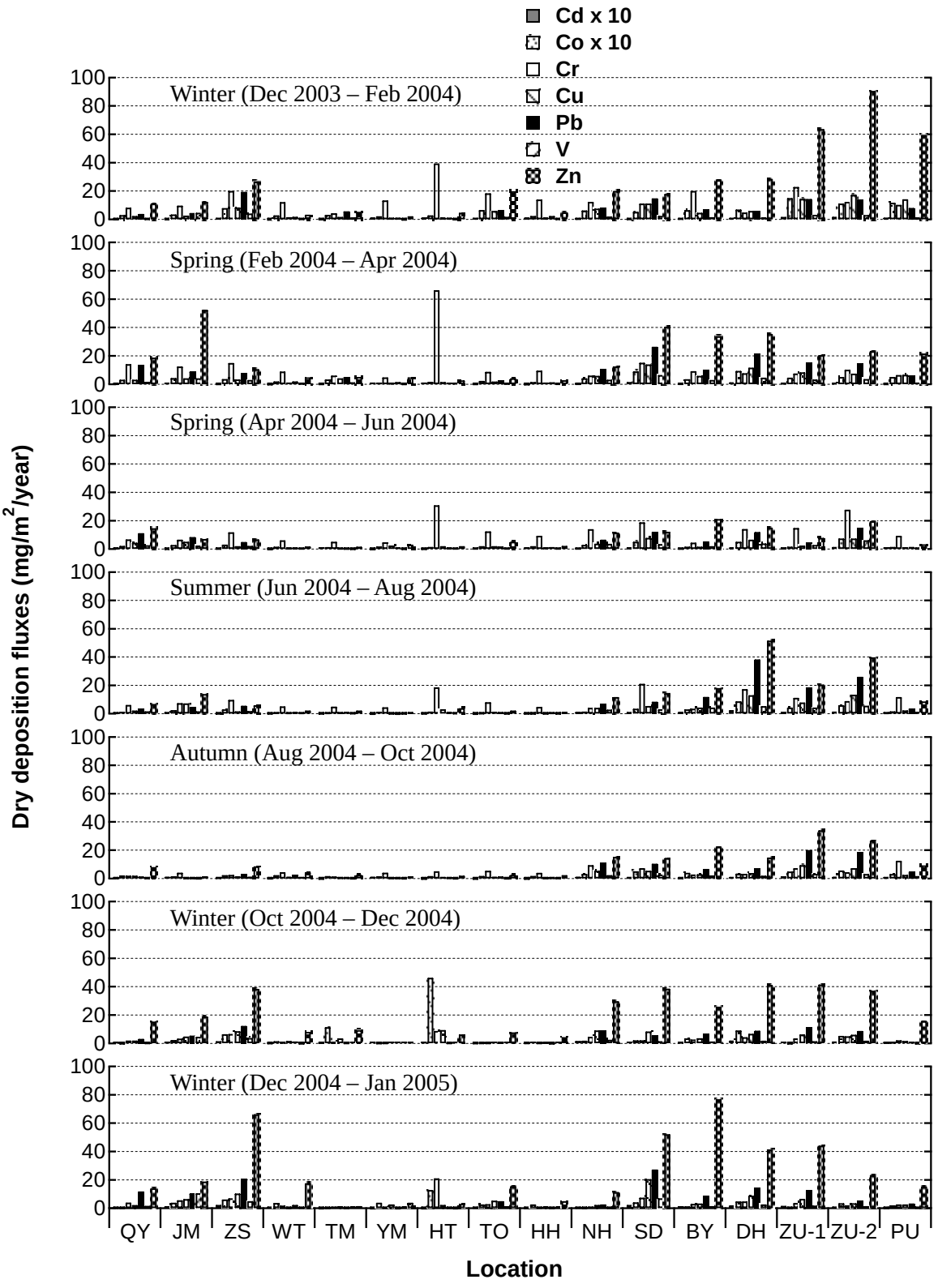
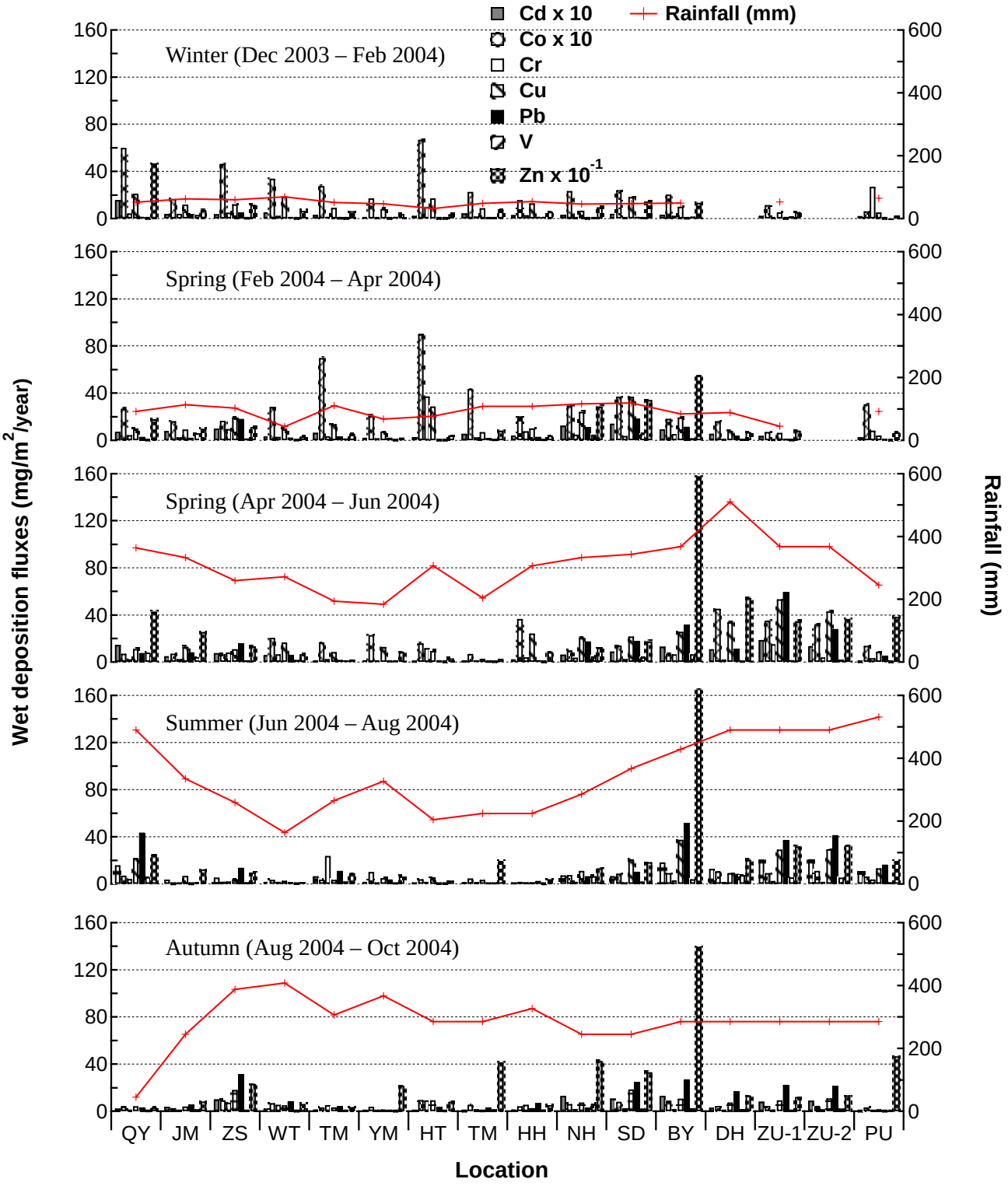


Figure 5-4: Temporal variation of wet deposition of heavy metals (mg/m^2/year) in the PRD region



5.5.1 Urban areas

The results from the statistical analysis are summarised in Table 5-7. There were significant seasonal differences for Cr ($P<0.01$) and Zn ($P<0.05$) in the dry depositions of the PRD urban areas (including DH, ZU-1, ZU-2 and PU). The highest dry deposition fluxes of Cr occurred during the spring and summer period (Apr 2004 – Aug 2004), and the dry deposition flux of Zn was the highest during the winter season (Dec 2003 – Feb 2004 and Oct 2004 – Jan 2005). For the wet depositions, significant variations were observed in trace metals, such as Co, Cu and Zn ($P<0.05$). The wet deposition fluxes of Co, Cu and Zn reached maxima during the spring and summer period (Apr 2004 – Aug 2004). During the summer and spring seasons, the rainfall amount was high. The enrichments of trace metals such as Co, Cu and Zn in wet depositions during the spring and summer periods may be attributed to a more significant wash out-effect by rain.

5.5.2 Suburban areas

There was no significant seasonal variability for all the heavy metal dry depositions ($P>0.05$) but there were significant seasonal variations in the wet deposition of Co and Cr ($P<0.05$). The highest wet deposition of Co and Cr occurred during the spring season (Feb 2004 – Apr 2004). The dry and wet depositions of most heavy metals such as Cd, Pb, V and Zn in the suburban areas showed less seasonal variability, suggesting that they were regularly deposited (by dry and wet depositions) to the terrestrial environment probably from some local sources in the PRD region.

5.5.3 Rural areas

Significant seasonal variability was observed in the dry depositions of trace metals such as Cr ($P<0.01$) and Co, Zn ($P<0.05$), which showed higher deposition fluxes during winter and spring period (Dec 2003 - Apr 2004 and Oct 2004 – Jan 2005) (Table 5-7). There were significant seasonal variation in Co and Cu wet deposition fluxes ($P<0.05$). The wet deposition of Co and Cu were relatively high during the winter and spring seasons (Dec 2003 - Apr 2004).

In general, the dry and wet deposition of trace metals such as Cd, Pb and V had less seasonal variability, showing that they were constantly deposited into the environment throughout the year. Some seasonal variability was observed for dry and wet deposits of Co, Cr, Cu and Zn. The dry deposition of Zn was found to be highly elevated particularly during winter, and the dry deposition of Cr was high during the spring and summer seasons. On the other hand, there were high wet depositions of Co, Cu and Zn during the summer season, probably due to the scavenging effect of rain which occurred most frequently during summer season in the PRD region.

Table 5-7: The statistical results from the Kruskal-Wallis test

	Urban areas			Suburban areas			Rural areas		
	Degree of freedom	Chi-Square	Sig.	Degree of freedom	Chi-Square	Sig.	Degree of freedom	Chi-Square	Sig.
Dry depositions									
Cd	6	3.702	0.717	6	6.857	0.334	6	10.411	0.108
Co	6	11.468	0.075	6	11.498	0.074	6	15.906	0.014*
Cr	6	18.163	0.006**	6	9.628	0.141	6	32.769	0.000**
Cu	6	9.059	0.170	6	5.177	0.521	6	9.725	0.137
Pb	6	6.200	0.401	6	3.775	0.707	6	9.863	0.131
V	6	7.397	0.286	6	8.693	0.192	6	8.460	0.206
Zn	6	13.493	0.036*	6	6.961	0.324	6	13.263	0.039*
Wet deposition									
Cd	4	8.797	0.066	4	8.267	0.082	4	7.105	0.130
Co	4	13.082	0.011*	4	10.900	0.028*	4	31.308	0.000**
Cr	4	5.337	0.254	4	9.767	0.045*	4	5.067	0.281
Cu	4	10.542	0.032*	4	8.900	0.064	4	16.497	0.002**
Pb	4	8.049	0.090	4	7.300	0.121	4	7.963	0.093
V	4	7.837	0.098	4	7.467	0.113	4	6.546	0.162
Zn	4	12.902	0.012*	4	5.300	0.258	4	0.782	0.941

** significance < 0.01

* significance < 0.05

5.6 Comparison between dry and wet deposition

Assuming that the total atmospheric deposition is the summation of the dry and wet deposition, the relative contribution of dry and wet deposition of major and trace elements (Al, Fe, Mg, Mn and Cd, Co, Cr, Cu, Pb, V and Zn) during the winter (Dec 2003 – Feb 2004) and summer (June 2004 – Aug 2004) seasons are tabulated in Table 5-8.

5.6.1 Al, Fe and Cr

The results showed that there was no variation on the major pathways of deposition in both winter and summer seasons. Elements such as Al, Fe and Cr, in urban, suburban and rural areas were mainly deposited through dry deposition, which accounted for 62.1 – 97.4 % of the total deposition (Table 5-8). These elements could be originated from natural or marine sources. Chromium was known to have low solubility in atmospheric deposition (dry and wet) (Morselli *et al*., 2003). Moreover, Al and Fe are crustal elements, showing that the depositions of these elements were probably associated with larger-sized particles, and hence they were readily removed from the atmosphere through dry deposition.

5.6.2 Cd, Co, Cu, Mg, Mn and Zn

Elements such as, Cd, Co, Cu, Mg, Mn and Zn showed a greater affinity to be deposited as wet depositions, especially during the summer season, which accounted for 66.4 – 94.7% of the total deposition (during summer season) (Table 5-8). During the winter seasons, most of the Cd, Co, Cu, Mg, Mn and Zn were deposited as wet depositions which accounted for about 26.6 – 92.2% of the

total deposition, but the deposition of Co, Cu and Zn in the rural areas was found to be mainly in the form of dry deposition. Cadmium and Zn were found to have relatively higher solubility in atmospheric deposition (dry and wet) (Morselli *et al*., 2003), and hence they can be more effectively removed from the atmosphere through the rain scavenging.

5.6.3 Pb and V

For Pb and V, the major deposition pathway was found to be varied during different seasons. The two elements were mainly deposited through dry deposition during the winter, which accounted for 76.2 – 97.7% of the total deposition, but the major way of deposition was wet deposition during the summer, which accounted for 52.4 – 64.0% of the total deposition (Table 5-8). Lead has been shown to have relatively low solubility in atmospheric deposition (wet and dry) (Morselli *et al*., 2003). Thus, it was mainly deposited through the dry deposition due to the relatively dry conditions and minimum rain scavenging process in the winter time. During the summer season, due to a higher amount of rainfall, a substantial amount of Pb was also deposited as wet deposition. The results showed that the major path of vanadium deposition during the winter season was dry deposition, despite its high solubility in wet deposition (Morselli *et al*., 2003). During the summer season, it was mainly deposited through wet deposition due to the more effective rain scavenging process.

Table 5-8: The relative contribution of dry and wet deposition fluxes of major and trace elements during winter and summer seasons

		Al	Cd	Co	Cr	Cu	Fe	Mg	Mn	Pb	V	Zn
Winter season												
Dry (%)	Urban (N=4)	87.3	7.8	11.7	80.7	17.5	72.7	19.7	12.8	76.2	78.6	10.4
	Suburban (N=3)	88.2	16.2	21.0	93.6	40.9	82.5	25.0	16.1	94.2	66.8	15.3
	Rural (N=4)	97.4	35.8	61.4	62.1	73.4	96.9	32.8	35.5	97.7	78.9	61.0
Summer season												
Dry (%)	Urban (N=4)	84.5	13.0	29.6	73.7	24.6	90.3	18.7	11.9	36.0	43.1	5.6
	Suburban (N=3)	79.5	9.0	22.9	72.6	19.2	96.0	21.5	12.8	38.5	47.6	5.3
	Rural (N=4)	84.4	8.3	33.6	83.1	31.5	96.4	24.1	19.6	43.0	46.3	10.3
Winter season												
Wet (%)	Urban (N=4)	12.7	92.2	88.3	19.3	82.5	27.3	80.3	87.2	23.8	21.4	89.6
	Suburban (N=3)	11.8	83.8	79.0	6.4	59.1	17.5	75.0	83.9	5.8	33.2	84.7
	Rural (N=4)	2.6	64.2	38.6	37.9	26.6	3.1	67.2	64.5	2.3	21.1	39.0
Summer season												
Wet (%)	Urban (N=4)	15.5	87.0	70.4	26.3	75.4	9.7	81.3	88.1	64.0	56.9	94.4
	Suburban (N=3)	20.5	91.0	77.1	27.4	80.8	4.0	78.5	87.2	61.5	52.4	94.7
	Rural (N=4)	15.6	91.7	66.4	16.9	68.5	3.6	75.9	80.4	57.0	53.7	89.7

5.7 Pb isotopic composition of dry and wet deposits

The Pb isotopic ratios ($^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$) of the dry deposits in the PRD region measured during the winter (Dec 2003 – Feb 2004) and summer (June 2004 – Aug 2004) seasons are tabulated in Table 5-9. The mean $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$ ratios of the dry deposits in winter season were 0.0636, 1.1671 and 2.4670, respectively, and that in summer time were 0.0636, 1.1692 and 2.4670, respectively. The mean Pb isotopic ratios of dry deposits were similar during the winter and summer seasons. Table 5-10 shows the Pb isotopic ratios of the wet deposits in the PRD region measured during the winter and summer seasons. The mean $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$ ratios of the wet deposits in winter season were 0.0644, 1.1602 and 2.4646, respectively, and that in summer time were 0.0638, 1.1691 and 2.4726, respectively. In general, the mean Pb isotopic ratios of wet deposits were found to be similar during the winter and summer seasons.

Table 5-9: The Pb isotopic ratios of dry depositions in the PRD region during the winter and summer seasons

Dry deposition Location	Winter $^{204}Pb/^{207}Pb$	Winter $^{206}Pb/^{207}Pb$	Winter $^{208}Pb/^{207}Pb$		Summer $^{204}Pb/^{207}Pb$	Summer $^{206}Pb/^{207}Pb$	Summer $^{208}Pb/^{207}Pb$
QY	0.0636	1.1677	2.4737		0.0633	1.1685	2.4591
JM	0.0635	1.1761	2.4714		0.0635	1.1784	2.4621
ZS	0.0636	1.1701	2.4707		0.0635	1.1799	2.4713
WT	0.0638	1.1641	2.4658		0.0634	1.1687	2.4632
TM	0.0631	1.1828	2.4847		0.0637	1.1715	2.4687
YM	0.0635	1.1637	2.4727		0.0641	1.1498	2.4303
HT	0.0637	1.1642	2.4566		0.0637	1.1579	2.4457
TO	0.0636	1.1653	2.4654		0.0638	1.1713	2.4569
HH	0.0635	1.1551	2.4597		0.0635	1.1665	2.4617
NH	0.0637	1.1686	2.4614		0.0636	1.1733	2.4619
SD	0.0635	1.1626	2.4587		0.0636	1.1713	2.4589
BY	0.0635	1.1649	2.4711		0.0637	1.1728	2.4600
DH	0.0638	1.1685	2.4659		0.0637	1.1662	2.4597
ZU-1	0.0634	1.1664	2.4676		0.0638	1.1732	2.4607
ZU-2	0.0638	1.1690	2.4667		0.0639	1.1727	2.4559
PU	0.0638	1.1648	2.4594		0.0635	1.1650	2.4572
Mean (N=16)	0.0636	1.1671	2.4670	Mean (N=16)	0.0636	1.1692	2.4583

Table 5-10: The Pb isotopic ratios of wet depositions in the PRD region during the winter and summer seasons

Wet deposition	Winter				Summer		
Location	$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$		$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
QY	0.0640	1.1665	2.4711		0.0637	1.1713	2.4653
JM	0.0632	1.1613	2.4620		0.0658	1.1665	2.4718
ZS	0.0637	1.1709	2.4647		0.0634	1.1754	2.4818
WT	0.0638	1.1569	2.4597		0.0636	1.1642	2.4712
TM	0.0658	1.1569	2.4595		0.0638	1.1738	2.4845
YM	0.0637	1.1586	2.4659		0.0639	1.1581	2.4824
HT	0.0634	1.1541	2.4643		0.0630	1.1668	2.4724
TO	0.0642	1.1629	2.4670		0.0632	1.1638	2.4655
HH	0.0636	1.1538	2.4605		0.0637	1.1653	2.4801
NH	0.0643	1.1608	2.4726		0.0639	1.1687	2.4616
SD	0.0638	1.1625	2.4670		0.0639	1.1720	2.4674
BY	0.0667	1.1599	2.4644		0.0639	1.1712	2.4558
DH	0.0637	1.1595	2.4584		0.0637	1.1726	2.4840
ZU-1	0.0676	1.1580	2.4723		0.0636	1.1706	2.4734
ZU-2	0.0641	1.1624	2.4667		0.0639	1.1736	2.4738
PU	0.0640	1.1576	2.4573		0.0637	1.1711	2.4700
Mean (N=16)	0.0644	1.1602	2.4646	Mean (N=16)	0.0638	1.1691	2.4726

To study the source of Pb in the dry and wet deposits, the $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$ ratios of the dry and wet deposits, the natural and anthropogenic sources in the PRD region were plotted in the same diagram (see Figure 5-5). The Pb isotopic ratios of the natural and anthropogenic sources in the PRD region and other environmental samples are tabulated in Table 5-11. As compared to the natural sources in the PRD region, such as the natural bedrocks and uncontaminated soils, the dry and wet deposits had lower Pb isotopic ratios (Figure 5-5). The Pb isotopic ratios of the PRD dry and wet deposits were found to be similar to those of the Pb ore (Fankou Pb-Zn ore), industrial aerosols, and road dusts of the PRD region. Although leaded petrol has been phased out in China since 2000, Pb can be emitted into the atmosphere from the wind-blown dust and soil particles due to historical uses of Pb in petrol. This showed that industrial use of Pb and road dusts were significant sources of anthropogenic Pb deposited (dry and wet deposition) in the PRD region. As seen from Figure 5-5, the ratios of the dry deposits measured during summer had a greater range than that measured during winter. The summer dry deposits in coastal areas, including YM and HT, had $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$ ratios as low as 1.150-1.160 and 2.430-2.450, respectively. The low Pb isotopic ratios of the dry deposits at the coastal sites were found to be similar to that of the Vietnam aerosols.

On the other hand, the Pb isotopic ratios of the wet deposits were similar during the winter and summer seasons (Figure 5-5). There was no significant seasonal difference in the Pb isotopic compositions of the wet deposits. The seasonal variability observed in the Pb isotopic compositions of the dry depositions could be attributed to the different synoptic conditions during the winter and summer season in the PRD region, especially in the coastal area. The PRD region was

subjected to the influence of the winter monsoon system during the winter period, during which the prevailing wind was the north and north-eastern winds from the inland China, and in summer, the prevailing wind was the south-western wind from the sea. The northern winds in winter season pass through the PRD region, bringing air mass to the coastal area of the PRD region. Hence the Pb isotopic ratios of dry deposits in winter assembled those of the anthropogenic sources in the PRD region (the Pb ore, industrial and vehicular sources). In summertime, the southern wind brings air mass from the sea. Some pollutants from the South Asian countries may be brought to the PRD region through the long range transportation.

Figure 5-5: The Pb isotopic composition of dry and wet depositions in the PRD region during the winter and summer seasons and other known environmental samples

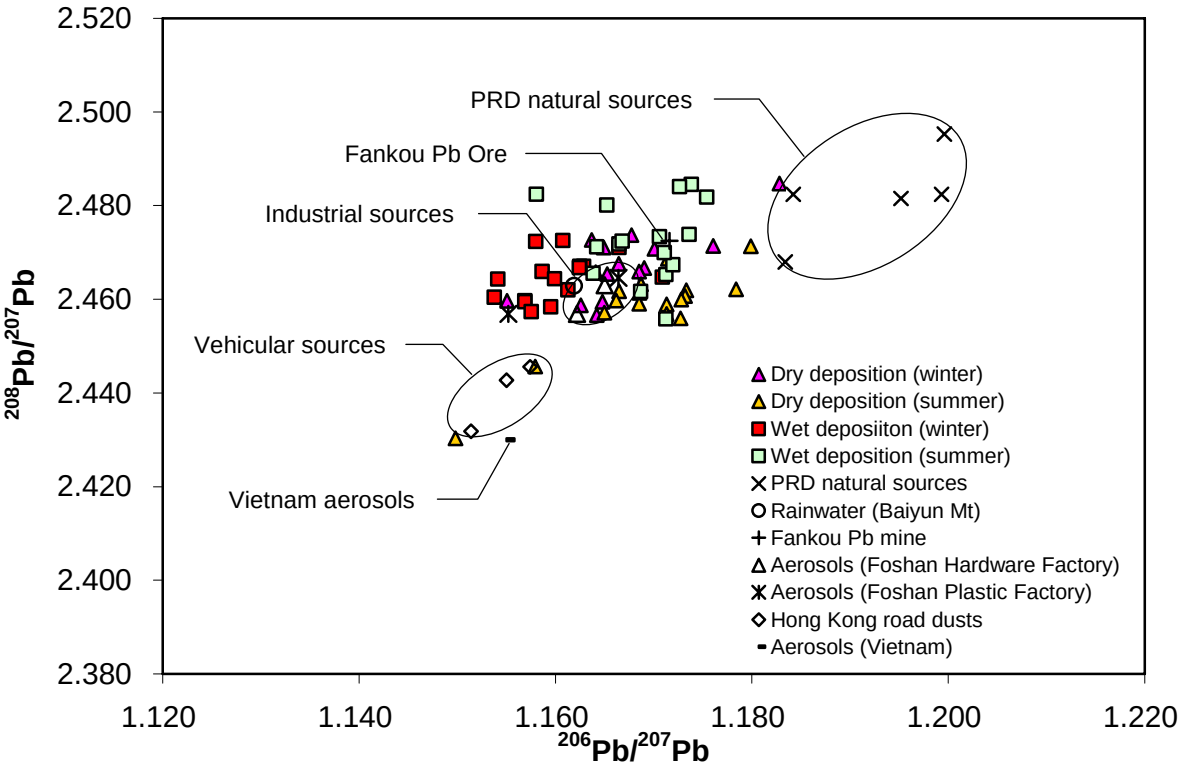


Table 5-11: The Pb isotopic composition of natural and anthropogenic sources in the PRD region and other environmental samples

	N	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	Reference
Natural sources				
Granite in the eastern Cathaysia	102	1.1834	2.4680	Zhu (1998)
PRD Granite	6	1.1842	2.4824	Zhu (1998)
Volcanic rocks in Foshan	8	1.1993	2.4824	Zhu *et al*. (1989)
Uncontaminated soils in PRD	2	1.1952	2.4815	Zhu *et al*. (2001)
Background soils in Hong Kong (country park soils)	11	1.1996	2.4953	Lee *et al*. (2006)
Anthropogenic sources				
Fankou Pb-Zn ore		1.1716	2.4725	Zhu (1998)
PRD automobile-exhaust		1.1604	2.4228	Zhu *et al*. (2001)
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	
Hong Kong road dusts				Duzgoren-Aydin *et al*. (2004)
- HKU car park	3	1.1514	2.4318	
- High Street	3	1.1574	2.4456	
- Mong Kok	3	1.1550	2.4427	
Other environmental samples				
Guangzhou rainwater (Baiyunshan Park)	1	1.1619	2.4629	Zhu *et al*. (2001)
Vietnam aerosols (Ho Chi Minh)	59	1.1550	2.4300	Bollhöfer and Rosman (2000)

5.8 pH of wet depositions

5.8.1 pH values

The average (and range) pH of wet depositions collected at 16 locations in the PRD region during the 1-year period of measurement are presented in Table 5-12. The pH measured in the wet deposition varied between 2.97 to 6.92, which are very acidic to about neutral. The average pH of wet depositions at all the locations showed values between 3.39 and 5.79, clearly showed that acidification of precipitation all over the PRD region. The pH values of the wet depositions in the PRD region was compared with other cities in China (see Table 5-13). As shown in Table 5-13, the pH of the urban areas in the PRD region was comparable to those in Shanghai, but was less acidic than those in the urban areas of South-western China cities (Chengdu, Chongqing and Guiyang). These South-western cities were highly industrialized with intensive mining (coal, copper, bauxite and others) and industrial activities (Lei *et al*., 1997), which could attribute to the high acidity in the precipitation. On the other hand, the pH in the urban areas of PRD was much lower than that in Beijing. The precipitation in Beijing has high concentrations of alkaline materials, resulted in neutral or alkaline rainwater in Beijing area (Feng *et al*., 2001).

Table 5-12: Average (range) pH of wet depositions in urban, suburban and rural areas of the PRD region

Location	Site characteristics	N	pH	Average Volume (mm)
QY	rural	5	4.62 (3.50-6.16)	208
JM	rural	5	4.73 (3.31-6.10)	218
ZS	rural	5	3.39 (2.97-3.78)	214
WT	rural	5	3.62 (3.51-3.78)	191
TM	rural	5	4.62 (3.50-6.31)	185
YM	rural	5	4.52 (3.51-5.86)	198
HT	rural	5	4.88 (3.84-5.89)	181
TO	rural	5	5.79 (5.03-6.36)	174
HH	rural	5	4.22 (3.57-5.73)	204
NH	suburban	5	3.79 (3.12-4.45)	205
SD	suburban	5	3.77 (3.51-4.35)	224
BY	suburban	5	4.18 (3.48-5.58)	243
DH	urban	4	4.78 (3.90-5.40)	344
ZU-1	urban	5	4.84 (3.45-6.92)	248
ZU-2	urban	3	4.61 (3.82-5.84)	381
PU	urban	5	4.66 (3.88-6.22)	244
PRD region				
	Overall	77	4.43 (2.97-6.92)	223
	urban	17	4.72 (3.45-6.92)	293
	suburban	15	3.91 (3.12-5.58)	224
	rural	45	4.49 (2.97-6.36)	197

Table 5-13: Comparison of pH of wet depositions in PRD region with other Chinese cities

Location	Site characteristics	N	pH average (range)	Reference
PRD	urban	17	4.72 (3.45-6.92)	The present study
(Dec2003-Jan2005)	suburban	15	3.91 (3.12-5.58)	The present study
	rural	45	4.49 (2.97-6.36)	The present study
Guangzhou (15-19 Mar1988)	urban	21	4.4 (3.8-5.7)	Lei *et al*. (1997)
Shanghai (21 June-11 July1986)	urban	66	4.7 (3.2-7.7)	Lei *et al*. (1997)
	suburban	66	5.1 (3.5-9.8)	
Chengdu (22-30 Sep1989)	urban	8	3.9 (3.3-6.8)	Lei *et al*. (1997)
Chongqing (3-9 Oct1989)	urban	22	3.9 (3.3-5.7)	Lei *et al*. (1997)
Guiyang (13-19 Oct1989)	urban	41	4.1 (3.4-6.0)	Lei *et al*. (1997)
Beijing (1998)	urban – Zhongguancun	-	6.77 (6.35-6.98)	Feng *et al*. (2001)
	rural – Mangshan	-	6.57 (6.35-7.52)	Feng *et al*. (2001)

5.8.2 Comparison of pH of wet depositions in urban, suburban and rural areas

The statistics Kruskal-Wallis test was applied to analyse the variations among the pH values of wet deposits in the urban, suburban and rural areas in the PRD. The results showed that the pH of wet depositions under the urban, suburban and rural settings were significantly different ($P<0.05$). The average pH values were ranked in the increasing order of suburban areas>urban areas>rural areas. The highest pH values were found in the suburban areas of the PRD region (average of 3.91). The Nanhai (NH) and Shunde (SD) towns had many small-middle scale industrial activities, the emissions of acidic gases and particulate matter in these areas may attribute to the acidity in these industrial towns. Moreover, the wet deposits in the rural areas were probably had more influenced from natural sources, which are enriched in crustal elements (see Table 5-6 in Section 5.3). Hence, the wet deposits in the rural areas had lower acidity due to the neutralisation effect of the crustal elements from the natural sources.

5.9 Summary

The elemental dry and wet deposition fluxes of Al, Cd, Co, Cr, Cu, Fe, Mg, Mn, Pb, V and Zn have been studied over one year period. The dry and wet depositions of most trace elements were found to be higher in the urban and suburban areas of the PRD region, as compared to those in the rural areas. The concentrations of the trace element wet deposition, including Cd, Co, Cr, Cu and Zn were found to be higher during the winter season, due to a lower amount of rainfall. The Pb concentrations of the wet depositions were higher during the summer season. The urban and suburban areas in the inland PRD region, near Guangzhou, were found to have the highest dry and wet depositions of heavy metals, particularly for Cd, Pb and Zn. The Zn wet deposition flux at suburban inland PRD region (Baiyun Mt.) was about 5-fold of the mean annual value, showing the severe sub-regional atmospheric deposition pollution in the inland PRD region.

Distinguished temporal variation was observed in the dry and wet depositions of most trace elements in the urban areas, but the seasonal variation of trace element deposition in the suburban and rural areas was less distinct. Higher dry deposition fluxes of Co, Cr, Cu and Zn in urban areas occurred during winter season, probably due to the influx of pollutants during the winter monsoon period and the relatively dry condition in winter. The wet deposition fluxes of Cd, Co, Cu, V and Zn in urban areas were observed to be higher in the summer season, attributed to a greater scavenging effect by rain. The predominant pathway of deposition varied for different trace elements. The differences in the mode of deposition may attribute to the associations of the trace elements with

particles of different sizes, and due to their different solubility in the dry and wet depositions. The Pb isotopic study showed that the Pb isotopic ratios of the most dry and wet deposits, during both winter and summer seasons, were similar to the anthropogenic sources of the PRD region, such as the Pb ore, industrial and vehicular emissions. The input of Pb could be originated from various anthropogenic sources in the PRD region. The Pb isotopic compositions of some summer deposits in the coastal PRD region were found to be similar to the Vietnam aerosols. Long-range transport of pollutants in summer from the South Asian countries could have some influences on the atmospheric dry depositions in the coastal areas of the PRD region.

Chapter 6 − Biomonitoring of trace metals in the atmosphere using mosses in the Nanling Mountains and the Pearl River Delta, Southern China

In this study, the heavy metal concentrations in the moss *Hypnum plumaeforme* in the Nanling Mountains were determined. Pb isotopic analysis was used to identify the potential anthropogenic inputs of heavy metals in mosses and aerosols collected in the surrounding areas. An intercomparison study was also carried out for the trace metal concentrations several moss species collected in the same location at the Dinghu Mountain in the PRD region, namely *Hypnum plumaeforme*, *Leucobryum chlorophyllosum*, *Pogonatum contorium*, *Thuidium tamariscinum* and *Bazzania tridens*, to assess their ability to absorb and retain heavy metals derived from atmospheric fluxes. The aim of the present research was to evaluate the suitability of several moss species, commonly found in the PRD region, for monitoring ambient air quality in a subtropical area.

6.1 Metal concentrations in mosses and aerosols in the Nanling Mountains

The total concentrations of metals in the moss and aerosol samples are presented in Table 6-1. The mean concentrations of heavy metals such as Cd, Cu, Ni, Pb and Zn in the NL-series (northern part of the Nanling range) were found to be 4.13 mg/kg, 34.3 mg/kg, 18.0 mg/kg, 183 mg/kg and 181 mg/kg, respectively. The corresponding values in the MS-series (the southern part of the Nanling range) were 1.82 mg/kg, 58.7 mg/kg, 23.6 mg/kg, 140 mg/kg and 143 mg/kg, respectively. The results showed that the Pb concentrations were highly elevated in both the NL- and MS-series, ranging from 40.5 mg/kg to 396 mg/kg. As no similar study using *Hypnum plumaeforme* for bimonitoring was found in the literature, the bioconcentrations of another similar species belonging to the same

class and being widely adopted in European moss surveys (Fernández *et al*., 2002; Ötvös *et al*., 2003), *Hypnum cupressiforme*, was used for comparison. In comparison with the results reported in Spain and Hungary, bioconcentrations in the moss *Hypnum plumaeforme* were much higher than in *Hypnum cupressiforme* (see Table 6-2). Previous studies on atmospheric deposition in the PRD showed that the atmospheric deposition of heavy metals was significantly greater than in the Great Lakes region in North America and the North Sea in Europe (Wong *et al*., 2003). The present study on heavy metals in dry and wet depositions (Chapter 5) also indicated the elevated atmospheric heavy metal deposition in the PRD region. Hence, the Nanling mosses could be expected to reflect the elevated concentrations of atmospheric heavy metals in the PRD compared with other regions. Nevertheless, the total amount of pollutants in the air, the relative humidity and wet deposition would also have significant effects on the capacity of mosses to absorb metals. The wide availability of the moss *Hypnum plumaeforme* in the Nanling Mountains and the PRD region, and their capacity in absorbing heavy metals makes it feasible for use in future biomonitoring programmes of atmospheric pollutants. A recent study on PAHs in these moss samples also demonstrated its suitability of monitoring POPs in the air of South China (Liu *et al*., 2006).

The results showed that of the three areas studied (Nanling, Guangzhou and Zhongshan), Guangzhou aerosols were found to have the highest mean concentrations of heavy metals (see Table 6-1). The concentrations of heavy metals in the aerosols of the PRD region, other cities of China and the surrounding regions were compared (see Table 6-3). The data showed that the air in Guangzhou was heavily contaminated with heavy metals, compared with other

areas in the PRD region and China, as well as surrounding Asian cities in Taiwan, Vietnam and India. The concentration of Pb in the air in Guangzhou was marginally within the National Ambient Air Quality Standard of China (NAAQS, 1996) of 1000 ng/m^3, and was lower than the limit specified in the Hong Kong Air Quality Objective (HKAQO, 1987), which is 1500 ng/m^3.

Table 6-1: Major and trace element concentrations (mg/kg) of the moss *Hypnum plumaeforme* in Nanling and element concentrations (ng/m^3) of aerosols in the Pearl River Delta (Nanling, Guangzhou and Zhongshan)

		Al	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	V	Zn
	(mg/kg)	Higher Elevation: >1100 m												
NL-series	Mean	2260	7660	1.71	0.46	9.99	27.8	898	1050	181	10.1	69.3	1.62	112
(N=4)	Std Dev	2190	2090	0.28	0.24	3.57	10.3	770	243	82.6	4.43	7.89	1.18	24.9
		Lower Elevation: <1100 m												
NL-series	Mean	2360	11400	6.55	0.63	40.1	40.8	1230	1390	175	25.9	296	2.64	249
(N=4)	Std Dev	2190	2090	0.28	0.24	3.57	10.3	425	243	52.7	16.2	89.5	2.08	45.4
		Higher Elevation: >1100 m												
MS-series	Mean	3110	10800	1.78	0.21	23.0	53.2	881	1020	200	16.2	106	2.60	144
(N=4)	Std Dev	2810	1060	0.74	0.14	17.1	29.4	447	135	147	6.39	50.3	1.69	18.3
		Lower Elevation: <1100 m												
MS-series	Mean	4990	9450	1.85	0.39	26.6	64.3	1450	902	175	30.9	175	1.67	141
(N=4)	Std Dev	2560	1180	0.67	0.43	23.6	53.5	747	144	142	28.3	82.6	0.58	26.3
PRD Aerosol														
Nanling	(ng/m^3)	Elevation: 1450 m												
YTH														
(North)	Mean	5630	3830	20.5	n.d.[a]	16.0	42.0	1480	336	n.d.[a]	30.5	615	17.5	5770
(N=2)	Std Dev	2870	605	7.29	n.d.[a]	10.1	1.64	375	89.2	n.d.[a]	24.8	255	5.87	2240
		Elevation: 802 m												
QY														
(South)	Mean	4640	6290	11.4	n.d.[a]	7.37	86.8	2270	573	n.d.[a]	23.9	452	39.2	3860
(N=2)	Std Dev	850	2880	2.81	n.d.[a]	4.60	71.1	1490	217	n.d.[a]	8.30	225	26.7	1070
		Elevation: 50 m												
Guangzhou	Mean	14600	22500	21.6	2.85	64.0	914	8860	1450	83.6	66.8	995	103	6440
(N=4)	Std Dev	1210	2460	7.3	1.96	40.1	462	1280	324	61.0	23.3	248	40.6	1880
		Elevation: 500 m												
Zhongshan	Mean	3400	3330	4.59	n.d.[a]	5.83	33.7	1190	292	n.d.[a]	20.3	147	21.1	3740
(N=4)	Std Dev	1340	960	2.16	n.d.[a]	4.55	14.4	287	149	n.d.[a]	5.3	39	8.6	2050

Note: [a] Not detectable

Table 6-2: Comparison of the mean concentrations (mg/kg) of heavy metals in the moss *Hypnum plumaeforme* in Nanling and the moss *Hypnum cupressiforme* in some European surveys

	Spain[a] (N=134)	Hungary[b] (N=116)	NL-series (N=8)	MS-series (N=8)
Cd	-	0.9	4.13	1.82
Cr	2.68	2.8	25.0	24.8
Cu	6.86	11.8	34.3	58.7
Ni	2.79	5.0	18.0	23.6
Pb	9.35	19.5	183	140
V	-	5.1	2.13	2.13
Zn	48.8	52	181	143

Note: [a] Fernández *et al*., 2002
[b] Ötvös *et al*., 2003

Table 6-3: Heavy metal concentrations of aerosols in the PRD (Nanling, Guangzhou and Zhongshan), other cities in China and in surrounding Asian countries

TSP		Mean concentration (ng/m^3)						
Location	Site characteristic	Cd	Cu	Ni	Pb	V	Zn	Reference
PRD								
Nanling (n=4)	rural	16.0	64.4	27.2	533	28.3	4810	present study
Guangzhou (n=4)	urban	21.6	914	66.8	995	103	6440	present study
Zhongshan (n=4)	suburban	4.59	33.7	20.3	147	21.2	3740	present study
Other cities in China								
Xian (n=75)	urban	-	830	810	4300	1100	3000	Zhang *et al.* (2002)
Harbin (n=5)	urban	-	-	-	282	-	-	Mukai *et al.* (2001)
Changchun (n=5)	urban	-	-	-	177	-	-	Mukai *et al.* (2001)
Beijing (n=2)	urban	-	-	-	119	-	-	Mukai *et al.* (2001)
Dalian (n=5)	urban	-	-	-	485	-	-	Mukai *et al.* (2001)
Nanjing (n=2)	urban	-	-	-	317	-	-	Mukai *et al.* (2001)
Shanghai (n=3)	urban	-	-	-	466	-	-	Mukai *et al.* (2001)
Taiwan								
Taichung (n=43)	urban	8.5	199	15.8	574	-	395	Fang *et al.* (2003)
India								
Sakinaka (n=45)	road junction	-	370	160	1060	-	-	Kumar *et al.* (2001)
Gandhinagar (n=45)	road junction	-	1550	100	820	-	-	Kumar *et al.* (2001)
Vietnam								
Ho Chi Minh City (n=43)	urban	-	1.28	-	146	7.3	203	Hien *et al.* (2001)

6.2 Elemental associations in mosses

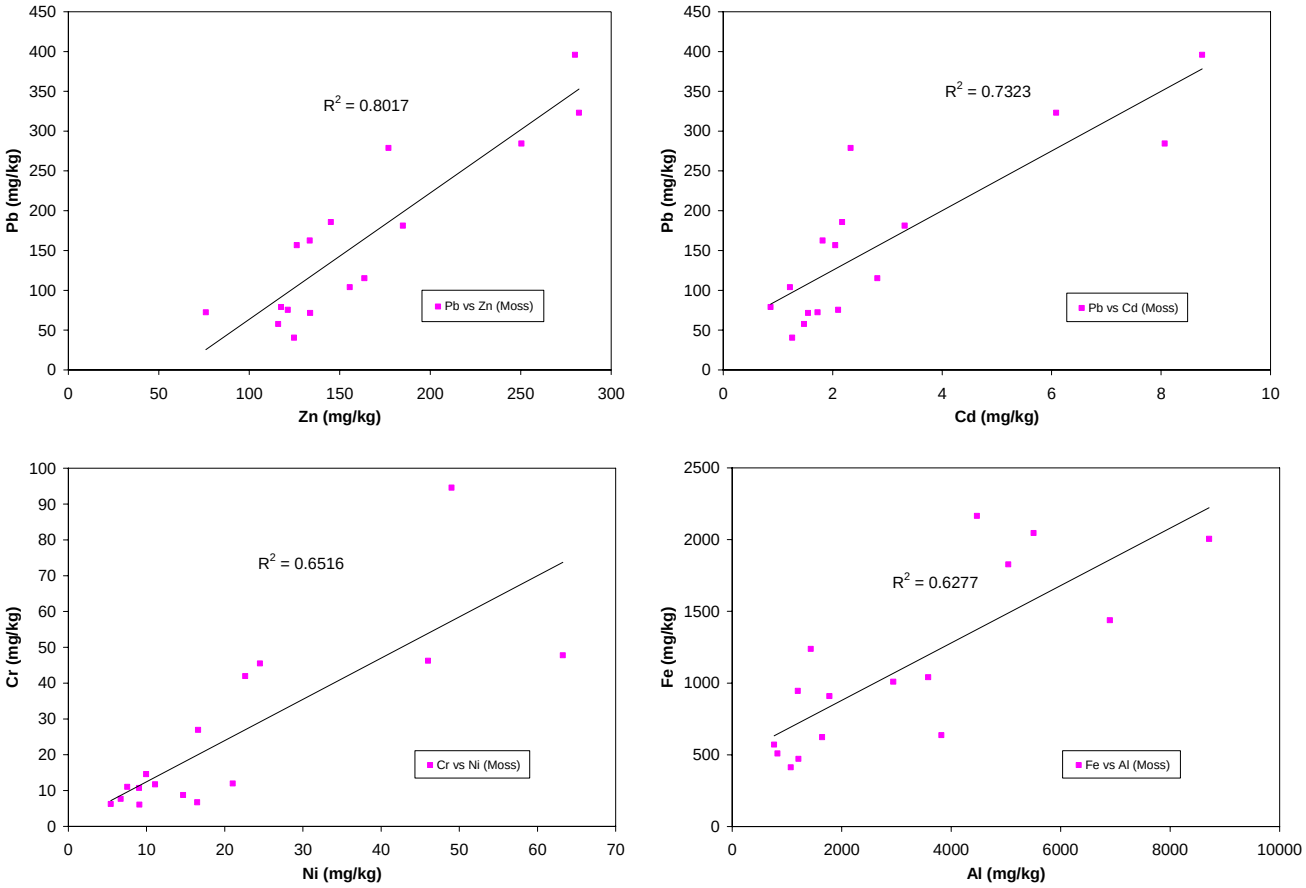
The results of the PC analysis for elemental concentrations of mosses are presented in Table 6-4. In the analysis, the major elements, such as Al and Fe, Ca and Mg, in the moss samples (see Table 6-4) were found to be closely correlated ($P<0.01$), possibly reflecting the geological origin of air particles. Elements such as Cd, Pb, Zn, and Cr, Cu and Ni were also shown to be strongly correlated ($P<0.01$), indicating potential anthropogenic inputs. The regression lines plotted for Pb vs Zn, Pb vs Cd, Cr vs Ni, Cu vs Ni, and Fe vs Al in the linear regression analysis showed that these elements were correlated significantly with $R^2>0.60$. Some of the results were presented in Figure 6-1, and they agreed well with the results from the PC analysis.

Table 6-4: Pearson correlation coefficient matrix between heavy metals and major elements of the moss *Hypnum plumaeforme* in the Nanling and PRD study areas

	Al	Ca	Cd	Cr	Cu	Fe	Mg	Ni	Pb	V
Ca	0.009									
Cd	-0.084	0.566*								
Cr	-0.110	0.566	0.474							
Cu	0.087	0.000	-0.079	0.320						
Fe	**0.792****	0.098	0.207	0.200	0.335					
Mg	-0.149	**0.654****	**0.668****	0.429	-0.273	0.153				
Ni	0.222	0.237	0.233	**0.807****	**0.668****	0.554*	0.103			
Pb	0.179	0.514*	**0.856****	0.293	0.013	0.316	0.399	0.228		
V	0.360	0.137	0.354	-0.165	0.039	0.499*	0.104	-0.016	0.361	
Zn	-0.076	0.663	**0.906****	0.385	0.005	0.497	0.612*	0.197	**0.895****	0.404

** $P<0.01$
* $P<0.05$

Figure 6-1: Elemental correlation in the Nanling mosses

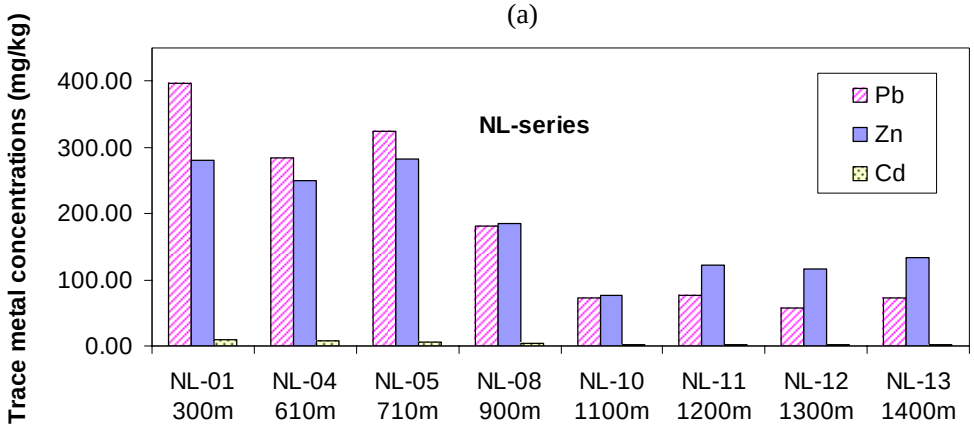


6.3 Topographical effect on moss metal concentrations

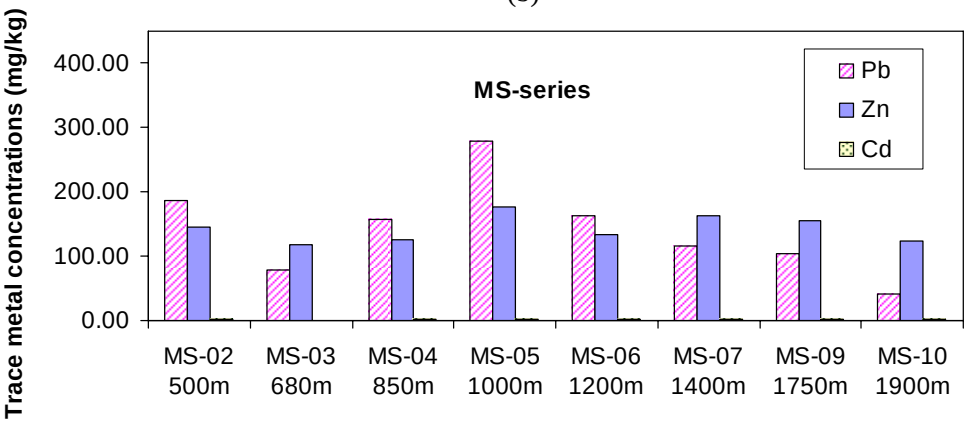
Mosses in the NL- and MS-series were collected at different elevations. The analytical results showed that the concentrations of elements such as, Cd, Pb and Zn, were significantly correlated with the elevations in the NL-series, but no significant correlation was observed in the MS-series (Figure 6-2a-c). At the elevations above 1100 m a.s.l., the concentrations of heavy metals became relatively constant. The results indicated that heavy metals such as Cd, Pb and Zn in the air tended to be associated with particles in areas of low elevation and close to sources of contamination and transport paths. Moreover, the statistical results from the Pearson correlation analysis showed that there was a strong elemental correlation among Cd, Pb and Zn in the Nanling mosses (see Table 6-4 and Figure 6-1), indicating a common source of anthropogenic inputs of these three heavy metals. The northern part of the Nanling Mountains was shown to be significantly enriched with heavy metals, possibly reflecting local sources of pollution and the effects of potential pathways for the long-range transport of air contaminants from northern China. In the southern part of the Nanling range, the elemental concentrations of Cd, Pb and Zn were relatively constant at various elevations, probably due to better mixing of the air because of coastal air flows from the South China Sea.

Figure 6-2: **(a) Cd, Pb and Zn concentrations of mosses in the NL-series; (b) Cd, Pb and Zn concentrations of mosses in the MS-series; (c) Linear plots of the Cd, Pb and Zn concentrations of mosses in the NL-series against elevation**

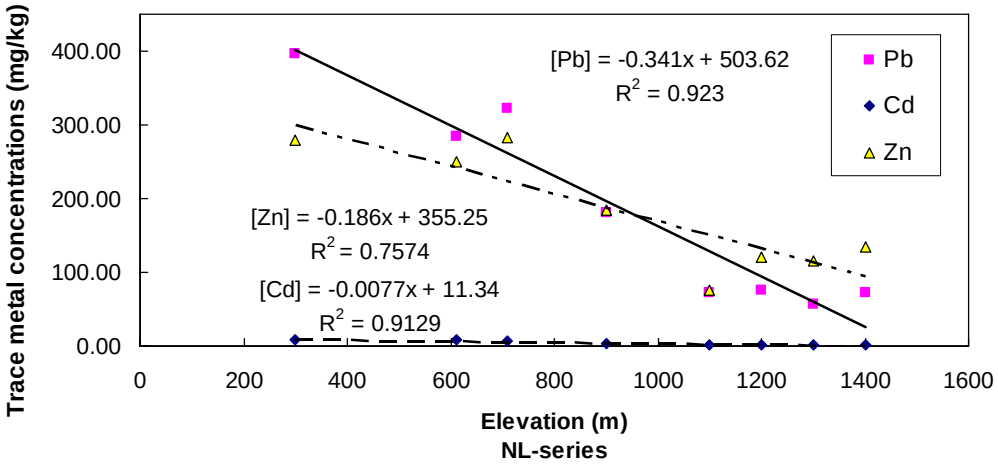
(a)



(b)



(c)



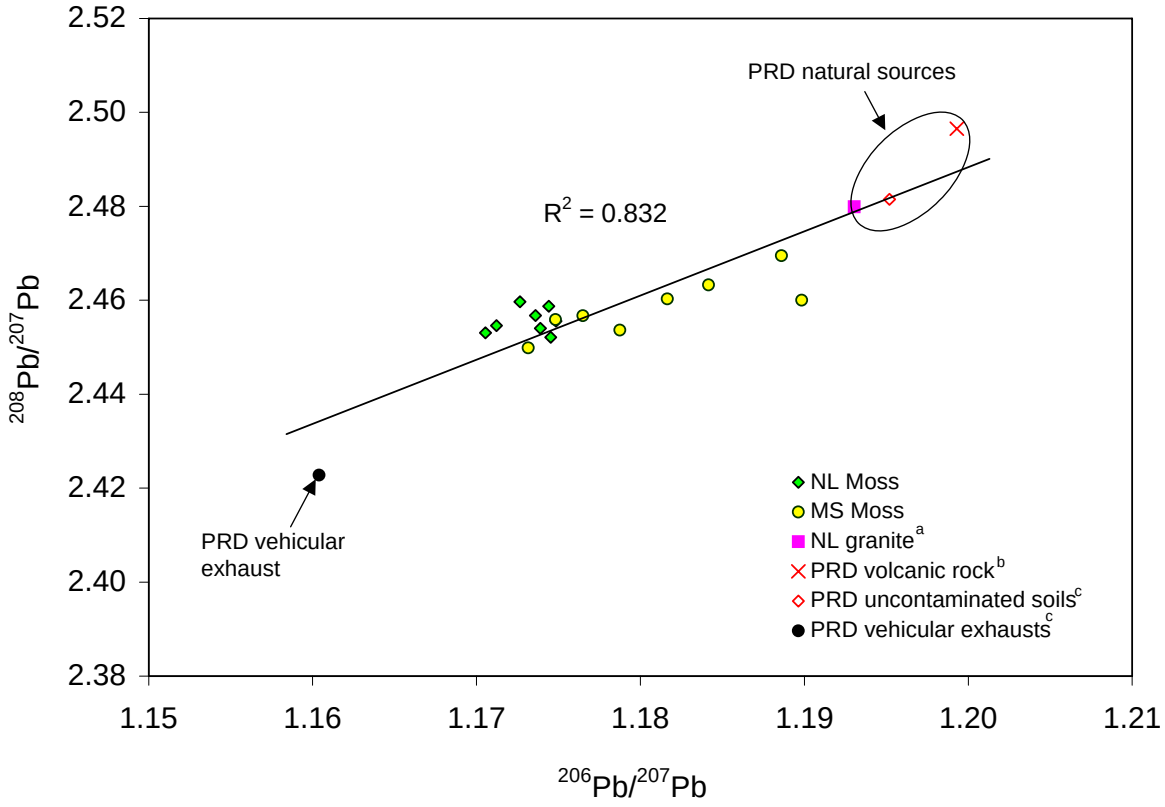
6.4 Pb isotopic compositions in mosses and aerosols

The Pb isotopic compositions of the Nanling mosses and the PRD aerosols are presented in Table 6-5. The ratios of $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in the Nanling mosses ranged between 0.0637-0.0642, 1.171-1.190 and 2.450-2.470, respectively. A comparison of the Pb isotopic ratios of known anthropogenic sources and the natural background may indicate the possible origins of Pb in the mosses. The Pb isotopic compositions of the mosses, the natural sources and vehicular emissions in the PRD are plotted in Figure 6-3. The Pb isotopic ratios of mosses were found to fit well between the natural sources and the vehicular emissions. The data points formed a linear correlation with R^2 = 0.832 (see Figure 6-3). The results indicated that vehicular emissions may be a major anthropogenic source of Pb in the Nanling mosses. The mosses in the Nanling mountain range showed $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of 1.171-1.190 and 2.450-2.470, which were relatively high compared with other moss species reported in European moss surveys (Weiss *et al*., 1999; Farmer *et al*., 2002). This is probably due to the different Pb compositions used in petrol and natural geological materials (e.g., uranium-rich granite) in the Nanling area (Zhang *et al*., 1993; Chen *et al*., 1999).

Table 6-5: Pb concentrations and isotopic compositions of the moss *Hypnum plumaeforme* in the Nanling Mountains and the aerosols in the PRD

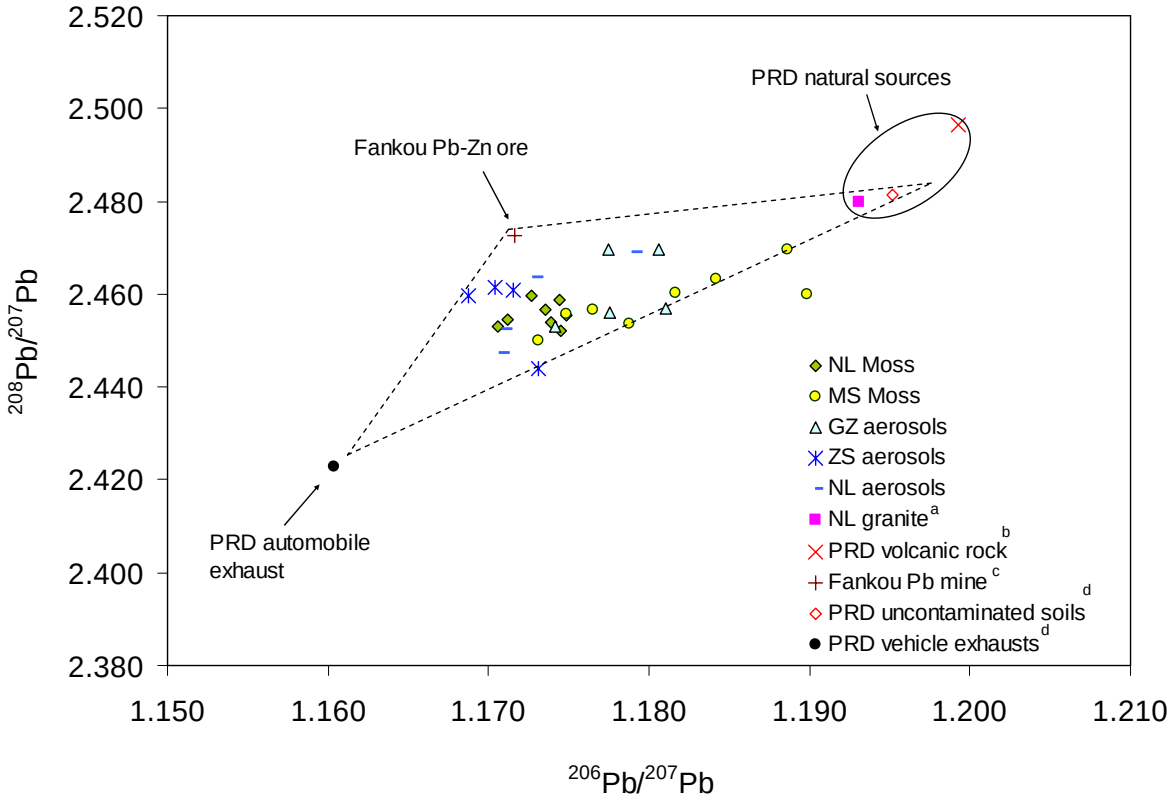
Nanling Moss					PRD Aerosol				
(N=16)	Sample ID	$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	(N=12)	Sample ID	$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
NL-series	NL-01	0.0641	1.171	2.455	*Nanling*	QY-01	0.0643	1.171	2.453
	NL-04	0.0642	1.171	2.453		QY-02	0.0642	1.173	2.464
	NL-05	0.0639	1.173	2.460		YTH-01	0.0644	1.179	2.469
	NL-08	0.0640	1.175	2.456		YTH-02	0.0643	1.171	2.447
	NL-10	0.0641	1.174	2.454					
	NL-11	0.0641	1.174	2.457		Mean	0.0643	1.173	2.458
	NL-12	0.0638	1.174	2.459					
	NL-13	0.0640	1.175	2.452	Guangzhou	GZ-01	0.0647	1.174	2.453
						GZ-03	0.0652	1.181	2.457
	Mean	0.0640	1.173	2.456		GZ-04	0.0651	1.181	2.470
						GZ-05	0.0644	1.178	2.470
MS-series	MS-02	0.0639	1.182	2.460					
	MS-03	0.0640	1.184	2.463		Mean	0.0649	1.178	2.462
	MS-04	0.0637	1.189	2.470					
	MS-05	0.0640	1.176	2.457	*Zhongshan*	ZS-01	0.0646	1.173	2.444
	MS-06	0.0638	1.190	2.460		ZS-02	0.0642	1.170	2.461
	MS-07	0.0640	1.175	2.456		ZS-03	0.0646	1.169	2.460
	MS-09	0.0641	1.179	2.454		ZS-04	0.0647	1.172	2.461
	MS-10	0.0640	1.173	2.450					
						Mean	0.0645	1.171	2.456
	Mean	0.0639	1.181	2.459					

Figure 6-3: **$^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of mosses in the Nanling Mountains ([a] Deng, 1987; [b] Zhu *et al*., 1989; [c] Zhu *et al*., 2001)**



To further assess the relationship of trace element concentrations in mosses with those in aerosols, the Pb isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) of aerosols were plotted in the same diagram as those of the mosses (see Figure 6-4). The ratios of $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in the aerosols at Nanling, Guangzhou and Zhongshan ranged between 0.0642-0.0652, 1.169-1.181 and 2.444-2.470, respectively (see Table 6-5). The Pb isotopic ratios of the PRD aerosols were similar to those of the Nanling mosses. The PRD aerosols were also affected by the anthropogenic Pb input from the vehicular emissions (Figure 6-4). In addition to this, the PRD aerosols were influenced by another source, which was the Pb-Zn ore in Fankou (industrial use of Pb in the region) (see Figure 6-4). The mixing of the isotopic signatures of Pb derived from both vehicular emissions and Pb-Zn ore contributed to the Pb isotopic composition of the PRD aerosols. As illustrated in Figure 6-4, the Pb isotopic compositions of the Nanling mosses resembled those of aerosols in Nanling and in the surrounding PRD region. This suggested that the Nanling and PRD aerosols were the major sources of the anthropogenic metal inputs in these mosses. The Nanling Mountains are located some distance away (> 60 km) from the nearest urban development, and the pollutants were probably derived from local sources and long-range transport of pollutants. The results showed that the Pb isotopic composition of mosses could reflect the Pb isotopic composition of the surrounding ambient air.

Figure 6-4: **$^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of aerosols in the Pearl River Delta, the Nanling mosses and other environmental samples in the Pearl River Delta ([a] Deng, 1987; [b] Zhu *et al.*, 1989; [c] Zhu, 1998; [d] Zhu *et al.*, 2001)**



6.5 Intercomparison of metal uptakes in different moss species at the Dinghu Mountain

Different moss species namely, *Hypnum plumaeforme*, *Leucobryum chlorophyllum*, *Pogonatum contorium*, *Thuidium tamariscinum and Bazzania tridens*, were collected at the same site in the Dinghu Mountain, PRD region, during May 2004. Table 6-6 summarises the major and trace elemental concentrations in the different moss species.

Table 6-6: Elemental concentrations of different moss species in PRD region

		Al	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	V	Zn
Hypnum plumaeforme	Mean	8700	3510	1.15	3.37	19.7	65.4	3110	899	51.1	40.0	219	10.6	280
(n=2)	Std dev	7360	1620	0.38	3.10	19.5	25.8	1720	58.7	23.3	33.7	110	2.48	33.3
Leucobryum chlorophyllum	Mean	8000	1570	0.62	1.69	8.87	13.5	4110	754	25.1	3.26	102	12.7	136
(n=13)	Std dev	4580	700	0.29	0.91	4.68	2.29	2290	170	9.94	1.01	39.1	5.41	121
Pogonatum contorium	Mean	13900	3500	1.81	1.14	10.0	21.4	4510	982	77.6	6.35	126	16.2	237
(n=8)	Std dev	2570	2350	0.82	0.32	2.95	8.53	1220	176	71.4	1.41	41.1	2.36	130
Thuidium tamariscinum	Mean	3860	3060	1.63	2.34	4.40	47.5	1770	796	70.2	11.6	218	11.7	209
(n=4)	Std dev	2190	865	0.55	2.14	2.14	11.1	756	208	26.0	3.18	74.9	2.41	75.9
Bazzania tridens	Mean	8770	3160	1.19	2.67	8.71	21.4	4540	1040	45.7	4.10	69.9	13.7	128
(n=2)	Std dev	1870	3590	0.69	2.71	2.00	19.6	1980	646	43.3	2.59	73.4	5.57	76.9

To further investigate on the variations between the elemental concentrations among different moss species, the Kruskal-Wallis Test was performed. The statistical results were depicted in Table 6-7. The mean concentrations of elements such as Cd, Cu, Ni ($P<0.01$) and Al, Mn, Pb ($P<0.05$) were found to be statistically different among the different species. The metal uptakes of Cd were in the order of *Pogonatum contorium*>*Thuidium tamariscinum*>*Bazzania tridens*>*Hypnum plumaeforme*> *Leucobryum chlorophyllum*. For Cu, Ni and Pb, the moss species *Hypnum plumaeforme* and *Thuidium tamariscinum* were found to contain significantly higher concentrations of these trace metals as compared to the other species, and the order of metal uptakes was *Hypnum plumaeforme*>*Thuidium tamariscinum*>> *Leucobryum chlorophyllum*≈ *Pogonatum contorium*≈ *Bazzania tridens*.

Table 6-7: Statistical results of the Kruskal-Wallis test on the elemental concentrations in different moss species at Dinghu Mountain, the PRD region

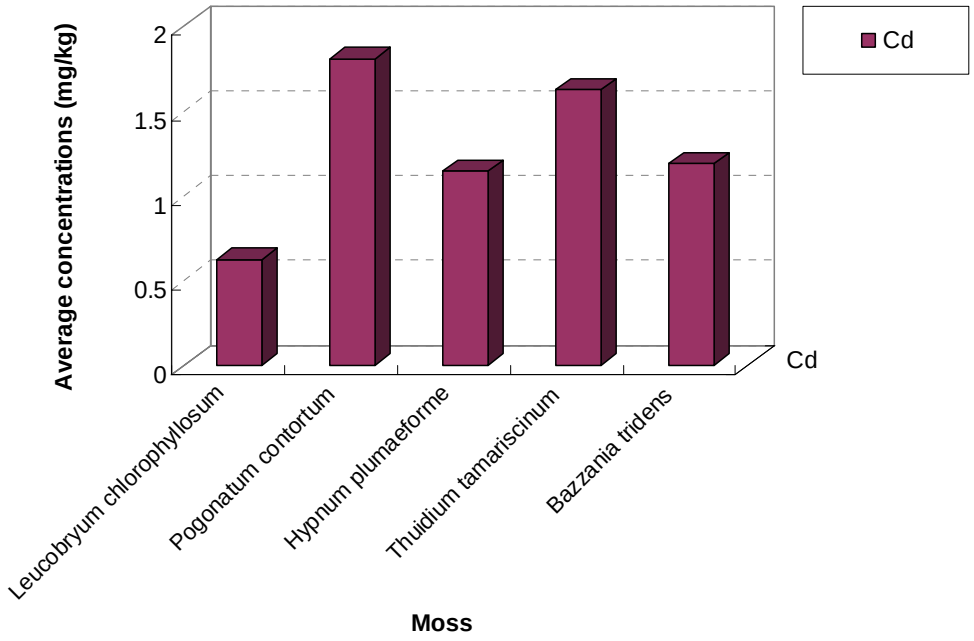
	Degree of freedom	Chi-Square	Significance
Al	4	11.915	0.018*
Ca	4	8.447	0.076
Cd	4	14.623	0.006**
Co	4	2.461	0.652
Cr	4	8.082	0.089
Cu	4	16.947	0.002**
Fe	4	8.554	0.073
Mg	4	6.701	0.153
Mn	4	9.996	0.040*
Ni	4	21.756	0.000**
Pb	4	12.042	0.017*
V	4	8.206	0.084
Zn	4	8.337	0.080

Note: **P<0.01
*P<0.05

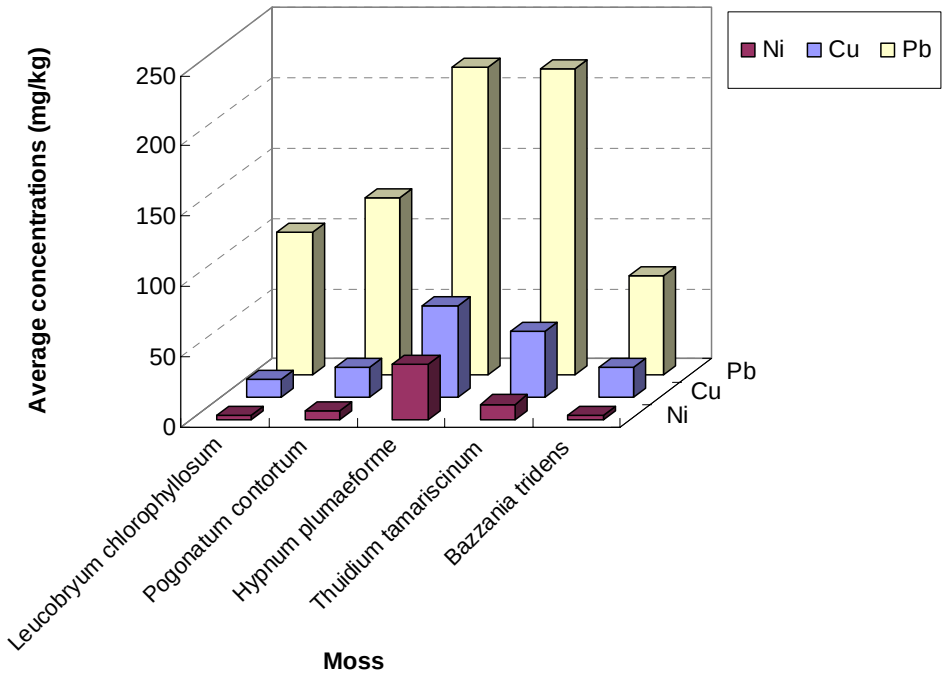
The average concentrations of Cd, Cu, Ni and Pb of the different moss species were compared in Figure 6-5a-b. The results showed that the moss species, *Hypnum plumaeforme* and *Thuidium tamariscinum* were suitable to be used as biomonitors of trace metals in the South China region, as they were found to have higher uptakes of most trace metals compared with other species. The moss *Pogonatum contorium* also has reasonably high uptakes of many trace metals (see Figure 6-5a-b). As indicated by previous researchers, the use of more than one species is necessary particularly in the large-scale surveys at national scale (Galsomiès *et al*., 2003). The moss species *Hypnum plumaeforme*, *Thuidium tamariscinum* and *Pogonatum contorium* were commonly found in China. *Hypnum plumaeforme* is also widely distributed in other Asian countries, including Japan, Korea, Nepal and Philippines, while *Pogonatum contorium* is also commonly found in India. The moss species *Hypnum plumaeforme*, *Thuidium tamariscinum* and *Pogonatum contorium*, hence have great potential use in the biomonitoring of trace metals in China and its surrounding regions.

Figure 6-5: Comparison of average concentrations of Cd, Ni, Cu and Pb in different moss species at Dinghu Mountain, the PRD region

(a)



(b)



6.6 Summary

The results in this chapter showed that trace metal concentrations in the moss *Hypnum plumaeforme*, *Thuidium tamariscinum* and *Pogonatum contorium* can be a good indicator for biomonitoring of atmospheric metal pollution in southern China. Trace elements such as Pb, Zn and Cd were found to be correlated with the elevations in northern Nanling. The concentrations of heavy metals decreased as the elevation increased, indicating that metal-rich particles were concentrated and transported in the lower air mass. The Pb isotopic compositions showed that vehicular emissions accounted for the major anthropogenic inputs of Pb in the mosses and aerosols, with some influences from the Pb ore used in the local industry. The moss *Hypnum plumaeforme*, *Thuidium tamariscinum* and *Pogonatum contorium* had high uptakes of trace metals, and were commonly found in the South China region. They showed a high-potential for use in the biomonitoring of trace element atmospheric pollution in South China, and possibly in other sub-tropical regions.

Chapter 7 − Integrated studies on the relationships of trace metals in particulate matter, dry and wet depositions and mosses, and the implications to regional environmental quality of the PRD region

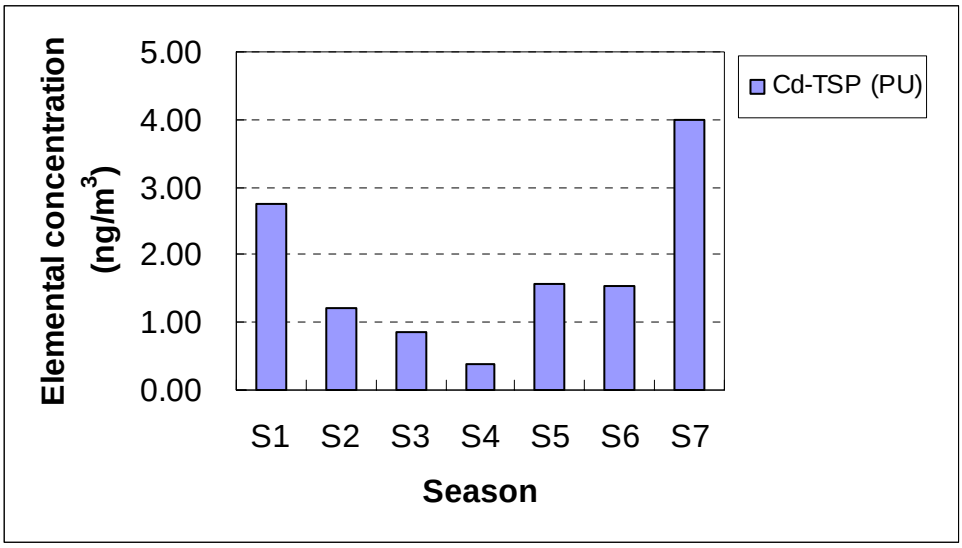
Trace metals in particulate matter, dry and wet depositions and mosses in the urban, suburban and rural areas of the PRD region have been assessed in the present study over one-year period of measurement. Once trace metals are emitted from their sources to the atmosphere, some may be removed close to their point of emission by contact with airborne droplets or the Earth's surface. Others can be carried high into the atmosphere and be transported to a great distance before they are ultimately removed from the atmosphere, mainly through two processes: wet deposition and dry deposition (Seinfeld and Pandis, 1998). In order to further investigate the environmental pathways of trace metals in the study region, and their impacts on human health and the ecosystem, the relationships of trace metals among the airborne TSP and those deposited as dry and wet depositions on the surface environment were studied. Moreover, the health risks associated with trace metals and the long-term implications on soils and water bodies were also evaluated.

7.1 Relationships of trace metals in particulate matter and atmospheric (dry and wet) depositions

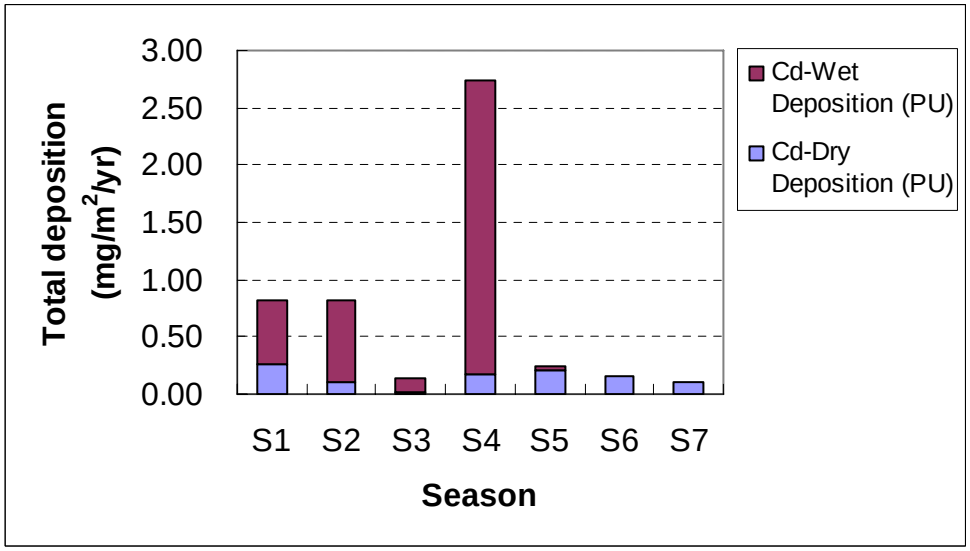
As described in the methodology section (Section 3.2), the sampling of particulate matter and dry and wet depositions were conducted on bi-weekly and bi-monthly basis, respectively, over 1-year period of measurement. The average trace metal concentrations in particulate matter over the same collection period (2 months) as the dry and wet depositions were calculated, and compared with

the total deposition (summation of dry and wet depositions) at the urban areas of Hong Kong and Guangzhou (PU and ZU). Figure 7-1a-b shows the average Cd concentrations (calculated on bi-monthly basis) in TSP and total deposition fluxes of Cd at PU. The average concentrations of Pb in TSP and total deposition flux of Pb at PU are depicted in Figure 7-2a-b. As illustrated in the figures, seasonal trends can be observed in the average trace metal concentrations of TSP at PU, with higher concentrations during the winter period (S1 and S7) and lower during the spring and summer period (S3 and S4). However, the total deposition was observed to be higher during the summer period (S4). The high trace metal loadings observed in total deposition during S4 were mostly attributed to the wet deposition. As discussed earlier in Chapter 5, this was due to a greater scavenging effect of rain during summertime. Similar observations were obtained when the average concentrations of trace metals, such as Cd, Pb, V and Zn, in particulate matter were compared with those in the total depositions at ZU. The average Cd concentrations in TSP and Cd total deposition fluxes at ZU are shown in Figure 7-3a-b. Figure 7-4a-b depicts the average Pb concentrations in TSP and Pb total deposition fluxes at ZU. The average trace metal concentrations, including Cd, Pb, V and Zn, in TSP were also plotted against the corresponding dry, wet and total deposition fluxes at PU and ZU. The linear relationships were not significant as shown by the low R^2 values, showing that no linear correlation was observed. This showed that there were no significant associations between the trace metals in particulate matter and those in dry, wet and total depositions. The total deposition of trace metals were dominated mostly by wet deposition. The rain scavenging effect was a predominant factor in the total deposition of trace metals in the PRD region.

Figure 7-1: Average Cd concentration of TSP and Cd total deposition fluxes at PU

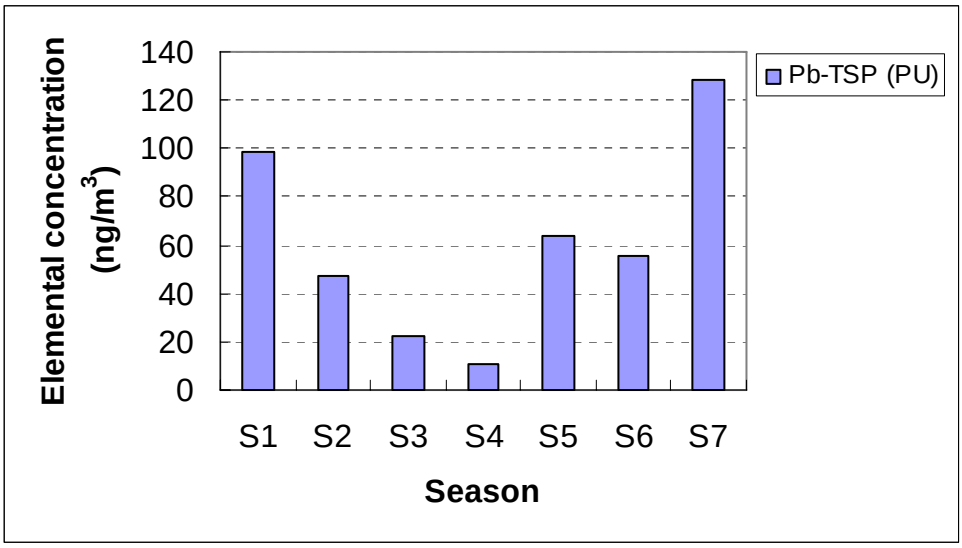


(a)

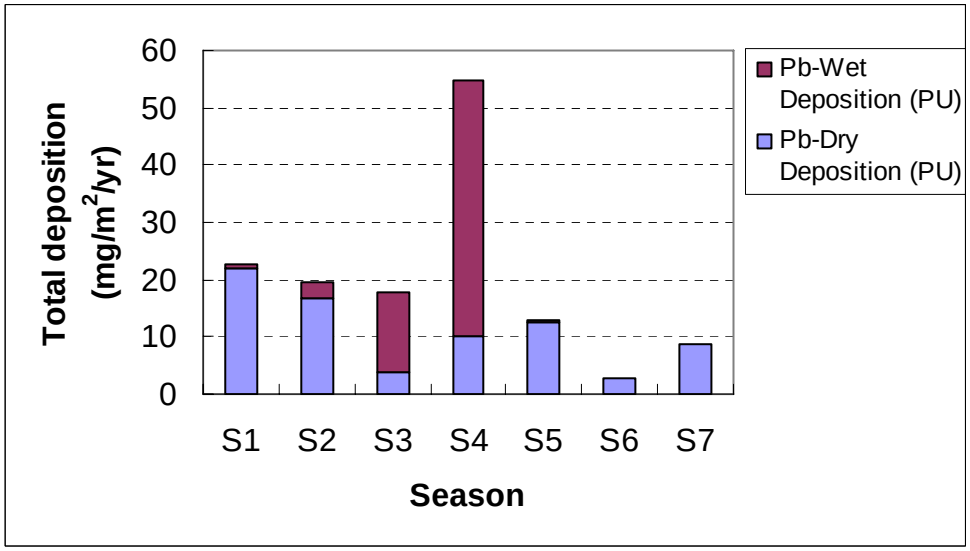


(b)

Figure 7-2: Average Pb concentration of TSP and Pb total deposition fluxes at PU

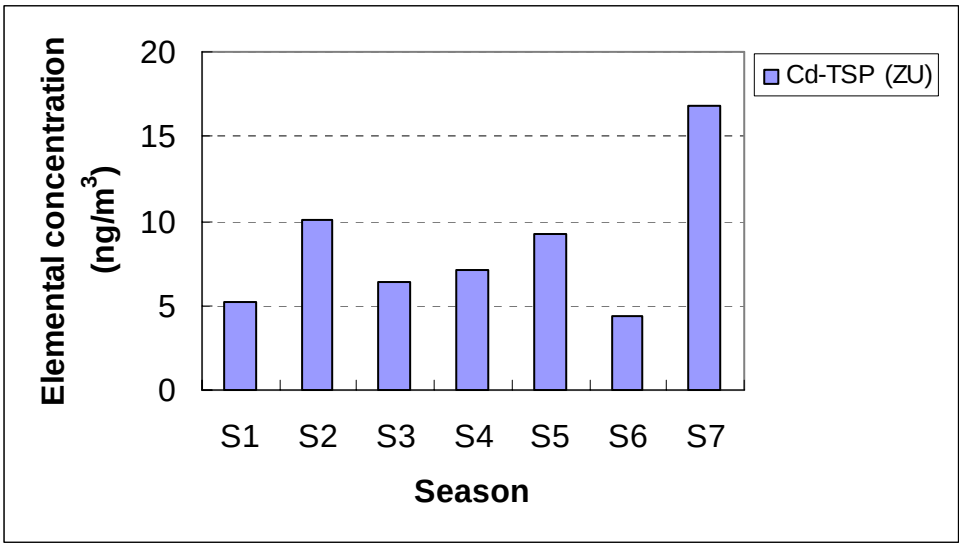


(a)



(b)

Figure 7-3: Average Cd concentration of TSP and Cd total deposition fluxes at ZU



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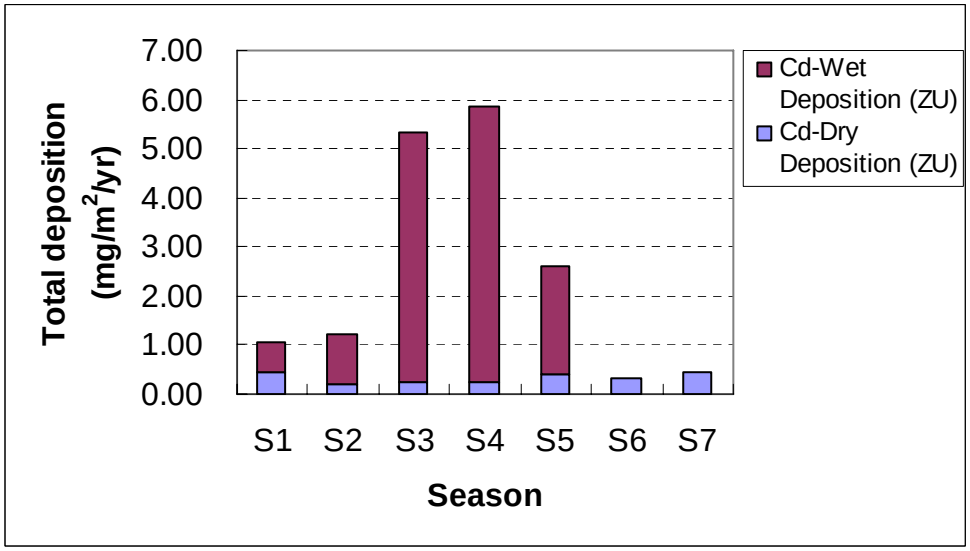
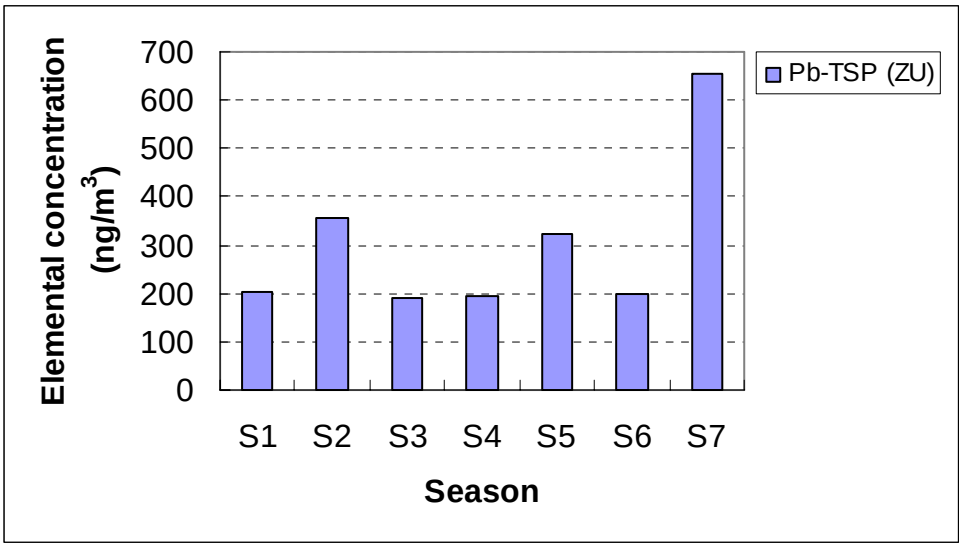


(b)

Figure 7-4: Average Pb concentration of TSP and Pb total deposition fluxes at ZU



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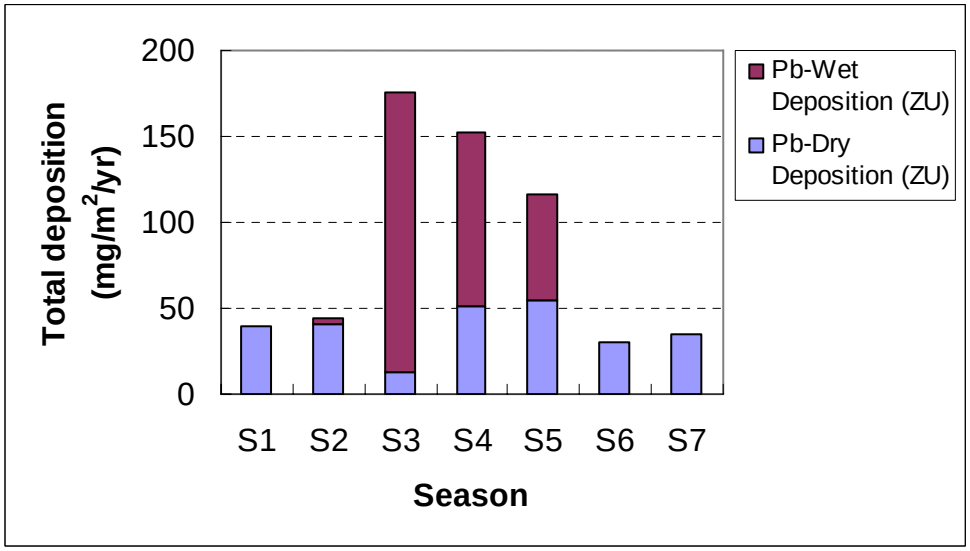

(b)

7.2 Deposition velocity of trace metals

The dry deposition velocity of trace metals was computed by dividing the dry deposition fluxes of trace metals with the corresponding values of the average trace metal concentrations in TSP. The dry deposition velocity of major and trace elements at PU and ZU are shown in Table 7-1.

Table 7-1: Average dry deposition velocities of major and trace elements at PU and ZU

(cm/s)		Al	Cd	Cr	Cu	Fe	Mg	Mn	Pb	V	Zn
PU											
Dry deposition velocity	Mean	1.98	0.15	2.02	0.27	1.75	0.36	0.62	0.33	0.34	0.19
n = 7	SD	1.97	0.17	1.36	0.31	1.35	0.20	0.34	0.35	0.35	0.15
ZU											
Dry deposition velocity	Mean	0.96	0.05	1.94	0.31	1.15	0.46	0.46	0.17	0.23	0.12
n = 7	SD	0.43	0.03	2.09	0.22	0.55	0.16	0.13	0.08	0.08	0.10

As depicted in Table 7-1, the dry deposition velocities of major elements, including Al, Fe, Mg and Mn, and trace metal, Cr, at PU and ZU were found to be relatively higher. On the other hand, trace metals, such as Cd, Cu, Pb, V and Zn, at both sites had relatively lower dry deposition velocities. This indicated that metals such as Cd, Cu, Pb, V and Zn were probably associated with finer particles which had lower deposition velocity.

Chromium and the major elements were generally associated with larger particles with higher deposition velocity. To further investigate on the differences of the

dry deposition velocities for major and trace elements (Al, Cd, Cr, Cu, Fe, Mg, Mn, Pb, V and Zn) at different sampling sites, the Student's T-test was performed. The statistical results showed that there was no significant differences in the dry deposition velocities of Al, Cd, Cr, Cu, Fe, Mg, Mn, Pb, V and Zn ($P>0.05$), showing that the dry deposition velocities of these elements were similar at Hong Kong and Guangzhou.

7.3 Relationships of trace metals in mosses and atmospheric (dry and wet) depositions

In this study, attempts were made to evaluate the relationships of trace metals in mosses and those in dry and wet depositions. Trace metals in mosses *Hypnum plumaeforme* and *Thuidium tamariscinum* at Dinghu Mountain in Zhaoqing of the PRD were compared with those in dry and wet depositions in the PRD region (average values), as no deposition samples were collected at Zhaoqing. Metal uptakes by moss from the atmosphere involve physical processes of sedimentation, impaction and diffusion, or via air particulate deposited in precipitation (Taylor and Witherspoon, 1972; Wallin, 1976; Onianwa *et al*., 2001). The process of metal uptakes by mosses are complex and it should be noted that this part of study mainly focuses on the relationships of trace metals in mosses and dry and wet depositions based on the current measurements in the study region. Table 7-2 shows the elemental ratios of trace metals such as Cd, Cu, Pb, V and Zn in mosses at Dinghu Mountain and those in dry and wet depositions in the PRD region.

Table 7-2: Elemental ratios in the mosses at Dinghu Mountain, and dry and wet depositions in the PRD region

		Zn/Cu	Zn/Pb	Zn/V	Pb/V	Pb/Cd
Moss						
Hypnum plumaeforme	n = 2	4.28	1.28	26.4	20.7	190
Thuidium tamariscinum	n = 2	4.40	0.96	17.9	18.6	134
Dry deposition PRD	n = 112	3.92	2.51	9.30	3.71	99.0
Wet deposition PRD	n = 77	18.5	25.0	133	5.32	15.6

The ratios of Zn/Cu, Zn/Pb, Zn/V, Pb/V and Pb/Cd in the mosses *Hypnum plumaeforme* and *Thuidium tamariscinum* were similar, showing that there was a close resemblance in the elemental associations of trace metals such as Cd, Cu, Pb, V and Zn in the two moss species. Since the mosses were collected at the same location, the results implied that the mosses *Hypnum plumaeforme* and *Thuidium tamariscinum* may have similar affinity in the uptakes of trace metals, such as Cd, Cu, Pb, V and Zn. The ratios of Zn/Cu, Zn/Pb and Pb/Cd in the mosses were in similar range as those in the dry depositions, and the ratio of Zn/V was in the range of those in the dry depositions and wet depositions. On the other hand, the Pb/V ratio was relatively higher in the mosses as compared with those in the dry and wet depositions. In overall, the elemental associations in the mosses were found to vary among different trace metals. Further investigation is needed to better understand the metal uptakes in the mosses from different atmospheric depositions in the region.

7.4 Potential health implications

Direct inhalation is an important pathway of trace metal intake in human, which may be associated with adverse health impacts such as inflammation in the airway and lungs (Ghio *et al*., 1999; Ghio and Devlin, 2001; Nel, 2005). In order to examine the health implications and the potential risks associated with inhalation of trace metals from contaminated air, calculations were conducted using Equation (3-1) presented in the methodology section (Section 3.4.6). Table 7-3 shows the reference exposure levels for selected trace metals for non-cancer chronic health effects recommended by California Air Pollution Control Officers Association (CAPCOA, 1993).

Table 7-3: Reference Exposure Level (REL) for chronic non-cancer health effects

Trace metals	Exposure Level ($\mu g/m^3$)
Cadmium	3.5
Copper and copper compounds	2.4
Lead and compounds	1.5
Zinc compounds	35

[Source: CAPCOA (1993)]

In the calculation of HI using the REL for chronic health effects, long-term measurement data was used, and in the present study the annual average trace metal concentrations were adopted. The calculation of HI_{mix} is based on the assumption of dose addition. The assumption of dose addition is most clearly justified when the mechanisms of action of the compounds under consideration are known to be the same (USEPA, 1986, 2000). In the calculation of the HI_{mix}, the trace metals are assumed to exhibit similar mechanisms of toxicity on health. Moreover, in the present study, the HI was calculated to evaluate the systemic

effects of trace metals. In reality, trace metals have different effects on various end point of concern (such as kidney, cardiovascular and respiratory system), and the health risks associated with different health end points should be evaluated.

Table 7-4 summarises the calculated HI_{single} of trace metals through inhalation using the annual mean concentrations of TSP in urban areas of the PRD region (PU and ZU). As shown in Table 7-4, the HI values of Cd, Cu, Pb and Zn at PU and ZU were all below 1.0, indicating that no significant health impacts were expected from the exposure to these trace metals in the air. However, relatively higher HI values were depicted for airborne Pb in the urban Guangzhou, which was 0.180. Hence, the potential long-term health risks associated with the exposure of airborne trace metals in the urban areas of the PRD region were relatively low.

Table 7-4: Health hazard indices (HI_{single}) of trace metals through inhalation

	PU		ZU	
	Annual mean concentration ($\mu g/m^3$)	Hazard Index (HI_{single})	Annual mean concentration ($\mu g/m^3$)	Hazard Index (HI_{single})
Cd	0.00161	0.0005	0.00784	0.0022
Cu	0.0708	0.0295	0.0823	0.0343
Pb	0.0565	0.0377	0.269	0.1795
Zn	0.298	0.0085	1.191	0.0340

The additive effects of trace metals on human health were further evaluated by calculating the HI_{mix} as defined earlier in the methodology section (Section 3.4.6). Table 7-5 shows the calculated HI_{mix} due to the long-term exposure of trace metals, including Cd, Cu, Pb and Zn, in the urban areas of the PRD region.

Table 7-5: Health hazard indices (HI_{mix}) of trace metals through inhalation

	PU	ZU
Hazard Index (HI_{mix})	0.0762	0.2501

As shown in Table 7-5, the calculated HI_{mix} at ZU was higher than PU, showing that the risks associated with trace metals in Guangzhou were relatively higher than that in Hong Kong. As the HI values were below 1.0 at both sites, no significant health impacts were expected for the exposures to these trace metals in the air. However, the above calculation was based on the average concentration values. During the episode days with high trace metal concentrations, the HI values are expected to be higher, which may impose greater risks on health. As discussed earlier the sources of airborne Pb were industrial emissions, the use of Pb from local ore and vehicular emissions in the region (see Section 4.4). The back trajectory analysis also indicate the potential transport of trace metals from northern inland areas of China and South Asian countries to the region (see Section 4.5). Considering the high population in mega cities such as Guangzhou and Hong Kong, the potential health risks from trace metal pollution will affect a great population and proper mitigation measures should be carried out to protect the public health.

7.5 Environmental impact of dry and wet depositions of trace metals

Inputs of pollutants into the terrestrial environment pose great burden on natural ecosystems. Trace metals in the air will eventually be deposited onto the soil and water surfaces, endanger the living organisms and abiotic sectors of ecosystems. Moreover, trace metals can enter the food chain and cause adverse health effects on human. The present study has evaluated the annual dry and wet depositions of trace metals, such as Cd, Co, Cr, Cu, Pb, V and Zn, in the PRD region. In order to investigate the potential implications of elevated deposition of atmospheric trace metals in the environment, attempts were made to estimate the metal enrichments in surface soils and water bodies within the PRD region.

The trace metals in agricultural and undisturbed soils in the PRD were 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 trace 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-yr period, the projected concentrations of Cu, Pb and Zn of the soils were calculated. The final concentrations of trace metals in soils due to dry, wet and total depositions were denoted as $C_{soil,\ wet}$, $C_{soil,\ dry}$ and $C_{soil,\ total}$, respectively, and $C_{soil,\ int}$ showed the initial concentrations in soils. The results of the above estimations are summarised in Table 7-6.

Table 7-6: Estimates of the increase of trace metal concentrations in undisturbed soils

	$C_{soil, int}$ mg/kg	$C_{soil, dry}$ mg/kg	increase %	$C_{soil, wet}$ mg/kg	increase %	$C_{soil, total}$ mg/kg	increase %
Cu	15	16.4	9.1%	19.0	26.9%	20.4	36.0%
Pb	30	32.1	7.1%	33.0	9.9%	35.1	17.0%
Zn	45	50.4	11.9%	119	165%	125	177%

As shown in Table 7-6, atmospheric dry deposition of Cu of 4.44 mg/m^2/yr lead to an increase of Cu concentration in the soils by 9.1% after 20-yr period. The increase in Cu concentration of the soils due to wet deposition (13.1 mg/m^2/yr) was 26.9%, and the total (dry and wet) deposition (17.5 mg/m^2/yr) amounted to 36.0% increase. For Pb, it was calculated that atmospheric dry deposition of 6.93 mg/m^2/yr caused an increase of Pb concentration of the soils by 7.1%. The increments of Pb concentration of the soils due to wet deposition (9.68 mg/m^2/yr) were 9.9%, and the total (dry and wet) deposition (16.6 mg/m^2/yr) was 17.0%. On the other hand, the Zn concentration of the soils would increase by 11.9% due to the atmospheric dry deposition of Zn of 17.4 mg/m^2/yr. The wet deposition of Zn of 242 mg/m^2/yr, and the total (dry and wet) deposition of Zn of 259 mg/m^2/yr would lead to 165% and 177% increase of Zn in the soils, respectively. The results showed that the dry and wet depositions of Cu, Pb and Zn in the PRD region caused approximately 17 to 177% increases in the trace metal concentrations of surface soils in the region over a 20-yr period. It has been shown that the region was susceptible to significant inputs of trace metals, such as Cu, Pb and Zn, among which the wet deposition of Zn was the most severe, amounted to 165% increase of Zn concentration. The estimates indicated that the atmospheric depositions of trace metals had significant long-term implication on

the soil quality in the PRD region.

The impact of elevated dry and wet depositions of trace metals in the PRD region has been evaluated by Ouyang *et al*. (2006). In this study, the dissolved trace metals in river water over major drainage basins in the PRD region have been investigated. The mean background concentrations of Cu, Pb and Zn in the river water were 5.82, 0.40 and 7.73 μg/l, respectively, and these were used in the present study as the background trace metal concentrations of freshwater in the PRD region. Assuming a water density of 1.0 g/cm^3 and that atmospheric deposition was the sole source of trace metal input, the enrichment of trace metals in the water body in the PRD region was calculated. Since no major lakes were found in the PRD region, the effects of trace metal depositions in a major reservoir in the PRD region was studied. The Huanglongdai reservoir is one of the largest reservoirs located in Guangzhou of the PRD region with a capacity of 94.6 million m^3 and dam height of 60 m (The Ministry of Water Resources, 2005). Unlike trace metals in soils which are relatively stable and retained at the soil surface over long period of time, the trace metals entered the reservoir are relatively mobile and was transferred down along the water column. In the present case study, it was assumed that trace metals entering the reservoir through dry and wet depositions became homogeneously mixed and undisturbed for 1-yr period. The enrichment of trace metals in the reservoir was then calculated. The final concentrations of trace metals of the reservoir water due to dry, wet and total depositions were denoted as $C_{water,\ dry}$, $C_{water,\ wet}$ and $C_{water,\ total}$, respectively, and $C_{water,\ int}$ represented the initial background concentrations of trace metals in the reservoir water. The results of the above estimations are shown in Table 7-7.

Table 7-7: Estimates of the increase of trace metal concentrations in reservoir water

	$C_{water, int}$ μg/l	$C_{water, dry}$ μg/l	increase %	$C_{water, wet}$ μg/l	increase %	$C_{water\ total}$ μg/l	increase %
Cu	5.82	5.89	1.3%	6.04	3.8%	6.11	5.0%
Pb	0.40	0.52	28.9%	0.56	40.3%	0.68	69.2%
Zn	7.73	8.02	3.8%	11.8	52.2%	12.1	55.9%

Table 7-7 shows that atmospheric deposition of Cu of 4.44 mg/m^2/yr caused an increase of Cu concentration of the reservoir water by 1.3% after 1-yr period. Alternatively, the wet deposition (13.1 mg/m^2/yr) and total (dry and wet) deposition (17.5 mg/m^2/yr) of Cu lead to 3.8% and 5.0% increase of Cu concentration in the reservoir water, respectively. For Pb, the atmospheric dry deposition of Pb of 6.93 mg/m^2/yr lead to an increase of Pb concentration of the reservoir water by 28.9%. The increments of Pb concentration of the reservoir water due to wet deposition and total (dry and wet) deposition were 40.3% and 69.2%, respectively. Furthermore, the atmospheric dry deposition of Zn of 17.4 mg/m^2/yr lead to an increase of Zn concentration of the reservoir water by 3.8%. The wet deposition (242 mg/m^2/yr) and total (dry and wet) deposition (259 mg/m^2/yr) of Zn resulted in 52.2% and 55.9% increase of Zn concentration of the reservoir water, respectively. The results showed that after 1-yr period, the trace metal concentrations of reservoir water increased by 5.0 to 69.2% in the PRD region. The dry and wet depositions could led to the significant increase of trace metal concentrations of reservoir water, especially the wet depositions of Pb and Zn, which were 40.3% and 52.2%, respectively. These estimates showed that the

elevated atmospheric depositions of trace metals had significant implications on the water quality in the PRD region.

7.6 Summary

The relationships of trace metals in particulate matter, dry and wet depositions and mosses have been investigated. No significantly direct relationship was found among trace metals in particulate matter and those in dry, wet and total depositions. The total deposition loadings of trace metals were found to be dominated by wet depositions. Furthermore, the deposition velocity of anthropogenic metals, including Cd, Cu, Pb, V and Zn, in Hong Kong and Guangzhou were lower than that of major elements, such as Al, Fe, Mg and Mn, and the trace metal Cr. Trace metals, such as Cd, Cu, Pb, V and Zn were probably associated with finer particles which had a lower deposition velocity. The moss *Hypnum plumaeforme* and *Thuidium tamariscinum* had similar affinity in the uptakes of trace metals, such as Cd, Cu, Pb, V and Zn. Moreover, the potential health risks associated with inhalation of trace metals in the PRD region have been evaluated. The risk assessments showed that no significant health impacts were expected for the current exposure to trace metals in the air in urban areas of Hong Kong and Guangzhou. The impacts on regional environmental quality have been projected based on the dry and wet deposition loadings in the present study.

Chapter 8 − Conclusions and Recommendations

8.1 Summary of major scientific findings

Trace metal contaminations in particulate matter, dry and wet depositions and mosses in the PRD region have been investigated. This study contributes toward our understanding of the atmospheric transport of trace metals and the impact of dry and wet depositions of metallic pollutants in the PRD region. The major findings on the trace metals in particulate matter in urban and suburban areas of the PRD are as follows:

1. Elevated concentrations of trace metals, especially Cd, Pb, V and Zn, were observed in the urban and suburban areas of Guangzhou, which were higher than those in Hong Kong, showing significant atmospheric trace element pollution in Guangzhou.

2. 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.

3. The TSP in Guangzhou were found to be dominantly influenced by local sources, as indicated by the lack of seasonal variations in metal concentrations and the similarity of Pb isotopic signatures to local pollution sources (e.g. local Pb ore and industrial sources).

4. 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 PRD region, and lower $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in summer, indicating the influence of Pb from the South Asia region and from marine sources.

5. The $PM_{2.5}$ in urban Guangzhou was found to be highly enriched with trace metals such as Pb, V and Zn. The PCA analysis showed that anthropogenic sources were the major contributors in the finer fractions ($PM_{2.5}$), while natural sources were dominant in the coarser fractions (TSP) in the urban areas of Guangzhou.

6. Trace elements, such as Cd, Cu, Ni, Pb, V and Zn, in $PM_{2.5}$ of Guangzhou had very high enrichment factors, ranging between 46 for Ni to 3400 for Cd. These elements were highly enriched in $PM_{2.5}$ as compared to the continental crustal materials, suggesting that they were originated from some anthropogenic sources.

7. The average $PM_{2.5}$/TSP ratios of Cd, Cu, Ni, Pb and V were high in the urban areas of Guangzhou, showing that they were dominant in the fine fraction.

8. The average concentrations of OC and EC in urban and suburban areas of Guangzhou were higher than those in Hong Kong, indicating the severe atmospheric pollution in Guangzhou and its surrounding areas.

9. Similar to the results for the trace metal concentrations, distinguished seasonal patterns were observed in the OC and EC concentrations in Hong Kong, with higher concentrations during the winter monsoon

period, and lower concentrations during summertime. In contracst, the OC and EC concentrations in Guangzhou exhibited less variability and remained high throughout the year.

10. Relatively high OC/EC ratios (>2.0) were depicted at PU, HT, ZU and BY, especially at HT, indicating the presence of relatively high secondary organic carbon (SOC).

The major findings on the trace metals in dry and wet depositions in the urban and rural areas of the PRD are as follows:

1. The dry and wet depositions of most trace elements were found to be higher in the urban and suburban areas of the PRD region, as compared to those in the rural areas.

2. The urban and suburban areas in the inland PRD region, near Guangzhou, were found to have the highest dry and wet depositions of heavy metals, particularly for Cd, Pb and Zn. The Zn wet deposition flux at the suburban inland PRD area (Baiyun Mt.) was about 5-fold of the regional mean annual value, showing the severe atmospheric deposition pollution of trace metals in the inland PRD region.

3. Distinguished temporal variation was observed in the dry and wet depositions of trace elements, such as Co, Cu and Zn, in the urban areas. Higher dry deposition flux of Zn in urban areas occurred during the winter season, probably due to the influx of pollutants during the winter monsoon period. The wet deposition fluxes of Co, Cu and Zn in urban

areas were observed to be higher in the summer season, attributed to a greater scavenging effect by rain.

4. The concentrations of the trace element wet deposition, including Cd, Co, Cr, Cu and Zn were found to be higher during the winter season, due to a lower amount of rainfall.

5. The mode of deposition was found to vary for different elements. Aluminium, Fe, Cr were found to be mainly deposited as dry depositions, and Cd, Co, Cu, Mg, Mn and Zn were primarily deposited as wet depositions, during both winter and summer seasons. The predominant pathway of deposition of Pb and V was dry deposition during the winter season and wet deposition during summer.

6. The Pb isotopic ratios of most dry and wet deposits, during both winter and summer seasons, were found to be similar to the anthropogenic sources of the PRD region, such as the Pb ore, industrial and vehicular emissions.

The major findings on the trace metals in mosses in the Nanling Mountains and the Dinghu Mountain are as follows:

1. The results showed that trace metal concentrations in the moss *Hypnum plumaeforme* can be a good indicator for bimonitoring of atmospheric metal pollution in Southern China.

2. The Pb isotopic compositions showed the ability of the moss *Hypnum*

plumaeforme to reflect the Pb isotopic composition of the surrounding ambient air. Vehicular emissions accounted for the major anthropogenic inputs of Pb in the mosses and aerosols, with some influences from the Pb ore used in the local industry.

3. A comparative study was conducted on the metal uptakes of different moss species, including *Hypnum plumaeforme, Leucobryum chlorophyllum, Pogonatum contorium*, *Thuidium tamariscinum* and *Bazzania tridens*. The results showed that the moss species, *Hypnum plumaeforme* and *Thuidium tamariscinum,* were suitable to be used as biomonitors of trace metals in the South China region and other subtropical areas.

Lastly, the major findings on the integrated studies on the relationships of trace metals in particulate matter, dry and wet depositions and mosses are as follows:

1. No significantly direct relationship was found among trace metals in TSP and those in dry, wet and total depositions.

2. The deposition velocity of anthropogenic metals, including Cd, Cu, Pb, V and Zn, in Hong Kong and Guangzhou were lower than that of major elements, such as Al, Fe, Mg and Mn, and the trace metal Cr. Trace metals, such as Cd, Cu, Pb, V and Zn, were probably associated with finer particles which had a lower deposition velocity.

3. The risk assessments based on hazard index (HI) showed that no significant health impacts were expected for the current exposure to

trace metals in the air in urban areas of Hong Kong and Guangzhou.

8.2 Recommendations

With respect to the study of trace metal contamination of the particulate matter, dry and wet depositions and mosses in the PRD region, several recommendations are made as follows:

1. Proactive pollution prevention and control measures should be adopted, especially in the urbanised areas of Guangzhou and other industrial zones within the PRD region, which were shown to suffer from severe atmospheric trace metal pollution.

2. Regional co-operations among the regulatory bodies in Hong Kong and Guangdong should be sought to improve the current cross-boundary trace metal pollution in the PRD region.

3. The implementation of environmental regulations should be improved or strictly enforced, especially in the emission control of vehicular and industrial sources and other uses of metals in the region.

4. Strategic environmental management plan should be formulated and implemented to solve the current air pollution problems in the PRD region.

5. Regular monitoring of trace metals and other contaminants in particulate matter, dry and wet depositions ought to be conducted to review the effectiveness of management procedures and control measures.

8.3 Future research

The atmospheric long-range transport of trace metals from the PRD region to other regions, such as the South Asian countries, during the winter monsoon should be further investigated to evaluate the regional impacts of the trace metal pollution from the PRD region. Moreover, bioavailability studies of trace metals in atmospheric depositions can provide further information on the potential hazards of metal uptakes by plants and other organisms in the terrestrial environment. Future scientific studies may emphasise on the promotion of the use of moss technique in monitoring of ambient air quality in the subtropical region, which is a cost-effective method and can provide valuable information on the influences of atmospheric pollutants on the surface environment. Furthermore, the application and development of deposition models for trace metals may be further explored, for prediction and strategic management of trace metal pollution in the PRD and other rapidly developing regions in the world.

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Biomonitoring of trace metals in the atmosphere using moss (*Hypnum plumaeforme*) in the Nanling Mountains and the Pearl River Delta, Southern China

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Abstract

Atmospheric particulates with elevated trace metals may have a serious impact on human health. Biomonitoring using moss is a well-developed technique employed in many parts of the world to assess the concentrations of trace elements in the atmosphere and their potential sources. The suitability of the moss *Hypnum plumaeforme* as a new biomonitor of atmospheric trace element pollution in southern China was evaluated in the present study. The results showed that the moss had a good capacity to absorb and retain heavy metals such as Cd, Co, Cu, Cr, Pb, V and Zn. The northern part of the Nanling mountain range was found to have more trace elements than the southern range, possibly reflecting the long-range transport of pollutants from northern China. The elemental concentrations of the mosses in the northern range were found to be well correlated with elevations. The concentrations of heavy metals decreased as elevations increased, and became relatively constant above 1100 m a.s.l. The Pb isotopic compositions indicated that atmospheric inputs of Pb in mosses were mainly derived from anthropogenic sources, including vehicular emissions and Pb used in local industries.

Keywords: Moss (*Hypnum plumaeforme*); Biomonitor; Aerosol; Heavy metals; Pb isotopes; Pearl River Delta; South China

1. Introduction

Atmospheric particulates have attracted great environmental concern over the last few decades because of evidence that this type of pollution can have severe long-term implications for respiratory illness in humans (Dockery and Pope, 1994). In particular, heavy metals adsorbed on ambient particles were found to cause damage to lung tissues (Dreher et al., 1997). Due to rapid urbanization and industrial development in recent years, atmospheric pollution has caused serious deterioration of the terrestrial environment in many countries. Thus, the monitoring of airborne metals in the urban environment has become an essential part of environmental planning and control programmes in many parts of the world. Biomonitoring is a technique using organisms or biomaterials to obtain (quantitative) information on certain characteristics of the biosphere

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(Wolterbeek, 2002). Mosses have been well studied as tools for the biomonitoring of atmospheric pollution. Unlike higher plants, mosses have no root system or cuticle layer; hence, mineral adsorption occurs over their entire surface (Rühling and Tyler, 1968). Mineral uptakes from soil play a minor role and the absorption of heavy metal is mainly derived from atmospheric flux on the surfaces of the moss. Therefore, mosses are excellent biomonitors for trace elements in air.

The technique of moss biomonitoring has been widely used in Europe (Rühling and Tyler, 1968, 1970; Markert et al., 1996; Zechmeister, 1998; Rühling and Steinnes, 1998; Aceto et al., 2003) and North America (Groet, 1976; Barclay-Estrup and Rinne, 1979; Percy, 1982) in the past few decades. The types of species recommended for use in European moss surveys include *Hylocomium splendens* and *Pleurozium schreberi* (Ross, 1990). Other moss species such as *Hypnum cupressiforme* and *Scleropodium purum* are more widespread and commonly used in southern Europe (Bargagli et al., 1995). In a large-scale sampling, the use of more than a single species is necessary. An interspecies study showed that the moss *Hypnum cupressiforme* accumulated 50–125% more Al, Co, Mo, Ni, Pb and Zn, as compared to other species such as *Pleurozium schreberi* as *Hypnum cupressiforme* grow in denser mats (Sucharová and Suchara, 1998). Similar results were obtained for elements such as Zn in the study by Galsomiés et al. (2003), whereas Rühling and Tyler (1968) showed that *Hypnum cupressiforme* contained only slightly more Pb than *Pleurozium schreberi*.

However, only limited attempts were found in the literature to use mosses as biomonitors for air pollution in China (Xiao et al., 1997), despite their wide application in other countries. Since the introduction of economic reform more than two decades ago, the Pearl River Delta (PRD) in southern China has become one of the fastest-developing regions. Urbanization and industrial development have led to some environmental pollution problems in the region, including the burning of coal, vehicular and industrial emissions. Recent studies have shown that there are relatively high concentrations of heavy metals in both aerosols and atmospheric depositions in the PRD region in comparison with many areas of the world (Cao et al., 2003; Wong et al., 2003). The moss *Hypnum plumaeforme* is commonly found in dense mats in many Asian countries, including China, Japan, Korea, Nepal and Philippines. The type of mat that the mosses form often affects their bioconcentration, and a denser mat is able to produce a higher rate of bioaccumulation as it is able to capture trace elements from the atmosphere more efficiently (Sucharová and Suchara, 1998).

In this study, the heavy metal concentrations in the moss *Hypnum plumaeforme* were determined. Pb isotopic analysis was used to identify the potential anthropogenic inputs of heavy metals in mosses and aerosols collected in the surrounding areas. The aim of the present research was to evaluate the suitability of the moss *Hypnum plumaeforme*, which is commonly found in the region, for monitoring ambient air quality in a subtropical area.

2. Materials and Method

2.1. The study area

The Nanling mountain range is located in southern China and straddles from west to east across the borders of Guangxi, Guangdong, Hunan and Jiangxi provinces for more than 1000 km (Fig. 1). The mountain range is an important boundary in south China between the temperate continent in the north and subtropical regions in the southeast coast. The area is the key pathway for the long-range transport of air pollutants from northern China to the PRD region, particularly during the dry winter monsoon period. To the south of the Nanling range lies the PRD region of Guangdong Province. The PRD region is one of the most urbanized areas in China, with a total population of more than 30 millions. It covers an area of 41,700 km^2. Major cities in the PRD include Guangzhou, Shenzhen, Dongguan, Foshan, Jiangmen, Zhuhai, Zhongshan and Huizhou, and all have different concentrations of industrial centres.

2.2. Moss sampling

Two sampling areas were selected in the upper northern part of the Nanling Mountains, the NL series; and the lower southern part of the mountain range, the MS series. Eight moss sampling sites were chosen in each area at various altitudes to study the topographical effect of metal concentrations in moss. Mosses were picked up with a plastic shovel and kept refrigerated at 5 °C in plastic bags. The green part of the moss 1–3 cm from the top was separated and thoroughly washed with tap water first, and then with DIW, until no soil particles adhered on the surfaces. The samples were dried in an oven at 60 °C for 3 days, and were subsequently ground in an agate pot until fine particles (< 200 μm) were obtained. The samples were stored in polyethylene bags in a desiccator.

2.3. Aerosol sampling

A total of 12 aerosol samples were collected in the Nanling Mountains, and in Guangzhou and Zhongshan of the PRD during the winter season (November 2002 January 2003). Two aerosol samples were collected at each location in the north (YTH series; at

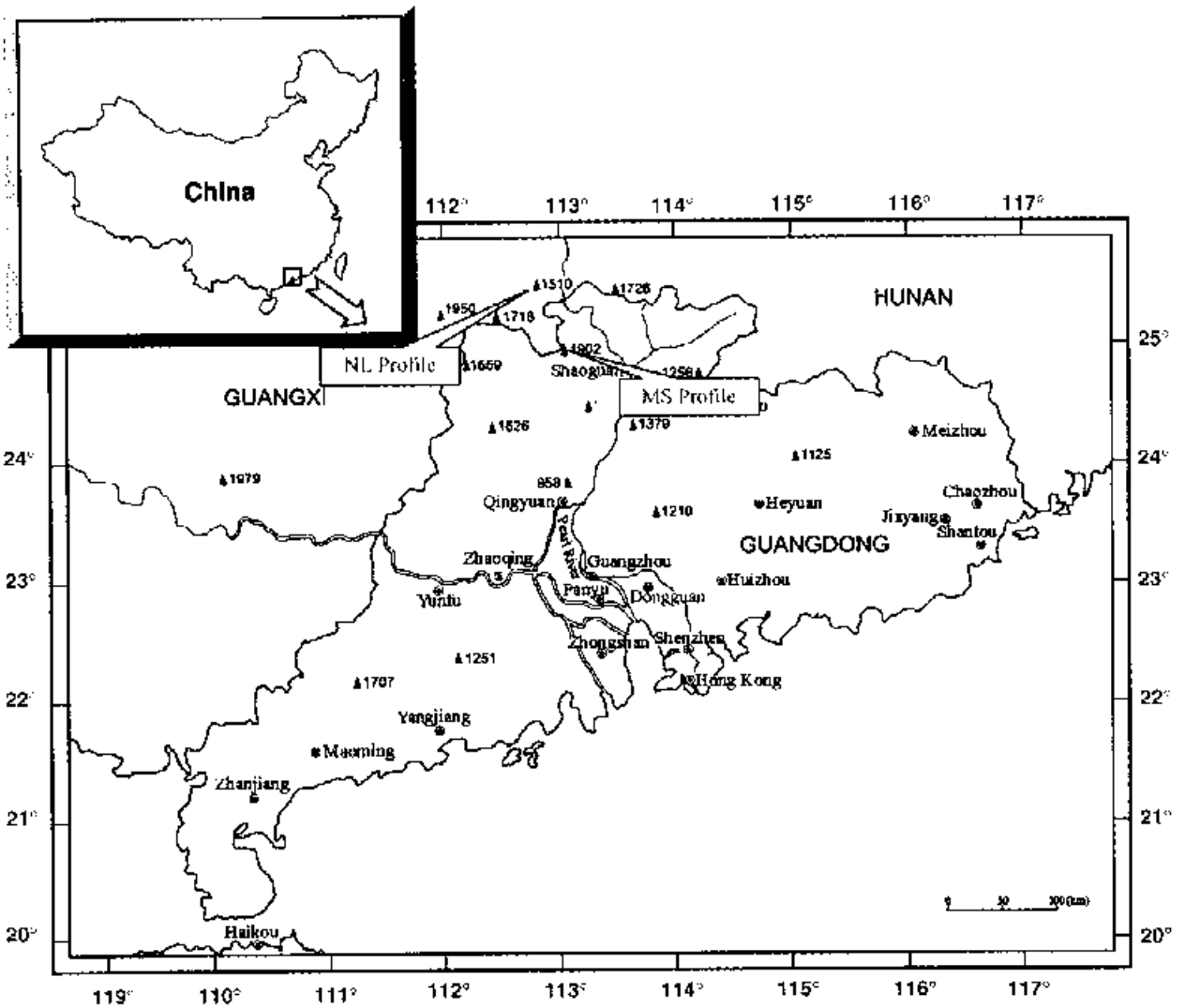

Fig. 1. Sampling locations.

1450 m) and south (QY series; at 802 m) of the Nanling Mountains. The Guangzhou aerosols were collected at the roof top of a building in the urban centre of Guangzhou (~50 m a.s.l.). The Zhongshan aerosols were sampled on a small mountain (~500 m a.s.l.), in a suburban area of Zhongshan city. The aerosols at Nanling, Guangzhou and Zhongshan, located at the northern, central and southern part of the PRD, represented the general atmospheric condition of the region. A high-volume sampler (Anderson-type) was deployed in the sampling sites to collect aerosol samples. The samplers were operated at a flow rate of 0.465 m ^{3}min^{-1} to collect the total aerosols on 20.3 cm × 25.4 cm glass fibre filters. A sampling duration of 12 h was adopted. The filters were then wrapped in aluminium foil and stored in polyethylene bags at 4 °C.

2.4. Heavy metal analysis

The moss and aerosol samples were analysed for major and trace metal concentrations using a strong acid digestion method (Shen et al., 2002; Wong et al., 2003). Approximately 0.350 g of the moss samples was weighted and placed into pre-cleaned Pyrex tubes. Twelve millilitres of concentrated high-purity nitric acid (HNO_3) and 4.0 ml of concentrated perchloric acid ($HClO_4$) were added. The mixtures were gently shaken and then heated progressively to 190 °C in an aluminium block for 24 h, until completely dry. After the test tubes

were cool, 10.0 ml of high-purity 5% (v/v) HNO_3 were added and heated at 70 °C for 1 h, with occasional mixing. Upon cooling, the mixtures were decanted into polyethylene tubes and centrifuged at 3500 rpm for 10 min.

Aerosol samples were carefully taken up from the aluminium foil using plastic tools and were cut into four equal portions using a pair of stainless steel scissors. A similar acid digestion method was employed for aerosol samples (Wong et al., 2003).

Elemental concentrations of the digested solutions for moss and aerosol samples were determined using an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES; Perkin-Elmer Optima DV 3300). The elemental concentrations of the procedural blanks were generally $<5\%$ of the mean analyte concentrations for all metals. Quality control standards were measured at every 10 samples to detect contamination and drift. Standard reference materials (NIST SRM 1515, apple leaves) were also incorporated in the analysis of the mosses. The precision assessed by SRM and duplicate samples was $<10\%$ for both trace and major elements in the analyses of the moss and aerosol samples. The recovery rates for the heavy metals and some major elements in the standard reference material (NIST SRM 1515) ranged from 86% to 115%.

2.5. *Pb isotopic composition analysis*

The moss and aerosol samples were analysed for Pb isotopic compositions using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS; Perkin-Elmer Sciex Elan 6100 DRC ^{plus}). Solutions from the acid digestion were diluted using 5% high-purity HNO_3. The analytical parameters were set as 250 sweeps per reading and 10 readings per sample solution. The Pb counts of the procedural blanks were generally $<0.5\%$ of the samples. The precision (%RSD) of the Pb isotopic ratios was typically $<0.5\%$. The NIST standard (NIST SRM 981, common lead) was used in the Pb isotopic analysis. The measured Pb ratios of $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ were 0.0647 ± 0.0001, 1.0936 ± 0.0014 and 2.3674 ± 0.0052, which were in good agreement with the standard reference values of 0.0645, 1.0933 and 2.3704, respectively.

2.6. *Statistical analysis*

The analytical results of the moss samples were compiled to form a multi-elemental database using Excel and SPSS®. A Pearson correlation (PC) was performed using SPSS® statistical software to obtain potential elemental correlations from the dataset. A linear regression analysis was also used to analyse the elemental correlations using the least-square method, in which regression lines were plotted.

3. Results and discussion

3.1. *Metal concentrations in mosses and aerosols*

The total concentrations of metals in the moss and aerosol samples are presented in Table 1. The mean concentrations of heavy metals such as Cd, Cu, Ni, Pb and Zn in the NL-series (northern part of the Nanling range) were found to be 4.13, 34.3, 18.0, 183 and 181 mg kg^{-1}, respectively. The corresponding values in the MS-series (the southern part of the Nanling range) were 1.82, 58.7, 23.6, 140 and 143 mg kg^{-1}, respectively. The results showed that the Pb concentrations were highly elevated in both the NL- and MS-series, ranging from 40.5 to 396 mg kg^{-1}. As no similar study using *Hypnum plumaeforme* for biomonitoring was found in the literature, the bioconcentrations of another similar species belonging to the same class and being widely adopted in European moss surveys (Fernández et al., 2002; Ötvös et al., 2003), *Hypnum cupressiforme*, was used for comparison. In comparison with the results reported in Spain and Hungary, bioconcentrations in the moss *Hypnum plumaeforme* were much higher than in *Hypnum cupressiforme* (see Table 2). Previous studies on atmospheric deposition in the PRD showed that the atmospheric deposition of heavy metals was significantly greater than in the Great Lakes region in North America and the North Sea in Europe (Wong et al., 2003). Hence, the Nanling mosses could be expected to reflect the elevated concentrations of atmospheric heavy metals in the PRD compared with other regions. Nevertheless, the total amount of pollutants in the air, the relative humidity and wet deposition would also have significant effects on the capacity of mosses to absorb metals. The wide availability of the moss *Hypnum plumaeforme* in the Nanling Mountains and the PRD region, and their capacity in absorbing heavy metals makes it feasible for use in future biomonitoring programmes of atmospheric pollutants.

The results showed that of the three areas studied (Nanling, Guangzhou and Zhongshan), Guangzhou aerosols were found to have the highest mean concentrations of heavy metals (see Table 1). The concentrations of heavy metals in the aerosols of the PRD region, other cities of China and the surrounding regions were compared (see Table 3). The data showed that the air in Guangzhou was heavily contaminated with heavy metals, compared with other areas in the PRD region and China, as well as surrounding Asian cities in Taiwan, Vietnam and India. The concentration of Pb in the air in Guangzhou was marginally within the National Ambient Air Quality Standard of China (NAAQS, 1996) of 1000 ng m^{-3}, and was lower than the limit specified in the Hong Kong Air Quality Objective (HKAQO, 1987), which is 1500 ng m^{-3}.

Table 1
Major and trace element concentrations (mg kg^{-1}) of the moss *Hypnum plumaeforme* in Nanling and element concentrations (ng m^{-3}) of aerosols in the Pearl River Delta (Nanling, Guangzhou and Zhongshan)

		Al	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	V	Zn
Nanling Moss														
	(mg kg^{-1})	Higher elevation: >1100 m												
NL-series	Mean	2260	7660	1.71	0.46	9.99	27.8	898	1050	181	10.1	69.3	1.62	112
($N = 4$)	Std dev	2190	2090	0.28	0.24	3.57	10.3	770	243	82.6	4.43	7.89	1.18	24.9
		Lower elevation: <1100 m												
NL series	Mean	2360	11400	6.55	0.63	40.1	40.8	1230	1390	175	25.9	296	2.64	249
($N = 4$)	Std dev	2190	2090	0.28	0.24	3.57	10.3	425	243	52.7	16.2	89.5	2.08	45.4
		Higher elevation: >1100 m												
MS-series	Mean	3110	10800	1.78	0.21	23.0	53.2	881	1020	200	16.2	106	2.60	144
($N = 4$)	Std dev	2810	1060	0.74	0.14	17.1	29.4	447	135	147	6.39	50.3	1.69	18.3
		Lower elevation: <1100 m												
MS-series	Mean	4990	9450	1.85	0.39	26.6	64.3	1450	902	175	30.9	175	1.67	141
($N = 4$)	Std dev	2560	1180	0.67	0.43	23.6	53.5	747	144	142	28.3	82.6	0.58	26.3
PRD Aerosol														
Nanling	(ng m^{-3})	Elevation: 1450 m												
YTH (North)	Mean	5630	3830	20.5	n.d.[a]	16.0	42.0	1480	336	n.d.[a]	30.5	615	17.5	5770
(N = 2)	Std dev	2870	605	7.29	n.d.[a]	10.1	1.64	375	89.2	n.d.[a]	24.8	255	5.87	2240
		Elevation: 802 m												
QY (South)	Mean	4640	6290	11.4	n.d.[a]	7.37	86.8	2270	573	n.d.[a]	23.9	452	39.2	3860
($N = 2$)	Std dev	850	2880	2.81	n.d.[a]	4.60	71.1	1490	217	n.d.[a]	8.30	225	26.7	1070
		Elevation: 50 m												
Guangzhou	Mean	14600	22500	21.6	2.85	64.0	914	8860	1450	83.6	66.8	995	103	6440
($N = 4$)	Std dev	1210	2460	7.3	1.96	40.1	462	1280	324	61.0	23.3	248	40.6	1880
		Elevation: 500 m												
Zhongshan	Mean	3400	3330	4.59	n.d.[a]	5.83	33.7	1190	292	n.d.[a]	20.3	147	21.1	3740
($N = 4$)	Std dev	1340	960	2.16	n.d.[a]	4.55	14.4	287	149	n.d.[a]	5.3	39	8.6	2050

[a]Not detectable.

Table 2
Comparison of the mean concentrations (mg kg^{-1}) of heavy metals in the moss *Hypnum plumaeforme* in Nanling and the moss *Hypnum cupressiforme* in some European surveys

	Spain[a] ($N = 134$)	Hungary[b] ($N = 116$)	NL-series ($N = 8$)	MS-series ($N = 8$)
Cd	—	0.9	4.13	1.82
Cr	2.68	2.8	25.0	24.8
Cu	6.86	11.8	34.3	58.7
Ni	2.79	5.0	18.0	23.6
Pb	9.35	19.5	183	140
V		5.1	2.13	2.13
Zn	48.8	52	181	143

[a]Fernández et al., 2002.
[b]Ötvös et al., 2003.

3.2. Elemental associations in mosses

The results of the PC analysis for elemental concentrations of mosses are presented in Table 4. In the analysis, the major elements, such as Al and Fe, Ca and Mg, in the moss samples (see Table 4) were found to be closely correlated ($P < 0.01$), possibly reflecting the geological origin of air particles. Elements such as Cd,

Table 3
Heavy metal concentrations of aerosols in the PRD (Nanling, Guangzhou and Zhongshan), other cities in China and surrounding Asian cities

TSP		Mean concentration (ng m^{-3})						
Location	Site characteristic	Cd	Cu	Ni	Pb	V	Zn	Reference
PRD								
Nanling ($n = 4$)	Rural	16.0	64.4	27.2	533	28.3	4810	Present study
Guangzhou ($n = 4$)	Urban	21.6	914	66.8	995	103	6440	Present study
Zhongshan ($n = 4$)	Suburban	4.59	33.7	20.3	147	21.2	3740	Present study
Other cities in China								
Xian ($n = 75$)	Urban	—	830	810	4300	1100	3000	Zhang et al. (2002)
Harbin ($n = 5$)	Urban			—	282			Mukai et al. (2001)
Changchun ($n = 5$)	Urban	—	—	—	177		—	Mukai et al. (2001)
Beijing ($n = 2$)	Urban			—	119	—	—	Mukai et al. (2001)
Dalian ($n = 5$)	Urban		—	—	485		—	Mukai et al. (2001)
Nanjing ($n = 2$)	Urban	—	—		317	—	—	Mukai et al. (2001)
Shanghai ($n = 3$)	Urban		—	—	466	—		Mukai et al. (2001)
Taiwan								
Taichung ($n = 43$)	Urban	8.5	199	15.8	574	—	395	Fang et al. (2003)
India								
Sakinaka ($n = 45$)	Road junction		370	160	1060	—	—	Kumar et al. (2001)
Gandhinagar ($n = 45$)	Road junction		1550	100	820			Kumar et al. (2001)
Vietnam								
Ho Chi Minh City ($n = 43$)	Urban		1.28	—	146	7.3	203	Hien et al. (2001)

Table 4
Pearson correlation coefficient matrix between heavy metals and major elements of the moss *Hypnum plumaeforme* in the Nanling and PRD study areas

	Al	Ca	Cd	Cr	Cu	Fe	Mg	Ni	Pb	V
Ca	0.009									
Cd	0.084	0.566*								
Cr	−0.110	0.566	0.474							
Cu	0.087	0.000	−0.079	0.320						
Fe	0.792**	0.098	0.207	0.200	0.335					
Mg	0.149	0.654**	0.668**	0.429	−0.273	0.153				
Ni	0.222	0.237	0.233	0.807**	0.668**	0.554*	0.103			
Pb	0.179	0.514*	0.856**	0.293	0.013	0.316	0.399	0.228		
V	0.360	0.137	0.354	−0.165	0.039	0.499*	0.104	−0.016	0.361	
Zn	−0.076	0.663	0.906**	0.385	0.005	0.497	0.612*	0.197	0.895**	0.404

** $P < 0.01$.
* $P < 0.05$.

Pb, and Zn, and Cr, Cu and Ni were also shown to be strongly correlated ($P < 0.01$), indicating potential anthropogenic inputs. The regression lines plotted for Pb vs. Zn, Pb vs Cd, Cr vs Ni, Cd vs Ni, and Fe vs. Al in the linear regression analysis showed that these elements were correlated significantly with $R^2 > 0.60$. Some of the results were presented in Fig. 2, and they agreed well with the results from the PC analysis.

3.3. Topographical effect on moss metal concentrations

Mosses in the NL- and MS-series were collected at different elevations. The analytical results showed that the concentrations of elements such as, Cd, Pb and Zn, were significantly correlated with the elevations in the NL-series, but no significant correlation was observed in the MS-series (Fig. 3a–c). At the elevations above

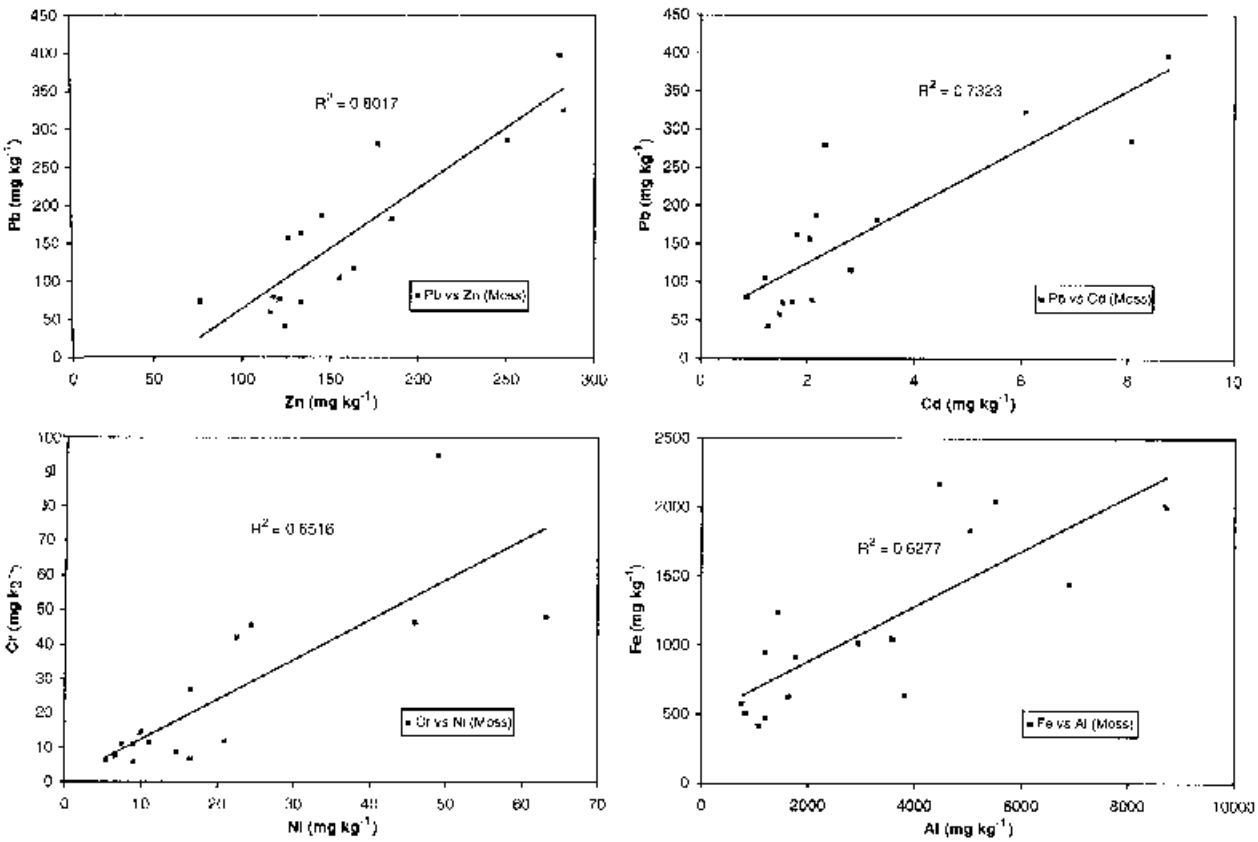

Fig. 2. Elemental correlation in the Nanling mosses.

1100 m a.s.l., the concentrations of heavy metals became relatively constant. The results indicated that heavy metals such as Cd, Pb and Zn in the air tended to be associated with particles in areas of low elevation and close to sources of contamination and transport paths. Moreover, the statistical results from the PC analysis showed that there was a strong elemental correlation among Cd, Pb and Zn in the Nanling mosses (see Table 4 and Fig. 2), indicating a common source of anthropogenic inputs of these three heavy metals. The northern part of the Nanling Mountains was shown to be significantly enriched with heavy metals, possibly reflecting local sources of pollution and the effects of potential pathways for the long-range transport of air contaminants from northern China. In the southern part of the Nanling range, the elemental concentrations of Cd, Pb and Zn were relatively constant at various elevations, probably due to better mixing of the air because of coastal air flows from the South China Sea.

3.4. Pb isotopic compositions in mosses and aerosols

The Pb isotopic compositions of the Nanling mosses and the PRD aerosols are presented in Table 5. The ratios of $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in the Nanling mosses ranged between 0.0637 and 0.0642, 1.171 and 1.190 and 2.450 and 2.470, respectively. A comparison of the Pb isotopic ratios of known anthropogenic sources and the natural background may indicate the possible origins of Pb in the mosses. The Pb isotopic compositions of the mosses, the natural sources and vehicular emissions in the PRD are plotted in Fig. 4. The Pb isotopic ratios of mosses were found to fit well between the natural sources and the vehicular emissions. The data points formed a linear correlation with $R^2 = 0.832$ (see Fig. 4). The results indicated that vehicular emissions may be a major anthropogenic source of Pb in the Nanling mosses. The mosses in the Nanling mountain range showed $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of 1.171–1.190 and 2.450–2.470, which were relatively high compared with other moss species reported in European moss surveys (Weiss et al., 1999; Farmer et al., 2002). This is probably due to the different Pb compositions used in petrol and natural geological materials (e.g., uranium-rich granite) in the Nanling area (Zhang et al., 1993; Chen et al., 1999).

To further assess the relationship of trace element concentrations in mosses with those in aerosols, the Pb isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) of aerosols were plotted in the same diagram as those of the mosses

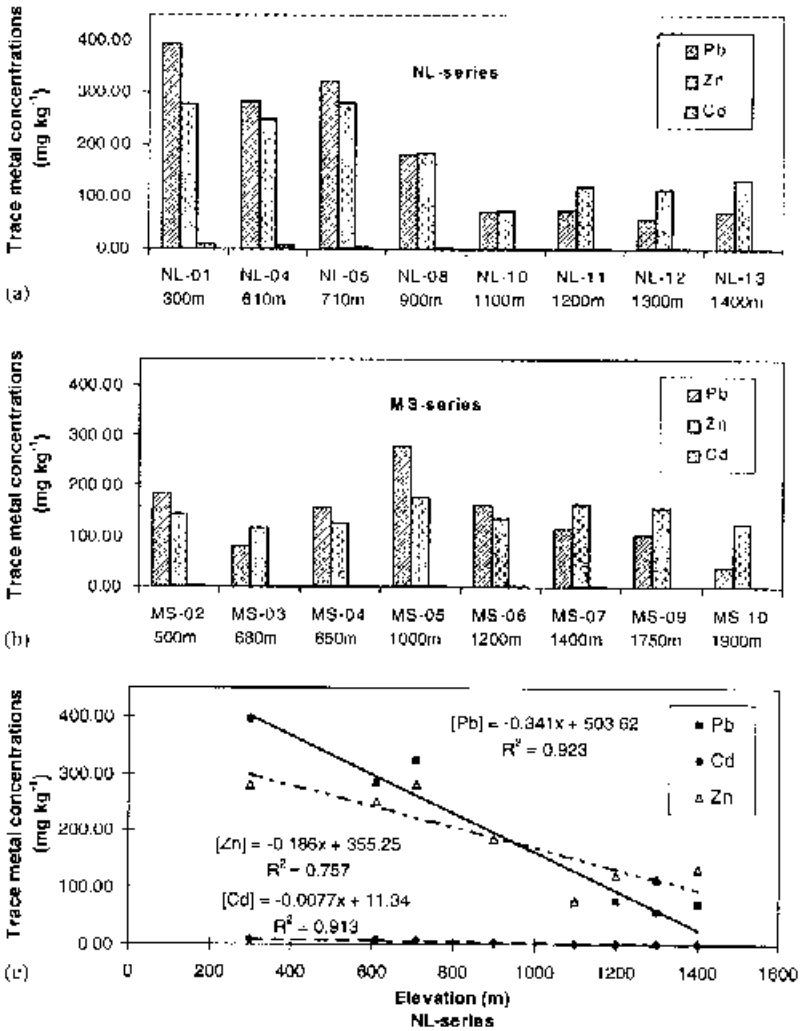

Fig. 3. (a) Cd, Pb and Zn concentrations of mosses in the NL-series; (b) Cd, Pb and Zn concentrations of mosses in the MS-series; (c) Linear plots of the Cd, Pb and Zn concentrations of mosses in the NL-series against elevation.

(see Fig. 5). The ratios of $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in the aerosols at Nanling, Guangzhou and Zhongshan ranged between 0.0642 and 0.0652, 1.169 and 1.181, and 2.444 and 2.470, respectively (see Table 5). The Pb isotopic ratios of the PRD aerosols were similar to those of the Nanling mosses. PRD aerosols were also affected by the anthropogenic Pb input from the vehicular emissions (Fig. 5). In addition to this, the PRD aerosols were influenced by another source, which was the Pb–Zn ore in Fankou (industrial use of Pb in the region) (see Fig. 5). The mixing of the isotopic signatures of Pb derived from both vehicular emissions and Pb–Zn ore contributed to the Pb isotopic composition of the PRD aerosols. As illustrated in Fig. 5, the Pb isotopic compositions of the Nanling mosses resembled those of aerosols in Nanling and in the surrounding PRD region. This suggested that the Nanling and PRD aerosols were the major sources of the anthropogenic metal inputs in these mosses. The Nanling Mountains are located some distance away (>60 km) from the nearest urban development, and the pollutants were probably derived from local sources and long-range transport of pollutants. The results showed that the Pb isotopic composition of mosses could reflect the Pb isotopic composition of the surrounding ambient air.

4. Conclusion

The results showed that trace metal concentrations in the moss *Hypnum plumaeforme* can be a good indicator for biomonitoring of atmospheric metal pollution in southern China. Trace elements such as Pb, Zn and Cd were found to be correlated with the elevations in northern Nanling. The concentrations of heavy metals

Table 5
Pb concentrations and isotopic compositions of the moss *Hypnum plumaeforme* in the Nanling Mountains and the aerosols in the PRD

Nanling Moss					PRD aerosol				
(N = 16)	Sample ID	$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	(N 12)	Sample ID	$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
NL-series	NL-01	0.0641	1.171	2.455	*Nanling*	QY-01	0.0643	1.171	2.453
	NL-04	0.0642	1.171	2.453		QY-02	0.0642	1.173	2.464
	NL-05	0.0639	1.173	2.46		YTH-01	0.0641	1.179	2.469
	NL-08	0.064	1.175	2.456		YTH-02	0.0643	1.171	2.447
	NL 10	0.0641	1.174	2.454					
	NL 11	0.0641	1.174	2.457		Mean	0.0643	1.173	2.458
	NL 12	0.0638	1.174	2.459					
	NL 13	0.064	1.175	2.452	*Guangzhou*	GZ-01	0.0647	1.174	2.453
						GZ-03	0.0652	1.181	2.457
	Mean	0.064	1.173	2.456		GZ-04	0.0651	1.181	2.47
						GZ 05	0.0644	1.178	2.47
MS-series	MS-02	0.0639	1.182	2.46					
	MS-03	0.064	1.184	2.463		Mean	0.0649	1.178	2.462
	MS-04	0.0637	1.189	2.47					
	MS-05	0.064	1.176	2.457	*Zhongshan*	ZS-01	0.0646	1.173	2.444
	MS-06	0.0638	1.19	2.46		ZS-02	0.0642	1.17	2.461
	MS-07	0.064	1.175	2.456		ZS-03	0.0646	1.169	2.46
	MS-09	0.0641	1.179	2.454		ZS 04	0.0647	1.172	2.461
	MS 10	0.064	1.173	2.45					
	Mean	0.0639	1.181	2.459		Mean	0.0645	1.171	2.456

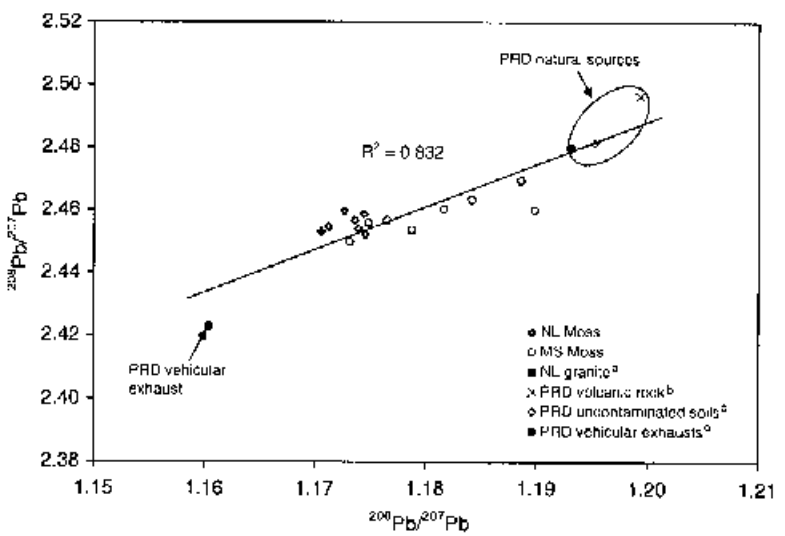

Fig. 4. $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of mosses in the Nanling Mountains ([a]Deng, 1987; [b]Zhu et al., 1989; [c]Zhu et al., 2001).

decreased as the elevation increased, indicating that metal-rich particles were concentrated and transported in the lower air mass. The Pb isotopic compositions showed that vehicular emissions accounted for the major anthropogenic inputs of Pb in the mosses and aerosols, with some influences from the Pb ore used in the local industry. The moss *Hypnum plumaeforme* showed a high-potential for use in the biomonitoring of trace element atmospheric pollution in south China, and possibly in other sub-tropical regions.

Acknowledgements

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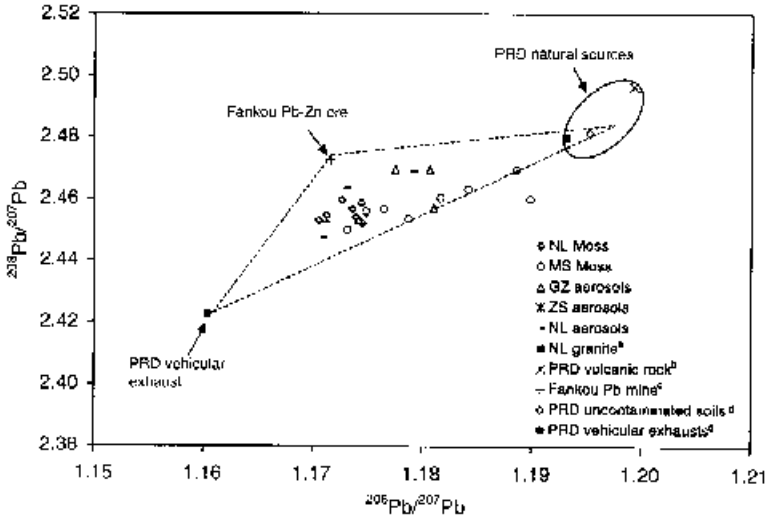

Fig. 5. $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of aerosols in the PRD, the Nanling mosses and other environmental samples in the PRD ([a]Deng, 1987; [b]Zhu et al., 1989; [c]Zhu, 1998; [d]Zhu et al., 2001).

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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 Pb from 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.

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

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(Lelieveld et al., 2002; Venkataraman et al., 2005). Particulate matter refers to solid and liquid particles that are suspended in the air. Epidemiological studies have indicated that elevated concentrations of fine-particulate matter 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). This results is in 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 catalyse 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), 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 concentrations of aerosols in urban and suburban coastal areas of the 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 (Fig. 1). Hong Kong is a highly urbanized metropolitan area situated at the south-eastern 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 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

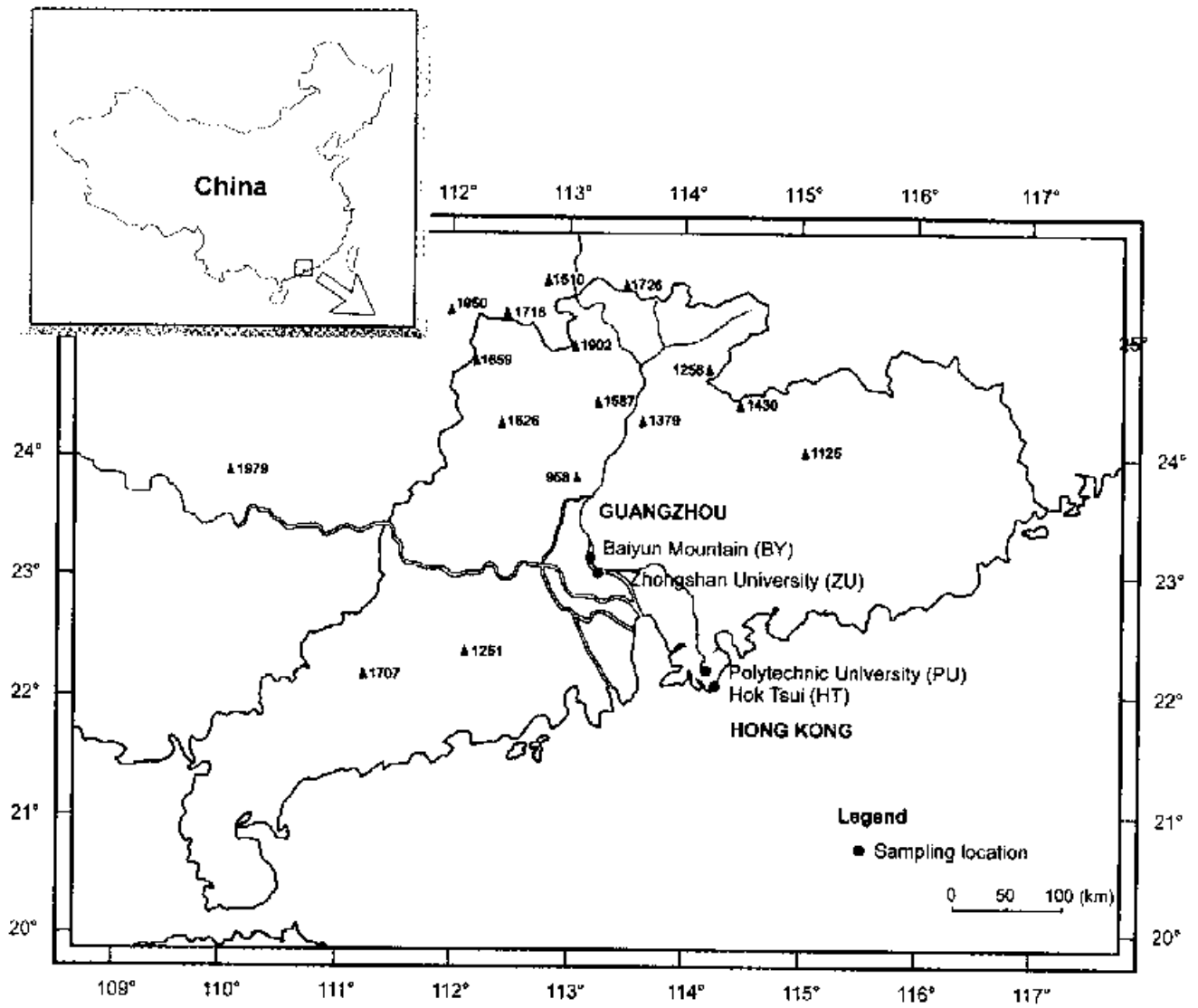

Fig. 1. Sampling locations.

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) (Fig. 1). The samples were taken on a bi-weekly basis over a 1-year period, from December 2003 to January 2005. They were collected on a pre-heated (4 h 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 h 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 h, 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 h. 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 $\mu g l^{-1}$ 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 10 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[36]. 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, 500 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

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 ± SD			
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 year) based on the annual average concentration.

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, respectively. 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 region (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 1-year period are plotted as a time-series in Fig. 2a–d. Distinguished seasonal patterns were found in the heavy metal concentrations of aerosols at PU and HT (Fig. 2a–b). The concentrations of most elements, Cd, Cu, Pb, V and Zn, during the winter seasons (December 2003—early

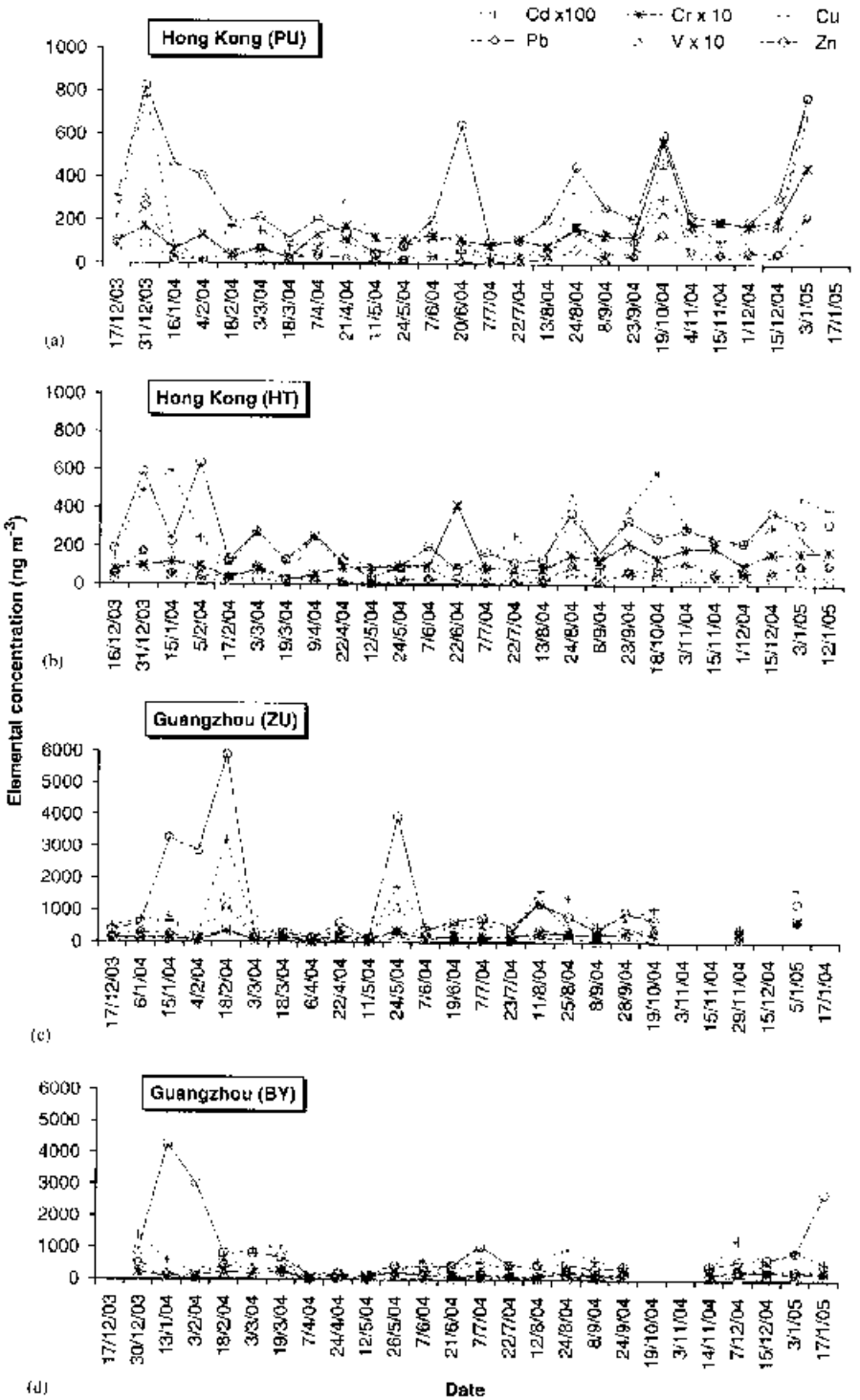

Fig. 2. Trace elemental concentrations of particulate matter (TSP) in urban and suburban areas of Hong Kong and Guangzhou, South China.

February 2004 and October 2004–January 2005) were significantly higher than that at other times. The heavy metal concentrations of aerosols were relatively low during the spring to summer season (March 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 relatively small. Therefore, the long-range transport due to Asian monsoon could be the most dominant effects to the seasonal variations in heavy metals at these sites (see further discussion in Section 3.5).

In Fig. 2c and 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 (January 2004–February 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 (December 2003–February 2004 and October 2004–January 2005) and low metal concentrations in the summer time (March 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 Fig. 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 (December 2003–February 2004 and October 2004–January 2005), and lower Pb isotopic ratios in the summer (March 2004–July 2004) (see Fig. 3a and 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 trajectory analysis showed that the air masses came from the east (on 24 May) and northeast (on 7 June) regions (classified as CT and CI in Fig. 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 (Fig. 3c and 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 Fig. 4).

Table 3
The Pb isotopic compositions of aerosols in 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
	($n = 11$)	SD	0.00026	0.0058	0.0081	82.6
	Summer[b]	Mean	0.06410	1.1549	2.4390	24.0
	($n = 10$)	SD	0.00044	0.0068	0.0087	19.7
	Annual	Mean	0.06386	1.1611	2.4506	56.5
	($n = 25$)	SD	0.00039	0.0084	0.0123	65.0
		95% CI[c]	0.06370–0.06402	1.1576–1.1645	2.4455–2.4557	
FT		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
	($n = 12$)	SD	0.00049	0.0059	0.0068	37.5
	Summer[b]	Mean	0.06408	1.1516	2.4360	23.6
	($n = 10$)	SD	0.00046	0.0141	0.0156	28.1
	Annual	Mean	0.06396	1.1606	2.4491	53.5
	($n = 26$)	SD	0.00045	0.0125	0.0149	43.1
		95% CI[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
	($n = 8$)	SD	0.00021	0.0044	0.0065	336
	Summer[b]	Mean	0.06360	1.1661	2.4519	147
	($n = 10$)	SD	0.00027	0.0054	0.0041	92
	Annual	Mean	0.06366	1.1677	2.4561	269
	($n = 22$)	SD	0.00024	0.0047	0.0062	238
		95% CI[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
	($n = 9$)	SD	0.00025	0.0033	0.0047	148
	Summer[b]	Mean	0.06369	1.1677	2.4549	167
	($n = 10$)	SD	0.00019	0.0069	0.0037	123
	Annual	Mean	0.06367	1.1690	2.4586	219
	($n = 23$)	SD	0.00022	0.0050	0.0054	133
		95% CI[c]	0.06358–0.06377	1.1668–1.1711	2.4563–2.4610	

[a]December 2003–February 2004 and October 2004–January 2005 (high metal concentrations observed in this study).
[b]March 2004–July 2004 (low metal concentrations observed in this study).
[c]95% confidence interval for annual means.

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 of the aerosols were relatively higher compared to other sampling times (see Fig. 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

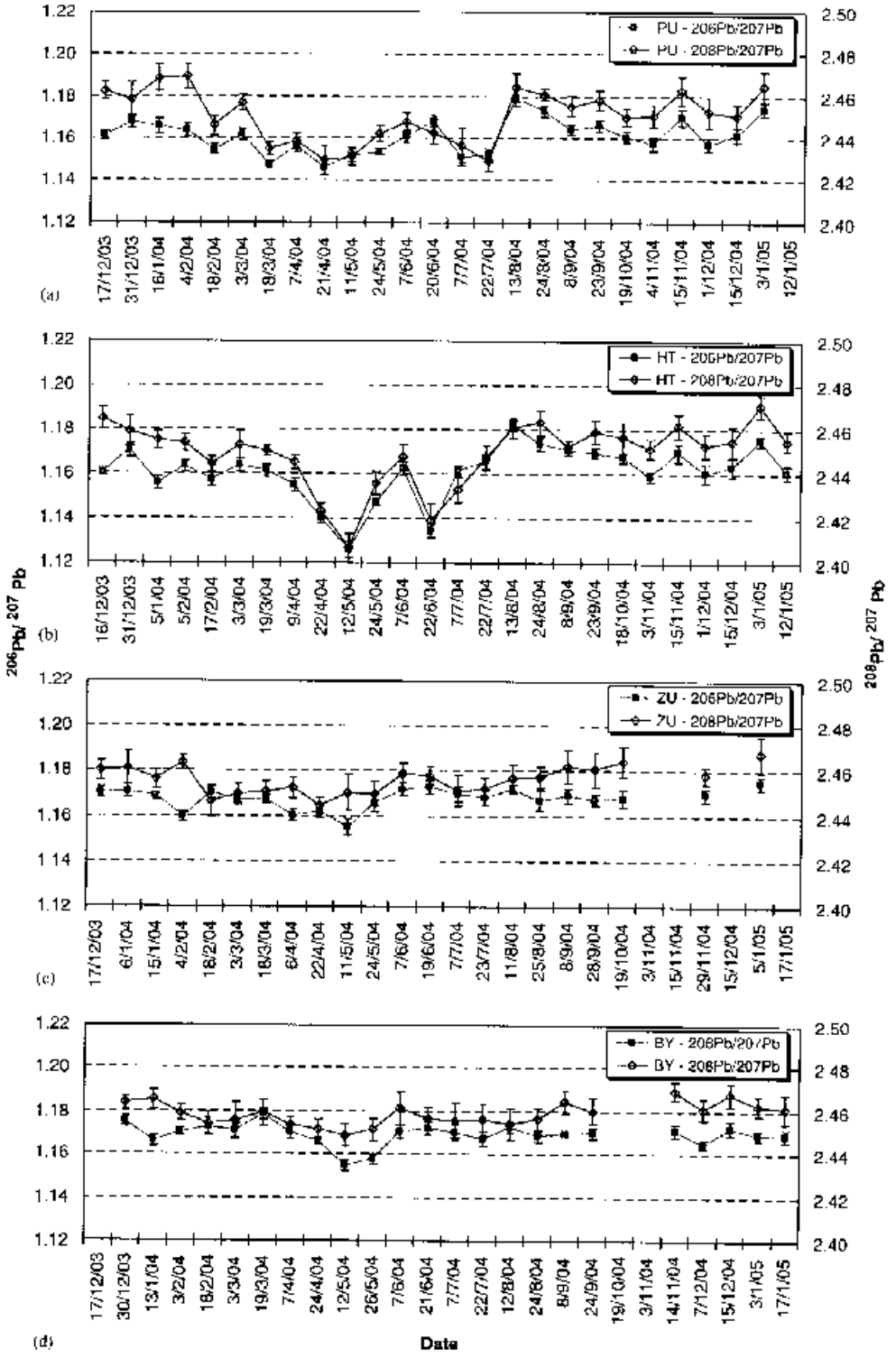

Fig. 3. Comparison of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in urban and suburban aerosols of Hong Kong and Guangzhou during the period December 2003–January 2005.

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

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	

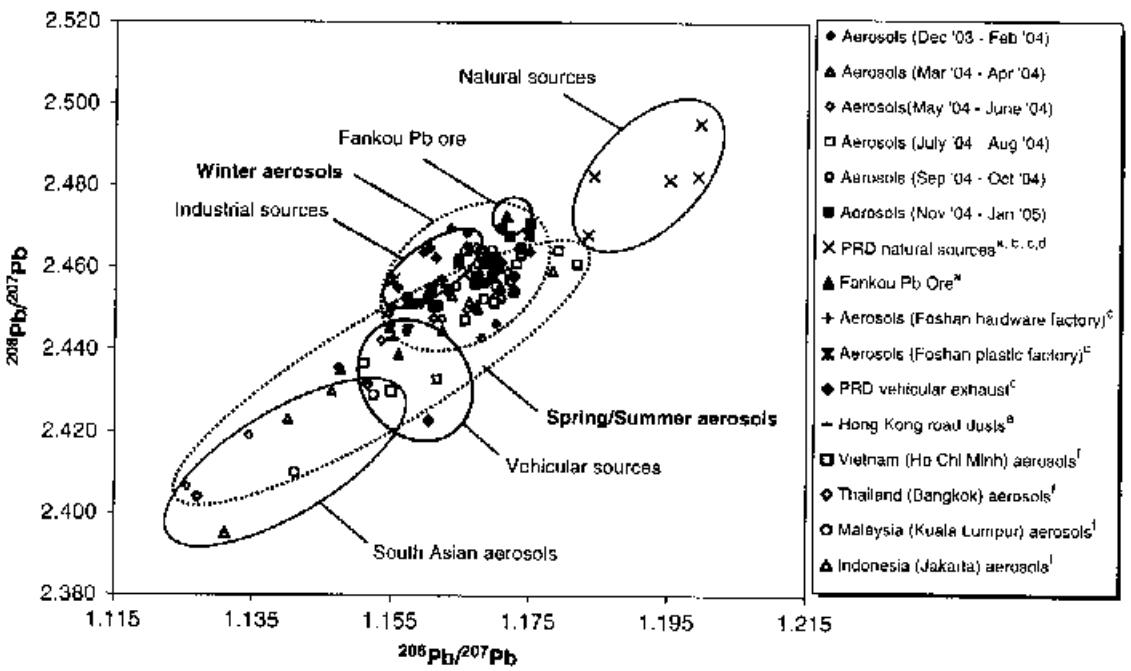

Fig. 4. Comparison of the Pb isotopic ratios of winter and spring/summer aerosols in the PRD region (PU, HT, ZU and BY) and other environmental samples ([a] Zhu et al., 1989; [b] Zhu, 1998; [c] Zhu et al., 2001; [d] Lee et al., 2006; [e] Duzgoren-Aydin et al., 2004; [f] Bollhöfer and Rosman, 2000).

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 Fig. 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 Fig. 4). During the spring and summer seasons, the prevailing winds in the PRD region were the oceanic winds from the south. Fig. 5a and 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 (11–12 May 2004 and 7 July 2004) (see Fig. 3a–d). The trajectory on 12 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 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 Fig. 4).

3.5. Back trajectory analysis

3.5.1. Air masses classification

Figs. 6a and b presents the plots of the seven-day back trajectories ending at Hong Kong and Guangzhou during the measurement period (December 2003–January 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

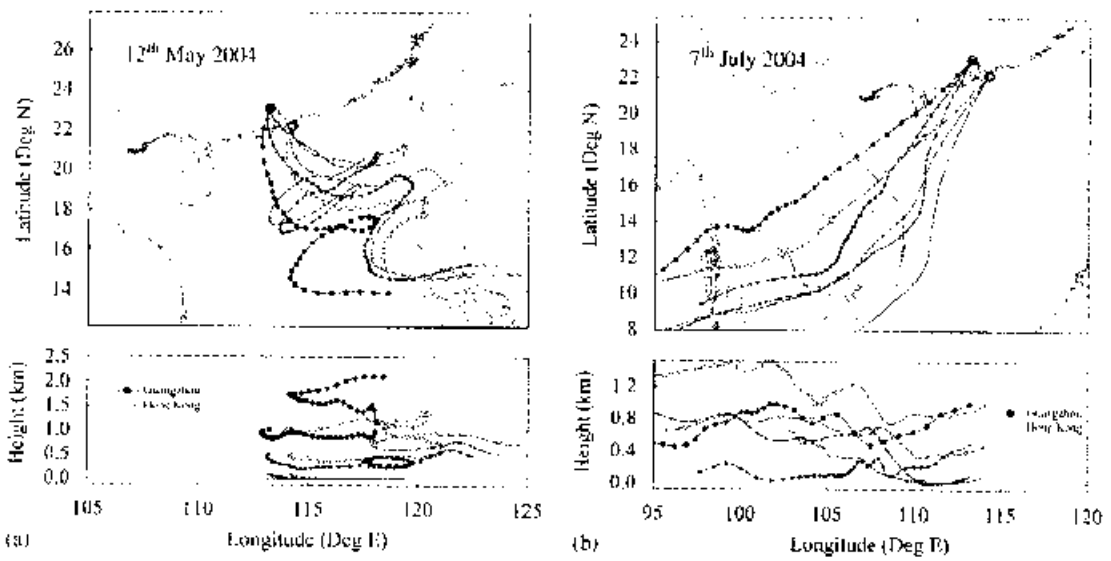

Fig. 5. Back trajectory plots on the days with low Pb isotopic ratios.

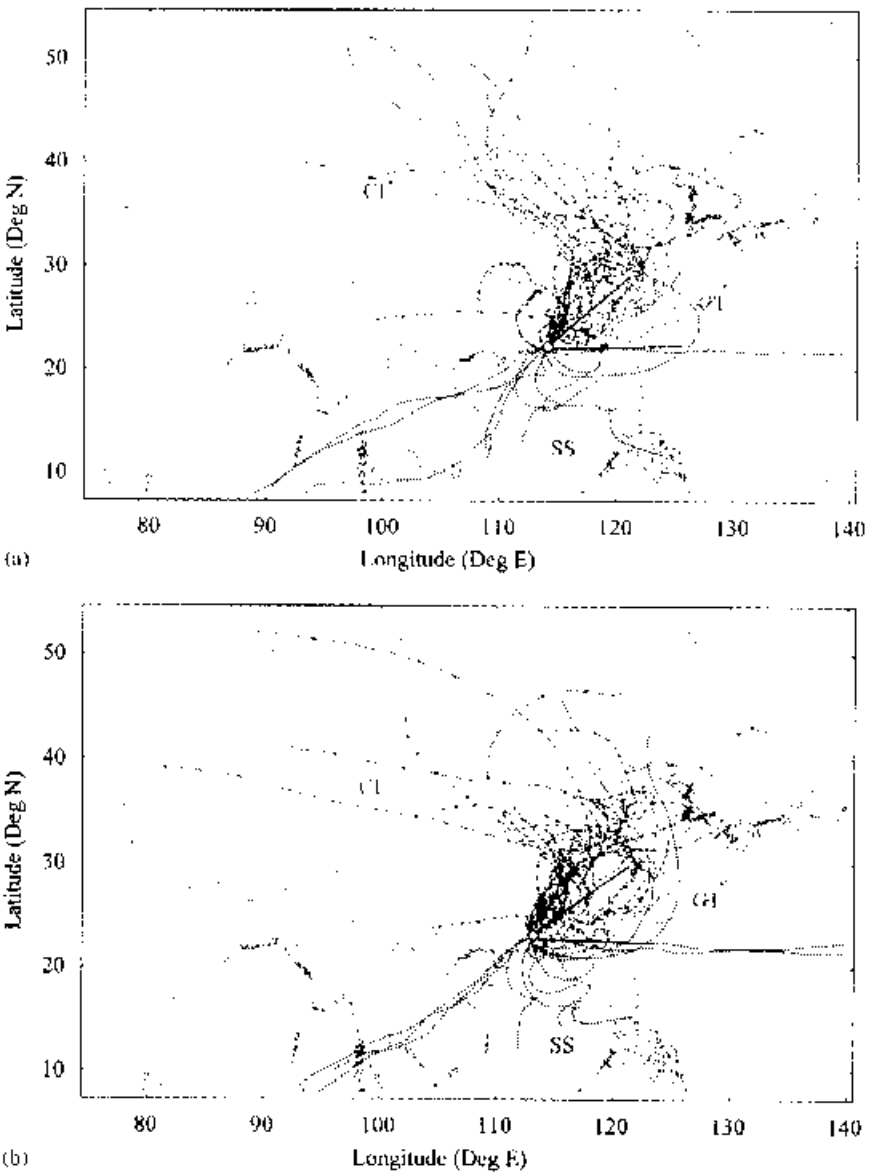

Fig. 6. The back trajectories of air masses in a) Hong Kong and b) Guangzhou. Air mass categories: CI—continental inland areas; CT—coastal areas; SS—marine sources.

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 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

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 (PU and HT)	CI	24	Mean	1490	2.85	16.5	68.7	1450	828	57.1	75.7	16.6	362
			SD	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
			SD	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
			SD	243	0.65	9.73	26.7	315	213	8.01	9.90	7.80	168
Guangzhou (ZU and BY)	CI	23	Mean	3200	7.58	20.1	78.5	2550	606	86.0	263	30.0	1190
			SD	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
			SD	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
			SD	1410	1.89	5.81	19.5	828	1750	22.4	65.3	19.8	288

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 CI 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 in 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 (Fig. 6).

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 1-year sampling

period (see Fig. 2a and 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, 500 and 1000 mAGL) over the sites are shown in Fig. 7.

Elevated heavy metal concentrations were observed on 31st December 2003 at both PU and HT (see Fig. 2a and 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. Fig. 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

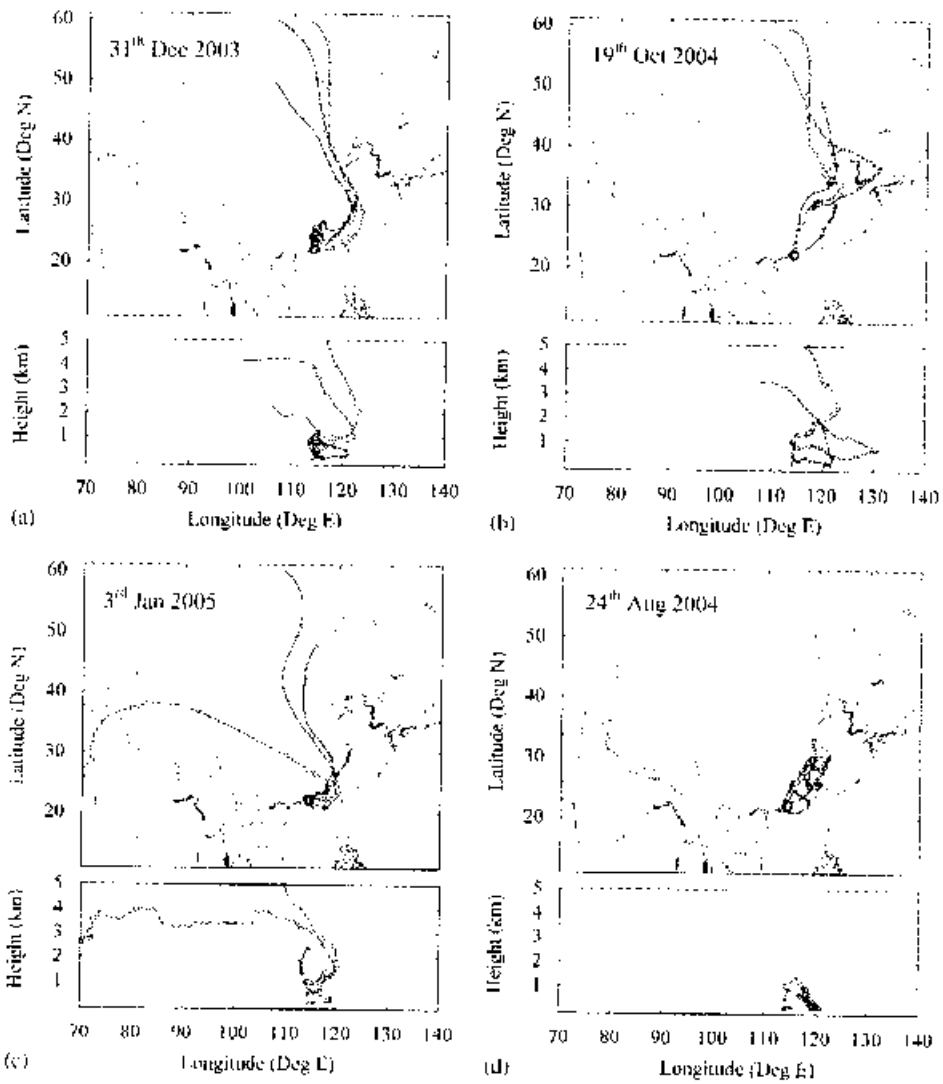

Fig. 7. Back trajectory plots (with increasing marker sizes to represent levels at 100, 500 and 1000 m, respectively) on the episodic days with elevated heavy metal concentrations.

concentrations were found at PU and HT (see Fig. 2a and 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 Fig. 7b and c). On the 24th August 2004, elevated heavy metal concentrations were observed at PU and HT (see Fig. 2a and b) during the summertime. Fig. 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 Fig. 2a and 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 metals 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.

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