The Hong Kong Polytechnic University

Department of Civil and Structural Engineering

ATMOSPHERIC TRANSPORT AND DEPOSITION OF TRACE METALS IN REMOTE RESERVOIRS OF THE SOUTH CHINA COASTAL REGION

By

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A thesis submitted in partial fulfillment of the requirements for the
Degree of Master of Philosophy

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CERTIFICATE OF ORIGINALITY

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JIANG Xunyi

Abstract of thesis entitled ‘Atmospheric Transport and Deposition of Trace Metals in Remote Reservoirs of the South China Coastal Region’ submitted by JIANG Xunyi for the Degree of Master of Philosophy at the Hong Kong Polytechnic University in July 2009.

ABSTRACT

In the past several decades, enormous economic development has taken place in the South China coastal region with intensive industrialization and urbanization. The increasing emissions of air pollutants from various anthropogenic sources have consequently resulted in substantial enrichment of heavy metals in the atmosphere and have deteriorated the air quality. The outflows of airborne heavy metals might have significant environmental implications for adjacent regions or countries. The present study aims to investigate the atmospheric transport and deposition of some major trace metals (Cu, Ni, Pb and Zn) in some remote areas of the South China coastal region, and to further elucidate the significance of potential outflows of air pollutants to the major receptors at the Western Pacific Rim.

Sediment cores were collected at four remote reservoirs (*i.e.* Tingxi Reservoir, Xinfengjiang Reservoir, Luokeng Reservoir and Songtao Reservoir) along the South China coastline to examine the historical inputs of heavy metals into the aqueous environment. Surface soil samples were collected in the reservoir catchment area to study the elemental concentrations of baseline soils in the drainage basin, and to provide background information of regional geochemical conditions. Moss samples were also collected simultaneously to assess the significance of current atmospheric deposition of trace metals in the study area.

The analytical results showed that the concentrations of heavy metals (*e.g.* Cu, Pb, and Zn) were elevated significantly in upper layers of sediments at Xinfengjiang Reservoir, reflecting the increasing inputs of regional air pollutants in recent years. The lead isotopic compositions of mosses imply that the atmosphere over the study area has been strongly influenced by the regional anthropogenic sources, which might contribute substantial amounts of anthropogenic heavy metals in the surface environment by atmospheric deposition. The intensive industrial activities processing lead-containing ores and coal combustion in the PRD region are probably the major contributing sources of anthropogenic lead at the reservoir. Moreover, the long persistence of past-released Pb, possibly from vehicle exhausts of leaded gasoline, may also contribute to the anthropogenic lead in the atmosphere. The increment of Pb concentrations in top sediments at Xinfengjiang Reservoir might thus be attributed to the increasing atmospheric deposition of anthropogenic pollutants released and transported from the PRD region in the past several years.

However, there is no obvious contamination sign of sediments at Tingxi Reservoir, Luokeng Reservoir and Songtao Reservoir, as the concentrations of trace elements were closely associated with the lithogenic major elements Al and Fe. The variations of trace metal concentrations along the sediment cores at these three reservoirs might be attributed to changes of the natural environment. When analyzing the moss samples, the concentrations of heavy metals accumulated in moss samples were found to be rather low at Songtao Reservoir, probably suggesting that the atmospheric deposition fluxes of heavy metals at this reservoir are less significant. In addition, the lead isotopic compositions of mosses at this reservoir were similar to the values of natural backgrounds, possibly reflecting that the air quality is well preserved in this area. The good air quality might be attributed to its specific topographic characteristics of the reservoir, which may prevent the intrusion of polluted air masses coming from the neighboring developing countries (*e.g.* Pakistan, Thailand, Vietnam, Indonesia) in Southeast Asia.

Although the sediments are not likely to be in contaminated level at Tingxi Reservoir and Luokeng Reservoir, the low ^{206}Pb/^{207}Pb ratios of mosses at these two reservoirs probably indicate that there are some anthropogenic inputs of Pb by atmospheric deposition from regional emission sources. The inappropriateness of using the reservoir sediments as geochemical archives of the environment changes might be attributed to the low transmission efficiency

through the reservoir catchments due to their small catchment areas, which may subsequently affect the deposition and accumulation of airborne heavy metals in the sediments of the two reservoirs. Further studies need to be conducted to provide additional evidence.

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CHAPTER 1 – INTRODUCTION

For many years, heavy metals have been among the most commonly investigated environmental pollutants, because they are harmful to the ecosystems due to their high toxicity and long persistence in the environment. It has been widely recognized that the ever-increasing emissions of airborne heavy metals from various anthropogenic sources have been endangering the air quality in both the urban and remote areas since the onset of industrial periods worldwide. The surface environment might be subsequently impaired due to atmospheric deposition of the air pollutants. As the metal associated air particles may be subject to regional or long-range atmospheric transport under certain circumstances, the atmospheric heavy metal pollution has inevitably become a global environmental issue.

1.1 Background

Nowadays, the Asian Continent has been regarded as one of the major contributing sources of anthropogenic air pollutants, as enormous economic development has taken place without strict enforcement of proper pollution prevention or control policies. The outflow of air toxics from the Asian Continent might exert adverse impacts on the environment of some major potential receptors, such as Japan, Korea, and southeast coastline of China.

Recently, successive evidence has been obtained on the long-range transport of air pollutants from the continental Asia (In and Park, 2003; Mori *et al.*, 2003; Bellis *et al.*, 2005; Jaffe *et al.*, 2005; Lee *et al.*, 2007).

The South China coastal region is one of the most rapidly developing and densely populated areas in China. Since the economic reform in the late 1970s, enormous economic development has taken place with intensive industrialization and urbanization, particularly in the Pearl River Delta (PRD) region. The potential environmental burdens imposed by the drastic development in the past three decades are causing increasing concerns. Recently, several investigations have been conducted to monitor the air pollution problem in South China (Wong *et al.*, 2003; Wang *et al.*, 2005; Hagler *et al.*, 2006; Choi *et al.*, 2008; Fang *et al.*, 2008). The findings suggested that not only the atmosphere in this region had been seriously deteriorated, but also the surface environment (*e.g.* urban soils, surface waters) which had been inevitably impaired as a consequence of atmospheric deposition. As the South China coastal region is situated in a typical subtropical monsoon area, it is expected that continuous fluxes of air pollutants might be delivered towards the downwind countries or regions by prevailing winds during monsoon seasons (Louie *et al.*, 2005). The air quality condition in this region might thus have significant implications for the environment of adjacent areas or countries, or locations even further away.

A variety of environmental analytical tools have been developed to investigate and monitor the atmospheric pollution of heavy metals. The most common examples include direct measurements of aerosols (Wong *et al.*, 2003; Hsu *et al.*, 2005; Witt *et al.*, 2006), indirect assessment of natural surface soils (Steinnes *et al.*, 1989; Monastra *et al.*, 2004), aquatic sediment cores (Blais and Kalff, 1993; Flower *et al.*, 1997; Yang *et al.*, 2002; Han *et al.*, 2007), and biological samples such as mosses and lichens (Reimann *et al.*, 1997; Szczepaniak and Biziuk, 2003; Harmens *et al.*, 2004; Ruhling and Tyler, 2004). Most of the previous investigations merely focused on a single environmental medium. However, certain limitations have been found in using each type of environment samples as an approach to monitor the air pollution, such as possible post-depositional disturbance in sediment cores (Weiss *et al.*, 1999; Jackson *et al.*, 2004), vulnerability to meteorological changes in ambient environment for passive air samples (Klanova *et al.*, 2008), and inadequacy in comparison between different species for mosses (Lee *et al.*, 2005). A multi-media approach by examining several different environmental components is thus considered as a more effective way to assess the pathway of trace metals in the environment, and to identify signatures of contamination from distinct sources and differentiate the relative contributions of these sources (Duzgoren-Aydin, 2007).

Although the issues concerning airborne heavy metal pollution in South China have been investigated in many studies recently (Fang *et al.*, 1999; Fang *et al.*, 2000; Zhu *et al.*, 2001; Lee *et al.*, 2007; Zhang *et al.*, 2007), most of them are confined to urban areas and they mainly focused on assessing the concentrations of airborne heavy metals, characterizing seasonal variation patterns, evaluating metal associated particle size distributions, or identifying their potential contributing sources. Limited studies have been conducted to assess regional or long-range atmospheric transport and deposition fluxes of heavy metals. The impacts of regional air pollution on ecosystems in rural or remote areas along the South China coastline also remain poorly understood. Moreover, the existing investigations generally assessed the current or recent situations of atmospheric heavy metal pollution. Information on the long-term atmospheric heavy metal deposition fluxes to the surface environment is still scarce.

In order to have a composite and comprehensive view of the situation in the South China coastal region as a whole, there is an emerging need to conduct a more systematic and intensive investigation on the atmospheric heavy metal pollution in a regional scale. Both the long-term variations and current significance of regional atmospheric deposition of trace metals will be assessed. Consequently, the elevated concentrations of airborne heavy metals, increasing regional deposition fluxes, as well as potential outflows of air toxics by long-range transport can be well monitored and controlled. All the findings will then be used for implementing proper mitigation measures and reasonable city planning to avoid or alleviate potential adverse impacts of hazardous trace metals in the coastal ecosystems.

1.2 Objectives

The aim of the study is to conduct a systematic and comprehensive investigation on the significance of regional atmospheric pollution of some major trace metals (Cu, Ni, Pb and Zn) in the South China coastal region, and further elucidate the potential continental outflow of the air toxics from the South China Coastline to the Western Pacific Rim Region.

The major objectives of this study are as follows:

1) To assess the historical records and variation trends of heavy metal inputs in well-dated sediment cores from remote reservoirs along the South China coastline.
2) To examine the significance of atmospheric deposition of trace metals in the remote area of South China by moss sample analysis.
3) To distinguish the input sources of trace metals between natural and anthropogenic sources by lead isotopic composition analysis and elemental association analysis.
4) To identify the potential contributing sources of anthropogenic air pollutants by conducting the air back trajectory analysis.
5) To establish a database to serve as the solid foundation for future regional

planning and pollution control programs.

1.3 Scopes

The thesis is mainly concerned with the atmospheric deposition of anthropogenic trace metals in the remote area of South China coastal region. The sampling locations were selected at four typical remote reservoirs along the South China coastline, including Tingxi Reservoir in Fujian Province, Xinfengjiang Reservoir in and Luokeng Reservoir in Guangdong Province, and Songtao Reservoir in Hainan Province. The reservoir sediment cores, and surface soil samples and moss samples from the reservoir catchment area were collected at each reservoir for subsequent laboratory analyses. All the samples will be digested by a strong acid mixture of HNO_3 (69%) and $HClO_4$ (70%), and the metal concentrations will be determined by the ICP-AES. Dating of undisturbed sediment cores will be conducted by using the ^{210}Pb dating technology. The long-term variations of metal concentrations along the sediment cores will then be examined to evaluate the enrichment of trace metals over time. Metal associations will be investigated by determining the Pearson correlation coefficients and plotting the relationships between the major and trace elements. Lead isotopic compositions of selected sediment samples, catchment soils and mosses will be analyzed by the ICP-MS. In addition, three-day air back-trajectory analysis will be performed by using the HYSPLIT4 model to identify the dominant air masses influencing the air quality in the study area and the potential anthropogenic sources of heavy metals.

1.4 Organization

The body of the thesis consists of six chapters:

1) Chapter 1 gives a general description of project background information and defines the major research objectives.
2) Chapter 2 presents a comprehensive literature review about the characteristics of trace metals and their adverse impacts, the metal biogeochemical cycling, the transport pathways of airborne trace metals in the atmosphere and the aqueous environment, the most commonly used technologies for monitoring of atmospheric deposition of heavy metals, as well as the existing investigations on atmospheric heavy metal pollution in the South China coastal region and other countries.
3) Chapter 3 illustrates the detailed information of the study area and describes the methodologies adopted for the present research study, including field sampling, sample preparations in laboratory, chemical analysis, air back-trajectory analysis, and statistical analysis.
4) Chapter 4 focuses on the results and discussion on the atmospheric deposition of anthropogenic heavy metals at Xinfengjiang Reservoir for implication of potential regional air pollution.
5) Chapter 5 compares the results from Tingxi Reservoir, Luokeng Reservoir,

and Songtao Reservoir with those at Xinfengjiang Reservoir to assess the air quality at these three reservoirs and discuss in detail the suitability of using the reservoir sediments as environmental archives for atmospheric deposition of anthropogenic heavy metals.

6) Chapter 6 provides a brief summary of the major findings from this research study and also proposes suggestions for improvements and further studies in future.
7) All the references supporting the evidence provided in the thesis are listed at the back in the section of References.
8) The raw data from which the results were derived are presented in Appendices A to C.

CHAPTER 2 – LITERATURE REVIEW

2.1 Metals & Environmental Geochemistry

Metals and metalloid elements are ubiquitous on the earth. They can be introduced into the environment from both natural and anthropogenic sources in a variety of forms. Environmental geochemistry is the discipline concerning physicochemical parameters and interaction processes that control the distribution of chemical elements over the earth's surface among four reservoirs, namely the lithosphere (the solid earth), atmosphere (the gaseous envelope), hydrosphere (oceans, rivers, streams, lakes, reservoirs, and ground waters), and biosphere (living organisms) (Eby, 2004). Understanding the transport and fate of the elements among various environmental medium can provide a basis for proper management and development of resources, and effective alleviation of the pollution problem.

2.1.1 Metals & adverse impacts of heavy metals

Nearly 99% of the earth's total crustal mass is made of eight elements, including O, Si, Al, Fe, Ca, Na, K, and Mg (Benjamin and Honeyman, 2000). Al, Fe, Ca, Na, K and Mg are therefore considered as major metals due to their large abundance in the crust. Trace elements are normally referred to as the metal elements which are residual and present in trace concentrations (*i.e.* several parts per million or even less) in the natural environment. Table 2.1 lists the typical concentrations of some major and trace metals in the continental and oceanic earth's crust and in abundant rock types.

Table 2.1 Elemental Concentrations in the Earth's Crust and in Abundant Rock Species (unit: ppm) (Wedepohl *et al.*, 1991)

	Mg	**Fe**	**Cd**	**Co**	**Cu**	**Cr**	**Mn**	**Ni**	**Pb**	**Zn**
Continental crust	16000	42000	0.10	19	35	88	800	45	15	69
Oceanic crust	50000	70000	0.13	45	81	317	12000	144	0.89	78
Shales	16000	48000	0.13	19	45	90	850	68	22	95
Greywackes	13000	38000	0.09	20	45	50	750	40	14	105
Limestones	26000	15000	0.16	2	4	11	700	15	5	23
Granites	6000	20000	0.09	4	13	12	325	7	32	50
Gneisses	13000	33000	0.10	13	23	76	600	26	16	65
Basalts	37000	86000	0.10	48	90	168	1390	134	3.5	100
Granulites	14000	38000	0.10	15	27	88	895	33	9.8	65

Generally, metals with atomic number 20 or greater are defined as heavy metals, the pollution of which has gained great environmental concern in recent years (Eby, 2004). Most of these elements belong to trace elements with the exception of Fe (Plant and Raiswell, 1983). Heavy metals can mainly be distinguished into two different groups: essential and non-essential elements. Essential heavy metals are regarded as micro-nutrients that are needed in micro-quantities (*i.e.* a few mg or µg per day) by critical human organs or other organisms to maintain good living or growing status, such as Co, Cu, Mn, Zn (Siegel, 2002). A deficiency of certain micronutrient may result in abnormal conditions or diseases in organisms. However, they could be toxic in case of excessive intake. Inhalation of fumes of volatilized metallic copper can result in nausea, gastric pain, or diarrhea (Scheinberg, 1991). High zinc intake may affect cholesterol metabolism in human beings (Bradl, 2005).

Non-essential heavy metals, such as Be, Cd and Pb, are not required by living organisms. Ingestion of these metals, even in trace levels, could be potentially toxic and harmful. Heavy metals are also well known for their long persistence in the environment. They can retain in the soft tissues of living organisms and thus bio-accumulate to certain levels that stunt plant growth and interfere with animal life (Schwedt, 2001). For instance, excessive Cd can affect kidneys and lungs, leading to protein-urea and emphysema. Long-term exposure to Pb could have poisoning effects on the hemoglobin synthesis, central nervous system and reproduction function (Bradl, 2005). Therefore, it is important to monitor heavy metal enrichment in the environment, and to control and alleviate the pollution problem.

The present study mainly focuses on four trace metals, including Cu, Ni, Pb and Zn. Cu, Ni and Zn are essential to plants, and/or to animals and human beings, but excesses can produce toxicity. Pb is potentially toxic and can exert adverse physiological impacts on living organisms even at trace concentrations. The major elements Al and Fe are also considered as they can play an important role in controlling the primary distribution and secondary dispersion of trace elements (Plant and Raiswell, 1983), and can also be used to assess the extent of heavy metal contamination.

2.1.2 Natural biogeochemical cycling of heavy metals

Unlike many of the synthetic organic compounds, metals are part of natural biogeochemical cycles (Benjamin and Honeyman, 2000). The metal cycling is initiated with the formation of plutonic rocks and ore minerals (Schwedt, 2001). Metal elements are incorporated into orderly internal crystalline structures of the igneous rock minerals upon cooling of magma, which is transported to the earth's surface by intensive geological processes (*e.g.* volcanism or plate tectonics). A wide range of minerals and chemical compositions can be found in the rocks forming at different cooling stages, and certain potentially toxic metals can form their own minerals or comprise large percent of a rock-forming mineral, such as Pb in galena (PbS) and Cr in chromite ($FeCr_2O_4$) (Siegel, 2002).

The metal elements can then be mobilized or redistributed via physical, chemical and biological weathering and other geochemical processes, and enter into other reservoirs (*i.e.* atmosphere, hydrosphere and biosphere) afterwards. With long-term weathering, rocks are disintegrated or decomposed into loose particles (sediments), which are then accumulated in sedimentary depositories (*e.g.* lakes) or consolidated into sedimentary rocks in geological time scales. Sedimentary rocks are porous and permeable, thus they can be invaded by ore-metal (*e.g.* Pb and Zn) bearing hydrothermal fluid and form ore deposits. The parent rocks could be transformed into metamorphic rocks under increased temperature and pressure conditions. With complicated physical and other geochemical processes, rocks can be further disintegrated into soils (Bradl, 2005). Soils originated from different types of rocks might have markedly varying chemical compositions, resulting in notable differences in natural background concentrations of metals between different regions. For example, soils formed from basalts are potentially enriched in Cr, Ni and Co (Siegel, 2002).

Metals are introduced into the aquatic system mainly in the following ways: 1) surface waters flow through soils and rocks and undergo complicated chemical processes; 2) ground water moves across disintegrated rock layers and receives leaching from overlying soils; 3) the water body receives metal inputs from atmospheric deposition (Bradl, 2005). The chemical compositions of rock-forming minerals or rocks which the water flows on or through can greatly influence its chemical properties. The subsequent fate of the metals in the water body is dependent on many different factors such as temperature, pH, redox potential, adsorption and desorption by suspended particles or bottom sediments, and metabolic processes by microorganisms (Schwedt, 2001).

Naturally, heavy metals in the atmosphere are mostly originated from mineral dusts (from ore deposits or soils), volcano eruptions, sea salt particles, thermal springs, and extraterrestrial matters (Bradl, 2005). They are mainly carried by particulates, aerosols, or gases in some cases (e.g Hg). After emission from the sources, metals may be dispersed and transported by prevailing air mass movement. During the transport process, they may be removed from the atmosphere from time to time by wet or dry deposition onto soils, waters and plants. Atmospheric inputs of metals to the surface environment are geographically different due to varying meteorological factors and distinctive residence time of a particular metal element in the atmosphere (Siegel, 2002).

The biosphere also plays an important role in metal cycling. Metals from waters and soils are capable of entering the food chain via microorganisms, plants and animals, and accumulating to as high concentrations as to be toxic to human beings. Generally, the lithosphere (*i.e.* parent rocks and metallic minerals) is the dominant source of all metals and also serves as the sink for these metals. The hydrosphere, atmosphere and biosphere act as temporary while important reaction reservoirs for the metal elements (Eby, 2004). It is therefore of great importance to study the interactions among the inter-related reservoirs (*i.e.* lithosphere, hydrosphere, atmosphere, and biosphere) in order to assess the transport and fate of heavy metals in the surface environment.

2.1.3 Anthropogenic sources of atmospheric heavy metals and the potential influences

In the previous section (Section 2.1.2), natural sources and biogeochemical cycling of heavy metals are introduced. The metal cycling was maintained basically in a steady state before the technological times. However, large amount of heavy metals, exceeding naturally occurring concentrations, have been released into the environment from many anthropogenic sources (human activities) since the onset of industrialization worldwide (Nyangababo *et al.*, 2005). Anthropogenic contributions to annual heavy metal emissions and environmental burdens were found to have significantly dominated over the natural emissions in many cases (Nriagu, 1989). In Table 2.2, the annual atmospheric emissions of heavy metals from natural and anthropogenic sources are listed and compared. Except Mn and Co, the anthropogenic inputs for the most important trace metals (*e.g.* As, Cd, Cu, Cr, Pb and Zn) exceeded the contributions from natural sources on the global scale, while natural emission rates were much higher for major elements. The natural biogeochemical cycling of heavy metals in many ecosystems has inevitably been overwhelmed, leading to enormous enrichment in soils (Romic *et al.*, 2003; Loska *et al.*, 2004; Krishna and Govil, 2005; Yang *et al.*, 2007), plants (Bech *et al.*, 1997; Rosen *et al.*, 2001; Al-Homaidan, 2007), aquatic sediments (Sanchez *et al.*, 1998; Huh and Chen, 1999; Li *et al.*, 2000; Feng *et al.*, 2004; Backstrom *et al.*, 2006), air (Deboudt *et al.*, 1999; Petaloti *et al.*, 2006; Tasdemir *et al.*, 2006), and resulting in subsequent accumulation of toxic metals in food chain and living organisms (Outridege *et al.*, 1997; Ip *et al.*, 2005). Besides altering the transferring rates of metals among different reservoirs, the interruption by human activities is also present in altering the form of metals from the originally deposited one, causing changes in metal speciation and potential metal remobilization (Benjamin and Honeyman, 2000).

Table 2.2 Comparison of Annual Atmospheric Emissions of Metal Elements from Natural and Anthropogenic Sources (unit: 10^3 ton) (Compiled from (a) Lantzy and Mackenzie, 1979; (b) Pacyna, 1986; (c) Salomons, 1986, reviewed by Morgan and Stumm, 1991)

Sources		**Al**	**Fe**	**As**	**Cd**	**Co**	**Cu**	**Cr**	**Mn**	**Ni**	**Pb**	**Zn**
(a)	Natural	48900	27800	2.8	0.3	7	19	58	605	28	5.9	36
	Anthropogenic	7200	10700	78	5.5	4.4	263	94	316	98	2030	840
	Anthropogenic / Natural	0.15	0.38	27.9	18.3	0.63	13.8	1.62	0.52	3.50	344	23.3
(b)	Natural	-	-	8	1	5	19	9	520	26	19	45
	Anthropogenic	-	-	24	7	-	56	-	-	47	450	310
	Anthropogenic / Natural	-	-	3.00	7.00	-	2.95	-	-	1.81	23.7	6.89
(c)	Natural	-	-	21	0.3	7	19	58	610	28	4	36
	Anthropogenic	-	-	78	6	5	260	94	320	98	400	840
	Anthropogenic / Natural	-	-	3.71	20.0	0.71	13.7	1.62	0.52	3.50	100	23.3

Historically, anthropogenic inputs of heavy metals can be dated back as early as ancient metal mining and smelting industry during the progression of civilization. Metallic ores were heated, pulverized, and dissolved, and toxic metals became environmentally labile and entered into the natural cycling process until their final deposition in sediments, soils, or biomass (Plant and Raiswell, 1983). In recent time, the major anthropogenic sources of heavy metals include agricultural activities, industrial activities, transportation and solid waste disposal. With development in agricultural productions, fertilizers and pesticides are widely applied to provide additional nutrients to crops and protect them from insects. Mineral (*e.g.* phosphate fertilizers) or micronutrient fertilizers may contain various amounts of potentially harmful heavy metals such as As, Cd, Cu, Pb and Zn (Saltali *et al.*, 2005; Nziguheba and Smolders, 2008). Zarcinas *et al.* (2003) found that the concentrations of As, Cd and Cu in soil samples collected in Peninsular Malaysia were closely correlated to the soluble soil phosphorus, suggesting the contributions of agricultural fertilizers to the enrichment of heavy metals in the soils.

Regarding industrial activities, metallurgical activities including mining, smelting, metal finishing, and others, coal and petroleum combustion for energy production and transportation are considered as the major contributors to the release of heavy metals into the environment, especially to the atmosphere (Bradl, 2005). Waste rocks from mine tailings normally contain high concentrations of As, Cd, Cu, Ni, Pb and Zn (Siegel, 2002). An investigation on heavy metal pollution near a copper smelting plant northeast Turkey showed significant elevation of Cu, Pb and Zn contents in soils, plants and waters nearby (Cubukcu and Tuysuz, 2007). Notable amount of toxic metals, such as Co, Cd, Ni, Pb and Zn, can be found in fly ash from coal combustion, particularly the burning of low quality lignite (Mehra *et al.*, 1998; Baba and Kaya, 2004). In India, the disposal of coal fly ash has been a major environmental concern due to a yearly production of over 100 million tonnes of ash (Praharaj *et al.*, 2002).

The road traffic is considered as another important contributor of heavy metal emissions to the air. The vehicle based sources, such as deicing salts, combustion exhaust, galvanized parts and railings, fuel and oil combustion, brake linings, and tire-wearing particles, are regarded to have released many anthropogenic heavy metals into the atmosphere. Lead (Pb) was once widely used as a gasoline additive (antiknock agent), and large amount of anthropogenic Pb in the atmosphere was attributed to the emission from vehicle exhausts (Monna *et al.*, 1999). Leaded gasoline has been gradually phased out in developed countries (*e.g.* western Europe and North America) since the late 1970s, and a declined trend of Pb contents in the aerosols was then observed, from 600 μg/g in 1979 to 200 μg/g in 1990 (Wang *et al.*, 2006). The phase-out of leaded gasoline was executed all over China in 2000. However, high Pb concentrations were still detected in the atmosphere over urban areas, possibly due to the long persistence of past-released Pb in different environmental medium or the existence of other potential Pb sources (Chen *et al.*, 2005). The metals of concern emitted from brake linings usually include Cd, Cr, Cu, Ni, Pb, Sb and Zn (Hjortenkrans *et al.*, 2006). Wear from vehicle tires is also a potential source for many toxic trace metals, especially for Zn (Councell *et al.*, 2004; Lim *et al.*, 2006). It was estimated that the traffic sector contributed about 90% of Cd, 40% of Cu, over

99% of both Cr and Ni, 85% of Pb, and 80% of Zn, out of the total diffuse metal emissions in Sweden (Hjortenkrans *et al.*, 2006).

Considerable amount of heavy metals can also stem from sewage effluents and solid wastes generated from both agricultural and industrial processes. Liu *et al.* (2005) reported that long-term irrigation with sewage effluent in Beijing had increased the amount and availability of heavy metals in soils. In southeastern Nigeria, which has had a 40-year disposal history of sewage wastes, heavy metal concentrations in soils were enriched high enough to exert health and phytotoxic risks, particularly for Cd, Cu, Pb and Zn (Udom *et al.*, 2004).

2.1.4 Pathways of accumulation and deposition of heavy metals in freshwater ecosystems and influencing factors

The present study is mainly concerned with issues of regional or long-range atmospheric heavy metal pollution. As mentioned in the introduction, anthropogenic inputs of heavy metals from various emission sources in continental Asia have been endangering the air quality in urban areas. The potential adverse impacts of heavy metal pollution in remote areas have also drawn increasing concerns. Aquatic sediments serve as important ultimate long-term conservative depository for heavy metals and might provide information on the historical trend and extent of atmospheric inputs of heavy metals in certain circumstances (*e.g.* remote lakes without point sources). In order to better interpret the sediment profiles, pathways of heavy metal accumulation and deposition in aquatic ecosystems need to be fully assessed, and possible factors influencing the transport and fate of the metal elements should also be examined. In the following part, the pathways of heavy metals will be described and illustrated through four sections, including emission by potential anthropogenic sources, transportation by prevailing air mass over vast distance, transfer mechanisms in a catchment area, and final deposition in lacustrine sediments. A comprehensive summary of heavy metal transferring processes in various stages is presented and illustrated in Fig. 2.1.

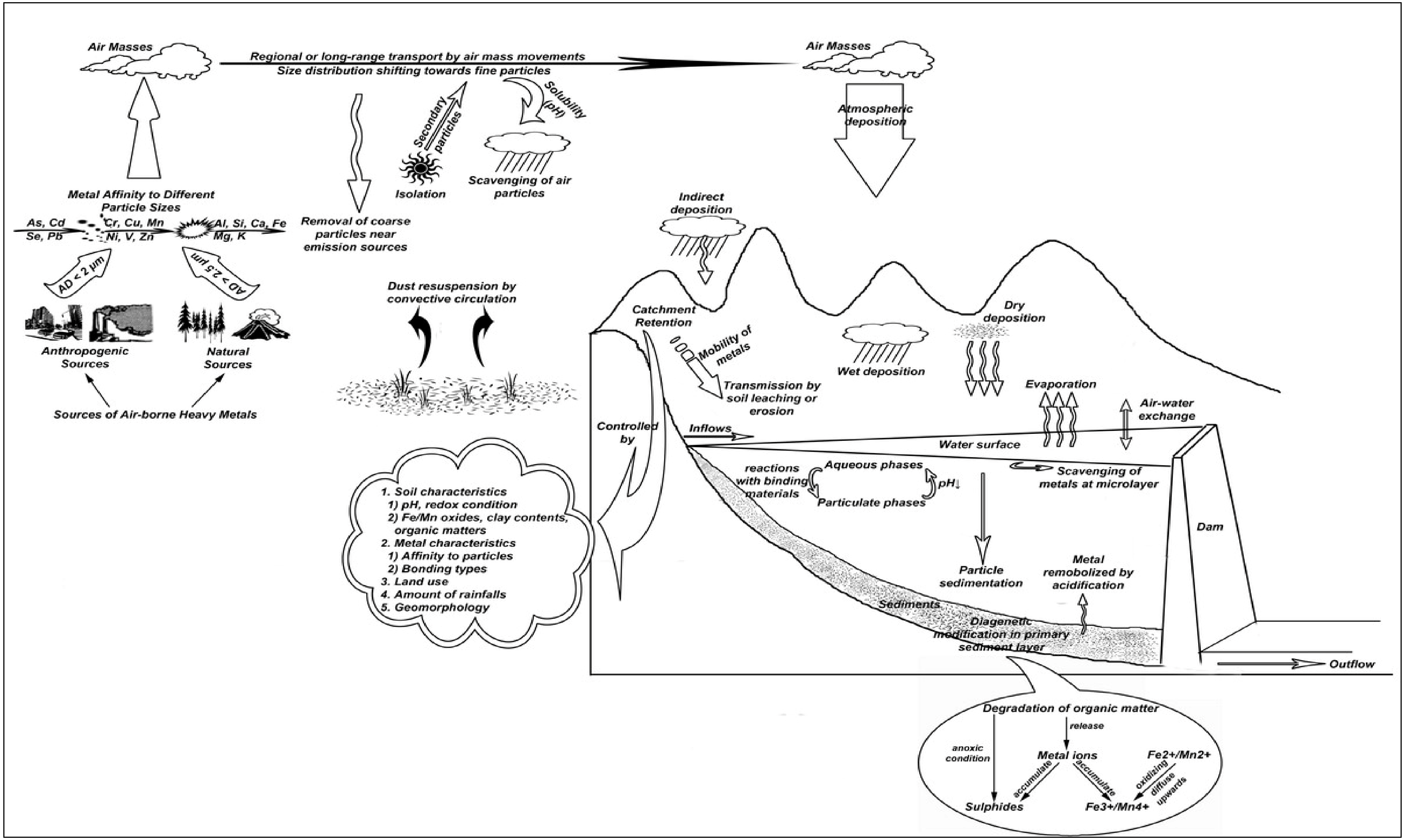


Figure 2.1 Pathways of accumulation and deposition of heavy metals in aquatic ecosystems and possible influencing factors.

2.1.4.1 Emission sources

Nature of emissions

The atmospheric occurrence of trace metals is firstly determined by the nature of emission sources. As mentioned in Section 2.1.3, there is a clear dominance of anthropogenic emissions for most trace elements on the global scale. Different types of natural and anthropogenic sources are also dominated by various types of trace metals. The annual global emissions of trace elements from some major natural sources and anthropogenic sources are presented in Table 2.3 and Table 2.4 respectively.

Table 2.3 The Annual Global Emissions of Trace Metals to the Atmosphere from Natural Sources (unit: 10^6 kg) (Hans, 1991)

Sources	**As**	**Cd**	**Cu**	**Cr**	**Mn**	**Ni**	**Pb**	**Zn**
Atmospheric Dust	0.24	0.25	12	50	425	20	10	25
Volcanoes	7	0.5	4	3.9	82	3.8	6.4	10
Forest Fires	0.16	0.01	0.3	-	-	0.6	0.5	0.5
Vegetation	0.26	0.2	2.5	-	5	1.6	1.6	10
Sea Spray	0.14	0.002	0.1	-	4	0.1	0.1	0.02

Table 2.4 The Annual Global Emissions of Trace Metals to the Atmosphere from Anthropogenic Sources (unit: 10^6 kg) (Hans, 1991)

Sources	**As**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**
Mining, nonferrous metals	0.013	0.002	0.8	-	8.2	1.6
Primary nonferrous metal production	15.2	4.71	20.8	9.4	76.5	107
Secondary nonferrous metal production	-	0.60	0.33	0.2	0.8	9.5
Iron and steel production	4.2	0.07	5.9	1.2	50	35
Industrial applications	0.02	0.05	4.9	1.9	7.4	26
Coal combustion	0.55	0.06	4.7	0.7	14	15
Oil and gasoline combustion	0.004	0.003	0.74	27	273	0.1
Wood combustion	0.60	0.20	12	3.0	4.5	75
Waste incineration	0.43	1.40	5.3	3.4	8.9	37
Phosphate fertilizer manufacture	2.66	0.21	0.6	0.6	0.05	1.8
Miscellaneous	-	-	-	-	5.9	6.7
Total	23.6	7.3	56	47	449	314

As the data show, atmospheric dusts are the dominant source of natural mineral particles containing Mn, Cu, Cr, Ni, Pb and Zn. Volcanoes are regarded as the major emission sources of As, Cd, Pb and Zn. Exudations from plants also contribute markedly to the natural fluxes of As, Cd and Zn compounds. Considering anthropogenic sources, Ni is found to be released mostly from oil combustion. Automobile exhaust emitted by fuel combustion is the predominant source for anthropogenic Pb in the atmosphere. As, Cd, Cu and Zn are mainly derived from non-ferrous smelting industries and secondary metal manufacturing plants, which are also important sources for Ni and Pb.

Size and compositions of source particles

Apart from Hg, which is mainly found in gaseous phase in the atmosphere, trace metals are usually associated with atmospheric particulates (aerosols) in the atmosphere (Witt, 2006). Aerosols can be derived from natural sources such as mineral dust, sea salt and volcanic activities, or are originated from a variety of anthropogenic processes (*e.g.* combustion, industrial activities and automobile) (Motelay-Massei *et al.*, 2005; Tasdemir *et al.*, 2006). It is also considered that secondary particulate matters, in addition to primary pollutants directly released from sources, could be produced during emission, transport and deposition processes. They are normally formed due to different physical and chemical processes such as homogeneous and/or heterogeneous nucleation (Querol *et al.*, 1996). Upon the formation of secondary aerosols, they may exert potentially adverse impacts on the environment, depending on their particle size and the associated acidity (Querol *et al.*, 1999).

The particle size of aerosols from different emission sources can vary significantly. Previous studies revealed that aerosols in coarser size fraction (aerodynamic diameter (*i.e.* AD) > 2.5 μm) are normally associated with natural sources or produced by mechanical processes, such as erosion or abrasion and during combustion of ash containing fuels (*e.g.* mineral dusts) (Hans, 1991). Although anthropogenic aerosols shows a broad size-distribution from 0.001 μm to 50 µm AD (see Fig. 2.2), most anthropogenic activities involve high-temperature processes, thus tending to generate much finer particles (*i.e.* with AD < 2 µm as the modal class) (Eleftheriadis and Colbeck, 2001; Espinosa *et al.*, 2001). Lam *et al.* (1999) observed $PM_{2.5}$ constituted up to 70% of the total PM_{10} when investigating the suspended particulate matters in Hong Kong. In such conditions, heavy metals are dominantly released to the atmosphere in their gaseous form and preferentially attached onto finer particles with largest surface areas. However, different heavy metals also show various affinities to different size fractions. It was observed that volatile trace elements such as As, Cd, Se and Pb are more likely to be enriched in fine particles (*i.e.* accumulation mode 0.3-0.8 µm AD), while oxides of Al, Si, Ca, Fe, Na, Mg and K exist predominantly in coarse particles. Cr, Cu, Mn, Ni, V and Zn exhibit an intermediate behavior and distribute in both fine and coarse particles, with slight enrichment in the finer particle fraction (1-5 µm AD) (Hans, 1991; Sweet *et al.*, 1998; Allen *et al.*, 2001). Fig. 2.3 shows the mass distribution of some typical major and trace metals according to size fractions. As can be noticed from the graph, $PM_{1.0}$ accounted for over 70% and $PM_{2.5}$ comprised over 90% of the total mass for Cd, Pb and Se. As for Zn, Ni, Co, Cu and Mn, the percent out of total mass for $PM_{1.0}$ was 43-62% and the PM_{10} fraction still exceeded 90%. The $PM_{1.0}$ fractions for Ba, Fe and Sr were all less than 20%.

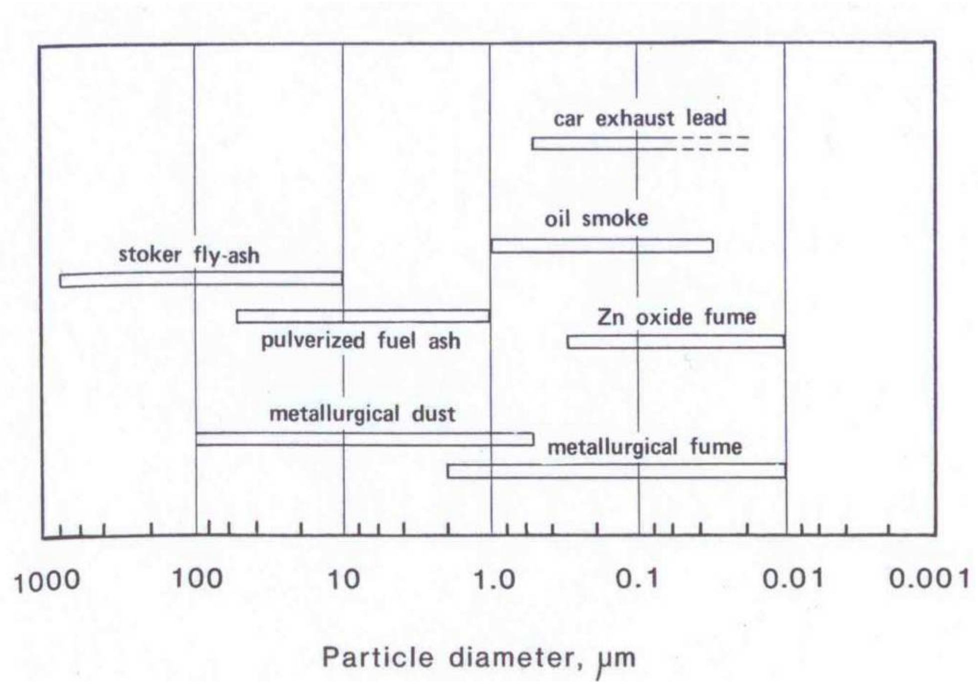


Figure 2.2 Particle size distributions of anthropogenic aerosols (Livett, 1988)

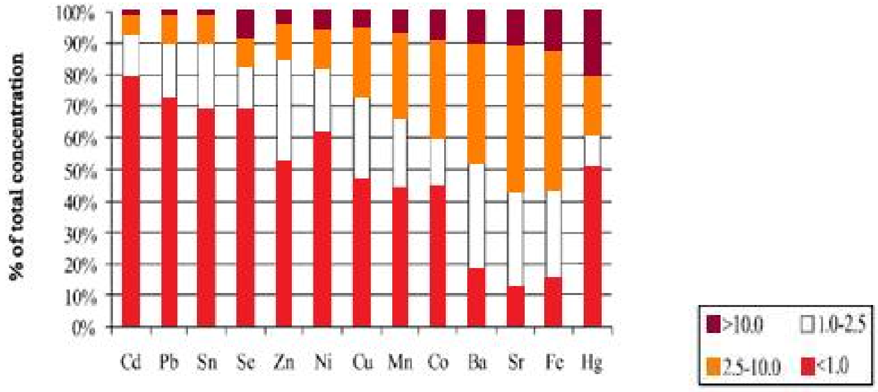


Figure 2.3 Size distribution of major and trace metals in atmospheric particulates in Central England (Allen *et al.*, 2001)

Many researchers suggested that particles less than 10 μm in diameter (*i.e.* respirable suspended particulates), especially those less than 2.5 μm, have high capability of respiratory penetration and retention, and are readily taken into human lungs, causing tissue damage and in turn increasing morbidity and mortality (Chan and Kwok, 2000; Cabada *et al.*, 2004; Fang *et al.*, 2005). The particle size distribution of heavy metal associated air particulates is thus considered of great importance in influencing the potential toxicity of the metal elements.

2.1.4.2 Atmospheric transport and deposition

<u>*Transport in the air*</u>

1) Particle size distribution

It has been realized that it is not merely the concentrations of total suspended air particulates and metals, but the particle size distribution and associated metal contents, can significantly influence the transport and fate of heavy metals, as well as the potential adverse impacts on human beings (Salma *et al.*, 2005; Srivastava and Jain, 2007). After emission into the atmosphere, aerosols can be carried and dispersed by atmospheric motions over a wide range of distances, and gradually removed from the atmosphere by either dry deposition (*e.g.* impaction or sedimentation) or wet deposition (*e.g.* rainout or washout) (Eby, 2004). The particle size is one of the most important controlling factors influencing the extent of metal dispersion via atmospheric transport (*i.e.* residence time in the atmosphere) and deposition rate of metals to the surface environment (Samara and Voutsa, 2005). Coarse particles are more readily removed from the atmosphere locally, while fine particles might be subject to atmospheric transport over vast distances and finally deposit at regions far away from the emission sources (Allen *et al.*, 2001). The size distribution away from sources is gradually shifted towards smaller particles (Mason *et al.*, 2002). It was reported that particles larger than 5 μm were generally absent in rural regions and heavy metals were most frequently associated with small aggregated particles of 0.1-1.0 μm in polar regions (Livett, 1988).

2) Meteorological parameters

The fate of atmospheric particles and behavior of heavy metals in the atmosphere are also greatly influenced by some meteorological parameters such as the temperature, humidity, rainfalls and winds (Ragosta *et al.*, 2002). These factors probably account for seasonal variations of concentrations of atmospheric suspended particles and associated heavy metals as investigated by many researchers (Querol *et al.*, 1998; Yatin *et al.*, 2000; Fang *et al.*, 2006; Shah *et al.*, 2008). Temperature might affect the levels of total suspended particles in the atmosphere. It was suggested that a higher temperature could favor resuspension of surface soils or dusts (Harrison *et al.*, 1997; Colombo *et al.*, 1999). Humidity and amount of rainfalls are also considered as important factors influencing levels of air particles. Harrison *et al.* (1997) observed that the concentrations of coarse particles were strongly correlated with wind-derived resuspension processes of dusts during drier seasons of the year and contributed substantially to the elevated levels of total suspended particulates. Higher precipitations were believed to cause more intense scavenging (wash-out) process of aerosols, resulting in lower levels of air particulates (Colombo *et al.*, 1999; Shaheen *et al.*, 2005; Shah *et al.*, 2008).

Another important parameter is the wind effect, which plays a significant role in controlling the transport and distribution patterns of atmospheric particulates, and the behavior of heavy metals in fine and coarse particle fractions. The wind effect mainly refers to the influences of wind speed, wind direction and the mixing height. The wind speed determines the frequency of surface winds from different source sectors. It is therefore closely correlated with the hourly concentrations of metal concentrations in the atmosphere (Ragosta *et al.*, 2002). A lower wind speed normally results in homogeneous distribution of metal concentrations in all sectors (Yatin *et al.*, 2000). Harrison *et al.* (1997) observed a negative correlation between the wind speed and the levels of fine particles all the year round. However, coarse particles from resuspension exhibited a positive dependence on the wind speed. As for wind direction, the episodic variations can switch on or off the contributions from a specific emission source, leading to seasonal, monthly or even weekly variations of concentrations of atmospheric particulates and associated metals (Ragosta *et al.*, 2002). This parameter is especially important for regions vulnerable to monsoon climate, which could cause significant changes of weather conditions (*e.g.* prevailing wind direction) and subsequently influence the concentrations of air pollutants (Cheng and Lam, 1998). The anemometric data are usually input in models for predicting the concentration maxima or estimating directions with the worst pollution conditions. In addition, change in the mixing height can cause common variations in all other meteorological parameters such as temperature, pressure and wind speed. The dependence of elemental concentrations on the mixing height is thus expected to occur. It was revealed that concentrations of metal elements were readily to decrease with increasing mixing height (Yatin *et al.*, 2000).

Moreover, the amount of air particles and associated heavy metals can also be subject to the concurrent influences of other meteorological factors, as well as the seasonal variations of emission source nature and strength (Yatin *et al.*, 2000). Querol *et al.* (1998) noticed that higher oxidation induced by higher insolation and oxidant levels in summer could increase the levels of secondary total suspended particles. They also suggested that higher convective circulation might increase levels of soil-related particles and primary anthropogenic particles.

Atmospheric deposition

There are four distinct processes of dry deposition based on the particle sizes of air particulates, namely gravitational settling, impaction, turbulent transfer, and transfer by Brownian motion (Livett, 1988). Gravitational settling is the major means of deposition for coarse particles, while the principal mechanisms for deposition of fine particles are impaction and turbulent transfer. The deposition efficiency of fine particles in remote areas is thus greatly dependent on the characteristics of the recipient surface. Table 2.5 shows the properties of some natural surfaces and their aerodynamic resistance to deposition. An area with a higher aerodynamic resistance factor is expected to have lower deposition efficiency.

Table 2.5 Microtopographic characteristics of some typical natural surfaces affecting dry deposition efficient of air particles (Livett, 1988)

Surface	**Geochemical monitoring equivalent**	**Canopy height (m)**	**Roughness length (cm)**	**Aerodynamic resistance (s cm^{-1})**
Smooth ice	Ice deposits	-	0.003	0.46
Ocean	Aquatic sediments	-	0.005	0.44
Tilled soil	Bare peat / rough snow	-	0.1	0.32
Thick grass	Vegetated peat (*e.g. Eriophorum vaginatum*)	0.1	2.3	0.19
Dwarf shrubs	Vegetated peat (*e.g. Ericaceae*)	< 1.0	-	-
Shrubs	-	1.5	20.0	0.10

As the data indicate, the dry deposition of air particles might be most effective for densely vegetated surfaces while least effective for snow and ice. The aerodynamic resistance of aquatic sediments is also found to be comparatively higher, approximately the value of ice deposits.

Wet atmospheric deposition (*e.g.* rainfalls and snows) mainly involves two processes, including nucleation (*i.e.* condensation of water vapor droplets), and within- or below-could scavenging of wetted aerosol particles by falling raindrops. Rainwater is regarded as the most effective scavenging agent for removing particulate or dissolved gaseous pollutants from the atmosphere (Al-Khashman, 2005). The scavenging of atmospheric particulates has a great influence on the chemical compositions and acidity (*i.e.* pH) of the rainwater via an interplay of the acidic and alkaline components. The acidic compounds generally come from gases given out by soil microbial activity, terrestrial and marine biological activity, and industrial and urban emissions, whilst alkaline components are mainly coarse aerosols (*e.g.* dusts) derived from soil resuspension (Datar *et al.*, 1996). The efficiency of wet deposition, described by washout factor (*i.e.* concentrations of an element in the precipitation vs. concentrations of an element in the air), depends on the solubility of the metals and their compounds, as well as the absolute concentration of impurities in the aerosol (Livett, 1988). Desboeufs *et al.* (2000) noticed that metals contained in carbonaceous aerosols were easier to be dissolved than those in aluminosilicated particles. As the metals associated with carbonaceous particles are very soluble, the dissolution is not likely to be dependent on the pH. However, metals associated with aluminosilicated particles are less soluble, especially for those constitutive of the matrix network (*e.g.* Fe, Mn), and have a dissolution highly influenced by the acidity. Normally, the highest concentrations of elements can be observed at the beginning of the rainfall season when large amounts of dust accumulated in the atmosphere are scavenged by rain (Al-Khashman, 2005). In case of clean air condition, the low concentrations of air impurities normally result in poor efficiency of atmospheric cleansing, leading to a close similarity of chemical compositions between the precipitation and air.

It was suggested that the atmospheric dry fluxes are more significant for crustal elements (*e.g.* Al, Fe and Mn), while trace elements (*e.g.* Cd, Cr, Cu, Pb and Zn) are predominant in wet fluxes (Church *et al.*, 2002). The percentage of heavy metal soluble fraction in dry deposition is generally lower than in wet deposition. Considering different trace metals, Cd, V, Cu and Zn exhibit a higher average solubility than Cr, Ni and Pb in both dry and wet deposition (Morselli *et al.*, 2003).

2.1.4.3 Deposition and transmission from the catchment

Atmospheric heavy metals can enter the freshwater system (*e.g.* lakes or reservoirs) either via direct fluxes to the surface water by dry or wet deposition, or by indirect transmission of atmospheric inputs through the watershed (Church *et al.*, 2002). The metals in the terrestrial drainage basin may be carried into the freshwater system by headwater stream discharges (both dissolved and particulate fluxes), or they may be leached through permeable soil layers (leaching fluxes) or dissolved in the groundwater (Schwedt, 2001). The contributions of atmospheric heavy metal inputs from the catchment might be appreciable, or even dominant over direct atmospheric deposition in case of high drainage ratio (catchment area vs. open surface water area) of the lake or reservoir (Shotbolt *et al.*, 2006). Ukonmaanaho *et al.* (2001) found that two thirds of the inputs of Cd, Ni, Pb and Zn to the receiving lake were from the terrestrial component of the catchment, with the remaining being directly from atmospheric deposition. Compared to natural lakes, water-supply reservoirs are more susceptible to the strong influences of metals exported from the catchment with relatively higher sedimentation rates, as they are generally located at regions where large catchment area can be utilized and preferably abundant precipitations are available (Shotbolt *et al.*, 2005). The significance of indirect loading of atmospheric heavy metals is closely related to the transmission/retention capacity of the catchment, which are mainly influenced by soil characteristics (*e.g.* pH, the abundance of Fe/Mn oxides and organic matters, clay content, surface area, and cation exchange capacity), chemical properties of the metal (e.g metal affinity to particles), geomorphology, land use, amount of rainfalls, and the basic hydrological characteristics (Schmitt and Sticher, 1991; Blais and Kalff, 1993; Church *et al.*, 2002). Organic-rich soils, such as forest soils, might be more effective for metal retention (Ukonmaanaho *et al.*, 2001). The flux of organic matter to the receiving water, on the other hand, significantly governs metal export from catchment soils (Dillon *et al.*, 1988). Metals can be present in the soil solution in the form of metal ions or of inorganic or organic complexes, and can also be adsorbed to the surface of clay minerals or clay-humus complexes. The bond type of heavy metals, and the redox condition and pH of soils can greatly affect the solubility and mobility of the metal elements (Schwedt, 2001). Metals in easily exchangeable forms might be more susceptible to pH changes so that accelerated deposition of strong acid or acid precursors (SO_2) is expected to cause increased mobility of the metals (Dillon *et* *al.*, 1988). Different metal elements exhibited distinctive behaviors in catchment soils due to different physico-chemical properties. Cr has a high mobility at pH > 7, while the solubility of Cd, Pb and Zn increases in more acidic conditions (Schwedt, 2001). Cr normally forms oxide anions in soils, which tend to be repelled by clays and Fe oxyhydroxides thus enhancing export fluxes from soils. Cu, Cr and Pb are found to be strongly correlated with dissolved organic carbon while Cd, Ni and Zn have a lower affinity for organic matters (Blais and Kalff, 1993; Ukonmaanaho *et al.*, 2001). Moreover, the catchment metal export behaviors are not consistent, possibly ascribed to particular geological conditions in different regions. Some researchers noticed that anthropogenic Cu, Pb and Zn could be effectively retained by catchments while Cr and Ni were readily exported (Dillon *et al.*, 1988; Blais and Kalff, 1993; Ukonmaanaho *et al.*, 2001). However, Church *et al.* (2002) observed that the atmospheric Pb inputs to the catchment were almost fully delivered to the receiving water, while Cr, Cu and Zn were retained by the terrestrial basin to certain extent and tended to be periodically remobilized by acidic precipitation events. In addition to the indirect fluxes of atmospheric heavy metals, metals exported from the terrestrial basin into the freshwater system can also be derived from erosion of natural catchment soils. The amount and particle size of the soils transported into the water body may vary temporally and spatially. This portion of inputs is considered of importance for particle-reactive elements, such as Fe (Church *et al.*, 2002). The fluxes of eroded materials from catchments with serious erosion could be high enough to the point of obscuring the evidence of atmospheric inputs, thus leading to unsuitability of the aquatic sediments as geochemical archives for historical aerial deposition of heavy metals (Yeloff *et al.*, 2005). The possible usage of solid control system can be used to reduce sedimentation rate, but might also alter the particle size distribution, possibly leading to shifting to finer-grained sediment components.

2.1.4.4 Transfer mechanisms in the aquatic system

Water column

The behavior of metals in the aquatic ecosystem is closely related to a number of distinct physical and chemical interactions between different components within both particulate and aqueous phases. Considerable amount of atmospheric heavy metals entering the aquatic environment are associated with fine particles (< 1 μm) or in soluble forms (Lion *et al.*, 1982; Livett, 1988). The interface between the water and the atmosphere (the uppermost thin water film with thickness of 50-100 μm) known as microlayer is regarded as the first site where complex physicochemical interactions could occur. Heavy metals concentrated in the surface microlayer might be derived from atmospheric deposition, or brought by bubble flotation from the water column (Cuong *et al.*, 2008). They are subject to scavenging by surface-active molecules in surface nanolayer (0.1-1.0 μm) or particulate matters and microorganisms enriched in surface microlayer (<10 μm) (Wurl and Obbard, 2004). The organic acids, proteinaceous materials, and other surface-active organic substances and particles might provide complexing sites for many heavy metals and thus be responsible for the transport and enrichment of these metals at the water surface (Duce *et al.*, 1972). Many researchers have reported the high enrichment of heavy metals in the microlayers relative to the bulk water column (Duce *et al.*, 1972; Wurl and Obbard, 2004; Cuong *et al.*, 2008).

In bulk water column, scavenging of heavy metals by particulate matters is the most important process controlling the accumulation and distribution of metals (Gonzalez-Davila, 1995). Heavy metals can be transferred from aqueous phases to particulate phases by several reactions, including precipitation and co-precipitation with hydroxides, sulphides or carbonates; cation exchange/sorption on clay minerals, iron/manganese oxides and sulphides, carbonates, phosphates and organic matters; and complexation with organic matters (Livett, 1988). These reaction processes are highly dependent on the binding characteristics of the particulate matters, such as the grain size. Marked grain size partitioning of heavy metal concentrations in the sediments has been widely recognized. Fine particles are believed to bind with metal ions more strongly than coarse particles as they provide much larger surface-active coating areas containing organic matters and Fe/Mn oxide (Yang *et al.*, 2002; Ip *et al.*, 2007). The efficiency of a distinct reaction also depends notably on the affinity of metal elements for a particular ligand and their respective concentrations, as well as the redox potential and pH. Organic matters, either natural dissolved or in particulate form, are regarded as critical scavengers of heavy metals in natural waters (Gonzalez-Davila, 1995). Serious impairment of the aquatic ecosystem might be caused by heavy metal enrichment during phytoplankton bloom periods (Admiraal *et al.*, 1995; Garcia-Hernandez *et al.*, 2005). Metals can be directly accumulated by the algae, or complexed by their extracellular metabolites, and significant amount of heavy metals may be subsequently incorporated into the sediments below (Garban *et al.*, 1999). The pH is another major factor influencing the behavior of heavy metals in the water column. A lower pH might increase the concentrations of soluble heavy metals, leading to decreased efficiency in scavenging mechanisms.

Sediments

Particles associated heavy metals will be gradually removed from the water column, and sink and accumulate in the underlying sediments. The newly deposited particulate matters form a layer over the primary sediment layer and may particularly susceptible to physical and chemical remobilization. The sediment redistribution (*i.e.* sediment focusing) triggered by thermal cycles or seasonal turbulence may consequently result in a proportionately greater loading of heavy metals in deeper layers of sediments (Yang *et al.*, 2002). The impacts of drawdown on sedimentation and sediment distribution are considered minor in deepwater sediments (Shotbolt *et al.*, 2005).

Heavy metal associations are subject to diagenetic modification when entering the primary sediment layer. Degradation of organic matters first occurs, which is especially faster in aerobic conditions. The released heavy metals usually accumulate in the top 1-3 cm of sediments. Fate of these metal elements greatly depends on the redox potential of the sediments and the overlying water column. For example, Cd, Cu, Ni and Pb are likely to be fixed in reducing conditions, while Fe and Mn are normally fixed in oxidizing conditions (Livett, 1988). The formation of sulphide in seasonal anoxic and eutrophic sediments from degradation of organic materials can accumulate large amount of heavy metals, which might be released to the water column in case of periodic oxidizing conditions (Canavan *et al.*, 2007). Coprecipitation with Fe/Mn oxides is another important mechanism influencing the accumulation, speciation and vertical distribution of heavy metals in sediments (Douglas and Adeney, 2000). Fe^{2+} and Mn^{2+} tend to diffuse upwards to the redox boundary and be oxidized to Fe^{3+} and Mn^{4+}, which are efficient scavengers of released heavy metals and can regulate the flux of metals into the overlying water column. The enrichment of Fe/Mn oxides can usually be observed at or near the sediment-water interface, and is mostly associated with peaks of heavy metal concentrations.

The acidity of bulk water and pore waters can also affect the fate of heavy metals in the sediments. In case the water body is suffering serious acidification, the lowered pH may not only reduce the efficiency of heavy metal scavenging by particulates, but also potentially remobilize metals from the surface sediments to the overlying water column, such as Cd, Ni and Zn (Fjeld *et al.*, 1994; Kjoller *et al.*, 2004). The distribution of heavy metals may also be significantly influenced by bioturbation. It may lead to mechanical mixing of surface sediments, or facilitate chemical remobilization of heavy metals by sediment aeration (Livett, 1988).

2.1.5 Long-range transport & monsoon activities

In the previous section (Section 2.1.4), the pathways of heavy metals from the emission sources to final deposition in sediments are described. It can be noticed that atmospheric transport of heavy metals by air mass movements (*i.e.* the wind effect) plays an important role in controlling the distribution and fate of anthropogenic air pollutants. In this section, two major issues considering the atmospheric transport of heavy metals are presented.

Recently, the term “long-range transport” (LRT) has gained great attention. It is widely recognized that LRT has promoted the globalization of environmental pollution. The cross-boundary transport of air pollutants was historically studied in European countries to assess the significance of acid deposition in the 1970s (Mukai *et al.*, 1994). The LRT was also recognized when investigating the Kosa phenomenon in spring, when yellow sands were blown from Asian Continent to Japan. It was then widely investigated by many researchers in North America, revealing the possible transport of airborne particulate matters from other regions (Kritz *et al.*, 1988; Parrish *et al.*, 1992; Jacob *et al.*, 1999; Jaffe *et al.*, 2003). They suggested that high levels of air toxics observed in North America might be attributed to two major influences: 1) 'events', whereby air masses containing relatively high concentrations of pollutants from Asia are rapidly transported across the Pacific; and 2) background and local contributions. Successive evidence has been released that trans-Pacific pollutant transport or inter-continental global transit could be expected to occur under some circumstances. However, most of the air toxics examined focused on dusts (Fang *et al.*, 1999; McKendry *et al.*, 2001; In *et al.*, 2003), non-seasalt sulfate (Berresheim, 1993), combined nitrogen (Nakamura *et al.*, 2005), CO (Jaffe *et al.*, 1997; Chan *et al.*, 2002; Goldstein *et al.*, 2004), mercury (Jaffe *et al.*, 2005), radon (Kritz *et al.*, 1988), ozone (Jacob *et al.*, 1999; Chan *et al.*, 2002), non-methane volatile organic compounds (Guo *et al.*, 2006), and peroxyacetyl nitrate (Jaffe *et al.*, 1999).

Considering trace metals, they are highly persistent in the environment and are not biodegradable. Since heavy metals of anthropogenic origins are normally associated with fine air particles or in gaseous form (*e.g.* Hg), they might be subject to possible LRT by prevailing air mass movements, and settled by dry or wet deposition in area far away from the source areas. Recently, more evidence on the possibility of long-range transport of heavy metals has been found (Reimann *et al.*, 1997; Steinnes *et al.*, 1997; Bellis *et al.*, 2005; Hsu *et al.*, 2005; Lee *et al.*, 2007). The outflow of heavy metals from continental Asia has been reported by many researchers. Bellis *et al.* (2005) observed that lead isotopic ratios of aerosols in Japan during winter were indicative of the contributions by certain lead ores and coals in continental Asia, reflecting the long-range transport of Pb from continental Asian to Japan. Lee *et al.* (2007) revealed that the enrichment of heavy metals in South China coastal region (*e.g.* Hong Kong and Guangzhou) was closely associated with the air masses from the northern inland areas of China by conducting the air back-trajectory analysis. Han *et al.* (2004) also attributed the increased atmospheric dry deposition of heavy metals in Korea mainly to the long-range transport of Al and Pb from major industrial areas and deserts of North China during yellow-sand events in spring. In North America, DesJardins *et al.* (2004) reported that the lead isotopic compositions in Kejimkujik National Park, Nova Scotia were influenced by the binary mixing of anthropogenic pollutants transported from both southeastern Canada and northeastern US. Moreover, it was revealed there was a strong outflow of Hg transported across the Pacific to North America (Jaffe *et al.*, 2005). Therefore, it is inevitable that the air quality in rural or remote areas might also be influenced greatly by the long-range transport of heavy metals from industrial and urbanized areas (Flower *et al.*, 1997; Fitzgerald *et al.*, 1998; Rose and Rippey, 2002). In certain circumstances, the aerosols from Norilsk and Kola Peninsula were even detected in the Arctic atmosphere (Shevchenko *et al.*, 2003).

It has been widely recognized that the long-range transport of heavy metals is dependent on seasonal variations of prevailing winds, caused by strong monsoon activities (Mukai *et al.*, 1994; Siefert *et al.*, 1999; Matsuki *et al.*, 2003; Lee *et al.*, 2007). Monsoons are normally described as the seasonal reversal of wind direction, caused by temperature differences between the land mass and ocean area. They play an important role in the management of global climates. Monsoons can affect the way that the land, sea and atmosphere regimes interact with each other and influence weather through the exchange of moisture and energy. Therefore, monsoons are considered to have a great impact on the atmospheric circulation and the geographic environment, thus affecting the source strength and pathways of air pollutants.

The Eastern China and South China coastal region are typical monsoon areas, which are sensitive to monsoon fluctuations and subject to significant seasonal climate changes (Ding, 1994). It was recently reported by Han *et al.* (2007) that the East Asian monsoon is a significant factor that affects atmospheric heavy metal deposition, as indicated by strong associations between the variations of heavy metal concentrations and climate changes in accordance with the East Asian monsoons.

In general, the summer monsoon corresponds to warm and wet climate, while the winter monsoon corresponds to dry and cold climate in China (Han *et al.*, 2007). During May to August, the summer monsoon prevails in China. It originates from three airflows: 1) the Indian summer monsoonal airflow; 2) the cross-equatorial airflow from Australian region flowing over Southeast Asia and the South China Sea; 3) the southeast monsoon coming from the southern flank of the subtropical high over the western Pacific (Ding, 1994). The summer monsoon advances northward in stepwise way with simultaneous northward movement of precipitation belts. When it finally comes to mid October, the summer monsoon completely withdraws from the Mainland and the winter monsoon prevails instead. The characteristic weather of winter monsoon is marked by the invasion of extremely dry and cold air and strong winds over Mongolia, northern China, and Korea. The Siberian high which intrudes into China has two tracks, the major one of which extends southeastward from the source region to the west of Lake Baikal, passing the middle Yellow River Valley, northern China, and the lower Yangtze River Valley, and eventually extends toward the sea region to the south of Japan or down to southern China (Ding, 1994).

For a long time, many researchers have been engaged in numerous studies to assess the impacts of monsoons on the weather and climate changes (An *et al.*, 2000). However, the studies of monsoons on air pollutants dispersion and transport, as well as atmospheric deposition are still scarce. As the study area of the present investigation are located in regions vulnerable to monsoons activities, it is necessary to take this factor into consideration when analyzing seasonal variations of long-range transport and atmospheric deposition of heavy metals. The results might help to effectively monitor the air quality and control regional pollutions.

2.2 Monitoring Atmospheric Heavy Metals

Nowadays, a variety of analytical tools (*i.e.* environmental materials) have been developed to investigate and monitor the atmospheric pollution of heavy metals. Examples include direct measurements of aerosols (Wong *et al.*, 2003; Hsu *et al.*, 2005; Witt *et al.*, 2006; Lee *et al.*, 2007), indirect assessment of natural surface soils (Steinnes *et al.*, 1989; Zhu *et al.*, 2001), rain and snow samples (Takeda *et al.*, 2000), ice cores, peat bogs, sediment cores (Blais and Kalff, 1993; Flower *et al.*, 1997; Yang *et al.*, 2002; Han *et al.*, 2007), and biological samples such as mosses and lichens (Reimann *et al.*, 1997; Szczepaniak and Biziuk, 2003; Harmens *et al.*, 2004; Ruhling and Tyler, 2004), tree trunk bark pockets (Satake *et al.*, 1996; Bellis *et al.*, 2005).

Monitoring of air pollution by a relatively systematic and quantitative analytical approach was pioneered by A. C. Smith in the mid-nineteenth century (Livett, 1988). It is not until the middle of twenties century that more attention began to focus on heavy metals, especially Pb, and conventional monitoring methods were established. Alternative monitoring means by biomonitors, such as lichens and mosses, were developed around the 1970s (Ruhling and Tyler, 1968, 1969)

In the following four sections, the most widely used approaches, namely aerosols, sediment cores, peat bogs, and mosses, are illustrated respectively.

2.2.1 Aerosols

Collection of aerosol samples by different sampling devices is the most direct approach to analyze the atmospheric pollution of heavy metals. The most commonly used sampling devices include low-volume air samplers (Mukai *et al.*, 2001), high-volume devices (Lee *et al.*, 2007), and passive bulk deposition samplers (Wong *et al.*, 2003).

With regard to low-volume and high-volume air sampling, air is actively drawn through filters, on which the air particles are retained and collected. This type of measurements could effectively provide information on the chemistry of aerosols suspended in the atmosphere. For years, active air sampling has been widely applied in combination with air back trajectory analysis and source attribution analysis to provide useful information on the long-range transport of trace metals (Mori *et al.*, 2003; Witt *et al.*, 2006; Lee *et al.*, 2007). However, it was reported (Guo *et al.*, 2003) that high-volume sampling on fiber filters is prone to sampling losses due to 'blow-off' effect on volatile species and filter-catalyzed oxidation. Therefore, the particulate phase of the target compounds is normally collected using a fiber or membrane filter (*e.g.* glass/quartz micro-fiber filters (GFF/QFF)), while the portion associated with gas phase is sampled using an adsorbent trap (*e.g.* polyurethane foam (PUF)) (Hart *et al.*, 1992). Moreover, active air sampling requires pumps, sampling heads, and electricity or other power sources to draw air samples actively, thus it is not applicable in remote sites.

The obtained data from active air sampling do not reflect the chemistry of aerosols removed from the atmosphere by dry or wet deposition. Therefore, passive air sampling technology by alternative samplers has been introduced. The collection of atmospheric depositions is merely dependent on the ambient environment and allows chemical accumulation via natural diffusion, which gives more reliable information as to the influences of atmosphere inputs of heavy metals on the surface environment (Wong *et al.*, 2003). Nevertheless, passive air sampling process normally takes much longer time and might also be sensitive to sudden changes of meteorological conditions such as wind speed and temperatures.

Considering the merits as well as drawbacks of both sampling technologies, passive air sampling is suggested to be a method complementary to the collection of high-volume active samples for monitoring long-term trends of heavy metal variations, which can enable the cost-effective collection of monthly or seasonally integrated air samples deployed throughout a large geographic region (Gouin *et al.*, 2005).

2.2.2 Mosses

If aerosols are considered to be a direct approach to analyze heavy metals, then analyzing organisms as bio-accumulators could be regarded as an indirect monitoring method. Biomonitoring of heavy metals in the atmosphere by mosses is a well-developed technique since the 1960s (Ruhling *et al.*, 2004). It has been widely applied in many parts of the world for monitoring airborne heavy metal deposition, especially in countries all over the Europe (Reimann *et al.*, 1997; Harmens *et al*, 2004) and North America (Schilling & Lehman, 2002).

The increasing use of mosses as a biomonitor is based on the fact that mosses have no root system and can receive water and nutrients merely from precipitation or dry deposition; thus the uptake of mineral substrates from soils is quite insignificant (Ruhling *et al.*, 2004). In addition, they do not have epidermis and cuticle, so metal ions can easily penetrate the cell wall and be strongly concentrated in mosses (Szczepaniak and Biziuk, 2003). Many moss species are geographically widespread and can grow in different environmental conditions. As this technique is easy to handle (fewer analytical problems than lichens and tree barks) and less costly, it has been widely adopted for surveys of atmospheric heavy metal deposition in large areas or even nations (Harmens *et al.*, 2004; Ruhling *et al.*, 2004; Lee *et al.*, 2005).

The most preferred species of mosses for the use in Europe are the carpet-forming mosses *Pleurozium schreberi* and *Hylocomium splendens* due to their great sensitivity to heavy metal pollutions (Szczepaniak and Biziuk, 2003). Other most frequently sampled species include *Hypnum cupressiforme* and *Scleropodium purum*, which are more widespread in south areas of Europe (Lee *et al.*, 2005). However, the studies on atmospheric deposition of heavy metals conducted based on mosses are still quite scarce in Asian countries. Recently, Lee *et al.* (2005) attempted to use the moss *Hypnum plumaeforme*, which is mostly commonly found in dense mats in many Asian countries (*e.g.* China, Japan, Korea, Nepal and Philippines), to analyze heavy metal deposition. The results turned out to be quite promising, for this type of moss is able to capture heavy metals from the atmosphere efficiently and presents high bioaccumulation rates.

However, when a moss survey is conducted over vast areas, it is inevitable that a wide range of moss species are involved. Therefore, data obtained from one certain specie of moss should be only comparable to similar species belonging to the same class. On the other hand, natural variability in ambient climate conditions, such as acidity, temperature, humidity, light and altitude, or ambient elemental occurrences, may affect the bioaccumulation behavior of mosses. Furthermore, the proliferation of indigenous moss is normally not encouraged in urbanized or contaminated areas (Wong *et al.*, 2003). The major disadvantage of the passive biomonitoring method is the difficulty in source identification. Since all processes and sources occur simultaneously, there is no possibility to separate them and look for a particular one (Szczepaniak and Biziuk, 2003).

2.2.3 Long-term historical record

The naturally occurring deposits, such as lake sediments, glacial ice, snow, and ombrotrophic peat bogs, have been most extensively used as historical archives to monitor long-term atmospheric deposition of heavy metals. However, each of them has certain drawbacks. For example, peat bogs and sediment cores might be subject to remobilization of heavy metals due to physical and chemical changes. All of them are thus required to meet with certain requisite criteria in order to serve as potential geochemical archives. They should receive only atmospheric inputs of anthropogenic heavy metals and be subject to minimal post-depositional migration of deposited substances. In addition, they must be able to accumulate sufficiently measurable concentrations of elements of interest (Benoit *et al.*, 1998).

2.2.3.1 Peat bogs

Recently, there is an increasing interest in the use of ombrotrophic peat bogs as geochemical archive. Peat consists of organic deposited matter produced by vegetation. In ombrotrophic peat bogs, the only source of water and nutrients is from atmosphere by wet and dry deposition (Weiss *et al.*, 1999), because the surface layers of ombrotrophic peat bogs are isolated from the underlying mineral soil or local ground and surface waters (Ukonmaanaho *et al.*, 2004).

Although mosses are more widely used as bioindicators of atmospheric pollutions, they only indicate current situations. In contrast, the vertical distribution of elements in peat bogs could provide information on recent deposition of trace elements and preserve historical records for temporal trends of atmospheric fluxes. They can be precisely dated using ^{14}C (bomb-pulse and traditional) or ^{210}Pb dating technologies (Le Roux *et al.*, 2005). Therefore, ombrotrophic peat bogs, together with glacial ice cores, are considered as the only archives recording exclusively atmospheric deposition of heavy metals in the last few hundred years. Nevertheless, measurement of heavy metals in ice cores has been found to be difficult due to the low concentrations (Benoit *et al.*, 1998; Weiss *et al.*, 1999). In addition, peatlands are widely distributed all over the world, thus the approach using peat bogs is applicable at many conditions for their high availability (Le Roux *et al.*, 2005). For another reason, peat formation in the northern hemisphere began after the retreat of glacial ice, which makes it possible to record the entire Holocene (Weiss *et al.*, 1999). Therefore, this method has been proved to be an effective tool to reconstruct the historical records of atmospheric deposition of heavy metals.

However, the possible importance of post-depositional migration in peat bogs still remains uncertain for most of the metals of interest (Weiss *et al.*, 1999; Shotyk *et al.*, 2000). Peat bog waters are naturally acidic and organic-rich, and may vary between oxic and anoxic, depending on the depth of the water table which fluctuates seasonally (Shotyk *et al.*, 2000). Hence, metal elements may be transformed chemically and liberated from peat bogs. There are even arguments about the accuracy of this approach when comparisons were made between atmospheric deposition rates and accumulation rates by peat bogs, and discrepancies were found (Le Roux *et al.*, 2005). Therefore, it is necessary to understand peat diagenetic processes in order to verify that the investigated elements are permanently immobilized in the peat and do not migrate after decomposition (Benoit *et al.*, 1998; Weiss *et al.*, 1999; Ukonmaanaho *et al.*, 2004). Meanwhile, validated sample preparation methods and certified standards reference material are still required to ensure high analytical accuracy and good data quality.

2.2.3.2 Sediment cores

In the absence of historic deposition measurements, undisturbed dated sediment cores may also act as useful geochemical archives and provide information on the atmospheric loading of heavy metals through time. Sediments are regarded as one of the major endpoints or sinks of many anthropogenic trace elements (Blais and Kalff, 1993; Yang *et al.*, 2002; Ip *et al.*, 2004). However, deep sea sediments are not normally used to assess short-term variations of atmospheric deposition due to low accumulation rates. Coastal or estuary sediments accumulate elements much faster than deep sea sediments, thus they are widely sampled to establish regional historical trends. Nevertheless, the possible biological or geological perturbations may have significant influences on metal distributions (Weiss *et al.*, 1999).

Comparatively, sediments in the freshwater ecosystems (*e.g.* lake sediments) are more widely and commonly used to analyze long-term accumulation history of pollutants including heavy metals. This technology has been well developed in Europe (Brannvall *et al.*, 1999; Renberg *et al.*, 2002; Yang and Rose, 2005; Shotbolt *et al.*, 2006) and North America (Blais and Kalff, 1993; Jackson *et al.*, 2004) to investigate atmospheric inputs of heavy metals into lake ecosystems.

Lake sediments can accumulate heavy metals by diverse pathways, of both natural and anthropogenic origins, such as natural weathering of bedrocks, catchment inwash, atmospheric deposition (Renberg *et al.*, 2002). Thus, concentration profiles (vertical distribution) of heavy metals in sediment cores not only reflect atmospheric inputs of the pollutants, but also demonstrate historical environmental changes (*e.g.* past drainage basin or land-use histories). Metals of different origins are not readily separable in the sediments. Among various types of anthropogenic sources, atmospheric deposition is considered as the major contributor for most of the trace elements of interest in case of a remote lake without direct point sources (Jackson *et al.*, 2004; Han *et al.*, 2007). In order to assess the significance of atmospheric deposition, it is necessary to distinguish non-geogenic components from geogenic trace element background. A comparison between measured concentrations and baseline values could result in clear pictures of historical changes of atmospheric inputs. Alternatively, this can also be achieved by using elemental normalizer to evaluate the pollution magnitude. Normally, Ti, Zr, loss on ignition (LOI), Si, Al and Fe are selected as the normalizers. It is also a general practice to identify different sources of air pollutants. Pb in terms of specific isotopic fingerprints can be used as a possible pollution tracer element to assess origins of heavy metals (Yang and Rose, 2005).

In most cases, the studied freshwater is located in remote areas, which is only for recreation use and not exposed industrial point sources of pollutants. It is thus assumed to receive anthropogenic pollutants mainly from atmospheric dry or wet deposition (Yang *et al.*, 2002). The obtained sediment records thus provide information on the significance of long-range atmospheric transport of anthropogenic heavy metals to the aqueous ecosystem (Fitzgerald *et al.*, 1998).

Dating of sediment cores by radiometric techniques can be performed by measuring independent chronological markers, among which ^{210}Pb, ^{137}Cs and ^{14}C are most frequently used (Eby, 2004). Hence, historical trends of atmospheric deposition can be clearly demonstrated with the combination of accurate chronology along the sediment core and concentration profiles of anthropogenic heavy metals. ^{14}C has a long half-life of 5.7×10^3 years, thus not accurate for recent deposits. ^{228}Th has very short half-life (1.91 years), which makes it adequate enough for dating sediments accumulated over the last decade or so. Dating by ^{210}Pb is most widely used for recent deposits of age around 100 years with the half-life of 22.3 years (Livett, 1988). However, one major disadvantage of this technique is that ^{210}Pb may be subject to remobilization, possibly leading to misestimate of ombrogenic ^{210}Pb.

Since sediments are also the potential future pollutant sources to water body and aquatic biota, it is important to investigate geochemical phases of trace elements in sediments and evaluate their bioavailabilities. The analysis is vital to the fate of heavy metals in the aquatic ecosystem and the subsequent impacts on the environment. Tessier *et al.* (1979) suggested a standard approach ‘sequential extraction analysis’ to determine five different geochemical phases of heavy metals in the sediments, namely 1) exchangeable; 2) bound to carbonates or specially adsorbed ; 3) bound to iron and manganese oxides; 4) bound to organic matter or sulphide; 5) residual.

However, sediment records are sometimes complicated and confounded by additional influencing factors. With much contaminated catchment soil inwash, sediment pollution level might be enhanced. On the other hand, the pollution signal may be diluted when less or no contaminated soils are released into the lake (Yang and Rose, 2005). Moreover, possible postdepositional remobilization processes (*e.g.* resuspension and bioturbation) might occur as a result of significant changes in pH or other geochemical conditions (Weiss *et al.*, 1999; Jackson *et al.*, 2004). Therefore, great attention should be paid during the whole process, from the selection of sampling locations, the sampling of sediment cores, sample preparations, to the final analyzing processes.

In case suitable lakes are not available around the area in question, sediments in reservoirs could be a possible alternative. Similar to the lake sediments, reservoir sediments are also important sinks for both catchment and atmospheric derived pollutants and might as well act as environmental archives for temporal changes of these inputs. However, while the use of lake sediments for assessing historical variations has been well established, reservoirs are less commonly used and even considered unsuitable due to the lack of understanding of the sedimentation processes involved (Shotbolt *et al.*, 2005).

Since reservoir sediments have the potential to provide additional information to reconstruct historical atmospheric deposition records of pollutants, many investigations have been conducted to examine the practicability of reservoir sediments (Park and Curtis, 1997; Van Metre and Callender, 1997; Shotbolt *et al.*, 2005; Yeloff *et al.*, 2005; Shotbolt *et al.*, 2006). It was reported that the major problem associated with reservoir sedimentary records is the uncertainty of post-depositional sediment redistribution. In case of water-level drawdown, particularly coinciding with a storm event, significant sediment redistribution might be caused, and the area of undisturbed sediments within the reservoir might also be reduced. Although it is believed that deep-water sediments are less vulnerable to water-level fluctuations, the existence of undisturbed and continuously deposited sediment cores is also considered critical to reconstruct past pollution trends. In addition, sediment distribution patterns are not readily known with rather complex bathymetry (Shotbolt *et al.*, 2006).

Nevertheless, reservoirs have much higher sedimentation rates due to their riverine hydrodynamic nature and large catchment/reservoir area ratio. Therefore, they have the advantage to give high-resolution temporal records of historical pollution inputs and minimize possible diagenesis process within sediment cores

(Yeloff *et al.*, 2005). The reservoir sediments also have the potential to provide historical records of atmospheric inputs and are regarded as valuable sources for further exploitations. It is generally suggested that assessment of sediment distribution should be conducted prior to site selection and sediment core collection, so that sediment cores of minimal stratigraphic disturbance could be sampled.

In summary, each approach mentioned above has its merits and disadvantages. Aerosols and mosses are most commonly used to provide current information on atmospheric heavy metal pollution. The active air sampling is the most effective and direct approach to monitor the airborne heavy metals except its infeasibility in remote sites without pumps and power sources. Passive air sampling, as a complementary method to the collection of active samples, allows chemical deposition and accumulation merely via natural diffusion. However, it is time-consuming and sensitive to changes of meteorological conditions. As an effective biomonitor of airborne heavy metals, mosses have been widely used as many moss species are geographically widespread. This technique is also easy to handle and costs less, and is especially effective for surveys over large areas or even nations. The major disadvantages of this approach are inadequacy in comparison between different species and vulnerability to natural variability in ambient climate conditions. On the other hand, the naturally occurring peat bogs and aqueous sediments can be used as historical archives to monitor long-term atmospheric deposition of heavy metals. However, they can only be applied in case the anthropogenic heavy metals are dominantly derived from atmospheric deposition. Moreover, they must be subject to minimal post-depositional substances to preserve the record. Therefore, a multi-media approach, including sampling of both mosses and sediment cores, was adopted in the present study to monitor both the current situation and long-term variations of atmospheric heavy metal deposition in remote areas of the South China coastal region. Sediment cores were collected in remote reservoirs without direct point sources of anthropogenic pollutants and were regarded adequate to provide historical records of atmospheric heavy metal inputs. As for monitoring the current situation, sampling of mosses is considered more appropriate than aerosol samples in remote areas.

2.3 Approaches for Pollution Source Identification

2.3.1 Lead isotopic analysis

Lead isotopes have been widely used to identify sources of atmospheric pollution and proved to be particularly useful in a variety of different environmental samples, including sediments (Farmer *et al.*, 1996; Kober *et al.*, 1999; Renberg *et al.*, 2002; Ip *et al.*, 2004; Jackson *et al.*, 2004), aerosols (Mukai *et al.*, 1993; Zhu *et al.*, 2001; Wong *et al.*, 2003; Bellis *et al.*, 2005; Witt *et al.*, 2006; Lee *et al.*, 2007), mosses (Farmer *et al.*, 2002; Lee *et al.*, 2005) .

Lead has four naturally occurring long-lived isotopes, namely ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. However, only ^{204}Pb is the stable isotope of lead, while ^{206}Pb, ^{207}Pb, and ^{208}Pb are radiogenic progenies of ^{238}U, ^{235}U, and ^{232}Th respectively. Therefore, the abundance of the last three isotopes can slowly change over long period and ratios among the four isotopes are also varying gradually. Each lead containing ore has specific lead isotopic ratios, which are dependent on the age and initial geological compositions of its parent rock (*e.g.* amount of co-existing U and Th). Normally, older lead ores experience less radioactive decay before separation from the parent rocks, thus they tend to have low $^{206}Pb/^{207}Pb$ ratio; vise versa (Witt *et al.*, 2006). Likewise, other natural materials, such as coal, also have unique values of lead isotopic ratios. These isotopic ratios are not subject to changes afterwards in the environment or during industrial productions, as no more fractionation takes place by chemical or biological processes. Lead in the atmosphere can be derived from many different origins, such as dust from natural ores, lead additives in gasoline, coal combustion, as well as various types of industrial emissions (Siegel, 2002; Bradl, 2005). Hence, lead isotopic ratios of different origins can be combined in various ways to result in other lead isotopic ratios. With comparisons between measured ratios of samples and known ratios of possible surrounding sources, origins of the pollutants could be identified. Therefore, lead is regarded as a useful tracer of environmental pollution since its isotopic compositions are specific to different emission sources.

2.3.2 Statistical analyses

Metals can occur naturally in silt and clay bearing minerals of terrestrial and marine geological deposits (Schiff and Weisberg, 1999). The natural occurrence of metals in the environment can complicate the evaluation of heavy metal enrichments contributed by anthropogenic sources, as the background metal concentrations might vary widely due to different parent materials and deposit properties (*e.g.* particle size) (Schropp *et al.*, 1990; Liu *et al.*, 2003). Therefore, elevated concentrations of heavy metals in aquatic sediments may not necessarily reflect anthropogenic contaminations. In order to distinguish the natural components, geochemical normalization of trace metal concentrations to a reference element has been commonly adopted to account for the natural mineralogical and granulometric variations and assess the presence and magnitude of anthropogenic enrichments of heavy metals (Weisberg *et al.*, 2000). The reference element (normalizer) is normally a fundamental or conservative tracer of the natural metal-bound phases, which is expected to have a uniform flux from natural sources and not sensitive to inputs from anthropogenic inputs (Liu *et al.*, 2003). They should not be vulnerable to physicochemical processes, such as reduction/oxidation, adsorption/desorption, or other diagenetic processes. The most widely used normalizers mainly include Al, Fe, Li, Sc, Cs, rare earth elements, radioisotope tracers, total organic carbon and the grain size (Van Metre

& Callender, 1997; Schiff and Weisberg, 1999).

Al has high natural concentration and minimal anthropogenic contamination. It is a structural element of clays. As a central component of clay (fine particles), Al can serve as a measure of clay content of sediments, with which bulk of trace elements are associated. Since trace metals tent to be absorbed on the surfaces of particles, their concentrations naturally increase as particle sizes decrease. However, Al has a much lower recovery rates for this study due to the adopted digestion method.

Fe is a clay mineral indicator element as an alternative to Al. It is not a matrix element like Al, but is like trace elements in being associated with surfaces. Fe geochemistry is similar to that of many trace metals both in oxic and anoixic environments. The direct association with trace elements and the fact that its natural concentrations in sediments are more uniform than Al, make it a promising normalizer. However, Fe has a great reduction potential in anaerobic sediments and may lead to an underestimation of the magnitude in anthropogenic enrichment of trace metals. Coprecipitation with Fe/Mn oxides is an important mechanism influencing the accumulation, speciation and vertical distribution of heavy metals in sediments. Fe^{2+} and Mn^{2+} tend to diffuse upwards to the redox boundary and be oxidized to Fe^{3+} and Mn^{4+}, which are efficient scavengers of released heavy metals. The reduction/oxidation process effectively concentrates iron in surface sediments at or near the sediment-water interface, and is mostly associated with peaks of heavy metal concentrations.

TOC serves as a matrix on particle surfaces for complex formation. TOC itself, however, is subject to considerable augmentation by human activity and is often a contamination. It is usually difficult to assess the background concentration.

Li is a constituent of fine-grained material of sediments, such as primary micas and ferromagnesium minerals and secondary clay minerals, and Li concentrations closely assoicated with clay contents. Like Al, Li has a low recovery rate in the present study.

It is assumed that the concentrations of natural occurring trace metals generally vary in proportion to that of the normalizer. The relationships between trace metals and the normalizers thus can be plotted to identify the presence of possible contaminations. A possible best normalizer for a particular metal element is usually the highest geochemically sensible tracer, referring the strongest correlator (Yang and Rose, 2005). The Pearson correlation coefficients between the metals and potential reference elements are usually calculated to identify the proper normalizers. Baseline relationships between the metal of interest and its most appropriate normalizer can be derived by establishing a simple linear regression model based on several selected uncontaminated samples in the study area. A close correlation between the major elements and trace metals is normally expected for uncontaminated sediments. The 95% prediction intervals are then derived from the linear regression models for the purpose of comparing individual samples to the baseline relationships. The linear regression lines and 95% prediction limits are then superimposed on scatter plots of heavy metals and the respective normalizers. It is suggested that any samples above the upper 95% prediction limit are probably contaminated by heavy metals from anthropogenic sources, while data points within the prediction limits are originated from natural sources. Moreover, the correlation coefficients between trace elements may provide additional information on source identification. Two closely correlated elements are supposed to have the same origin.

The Principal Component Analysis (PCA) together with the Pearson correlations is another useful multivariate analytical tool that is frequently performed to identify the anthropogenic sources of enriched heavy metals (Singh *et al.*, 2005; Wu *et al.*, 2007). It evaluates the inter-correlations between the variables in the original data set and enables a data reduction into a few independent underlying factors that account for the majority of total variance and allow easier interpretation (DelValls *et al.*, 1998). The extracted principal components (PC) are those whose eigenvalue is higher than 1 (Loska and Wiechula, 2003). As heavy metal concentrations normally varies by different orders of magnitude, PCA can be applied to the correlation matrix and normalize each variable to unit variance (Han *et al.*, 2006). Varimax normalized rotation can be further conducted to maximize the variances of factor loadings and eliminate invalid components, which makes the results more easily interpretable (Loska and Wiechula, 2003). Each PC provides information on loadings of the metal elements (variables) indicating the relative contribution of each element. The dominance of metal elements in each component can be identified and origins of heavy metals can thus be implicated.

2.3.3 Air back-trajectory analysis

In order to identify the origins of specific pollutants, it is necessary to examine the exact paths of air mass transport. The air mass back trajectories have thus been frequently used to investigate the potential sources of contaminants (Siefert *et al.*, 1999; Bellis *et al.*, 2005; Witt *et al.*, 2006; Lee *et al.*, 2007). Since air mass trajectory models may include many possible source areas, it is normally used in combination with other source apportioning methods, such as isotopic signatures. The analysis is generally conducted with the aid of computer models. It was found that the type and concentration of air-borne pollutants at certain sampling locations vary in accordance with wind directions. In addition, air mass trajectory could change as a function of time, even the general wind pattern is known (Eby, 2004). Thus, many important components, such as meteorological data, should be considered and included in the computer model to give accurate calculations.

After obtaining plots of air mass back trajectories, it is possible to identify places that air mass has traveled across and thus locate possible sources of the air pollutants. However, the time range for back trajectory calculation should be carefully considered in order to get reliable results and solid interpretations.

2.4 Atmospheric Heavy Metal Pollution in South China & Worldwide

As mentioned in Section 2.1.3, the ever intensive human activities have brought abundant potentially hazardous heavy metals into the environment since the onset of industrialization worldwide, which might pose adverse impacts on the ecosystems. In the past several decades, numerous studies have been conducted to assess atmospheric heavy metal contamination and evaluate the significance of atmospheric depositions of heavy metals, particularly in European countries (Guieu *et al.*, 1997; Injuk *et al.*, 1998; Motelay-Massei *et al.*, 2005; Rossini *et al.*, 2005; Lavilla *et al.*, 2006) and North America (Golomb *et al.*, 1997; Sweet *et al.*, 1998; Riget *et al.*, 2000; Schilling and Lehman, 2002). Increasing evidence has revealed that the air quality in not only urban areas (Wong *et al.* 2003; Tasdemir *et al.*, 2006) but also remote areas (Lee *et al.*, 2005; Yang and Rose, 2005) has been deteriorated seriously. Atmospheric emissions and depositions of anthropogenic heavy metals have been regarded as significant contributors to the accumulation and enrichment of toxic trace metals in the surface environment, such as lake sediments (Dauvalter *et al.*, 1994; Kober *et al.*, 1999) and surface soils (Steinnes *et al.*, 1993; Lee *et al.*, 2006).

Many attempts have been made to determine the annual atmospheric fluxes by assessing passive bulk deposition samples. In Table 2.6, the significance of atmospheric heavy metal inputs in several study areas are listed and compared.

As the data indicate, the atmospheric deposition fluxes of heavy metals in urban or industrial areas are generally greater than the amounts in rural or relatively remote areas. By comparison among different regions, it can also be noticed that the atmospheric deposition fluxes of anthropogenic heavy metal in the South China coastal region have been significantly enhanced, which are comparable or even stronger than some industrial areas in Europe and North America, especially for Cr, Ni and Pb. The South China coastal region, particularly the Pearl River Delta region, is one of the most rapidly economically developing and densely populated areas in China. The economic reform since the late 1970s has brought about enormous economic bloom with intensive industrialization and urbanization. The potential environmental burdens imposed by the drastic development in the past three decades are causing increasing concerns. Recent studies regarding the air pollution in South China revealed that not only the atmosphere in this region has been seriously deteriorated, but also the surface environment (*e.g.* urban soils, surface waters) has been inevitably impaired as a consequence of atmospheric deposition (Wong *et al*, 2003; Wang *et al.*, 2005; Hagler *et al.*, 2006; Choi *et al.*, 2008; Fang *et al.*, 2008). The contamination by anthropogenic Cu, Pb and Zn in the PRD region needs particular attention (Fang *et al.*, 1999; Fang *et al.*, 2000; Zhu *et al.*, 2001; Lee *et al.*, 2007; Zhang *et al.*, 2007).

The atmospheric heavy metal pollution has also been widely investigated by analysis of terrestrial mosses to assess the current atmospheric fluxes of heavy metals. The most commonly used moss species include *Hylocomium splendens* and *Pleurozium schreberi* in European countries (Zechmeister, 1995; Berg and Steinnes, 1997; Harmens *et al.*, 2004), *Thuidium delicatulum* in southeastern US (Schilling and Lehman, 2002), and *Hypnum plumaeform* in Asian countries (Lee *et al.*, 2005). This technology has been well developed especially in western countries, where moss surveys over several decades were conducted to assess the temporal deposition trends and to identify the potential sources (Kubin and Lippo, 1996; Rosman *et al.*, 1998; Harmens *et al*, 2004; Ruhling and Tyler, 2004; Shotbolt *et al.*, 2007). The findings revealed that the highest concentrations of heavy metals in mosses by atmospheric depositions occurred in the 19th century (Shotbolt *et al.*, 2007) and there was a continuous decrease of metal concentrations since the end of 1970s due to the reduction of industrial emissions (Ruhling and Tyler, 2004). The decline of atmospheric lead levels was particularly evident since the ban of leaded petrol in the 1960s (Berg and Steinnes, 1997; Farmer *et al.*, 2002). The long-range trans-boundary transport of air pollutants from industrial sites might account for the elevated airborne heavy metal concentrations in remote areas. The studies conducted in China are quite limited. Past investigations were mostly confined to using the moss technology to monitor the dry deposition fluxes of heavy metals near some emission sources (Xiao *et al.*, 1998; Tan *et al.*, 2000; Bi *et al.*, 2006) or in relatively remote areas (Lee *et al.*, 2005), and to identify potential sources. Limited studies focus on examining the temporal variations of airborne heavy metal concentrations. One recent study by Cao *et al.* (2008) reported that the levels of heavy metals in the atmosphere in Shanghai were distinctly elevated from 1965 to 2005, especially after the 1980s.

It has been widely recognized that aquatic sediment cores collected from lakes or reservoirs could preserve a historical record of heavy metal concentrations with accurate chronological dating (Renberg *et al.*, 2002; Yang and Rose, 2005; Shotbolt *et al.*, 2006). In case of a freshwater system without direct point sources, the obtained sediment records are considered suitable to provide information on the atmospheric transport and deposition of heavy metals to the aqueous ecosystem at regional scales (Fitzgerald *et al.*, 1998). Regarding this, sediment profiles of heavy metal concentrations have been widely investigated to monitor the long-term atmospheric inputs of heavy metals in both urban and remote areas in Europe (Foster *et al.*, 1991; Fitzgerald *et al.*, 1998; Brannvall *et al.*, 1999; Renberg *et al.*, 2001; Yang *et al.*, 2002; Shotbolt *et al.*, 2006) and North America (Chillrud *et al.*, 1999; Belzile *et al.*, 2004; Jackson *et al.*, 2004). The sediment records clearly showed that the atmospheric emissions and deposition fluxes of anthropogenic heavy metals have been markedly increased since the onset of the industrialization period. However, some studies revealed that the Pb concentrations appeared to have a decreasing trend in recent sediments due to reduced Pb emissions from vehicle exhausts, though they were still much higher than the background values (Renberg *et al.*, 2002). Nevertheless, the recovery signal of anthropogenic Pb concentrations in sediments was not recorded at some other sampling sites (Kober *et al.*, 1999; Shotbolt *et al.*, 2006; Yang *et al.*, 2007). This might be attributed to the fact that anthropogenically derived Pb initially deposited onto drainage basin soils keeps entering the freshwater system via erosion and leaching processes. The catchment soils began to act as a contributing source of heavy metals instead of a major depository sink. While the temporal trends of atmospheric heavy metal depositions have been well established in western countries, the investigations on monitoring of atmospheric heavy metal pollution by aquatic sediments in China are still quite scarce (Han *et al.*, 2007). The sediment profiles of metal concentrations have been mostly used to assess potential contamination of sediments with direct discharges of municipal and industrial wastewater (Huh and Chen, 1998; Liu *et al.*, 2003; Feng *et al.*, 2004; Ip *et al.*, 2004). Several recent studies suggested that the sediment levels of heavy metal concentrations in coastal and estuarial sediments are comparable or even higher than the values reported in urban areas of the western countries. Although the enrichment of heavy metals is dominantly ascribed to wastes discharged from point sources, the increasing atmospheric input of anthropogenic pollutants is also considered as a potential source. Regarding the ever-increasing emissions of air pollutants in China, there is an urgent need to quantify the deposition fluxes of airborne heavy metals and establish long-term records of heavy metal concentrations in aquatic sediments from lakes or reservoirs without direct point sources.

Table 2.6 Bulk atmospheric deposition fluxes (mg/m^2/yr) for heavy metals obtained from various studies worldwide

	Location	**Period**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Remarks**
Europe	Le Havre, France [a]	2001 – 2002	0.36	--	9.4	4.1	18.4	1172	Industrialized area
	NDG, France [a]	2001	0.23	--	5.2	2.0	4.8	59	Urban area
	Rouen, France [a]	2001 – 2002	0.19	--	2.8	0.44	3.0	27	Urban city center
	Evreux, France [a]	2001 – 2002	0.20	--	7.5	0.34	1.7	38	Semi-rural area
	Paris, France [a]	2001 – 2002	0.24	--	6.0	0.62	4.2	30	Very urbanized and industrialized area
	Ligurian Sea [b]	1997 – 1998	0.06	0.62	1.28	1.10	1.20	41.2	Coastal area
	North Sea [c]	1993 – 1994	--	2.43	1.30	1.21	3.69	6.50	Coastal area
	Irish Sea [d]	1993 – 1994	--	--	2.60	--	1.62	--	Coastal area
	Mediterranean Coast [e]	1988 – 1993	0.31 – 1.3	2.5	2.7	0.9	3.2	2.0	Coastal area
	Lagoon of Venice [f]	1998 - 1999	0.15	--	4.3	1.9	3.6	29	Coastal area
North America	Lake Superior [g]	1993 – 1994	0.46	0.22	3.1	--	1.5	8.8	Away from sources
	Lake Michigan [g]	1993 – 1994	0.45	0.20	1.9	--	1.6	6.0	Away from sources
	Lake Erie [g]	1993 – 1994	0.49	1.10	4.2	--	1.8	17.0	Near industrial and urban emissions
	Massachusetts Bay [h]	1992 - 1993	0.45	2.7	3.5	7.2	2.7	7.8	No point sources
Asia	Pearl River Delta [i]	2001 – 2002	0.07	6.43	18.6	8.35	12.7	104	Urban/suburban/rural without point sources
	Xinghua Bay [j]	2004 – 2005	0.08	11.63	2.72	7.81	3.83	14.39	Coastal area
	Quanzhou Bay [k]	2004 – 2005	0.08	5.62	2.79	6.28	3.5	11.47	Coastal area

a. Motelay-Massei *et al.*, 2005; b. Sandroni and Migon (2002); c. Injuk *et al.*, 1998; d. Williams *et al.*, 1998; e. Guieu *et al.*, 1997; f. Rossini *et al.*, 2005; g. Sweet *et al.*, 1998; h. Golomb *et al.*, 1997; i. Wong *et al.*, 2003; j. Wu *et al.*, 2006(a); k. Wu *et al.*, 2006(b).

CHAPTER 3 – STUDY AREA & METHODOLOGY

In this chapter, detailed descriptions of the project study area are presented, including geographical locations, geochemical characteristics, and historical economic and industrial developments. In addition, the sampling procedures and analytical methods adopted during the study are also illustrated.

3.1 Study Area & Geochemical Characteristics

The present study was conducted in three major southeastern provinces along the South China coastline, including Fujian, Guangdong, and Hainan (Fig. 3.1). The South China coastal region is one of the most rapidly developing and densely populated areas in East Asia. Enormous economic development has taken place since the economic reform in the late 1970s. However, most of the economic achievements have been made at the cost of environmental degradation in the past several decades.

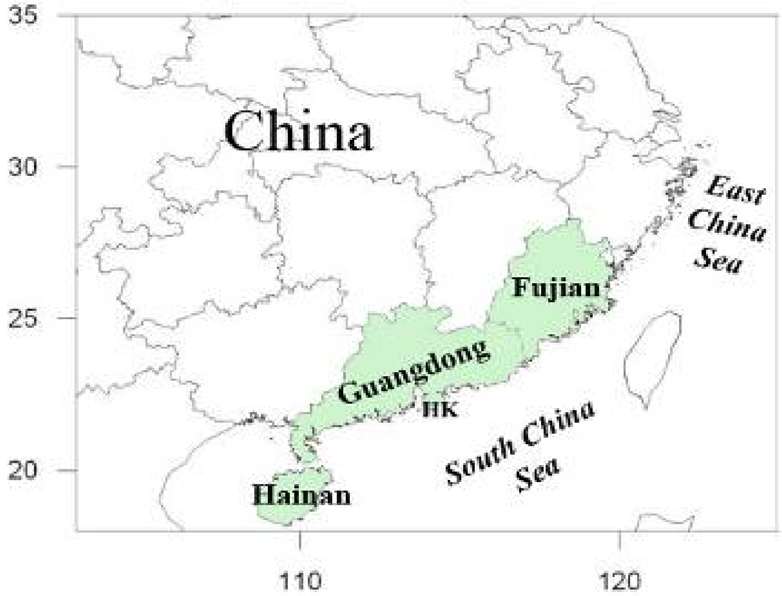


Figure 3.1 Map of the study area (colored in green)

3.1.1 Fujian Province

Fujian Province is located on the southeast coast of China (23°31'～28°18'N; 115°50'～120°43'E), lying along the East China Sea to the east, South China Sea to the south, and Taiwan Strait to the southeast. It has a total land area of 121,400 km^2 and supports a population of 35.81 millions (Fujian Gov., 2008). Over 80% of Fujian's land area is mountainous with two major mountain belts striding over the province longitudinally in the west and the center area. Plain areas are generally located at coastal regions, mainly Fuzhou Plain, Putian Plain, Quanzhou Plain, and Zhangzhou Plain, which are the most economically developed and urbanized areas in Fujian Province. Fujian has the most complicated and the second longest coastline in China, facilitating the formation of many deep bays as natural harbors. Although it is situated at a typical sub-tropic zone and is sensitive to the impact of East Asia monsoon activities, Fujian has a relatively mild and humid climate with abundant rainfalls. The Mountain Wuyi lying across the northwest part of Fujian prevents the intrusion of dry and cold winter monsoons from North China, while sufficient moisture is brought inland from the ocean in summer. According to Fujian Statistical Yearbook 2008, the annual average temperatures and precipitations are 15.8-22.6 ºC and 932.7-2265.2 mm respectively (Fujian Gov., 2008).

Situated at the jointing boundary of the Eurasia Plate and Pacific Ocean Plate, Fujian is characterized by complicated geological formations and dominated by igneous rocks. Granite is the most widely spread rock type in the province, accounting for nearly 1/3 of the total land area, particularly at coastal hills and mesas. The coastal estuary plains and harbor areas are characterized by sedimentary rocks, while the northwest region is mainly composed of metamorphic rocks and igneous rocks. Due to historical intrusions of abundant granites, elements such as U, Th, La, Y, Zr, W, Sn, Mo, Ag, Pb and Zn are greatly enriched in the lithosphere while Fe is relatively lacked (Fujian Bureau of Geology, 2008). As Fujian has plentiful rainfalls with a humid sub-tropic climate, some elements like Sr and Cu are drained away significantly. Table 3.1 summarizes the background elemental concentrations in aqueous sediments in Fujian compared to the national average background levels.

Table 3.1 Background elemental concentrations in Fujian aqueous sediments compared to national background levels (unit: μg/g, otherwise indicated) (Fujian Bureau of Geology, 2008)

Elements	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Mn**	**Ni**
Fujian Mean	3.47	0.15	7.63	22.44	9.78	602	8.48
National Background	9.08	0.15	12.32	58.45	21.56	678	24.41

Elements	**Pb**	**Zn**	**Al_2O_3 (%)**	**Fe_2O_3 (%)**	**CaO (%)**	**MgO (%)**
Fujian Mean	42.65	78.8	14.42	3.48	0.25	0.45
National Background	25.96	68.47	12.97	4.44	1.76	1.31

Fujian’s economy was mainly dependent on farming, forestry, animal husbandry and fishery until the adoption of the economic reform in the 1970s. As Fig. 3.2 indicates, industries have been developing enormously since the mid 1970s, and gradually replaced the dominance of agriculture. According to Fujian Statistical Yearbook 2008, the percentage of industries in the entire economic output is increasing continuously every year and reaches 89.5% in 2007. Nowadays, electronic industry, petrochemical industry and mechanical industry have become the three leading industries in Fujian. With large-scale industrial productions, however, excessive amount of pollutants have been released into the atmosphere. It was reported (Fujian Environment Protection Bereau, 2008) that the annual discharges of soots, and industrial powders/dusts in 2006 amounted to 129,500 tons and 173,000 tons respectively, which exerted potential adverse impacts on the ecosystems. Fig. 3.3 presents the air quality conditions in some major cities of Fujian in 2006 reported by the Fujian Environment Protection

Bereau. As the figure shows, the air pollution problem is particularly serious in Sanming and Longyan where metallurgical and mining industrial activities are intensive. Since air pollutants might travel over vast areas and finally deposit far away from the emission sources, it is thus important to investigate the potential atmospheric outflows and inputs of anthropogenic pollutants to the surrounding areas.

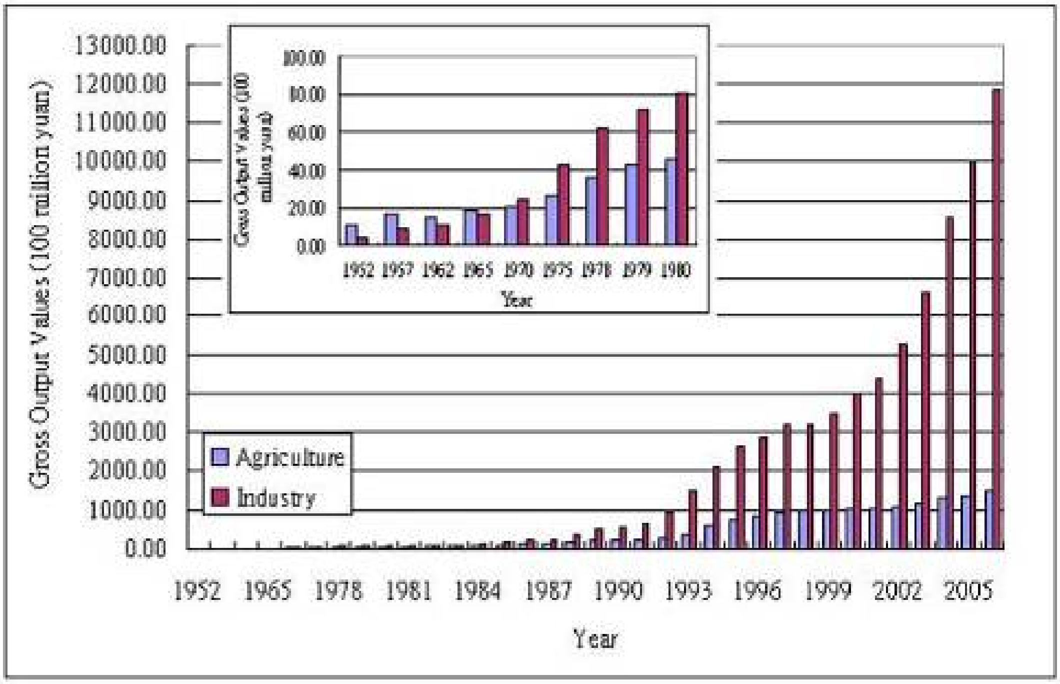


Figure 3.2 Gross output values of agriculture and industry from 1952 to 2006 (Fujian Bureau of Statistics, 2008)

Figure 3.3 Air quality in several major cities of Fujian Province in 2006 (Gazette 2006 of Fujian Environment Protection Bureau, 2008). Grade I represents the best air quality, while Grade III represents the worst (National Ambient Air Quality Standard).

3.1.2 Guangdong Province

Bordering Fujian on the northeast, Guangdong Province (20°13’～25°31’N; 109°39’～117°19’E) is situated at low-lying areas along the South China coastline towards the South China Sea. It has a total land area of 179,800 km^2 and owns the longest coastline in China. The Tropic of Cancer runs through the province, which results in a subtropical climate in the north part while a tropic climate in the south part. Generally, it is warm and humid all year round with annual average temperatures and precipitations of 19-24 ℃ and 1300-2500 mm respectively (Guangdong Gov. 2008). Mountains in Guangdong are mostly located in the northwest region, most of which run in a northeast-to-southwest direction. Similar to Fujian, granite is the most common rock type in Guangdong as well, followed by sandstones and metamorphic rocks. Moreover, certain amount of limestone is scattered in the northwest area.

Guangdong is one of the most densely populated provinces in China and supports a population of almost 94.5 millions (Guangdong Gov., 2008), especially concentrated in the Pearl River Delta Region. In 2006, the town population in nine major cities (*i.e.* Guangzhou, Shenzhen, Zhuhai, Foshan, Jiangmen, Dongguan, Zhongshan, Huizhou, and Zhaoqing) in the PRD region amounted to 62.84% of the total town population in Guangdong Province. The Pearl River Delta is the second largest delta in China, where three inland rivers East River, Pearl River and West River converge and discharge into the South China Sea. Bordering on the east side of the Pearl River Estuary, Hong Kong is a well known international metropolis which is highly developed and urbanized. With a total land area of 1,104 km^2, Hong Kong supports a population of almost 6.92 millions (HKSAR Gov., 2008). In the past several decades, a large fraction of Hong Kong's heavy industries have been relocated to Guangdong Province, which has stimulated its economic bloom. Figure 3.4 depicts the industrial development in Guangdong since the economic reform in 1978 (Guangdong Bureau of Statistics, 2008). The gross output values of industries have been rising exponentially ever since. Nowadays, the PRD region has developed as one of the leading economic centers in China, with massive manufacturing capacities. Electronic industry, mechanical industry, petrochemical industry, and automobile manufacturing industry are growing into the main heavy industry sectors in the delta region.

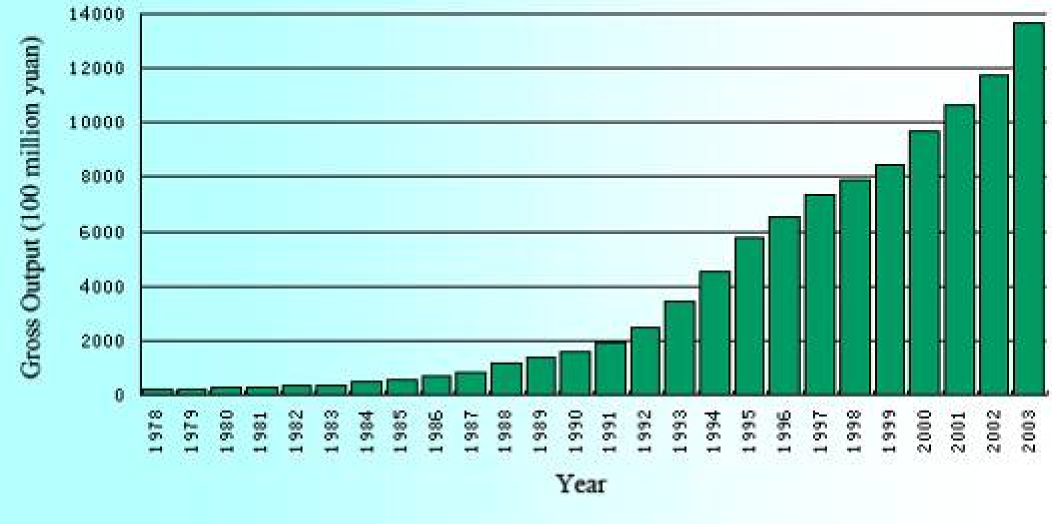


Figure 3.4 Gross output values of Guangdong industrial productions since 1978 (Guangdong Bureau of Statistics, 2008).

However, pollution problems become increasingly serious with extensive and intensive industrial activities, especially in recent years (see Fig. 3.5). The air quality, particularly over the PRD region, has been severely deteriorated. Traffic exhausts, intensive industrial activities and emissions from power plants have been regarded as the major anthropogenic sources of air pollutants in the PRD region (HK EPD, 2008). According to the record of Regional Air Quality Indexes (RAQI) released by Guangdong and HK Governments during Jan-Jun 2007, nearly 30% of the data exceeded Grade II of National Ambient Air Quality Standard (Fig. 3.6). In addition, Guangdong is located in the East Asian monsoon zone and is vulnerable to the impacts of monsoon activities, which might influence the transport of air pollutants and lead to variations in spatial and temporal distributions. Numerous evidences revealed that the adverse impacts of air pollution concern the entire PRD region rather than merely the local area. Moving and re-allocating heavy industries to remote areas thus can never be a long-term solution. Maximum concentrations of air pollutants usually occur in winter, while abundant precipitations brought from the ocean in summer normally result in much better air quality and the higher mixing layer height also facilitates the dispersion of air pollutants.

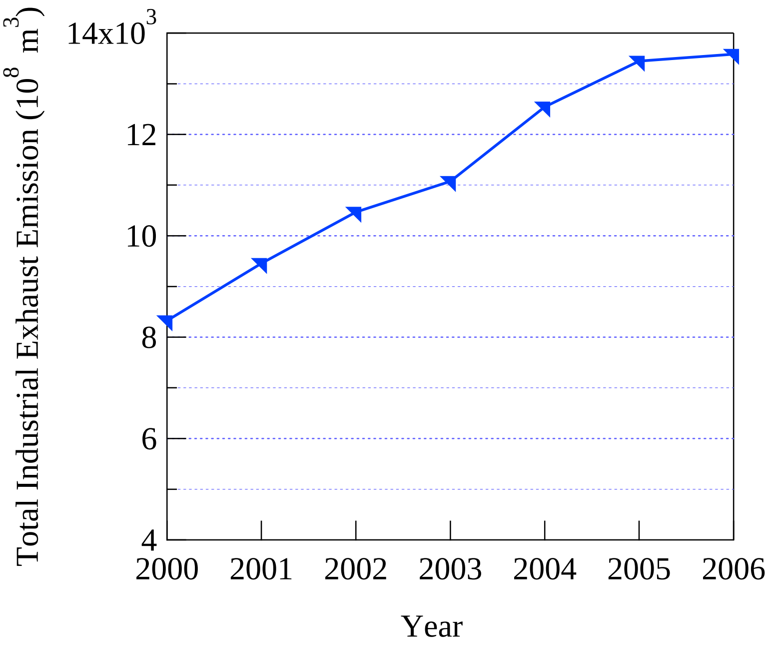


Figure 3.5 Increasing amount of total industrial exhaust emission into the atmosphere during 2000-2006 in Guangdong Province (Guangdong EPD, 2008)

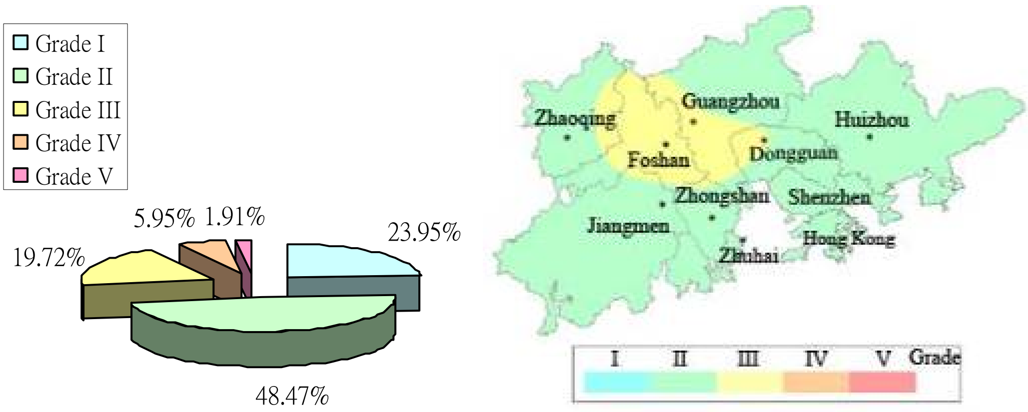


Figure 3.6 Statistics of Regional Air Quality Indexes recorded during January – June, 2007. (a) Percentages of each air quality grade; (b) Spatial distribution of mean air quality indexes. (Guangdong EPD, 2008)

3.1.3 Hainan Province

Being at the southmost end of China, Hainan Province is located off the southern coastline of China, separated from the Leizhou Peninsula (Guangdong Province) by Qiongzhou Strait. The total land area of Hainan Province is 35,400 km^2, dominated by Hainan Island of 33,900 km^2. Hainan Island (18°10’～20°10’N; 108°37’～111°03’E) is located at the north margin of the tropical zone, characterized by a moist monsoonal climate. The annual average temperature ranges from 22 ºC to 26 ºC. The island is usually in the path of typhoons, which bring about numerous precipitations from the South China Sea. The annual average precipitations are around 1111-2150 mm, particularly concentrated during May-October (Hainan Gov., 2008). Topographically, Hainan Island is elevated in the central region and gradually leveled off peripherally. Most of the rivers are originated from mountains in the central area and flow radially in different directions. Igneous rocks are widely spread in Hainan Island due to intensive geotectonic and diastrophic activities, accounting for over 50% of the total land area. Ferrallitic soils or ferruginous soils are the dominant soil types on the island under the humid and hot environmental condition (Zhao *et al.*, 2005).

Compared to the previous two provinces, Hainan is much less densely populated. Till the end of 2004, the population in Hainan Province is about 8.18 millions (Hainan Gov., 2008). Historically, agriculture had played the major role in the economic development of the island in early years. It still kept the dominance (over 50%) in the whole economic gross output even in the early 1990s. Recently, enormous economic development, especially industries and tourism, has occurred resulting in great economic structure reform. According to the government yearbook (Hainan Gov., 2008), the ratios between three main productions were 36:26:38 in 2005. Petrochemical industry, automobile industry, medicines and drugs, as well as paper production industry have gradually become the pillar industries. For many years, Hainan Province is among the provinces with best air quality in China. The air quality in most cities of Hainan meets Grade I of National Air Quality Standard. As the government reported (Hainan Gov., 2008), SO_2, NO_2 and suspended particulates only accounted for 9%, 27%, 21% of the national average levels in 2002. However, there appears an increasing trend for the concentration of suspended particulates, especially in the western areas, such as Haikou, Sanya, Danzhou and Qionghai (Hainan Gov., 2008). Moreover, the lead-free petroleum was still not widely introduced till the end of the twenties century. Considering the ever-increasing industrial productions, the air pollution problem cannot be neglected any longer, and the daily air quality should be monitored for effective environmental management.

All the three provinces are situated in typical monsoon zone and sensitive to monsoon fluctuations, which might facilitate the long-range transport of air pollutants from inland area of the continental Asia. Han *et al.* (2007) found a strong association between variations of heavy metal concentrations and climate changes in accordance with East Asia monsoons. Hsu *et al.* (2005) and Lee *et al.* (2007) recently provided evidence on possible long-range transport of air pollutants from northern China by monsoon activities. Therefore, the South China coastal region might be subject to air pollutants released from both local and regional sources via the long-range transport.

3.2 Sampling Locations & Sample Collection

The sampling work was conducted during September – November of 2006, including sampling of reservoir sediment cores, catchment surface soils, and mosses. The sampling locations were selected at four drinking water reservoirs in the remote areas of the South China coastal region, namely Xiamen Tingxi Reservoir in Fujian Province, Heyuan Xinfengjiang Reservoir and Maoming

Luokeng Reservoir in Guangdong Province, and Danzhou Songtao Reservoir in Hainan Province (see Fig. 3.7).

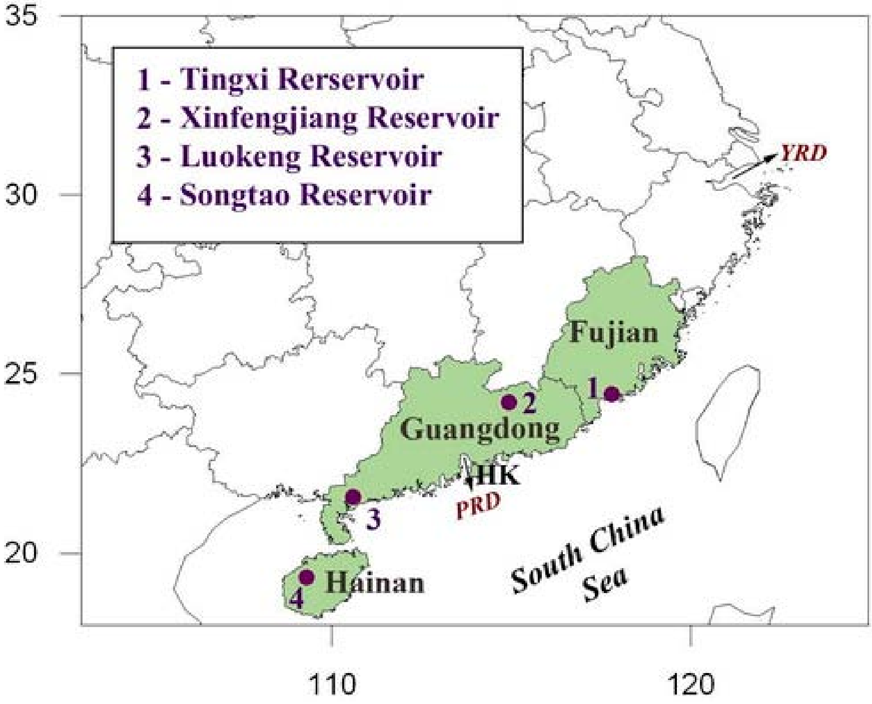


Figure 3.7 Map of sampling sites along the South China coastline

3.2.1 Descriptions of reservoirs

These selected reservoirs were all constructed between the 1950s – 1960s. Sediments are thus supposed to have a historical accumulation of around 50 years. All the sampling sites are far away from intensive industrial areas, avoiding direct inputs of anthropogenic pollutants. It is therefore reasonable to assume the major contribution of trace metal concentrations in the sediments is from the atmospheric deposition. In addition, the reservoirs are generally free from significant human activities, facilitating the formation of laminated sediments under natural conditions without much disturbance.

3.2.1.1 Tingxi Reservoir

Tingxi Reservoir (Fig. 3.8) is located in Tong'an of Xiamen, Fujian Province, about 7 km away from the urban area. It is an important source of fresh water and serves as one of the four major drinking-water supplies in Xiamen. Tingxi Reservoir was constructed in 1956 and expanded in 1966 to increase its capacity. At present, the total water storage volume amounts to 48.45 million m^3 with effective reservoir volume of 37.63 million m^3 (Yu *et al.*, 2006). The catchment area is about 100.8 km^2. The main function of Tingxi Reservoir is to provide water for irrigation in the districts of Tong'an and Xiang'an. It also plays an essential role in floods prevention, drinking water supply, electricity generation, as well as aquatics breeding (Lv, 2007). Topographically, Tingxi Reservoir is elevated in the north region and gradually descended southwards. Most of the inhabitants living in the upper reach are involved in agricultural activities. Due to the increasing scale of agriculture productions and livestock raising activities, the water quality of the reservoir has been greatly deteriorated in recent years. In addition, soil erosion problem becomes increasing serious caused by excessive felling of trees in the upriver and decreasing forest cover in the surrounding area (Lv, 2007).

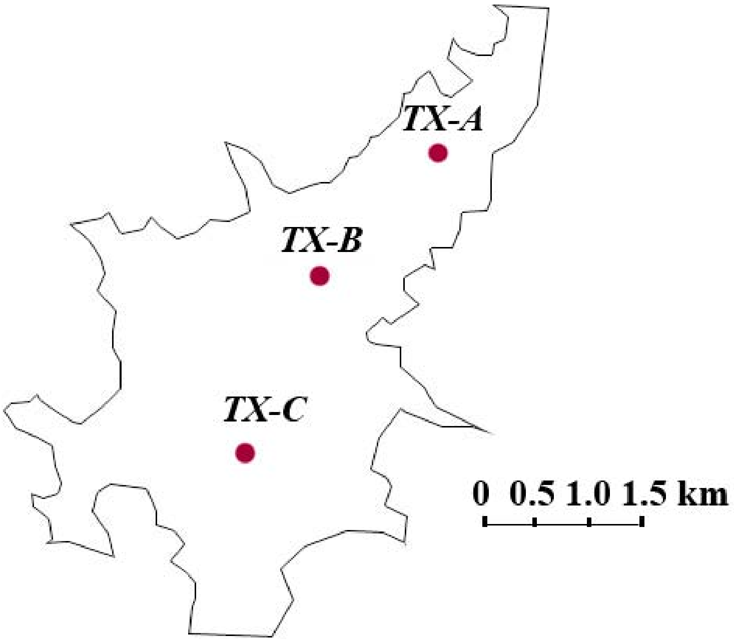


Figure 3.8 Sampling locations of sediment cores at Tingxi Reservoir

3.2.1.2 Xinfengjiang Reservoir

Xinfengjiang Reservoir (see Fig. 3.9) is the largest reservoir in South China with water area of 370 km^2 and storage volume of 13.9 billion m^3 (Ye, 2000). It is located in a remote mountainous area of Guangdong Province, at a distance of around 150 km away from the capital city Guangzhou. The reservoir was constructed during 1958-1962 by damming up Xinfengjiang River downstream at Yaposhan Valley. The total catchment area amounts to 5,734 km^2 with the forest cover around 1,100 km^2 (Chen, 1999). The dam of the reservoir is 124 m in height and 440 m in length. In normal conditions, the characteristic water level (*i.e.* altitude) of the reservoir is around 116 m (Guangdong Bureau of Hydrology, 2008). As a multifunctional reservoir, Xinfengjiang Reservoir has played significant roles in electricity generation (annual yield up to 0.9 billion kw·h), irrigation, shipping, flood prevention, and water supply. It is one of the major tributaries of East River, bearing a huge responsibility of providing high-quality water for people living in the PRD region.

The East River basin was originally dominated by agricultural production, and the natural environment and ecosystems were well conserved. During the late 1970s and mid 1980s, however, rapid industrialization and urbanization occurred firstly in the downstream PRD region and then gradually expanded to the whole East River region. The economy has boosted at the cost of ecological degradation and environmental pollution, potentially endangering the water and air quality at Xinfengjiang Reservoir (Chen, 1999; Ye, 2000; Che, 2004). In 1988, a large cement factory was established beside the reservoir, which produced numerous industrial dusts and powders and inevitably resulted in serious air and water pollutions. Being aware of the seriousness of ecocrisis, Guangdong government took immediate measures and shut down the cement factory in 1996. Nowadays, certain mining activities in the upriver region are still in operation (Ye, 2000). Around 232 ships or boats run across the reservoir every day for tourism or shipping activities. The discharges of untreated domestic sewages by around 40 thousand residents from the surrounding towns (*e.g.* Xichang, Huilong, Jiantou and Banjiang) are not properly managed. The intensively urbanized PRD region is located just within 200 km from the reservoir, and the air pollutants (*e.g.* heavy metals) released and transported from the PRD region might have adverse impacts on the ecosystems at the reservoir.

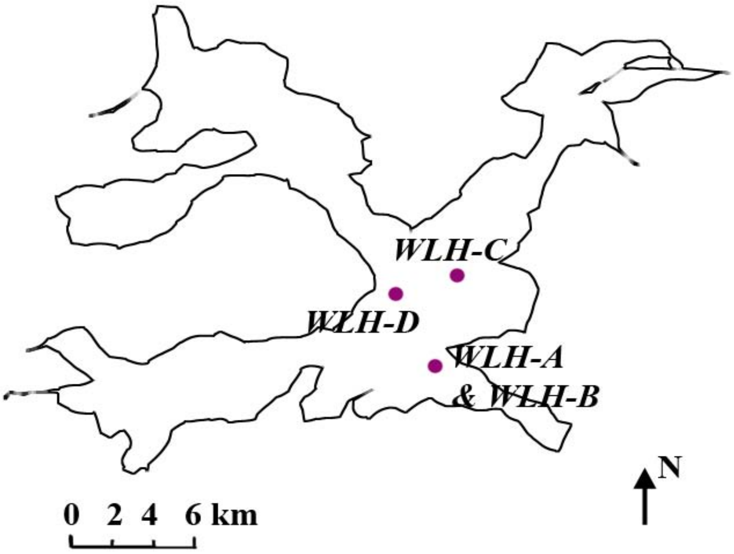


Figure 3.9 Sampling locations of sediment cores at Xinfengjiang Reservoir

3.2.1.3 Luokeng Reservoir

Luokeng Reservoir, constructed in 1960, is one of the three major reservoirs in western Guangdong Province (see Fig. 3.10). It is originated from Ehuangzhang Mountain in the northeast part of Maoming City, and has a total reservoir storage capacity of 114.7 million m^3 and catchment area of 77 km^2. The normal water level is about 114 m. Luokeng Reservoir is situated in the remote area, at a distance of around 60 km from the downtown region. As it is far away from the industrial zone and surrounded by large mountain ranges, a good air quality is likely to be preserved over the reservoir area.

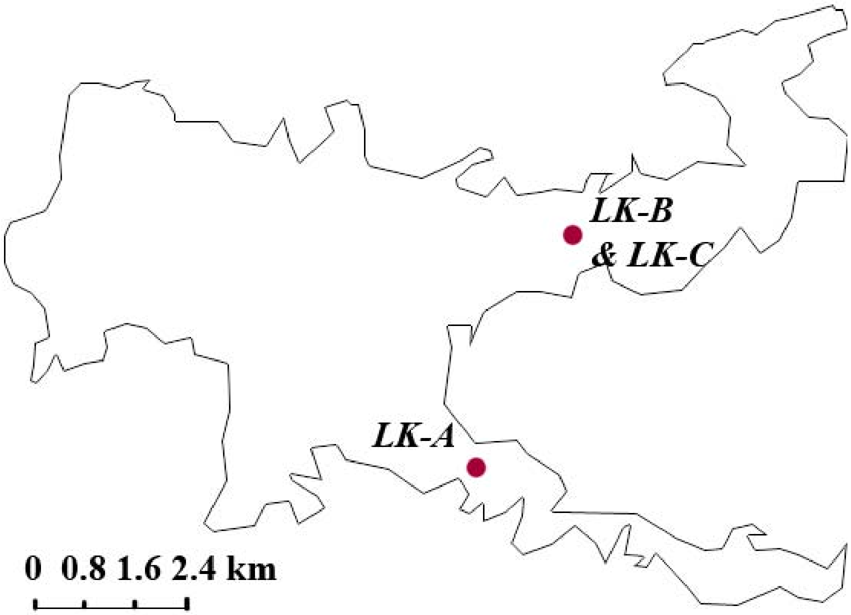


Figure 3.10 Sampling locations of sediment cores at Luokeng Reservoir

3.2.1.4 Songtao Reservoir

As one of the ten largest reservoirs in China, Songtao Reservoir (see Fig. 3.11) is located in Danzhou, Hainan Province, about 20 km southeast of Danzhou urban area. Construction of the reservoir initiated in 1958 and lasted over 10 years till 1969, with a dam built at Qinzukou Valley, the upper reach of Nandujiang River (Zeng, 2000). The river flows northward into the reservoir, and then turns eastward (Deng *et al.*, 2007). Songtao Reservoir has a total reservoir area of 130.5 km^2, and water storage capacity of 3,345 million m^3. The drainage area of the reservoir amounts to 1,496 km^2. As a multifunctional reservoir, it is dominantly used for irrigation and also functions for water supply, electricity generation, flood prevention, aquatic breeding and shipping (Yang *et al.*, 2007). It is responsible for irrigation of agricultural lands up to 136,700 hm^2, and water supply for over two millions inhabitants in Baisha, Danzhou, Lingao, Chengmai, Haikou (Yue *et al.*, 2005). The reservoir drainage region is relatively backward in economy and most of the residents are involved in agricultural activities. With rapid economic development and improvement of people's living conditions in recent years, however, the water and air quality at Songtao Reservoir are gradually endangered by the pollutions from industrial, domestic, agricultural sources, and shipping activities (Yue *et al.*, 2005). Although the overall water quality still reaches Grade II of National Surface Water Quality Standard, some water regions can only meet Grace IV or even Grade V. Most of the existing studies focused on merely the water quality of Songtao Reservoir, while the investigations on air quality over the reservoir area are rather scarce. The results from this present study can thus be used to examine the air quality at the reservoir, as well as the surrounding areas.

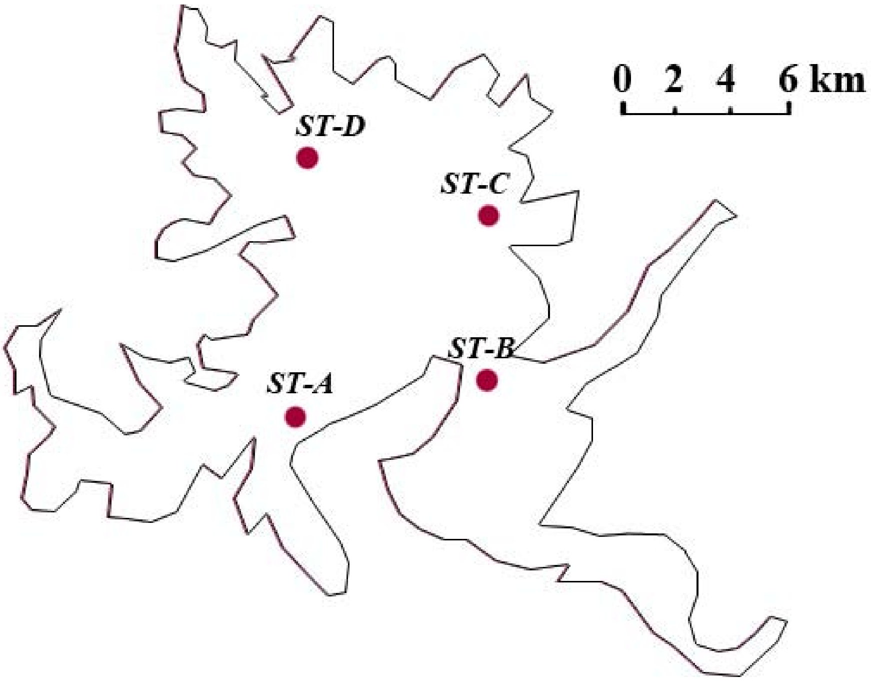
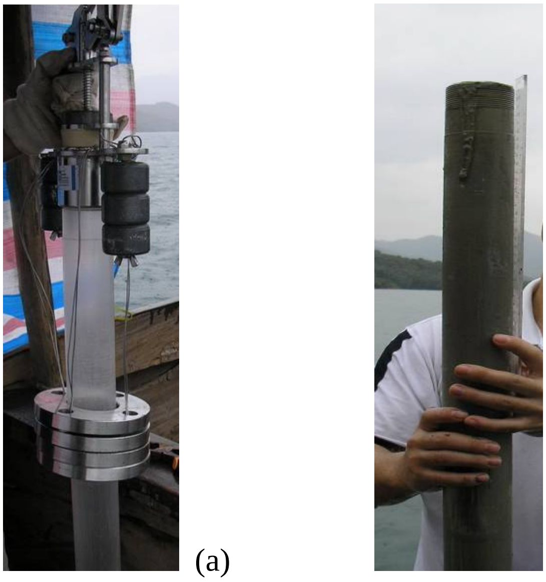


Figure 3.11 Sampling locations of sediment cores at Songtao Reservoir

3.2.2 Sample collection

Sediment cores were collected at locations with relatively deeper water depth at each reservoir, using a portable Kajak gravity corer with an automatic clutch and reverse catcher. In Fig. 3.8 – 3.11, the sampling locations of sediment cores are indicated for the four reservoirs respectively. The corer was first released and driven into the sediments by gravity. The sediments were then retained in a PVC tube of 70 mm in its inner diameter. After collection, the sediment cores, except the case of Xinfengjiang Reservoir, were immediately sliced into sub-samples at 1-cm intervals in situ. At Xinfengjiang Reservoir, the sediment cores were sliced into sub-samples at 0.5-cm intervals for the top 10 cm and at 1-cm intervals for the remaining parts. Table 3.2 summarizes the details for sediment cores at the four reservoirs, including locations, core lengths and sampling conditions.



(a) (b)

Figure 3.12 Pictures of a) portable Kajak gravity corer; b) one collected sediment core to be sliced into sub-samples in-situ immediately

Table 3.2 Details of sediment cores collected in the four reservoirs

Name of Reservoir	**Time of Foundation**	**Sampling Time**	**Sediment Cores**	**Latitude**	**Longitude**	**Length (cm)**	**Water Depth (m)**
Tingxi Reservoir	Jun., 1956	Sep. 18, 2006	TX-A	24°48.48'N	118°08.53'E	32	25
			TX-B	24°48.20'N	118°08.36'E	46	30
			TX-C	24°47.85'N	118°08.23'E	30	27
Xinfengjiang Reservoir	Oct., 1959	Sep. 8, 2006	WLH-A	23°45.75'N	114°34.93'E	32	60
			WLH-B	23°45.75'N	114°34.93'E	26	60
			WLH-C	23°48.09'N	114°35.63'E	21	65
			WLH-D	23°47.51'N	114°34.10'E	37	80
Luokeng Reservoir	1960	Sep. 14, 2006	LK-A	21°49.08'N	111°16.68'E	37	30
			LK-B	21°49.66'N	111°17.28'E	40	25
			LK-C	21°49.66'N	111°17.28'E	50	25
Songtao Reservoir	1969	Nov. 10, 2006	ST-A	19°21.69'N	109°32.36'E	56	35
			ST-B	19°21.33'N	109°33.80'E	55	36
			ST-C	19°22.51'N	109°33.45'E	50	37
			ST-D	19°23.40'N	109°31.75'E	45	30

Surface soil samples were collected in the reservoir catchment area to study the elemental concentrations of baseline soils in the drainage basin, and to provide background information of regional geochemical conditions. Moss samples were also collected simultaneously to assess the significance of current atmospheric deposition of trace metals in the study area. The total number of mosses and surface soils collected are listed in Table 3.3. All the samples were stored in zipped polyethylene bags at 4 ºC before laboratory analysis.

Table 3.3 Number of moss and surface soil samples collected at the four remote reservoirs

	Tingxi Reservoir	**Xinfengjiang Reservoir**	**Luokeng Reservoir**	**Songtao Reservoir**
Moss	N = 5	N = 9	N = 3	N = 4
Surface Soil	N = 4	N = 5	--	N = 11

3.3 Sample Preparation and Analyses

3.3.1 Sample preparation

Prior to the chemical analysis, sediment samples were kept at around -26 ºC to prepare for the subsequent freeze-drying process. The sediments were then freeze-dried at -45 ºC for about three days. Freeze-drying was preferred to air drying in order to prevent baking of clay-rich samples at higher temperatures (Bradl, 2005). Weights before and after drying were determined for each sample to calculate dry densities. After drying, sediments were ground into fine particles in an agate grinder by a grinding roll, avoiding contamination caused by abrasion from the material of the grinding equipment. Soil samples were air-dried and grinded in a similar way. The impurities (*e.g.* stones, coarse materials, and other debris) in soil samples were screened out and removed before grinding. Mosses were pretreated by washing thoroughly with tap water first and then with distilled water ultrasonically for three times to remove soil particles in a modified method of Lee *et al.* (2005). The samples were subsequently air-dried at 60 ºC and grinded until fine particles were obtained. The grinded samples were then stored in a desiccator, prepared for subsequent chemical analysis.

3.3.2 Determination of total metal concentrations

For analytical purpose, all the sample materials should be digested and transferred to a solution for final instrumental determination of elemental concentrations. Several concentrated acids and oxidizing reagents are suitable for acid digestion, such as hydrofluoric acid (HF), perchloric acid ($HClO_4$), nitric acid (HNO_3), sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2). The selection of acids depends on the constituents of the material for decomposition and the interference effect during the equipment analysis. To perform a complete decomposition of lattic constituents in a sample, HF should be used to break down the silicate structures. Other digestion methods without HF are considered as the pseudo-acid digestion. These methods can also provide consistent results and nearly total concentrations for most of the trace metals across the samples. The pseudo-acid digestion can give an assessment of the maximum potentially soluble or mobile contents of metals which are usually not bound in silicates. These metal contents most likely reflect the maximum potential hazard that could occur in the long term, or in extreme environmental regimes.

In the laboratory, a strong acid mixture of HNO_3 (69%) and $HClO_4$ (70%) was used for the sample digestion (Ip *et al.*, 2004). For sediments and soils, a representative aliquot (about 0.25 g) of the sample was weighted and digested by 10 ml HNO_3 (69%) and 2.5 ml $HClO_4$ (70%) in a pre-cleaned Pyrex test tube. The digestion process was conducted in a specially designed exhaust by using an aluminum heating block, which heated from 50 ºC up to 190 ºC progressively for around 16 hours until complete dryness of the sediments. The residues were dissolved in 10 ml of 5% HNO_3 by leaching at 70 ºC for 1 hour after cooling down. Digestion of moss samples was conducted in a similar way with 8 ml HNO_3 and 2 ml $HClO_4$. The solutions were then analyzed for the total concentrations of trace metals (*e.g.* Cd, Cu, Pb, Ni, Zn) and lithogenic major elements (*e.g.* Al, Fe) by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES, Perkin Elmer Optima 3300DV) according to the method of Ip *et al.* (2007). The general detection limits of ICP-AES for different metal elements are listed in Table 3.4.

Table 3.4 The general detection limits of ICP-AES for different metal elements (unit: ppb)

Element	**Al 308.215**	**Ca 317.933**	**Cd 228.802**	**Co 228.616**	**Cr 283.563**
D.L.	28	10	3	7	7

Element	**Cu 327.393**	**Fe 238.204**	**Li 670.784**	**Mg 280.271**	**Mn 260.568**
D.L.	10	5	3	2	2

Element	**Ni 231.604**	**Pb 220.353**	**V 292.402**	**Zn 213.857**
D.L.	15	42	9	6

A set of quality assurance and quality control measures was strictly implemented throughout the whole process from sampling, sample preparation, acid digestion, to final concentration determination. Precautions were taken to prevent possible cross contamination between different samples. All the Pyrex test tubes were pre-soaked in 10% HNO_3 acid batch overnight and then rinsed with plenty of distilled deionized water (DIW) before use. For sample digestion, reagent blanks, sample duplicates, and standard reference material (*i.e.* NIST 1646a for sediments, NIST 2709 for soils, NIST 1515 for mosses, and laboratory internal standards) were inserted among samples in each batch to examine the reliability of the analytical method, and accuracy and precision of obtained data. During the analytical process by ICP-AES, a standard solution (prepared from Comb 21 of Perkin Elmer Ltd.) was measured every ten samples to monitor the equipment performance and control the drifting of data within 10%. It was shown that the relative standard deviations of duplicate samples were basically within 10%. There was no sign of contamination by the results from blank samples. Recovery rates of major and trace elements from standard reference material were generally over 80% except aluminum and lead. The amount of aluminum bound to silicates can not be effectively digested by the current method, while the relatively poor recovery of lead might be due to the low lead concentrations in the standard materials approaching the detection limit. By examining laboratory internal standards, nevertheless, the recovery rates of both elements were found to be around 80%-100%.

3.3.3 Lead-210 dating of sediment cores

Lead-210 occurs naturally as one of the radioisotopes in the ^{238}U decay series, which has a half-life of 22.26 years. ^{210}Pb dating technology is considered as a useful geochronological tool for the determination of time-stratigraphy in undisturbed sediments and was applied to date the sediment cores during the study. Sediment subsamples were isolated for a period of around two half-lives (9 ~ 10 months) of ^{210}Po (Smith and Walton, 1980) so that ^{210}Po could accrue sufficiently from its grandparent ^{210}Pb, and a secular equilibrium between them was supposed to achieve. ^{210}Pb activity was therefore indirectly determined by measuring ^{210}Po activity using alpha radioactivity counting. All the selected samples for dating were assayed in a high-resolution alpha spectrometer equipped with silicon surface barrier detectors and a multi-channel analyzer with ^{209}Po used as an internal yield tracer (Turner and Delorme, 1996). ^{210}Po and ^{209}Po were extracted, purified, and plated onto silver discs from 0.5 M HCl solution at 70 – 80 ºC (Smith and Walton, 1980). Chemical yields, which were estimated from the recovery of ^{209}Po, were also evaluated. The supported ^{210}Pb activity was determined by measuring the activity of its parent nuclide ^{226}Ra. Because of small variations in ^{226}R activity through each core, the supported ^{210}Pb activity was taken to be equal to the average ^{226}R activity for samples from the top, middle, and bottom portions of the cores.

It is assumed that atmospheric deposition of ^{210}Pb is reasonably constant when averaged over several years. As an exponential decline in ^{210}Pb activity with depth was characterized in the present study, the Constant Flux – Constant Sedimentation Rate (CF:CS) model was applied to calculate the sedimentation rate of sediments in the reservoirs (Appleby and Oldfield, 1992).

3.3.4 Lead isotopic composition analysis

Lead isotopic analysis was conducted for selected sediment samples, soil samples, and moss samples to identify the anthropogenic sources of the pollutants and quantify the contribution of anthropogenic inputs. Lead isotopic ratios $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$, and $^{208}Pb/^{207}Pb$ were determined by Inductively Coupled Plasma – Mass Spectrometry (ICP – MS, Perkin Elmer ELAN 6100 DRC^{plus}). The solutions (after sample digestion) were diluted with 5% high purity HNO_3 to around 25 μg Pb/l depending on the daily instrument performance. Meanwhile, standard solution of a reference material (NIST 981) was also prepared and measured every five samples and also at the very beginning and the end of the whole batch. The analyses were performed with 150 sweeps for each reading and ten measurements were taken for each sample. The relative standard deviation of duplicate readings was generally within 0.5%. The measured mean ratios $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$, and $^{208}Pb/^{207}Pb$ of QCs were 0.0646±0.0001, 1.0931±0.0016, 2.3702 ±0.0029 respectively and drifts of all QCs were well below 0.5%. The results were in good agreement with the certified values

(0.0646, 1.0933, and 2.3704 respectively).

3.3.5 Air back-trajectory analysis

To investigate origins and transport pathways of air masses entering the study areas, air back-trajectories were calculated using nesting meteorological data by the Hybrid Single-Particle Lagrangian Integrated Trajectory, Version 4.7 (HYSPLIT4 model) developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (Wang *et al.*, 2006). The ending position (*i.e.* latitude and longitude) of each reservoir was determined by taking the mean values of all the sampling sites. The trajectories were set to end at the height of 500 m above the ground level (AGL), which is normally half of the height of the mean daytime planet boundary layer (PBL) and represents the general transport condition in the PBL (Lee *et al.*, 2007). To assess potential seasonal variations of prevailing air mass movements, trajectories were evaluated every six hours (*i.e.* 0:00, 6:00, 12:00, and 18:00 for local times) per day during the period of Jan. 2006 – Feb. 2007. Cluster means of the trajectories for each season were calculated to identify the dominant air masses. Details regarding the trajectory setup for the four reservoirs were listed in Table 3.5.

Table 3.5 Setup details of air back-trajectories calculated for the four reservoirs

Reservoirs	Latitude	Longitude	Height (m)	Starting Time
Tingxi Reservoir	24.80ºN	118.14ºE	500	0:00, 6:00, 12:00, 18:00
Xinfengjiang Reservoir	23.79ºN	114.57ºE	500	0:00, 6:00, 12:00, 18:00
Luokeng Reservoir	21.83ºN	111.29ºE	500	0:00, 6:00, 12:00, 18:00
Songtao Reservoir	19.36ºN	109.54ºE	500	0:00, 6:00, 12:00, 18:00

3.3.6 Statistical analyses

Several statistical analyses were conducted to better interpret the obtained data. Two-sample t-test statistics was adopted to assess the variation of trace metal concentrations or historical fluxes between independent samples at different sampling locations. The association between each two metal elements was assessed by calculating the Pearson correlation coefficient. In this study, SPSS® for Windows Release 13.0 was utilized to perform all the statistical analyses.

CHAPTER 4 – ATMOSPHERIC DEPOSITION OF ANTHROPOGENIC HEAVY METALS AT XINFENGJIANG RESERVOIR – IMPLICATION OF REGIONAL AIR POLLUTION

The present study was conducted at Xinfengjiang Reservoir in a remote area of South China with systematic sampling of reservoir sediment cores, mosses, and surface soils in the catchment area. The objectives are: 1) to investigate historical variations of heavy metal concentrations by assessing the vertical profiles of sediment cores; 2) to identify the input sources of trace metals by lead isotopic composition analysis and elemental association analysis; 3) to assess the impact of current air pollution on the ecosystem in a typical remote area of South China.

4.1 Metal concentrations in sediment profiles

The elemental profiles of Al, Fe, Cu, Ni, Pb and Zn in the four sediment cores from Xinfengjiang Reservoir are presented in Fig. 4.1. The distribution of major elements Al and Fe were generally stable above 18 cm in all the sediment cores, followed by a sharp drop of concentrations with increasing depth occurred below 15 cm (Fig. 4.1a and 4.1b). WLH-A showed the slowest decreasing rate while the slopes of WLH-B and WLH-C were generally similar and comparatively steeper than WLH-A. The metal concentrations declined fastest in WLH-D and reached the minimum values at around 20 cm. A peak was observed around 25-30 cm, below which the concentrations were kept constant back to the minimum values.

A continuous decreasing trend of heavy metal concentrations with increasing depth was observed within the depth of 0-20 cm (Fig. 4.1c-4.1f), in contrast to the generally constant concentrations of major elements. However, the distribution patterns of Cu, Ni, Pb and Zn in deep layers were found to be similar to those of Al and Fe, except for WLH-A. In WLH-A, the concentrations of Cu and Ni showed an increasing trend below 20 cm until they tended to decrease at 30 cm. Zn concentrations in the lower profiles of sediments did not vary much. Heavy metal concentrations in the bottom sediments of WLH-A were also comparatively higher than the values in sediments at the same levels of the other three cores. It is also noticed that the distribution patterns of these trace elements in top sediments were not exactly the same although they had a common variation trend (*i.e.* decreasing trend of heavy metal concentrations with increasing depth). Cu, Ni and Zn concentrations were found to be sharply elevated in the top 5 cm of the sediment cores while the variations of Pb concentrations showed a generally uniform descending trend along the whole length, with the only exception of two abnormally high concentrations at 23 cm and 26 cm observed in WLH-B.

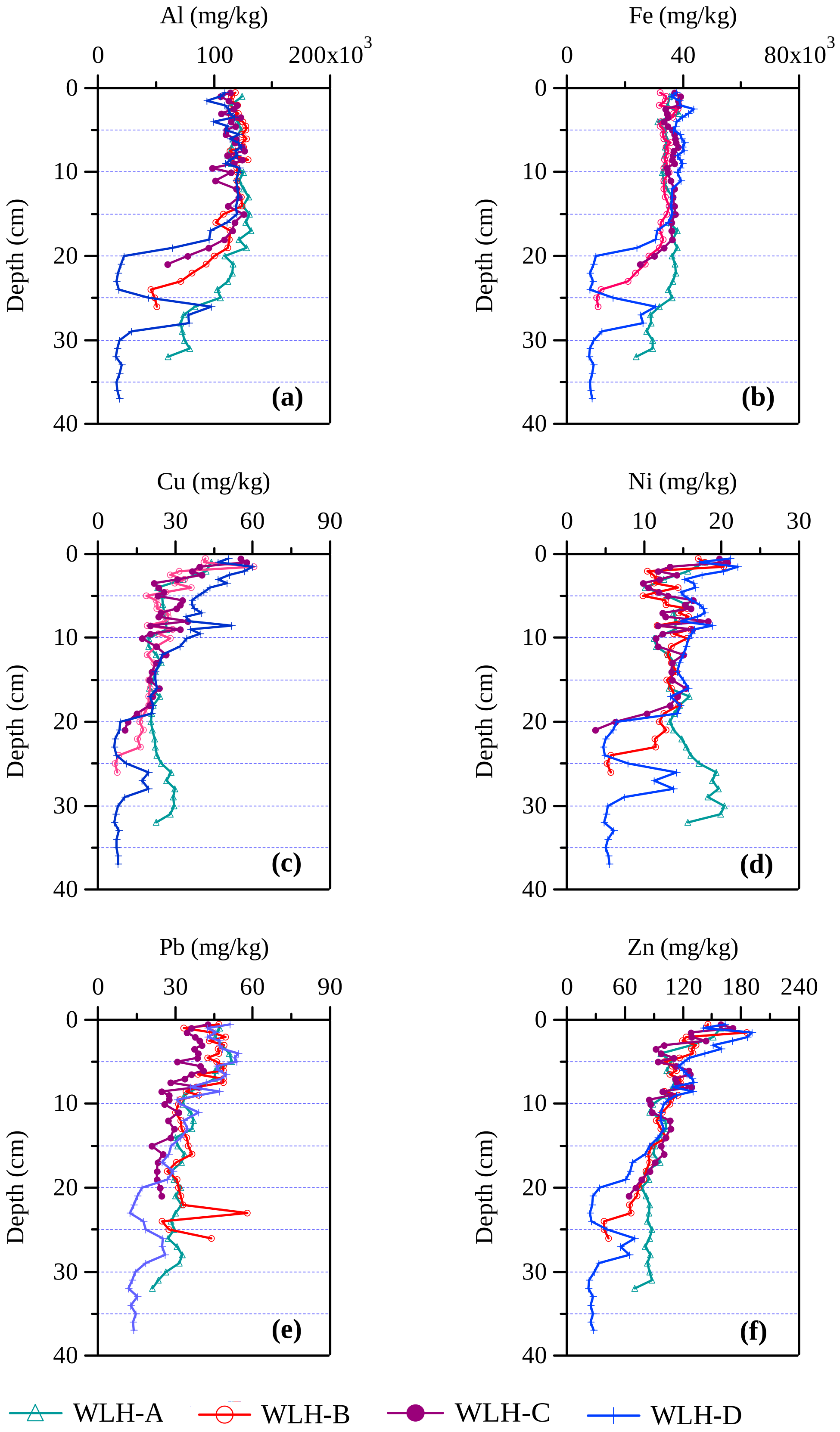


Figure 4.1 Concentration profiles of major elements Al (a) and Fe (b), and trace elements Cu (c), Ni (d), Pb (e), and Zn (f) in sediment cores from Xinfengjiang Reservoir

4.2 Enrichment of heavy metals

As can be seen from the sediment profiles, the decreasing rate of metal concentrations in bottom layers of sediments (below 15 cm) of Core WLH-A was much slower than those of other cores, suggesting the sedimentation rate at the location of WLH-A might be much higher than other sampling locations. In addition, the distinctive distribution patterns of trace elements (*e.g.* Cu and Ni) in WLH-A from other sediment cores possibly indicate that post-depositional disturbance occurred in bottom sediments. Considering the abnormal condition of Core WLH-A, the other three sediment cores, including WLH-B, WLH-C and WLH-D, were selected for further analysis. In Fig. 4.2, the means and standard deviations of heavy metal concentrations at various depths along the sediment cores at Xinfengjiang Reservoir are presented. Statistical significance of differences in metal concentrations between different layers of sediments was also assessed. As the results showed, heavy metals were gradually enriched in upper layers. The concentrations of Cu, Ni, Pb and Zn in surface sediments (0-5 cm) reached 39.6 mg/kg, 14.9 mg/kg, 43.3 mg/kg and 138 mg/kg respectively. Metal concentrations at 0-5 cm ($n = 29$) were significantly higher than those below 30 cm ($n = 8$) ($p < 0.01$), particularly for Cu and Zn. Cu and Zn concentrations in the surface sediments were over fourfold higher than the values in bottom layers, while Pb concentrations were also elevated almost threefold. Compared with the three trace elements, the enrichment of Ni was relatively small, which was less than twofold. In the upper 20 cm of sediments, the concentrations of Cu, Pb and Zn showed a significant decreasing trend while variations of Ni concentrations was not significant. There were no significant differences in heavy metal concentrations at the peak of 26-30 cm, compared to the overlying sediment layers (*i.e.* 21-25 cm).

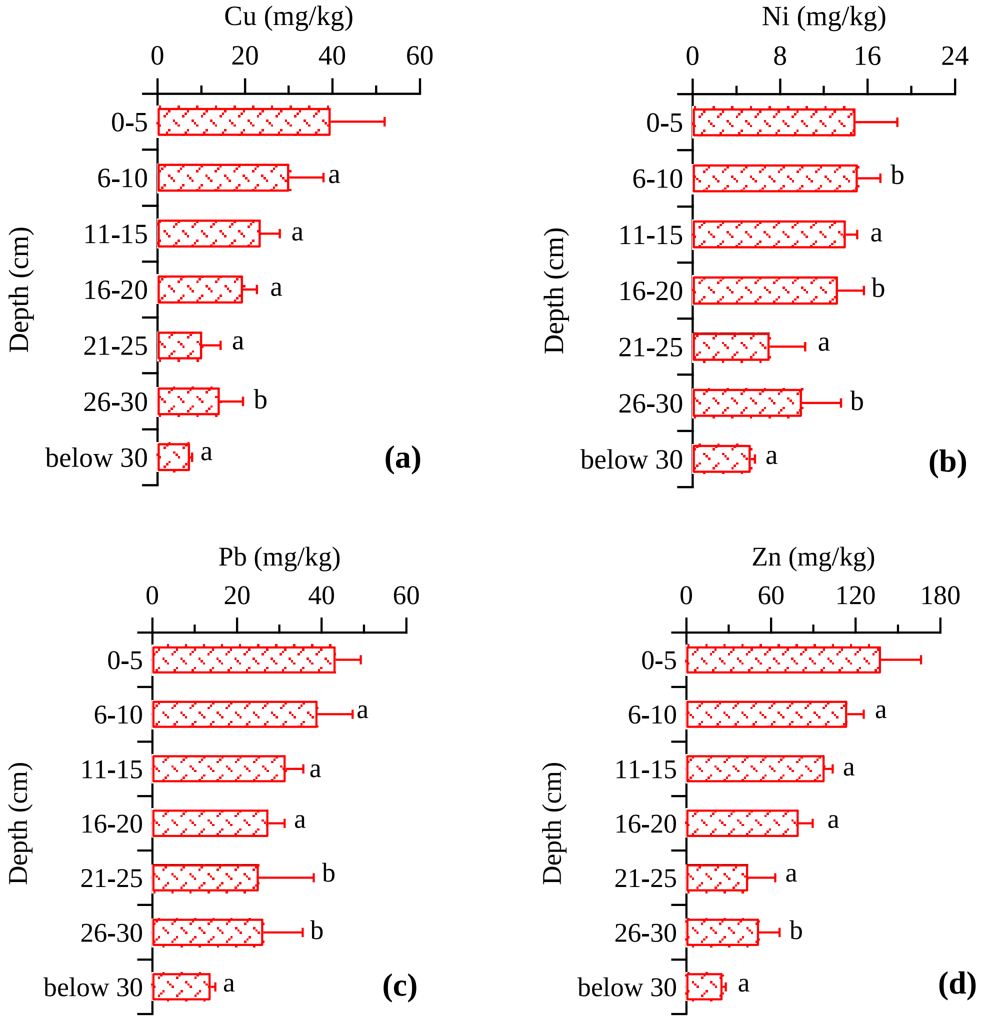


Figure 4.2 Variations of heavy metal concentrations at different depths of the sediment cores at Xinfengjiang Reservoir: Cu (a), Ni (b), Pb (c), and Zn (d). The annotation 'a' indicates a significant difference of metal concentrations with the above sediment layer at $p < 0.05$ level, while 'b' implies no statistically significant difference between the two adjacent layers.

Although the heavy metals, especially Cu, Pb and Zn, were found to be significantly enriched in sediments, the raw data of heavy metal concentrations are not sufficient enough to infer the presence or quantify the intensity of contamination in sediments (Schropp *et al.*, 1990; Aloupi and Angelidis, 2001). Changes in sediment properties, such as granulometric (particle size) and mineralogical (rock type) variations, can affect the natural background concentrations of metals in sediments (Tam & Yao, 1998; Schiff & Weisberg, 1999). The enrichment of trace metal concentrations in sediments of Xinfengjiang Reservoir might be attributed to natural environmental changes or the contamination due to increasing inputs of anthropogenic pollutants from catchment areas or transported from industrial or urban areas.

The lithogenic major elements Fe and Al are abundant in the crust and are mostly derived from natural materials, thus reflecting the natural environmental conditions. A high correlation of the lithogenic elements and the trace metals is normally expected for uncontaminated sediments and vice versa. Considering the longest core WLH-D, the trace elements were found to be closely correlated with the major elements in sediments below 15 cm ($r_{Cu\text{-}Fe} = 0.983$; $r_{Ni\text{-}Fe} = 0.977$; $r_{Pb\text{-}Fe} = 0.960$; $r_{Zn\text{-}Fe} = 0.989$). Therefore, the large increment of trace metal concentrations at 15-20 cm is probably attributed to the natural environmental changes. On the other hand, the trace metal concentrations had poor relationships with the major elements above 15 cm ($r_{Cu\text{-}Fe} = 0.406$; $r_{Ni\text{-}Fe} = 0.240$; $r_{Pb\text{-}Fe} = 0.275$;

$r_{Zn\text{-}Fe}$ = 0.416), suggesting that the enrichment of trace metals in the top sediments (0-15 cm) are mainly derived from anthropogenic sources. To identify the significance of the anthropogenic inputs, the enrichment factors of Cu, Ni, Pb and Zn concentrations in top sediments were determined by comparing the trace metal concentrations at 0-2 cm (47.3 mg/kg, 17.4 mg/kg, 42.2 mg/kg, and 153.2 mg/kg respectively) and at 14-15 cm (21.4 mg/kg, 13.9 mg/kg, 30.9 mg/kg, and 97.3 mg/kg respectively). It can be noticed that the enrichment of anthropogenic Cu was most significant at the reservoir. The Cu concentrations in surface sediments were over twofold of the concentrations at 14-15 cm. The Zn concentrations were also elevated by nearly 60%. The Pb and Ni appeared relatively less enriched (*i.e.* 37% for Pb and 25% for Ni) in surface sediments by anthropogenic inputs.

As mentioned in Section 2.3.2, geochemical normalization of metal concentrations to a reference element (normalizer) can be used to distinguish natural contributions from the anthropogenically enriched metal concentrations. In order to further examine the extent of metal contaminations in the sediments, proper normalizers were identified to reduce the natural effects. In Table 4.1, the Pearson correlation coefficients between major (Al and Fe) and trace elements (*i.e.* Cu, Ni, Pb and Zn) in the sediment cores are summarized. The results showed that three trace elements, including Cu, Ni and Zn, had much stronger correlations with Fe. The correlation coefficients between Pb and the two major elements were similar ($r_{Pb\text{-}Al}$ = 0.665; $r_{Pb\text{-}Fe}$ = 0.663). Normally, a possible best normalizer is the highest geochemically sensible tracer, referring the strongest correlator (Yang and Rose, 2005). Fe was thus considered as a better normalizer for Cu, Ni and Zn, while Al and Fe were regarded both appropriate for Pb normalization.

Table 4.1 Pearson correlation coefficients between elemental concentrations in sediment cores at Xinfengjiang Reservoir (n = 114)[a]

Element	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
Al	1					
Fe	0.947	1				
Cu	0.613	0.732	1			
Ni	0.762	0.834	0.861	1		
Pb	0.665	0.663	0.721	0.641	1	
Zn	0.784	0.847	0.933	0.857	0.782	1

a. All the correlations are significant at the 0.01 level (2-tailed).

A set of uncontaminated samples needs to be identified to obtain reliable baseline conditions for defining metal-normalizer relationships. As the concentrations of Cu, Ni, Pb and Zn in sediments below 15 cm of Core WLH-D were found to be highly correlated with Al and Fe ($r_{Cu\text{-}Fe}$ = 0.983; $r_{Ni\text{-}Fe}$ = 0.977; $r_{Pb\text{-}Fe}$ = 0.960; $r_{Zn\text{-}Fe}$ = 0.989), they were regarded as uncontaminated sediments. The baseline metal-normalizer reference element relationships (simple linear regression lines) for the study area were then established based on metal concentrations in sediments over 15-38 cm of Core WLH-D. The 95% prediction intervals were subsequently derived from the linear regression models for the purpose of comparing individual samples to the baseline relationships.

The scatter plots of heavy metals and the respective normalizers are presented in Fig. 4.3. The linear regression lines and 95% prediction intervals are superimposed on the data. Sediment samples were then assessed depending on the plotted positions relative to the regression lines and prediction intervals. It was suggested that any samples above the upper 95% prediction limit (with high excursions) are probably contaminated by heavy metals from anthropogenic sources, while data points within the prediction limits are usually originated from natural sources (Daskalakis and O'Connor, 1995; Schiff and Weisberg, 1999; Aloupi and Angelidis, 1999). It can be noticed that large amount of samples in upper sediment cores exceeded the prediction limits; while samples in lower layers at low concentrations were generally within the natural ranges. The deviations were larger when the concentrations of heavy metals were higher. These findings probably suggest that trace elements in the sediments of Xinfengjiang Reservoir are derived from natural sources in the early stage. However, the sediments are likely to be anthropogenically contaminated by heavy metals in the upper layers (especially in top 10 cm) where significant elevation of heavy metals occurred. Additional evidence could be obtained from the sediment profiles. The similar distribution patterns and high correlations between heavy metals (*i.e.* Cu, Ni, Pb and Zn) and major elements (*i.e.* Al and Fe) in lower sediment layers also suggest the natural origin of the trace elements. In upper layers, heavy metals were greatly enriched while Al and Fe concentrations generally remained constant. The poor correlation between major and trace elements further reflects the possible contamination of sediments.

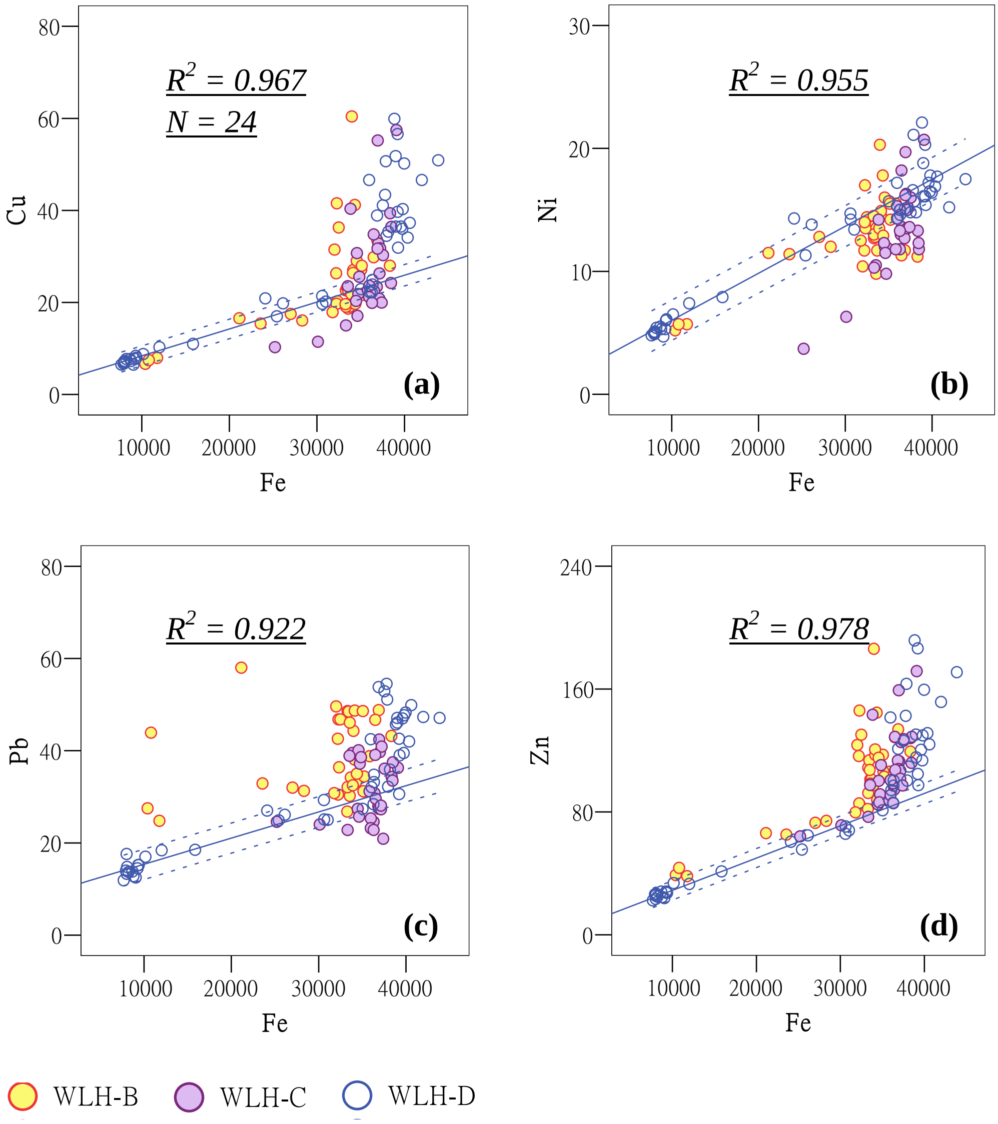


Figure 4.3 Scatter plots of Cu-Fe (a), Ni-Fe (b), Pb-Fe (c) and Zn-Fe (d) relationships in sediments of Xinfengjiang Reservoir. Linear regression baselines (obtained based on the metal concentrations in bottom sediments (*i.e.* 15-38 cm) of Core WLH-D) with 95% confidence intervals are superimposed on the data for comparison.

Till now, few studies have been conducted on historical variations of heavy metal concentrations in lacustrine sediments in remote area of South China. The existing studies mainly focused on the heavy metal contamination in sediments of the Pearl River Estuary and the surrounding coastal area (Li *et al.*, 2000; Liu *et al.*, 2003; Ip *et al.*, 2004). The heavy metal contents in sediment cores were found to have generally increased over the last three decades due to the recent rapid industrial development and urbanization in the estuarine region. Although the enrichment of heavy metals in the coastal and estuarine sediments was dominantly ascribed to wastes discharged from point sources, the increasing atmospheric input of anthropogenic pollutants was also considered as an important contributing source, particularly for Pb.

As Figure 4.3 also indicated, much more data points were found beyond the natural ranges in Cu-Fe, Pb-Fe and Zn-Fe plots. This reflects that heavy metal pollution at the reservoir is particularly serious for Cu, Pb and Zn, although the total enrichment of anthropogenic Pb in upper layer sediments was not as high as that of Cu and Zn. Considering the Ni-Fe plot, only a few samples were observed above the prediction interval, indicating relatively less significant enrichment of anthropogenic Ni in surface sediments. As the contamination of Ni by anthropogenic sources appears not serious in sediments of Xinfengjiang Reservoir, the following discussion will focus on Cu, Pb and Zn.

4.3 Contributions of potential sources to the enrichment

Without obvious direct discharges of pollutants from point sources, heavy metals in the reservoir sediments are supposed to be mainly derived from direct atmospheric deposition over the reservoir area and contributed by inputs from the catchment area via inflow streams, surface runoff, soil leaching or erosions. Due to the high drainage ratio (catchment area vs. open surface water area) of Xinfengjiang Reservoir, which is 15.5:1, the contributions from the catchment might be appreciable, or even more significant than the direct atmospheric inputs (Yang *et al.*, 2002; Shotbolt *et al.*, 2006).

As illustrated in Section 4.2, the concentrations of heavy metals in lower sediment layers (generally below 15 cm) had high correlations with the major elements. The elevated heavy metal concentrations are thus probably attributed to the accelerated erosion rate of natural soils from the watershed, as the increase of natural weathering normally results in accumulation of rock-forming elements (Ip *et al.*, 2004). This was well reflected by the simultaneously elevated Al and Fe concentrations in the lower parts of the sediment cores (see Fig. 4.1).

The results also indicate, however, that the upper layer sediments of the reservoir are anthropogenically enriched in heavy metals. Considering the catchment soils, no significant differences in concentrations of Cu and Pb existed between the surface soils and reservoir bottom sediments. The latter one probably indicates the background levels of the study area. The catchment soils are thus not likely to be contaminated by anthropogenic Cu or Pb. Although Zn concentrations were much higher in surface soils, strong correlations were observed between Zn and the major elements ($r_{Zn\text{-}Al} = 0.954$; $r_{Zn\text{-}Fe} = 0.831$), suggesting its geological origin. Moreover, no sign of enrichment of major elements was noticed in upper layers of the reservoir sediments. The upper layer sediments are thus considered to be mainly contaminated by anthropogenic heavy metals from atmospheric deposition, which concurrently occurred in both the terrestrial catchment and at the reservoir.

The surface sediments were assumed to be deposited in recent years without post-depositional disturbance of the sediments at the reservoir. As mentioned in Chapter 1, enormous economic development has taken place in South China in the past three decades. The great amount of anthropogenic pollutants released into the atmosphere in the intensively industrialized and urbanized area might be transported over vast distance to the remote area. During May to August, the eastern China and South China coastal region is normally prevailed by the summer monsoon, which advances northward in stepwise way with simultaneous northward movement of precipitation belts (Ding, 1994). Consequently, the air masses transported from the South China coastal region would just sweep across the central and northern Guangdong Province, including Xinfengjiang Reservoir. Previously, Lee *et al.* (2005) assessed the mosses and aerosols in Nanling

Mountains lying along the north border of Guangdong Province, and noticed that the area was susceptible to the strong influences of air pollutants originated from the PRD region. This further suggests that the enrichment of heavy metals in surface sediments of the reservoir is probably ascribed to the increasing atmospheric inputs of air pollutants from regional anthropogenic sources in recent years.

In this study, mosses were collected and analyzed to assess the significance of atmospheric heavy metal deposition recently (around 2-3 years). Most of the samples belong to the species *Pogonatum contortum*, which is commonly found in China (*e.g.* Guangdong, Guangxi, Hainan, Sichuan, Henan and the northeast region), Russia (the far east region), Japan and North America (west coast) (Yuan *et al.*, 2006). Although there have been no previous records available for using *Pogonatum contortum* to biomonitor the airborne heavy metal concentrations, the results from this study indicate that this type of mosses is effective in accumulating airborne heavy metals. The mean concentrations and standard deviations of trace elements Cu, Pb and Zn in the mosses were 10.5 ± 4.36 mg/kg, 47.1 ± 27.9 mg/kg, and 133 ± 44.7 mg/kg respectively. In Europe, several studies have been conducted to monitor the airborne heavy metals by mosses in relatively remote areas (Reimann *et al.*, 2001; Ruhling *et al.*, 2004). They reported that the Cu, Pb and Zn concentrations accumulated in moss samples were generally around 4.5 mg/kg, 4.2 mg/kg, and 32.3 mg/kg. In comparison, the heavy metal concentrations in mosses of this study were found to be much higher than the values reported in Europe (*i.e.* twofold for Cu, eleven-fold for Pb, and fourfold for Zn), especially for Pb. This probably suggests that the regional atmospheric deposition of air pollutants in South China is much more significant and might contribute substantial amounts of anthropogenic heavy metals in the surface environment of the study area.

As suggested by Schilling *et al.* (2002), different moss species in distinct meteorological and topographical conditions may have varied cation exchange capacities, which might subsequently influence the metal accumulation in mosses. Therefore, a multi-media approach was adopted in the present study to monitor the atmospheric heavy metals by considering the results of both mosses and reservoir sediment cores. The concentrations of Cu in mosses were noticed to be closely correlated with Zn ($r_{Cu\text{-}Zn} = 0.692$), suggesting these two elements are likely to be originated from common pollution sources. However, the relationships between Pb and these two trace elements were not strong ($r_{Pb\text{-}Cu} = -0.053$; $r_{Pb\text{-}Zn} = 0.266$), which might be attributed to their different origins or associated particle sizes of the emission sources. Lead is mostly associated with fine atmospheric particles while Cu and Zn are distributed in both fine and coarse particulates (Sweet *et al.*, 1998). Similar elemental association relationships were observed in surface sediments. Cu and Zn were also found to be strongly interrelated ($r_{Cu\text{-}Zn} = 0.953$) in the top sediments (0-5 cm) while no close relationship was observed between Pb and these trace elements (r_{Pb-Cu} = 0.107; r_{Pb-Zn} = 0.142). The consistency of results from both types of environmental materials further reflects that the significant atmospheric fluxes (including the indirect inputs from the catchment) are probably the dominant input sources of anthropogenic heavy metals in upper layer sediments of the reservoir.

4.4 Identification of regional sources

In order to identify possible origins of the air pollutants, lead isotopic compositions were determined to distinguish between different sources, as each lead containing ore or other natural materials has specific lead isotopic signature and the values are not subject to large changes by chemical or biological fractionation (Renberg *et al.*, 2002; Duzgoren-Aydin *et al.*, 2004). Duzgoren-Aydin *et al.* (2004) stated that anthropogenic lead in the atmosphere was mainly derived from combustion of leaded petrol, industrial discharges, and coal burning. In Table 4.2, data of available backgrounds (*e.g.* natural bedrocks), potential anthropogenic sources (*e.g.* ore deposits, automobile exhausts), as well as the values of aerosols and mosses collected in the PRD region and other surrounding areas retrieved from previous literatures are listed for comparison. The relationships between different types of samples are plotted and depicted in Figure 4.4.

Table 4.2 Lead isotopic compositions of potential natural and anthropogenic sources.

Nature of Sample	**$^{206}Pb/^{207}Pb$**	**$^{208}Pb/^{207}Pb$**
Regional Natural Background		
Volcanic rock (HK) [a]	1.221	2.529
Volcanic rock (PRD) [b]	1.199	2.497
Uncontaminated soils (PRD) [b]	1.195	2.482
Regional Pollution Sources		
Automobile exhausts (PRD) [b]	1.160	2.423
Fankou Pb-Zn ore deposit [b]	1.172	2.473
Aerosols and Mosses in South China		
PRD aerosols [c]	1.161-1.177	2.366-2.501
Foshan aerosols (urban) [b]	1.155-1.170	2.457-2.474
Zhongshan aerosols (suburban) [d]	1.169-1.173	2.444-2.461
Nanling mosses (rural) [d]	1.171-1.190	2.452-2.463
Nanling aerosols (rural) [d]	1.171-1.179	2.447-2.469

a. Duzgoren-Aydin *et al.*, 2004;
b. Zhu *et al.*, 2001;
c. Wong *et al.*, 2003;
d. Lee *et al.*, 2005.

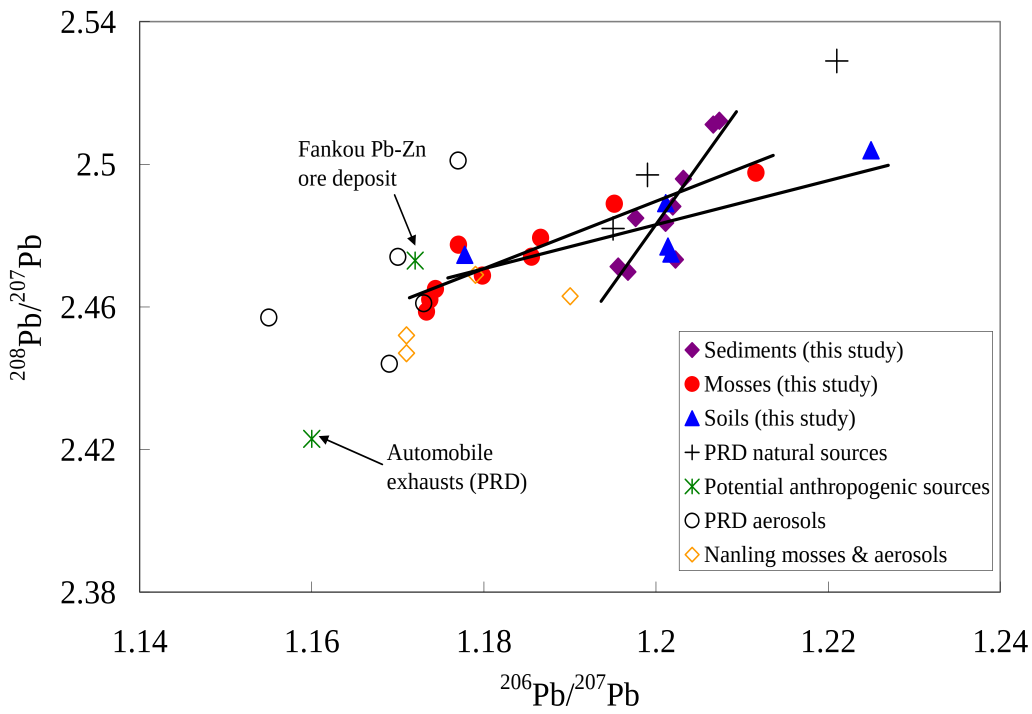


Figure 4.4 Comparisons of Pb isotopic compositions between sediments, mosses, and surface soils at Xinfengjiang Reservoir, with reference to available data of backgrounds and potential anthropogenic sources in the PRD region

The results showed that the lead isotopic compositions of mosses and soils varied over large ranges (*i.e.* 1.173-1.212 and 1.178-1.225, respectively), possibly indicating the influences of various types of lead sources. However, each of the data set presented a good linear relationship between the natural sources and anthropogenic sources (see Fig. 4.4), indicating a binary mixing effect of geogenic Pb and anthropogenic Pb. The anthropogenic Pb emitted from industrial processes using lead-containing ores and coal combustion (with similar lead isotopic compositions to some of the lead ores) in the PRD region are probably the dominant contributing sources. Although leaded gasoline has been gradually phased out in China since 2000, the lead isotopic compositions of moss and soil samples also appeared to be influenced by the automobile lead emissions. This might suggest that Pb emitted in the past by the usage of leaded petrol still remains due to its long persistence in the environmental medium (e.g. catchment soils), which becomes another important source of anthropogenic Pb (Bollhofer and Rosman, 2001; Chen *et al.*, 2005). Compared with mosses and soils, the range of values in sediments was much narrower (*i.e.* 1.196-1.207) with the ratios slightly decreased towards the surface (*i.e.* no large variations). This is possibly attributed to the mixing effects of both natural inputs from the catchment (*e.g.* erosion of catchment soils and bedrocks) and atmospheric deposition of anthropogenic pollutants. Moreover, substantial anthropogenic Pb might be retained in the terrestrial catchment caused by its large retention capacity (*i.e.* large catchment area).

As the figure also illustrates, the lead isotopic ratios of mosses were consistent with the reported values of aerosols and mosses in Nanling Mountain, which is situated in a relatively remote area of South China as well. Lee *et al.* (2005) suggested that the lead isotopic compositions of mosses could reflect the isotopic signature of lead of the surrounding ambient air. Therefore, the atmosphere over the study area is regarded to be significantly influenced by regional anthropogenic sources. The increment of Pb concentrations in top layers of sediment cores at Xinfengjiang Reservoir might thus be attributed to the increasing atmospheric deposition of anthropogenic pollutants emitted and transported from the PRD region in recent years. Further investigations are required, however, to provide additional evidence on anthropogenic sources of the heavy metals in sediments of Xinfengjiang Rerservoir. The results would be of great importance for establishing proper management policies to alleviate potential impairment of environment and ecosystems at Xinfengjiang Reservoir.

CHAPTER 5 – THE SUITABILITY OF USING RESERVOIR SEDIMENTS AS GEOCHEMICAL ARCHIVES OF ATMOSPHERIC HEAVY METAL INPUTS – FACTORS INFLUENCING TRANSPORT AND DEPOSITION OF AIRBOREN HEAVY METALS

In the present study, the atmospheric heavy metal pollution was assessed at four typical reservoirs (*i.e.* Tingxi Reservoir, Xinfengjiang Reservoir, Luokeng Reservoir and Songtao Reservoir) located in the remote area of the South China coastal region. It is considered that these reservoirs might present different signatures as to the impacts of atmospheric heavy metal pollution due to their distinctive locations, topographical and meteorological conditions, as well as the specific physicochemical conditions of the reservoirs and their catchments. Therefore, the major objectives of this chapter are 1) to assess the long-term variations of heavy metal concentrations in sediments of each reservoir; 2) to evaluate the significance of metal enrichments in recent years; 3) to identify the dominant contributing sources of heavy metal inputs in the sediments; 4) to examine the possible influencing factors affecting atmospheric deposition of anthropogenic heavy metals in sediments of reservoirs in remote areas.

5.1 Concentration Profiles of Metals in Sediment Cores at Different Reservoirs in the Remote Area

The concentration profiles of metals in the sediment cores were assessed at the four reservoirs respectively. Assuming no post-depositional disturbances, the sediment profiles probably mirror the long-term variations of heavy metal inputs in the reservoir.

5.1.1 Tingxi Reservoir

At Tingxi Reservoir, three sediment cores were collected at relatively deep locations across the reservoir. The concentration profiles of some major metals (*i.e.* Al and Fe) and trace elements (*i.e.* Co, Ni, Pb and Zn) in the sediments are presented in Fig. 5.1. As the low Cu concentrations in sediments from Tingxi Reservoir were approaching the detection limit, the data were not used for further discussion.

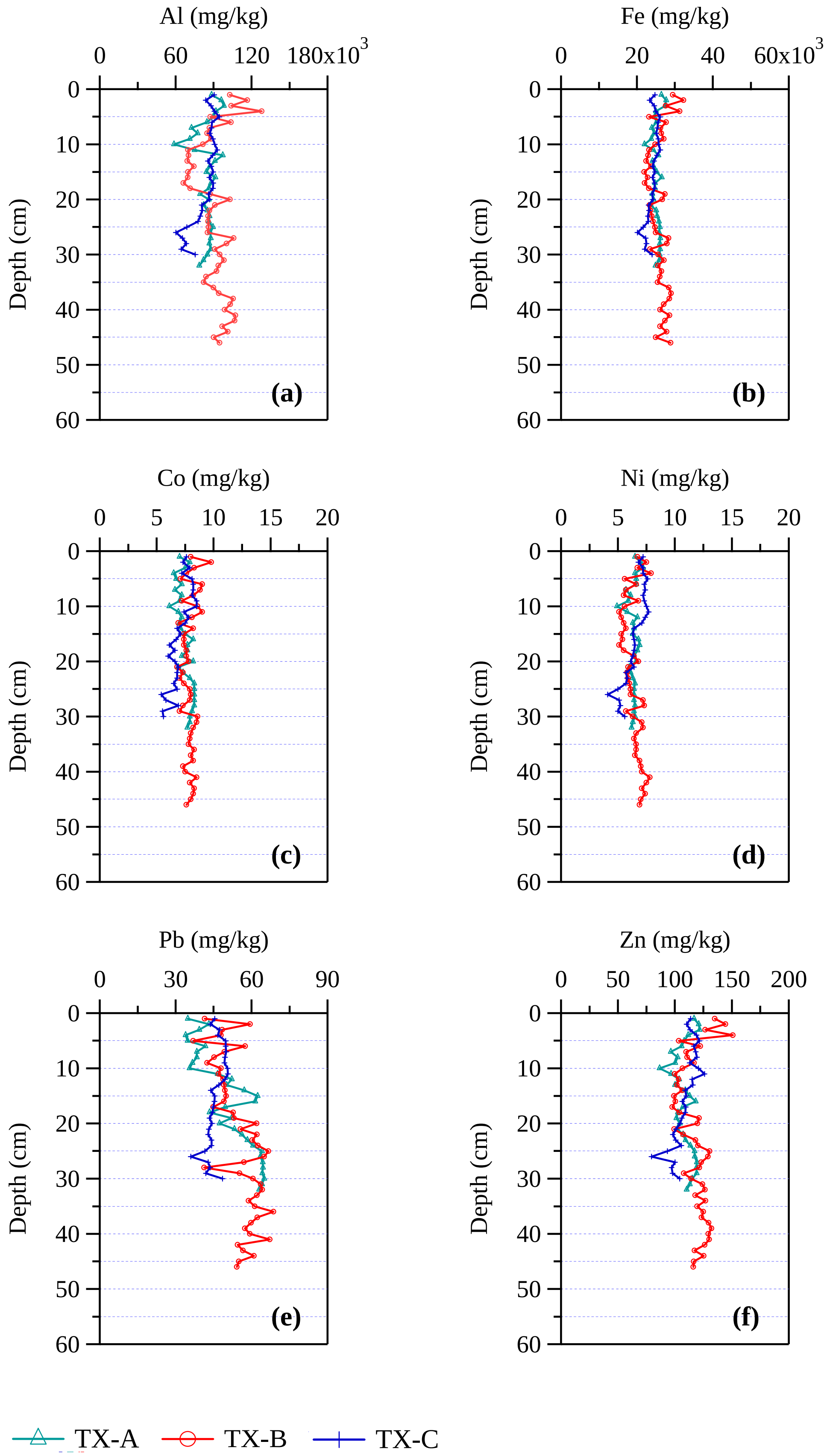


Figure 5.1 Concentration profiles of major elements Al (a) and Fe (b), and trace elements Co (c), Ni (d), Pb (e), and Zn (f) in sediment cores from Tingxi Reservoir

It can be noticed that the distribution patterns of major element Al in the three sediment cores varied much from each other. In Core TX-A, the Al concentration decreased gradually in the top 10 cm and then turned to increase until it reached about 97×10^3 mg/kg at 12 cm, below which the concentration generally kept constant. Similar variation pattern of Al concentration was observed in the longest Core TX-B, however, the sedimentation rate at this location was probably slower. The concentration firstly decreased continuously until it reached about 70×10^3 mg/kg at 11 cm, which was kept steady for the next 6 cm. It then increased sharply to 100×10^3 mg/kg at 17-20 cm. Below 20 cm, there was no large variation of Al concentration with the values kept around 95×10^3 mg/kg. Considering Core TX-C, the concentration was generally constant in the top 20 cm. It then decreased slightly to 60×10^3 mg/kg at 26 cm, below which the concentration was gradually raised back to 75×10^3 mg/kg. Compared to Al, a generally uniform distribution pattern of Fe concentrations was observed in all the three cores. The concentration was kept around 25×10^3 mg/kg, with only a slight elevation in Core TX-B in the top 5 cm.

The concentration profiles of four selected trace elements Co, Ni, Pb and Zn are shown in Fig. 5.1(c)-(f). As the figures show, the concentrations of Co and Ni were generally kept constant along the sediment cores. The distribution patterns were quite similar to the major element Fe. The variation trends of Zn concentrations in the three cores were also found to be similar to those of Al concentrations. However, the concentration profiles of Pb appeared quite different from other heavy metals. Large variations of Pb concentrations were observed along the whole length of the sediment cores in TX-A and TX-B. Moreover, a reserved trend with relatively higher concentrations in the bottom sediments was observed. The only exception was Core TX-C, in which the variation of Pb concentrations was similar to those of both major (*i.e.* Al and Fe) and other trace elements (*i.e.* Co, Ni and Zn).

The results from Pb^{210} dating analysis indicate that Core TX-B is probably subject to some post-depositional disturbances. The ^{210}Pb activity was found to be abnormally lower in deeper sediment layers (see Fig. 5.2). The sediment profiles of Core TX-B are thus not suitable as a geochemical archive and cannot provide information on the long-term variations of heavy metal concentrations at the reservoir. The similar distribution patterns of metals in Core TX-A, especially the irregular variation trend of Pb, probably suggests this sediment core is also disturbed to a certain extent. Only Core TX-C is supposed to be well preserved. Both the major and trace elements were uniformly distributed along the sediment core. There were no significant differences in metal concentrations between the top (0-5 cm, $n = 5$) and bottom (below 25 cm, $n = 5$) sediments ($p > 0.1$). The mean concentrations of Co, Ni, Pb and Zn in the surface sediments were 7.62±0.38 mg/kg, 7.20±0.29 mg/kg, 46.6±2.27 mg/kg, and 116±4.48 mg/kg. The Pearson correlation coefficients between the metal elements were determined to assess the origins of heavy metals in the sediments at the reservoir (see Table 5.1). The results showed that all the examined heavy metals were strongly correlated with major elements. A close relationship between major and trace elements normally reflects that the sediments are not significantly contaminated by anthropogenic inputs. The heavy metals in the sediments at Tingxi Reservoir are thus expected to be mainly originated from natural sources. There is no obvious sign of heavy metal enrichment in reservoir sediments caused by atmospheric deposition of anthropogenic air pollutants (including the indirect inputs from the catchment). Therefore, the possible adverse impacts of either local or regional air pollution of heavy metals on the ecosystems of Tingxi Reservoir cannot be clearly observed by examining the sediment profiles.

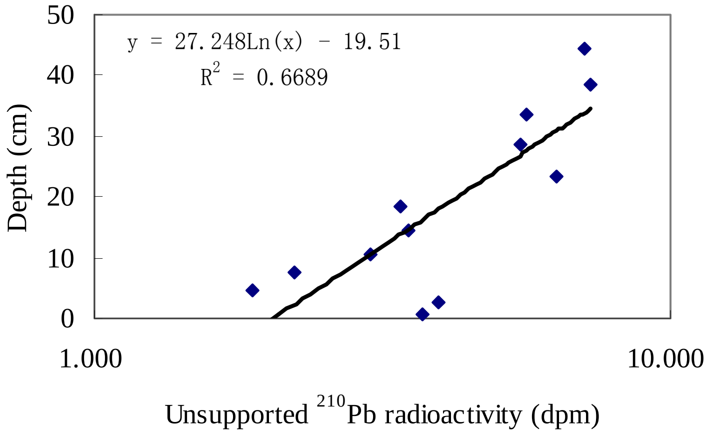


Figure 5.2 Plot of the unsupported ^{210}Pb radioactivity against the depth of the sediment core LK-B from Luokeng Reservoir

Table 5.1 Pearson correlation coefficients between elemental concentrations in sediments of Tingxi Reservoir (n = 30)[a]

Element	**Al**	**Fe**	**Co**	**Ni**	**Pb**	**Zn**
Al	1					
Fe	0.923	1				
Co	0.680	0.734	1			
Ni	0.911	0.933	0.833	1		
Pb	0.727	0.911	0.760	0.857	1	
Zn	0.862	0.944	0.747	0.951	0.902	1

a. All the correlations are significant at the 0.01 level (2-tailed).

5.1.2 Luokeng Reservoir

At Luokeng Reservoir, the concentration profiles of Al, Fe, Cu, Pb and Zn are plotted for two selected sediment cores LK-B and LK-C in Fig. 5.3(a) – 5.3(f) respectively.

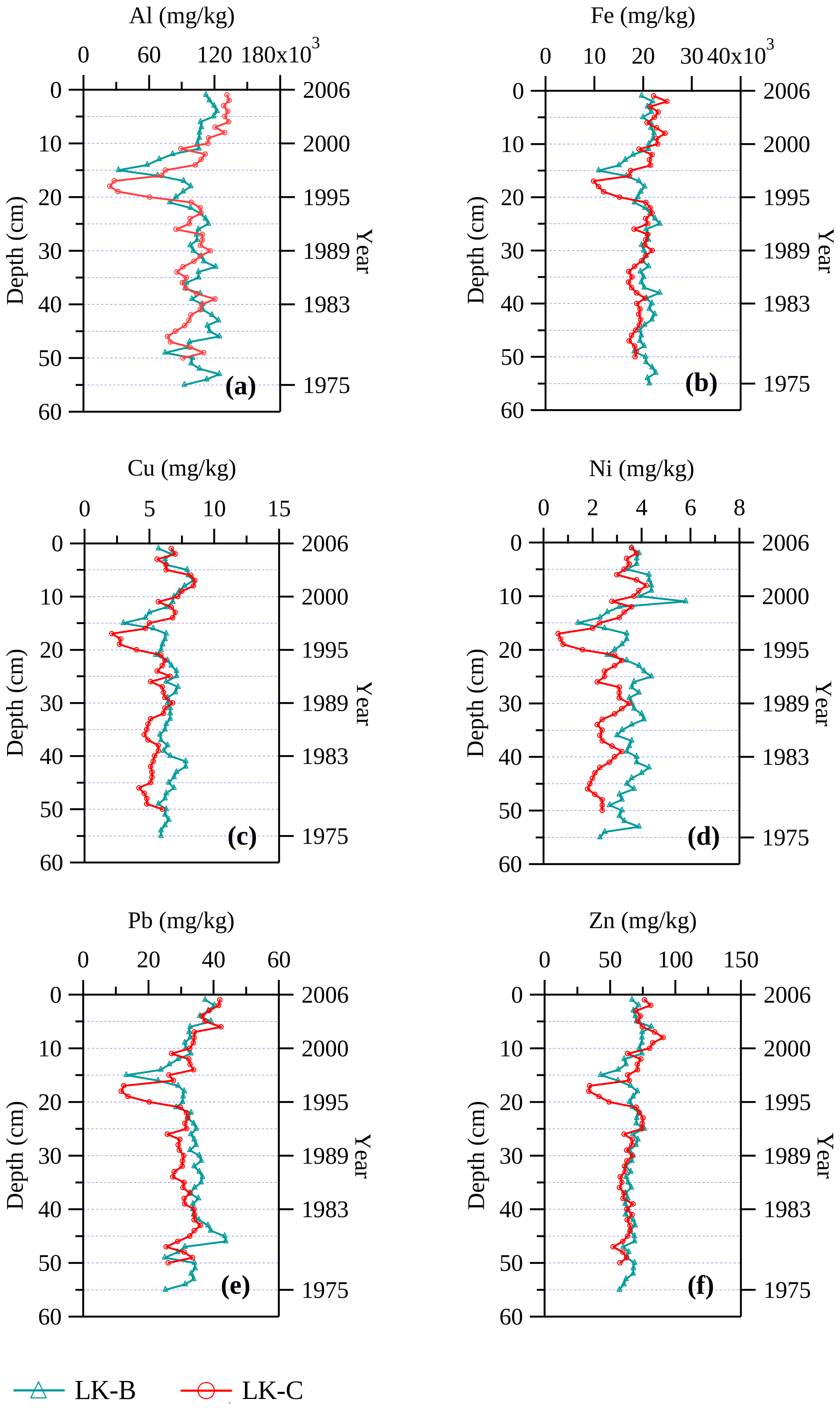


Figure 5.3 Concentration profiles of major elements Al (a) and Fe (b), and trace elements Cu (c), Ni (d), Pb (e), and Zn (f) in sediment cores from Luokeng Reservoir

It can be noticed that the variation trends of both major (*i.e.* Al and Fe) and trace elements (*i.e.* Cu, Ni, Pb and Zn) in the two sediment cores closely resembled each other, possibly indicating their similar sedimentation conditions. The Al concentrations gradually decreased with increasing depth in top sediments until they reached the minimum values at around 17 cm. The concentrations were then elevated sharply back to 105×10^3 mg/kg at 20 cm and kept generally constant in the bottom sediments. Similar distribution patterns of Fe concentrations were observed except that Fe concentrations in the top 10 cm were also kept stable, which was around 20×10^3 mg/kg.

Considering the trace elements, the variation trends of Cu, Ni, Pb and Zn were found to be similar to those of major elements Al and Fe. The concentrations of the four heavy metals reached their minimum values at around 15-17 cm and then gradually increased back to the values prior to the decrement. Likewise, the concentrations in sediments below 20 cm were generally kept constant. However, the distribution patterns of trace elements in the top 15 cm of sediments varied from each other. In the sediment profiles of Cu, Ni and Zn, a peak, which was most obvious for Cu, was observed at the depth of 5-10 cm. As for Pb, however, the concentration decreased continuously in the top 15 cm until the minimum value was obtained.

Dating of the sediment core LK-B was conducted by using ^{210}Pb dating technology to assess the time-stratigraphy. The results were shown in Table C-2 of Appendix C. The unsupported ^{210}Pb was found to vary exponentially with the depth of the sediments (see Fig. 5.4). Therefore, the Constant Flux – Constant Sedimentation Rate (CF:CS) model was applied to date the sediment core (Appleby and Oldfield, 1992). The calculation was conducted based on the following equation: $t = \frac{1}{\lambda}\ln\left(\frac{^{210}Pb^{0}}{^{210}Pb}\right) = 32.15 \times \ln\left(\frac{^{210}Pb^{0}}{^{210}Pb}\right)$, where t represents the age, λ is the radioactive decay constant of ^{210}Pb ($\lambda = 3.11 \times 10^{-2}$ y^{-1}), ^{210}Pb^{0} is the initial activity of unsupported ^{210}Pb, and ^{210}Pb is the measured (present-day) activity of unsupported ^{210}Pb. According to the results from the dating analysis, the annual sedimentation rate at Luokeng Reservoir = 56.313/32.15 = 1.75 cm/year. The ages were then determined based on the sedimentation rate and the corresponding depths. The obtained results were superposed on the sediment profiles in Fig. 5.2. The longest core LK-B was found to have accumulated sediments for a period of 25 years. As the figure presents, the distribution of metals in the sediments at Luokeng Reservoir was generally stable prior to 1995. A common drop of concentrations of both major and trace elements occurred around 1996-1997. During the recent ten years, relatively higher concentrations of Cu, Ni and Zn were noticed in 2002 while Pb concentrations were continuously elevated as time went on.

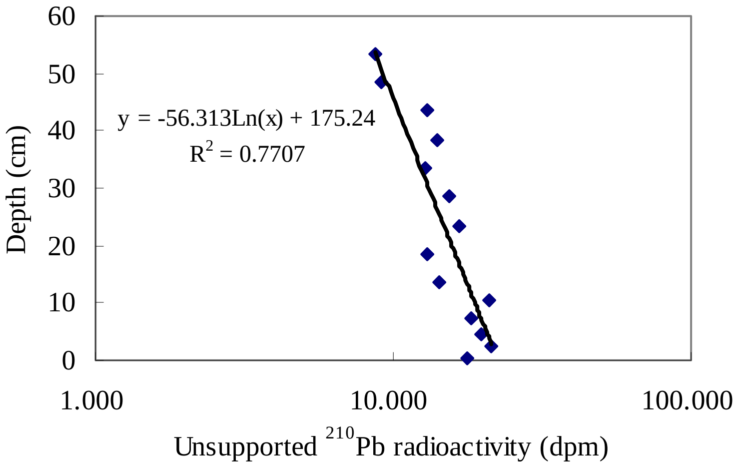


Figure 5.4 Plot of the unsupported ^{210}Pb radioactivity against the depth of the sediment core LK-B from Luokeng Reservoir

The average concentrations of heavy metals Cu, Ni, Pb and Zn in the surface sediments (0-5 cm, n = 10) were 6.45±0.67 mg/kg, 3.60±0.22 mg/kg, 38.7±2.08 mg/kg, and 71.8±4.88 mg/kg respectively, while the concentrations in bottom sediments (below 45 cm, n = 15) were 5.77±0.79 mg/kg, 2.81±0.61 mg/kg, 31.1±4.86 mg/kg, and 62.2±4.72 mg/kg. There have been only slight elevations of heavy metal concentrations (*i.e.* 12% for Cu, 29% for Ni, 24% for Pb, and 17% for Zn) in the past 25 years. The elemental associations were analyzed by calculating the Pearson correlation coefficients. The results are shown in Table 5.2 as follows. The significant correlations between major elements and heavy metals probably indicate that the variations of heavy metals in the sediment profiles are attributed to natural changes. The sediments at Luokeng Reservoir are thus not likely to be significantly contaminated by anthropogenic heavy metals.

Table 5.2 Pearson correlation coefficients between elemental concentrations in sediment cores at Luokeng Reservoir (n = 105)[a]

Element	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
Al	1					
Fe	0.900	1				
Cu	0.788	0.858	1			
Ni	0.759	0.810	0.863	1		
Pb	0.891	0.770	0.704	0.680	1	
Zn	0.780	0.864	0.828	0.740	0.714	1

a. All the correlations are significant at the 0.01 level (2-tailed).

5.1.3 Songtao Reservoir

At Songtao Reservoir, three sediment cores, including ST-A, ST-B, and ST-D, were used to assess the long-term variations of metal concentrations in the reservoir sediments. The concentration profiles of Al, Fe, Cu, Ni, Pb and Zn in the sediment cores are presented in Fig. 5.5 (a)-(f) respectively.

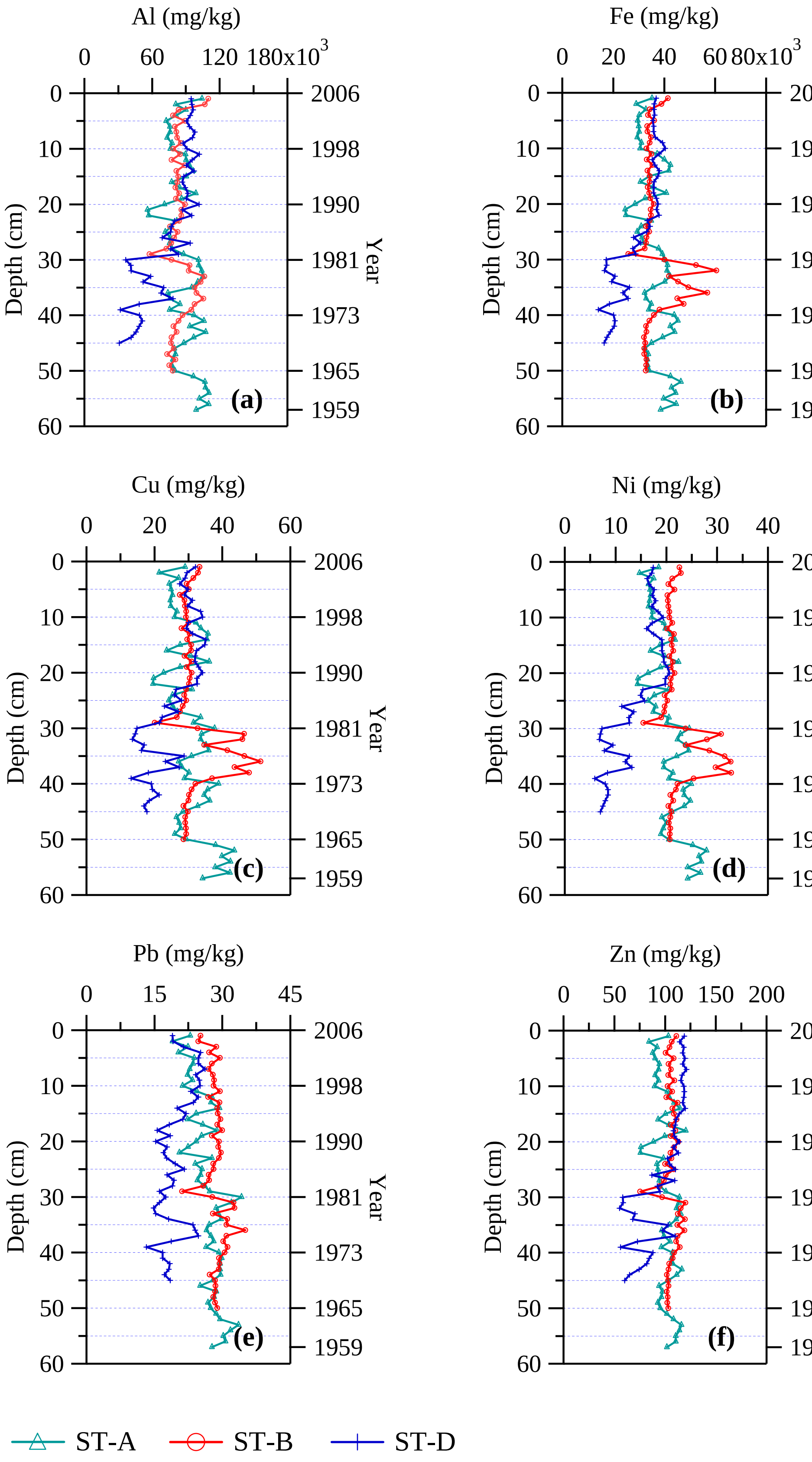


Figure 5.5 Concentration profiles of major elements Al (a) and Fe (b), and trace elements Cu (c), Ni (d), Pb (e), and Zn (f) in sediment cores from Songtao Reservoir

As the figures show, the distribution patterns of the metal elements in upper layer sediments of the three cores were generally similar, while they were rather scattered in the bottom sediments below 30 cm. In Core ST-A, a reversed variation trend was observed for the major elements Al and Fe, the concentrations of which were found to be slightly higher in deep layers than in the surface sediments. The variations of lithogenic metals normally indicate changes of the natural environment. It was suggested that the increase of natural weathering of soil materials in the watershed normally result in accumulation of lithogenic elements in aqueous sediments (Ip *et al.*, 2004). Therefore, the reduced concentrations of major metals towards the surface sediments in Core ST-A of Songtao Reservoir might be caused by decelerated soil erosions from the catchment area over time. Considering Core ST-B, the metal concentrations of Al and Fe were generally kept stable around 80×10^3 mg/kg and 35×10^3 mg/kg respectively, except for several peaks occurring at the depth of 30-40 cm. These peaks might be attributed to accelerated weathering of natural soils from the catchment during that period of time. In Core ST-D, the concentrations of Al and Fe were relatively lower in sediments below 30 cm compared to the values in upper layers. The concentrations decreased gradually between 20-30 cm until they reached the minimum values at 30 cm. Below 30 cm, the concentrations fluctuated irregularly with two peaks formed at 35 cm and 40 cm respectively. With regard to the trace elements, the variation trends of Cu, Ni, Pb and Zn appeared similar to those of the major elements.

The ^{210}Pb dating analysis was conducted to assess the time-stratigraphy of sediment cores at Songtao Reservoir. Similar to Luokeng Reservoir, the CF:CS model was applied to date the sediment cores at Songtao Reservoir, as the unsupported ^{210}Pb also varied exponentially with depth of the sediments (see Fig. 5.6). Core ST-A was found to have been well preserved, providing a historical record of metal concentrations of nearly 50 years. The results were shown in Table C-3 of Appendix C. The annual sedimentation rate was 1.22 cm/year (*i.e.* 39.345/32.15), which was determined in a similar approach as Luokeng Reservoir. The ages were then calculated and plotted in correspondence with the depths in the sediment profiles (see Fig. 5.4 Y2-axis). The distribution patterns of metal elements at the Songtao Reservoir were found to be generally uniform since the 1980s. However, the sedimentation conditions across the reservoir varied much in early years. Regarding the peaks observed in both Core ST-B and ST-D around 30-40 cm, they are probably caused by accelerated catchment soil erosions due to intensive deforestation activities in the mid to late 1970s.

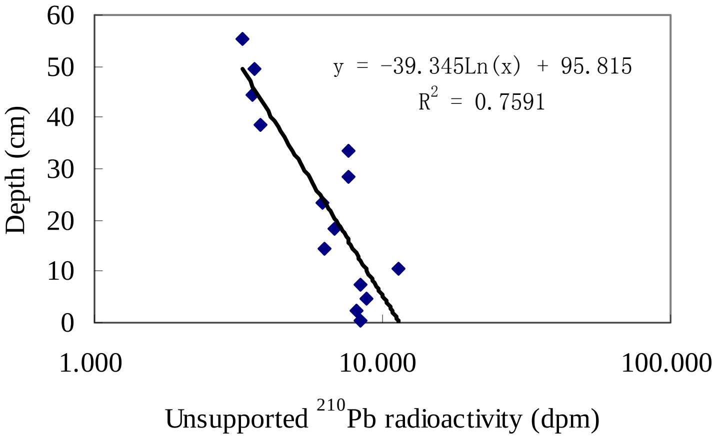


Figure 5.6 Plot of the unsupported ^{210}Pb radioactivity against the depth of the sediment core ST-A from Songtao Reservoir

The mean concentrations of trace metals at different depths along the sediment cores were then determined for ST-A and ST-B, which had accumulated sediments for a longer history. The elemental concentrations of Cu, Ni, Pb and Zn in surface sediments (0-5 cm, n = 10) were 28.4±3.91 mg/kg, 19.3±2.85 mg/kg, 24.4±3.42 mg/kg, and 98.9±9.56 mg/kg respectively. On the other hand, the concentrations of the four trace elements in bottom sediments (below 45 cm, n = 17) were 33.0±6.24 mg/kg, 22.5±3.12 mg/kg, 28.9±1.95 mg/kg, and 103±6.93 mg/kg. The results indicate that there has been no large enrichment of heavy metal concentrations (*i.e.* 16% for Cu, 17% for Ni, 18% for Pb, and 4% for Zn) in sediments of Songtao Reservoir in the past fifty years, with the concentrations gradually and slightly decreased towards the surface. The Pearson correlation coefficients between the metal elements were determined to assess the elemental associations (see Table 5.3). It can be seen that all the metal elements were strongly correlated with each other, reflecting the variations of heavy metals over time are probably attributed to the natural changes. The sediments at Songtao Reservoir are thus not likely to be contaminated by heavy metals from anthropogenic sources.

Table 5.3 Pearson correlation coefficients between elemental concentrations in sediment cores at Songtao Reservoir (n = 107)[a]

Element	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
Al	1					
Fe	0.785	1				
Cu	0.780	0.952	1			
Ni	0.735	0.901	0.965	1		
Pb	0.557	0.700	0.769	0.813	1	
Zn	0.783	0.757	0.795	0.799	0.848	1

a. All the correlations are significant at the 0.01 level (2-tailed).

5.1.4 Xinfengjiang Reservoir

As discussed in Chapter 4, the concentrations of heavy metals Cu, Pb and Zn were found to be elevated significantly in upper layers of sediments at Xinfengjiang Reservoir, reflecting the increasing inputs of regional air pollutants in recent years. The lead isotopic compositions of mosses imply that the atmosphere over the study area has been strongly influenced by the regional anthropogenic sources. Industrial use of lead-containing ores and past released Pb from leaded gasoline in the PRD region are regarded as the major contributors of substantial amount of anthropogenic lead at the reservoir. The increment of Pb concentrations in top sediments at Xinfengjiang Reservoir might thus be attributed to the increasing atmospheric deposition of anthropogenic pollutants from intensive industrial activities and heavy traffic in the PRD region in the past several years.

All the four reservoirs are located in remote area of the South China coastal region. While the sediment cores from Xinfengjiang Reservoir showed enriched heavy metal concentrations due to increasing atmospheric inputs over time and strong influences of regional anthropogenic sources in recent years, there was no obvious contamination sign of sediments at the other three reservoirs. However, this cannot directly indicate the atmosphere at Tingxi Reservoir, Luokeng Reservoir, and Songtao Reservoir is not impaired by the increasing local or regional emissions of air pollutants in the past several decades. In order to further assess the air quality in the four remote areas, moss samples will be analyzed by determination of metal concentrations and lead isotopic compositions in the following section.

5.2 Biomonitoring of the Air Quality by Mosses

5.2.1 Metal concentrations in mosses

Five moss samples were collected at the catchment area of Tingxi Reservoir. Most of them belong to the species *Hypnum plumaeform*, which is commonly found in dense mats in many Asian countries, such as China, Japan, Korea, Nepal and Philippines. Past investigations have suggested that this type of mosses is effective in accumulating airborne heavy metals (Lee *et al.*, 2005). In the present study, the average concentrations of trace elements Co, Cu, Ni, Pb and Zn in the mosses were 1.32±0.49 mg/kg, 45.1±14.1 mg/kg, 3.96±0.87 mg/kg, 59.0±13.4 mg/kg, and 169 ± 27.6 mg/kg, respectively. The Ni and Pb concentrations were found to be much lower than the values reported in Nanling Mountains, while Cu and Zn concentrations were comparable (Lee *et al.*, 2005). This might be due to the fact that Nanling Moutain is at the key pathway for the long-range transport of air pollutants from northern China to the RPD region, particularly during the dry winter monsoon period. As the sampling work of the two studies was conducted during different time periods, the comparison of metal concentrations in mosses from the two study areas was only for general indication.

At Xinfengjiang Reservoir, a total of nine moss samples were collected and analyzed to assess the significance of atmospheric heavy metal deposition. As illustrated in Section 4.3, most of the samples belong to the species *Pogonatum contortum*, which is considered effective in accumulating airborne heavy metals. The mean concentrations and standard deviations of trace elements Cu, Ni, Pb and Zn in the mosses were 10.5±4.36 mg/kg, 5.00±1.82 mg/kg, 47.1±27.9 mg/kg, and 133±44.7 mg/kg respectively. When compared to the values reported in some remote areas of the Europe, the heavy metal concentrations in mosses at Xinfengjinag Reservoir appeared much higher (Reimann *et al.*, 2001; Ruhling *et al.*, 2004).

Three moss samples of three different species (*i.e. Thuidium glaucinum, Claopodium assurgens, and Claopodium aciculum*) were sampled at Luokeng

Reservoir. The average concentrations of Cu, Ni, Pb and Zn in the mosses were 9.23±1.81 mg/kg, 1.63±0.25 mg/kg, 36.4±19.5 mg/kg, and 86.4±19.4 mg/kg, respectively. There have been no previous records of using these species as biomonitors of heavy metals. The results showed that considerable Pb and Zn concentrations were accumulated in the moss samples.

At Songtao Reservoir, four moss samples were collected at the height of 650 m of Jianfengling Mountain. All the samples belong to the species *Pogonatum contortum*, which is the same as the samples collected at Xinfengjiang Reservoir. The average concentrations of the trace metals Cu, Ni, Pb and Zn in the mosses were 5.75±0.21 mg/kg, 1.65±0.17 mg/kg, 34.8±3.46 mg/kg, and 59.9±1.42 mg/kg respectively.

In Fig. 5.7, the heavy metal concentrations in mosses from different reservoirs are compared. It can be noticed that the concentrations of most heavy metals (*e.g.* Cu, Pb and Zn) in mosses from Tingxi Reservoir were much higher than the values in other reservoirs. The concentrations were found to be lowest in the mosses collected at Songtao Reservoir. There was no large difference in concentrations of Ni between the four reservoirs and the Ni contents in mosses were rather low compared to other elements. However, the raw data of metal concentrations in mosses may not directly reflect the relative significance of air pollution in the study area. Different moss species might have varied cation exchange capacities, which would affect metal accumulation in mosses (Schilling *et al.*, 2002). Fortunately, the mosses collected at Xinfengjiang Reservoir and Songtao Reservoir were of the same species. The results showed that the heavy metal concentrations in mosses from Xinfengjiang Reservoir were much higher (*i.e.* 1.4 times for Pb, twofold for Cu and Zn, and threefold for Ni) than the values at Songtao Reservoir. This probably reflects that the atmospheric deposition of heavy metals is more significant at Xinfengjiang Reservoir. It was reported that the variations in meteorological and topographical conditions (*e.g.* temperature, humidity, altitude) might have an influence on metal accumulation in the moss samples (Wolterbeek, 2002). In this study, the meteorological conditions at Songtao Reservoir and Xinfengjiang Reservoir are quite similar. The former one has a tropical monsoon climate with average annual temperature around 23.3 ºC, while the later one has a subtropical monsoon climate with the average temperature of 19.6 – 21.3 ºC. Both of them have abundant annual rainfalls. These two reservoirs are both located at low altitude, which is around 100-200 m. Considering their similar site conditions, the comparison of moss data between the two reservoirs should be rather reliable.

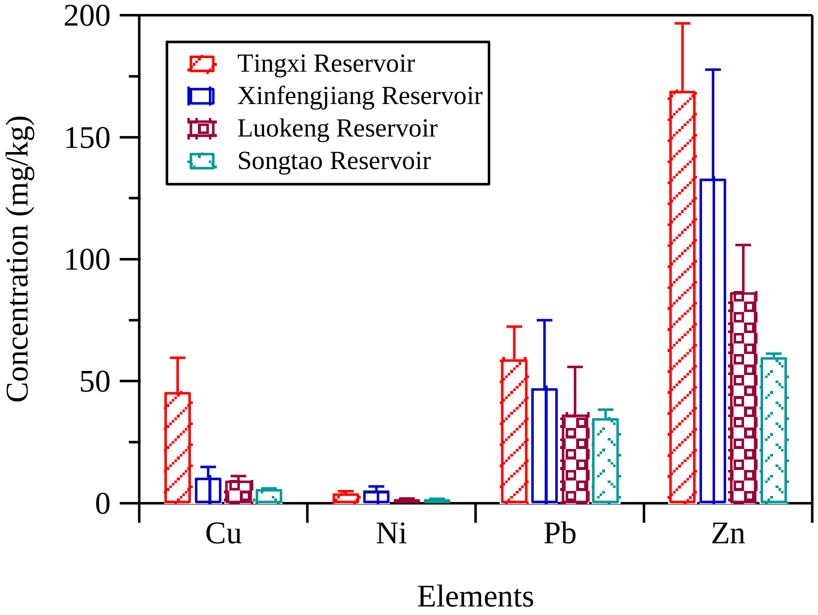


Figure 5.7 Comparison of concentrations of trace elements Cu, Ni, Pb and Zn in moss samples collected at different reservoirs

5.2.2 Lead isotopic compositions

In order to further investigate the potential impacts of regional atmospheric heavy metal pollution on the air quality in remote areas, the lead isotopic compositions of mosses were determined to provide information on possible origins of lead in mosses. Meanwhile, the collected catchment soils were also analyzed to assess the natural geological conditions of the study area. The lead isotopic ratios of selected sediment samples at the reservoirs were also determined for comparison. The obtained results (in terms of ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb) are listed in Table 5.4, compared to the values of available backgrounds (*e.g.* natural bedrocks), potential anthropogenic sources (*e.g.* ore deposits, aerosol samples, and mosses) from previous literature.

Table 5.4 Lead isotopic compositions of the moss, catchment soil and selected sediment samples at the four reservoirs, compared to potential natural and anthropogenic sources

Nature of Samples	**^{206}Pb/^{207}Pb**	**^{208}Pb/^{207}Pb**
Tingxi Reservoir		
Sediments (n = 4)	1.187 ~ 1.189	2.468 ~ 2.473
Surface soils (n = 4)	1.175 ~ 1.184	2.465 ~ 2.474
Mosses (n = 5)	1.168 ~ 1.175	2.456 ~ 2.467
Xinfengjiang Reservoir		
Sediments (n = 9)	1.196 ~ 1.207	2.470 ~ 2.512
Surface soils (n = 5)	1.178 ~ 1.225	2.475 ~ 2.504
Mosses (n = 9)	1.173 ~ 1.212	2.459 ~ 2.498
Luokeng Reservoir		
Sediments (n = 4)	1.227 ~ 1.234	2.500 ~ 2.533
Mosses (n = 3)	1.183 ~ 1.228	2.472 ~ 2.529
Songtao Reservoir		
Sediments (n =9)	1.196 ~ 1.203	2.452 ~ 2.486
Surface soils (n = 11)	1.208 ~ 1.224	2.507 ~ 2.568
Mosses (n = 4)	1.198 ~ 1.203	2.505 ~ 2.511
North China		
Beijing aerosols (urban) [a]	1.148	2.444
Dalian aerosols (urban) [a]	1.136	2.441
Major Pb-Zn ore deposits [b]	1.091 ~ 1.140	2.425 ~ 2.456
Background [b]	1.040 ~ 1.160	2.373 ~ 2.489
Yangtze River Delta Region		
Shanghai aerosols (urban) [a]	1.157	2.449
Nanjing aerosols (urban) [a]	1.163	2.460
Major Pb-Zn ore deposits [b]	1.130 ~ 1.164	2.370 ~ 2.458
Background [b]	1.152 ~ 1.170	2.449 ~ 2.456
Southeast China		
PRD aerosols [c]	1.161 ~ 1.177	2.366 ~ 2.501
Zhongshan aerosols (suburban) [d]	1.171	2.456
Nanling mosses (rural) [d]	1.171 ~ 1.190	2.452 ~ 2.463
Automobile exhausts (PRD) [e]	1.160	2.423
Fankou Pb-Zn deposit [e]	1.172	2.473
Fujian basalts [f]	1.189	2.486
Fujian granites [f]	1.188	2.481

Nature of Samples	**^{206}Pb/^{207}Pb**	**^{208}Pb/^{207}Pb**
Southeast China (cont.)		
Volcanic rock (HK) [g]	1.221	2.529
Volcanic rock (PRD) [e]	1.199	2.497
Uncontaminated soils (PRD) [e]	1.195	2.482
South China		
Hainan Au deposits [h]	1.213 ± 0.022	2.482 ± 0.014
Leizhou basalts [f]	1.190	2.482
Hainan Basalts [i]	1.196 ± 0.004	2.491 ± 0.002
South Asia		
Vietnam – Hanoi [j]	1.167	2.453
Vietnam – Ho Chi Minh [j]	1.155	2.430
Tailand – Bangkok [j]	1.127	2.404
Malaysia – Kuala Lumpur [j]	1.141	2.410

a. Mukai *et al.*, 2001; b. Zhu *et al.*,2003; c. Wong *et al.*, 2003; d. Lee *et al.*, 2005; e. Zhu *et al.*, 2001; f. Zhu *et al.*, 1995; g. Duzgoren-Aydin *et al.*, 2004; h. Chang *et al.*, 2002; i. Flower *et al.*, 1991; j. Bollhofer, 2001.

As Zhu *et al.* (1995) previously reported, the ^{206}Pb/^{207}Pb ratios of natural sources in Fujian Province (*i.e.* Fujian basalts and Fujian granites) were around 1.189. Similar results were obtained in the present study, as the upper bound value of the catchment surface soils at Tingxi Reservoir was found to be 1.184. It can be noticed that the lead isotopic compositions of reservoir sediments at Tingxi Reservoir were all kept around the background values, possibly reflecting that the sediments are not contaminated by anthropogenic lead. This is consistent with the generally constant distribution pattern of lead in the sediment profile of Core TX-C as illustrated in Section 5.1.1. However, the ^{206}Pb/^{207}Pb ratios of mosses collected at Tingxi Reservoir were much lower, ranging from 1.168 to 1.175. The results might indicate that there are some anthropogenic inputs of lead in mosses as the lead isotopic ratios of anthropogenic sources are normally much lower than the values of geochemical backgrounds (*e.g.* automobile exhausts in the PRD region, aerosols in Beijing and Shanghai). In Fig. 5.8, the lead isotopic ratios of mosses, soils and sediments are plotted in comparison with the values of natural geological sources. As the figure presents, the samples formed a good linear relationship, further reflecting the concurrent contributions of both natural and anthropogenic sources at the reservoir. Since the uptake of mineral substrates from soils is insignificant, the metal contents in mosses are expected to be mainly derived from precipitation or dry deposition (Ruhling *et al.*, 2004). Therefore, the anthropogenic lead in mosses is probably contributed by atmospheric deposition of air pollutants over the whole catchment of Tingxi Reservoir. Additional investigations are needed, however, to identify the potential sources of anthropogenic heavy metals.

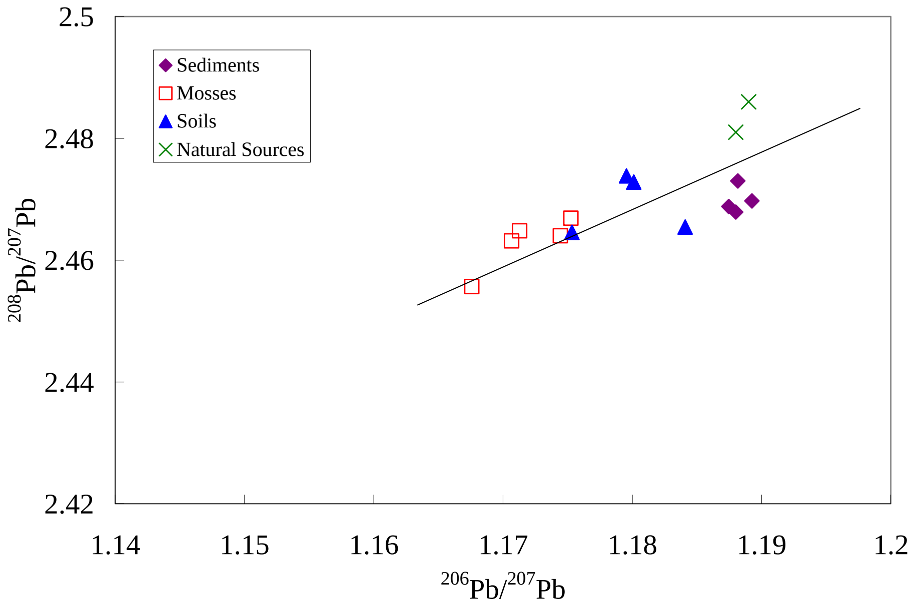


Figure 5.8 Comparisons of Pb isotopic compositions between sediments, mosses, and surface soils at Tingxi Reservoir

The lead isotopic compositions of the various samples collected at Xinfengjiang Reservoir have previously been discussed in Section 4.4. The results suggest that the air quality at Xinfengjiang Reservoir is deteriorated by the strong influences of regional air pollution. Industrial use of lead-containing ores in the PRD region and possible existence of Pb from past usage of leaded gasoline might have contributed substantial amount of anthropogenic lead in mosses and soils in the study area.

Luokeng Reservoir is located in the southwest region of Guangdong Province. Past investigations revealed that the lead isotopic ratios $^{206}Pb/^{207}Pb$ of geological materials in Guangdong, such as volcanic rocks and natural soils, generally ranged from 1.195 to 1.221 (Zhu *et al.*, 2001; Duzgoren-Aydin *et al.*, 2004). The results from the present study showed that the $^{206}Pb/^{207}Pb$ ratios of sediment samples were generally in the range of 1.227 ~ 1.234, which were slightly higher than the values of natural sources reported previously in Guangdong Province. Therefore, the sediments at Luokeng Reservoir are not likely to be contaminated significantly by anthropogenic lead, which can also be indicated by the high correlations between lead and major elements in the sediment profiles at the reservoir. The $^{206}Pb/^{207}Pb$ ratios of sediments thus possibly represent the values of geochemical backgrounds in the study area. The lead isotopic ratios of moss samples varied over a wide range from 1.183 to 1.228. The upper bound value was similar to those of the natural backgrounds while the lower bound value was lower. This might indicate some inputs of anthropogenic lead in mosses at Luokeng Reservoir. The anthropogenic lead is probably derived from the atmospheric inputs of air pollutants from regional emission sources.

In Hainan Province, several studies have been conducted to examine the lead isotopic compositions of geochemical backgrounds such as Au deposits and basalts. The ^{206}Pb/^{207}Pb ratios of the natural materials generally ranged from 1.190 to 1.213 (Tu *et al.*, 1991; Zhu *et al.*, 1995; Chang *et al.*, 2002). In the present study, the ^{206}Pb/^{207}Pb ratios of surface soils collected at Jianfengling Mountain near the Songtao Resevoir were found to be around 1.208 ~ 1.224, similar to the values reported in previous studies. The ^{206}Pb/^{207}Pb ratios of sediments at Songtao Reservoir were generally around 1.20, as high as the values of the natural sources. The sediments are thus not expected to be contaminated by anthropogenic lead. As previous results also indicated, the lead concentrations along the sediment cores were closely correlated with the major elements, reflecting the natural origin of lead in the sediments. Considering the moss samples, the lead isotopic compositions (*i.e.* ^{206}Pb/^{207}Pb ratios around 1.20) were also found to be quite similar to the values of reservoir sediments. This might reflect that the lead accumulated in mosses is derived from natural sources. There is thus no obvious sign of deterioration of air quality in the study area (*i.e.* Songtao Reservoir).

Based on the previous results (*i.e.* heavy metal distribution patterns, Pearson correlation analysis and lead isotopic analysis), it can be noticed that the sediments at Tingxi and Luokeng Reservoir are not likely to be contaminated by anthropogenic lead. However, the low $^{206}Pb/^{207}Pb$ ratios of mosses at these two reservoirs probably indicate that there are some anthropogenic inputs of lead from atmospheric deposition at the two reservoirs. Considering Songtao Reservoir, the $^{206}Pb/^{207}Pb$ ratios of both sediments and mosses were close to the values of natural backgrounds, possibly reflecting both the air quality and the aqueous environment are well conserved in this area. In contrast, the sediments at Xinfengjiang Reservior are significantly enriched by heavy metals, such as Cu, Pb and Zn. The atmospheric depositions of air pollutants from regional anthropogenic sources are considered to be the main contributing sources in this area. In summary, the air quality at Tingxi Reservoir, Luokeng Reservoir, and Xinfengjiang Reservoir is likely to be impaired in recent times, although no obvious contamination sign can be observed in sediment profiles of Tingxi Reservoir and Luokeng Reservoir. The only exception among the four remote reservoirs is Songtao Reservoir. It would be interesting to further investigate the air masses passing through these four reservoirs, which might have an influence on the air quality of the study areas.

5.3 Classification of Influencing Air Masses

Transport paths of air masses potentially influencing the study areas were analyzed by conducting air back-trajectory analysis. The three-day back trajectories ending at the four reservoirs were analyzed every six hours (local time 0, 6, 12, 18) for each day during the period of January 2006 to February 2007.

In Fig. 5.9(a) – (e), the mean clusters of back-trajectories of dominant air masses ending at Tingxi Reservoir are plotted for five representative time periods respectively. It can be seen that the reservoir was periodically influenced by four major air masses at an annual cycle, including 1) NIM – air masses originated from the inland Mongolia area, North and Northeast China; 2) NEC – air masses coming from the northeast region of Asia, advancing southwards along the southeast coastline; 3) SCS – air masses from the South China Sea; 4) SEA – air masses coming from the inland area or coastal regions of Southeast Asia. During January-March of 2006, the reservoir was mainly controlled by the air masses NIM and NEC, which were closely associated with the winter monsoons (Ding, 1994). Since the early April, the air masses SCS began to influence this area, concurrently with the impacts of air masses NEC. In July, the region was mostly dominated by air masses SCS and SEA, subject to strong impacts of Asian summer monsoons. The situation was maintained for about two months until the air masses NEC were back to prevail in late August. Since November till

February of the next year, the region was again markedly influenced by the intrusion of Siberian high from the north inland area of Asia. The periodic fluctuation of dominant air mass at Tingxi Reservoir was highly related to the season changes of climate with Asian monsoon activities. As it can also be noticed that the area was dominated by air masses NIM for nearly half of the year, suggesting its strong influences on the air quality of the study area.

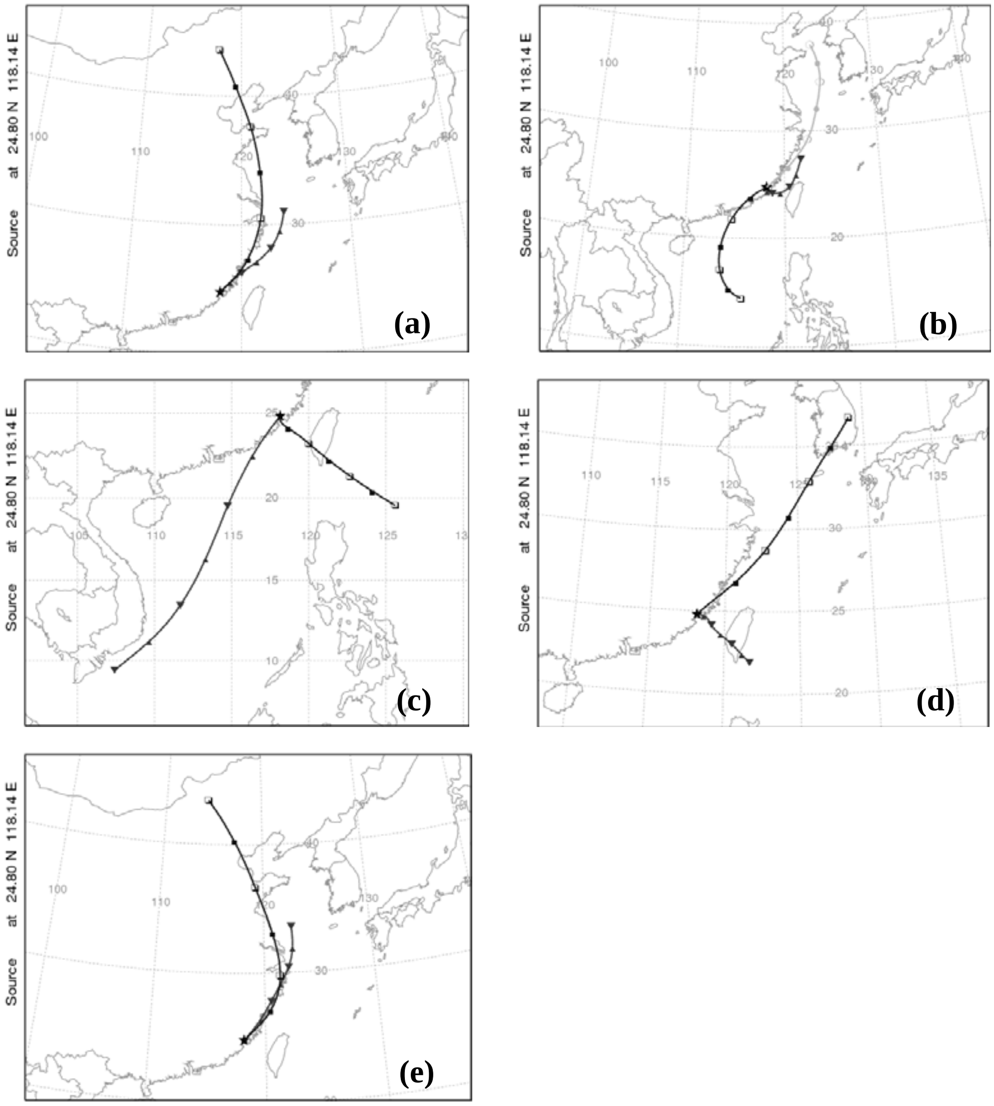


Figure 5.9 Cluster means of back trajectories ending at Tingxi Reservoir during different time periods: (a) Jan. 2006 – Mar. 2006; (b) Apr. 2006 – May. 2006; (c) Jun. 2006 – Jul. 2006; (d) Aug. 2006 – Oct. 2006; (e) Nov. 2006 – Feb. 2007

In Fig. 5.10(a) – (e), the mean clusters of dominant air back-trajectories ending at Xinfengjiang Reservoir during five different time periods are plotted respectively. The seasonal variation of prevailing air masses (*i.e.* NIM, NEC, SCS and SEA) at the reservoir was generally similar to that at Tingxi Reservoir, shifting in accordance with the seasonal advances and withdraws of Asian monsoons. Similar classifications of air masses were reported by Lee *et al.* (2005) in Nanling Mountain located in northern Guangdong.

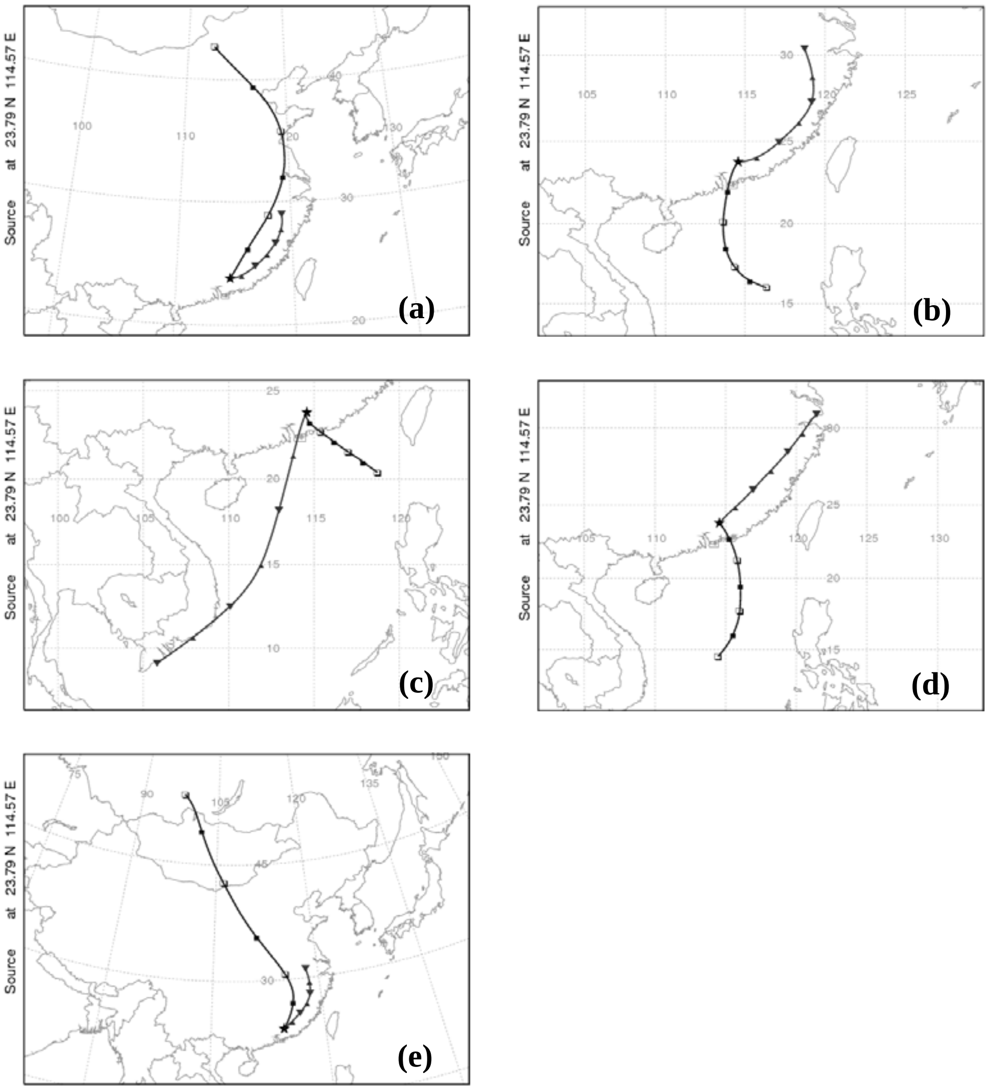


Figure 5.10 Cluster means of back trajectories ending at Xinfengjiang Reservoir during different time periods: (a) Jan. 2006 – Mar. 2006; (b) Apr. 2006 – May. 2006; (c) Jun. 2006 – Jul. 2006; (d) Aug. 2006 – Oct. 2006; (e) Nov. 2006 – Feb. 2007

In Fig. 5.11, the mean back-trajectories clusters of dominant air masses ending at Luokeng Reservoir during four representative time periods are presented. As the figures show, the reservoir was also influenced by the same prevailing air masses annually, including NIM, NEC, SCS and SEA. Although the seasonal variation patterns were generally similar to the previous two reservoirs, the durations of dominances by different air masses differed a bit. As the reservoir is located to the south of the Tropic of Cancer, the air masses NIM was dominant for only three months (from Nov. 2006 to Jan. 2007), which was much shorter compared to the cases at Tingxi and Xinfengjiang Reservoir. Starting from the February of 2006, the area had been dominated by the air masses NEC and SCS till the May. The area was then mostly controlled by the SCS and SEA during June-August, following which the air masses NEC began to prevail again. The dominance by air masses NEC at Luokeng Reservoir was observed for six months of a year.

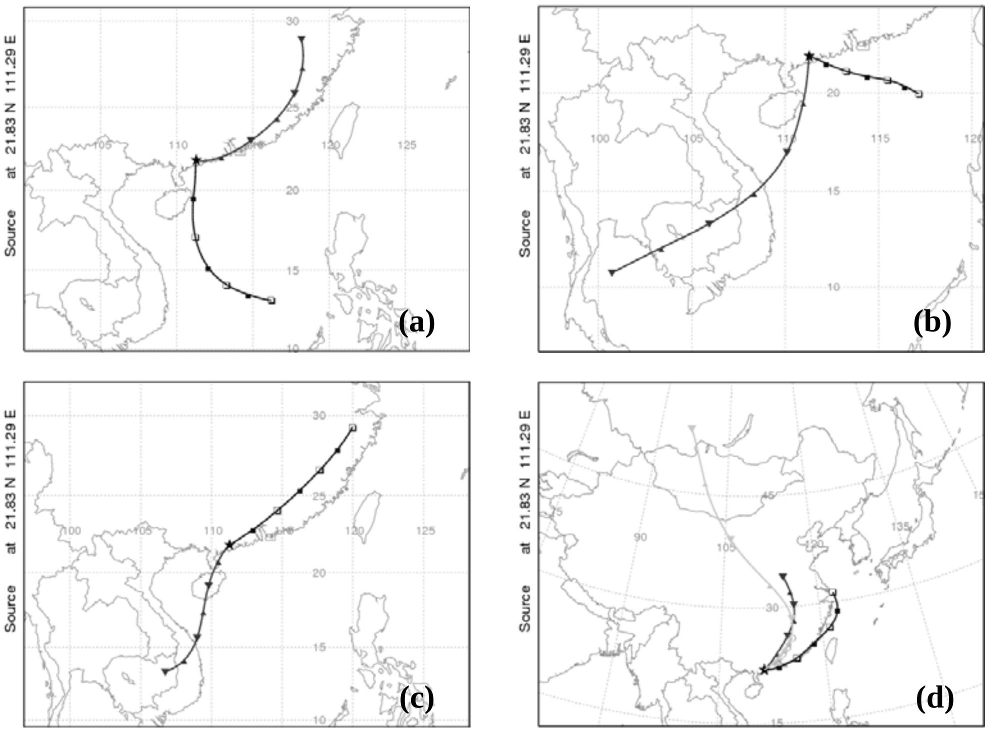


Figure 5.11 Cluster means of back trajectories ending at Luokeng Reservoir during different time periods: (a) Feb. 2006 – May. 2006; (b) Jun. 2006 – Aug. 2006; (c) Sep. 2006 – Oct. 2006; (d) Nov. 2006 – Jan. 2007

The mean clusters of dominant air back-trajectories influencing Songtao Reservoir are shown in Fig. 5.12(a) – (d) for four representative time periods respectively. The prevailing air masses and seasonal variation patterns were generally similar to those of Luokeng Reservoir, except that the time period dominated by the air masses NIM was further shortened to two months from December to January.

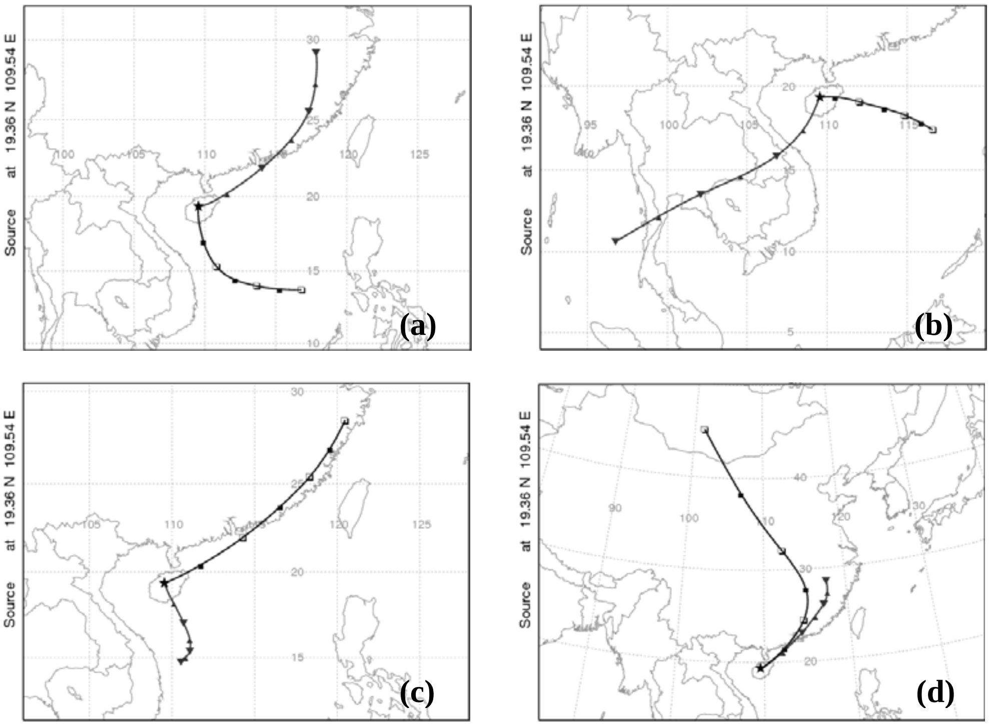


Figure 5.12 Cluster means of back trajectories ending at Songtao Reservoir during different time periods: (a) Feb. 2006 – May. 2006; (b) Jun. 2006 – Aug. 2006; (c) Sep. 2006 – Nov. 2006; (d) Dec. 2006 – Jan. 2007

In summary, all the four reservoirs are located in typical monsoon regions subject to seasonal variations of the climate. Tingxi Reservoir was dominantly influenced by air masses NIM originated from north inland area of Asia (*e.g.* Mongolia area and North China) and air masses NEC advancing southwards along the southeast coastline. The air masses SCS and SEA prevailed only for short periods and mostly came from the south coastal area. The air quality in this area might be influenced by air pollution from both the YRD region and PRD region. The situation was generally similar at Xinfengjiang Reservoir. However, the reservoir is located at a much shorter distance (about 150 km) from the PRD region than Tingxi Reservoir (over 500 km). Therefore, the impacts of air pollution from intensively industrialized PRD region on the air quality at

Xinfengjiang Reservoir might be more significant. At Luokeng Reservoir, the air masses NEC dominated for over half year time, suggesting strong potential impacts on the air quality at this reservoir. The air masses normally transported along the southeast coastal region, including the PRD region located at 260 km northeast of the reservoir. The intrusion period of air masses NIM during winter monsoons was comparatively shorter. Moreover, this area was also influenced by air mass SEA from inland or coastal regions of Southeast Asian countries. It was generally the same case at Songtao Reservoir except that this area was much farther away from the PRD region (around 560 km) while it was quite near to the Southeast Asian region (350-400 km). Therefore, the air pollutants released in Southeast Asian countries are possibly important contributing sources for potential impairment of air quality at Songtao Reservoir. As mentioned in Section 5.1.3, however, no obvious sign of air pollution was observed at this reservoir. This might be due to other influencing factors, which will be discussed in detail in the following section.

5.4 Other Possible Influencing Factors

As demonstrated in the previous section, the air quality of a specific remote area might be strongly affected by the prevailing air masses, especially those originated from or passing through intensively urbanized or industrialized areas. However, the case of Songtao Reservoir was an exception. On the other hand, many previous investigations revealed that undisturbed sediment cores were capable to assess the long-term atmospheric inputs of heavy metals into the freshwater ecosystems in the remote area (Blais and Kalff, 1993; Brannvall *et al.*, 1999; Renberg *et al.*, 2002; Yang and Rose, 2005; Shotbolt *et al.*, 2006). In the present study, nevertheless, the sediment cores at Tingxi and Luokeng Reservoir did not reflect the recent deterioration of air quality. It is then considered that there might be other influencing factors affecting the atmospheric transport, deposition and accumulation of heavy metals in aqueous sediments, such as the topographical conditions, climate, and specific characteristics of the reservoirs and their catchments. In Table 5.5, the key characteristics of the four remote reservoirs are listed and compared.

Table 5.5 Comparison of key characteristics of the four remote reservoirs

	Tingxi Reservoir	**Xinfengjiang Reservoir**	**Luokeng Reservoir**	**Songtao Reservoir**
Topographical conditions	Elevated in the north	Elevated in the north	Elevated in the northeast	Elevated in the northwest
Characteristic water level (m)	38.96 – 70.85 [a]	93 – 116 [b]	92.38 – 114 [b]	165 – 190
Climate	Subtropical monsoon	Subtropical monsoon	Tropical monsoon	Tropical monsoon
Temperature (ºC)	21 [c]	19.6 – 21.3 [d]	23 [e]	23.3 [f]
Annual precipitations (mm)	1059-2011.7 [c]	1694 – 1936 [d]	> 1600 [e]	1896.1 [g]
Area of reservoir water surface (km^2)	N.A.	370 [h]	N.A.	130 [g]
Catchment area (km^2)	100.8 [a, i]	5740 [b, h]	77 [b]	1496 [g]
Drainage ratio	N.A.	15.5	N.A.	11.5

a. Fujian College of Water Conservancy and Electric Power Website (assessed in August 2008);
b. Guangdong Bureau of Hydrology Official Website (assessed in August 2008);
c. Fujian Government Website in Agriculture and Technology (assessed in August 2008)
d. Heyuan Government Website in Agriculture (assessed in August 2008)
e. Maoming Bureau of Hydrology Official Website (assessed in August 2008)
f. Danzhou Government Official Website (assessed in August 2008)
g. Yang *et al.*, 2007
h. Ye, 2000;
i. Lv, 2007;

The topographical condition might be the most important factor influencing the transport of air masses and subsequently the entry of air pollutants in the study area. As the air back-trajectories shows, the air quality at Songtao Reservoir was likely to be influenced by polluted air masses coming from the Southeast Asia. Past investigations revealed that the leaded gasoline was still the major source of anthropogenic Pb in the atmosphere in most of the developing countries in the Southeast Asia, such as Thailand, Vietnam, Sri Lanka and Indonesia (Mukai *et al.*, 1993; Bollhofer and Rosman, 2002). However, it was noticed that Songtao Reservoir was elevated in the northwest region, which might prevent the intrusion of air masses transported from the Southeast Asia. In addition, the impacts from the PRD region might be insignificant due to the long distance (around 560 km). These possibly explain why a good air quality can be preserved at Songtao Reservoir.

Previous results suggest that the air quality at the other three reservoirs, namely Tingxi Reservoir, Xinfengjiang Reservoir, and Luokeng Reservoir, is probably deteriorated recently. Based on the data provided in Table 5.5, the altitude of the Xinfengjiang Reservoir is around 100 m, which is around the same level as Luokeng Reservoir. Compared to these two reservoirs, Tingxi Reservoir is located relatively lower. Nevertheless, the three reservoirs all belong to low-altitude reservoirs that air pollutants from both local and regional (or even by long-range transport) sources are readily to enter and influence the atmosphere over the study area. As the results from sediment profiles of metal concentrations indicated, however, that only the heavy metals in surface sediments of Xinfengjiang Reservoir were significantly elevated while the sediments at the other two reservoirs were not likely to be contaminated. It has been suggested that the fate of atmospheric particles and behavior of heavy metals in the atmosphere might be greatly influenced by some meteorological parameters, such as the temperature, humidity, rainfalls and winds (Querol *et al.*, 1997; Yatin *et al.*, 2000; Ragosta *et al.*, 2002). It can be noticed that the meteorological conditions are generally similar at these three reservoirs, including the monsoon climate, annual average temperature, and amount of precipitations. Therefore, the meteorological conditions are possibly not important influencing parameters.

As mentioned in Chapter 2, the reservoir catchment might play a significant role in deposition and transmission of heavy metals at both the terrestrial drainage basin and the freshwater system due to the specific characteristics of the natural surfaces, such as the soil pH, the abundance of Fe/Mn oxides and organic matters, clay content, cation exchange capacity with metal elements, and type of land use (Dillon *et al.*, 1988; Livett, 1988; Blais and Kalff, 1993; Church *et al.*, 2002; Shotbolt *et al.*, 2005). The contributions of atmospheric heavy metal inputs from the catchment might be appreciable in case of a reservoir with a large drainage ratio. As the data show in Table 5.5, the catchment area of Xinfengjiang Reservoir amounts to 5740 km^2, nearly 60-fold of the catchment area of Tingxi Reservoirs and over 70-fold of Luokeng Reservoir. Therefore, the transmission efficiency through the catchment might be a potential factor affecting the deposition and accumulation of heavy metals in the freshwaters, which may explain the different phenomena in sediment cores from the three reservoirs (*i.e.*

Tingxi Reservoir, Xinfengjiang Reservoir, and Luokeng Reservoir).

The subsequent accumulation and distribution of heavy metals in reservoir sediments involve many complicated reaction processes, which depend notably on the amount of scavenging materials, the affinity of metal elements for a particular ligand and their respective concentrations, as well as the redox potential and water pH (Livett, 1988; Gonzalez-Davila, 1995). Once more information on the aquatic environment is available, the distinct behaviors of heavy metals in the freshwater and sediments could be further investigated, which might be useful for explaining the inadequacy of sediment profiles as the geochemical archive to monitor historical atmospheric inputs of heavy metals at Tingxi Reservoir and Luokeng Reservoir.

CHAPTER 6 – CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Since the onset of industrialization periods worldwide, the drastic emissions of anthropogenic heavy metals have been endangering the air quality in both the urban and remote areas. Based on a multi-media approach, the present study was conducted to investigate the potential impacts of air pollution on the ecosystems of four typical remote areas (*i.e.* Tingxi Reservoir, Xinfengjiang Reservoir, Luokeng Reservoir, and Songtao Reservoir) along the South China coastal region, one of the most rapidly developing areas in China.

By analyzing the reservoir sediment cores, catchment soils, as well as moss samples, the major findings obtained at Xinfengjiang Reservoir were as follows:

1) At Xinfengjiang Reservoir, the trace metal concentrations were significantly elevated in surface sediments, especially for Cu, Pb and Zn. The Cu and Zn concentrations in the surface sediments were over fourfold higher than the values in bottom layers, while Pb concentrations were also elevated almost threefold. The enrichment of Ni was relatively insignificant.
2) The distribution patterns of major and trace elements were generally similar in bottom sediments. However, there was a decreasing trend of trace metal

concentrations with increasing depths in upper layers of sediments (0-20 cm) while a uniform pattern was observed for major elements.

3) When analyzing the relationships between trace metals and their respective normalizers (*e.g.* Fe), much more data points were found beyond the prediction intervals in the Cu-Fe, Pb-Fe and Zn-Fe plots; while only a few samples were observed above the upper limit in the Ni-Fe plot.
4) The type of moss species *Pogonatum contortum* collected in the present study were found to be effective in accumulating airborne heavy metals, thus would be a promising bioindicator for monitoring atmospheric heavy metal pollution.
5) By comparison of heavy metal concentrations in mosses between different regions, the atmospheric inputs of air pollutants in remote area of South China were found to be more significant than those in European countries.
6) The data set of lead isotopic compositions of mosses and soils presented a good linear relationship between the natural sources and anthropogenic sources.

The results from the other three remote reservoirs (*i.e.* Tingxi Reservoir, Luokeng Reservoir and Songtao Reservoir) when compared to the results at Xinfengjiang Reservoir revealed that:

1) There was no obvious contamination sign of sediments at Tingxi Reservoir, Luokeng Reservoir and Songtao Reservoir as the concentrations of trace

elements were closely associated with the lithogenic major elements Al and Fe.

2) The Cu, Pb and Zn concentrations in moss samples were found highest at Tingxi Reservoir, followed by Xinfengjiang Reservoir. The lowest heavy metal concentrations were observed in mosses from Songtao Reservoir.
3) The lead isotopic compositions of mosses at Songtao Reservoir were similar to the values of natural backgrounds. However, low ^{206}Pb/^{207}Pb ratios (around 1.17) were observed in mosses collected from Tingxi Reservoir and Luokeng Reservoir.
4) By air back-trajectory analyses, it was observed that the dominant influencing air masses and their seasonal patterns were generally similar at the four reservoirs. However, Xinfengjiang Reservoir might be subject to strong influences from the PRD region, while Songtao Reservoir was mainly influenced by air masses from South China Sea and Southeast Asia (*i.e.* far away from the PRD region).

Therefore, it can be concluded from this study that:

1) At Xinfengjiang Reservoir, the sediments are considered to be anthropogenically contaminated in the upper layers where significant elevation of heavy metal concentrations (*e.g.* Cu, Pb and Zn) occurred.
2) The enriched anthropogenic heavy metals in top sediments of Xinfengjiang Reservoir are probably derived from increasing atmospheric deposition of air

pollutants in recent years, which concurrently occurred in both the terrestrial catchment and the reservoir.

3) The regional transport of anthropogenic Pb emitted from industrial processes using lead-containing ores and coal combustion (with similar lead isotopic compositions to some of the lead ores) in the PRD region is probably the dominant contributing source at Xinfengjiang Reservoir. The long persistence of past-released Pb, possibly from vehicle exhausts of leaded gasoline, may also contribute to the total anthropogenic lead in the atmosphere.
4) The sediments at Tingxi Reservoir, Luokeng Reservoir, and Songtao Reservoir are not likely to be contaminated by anthropogenic heavy metals. However, the low ^{206}Pb/^{207}Pb ratios of mosses at Tingxi Reservoir and Luokeng Reservoir indicate that the atmosphere at the two reservoirs is probably impaired and there are some anthropogenic inputs of Pb in the surface environment via atmospheric deposition.
5) The inadequacy of the reservoir sediments as geochemical archives of the environment changes at Tingxi Reservoir and Luokeng Reservoir might be attributed to the low transmission efficiency through the reservoir catchments due to their small catchment areas, which may subsequently affect the deposition and accumulation of airborne heavy metals in the sediments of the two reservoirs. Further investigations need to be conducted to provide additional evidences.

6) The air quality is well preserved at Songtao Reservoir, which might be ascribed to the fact that the specific topographical condition of the reservoir (*i.e.* elevated in the northwest region) prevents the intrusion of polluted air masses coming from the Southeast Asia. Moreover, the impacts from the PRD region are possibly less significant due to the long distance.

6.2 Recommendations

With regard to the major findings obtained from the present study, several recommendations were proposed as follows:

1) Strict regulations or guidelines on emissions of air particulates from various anthropogenic sources, especially from industrial activities and vehicle exhaust emissions, should be established and enforced to alleviate further deterioration of air quality in South China.
2) As an important freshwater supply reservoir for residents living in the PRD region, the sediment quality at Xinfengjiang Reservoir should be carefully controlled to prevent potential impairment of water quality or adverse impacts on the ecosystems of the reservoir area.
3) The air quality in remote areas along the South China coastal region should be closely monitored to assess the significance of trans-boundary outflow fluxes of air pollutants (*e.g.* anthropogenic heavy metals).
4) As air pollution has become a global environmental issue, the governments in

adjacent regions or even countries should cooperate and coordinate together to work on effective pollution prevention and control measures.

5) The awareness of environmental pollution and its potential adverse impacts should be further promoted among the governments and the general public.
6) Considering selection of proper reservoirs as geochemical archives for environmental changes, the reservoirs with large catchment areas available (or large drainage ratios) should be preferred.

6.3 Future research

Based on the findings from this study, some suggestions for future research work are proposed.

1) The variation trend of heavy metal concentrations along the sediment cores at Xinfengjiang Reservoir was clearly shown by the sediment profiles. However, limited quantities of sediment samples did not allow the assessment of the chronology of collected sediment cores (*e.g.* the longest core WLH-D) by ^{210}Pb dating analysis. The selected sediment cores WLH-B, WLH-C and WLH-D for discussion were assumed to be accumulated without post-depositional disturbances. It is therefore suggested that some additional sediment cores could be collected for dating analysis, which may help to better interpret the historical variation trend of heavy metal inputs in sediments at Xinfengjiang Reservoir

2) In the present study, geochemical normalization of trace metal concentrations to a proper reference element (*i.e.* Fe) was adopted to account for the natural mineralogical and granulometric variations, and assess the magnitude of anthropogenic enrichments of heavy metals in the sediments at Xinfengjiang Reservoir. Nevertheless, the particle size distributions of the sediment samples were not determined. If additional sediment cores could be collected during future research study, it would be very useful to evaluate the size distribution of sediment particles, and assess the associations between metal concentrations and different particle sizes, which may provide further evidence on the influences by natural factors.
3) The sediment profiles of heavy metal concentrations at Xinfengjiang Reservoir showed that the heavy metals were significantly enriched by anthropogenic sources in upper layers of sediments, especially for Cu and Zn. While being a major sink for heavy metals, the sediments may also act as potential pollutant sources to the water body and aquatic biota. Therefore, further investigations on chemical partitioning of trace metals (*e.g.* Cu, Pb and Zn) in contaminated sediments of the reservoir by sequential extraction analysis are needed to investigate geochemical phases of trace elements in sediments, and provide information on the their mobility, bio-availability to living organisms, as well as the potential adverse impacts to the aquatic ecosystem.
4) The air qualities at the four remote reservoirs were effectively biomonitored

by moss samples in this study. However, most of the mosses collected belong to different species. It was thus infeasible to make direct comparisons of heavy metal concentrations in mosses between different sampling locations to assess the relative significance of atmospheric heavy metal deposition in the study area. It is suggested that a suitable widespread moss species should be selected as the biomarker for extensive and comprehensive moss survey at a national or even continental scale to provide a clearer picture of the current situation of atmospheric heavy metal pollution in remote areas of the South China coastal region. Moreover, additional information can also be obtained by simultaneous collection of aerosol samples in the study area.

5) Regarding the results of sediment cores and mosses at Tingxi Reservoir and Luokeng Reservoir, the sediment cores were found to be inadequate as environmental archives to reflect historical variations of atmospheric heavy metal inputs at these two reservoirs. It would thus be of great value to examine the causes by assessing the metal budgets of the whole reservoir systems, including the reservoir water areas and their catchments. The total atmospheric depositions to the receiving water and the terrestrial catchment area need to be determined by air sampling. Stream discharge and leaching fluxes from the catchment should also be evaluated. In addition, the catchment soil characteristics also need to be investigated. As a result, the retention capacity of the catchment and the net deposition fluxes of atmospheric heavy metals in the freshwater system can be estimated for

better understanding of the biogeochemical processes of heavy metals in the whole system.

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APPENDIX A – ANALYTICAL RESULTS OF SEDIMENT CORES

Table A-1 Metal concentrations (unit: mg/kg, dry weight) in sediment core TX-A from Tingxi Reservoir.

Depth (cm)	**Al**	**Fe**	**Co**	**Ni**	**Pb**	**Zn**
1	88300	26400	7.05	6.50	34.8	117
2	96100	27700	7.89	7.05	43.1	121
3	98200	27400	7.50	7.16	39.4	122
4	91800	25000	6.49	6.51	34.0	112
5	89800	24600	6.73	6.59	34.7	108
6	84700	25200	7.17	6.55	41.8	106
7	72600	23900	6.65	5.74	38.4	96.5
8	77300	24600	7.20	6.08	38.4	102
9	71300	23800	7.04	5.86	36.7	100
10	58700	22000	6.12	4.86	35.5	86.5
11	75090	24300	6.92	5.83	46.6	96.6
12	97200	25600	7.22	6.73	52.2	104
13	91000	24100	6.96	6.28	50.2	100
14	87000	24400	7.15	6.36	57.1	109
15	84200	25200	7.45	6.32	62.4	113
16	91500	26600	8.24	6.82	61.4	118
17	88000	24800	7.74	6.87	49.6	107
18	86300	24700	7.65	6.75	43.4	103
19	79300	24000	7.19	6.41	52.1	101
20	86300	24400	8.16	6.57	47.4	104
21	82200	23700	6.91	6.01	53.2	102
22	85100	25100	7.29	6.07	56.1	107
23	86700	25300	7.91	6.33	58.4	109
24	86300	25800	8.27	6.47	60.6	114
25	89500	26000	8.26	6.40	64.1	117
26	87400	25800	8.32	6.41	63.5	118
27	87800	26100	8.33	6.36	64.4	120
28	86600	26000	8.26	6.49	64.5	119
29	87800	26100	8.13	6.36	64.2	119
30	85100	26000	7.86	6.50	65.0	115
31	82000	25900	7.87	6.27	64.1	113
32	79000	25000	7.68	6.20	63	111

Table A-2 Metal concentrations (unit: mg/kg, dry weight) in sediment core TX-B from Tingxi Reservoir.

Depth (cm)	**Al**	**Fe**	**Co**	**Ni**	**Pb**	**Zn**
1	103000	29500	8.04	6.73	41.5	135
2	117000	32300	9.76	7.54	59.4	144
3	104000	27600	8.34	6.71	48.4	127
4	128000	31300	7.64	7.92	47.9	151
5	87400	23200	7.11	5.61	36.9	103
6	104000	27700	9.02	6.65	57.5	122
7	86900	26200	8.80	5.68	49.3	110
8	84900	26400	8.21	5.49	45.2	111
9	87900	27100	7.17	6.83	42.4	117
10	81600	24800	8.55	5.61	47.9	107
11	69900	23200	8.95	5.06	47.0	99.8
12	70200	22900	8.06	5.33	48.8	103
13	69200	22500	6.86	5.49	49.1	102
14	74400	23800	8.20	5.72	49.5	107
15	69900	21900	7.45	5.30	50.0	99.3
16	69700	22800	7.43	5.40	49.1	100
17	66200	22100	7.36	5.06	44.9	98
18	71600	23100	7.63	5.48	52.8	104
19	87400	27400	7.58	6.38	53.1	121
20	103000	26700	7.85	6.77	62.0	120
21	91000	23300	6.76	5.91	55.7	99
22	86800	23600	7.26	5.79	62.1	108
23	85600	23900	6.99	5.94	60.3	118
24	85600	24200	7.45	6.00	62.5	120
25	86000	24700	7.87	6.12	66.7	131
26	85200	24900	8.01	6.08	65.0	129
27	106000	28400	7.90	7.18	57.0	123
28	100000	27900	7.28	7.28	41.3	121
29	90900	23400	7.03	5.74	55.3	108
30	94900	25600	8.61	6.29	60.6	114
31	98100	27100	8.48	7.13	63.7	124
32	93700	25500	8.15	7.19	64.2	126
33	92400	26500	8.01	6.64	62.1	118
34	84000	26000	7.94	6.41	58.8	127
35	82100	25500	7.78	6.57	61.3	120
36	89800	28400	8.31	6.63	68.7	125
37	94100	29000	8.02	6.52	62.3	124
38	106000	28600	8.18	6.90	59.8	130
39	103000	27100	7.35	6.98	57.4	132

(cont.)

Depth (cm)	**Al**	**Fe**	**Co**	**Ni**	**Pb**	**Zn**
40	98700	26100	7.54	7.09	59.3	129
41	107000	28600	8.53	7.78	67.2	130
42	107000	27400	7.92	7.52	54.5	126
43	96900	26100	8.26	7.08	56.6	117
44	101000	27900	8.16	7.41	61.0	126
45	90100	24900	8.02	7.02	55.0	117
46	94700	28900	7.63	6.91	54.2	116

Table A-3 Metal concentrations (unit: mg/kg, dry weight) in sediment core TX-C from Tingxi Reservoir.

Depth (cm)	**Al**	**Fe**	**Co**	**Ni**	**Pb**	**Zn**
1	90500	24800	7.59	7.18	45.4	114
2	83700	23300	7.30	6.78	43.7	110
3	88100	24600	7.86	7.20	47.3	113
4	90800	25000	7.22	7.24	46.7	119
5	94500	26100	8.11	7.58	49.8	121
6	88800	25600	8.23	7.32	49.8	117
7	88300	25400	8.21	7.38	50.0	118
8	87100	25100	8.10	7.25	49.5	120
9	89500	25700	8.52	7.29	49.3	113
10	90900	25700	8.46	7.49	50.5	121
11	92900	26200	7.37	7.73	50.6	126
12	89400	25200	7.80	7.45	49.5	115
13	85500	24500	7.52	7.11	47.1	116
14	88200	24200	6.82	6.36	43.9	109
15	89700	24700	7.05	6.34	45.4	110
16	86600	24100	6.75	6.40	45.3	106
17	89700	24600	6.14	6.53	44.9	109
18	89500	24700	6.56	6.41	44.6	109
19	86000	24000	6.05	6.27	43.4	106
20	86800	24300	6.61	6.13	44.4	105
21	80500	23100	6.91	6.36	43.1	101
22	89000	23200	6.78	5.72	42.8	98.2
23	79500	22900	6.78	5.82	44.2	101
24	77700	23000	6.46	5.68	44.2	106
25	68800	21600	6.77	4.98	41.6	93.5
26	60200	20100	5.43	4.07	36.0	79.5
27	65300	22300	5.75	5.14	42.8	100
28	68500	22500	6.93	5.19	43.6	97.2
29	64400	22000	5.46	4.96	42.0	97.9
30	75500	24000	5.63	5.65	48.5	104

Table A-4 Metal concentrations (unit: mg/kg, dry weight) in sediment core WLH-A from Xinfengjiang Reservoir.

Depth (cm)	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
0.5	--	--	--	--	--	--
1.0	124000	35600	44.0	17.8	47.3	159
1.5	--	--	--	--	--	--
2.0	114000	34800	42.1	15.6	45.3	152
2.5	--	--	--	--	--	--
3.0	119000	38500	33.1	12.5	48.1	129
3.5	--	--	--	--	--	--
4.0	120000	31500	23.2	10.1	50.9	97
4.5	--	--	--	--	--	--
5.0	124000	33600	25.0	12.9	51.9	108
5.5	--	--	--	--	--	--
6.0	117000	34600	25.2	15.5	45.3	104
6.5	--	--	--	--	--	--
7.0	115000	33800	25.8	13.8	45.2	112
7.5	--	--	--	--	--	--
8.0	112000	33800	26.4	14.1	39.2	110
8.5	--	--	--	--	--	--
9.0	115000	33900	26.6	14.0	33.6	103
9.5	--	--	--	--	--	--
10	125000	33000	19.8	11.3	33.0	88.4
11	121000	33400	19.7	11.6	35.9	85.9
12	126000	34400	22.7	13.1	37.0	102
13	130000	36400	24.5	13.9	36.5	103
14	125000	35600	22.2	13.7	30.0	95.9
15	130306	36900	21.3	13.3	31.0	91.4
16	127172	35400	19.9	13.2	33.5	89.8
17	132000	38000	24.1	15.8	32.5	96.3
18	122000	36600	21.3	14.6	28.3	82.1
19	128000	38000	20.7	13.9	29.4	85.0
20	109000	36200	20.5	13.3	32.2	77.3
21	116000	37300	21.0	13.8	30.1	82.1
22	116000	37500	21.9	14.9	32.3	85.6
23	112000	36500	22.4	15.4	30.2	85.1
24	103000	35100	23.0	16.0	28.5	83.7
25	105000	36300	24.6	17.1	29.4	88.2
26	83600	31800	28.3	19.3	27.1	85.3
27	74300	28900	26.7	18.8	30.7	80.7
28	71400	29200	29.8	19.6	32.6	86.3
29	72900	27600	29.2	18.2	31.5	83.4

(cont.)

Depth (cm)	**Al**	**Fe**	**Co**	**Ni**	**Pb**	**Zn**
30	74900	29500	29.5	20.4	26.4	85.6
31	79100	29600	28.0	19.9	23.3	87.7
32	60600	23900	22.7	15.6	21.2	70.5

Table A-5 Metal concentrations (unit: mg/kg, dry weight) in sediment core WLH-B from Xinfengjiang Reservoir.

Depth (cm)	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
0.5	118000	32300	41.5	17.0	46.8	146
1.0	115000	34300	41.2	17.8	33.3	145
1.5	115000	34000	60.4	20.3	44.3	186
2.0	120000	32000	31.5	10.4	49.6	124
2.5	114000	38300	28.0	11.2	43.2	119
3.0	121000	36900	33.6	11.7	48.8	134
3.5	115000	36500	29.8	11.3	46.7	129
4.0	125000	32500	36.3	14.4	46.8	130
4.5	127000	32200	26.3	11.7	42.6	116
5.0	127000	33600	18.7	9.8	46.1	101
5.5	124000	33300	22.6	12.7	48.6	109
6.0	128000	33400	23.2	12.8	48.5	114
6.5	124000	35800	22.7	15.5	38.8	106
7.0	125000	34100	27.0	14.5	48.7	117
7.5	114000	35100	27.1	15.7	48.6	117
8.0	118000	34100	26.4	14.9	38.1	121
8.5	129000	33700	19.1	11.7	34.2	101
9.0	116000	34500	29.0	16.0	39.0	115
9.5	120000	33500	23.4	13.8	31.9	107
10	120000	35100	28.0	15.5	31.2	106
11	120000	33600	22.5	13.5	30.2	98.5
12	119000	33300	19.1	13.0	32.1	92.3
13	123000	33900	21.8	13.5	32.5	97.3
14	124000	35200	21.6	14.2	34.4	103
15	108000	34400	19.7	12.9	35.0	87.7
16	101000	32300	20.3	13.5	36.4	84.4
17	114000	32200	19.7	14.0	30.5	85.5
18	113000	33300	19.6	14.5	26.8	81.9
19	112000	31800	17.9	12.5	30.8	79.7
20	100000	28300	16.1	12.0	31.3	74.2
21	93200	27000	17.5	12.8	32.0	72.9
22	81100	23600	15.4	11.4	32.9	65.2
23	71100	21100	16.6	11.5	58.0	66.2
24	45400	11800	7.96	5.65	24.8	38.2
25	49100	10400	6.68	5.19	27.5	38.9
26	50600	10800	7.47	5.65	43.9	43.6

Table A-6 Metal concentrations (unit: mg/kg, dry weight) in sediment core WLH-C from Xinfengjiang Reservoir.

Depth (cm)	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
0.5	114000	36900	55.2	19.7	42.4	159
1.0	106000	39100	57.5	20.7	36.3	172
1.5	113000	38400	39.4	13.3	34.3	128
2.0	120000	38500	36.4	11.8	37.5	129
2.5	117000	33800	40.4	14.2	39.5	143
3.0	106000	34600	30.7	12.0	40.1	100
3.5	123000	34700	21.8	9.81	37.2	91.5
4.0	114000	33500	23.5	10.5	38.9	97.5
4.5	118000	34800	25.6	11.9	38.6	111
5.0	110000	36400	23.3	13.0	30.8	94.5
5.5	110000	37000	32.8	16.3	39.7	113
6.0	119000	37200	31.8	15.2	40.9	126
6.5	118000	37500	30.3	16.0	36.1	127
7.0	124000	38500	24.2	12.3	33.5	112
7.5	126000	36800	23.4	12.7	28.0	114
8.0	111000	36500	34.8	18.2	39.1	129
8.5	124000	36300	20.4	11.8	24.6	98.6
9.0	117000	36900	31.7	16.2	27.4	108
9.5	98400	34500	20.3	12.3	27.4	84.8
10	114000	34600	17.1	11.5	25.7	86.3
11	101000	35800	22.7	11.8	31.2	87.6
12	118000	37100	26.3	15.0	27.3	107
13	122000	36500	22.4	13.6	29.6	107
14	112000	37100	20.8	13.5	28.1	102
15	125000	37400	20.0	13.6	20.9	97.2
16	118000	36000	23.7	15.3	25.3	101
17	116000	36000	21.2	14.3	23.2	90.9
18	109000	36300	19.9	13.3	22.8	85.7
19	95000	33300	15.0	10.3	22.8	76.8
20	77400	30100	11.5	6.35	24.0	71.3
21	59800	25200	10.3	3.69	24.6	64.1

Table A-7 Metal concentrations (unit: mg/kg, dry weight) in sediment core WLH-D from Xinfengjiang Reservoir.

Depth (cm)	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
0.5	--	--	--	--	--	--
1.0	109000	37900	50.7	21.1	51.1	163
1.5	105000	36000	46.6	17.2	42.5	142
2.0	93700	38800	59.9	22.1	45.7	192
2.5	109000	39200	56.6	20.3	42.6	187
3.0	113000	43900	50.9	17.5	47.1	171
3.5	114000	42000	46.6	15.2	47.3	152
4.0	118000	40000	50.2	16.4	48.3	160
4.5	99800	37800	43.4	16.6	54.5	143
5.0	112000	37500	41.1	14.8	52.9	126
5.5	110000	36900	38.9	15.1	53.8	121
6.0	121000	39000	36.5	16.1	46.1	116
6.5	114000	39600	36.5	17.2	47.0	121
7.0	121000	40600	37.3	17.7	49.9	124
7.5	124000	39800	40.3	17.8	47.7	130
8.0	118000	40400	34.1	16.9	42.0	131
8.5	120000	38200	35.4	14.8	35.9	110
9.0	115000	39000	51.8	18.8	47.1	130
9.5	110000	39700	36.0	16.5	39.5	114
10	122000	39200	39.7	16.1	30.6	105
11	121000	37900	34.5	15.7	32.2	100
12	119000	39300	31.9	15.4	39.0	97.4
13	120000	36300	24.9	15.0	33.2	97.1
14	121000	36300	23.9	14.6	34.8	100
15	119000	36100	22.2	14.3	32.1	94.2
16	120000	36300	22.2	15.0	28.4	86.0
17	112000	35000	22.9	15.7	27.4	81.1
18	97200	31000	20.2	13.4	25.0	68.0
19	95700	30600	21.4	14.7	29.3	65.8
20	64400	24100	20.9	14.3	27.0	60.6
21	22800	10200	8.80	6.50	17.0	33.7
22	20100	9320	8.40	6.00	15.2	27.3
23	17100	7930	6.70	5.00	14.0	26.3
24	16400	9050	6.50	4.70	12.5	23.9
25	18000	8000	7.20	4.90	17.6	25.5
26	44000	15900	11.0	7.90	18.5	41.3
27	97600	30600	19.7	14.2	25.1	70.5
28	77900	25400	17.0	11.3	24.9	55.5
29	78200	26100	19.8	13.8	26.1	64.7

(cont.)

Depth (cm)	**Al**	**Fe**	**Co**	**Ni**	**Pb**	**Zn**
30	29100	12000	10.3	7.40	18.4	33.1
31	18400	9260	7.70	5.30	14.5	28.2
32	17000	8020	6.90	5.10	13.3	23.4
33	15600	7680	6.50	4.80	11.9	22.4
34	20900	9380	8.00	6.10	15.2	27.3
35	18900	8790	7.30	5.30	12.8	24.6
36	16300	8050	7.30	5.00	14.8	26.8
37	17000	8230	7.70	5.40	13.7	24.8
38	18600	8670	7.70	5.50	13.8	28.1

Table A-8 Metal concentrations (unit: mg/kg, dry weight) in sediment core LK-A from Luokeng Reservoir.

Depth (cm)	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
1	124000	25700	5.71	3.99	36.2	70.2
2	105000	26400	6.92	4.36	33.8	68.9
3	124000	26500	5.67	4.58	24.1	76.3
4	116000	27500	6.51	4.50	23.9	81.1
5	124000	28200	5.56	4.75	21.5	80.5
6	113000	27800	6.59	4.72	24.8	75.9
7	117000	27200	5.51	4.40	22.9	77.0
8	107000	26500	6.02	4.01	24.0	76.3
9	99300	25800	4.98	3.13	21.9	78.8
10	93400	25400	3.95	2.61	19.9	79.1
11	91600	26000	6.54	2.33	17.7	84.6
12	84900	24800	4.49	2.18	18.4	81.7
13	83300	24700	4.70	2.26	18.1	80.1
14	95200	25700	4.65	2.98	17.7	75.2
15	112000	27600	6.19	4.06	19.7	74.6
16	104000	25700	4.27	3.50	18.6	73.1
17	99700	25700	3.58	2.92	18.0	75.1
18	80800	24800	3.03	2.19	18.5	77.6
19	89700	24800	3.31	2.56	16.4	74.6
20	110000	26500	4.67	4.03	18.5	72.8
21	115000	27300	5.48	4.78	20.6	72.2
22	107000	24400	3.74	3.49	17.9	68.3
23	112000	24900	4.31	3.88	20.9	67.3
24	109000	25200	5.80	3.74	19.8	65.9
25	115000	26200	5.17	4.27	20.9	67.5
26	119000	25700	4.68	3.88	23.0	72.3
27	114000	24800	3.74	3.72	26.5	68.0
28	121000	24900	3.83	3.90	27.7	71.5
29	113000	24600	2.60	3.61	23.4	69.0
30	103000	23500	3.48	3.49	20.3	65.9
31	60500	16600	1.95	1.60	14.4	55.3
32	57600	16000	2.12	1.35	11.2	52.4
33	50700	16200	2.80	1.13	15.3	54.1
34	42800	12300	2.39	0.91	12.5	41.1
35	38500	11000	2.34	0.86	11.7	38.6
36	38900	11200	1.78	1.00	12.2	42.1
37	39700	10900	3.27	1.01	10.8	40.5

Table A-9 Metal concentrations (unit: mg/kg, dry weight) in sediment core LK-B from Luokeng Reservoir.

Depth (cm)	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
1	112000	19700	5.67	3.60	37.4	66.8
2	115000	21900	6.66	3.91	40.3	71.9
3	119000	20900	6.17	3.84	38.4	67.8
4	122000	21700	6.29	3.82	35.8	69.3
5	119000	20000	7.95	3.37	39.2	70.2
6	107000	21600	8.03	4.32	32.8	81.7
7	108000	21600	8.37	4.28	32.5	74.5
8	106000	22200	7.67	4.41	32.9	74.4
9	106000	22100	7.30	4.40	31.1	74.3
10	104000	21200	6.91	3.94	31.5	72.3
11	106000	21100	6.78	5.84	33.0	74.4
12	81600	17900	6.34	3.11	29.1	60.7
13	69100	16300	4.97	2.59	26.4	62.3
14	58300	15000	4.73	2.26	23.8	56.2
15	32000	10900	2.96	1.40	13.2	42.8
16	67800	16600	5.29	2.52	22.9	56.1
17	91600	19200	6.26	3.38	29.1	65.6
18	98200	20300	6.25	3.41	31.0	71.0
19	91200	19500	5.96	3.25	30.6	67.7
20	84700	18900	5.85	2.93	30.5	64.9
21	79000	18200	5.52	2.63	28.5	67.1
22	98000	20400	6.42	3.36	33.1	72.2
23	107000	21400	6.72	3.89	32.1	70.4
24	112000	22500	7.12	4.11	33.9	70.0
25	114000	23400	7.08	4.39	34.7	76.2
26	105000	20600	6.26	3.75	33.0	67.5
27	104000	20900	7.17	3.58	34.0	71.2
28	104000	21100	6.99	3.95	34.6	69.8
29	97600	19700	6.37	3.47	32.7	64.7
30	101000	20200	6.43	3.56	35.6	67.5
31	108000	20700	6.58	3.71	36.2	66.5
32	110000	19900	6.58	3.99	34.0	61.9
33	121000	21100	6.60	4.13	35.6	65.8
34	105000	19500	6.33	3.59	36.6	62.2
35	105000	20100	6.17	3.23	36.1	63.8
36	94100	19600	5.80	2.97	34.2	66.2
37	93100	20300	5.92	3.59	32.7	61.8
38	107000	23400	6.35	3.52	35.3	63.4
39	99200	20700	6.13	3.38	33.7	61.4

(cont.)

Depth (cm)	**Al**	**Fe**	**Co**	**Ni**	**Pb**	**Zn**
40	109000	21800	6.59	3.79	33.6	63.6
41	109000	21300	7.82	3.84	33.9	61.9
42	118000	22400	7.82	4.30	35.5	67.7
43	124000	21800	7.05	4.01	38.2	69.1
44	113000	20300	6.91	3.60	39.1	65.2
45	115000	19300	6.54	3.37	43.4	68.6
46	124000	19600	6.90	3.71	43.7	68.8
47	97000	19300	6.30	3.09	31.2	60.0
48	95500	20200	6.15	3.25	29.0	64.2
49	74600	18200	5.69	2.66	25.0	62.7
50	99900	20500	6.34	3.15	34.1	68.8
51	98600	20600	6.24	3.14	34.3	67.8
52	106000	21900	6.51	3.32	33.1	67.6
53	124000	22600	6.22	3.91	33.9	62.2
54	113000	20900	5.89	2.55	31.3	60.6
55	92200	21300	5.88	2.33	25.2	57.2

Table A-10 Metal concentrations (unit: mg/kg, dry weight) in sediment core LK-C from Luokeng Reservoir.

Depth (cm)	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
1	131000	22200	6.65	3.57	41.9	76.4
2	134000	24900	6.96	3.78	41.6	81.0
3	128000	21400	5.64	3.35	38.7	69.8
4	132000	23100	6.30	3.50	36.4	73.2
5	130000	22300	6.25	3.31	37.4	71.4
6	133000	20900	8.23	2.95	42.3	74.7
7	121000	22800	8.54	3.81	34.1	84.2
8	129000	24500	8.41	4.23	34.0	90.6
9	114000	22800	7.48	3.86	33.8	82.7
10	114000	23000	7.17	3.74	32.7	80.3
11	89200	19200	5.67	2.84	27.1	63.5
12	111000	21900	6.71	3.58	32.4	73.7
13	108000	21300	6.97	3.33	32.8	70.9
14	103000	21600	6.84	3.07	33.9	71.1
15	75000	17500	5.01	2.26	26.3	63.5
16	71600	17200	4.72	1.98	27.7	64.7
17	28300	9880	2.12	0.63	12.5	34.5
18	24100	10900	2.81	0.73	11.7	34.0
19	31600	11900	2.71	0.82	13.8	41.7
20	60500	15200	4.05	1.58	20.3	49.3
21	98800	20600	5.86	2.87	29.8	70.0
22	107000	21500	6.24	3.15	31.7	72.5
23	108000	21800	5.98	2.89	32.1	75.3
24	97700	20600	5.60	2.49	31.2	74.8
25	96800	21000	6.64	2.46	31.7	74.5
26	84800	18200	5.15	2.17	25.8	60.8
27	109000	21000	5.96	3.11	29.7	67.1
28	109000	20500	6.13	3.12	29.2	66.8
29	107000	20300	6.24	3.14	29.5	62.8
30	116000	21900	6.76	3.50	30.8	67.2
31	107000	20500	6.22	3.20	30.5	63.0
32	101000	19700	6.08	2.88	30.4	61.1
33	91300	18300	5.07	2.38	27.9	61.4
34	85500	17100	4.86	2.19	27.5	57.8
35	94300	17800	4.75	2.39	31.0	59.1
36	90600	17000	4.64	2.29	30.6	57.4
37	93800	17700	4.95	2.37	32.8	60.8
38	104000	18700	5.70	2.84	31.0	60.0
39	121000	20400	5.66	3.17	31.1	67.7

(cont.)

Depth (cm)	**Al**	**Fe**	**Co**	**Ni**	**Pb**	**Zn**
40	108000	18700	5.43	2.93	34.0	62.8
41	107000	19400	5.27	2.70	34.2	67.0
42	98500	19200	5.09	2.31	34.0	63.1
43	96700	19600	5.17	2.11	36.0	65.3
44	92800	19300	5.19	2.01	34.1	65.4
45	84100	18500	5.07	1.88	32.7	63.4
46	77100	17700	4.18	1.81	29.0	59.8
47	79600	17200	4.59	2.06	25.5	52.4
48	97700	18300	4.84	2.36	31.0	59.9
49	110000	18600	4.82	2.39	33.5	62.7
50	91300	18400	5.96	2.37	26.1	57.6

Table A-11 Metal concentrations (unit: mg/kg, dry weight) in sediment core ST-A from Songtao Reservoir.

Depth (cm)	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
1	104000	35200	29.0	18.5	22.9	103
2	81000	29100	21.4	14.7	19.0	84.2
3	89800	32800	27.1	17.5	22.4	92.1
4	81100	30100	24.4	16.5	20.3	87.7
5	72500	29600	24.9	16.8	23.8	90.3
6	75700	30000	25.3	16.9	23.5	94.4
7	75900	30100	24.7	16.7	22.8	93.5
8	73300	29400	24.8	16.5	22.3	90.1
9	77600	31100	26.6	17.3	23.4	93.7
10	76200	30500	25.9	17.1	21.2	89.8
11	89800	37200	32.2	19.5	24.4	102
12	90200	40100	33.7	19.8	27.7	104
13	93200	42400	35.8	20.9	27.5	109
14	96500	41800	35.5	21.7	29.4	115
15	90400	34300	27.6	18.7	24.2	100
16	77200	30700	23.6	16.9	22.3	93.0
17	84400	35600	30.7	19.7	25.7	104
18	98900	40900	36.1	22.4	28.8	121
19	86300	32500	27.6	18.8	25.4	99.6
20	70900	28600	22.7	16.4	24.2	88.5
21	56000	24700	19.7	14.4	22.4	76.2
22	57000	25000	19.6	14.3	20.5	75.8
23	81900	34900	31.1	20.4	27.7	98.4
24	76800	31000	25.3	17.6	24.0	91.9
25	71500	29400	24.2	16.4	25.5	92.8
26	76100	31300	25.4	17.9	25.2	93.2
27	75600	31700	26.7	17.4	24.5	94.4
28	77700	37800	33.6	20.5	26.1	95.1
29	88000	39300	31.5	20.1	27.2	101
30	101000	40000	37.7	24.5	34.2	114
31	101000	41300	33.9	22.8	32.0	114
32	104000	41200	33.6	22.2	28.6	111
33	105000	42300	35.2	23.9	29.1	116
34	101000	40300	36.0	24.4	29.7	111
35	95000	35500	30.9	22.0	27.1	104
36	74100	32300	27.1	19.5	26.5	96.7
37	75800	32900	28.1	19.5	27.5	99.0
38	84600	35000	30.2	21.3	28.1	105
39	75600	33900	28.8	20.5	26.4	96.3

(cont.)

Depth (cm)	**Al**	**Fe**	**Co**	**Ni**	**Pb**	**Zn**
40	97100	44000	38.9	24.9	29.2	107
41	106000	45400	35.7	23.3	29.9	106
42	93300	42400	34.6	23.5	29.5	108
43	108000	44100	36.3	24.7	29.5	117
44	96800	39300	32.7	23.5	29.6	111
45	88200	35100	28.4	21.1	27.9	103
46	79600	32400	26.5	19.1	25.1	94.0
47	80700	33800	27.3	20.0	28.7	97.5
48	78300	33400	27.7	19.4	28.2	96.4
49	77600	33400	26.0	18.9	26.8	92.8
50	80300	34100	29.4	20.5	27.4	95.2
51	96700	42500	38.0	25.2	28.6	102
52	107000	46600	43.5	27.9	29.5	108
53	107000	42800	39.8	26.4	33.6	116
54	110000	44500	42.4	26.9	31.8	114
55	102000	39800	37.9	24.2	30.2	111
56	110000	44700	42.2	26.7	30.7	111
57	99000	38600	34.2	24.2	27.7	102

Table A-12 Metal concentrations (unit: mg/kg, dry weight) in sediment core ST-B from Songtao Reservoir.

Depth (cm)	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
1	110000	41500	33.3	22.6	25.2	111
2	107000	39000	32.9	22.9	24.7	107
3	83500	34300	31.5	21.2	28.7	104
4	78600	33700	29.5	20.4	27.1	101
5	89200	36100	30.2	21.6	29.5	109
6	80300	33400	27.5	20.2	27.7	103
7	81700	33500	28.9	20.3	27.0	106
8	82300	34800	29.0	20.4	27.9	103
9	85400	34300	29.4	20.6	28.2	109
10	78800	33100	29.3	20.6	28.1	103
11	84800	35000	30.0	21.2	29.5	107
12	77200	33100	28.0	20.1	26.9	101
13	88800	35400	30.4	21.5	29.4	113
14	81600	33500	29.7	21.0	28.9	107
15	83100	34400	30.8	21.1	29.0	109
16	82500	34400	30.8	21.4	29.6	112
17	80700	33500	28.9	20.6	28.9	106
18	84100	34200	31.0	21.3	30.0	110
19	81100	34700	29.5	20.9	27.7	106
20	89200	35900	31.0	21.6	29.3	113
21	86100	34700	30.4	20.9	29.1	109
22	86100	34800	30.2	20.8	29.7	105
23	83900	34300	29.4	21.1	29.3	106
24	75900	32900	28.8	19.7	28.0	100
25	82800	34200	29.4	20.2	28.1	108
26	79700	33100	28.4	19.7	27.0	101
27	77000	32900	27.6	19.6	27.1	98.9
28	72700	32400	26.6	19.0	25.8	94.8
29	57600	26000	20.1	15.5	21.1	75.5
30	77200	40200	32.7	23.8	27.8	97.1
31	93400	52500	46.4	30.8	32.5	120
32	92500	60600	45.9	28.0	32.7	115
33	107000	41900	34.7	23.8	27.9	113
34	103000	45400	41.5	28.5	31.1	120
35	97800	49600	46.5	31.5	30.9	112
36	99500	56900	51.3	32.7	35.1	119
37	106000	45200	43.6	29.7	30.9	112
38	97600	47600	47.9	32.8	30.2	111
39	94900	38200	37.0	25.4	31.2	115

(cont.)

Depth (cm)	**Al**	**Fe**	**Co**	**Ni**	**Pb**	**Zn**
40	87000	35900	32.1	22.2	30.5	109
41	83600	34300	31.0	21.9	29.3	108
42	79000	32900	30.2	20.8	29.4	104
43	81900	33100	30.0	21.4	29.2	103
44	77200	32200	28.6	20.4	27.2	102
45	76800	32700	29.9	21.0	28.4	103
46	79200	32200	29.1	20.8	28.5	104
47	73300	32200	29.1	20.5	28.4	102
48	80800	33100	29.3	20.8	28.0	103
49	75300	33000	29.4	20.7	28.4	102
50	78400	32800	28.6	20.7	28.9	103

Table A-13 Metal concentrations (unit: mg/kg, dry weight) in sediment core ST-C from Songtao Reservoir.

Depth (cm)	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
1	97400	34300	24.3	17.2	13.0	101
2	91700	34800	26.8	18.1	15.9	103
3	93200	40100	31.8	20.9	21.6	115
4	97100	43200	35.7	21.7	19.2	123
5	86100	41200	33.3	21.0	22.9	116
6	84600	36000	26.3	18.5	16.5	103
7	89600	36100	27.4	19.2	15.5	107
8	72300	34400	30.0	19.6	24.4	103
9	73400	34400	29.7	19.5	23.9	102
10	98000	37200	31.5	21.1	21.0	110
11	98400	37100	30.7	21.4	21.6	113
12	98700	38100	32.0	21.4	23.5	113
13	88900	37000	32.6	21.5	22.1	113
14	96300	39400	33.9	22.0	20.1	114
15	99100	41400	34.9	21.8	16.7	111
16	97200	41500	31.0	21.1	17.1	107
17	88000	40700	32.7	21.2	21.5	109
18	93900	38500	30.4	21.3	20.8	110
19	81500	37200	34.6	22.1	22.4	108
20	98900	38700	32.4	22.0	16.7	108
21	105000	41200	36.4	23.5	18.3	112
22	98200	39600	34.8	23.0	19.9	112
23	97200	38500	33.5	22.6	21.7	112
24	97800	38300	35.2	22.8	19.4	112
25	101000	38900	35.4	22.4	16.2	108
26	81600	39300	36.3	22.9	21.9	106
27	99500	38100	32.4	20.1	14.3	101
28	95800	36500	29.9	19.8	14.3	101
29	89900	35600	29.6	19.8	14.8	95.7
30	95000	35800	29.9	19.6	13.5	98.0
31	90100	35000	30.7	20.0	13.6	95.1
32	95000	35300	29.7	19.4	14.9	93.5
33	90100	32700	25.7	18.2	14.0	83.0
34	85900	30900	24.7	17.4	13.2	80.9
35	79600	29500	23.4	16.6	14.2	80.6
36	72200	28200	20.4	15.3	14.2	75.2
37	72900	29900	23.4	17.0	14.9	83.0
38	70700	29800	21.0	16.3	14.4	83.8
39	83000	34600	26.5	18.5	12.2	98.2

(cont.)

Depth (cm)	**Al**	**Fe**	**Co**	**Ni**	**Pb**	**Zn**
40	85000	35300	27.0	18.9	12.6	98.9
41	88800	36400	27.3	19.0	12.5	102
42	92400	37700	28.8	19.3	10.7	103
43	94000	38700	29.8	19.8	11.3	107
44	92700	38500	29.2	19.6	12.1	105
45	90700	37700	27.4	19.0	12.1	103
46	82200	35500	25.9	17.9	11.9	94.5
47	67300	31600	22.4	16.3	14.4	83.0
48	69900	30400	23.2	16.5	12.1	85.2
49	67500	29200	21.2	15.4	14.0	81.7
50	67900	28700	20.6	15.2	15.0	81.8
51	56200	24500	16.5	12.8	13.4	74.4

Table A-14 Metal concentrations (unit: mg/kg, dry weight) in sediment core ST-D from Songtao Reservoir.

Depth (cm)	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
1	94600	36800	32.1	17.4	19.0	119
2	95200	36100	29.6	17.1	19.1	114
3	96500	35900	29.0	16.2	21.4	118
4	93900	36200	27.4	16.6	25.2	117
5	90500	35500	29.9	17.6	24.7	120
6	93200	35900	28.8	17.2	24.7	117
7	98000	35800	31.2	17.9	26.2	121
8	95700	36500	29.8	17.1	24.1	117
9	87400	39400	33.6	18.4	24.9	116
10	90900	40500	34.2	19.4	25.1	119
11	102000	38000	30.0	17.2	23.0	119
12	95600	35300	29.4	16.1	24.7	118
13	90200	36400	31.3	17.5	23.6	117
14	97200	38100	35.1	19.1	20.0	120
15	88000	37500	34.8	19.2	22.0	114
16	86800	36000	32.4	19.1	21.3	111
17	89400	35900	32.0	19.5	18.3	110
18	91900	35800	31.9	19.5	15.6	108
19	90400	37000	33.0	20.2	18.5	109
20	102000	37600	34.2	20.6	15.3	114
21	87000	37000	32.5	19.8	17.8	108
22	95200	38000	32.6	19.8	17.0	113
23	80000	33400	26.4	15.4	17.7	102
24	77200	34400	25.9	14.9	19.6	105
25	76400	33100	28.0	15.7	21.6	110
26	68900	28000	22.9	11.2	17.8	87.0
27	93800	30800	27.0	13.6	19.3	110
28	76500	27600	22.3	12.6	19.0	92.4
29	83400	28800	21.5	12.7	16.1	95.0
30	36600	17200	14.9	7.26	17.5	58.2
31	41000	17400	14.4	7.02	16.1	58.8
32	41400	16500	13.5	6.78	14.8	55.1
33	58800	20700	17.0	9.47	15.3	70.4
34	52000	19300	16.2	7.77	18.1	68.1
35	70300	26400	28.7	12.7	23.5	103
36	68000	23800	23.2	11.9	24.0	97.7
37	78700	25800	27.3	13.2	24.7	110
38	48600	18500	18.2	8.39	18.7	72.8
39	31800	14100	13.1	5.93	13.2	56.0

(cont.)

Depth (cm)	**Al**	**Fe**	**Co**	**Ni**	**Pb**	**Zn**
40	48800	20100	19.1	8.04	16.8	88.0
41	51400	20700	19.4	8.55	16.8	84.5
42	48500	20400	21.4	8.53	18.4	81.9
43	45700	18900	18.5	8.04	18.2	74.4
44	41200	17500	16.9	7.51	17.2	65.0
45	30800	16400	17.8	7.04	18.5	60.2

Table A-15 Lead isotopic compositions of selected sediment samples from the reservoirs.

Sample Name	Pb Isotopic Mean Ratio			RSD (%)		
	$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
TX-A-Sd4	0.06414	1.18925	2.46972	0.4999	0.2486	0.2600
TX-A-Sd14	0.06399	1.18800	2.46790	0.5187	0.2697	0.2548
TX-A-Sd20	0.06406	1.18816	2.47300	0.4177	0.2997	0.3003
TX-A-Sd30	0.06392	1.18746	2.46880	0.5273	0.3866	0.3130
WLH-B-Sd3	0.06365	1.19764	2.48494	0.5976	0.3713	0.3575
WLH-B-Sd11	0.06375	1.20317	2.49587	0.4191	0.2497	0.3470
WLH-B-Sd21	0.06397	1.20110	2.48358	0.5481	0.3559	0.3637
WLH-B-Sd33	0.06365	1.20735	2.51221	0.6053	0.3854	0.4189
WLH-B-Sd36	0.06352	1.20665	2.51114	0.3737	0.2992	0.2379
WLH-C-Sd2	0.06385	1.19673	2.46986	0.4131	0.3359	0.2923
WLH-C-Sd13	0.06399	1.19561	2.47133	0.5061	0.3160	0.2686
WLH-C-Sd20	0.06408	1.20224	2.47330	0.3923	0.2905	0.0954
WLH-C-Sd30	0.06392	1.20194	2.48816	0.3631	0.2703	0.2324
LK-A-Sd2	0.06393	1.22679	2.49962	0.2510	0.3002	0.2133
LK-A-Sd11	0.06380	1.22976	2.51551	0.4608	0.1877	0.2916
LK-A-Sd27	0.06373	1.22961	2.51283	0.3750	0.1948	0.1663
LK-A-Sd36	0.06344	1.23422	2.53317	0.3707	0.2690	0.2276
ST-C-Sd2	0.06420	1.19579	2.46015	0.4382	0.2205	0.1934
ST-C-Sd21	0.06389	1.20016	2.47307	0.6559	0.2369	0.1620
ST-C-Sd32	0.06389	1.19727	2.47414	0.3900	0.2356	0.1462
ST-C-Sd49	0.06417	1.20037	2.47038	0.4170	0.2623	0.2018
ST-D-Sd2	0.06436	1.19950	2.45242	0.2779	0.1504	0.2189
ST-D-Sd8	0.06423	1.20224	2.45838	0.4805	0.2536	0.2062
ST-D-Sd20	0.06438	1.20298	2.45860	0.3896	0.2820	0.2009
ST-D-Sd37	0.06420	1.20133	2.46813	0.4502	0.2630	0.1973
ST-D-Sd44	0.06411	1.19748	2.48635	0.3040	0.2587	0.1706

APPENDIX B – ANALYTICAL RESULTS OF SURFACE SOILS & MOSSES

Table B-1 Concentrations (unit: mg/kg, dry weight) of surface soils from the catchment of the reservoirs.

Sample Name	**Al**	**Fe**	**Cu**	**Ni**	**Pb**	**Zn**
TX 100	23200	8910	32.5	5.40	47.6	102
TX 150	18800	6540	44.2	5.02	53.2	110
TX 250	15100	5000	37.7	3.85	38.2	86.8
TX 290	24600	5570	20.4	3.00	23.0	52.1
WLH 200	42100	16500	6.70	3.37	10.4	32.4
WLH 290	47100	9750	3.26	0.08	27.9	63.5
WLH 400	31800	11100	3.64	6.85	9.95	22.0
WLH 490	58800	21500	13.9	7.81	8.65	55.9
WLH 550	66200	26800	7.02	6.98	19.0	78.4
WLH 615	88000	45100	8.69	12.9	0.00	105
ST – I	58400	14600	1.51	2.37	1.36	26.8
ST – II	57100	13900	1.51	2.28	2.64	27.9
ST – III	56800	14100	1.28	2.35	3.08	25.9
ST – IV	49500	12200	1.29	2.14	3.02	24.1
ST – JFL no. 1	44900	11500	3.00	0.08	28.7	24.6
ST – JFL no. 2	64100	17200	8.69	0.00	19.1	49.3
ST – JFL no. 3	36400	8440	1.66	0.00	6.27	20.5
ST – JFL no. 4	45200	10800	2.93	0.82	7.26	26.8
ST – JFL no. 5	39600	9670	2.56	0.66	6.22	24.7
ST – JFL no. 6	63300	12100	1.80	1.91	26.5	25.2

Table B-2 Concentrations (unit: mg/kg, dry weight) of moss samples collected from the catchment of the reservoirs.

Sample Name	**Name of Moss Species**	**Cu**	**Ni**	**Pb**	**Zn**
XMTX – A	*Hypnum plumaeforme Wils.*	47.2	3.46	65.0	199
XMTX – B	*Hypnum plumaeforme Wils.*	32.1	3.10	53.9	163
XMTX – C	*Hypnum plumaeforme Wils.*	34.2	3.58	61.8	174
XMTX – D	*Hypnum plumaeforme Wils.*	68.1	5.48	74.3	180
XMTX – E	*Entodon macropodus(Hedw.)C.Muell.*	42.2	3.80	38.3	125
WLH-GS 200	*Pogonatum contortum(Brid.)Lesq.*	7.92	2.77	34.3	164
WLH-GS 290	*Pogonatum contortum(Brid.)Lesq.*	9.27	4.00	116	152
WLH-GS 400	*Pogonatum contortum(Brid.)Lesq.*	7.15	5.73	41.0	103
WLH-GS 490	*Pogonatum contortum(Brid.)Lesq.*	7.93	3.30	45.9	82.0
WLH-GS 550	*Pogonatum contortum(Brid.)Lesq.*	8.18	3.81	56.2	132
WLH-GS 600	*Plagiochila dendroides(Nees)Lindenb.*	12.7	5.43	36.7	164
WLH-GS 615	*Pogonatum contortum(Brid.)Lesq.*	9.55	4.55	23.0	111
WLH-GS 700	*Thudium cymbifolium(Doz.et Molk.)Doz.et Molk.*	11.0	7.00	23.7	78.6
WLH-GS 760	*Thudium cymbifolium(Doz.et Molk.)Doz.et Molk.*	21.2	8.43	47.8	216
LK270	*Thuidium glaucinum(Mitt.)Bosch. et Scande Lac.*	11.3	1.86	58.6	108
LK340	*Claopodium assurgens(sull.et Lesq.)Card.*	8.50	1.62	21.8	80.5
LK360	*Claopodium aciculum(Broth.)Broth.*	7.89	1.42	28.9	70.7
ST – I	*Pogonatum contortum(Brid.)Lesq.*	5.50	1.78	29.8	59.0
ST – II	*Pogonatum contortum(Brid.)Lesq.*	5.72	1.69	36.9	60.9
ST – III	*Pogonatum contortum(Brid.)Lesq.*	5.99	1.45	35.2	61.2
ST – IV	*Pogonatum contortum(Brid.)Lesq.*	5.79	1.68	37.3	58.3

Table B-3 Lead isotopic compositions of surface soil samples collected from the catchment area of the reservoirs.

Sample Name	**Pb Isotopic Mean Ratio**			**RSD (%)**		
	^{204}Pb/^{207}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	^{204}Pb/^{207}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb
TX 100	0.06383	1.18011	2.47282	0.4551	0.3239	0.3897
TX 150	0.06391	1.17955	2.47382	0.6915	0.3628	0.2886
TX 250	0.06388	1.17533	2.46457	0.7002	0.3574	0.3768
TX 290	0.06394	1.18409	2.46544	0.3701	0.3899	0.3555
WLH 200	0.06380	1.20138	2.47694	0.3542	0.2836	0.2199
WLH 290	0.06362	1.22499	2.50396	0.4526	0.2415	0.4097
WLH 400	0.06412	1.17778	2.47461	0.4492	0.3046	0.3127
WLH 490	0.06396	1.20174	2.47499	0.4758	0.2635	0.2097
WLH 550	0.06389	1.20112	2.48908	0.4881	0.2321	0.2720
WLH 615	--	--	--	--	--	--
ST – I	0.06438	1.20822	2.50673	0.4496	0.2087	0.2489
ST – II	0.06436	1.20869	2.51155	0.2730	0.2925	0.3063
ST – III	0.06422	1.20921	2.52424	0.1954	0.2996	0.1737
ST – IV	0.06367	1.21300	2.53387	0.4350	0.2268	0.3037
ST – JFL no. 1	0.06391	1.21005	2.52877	0.3139	0.2510	0.2301
ST – JFL no. 2	0.06398	1.21600	2.55082	0.4257	0.3886	0.2356
ST – JFL no. 3	0.06391	1.22155	2.56819	0.3584	0.2875	0.3090
ST – JFL no. 4	0.06402	1.21881	2.55009	0.6471	0.1806	0.3574
ST – JFL no. 5	0.06402	1.22431	2.53670	0.3740	0.1719	0.4177
ST – JFL no. 6	0.06371	1.22362	2.52590	0.3217	0.3095	0.2857

Table B-4 Lead isotopic compositions of moss samples collected from the catchment area of the reservoirs.

Sample Name	**Pb Isotopic Mean Ratio**			**RSD (%)**		
	^{204}Pb/^{207}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	^{204}Pb/^{207}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb
XMTX – A	0.06429	1.17129	2.46483	0.3718	0.3529	0.3661
XMTX – B	0.06405	1.17444	2.46399	0.6063	0.2715	0.3951
XMTX – C	0.06403	1.17525	2.46689	0.5242	0.2471	0.3213
XMTX – D	0.06413	1.17066	2.46317	0.4607	0.2165	0.2457
XMTX – E	0.06385	1.16758	2.45566	0.4092	0.3648	0.3215
WLH-GS 200	0.06384	1.18553	2.47409	0.4989	0.2840	0.3238
WLH-GS 290	0.06381	1.21162	2.49761	0.4479	0.3245	0.3538
WLH-GS 400	0.06408	1.17705	2.47743	0.4591	0.3506	0.3671
WLH-GS 490	0.06367	1.19516	2.48889	0.3578	0.2582	0.2456
WLH-GS 550	0.06377	1.18659	2.47935	0.2076	0.1419	0.1853
WLH-GS 600	0.06387	1.17437	2.46498	0.4407	0.3175	0.2579
WLH-GS 615	0.06385	1.17982	2.46877	0.3834	0.1942	0.2073
WLH-GS 700	0.06385	1.17333	2.45865	0.5048	0.2676	0.2890
WLH-GS 760	0.06383	1.17370	2.46201	0.7091	0.4150	0.4599
LK270	0.06401	1.18334	2.47226	0.4176	0.3895	0.2993
LK340	0.06384	1.19862	2.48899	0.4476	0.2807	0.3325
LK360	0.06370	1.22842	2.52902	0.5605	0.2637	0.3067
ST – I	0.06376	1.19777	2.50486	0.5132	0.2318	0.2739
ST – II	0.06389	1.20219	2.51099	0.6586	0.6008	0.4093
ST – III	0.06415	1.20167	2.50972	0.2501	0.3027	0.1960
ST – IV	0.06389	1.20324	2.51011	0.4721	0.2746	0.3657

APPENDIX C – ANALYTICAL RESULTS OF ^{210}Pb DATING ANALYSIS

Table C-1 The concentrations of unsupported ^{210}Pb against the depths of the sediment core TX-B at Luokeng Reservoir by ^{210}Pb dating analysis

Depth (cm)	Pb (dpm)	Ra (dpm)	Unsupported Pb(dpm)	Average Depth (cm)
1	5.789	2.093	3.697	0.5
3	6.031	2.084	3.946	2.5
5	4.333	2.460	1.874	4.5
8	4.466	2.236	2.230	7.5
11	5.046	2.043	3.003	10.5
15	5.415	1.902	3.513	14.5
19	5.675	2.268	3.407	18.5
24	8.871	2.514	6.357	23.5
29	7.375	1.865	5.509	28.5
34	6.664	1.023	5.642	33.5
39	8.986	1.720	7.266	38.5
45	9.438	2.329	7.109	44.5

Note: 1 dpm (decay per minute) = 1/60 Bq (becquerel) = 0.45045 picocurie (pCi)

Table C-2 The concentrations of unsupported ^{210}Pb against the depths of the sediment core LK-B at Luokeng Reservoir by ^{210}Pb dating analysis

Depth (cm)	**Pb (dpm)**	**Ra (dpm)**	**Unsupported Pb(dpm)**	**Average Depth (cm)**	**Year**
1	20.704	3.103	17.601	0.5	2005
3	24.623	3.258	21.365	2.5	2004
5	22.682	3.065	19.616	4.5	2003
8	21.033	2.765	18.268	7.5	2001
11	23.795	2.639	21.156	10.5	2000
15	16.841	2.549	14.292	13.5	1998
19	15.456	2.487	12.970	18.5	1995
24	19.145	2.468	16.677	23.5	1992
29	18.096	2.685	15.411	28.5	1989
34	15.333	2.499	12.834	33.5	1987
39	16.642	2.689	13.952	38.5	1984
45	15.745	2.759	12.986	43.5	1981
50	12.452	3.285	9.168	48.5	1978
56	11.573	2.927	8.645	53.5	1975

Note: 1 dpm (decay per minute) = 1/60 Bq (becquerel) = 0.45045 picocurie (pCi)

Table C-3 The concentrations of unsupported ^{210}Pb against the depths of the sediment core ST-A at Songtao Reservoir by ^{210}Pb dating analysis

Depth (cm)	**Pb (dpm)**	**Ra (dpm)**	**Unsupported Pb(dpm)**	**Average Depth (cm)**	**Year**
1	9.210	0.821	8.389	0.5	2005
3	9.290	1.155	8.136	2.5	2004
5	10.437	1.627	8.810	4.5	2002
8	9.853	1.449	8.404	7.5	1999
11	13.139	1.685	11.454	10.5	1997
14	7.130	0.795	6.335	14.5	1994
19	7.558	0.777	6.782	18.5	1990
24	6.921	0.744	6.177	23.5	1986
29	8.945	1.298	7.647	28.5	1982
34	9.248	1.635	7.613	33.5	1978
39	5.327	1.545	3.782	38.5	1974
44	5.314	1.795	3.519	44.5	1969
49	5.207	1.610	3.597	49.5	1965
54	4.986	1.747	3.240	55.5	1960

Note: 1 dpm (decay per minute) = 1/60 Bq (becquerel) = 0.45045 picocurie (pCi)