Biomonitoring of Trace Metals in the Atmosphere using Moss (*Hypnum plumaeforme)* in the Nanling Mountains and the Pearl River Delta, Southern China

Siu Lan Lee[a], Xiangdong Li[a*], Gan Zhang[b], Xinzhi Peng[b] and Li Zhang[c]
[a]*Department of Civil and Structural Engineering, The Hong Kong Polytechnic University Hung Hom, Kowloon, Hong Kong*

[b]*State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*

[c]*South China Institute of Botany, Chinese Academy of Sciences, Guangzhou 510650, China*

Abstract

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

Keywords: Moss (*Hypnum plumaeforme*), biomonitor, aerosol, heavy metals, Pb isotopes, Pearl River Delta, south China

1. Introduction

Atmospheric particulates have attracted great environmental concern over the last few decades because of evidence that this type of pollution can have severe long-term implications for respiratory illness in humans (Dockery and Pope, 1994). In particular, heavy metals adsorbed on ambient particles

*Corresponding author (X. D. Li); email cexdli@polyu.edu.hk; fax: (852) 2334 6389; tel.: (852) 2766 6041

were found to cause damage to lung tissues (Dreher et al., 1997). Due to rapid urbanization and industrial development in recent years, atmospheric pollution has caused serious deterioration of the terrestrial environment in many countries. Thus, the monitoring of airborne metals in the urban environment has become an essential part of environmental planning and control programmes in many parts of the world. Biomonitoring is a technique using organisms or biomaterials to obtain (quantitative) information on certain characteristics of the biosphere (Woltebeek, 2002). Mosses have been well studied as tools for the biomonitoring of atmospheric pollution. Unlike higher plants, mosses have no root system or cuticle layer; hence, mineral adsorption occurs over their entire surface (Rühling and Tyler, 1968). Mineral uptakes from soil play a minor role and the adsorption of heavy metal is mainly derived from atmospheric flux on the surfaces of the moss. Therefore, mosses are excellent biomonitors for trace elements in air.

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

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

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

2. Materials and Method

2.1. The study area

The Nanling mountain range is located in southern China and straddles from west to east across the borders of Guangxi, Guangdong, Hunan and Jiangxi provinces for more than 1,000 km (Fig. 1). The mountain range is an important boundary in south China between the temperate continent in the north and subtropical regions in the southeast coast. The area is the key pathway for the long-range transport of air pollutants from northern China to the PRD region, particularly during the dry winter monsoon period. To the south of the Nanling range lies the Pearl River Delta (PRD) region of Guangdong Province. The PRD region is one of the most urbanized areas in China, with a total population of more than 30 millions. It covers an area of 41,700 km^2. Major cities in the PRD include Guangzhou, Shenzhen, Dongguan, Foshan, Jiangmen, Zhuhai, Zhongshan and Huizhou, and all have different concentrations of industrial centres.

2.2. Moss sampling

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

2.3. Aerosol sampling

A total of 12 aerosol samples were collected in the Nanling Mountains, and in Guangzhou and Zhongshan of the PRD during the winter season (November 2002–January 2003). Two aerosol samples were collected at each location in the north (YTH series; at 1408 m) and south (QY series; at 840 m) of the Nanling Mountains. The Guangzhou aerosols were collected at the roof top of a building in the urban centre of Guangzhou (~50 m). The Zhongshan aerosols were sampled on a small mountain (~500 m), in a suburban area of Zhongshan city. The aerosols at Nanling, Guangzhou and Zhongshan, located at the northern, central and southern part of the PRD, represented the general atmospheric condition of the region. A high-volume sampler (Anderson-type) was deployed in the sampling sites to collect aerosol samples. The samplers were operated at a flow rate of 0.465 m^{-3} min^{-1} to collect the total aerosols on 20.3 cm x 25.4 cm glass fibre filters. A sampling duration of 12 hrs was adopted. The filters were then wrapped in aluminium foil and stored in polyethylene bags at 4°C.

2.4. Heavy metal analysis

The moss and aerosol samples were analysed for major and trace metal concentrations using a strong acid digestion method (Shen et al., 2002; Wong et al., 2003). Approximately 0.350 g of the moss samples was weighted and placed into pre-cleaned Pyrex tubes. Twelve ml of concentrated high-purity nitric acid (HNO_3) and 4.0 ml of concentrated perchloric acid ($HClO_4$) were added. The mixtures were gently shaken and then heated progressively to 190 °C in an aluminium block for 24 hr, until completely dryness. After the test tubes were cool, 10.0 ml of high-purity 5% (v/v) HNO_3 were added and heated at 70°C for 1 hr, with occasional mixing. Upon cooling, the mixtures were decanted into polyethylene tubes and centrifuged at 3500 rpm for 10 min.

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

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

2.5. Pb isotopic composition analysis

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

2.6. Statistical analysis

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

3. Results and Discussion

3.1. Metal concentrations in mosses and aerosols

The total concentrations of metals in the moss and aerosol samples are presented in Table 1. The mean concentrations of heavy metals such as Cd, Cu, Ni, Zn and Pb in the NL-series (northern part of the Nanling range) were found to be 4.13 mg kg^{-1}, 34.3 mg kg^{-1}, 18.0 mg kg^{-1}, 183 mg kg^{-1} and 181 mg kg^{-1}, respectively. The corresponding values in the MS-series (the southern part of the Nanling range) were 1.82 mg kg^{-1}, 58.7 mg kg^{-1}, 23.6 mg kg^{-1}, 140 mg kg^{-1} and 143 mg kg^{-1}, respectively. The results showed that the Pb concentrations were highly elevated in both the NL- and MS-series, ranging from 40.5 mg kg^{-1} to

396 mg kg^{-1}. As no similar study using *Hypnum plumaeforme* for bimonitoring was found in the literature, the bioconcentrations of another similar species belonging to the same class and being widely adopted in European moss surveys (Fernández et al., 2002; Ötvös et al., 2003), *Hypnum cupressiforme,* was used for comparison. In comparison with the results reported in Spain and France, bioconcentrations in the moss *Hypnum plumaeforme* were much higher than in *Hypnum cupressiforme* (see Table 2). Previous studies on atmospheric deposition in the PRD showed that the atmospheric deposition of heavy metals was significantly greater than in the Great Lakes region in North America and the North Sea in Europe (Wong et al., 2003). Hence, the Nanling mosses could be expected to reflect the elevated concentrations of atmospheric heavy metals in the PRD compared with other regions. Nevertheless, the total amount of pollutants in the air, the relative humidity and wet deposition would also have significant effects on the capacity of mosses to absorb metals. The wide availability of the moss *Hypnum plumaeforme* in the Nanling Mountains and the PRD region, and their capacity in absorbing heavy metals makes it feasible for use in future biomonitoring programmes of atmospheric pollutants.

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

3.2. Elemental associations in mosses

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

>0.60. Some of the results were presented in Fig. 2, and they agreed well with the results from the Pearson correlation analysis.

3.3. Topographical effect on moss metal concentrations

Mosses in the NL- and MS-series were collected at different elevations. The analytical results showed that the concentrations of elements such as, Cd, Pb and Zn, were significantly correlated with the elevations in the NL-series, but no significant correlation was observed in the MS-series (Fig. 3a-c). At the elevations above 1100 m a.s.l., the concentrations of heavy metals became relatively constant. The results indicated that heavy metals such as Cd, Pb and Zn in the air tended to be associated with particles in areas of low elevation and close to sources of contamination and transport paths. Moreover, the statistical results from the Pearson correlation analysis showed that there was a strong elemental correlation among Cd, Pb and Zn in the Nanling mosses (see Table 4 and Fig. 2), indicating a common source of anthropogenic inputs of these three heavy metals. The northern part of the Nanling Mountains was shown to be significantly enriched with heavy metals, possibly reflecting local sources of pollution and the effects of potential pathways for the long-range transport of air contaminants from northern China. In the southern part of the Nanling range, the elemental concentrations of Cd, Pb and Zn were relatively constant at various elevations, probably due to better mixing of the air because of coastal air flows from the South China Sea.

3.4. Pb isotopic compositions in mosses and aerosols

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

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

4. Conclusion

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

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References

Aceto, M., Abollino, O., Conca, R., Malandrino, M., Mentasti, E., Sarzanini, C., 2003. The use of mosses as environmental metal pollution indicators. Chemosphere 50, 333-342.

Barclay-Estrup, P., Rinne, R.J.K., 1979. Trace element accumulation in a feather moss and in soil near a kraft paper mill in Ontario. Bryologist 82, 599-602.

Bragagli, R., Brown, H., Nelli, L., 1995. Metal biomonitoring with mosses: procedures for correcting for soil contamination. Environmental Pollution 89, 169-175.

Cao, J.J., Lee, S.C., Ho, K.F., Zhang, X.Y., Zou, S.C., Fung, K., Chow, J.C., Watson, J.G., 2003. Characteristics of carbonaceous aerosol in Pearl River Delta Region, China during the 2001 winter period. Atmospheric Environment 37, 1451-1460.

Chen, G.H., Chen M.Z., Di, R.J., 1999. Assessment of prospecting potentiality for superlarge continental volcanic rock-type uranium deposits in China. Chinese Journal of Geochemistry 18, 350-360.

Deng, F.L., 1987. Isotopic geochronology in southern Zhuguangshan granitoid batholith. Geochemistry (China) 2, 141-152. (in Chinese)

Dockery, D.W., Pope, C.A., 1994. Acute respiratory effects of particulate air pollution. Annual Reviews and Public Health 15, 107-132.

Dreher, K.L., Jaskot, R.H., Lehmann, J.R., Richards, J.H., McGee, J.K., Ghio, A.J., Costa, D.L., 1997. Soluble transition metals mediate residual oil fly ash induced acute lung injury. Journal of Toxicology in Environmental Health 50, 285-305.

Fang, G.C., Chang, C.N., Chu, C.C., Wu, Y.S., Fu, P.P.C., Yang, I L., Chen, M.H., 2003. Characterization of particulate, metallic elements of TSP, $PM^{2.5}$ and $PM^{2.5\text{-}10}$ aerosols at a farm sampling site in Taiwan, Taichung. The Science of the Total Environment 308, 157-166.

Farmer, J.G., Eades, L.J., Atkins, H., Chamberlain, D.F., 2002. Historical trends in the lead isotopic composition of archival sphagnum mosses from Scotland (1838-2000). Environmental Science and Technology 36, 152-157.

Fernández, J.A., Ederra, A., Núñez, E., Martinez-Abaígar, J., Infante, M., Heras, P., Elías, M.J., Mazimpaka, V., Carballeira, A., 2002. Biomonitoring of metal deposition in northern Spain by moss analysis. The Science of the Total Environment 300, 115-127.

Galsomiés, L., Ayrault, S., Carrot, F., Deschamps, C., Letrouit-Galinou, M.A., 2003. Interspecies calibration in mosses at regional scale – heavy metal and trace elements results from Ile-de-France. Atmospheric Environment 37, 241-251.

Groet, S.S., 1976. Regional and local variations in heavy metal concentrations of bryophytes in the northeastern United States. Oikos 27, 445-456.

Hien, P.D., Binh, N.T., Truong, Y., Ngo, N.T., Sieu, L.N., 2001. Comparative receptor modelling study of TSP, PM_2 and $PM_{2\text{-}10}$ in Ho Chi Minh City. Atmospheric Environment 35, 2669-2678.

HKAQO, Hong Kong Air Quality Objectives, 1987. Environmental Protection Department of Hong Kong, Hong Kong SAR Government.

Kumar, A.V., Patil, R.S., Nambi, K.S.V., 2001. Source apportionment of suspended particulate matter at two traffic junctions in Mumbai India. Atmospheric Environment 35, 4245-4251.

Markert, B., Herpin, U., Siewers, U., Berlekamp, J., Leith, H., 1996. The German heavy metal survey by means of mosses. The Science of the Total Environment 182, 159-168.

Mukai, H., Tanaka, A., Fujii, T., 2001. Regional characteristics of sulfur and lead isotope ratios in the atmosphere at several Chinese urban sites. Environmental Science and Technology 33, 2517-2523.

NAAQS, National Ambient Air Quality Standard, 1996. State Environmental Protection Agency of China.

Ötvös, E., Pázmándi, T., Tuba, Z., 2003. First national survey of atmospheric heavy metal deposition in Hungary by the analysis of mosses. The Science of the Total Environment 309, 151-160.

Percy, K.E., 1982. Heavy metal and sulphur concentrations in *Sphagnum Magellanicum* Brid. In the maritime provinces, Canada. Water, Air, and Soil Pollution 19, 341-349.

Ross, H.B., 1990. On the use of mosses (*Hylocomium splenders and Pleurozium schreberi*) for estimating atmospheric trace metal deposition. Water, Air, and Soil Pollution 50, 63-76.
Rühling, Å., Taylor, G., 1968. An ecological approach to the lead problem. Botanical Notes 121, 321-342.
Rühling, Å., Taylor, G., 1970. Sorption and retention of heavy metals in the woodland moss *Hylocomium splenders* (Hedw.). Oikos 21, 92-97.
Rühling, Å., Steinnes, E., 1998. Atmospheric heavy metal deposition in Europe 1995-1996. NORD 15, 66.
Shen, Z.G., Li, X.D., Wang, C.C., Chen, H.M., Chua, H., 2002. Lead phytoextraction from contaminated soil with high-biomass plant species. Journal of Environmental Quality 31, 1893-1900.
State Environmental Protection Administration of China. 2001. Report on the State of the Environment in China, 2001.
Sucharová, J., Suchara, I., 1998. Atmospheric deposition levels of chosen elements in the Czech Republic determined in the framework of the International Bryomonitoring Program 1995. The Science of the Total Environment 223, 37-52.
Weiss, D., Shotyk, W., Kramers, J.D., Gloor, M., 1999. Sphagnum mosses as archives of recent and past atmospheric lead deposition in Switzerland. Atmospheric Environment 33, 3751-3763.
Wolterbeek, B., 2002. Biomonitoring of trace element air pollution: principles, possibilities and perspectives. Environmental Pollution 120 11-21.
Wong, C.S.C., Li, X.D., Zhang, G., Qi, S.H., Peng, X.Z., 2003. Atmospheric deposition of heavy metals in the Pearl River Delta, China. Atmospheric Environment 37, 767-776.
Xiao, Z., Sommar, J., Lindqvist, O., 1997. Atmospheric mercury deposition on Fanjing mountain nature reserve, Guizhou, China. Chemosphere, 36, 2191-2200.
Zechmeister, H.G., 1998. Annual growth of four Pleurocarpous moss species and their applicability for biomonitoring heavy metals. Environmental Monitoring and Assessment 52, 441-451.
Zhang, L.G., Wang K.F., Chen, Z.S., 1993. Mesozoic Pb isotopic provinces in eastern China and dynamics of crust and mantle. Chinese Science Bulletin 38, 254-257. (in Chinese)
Zhang, X.Y., Cao, J.J., Li, L.M., Arimoto, R., Cheng, Y., Huebert, B., Wang, D., 2002. Characterization of atmospheric aerosol over Xian in the south margin of the Loess Plateau, China. Atmospheric Environment 36, 4189-4199.
Zhu, B.Q., Wang, H.F., Mao, C.X., Zhui, N.J., Huang, R.S., Peng, J.H., 1989. Geochronology of and Nd-Sr-Pb isotopic evidences for mantle source in the ancient subduction zone beneath Sanshui Basin, Guangdong Province, China. Chinese Journal of Geochemistry 8, 65-71.
Zhu, B.Q., 1998. Theory and Application of Isotopic Systematic in Earth Science. Science Press, Beijing (in Chinese).
Zhu, B.Q., Chen, Y.W., Peng, J.H., 2001. Lead isotope geochemistry of the urban environment in the Pearl River Delta. Applied Geochemistry 16, 409-417.

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

		Al	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	V	Zn
Nanling Moss														
	(mg kg^{-1})	Higher Elevation: >1100 m												
NL-series (N=4)	Mean	2260	7660	1.71	0.46	9.99	27.8	898	1050	181	10.1	69.3	1.62	112
	Std Dev	2190	2090	0.28	0.24	3.57	10.3	770	243	82.6	4.43	7.89	1.18	24.9
		Lower Elevation: <1100 m												
NL-series (N=4)	Mean	2360	11400	6.55	0.63	40.1	40.8	1230	1390	175	25.9	296	2.64	249
	Std Dev	2190	2090	0.28	0.24	3.57	10.3	425	243	52.7	16.2	89.5	2.08	45.4
		Higher Elevation: >1100 m												
MS-series (N=4)	Mean	3110	10800	1.78	0.21	23.0	53.2	881	1020	200	16.2	106	2.60	144
	Std Dev	2810	1060	0.74	0.14	17.1	29.4	447	135	147	6.39	50.3	1.69	18.3
		Lower Elevation: <1100 m												
MS-series (N=4)	Mean	4990	9450	1.85	0.39	26.6	64.3	1450	902	175	30.9	175	1.67	141
	Std Dev	2560	1180	0.67	0.43	23.6	53.5	747	144	142	28.3	82.6	0.58	26.3
PRD Aerosol														
Nanling	(ng m^{-3})	Elevation: 1408 m												
YTH (North) (N=2)	Mean	5630	3830	20.5	n.d.[a]	16.0	42.0	1480	336	n.d.[a]	30.5	615	17.5	5770
	Std Dev	2870	605	7.29	n.d.[a]	10.1	1.64	375	89.2	n.d.[a]	24.8	255	5.87	2240
		Elevation: 804 m												
QY (South) (N=2)	Mean	4640	6290	11.4	n.d.[a]	7.37	86.8	2270	573	n.d.[a]	23.9	452	39.2	3860
	Std Dev	850	2880	2.81	n.d.[a]	4.60	71.1	1490	217	n.d.[a]	8.30	225	26.7	1070
		Elevation: 50 m												
Guangzhou (N=4)	Mean	14600	22500	21.6	2.85	64.0	914	8860	1450	83.6	66.8	995	103	6440
	Std Dev	1210	2460	7.3	1.96	40.1	462	1280	324	61.0	23.3	248	40.6	1880
		Elevation: 500 m												
Zhongshan (N=4)	Mean	3400	3330	4.59	n.d.[a]	5.83	33.7	1190	292	n.d.[a]	20.3	147	21.1	3740
	Std Dev	1340	960	2.16	n.d.[a]	4.55	14.4	287	149	n.d.[a]	5.3	39	8.6	2050

[a] not detectable

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

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

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

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

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

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

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

** P<0.01
* P<0.05

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

Nanling Moss (N=16)	Sample ID	$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
NL-series	NL-01	0.0641	1.171	2.455
	NL-04	0.0642	1.171	2.453
	NL-05	0.0639	1.173	2.460
	NL-08	0.0640	1.175	2.456
	NL-10	0.0641	1.174	2.454
	NL-11	0.0641	1.174	2.457
	NL-12	0.0638	1.174	2.459
	NL-13	0.0640	1.175	2.452
	Mean	0.0640	1.173	2.456
MS-series	MS-02	0.0639	1.182	2.460
	MS-03	0.0640	1.184	2.463
	MS-04	0.0637	1.189	2.470
	MS-05	0.0640	1.176	2.457
	MS-06	0.0638	1.190	2.460
	MS-07	0.0640	1.175	2.456
	MS-09	0.0641	1.179	2.454
	MS-10	0.0640	1.173	2.450
	Mean	0.0639	1.181	2.459

PRD Aerosol (N=12)	Sample ID	$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Nanling	QY-01	0.0643	1.171	2.453
	QY-02	0.0642	1.173	2.464
	YTH-01	0.0644	1.179	2.469
	YTH-02	0.0643	1.171	2.447
	Mean	0.0643	1.173	2.458
Guangzhou	GZ-01	0.0647	1.174	2.453
	GZ-03	0.0652	1.181	2.457
	GZ-04	0.0651	1.181	2.470
	GZ-05	0.0644	1.178	2.470
	Mean	0.0649	1.178	2.462
Zhongshan	ZS-01	0.0646	1.173	2.444
	ZS-02	0.0642	1.170	2.461
	ZS-03	0.0646	1.169	2.460
	ZS-04	0.0647	1.172	2.461
	Mean	0.0645	1.171	2.456

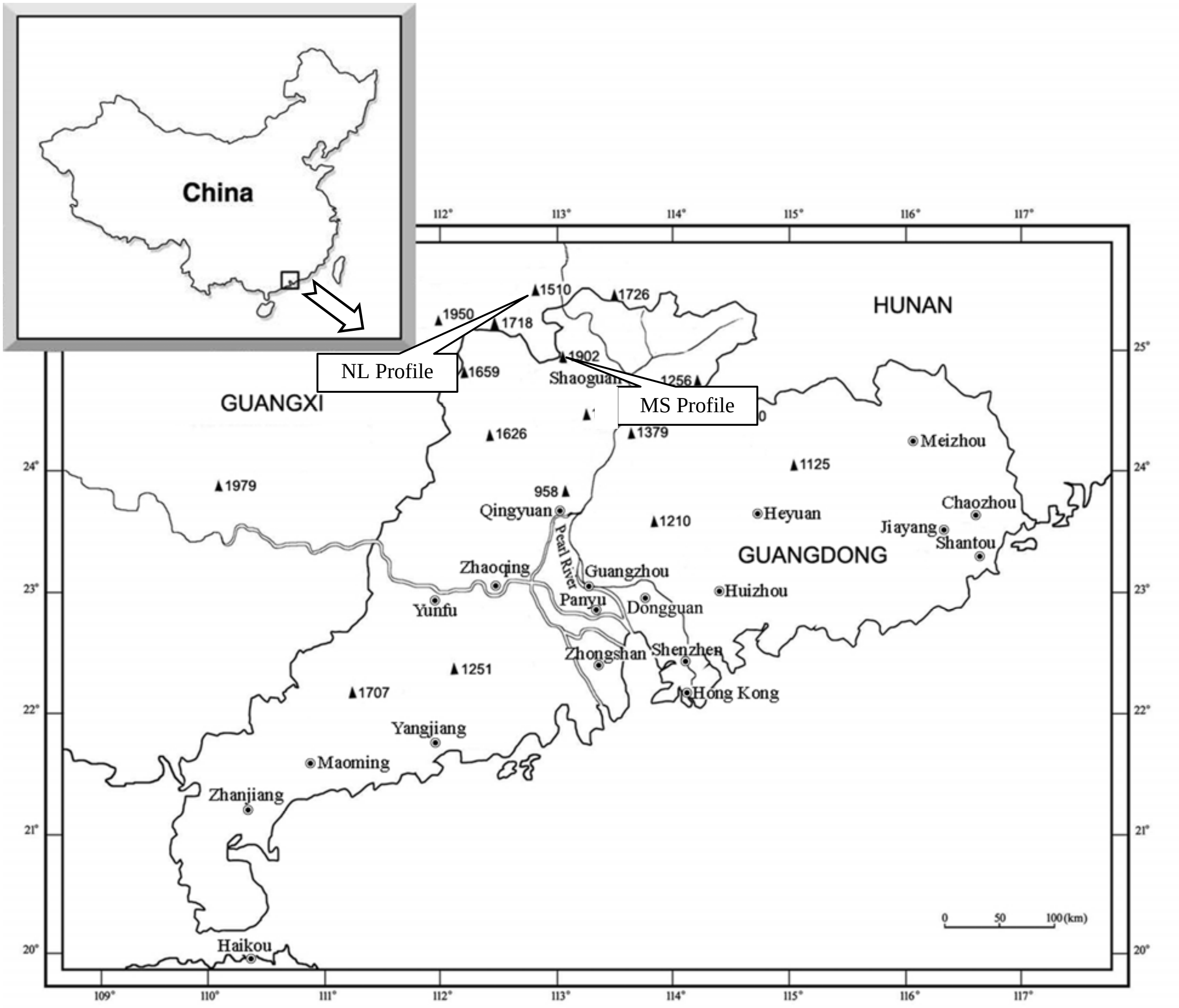


Fig. 1. Sampling locations

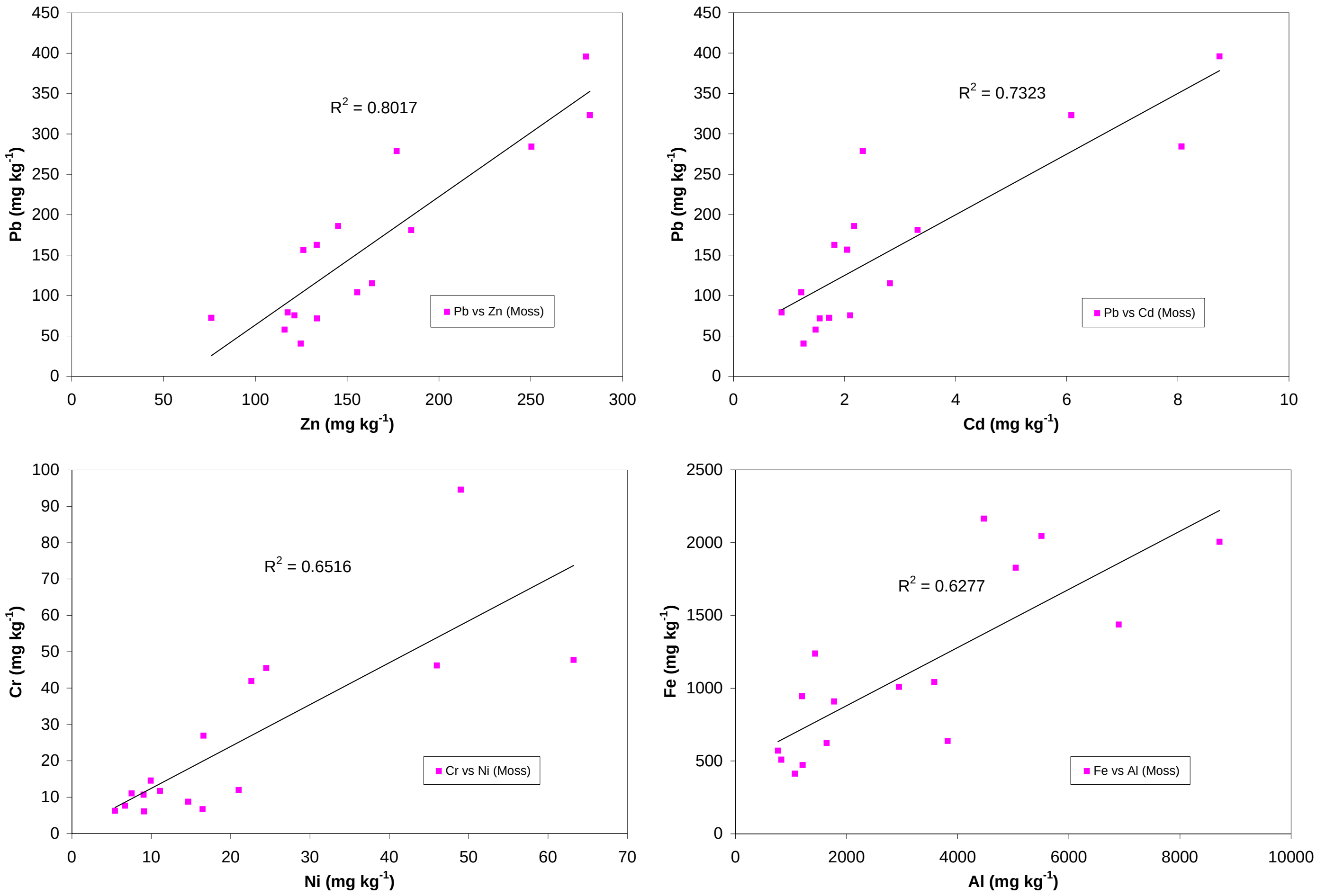


Fig.2. Elemental correlation in the Nanling mosses

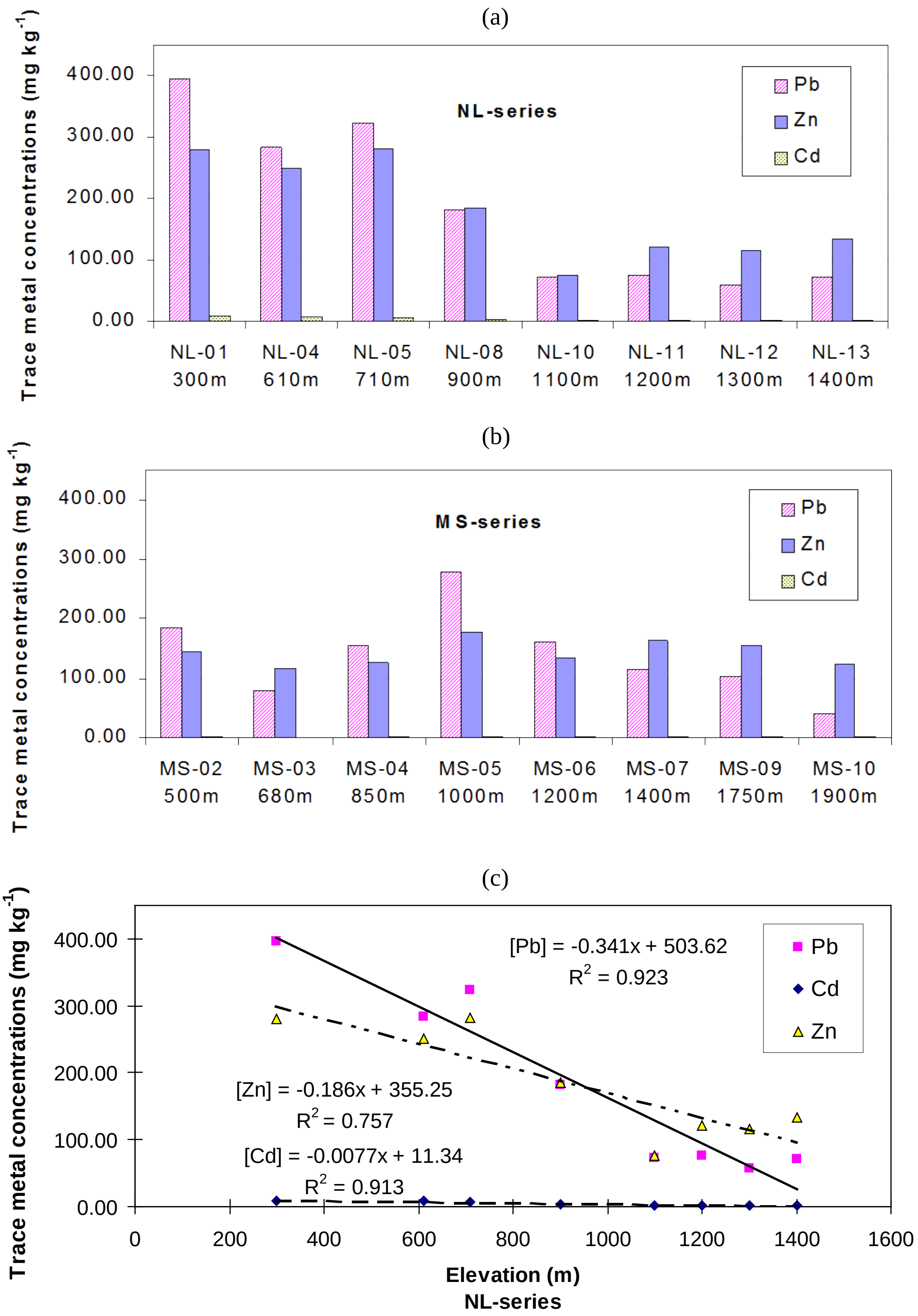


Fig. 3. (a) Cd, Pb and Zn concentrations of mosses in the NL-series; (b) Cd, Pb and Zn concentrations of mosses in the MS-series; (c) Linear plots of the Cd, Pb and Zn concentrations of mosses in the NL-series against elevation

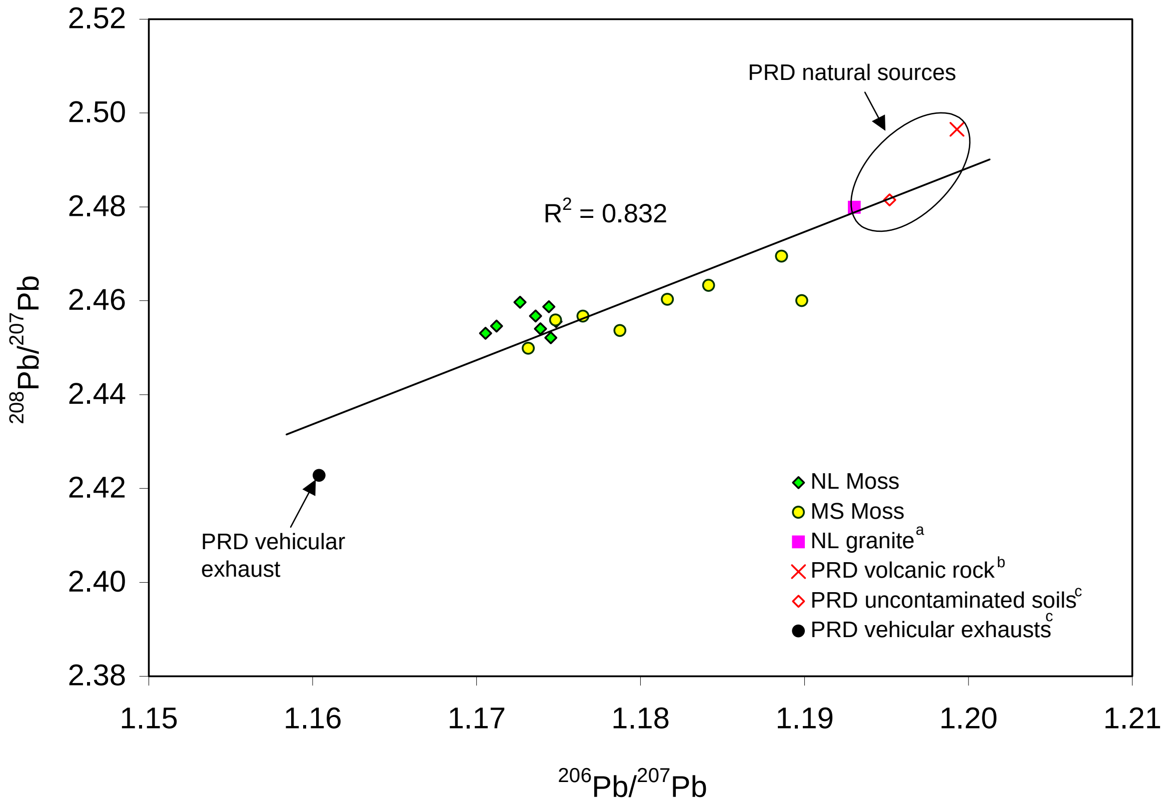
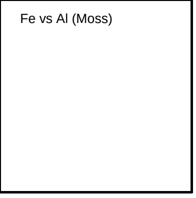


Fig. 4. $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of mosses in the Nanling Mountains ([a] Deng ,1987; [b] Zhu et al.,1989; [c] Zhu et al. 2001)



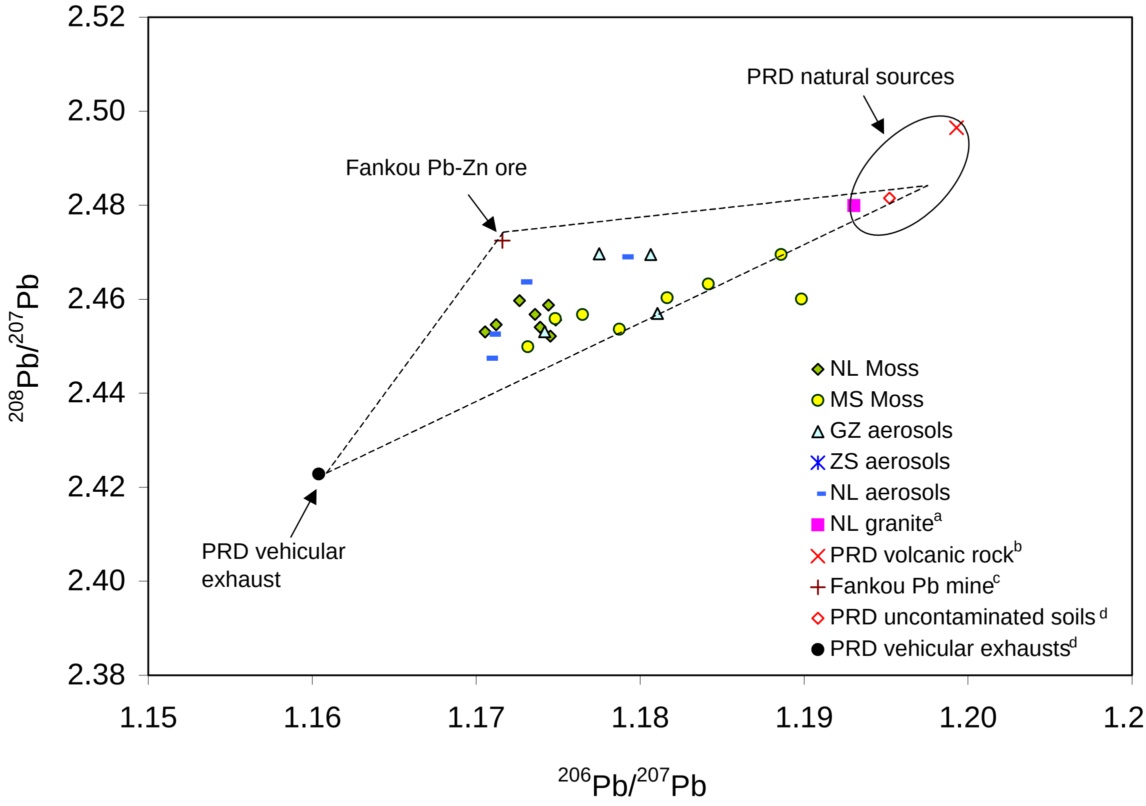


Fig. 5. $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of aerosols in the Pearl River Delta, the Nanling mosses and other environmental samples in the Pearl River Delta ([a] Deng ,1987; [b] Zhu et al.,1989; [c] Zhu, 1998; [d] Zhu et al., 2001)