Human and Ecological Risk Assessment, 12: 374–389, 2006

ISSN: 1080-7039 print / 1549-7680 online
DOI: 10.1080/10807030500538005

Fate of Heavy Metal Contaminants in Road Dusts and Gully Sediments in Guangzhou, SE China: A Chemical and Mineralogical Assessment

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ABSTRACT

The urban environment of Guangzhou, the largest industrialized center in SE China, has elevated levels of heavy metals. In places, Cu, Pb, and Zn contents exceed 490, 920, and 1,820 mg/kg, respectively. The accumulation of these contaminants is likely to accelerate as a consequence of rapid economic and industrial growth in the region. Understanding of the possible fate of the contaminants is therefore imperative in order to assess their potential long-term ecological impacts. This article documents the results of a sequential extraction procedure involving five operationally defined fractions to determine the chemical partitioning of Cu, Pb, and Zn in the urban deposits represented by road dusts and corresponding gully sediments. Special emphasis was given to the mineralogical characteristics of the urban deposits. Road dusts were mainly composed of quartz, K-Feldspar, plagioclase, and calcite, and contained minor amounts of mica and clay minerals. The corresponding gully sediments, however, typically contained minor amounts of calcite, mica, and clay minerals, and were dominated by quartz and K-feldspar. The road dusts and gully sediments exhibited comparable chemical partitioning patterns of Cu, Pb, and Zn, despite significant differences in the relative abundances of minerals, especially of calcite. Lead and Zn occurred mainly in the operationally defined carbonate/ specifically adsorbed (Pb: 48%; Zn: 50%) and Fe-Mn (Pb: 36%; Zn: 27%) phases, whereas Cu was largely associated with the organic (70%) and residual (15%) phases. In general, the residual phases of the heavy metal contaminants were equal or less than 15%, suggesting their dominantly anthropogenic origin. The relative mobility and bioavailability of the heavy metals in the urban deposits of Guangzhou was:

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Pb ~ Zn > Cu. The ever-increasing accumulations of heavy metals may pose a threat in the region both to the environment and to human health.

Key Words: environmental quality, urban environment, Pb, Zn, Cu, road dust.

INTRODUCTION

Urban deposits, road dusts, and gully sediments are useful indicators of the level and distribution of heavy metal contamination in the surface environment. The relative ease of sampling of these deposits has led to their increasing utilization in research on urban environmental quality in the past two decades (Gibson and Farmer 1986; Tam *et al.* 1987; Charlesworth and Lee 1999; Sutherland 2003). Elevated concentrations of heavy metals are universal in urban environments as a result of a wide range of anthropogenic activities, including municipal, industrial, agricultural, residential, and traffic-related uses (Thornton 1990; Alloway 1990). Heavy metals are non-degradable and their accumulation not only contaminates the surface environment but also contributes to air pollution, as they may become airborne and eventually enter the drainage system to affect aquatic ecosystems. As the urban environment is becoming an increasingly dominant habitat for humans, the level and variety of these contaminants are increasing exponentially, demanding a better understanding of their sources, transport, and transformation processes. This is a particularly urgent task for regions undergoing rapid industrial development.

Guangzhou, the capital of Guangdong province (Figure 1), is the largest industrial center and one of the fastest expanding cities in China. Rapid urbanization and industrialization have led to degradation of air, water, and soil quality in the region (Wong *et al.* 2002). A recent study based on total metal concentrations in urban deposits from Guangzhou indicated that the city's surface environment has been drastically contaminated with heavy metals, especially Cu, Pb, and Zn (Duzgoren-Aydin *et al.* 2004a, 2004b). The accumulation of these contaminants is likely to accelerate as a consequence of continuing economic and industrial growth in the region. It is therefore imperative to understand the fate of these contaminants in the surface environment of Guangzhou in order to assess their potential long-term impacts on the receiving aquatic system (the Pearl River).

It has been established that total concentrations are not sufficient to evaluate the ecotoxicological significance of heavy metals in the environment. The mobility and bioavailability of heavy metals is a function of their physicochemical properties of the binding forms (species) in which they occur (Harrison *et al.* 1981). Among the methods for investigating partitioning of contaminants in solid phase, the use of chemical extraction (sequential selective chemical extractions, also called "speciation schemes") is the most common (Fergusson 1991). The sequential extraction methods are based on the rational use of a series of increasingly aggressive reagents to dissolve successively different solid fractions (*e.g.,* mineral) believed to be responsible for retaining the elements. The procedure described by Tessier *et al.* (1979) is probably one of the most vigorously tested and widely used sequential extraction procedures. It is an operationally defined method, which sequentially differentiates heavy metals into five fractions: (i) exchangeable; (ii) bound to carbonates or

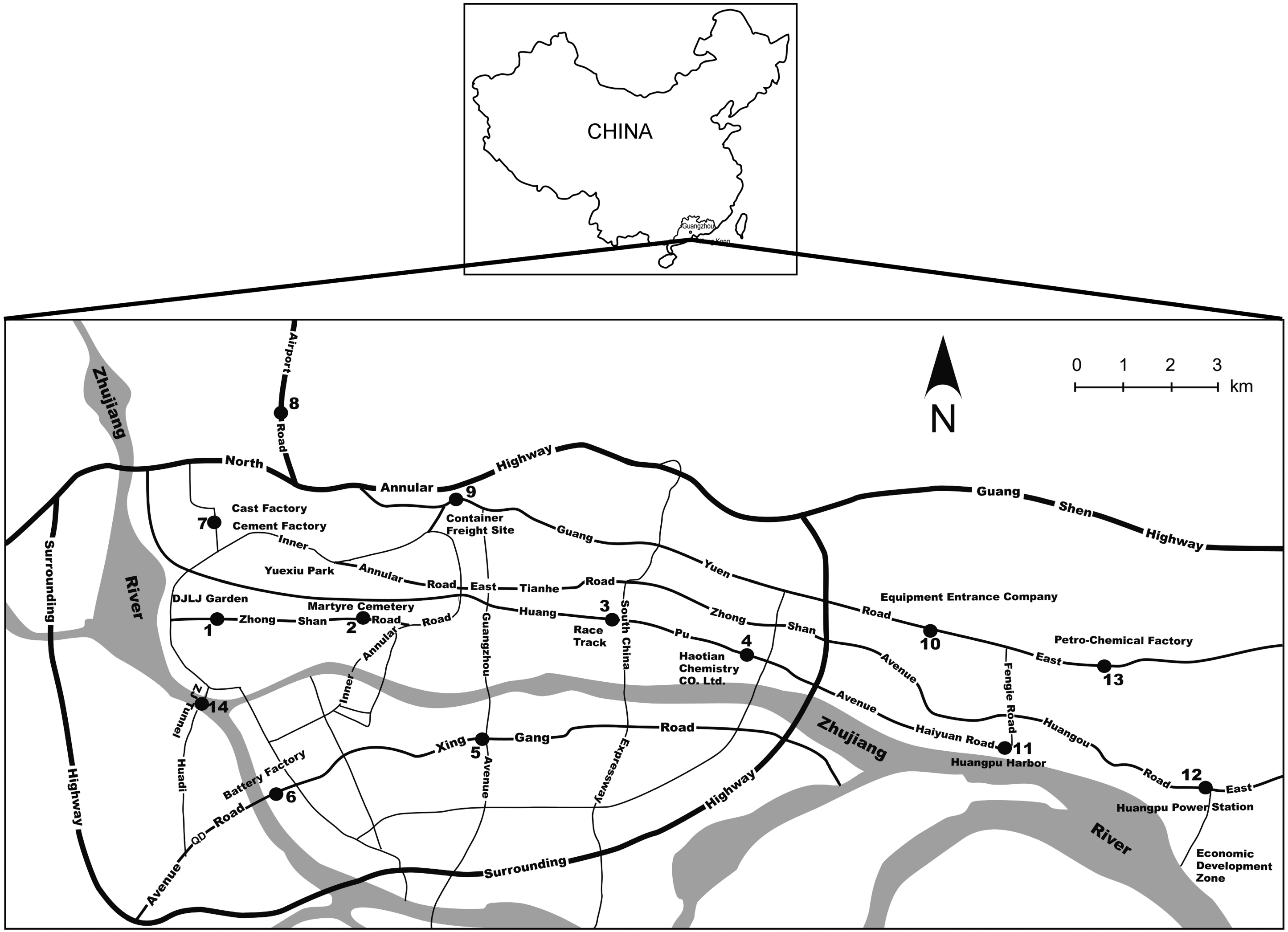

Figure 1. Guangzhou, the capital of Guangdong province.

specifically absorbed; (iii) bound to Fe-Mn oxides; (iv) bound to organic matter/ sulfides; and (v) residual.

Chemical partitioning of heavy metals in road dusts and urban soils has been investigated by various researchers (*e.g.,* Wang *et al.* 1998; Charlesworth and Lee 1999; Li *et al.* 2001; Banerjee 2003). However, studies of partitioning of heavy metals in road dusts and their corresponding gully sediments in the same urban setting are rare. As road dusts are transported into the receiving aquatic body through gully systems, they can undergo considerable physical and chemical transformations (de Miguel *et al.* 1999). Chemical partitioning of the contaminants in both road dusts and gully sediments can therefore be useful to evaluate the long-term fate of the contaminants in the urban system.

Only a few studies have reported the mineralogical composition and/or contaminant mineralogy of the road dust samples (Biggins and Harrison 1980; Linton *et al.* 1980; Harrison *et al.* 1981; Kuang *et al.* 2004). This is mainly because the application of direct instrumental techniques, particularly X-ray diffraction (XRD), has had limited success in identifying contaminant mineralogy. It has been established that only a minor portion of heavy metal contaminants in urban deposits exists in a crystalline form suitable for XRD analysis (*e.g.,* Biggins and Harrison 1980). It can be difficult to identify other phases, such as Fe-Mn oxyhydroxides, which play an important role in retaining heavy-metal contaminants due to their poorly crystallized nature or frequent presence in only low quantities. As a result, the overall mineralogical content of road dusts and the mineralogy of heavy-metal contaminants have been inferred primarily by using chemical extraction procedures (Harrison *et al.* 1981; Li *et al.* 1995). However, Ca-bearing minerals (*e.g.,* calcite), which are among the most common minerals in the urban environment and are strongly linked to the operationally defined carbonate/specifically adsorbed phase (Harrison *et al.* 1981), can be easily identified by XRD due to their crystalline nature and presence in sufficiently high quantities.

This article documents the results of a sequential extraction procedure involving five operationally defined fractions to determine the chemical partitioning of Cu, Pb, and Zn in the urban deposits of Guangzhou. Special emphasis was given to the mineralogical characteristics of these urban deposits. Integrated assessments based on the chemical speciation of Ca and the actual mineralogy of Ca-bearing phases were also performed in order to improve our understanding of the potential processes affecting the mobility of certain contaminants (such as Pb and Zn) known to be strongly associated with the operationally defined carbonate fraction.

MATERIALS AND METHODS

A total of 28 composite samples from road dusts and corresponding gully sediments were collected in March 2003 along the major roads running through the main commercial, residential, and industrialized districts of the city (Figure 1). Guangzhou has a mild, subtropical climate, with hot and humid summers and dry and cool winters. The mean temperature in the wet and dry seasons is around 28°C

Table 1. Sampling locations and corresponding annual daily traffic (ADT).

Sampling location	ADT*	Location ID	Sample ID**
Zhongshan Road near Li-Jin-Yuan bus station	60,000	GZ-1	RD-1; GU-1
Zhongshan Road near Martyr Cemetery	60,000	GZ-2	RD-2; GU-2
Huangpu Avenue near Race Course	60,000	GZ-3	RD-3; GU-3
Huangpu Avenue near Haotian Chemical Limited	60,000	GZ-4	RD-4; GU-4
Xin-Gang Road near Ke-Cun Bridge	50,000	GZ-5	RD-5; GU-5
Xin-Gang Road near He-Tong Bridge	50,000	GZ-6	RD-6; GU-6
Xi-Wan Road near a Cement Factory	60,000	GZ-7	RD-7; GU-7
Airport Highway to Bai-Yun Airport	70,000	GZ-8	RD-8; GU-8
Guangyuan Road near Guangzhou Eastern Train Station	70,000	GZ-9	RD-9; GU-9
Guangyuan Road near Car Factory	70,000	GZ-10	RD-10; GU-10
Huangpu Dock Road near Huangpu Dock	20,000	GZ-11	RD-11; GU-11
Zhongshan Avenue near Guangzhou Power Plant	70,000	GZ-12	RD-12; GU-12
Petrochemical Factory		GZ-13	RD-13

**RD = road dust; GU = gully sediment.

and 13°C, respectively. Annual total rainfall is around 1,682 mm, most of which falls between April and September.

The average daily traffic (ADT) of the sampling sites was estimated to range from 20,000–70,000 vehicles per day. The sample locations and corresponding ADT are given in Table 1. The road dust samples were collected using a plastic brush and a dustpan, whereas the gully sediments were retrieved with a plastic scoop. These samples were oven-dried at 35°C for 3 days and then sieved through a 2 mm plastic sieve to remove coarse debris and other gravel-sized materials. The dried and sieved samples were then homogenized with an agate mortar and pestle, and stored in a dessicator prior to chemical analysis.

Calcium, Cu, Pb, and Zn concentrations of the extracted solutions were measured using ICP-AES (Perkin Elmer Optima 3300 DV). Analytical procedures and measures for quality control and assurance were as described by Wong *et al.* (2002). A modified Tessier's method, as described by Li *et al.* (1995), was used. Blanks and replicates represented 10% and 20%, respectively, of the sample population. Two standard reference materials from National Institute of Standardization and Testing (NIST 2709 San Quan Soil and NIST 2711 Soil tainted with Pb from leaded paint) were also inserted into the batch. The percentage recoveries of NIST 2709 and NIST 2711 were 72.1 and 70.1 for Ca, 102.2 and 103.4 for Cu, 63.5 and 87.3 for Pb, and 89.1 and 86.7% for Zn, respectively. The percentage recoveries (the sum of five fractions/independent total concentration) from the samples were 83.1 for Ca, 98.7 for Cu, 86.4 for Pb, and 90.2 for Zn. The mineralogical compositions of the samples were examined by X-ray diffraction (XRD) using a Philips PW3040 instrument with Cu ($K\alpha$) radiation at 40 kV and 40 mA operating conditions using a step size 0.02° 2θ. The pH of the road dusts and gully sediments were measured in a solution (4 g of sample in 10 mL dionized water) after 30 min of shaking and centrifuging.

Table 2. Elemental concentrations and pH values of road dusts in Guangzhou (mg/kg).

Sample ID	Ca	Cu	Pb	Zn	pH
RD-1	27800	339	74.8	492	8.2
RD-2	29600	53	166	239	9.4
RD-3	24600	93	199	350	9.8
RD-4	19800	45	185	211	11.7
RD-5	33100	34	76	232	10.9
RD-6	24300	59	153	360	10.6
RD-7	96100	67	112	237	8.6
RD-8	22800	61	234	327	10.6
RD-9	21200	282	220	720	10.2
RD-10	28800	94	268	540	7.9
RD-11	24400	422	926	1826	NA
RD-12	29000	669	323	1347	11.5
RD-13	34600	294	375	740	9.1
Mean	32008	193	255	586	9.9
Median	27800	93	199	360	10.0
Stdev	19751	195	220	487	1.3

RESULTS

Elemental Concentrations

The concentrations of Ca, Cu, Pb, and Zn of road dusts and corresponding gully sediments and their pH values are summarized in Tables 2 and 3, respectively. The

Table 3. Elemental concentrations and pH values of gully sediments in Guangzhou (mg/kg)

Sample ID	Ca	Cu	Pb	Zn	pH
GU-1	20800	24.7	338	722	ND
GU-2	31200	31.3	70.2	129	8.0
GU-3	20800	105	189	354	7.3
GU-4	18800	49.8	109	161	8.0
GU-5	21300	40	74.3	205	8.1
GU-6	34300	123	197	2640	8.0
GU-7	75200	82.2	110	368	9.8
GU-8	30200	201	189	596	8.4
GU-9	24000	114	144	377	NA
GU-10	24600	80.8	214	409	8.0
GU-11	22900	162	490	1720	9.1
GU-12	28200	147	253	915	7.4
Mean	29358	97	198	716	8.2
Median	24300	93.6	189	393	8.0
Stdev	15217	56	120	747	0.8

ND: Not determined.

Table 4. Heavy metal concentrations of road dusts in Guangzhou and other cities (mg/kg).

Location	Reference		Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Guangzhou	Duzgoren-Aydin *et al.* 2005	Mean	176	240	586
		Std	186	208	452
		Range	(34–669)	(75–926)	(211–1826)
Hong Kong	Yim and Nau (1987)	Mean	635	1287	2902
	Wang *et al.* 1998	Mean	296	652	2305
	Li *et al.* 2001	Mean	173	181	1450
		Std	190	93	869
Beijing	Kuang *et al.* 2004	Mean	42	57	193
		Std	13	27	69
		Range	(25–79)	(27–176)	(114–360)
Delhi	Banerjee 2003	Mean	721	598	366
		Std	617	1153	78
		Range	(129–1903)	(128–3670)	(242–499)
London	Harrison 1979	Mean	112	1914	571
	Thornton 1991	Mean	115	1354	513
	Wang *et al.* 1998	Mean	300	897	1866
Birmingham	Charlesworth *et al.* 2003	Mean	467	48	534
		Range	(16–6688)	(0–146)	(81–3165)
Coventry	Charlesworth *et al.* 2003	Mean	226	47	385
		Range	(49–815)	(0–199)	(93–3038)

heavy metal concentrations of the road dust samples in Guangzhou were compared with those in other major cities (Table 4) including Hong Kong (Yim and Nau 1987; Li *et al.* 2001), Beijing (Kuang *et al.* 2004), London (Thornton 1990; Wang *et al.* 1998), Birmingham and Coventry (Charlesworth *et al.* 2003), and Delhi (Banerjee 2003).

In general, the heavy metal contents of the samples taken from the eastern side of Guangzhou (where most of its industry is concentrated) were noticeably higher than those of the samples collected from the western side (the mainly residential and commercial districts). The highest Pb and Zn concentrations (926 and 1,826 mg/kg, respectively) were detected at Huangpu Dock Road (GZ-11), where the nature of traffic involved frequent brake and stop-start maneuvers, and were mainly due to vehicle exhaust emissions. However, elevated Cu and Zn concentrations (339 and 492 mg/kg, respectively) were also found at locations where similar traffic flows existed, indicating that vehicle corrosion and wear and tear on tires were also important sources of heavy metal contaminants. On the other hand, significantly high Cu and Zn concentrations (669 and 1,350 mg/kg, respectively) were found at GZ-12, close to the Guangzhou Power Plant, probably resulting from discharges from coal combustion as well as traffic–related activities. In general, Ca concentrations remained relatively constant, except in the case of the sampling site near the cement factory (GZ-7), where Ca concentrations (96,100 mg/kg) were four times higher than at the other sites.

Table 5. Mineralogical compositions of road dusts in Guangzhou.

Sample ID	Quartz	K-feldspar	Plagioclase	Illite-Mica	Kaolin	Calcite	Hematite
RD-1	D	A	A	mn	mn	mn	—
RD-2	D	A	A	mn	mn	A	Tr
RD-3	D	A	mn	mn	mn	A	Tr
RD-4	D	A	M	mn	Tr	mn	Tr
RD-5	D	A	A	mn	Tr	A	—
RD-6	D	A	A	mn	Tr	A	Tr
RD-7	D	A	mn	mn	Tr	D	Tr
RD-8	D	A	A	mn	Tr	A	—
RD-9	D	A	A	mn	Tr	A	—
RD-10	D	A	mn	mn	Tr	mn	Tr
RD-11	D	A	A	mn	Tr	mn	mn
RD-12	D	D	mn	A	Mn	mn	—

Abbreviations: D: Dominant; A: Abundant; mn: minor; Tr: trace. Order of relative abundance D>A>mn>tr.

Guangzhou's urban deposits were slightly to noticeably alkaline (Tables 2 and 3). Overall, the pH values of road dusts varied from 7.9–11.5, with a mean value of 9.9 ± 1.3, whereas the pH values of gully sediments changed from 7.3–9.8, with a mean value of 8.2 ± 0.8. However, at any given sampling location road dusts were slightly more alkaline than the corresponding gully sediments (at 90% level of confidence, $p < .05$).

Mineralogical Characteristics

The mineralogical compositions of the road dusts and gully sediments of Guangzhou are summarized in Tables 5 and 6, respectively. Minerals commonly found in the samples included quartz, K-feldspar, plagioclase, calcite, mica, and clay minerals. Quartz, the most resistant mineral to physical and chemical weathering,

Table 6. Mineralogical compositions of gully sediments in Guangzhou.

Sample ID	Quartz	K-feldspar	Plagioclase	Illite-Mica	Kaolin	Calcite	Hematite
GU-1	D	A	A	mn	Tr	mn	—
GU-2	D	A	A	mn	Tr	mn	—
GU-3	D	D	mn	mn	Tr	mn	—
GU-4	D	A	mn	mn	Tr	mn	Tr
GU-5	D	A	A	mn	Tr	mn	—
GU-6	D	A	mn	A	mn	mn	—
GU-7	D	A	Tr	mn	Tr	A	—
GU-8	D	A	A	mn	Tr	mn	Tr
GU-9	D	A	mn	mn	Tr	mn	—
GU-10	D	A	A	mn	Tr	mn	Tr
GU-11	D	A	A	mn	Tr	mn	Tr
GU-12	D	A	mn	mn	Tr	mn	—

Abbreviations: D: Dominant; A: Abundant; mn: minor; Tr: trace. Order of relative abundance D>A>mn>tr.

dominated the overall mineralogy of the urban deposits. K-feldspar was also found in copious amounts in all urban deposits. There were slight variations in the amounts of plagioclase in the various samples, and more noticeable variations in the amounts of calcite. In general calcite was one of the most abundant minerals in the road dusts, and was probably derived from the erosion of concrete pavements and other construction materials or from the cement factory (Harrison *et al.* 1981; Tossavainen and Forssberg 1999). In the gully sediments, however, calcite was a minor mineral phase except near the cement factory (GU-7).

Trace amounts of mica and clay minerals were ubiquitous in the urban environment. Neither Fe- nor Mn-bearing minerals were recognized by XRD, probably due to their amorphous nature or presence in only low quantities (cf. Harrison *et al.* 1981).

Chemical Partitioning

The chemical partitioning patterns of Ca, Cu, Pb, and Zn in the road dusts and gully sediments are shown in Figures 2 and 3, respectively. The results are expressed as percentage distributions of the elements within each fraction. Despite noticeable variations in the abundance of minerals and significant differences in elemental concentrations within and between the road dusts and corresponding gully sediments, the speciation patterns in general display considerable similarities.

Copper in the road dusts and gully sediments was mainly concentrated in the organic phase (~70%), and showed weaker association with the residual (15%) and Fe-Mn (10%) phases. The percentages of Cu related to carbonate and exchangeable phases were around 5% and 2%, respectively. Lead was strongly associated with the carbonate/specifically adsorbed (48%) and Fe-Mn phases (36%), with small amounts in the residual and organic fractions (10% and 5%, respectively). The percentage of exchangeable Pb fraction was less than 1%. Similar to Pb partitioning patterns, the chemical association of Zn was dominated by carbonate/specifically adsorbed (~50%) and Fe-Mn (27%) phases, with organic (11%) and residual (10%) fractions being of secondary importance. The exchangeable Zn phase was also less than 1%. Overall, these results are in good agreement with those reported in road dust studies of other regions around the world (Harrison *et al.* 1981; Li *et al.* 2001; Charlesworth *et al.* 2003). Calcium in the road dusts and gully sediments was strongly associated with the carbonate/specifically adsorbed (~70%) fraction. The remaining Ca was mostly in exchangeable (17%) and Fe-Mn (10%) phases, with small amounts in the residual (~4%) and organic (<1%) phases.

DISCUSSION

Heavy Metal Concentrations

Overall, the values of the concentrations of Cu, Pb, and Zn in Guangzhou's urban deposits varied widely. As the focus of this article was to discuss the potential fate of selected heavy metal contaminants, the level and distribution of heavy metals have been extensively discussed in another manuscript (Duzgoren-Aydin *et al.* 2005). Briefly, it was documented that the type and extent of contamination in the surface

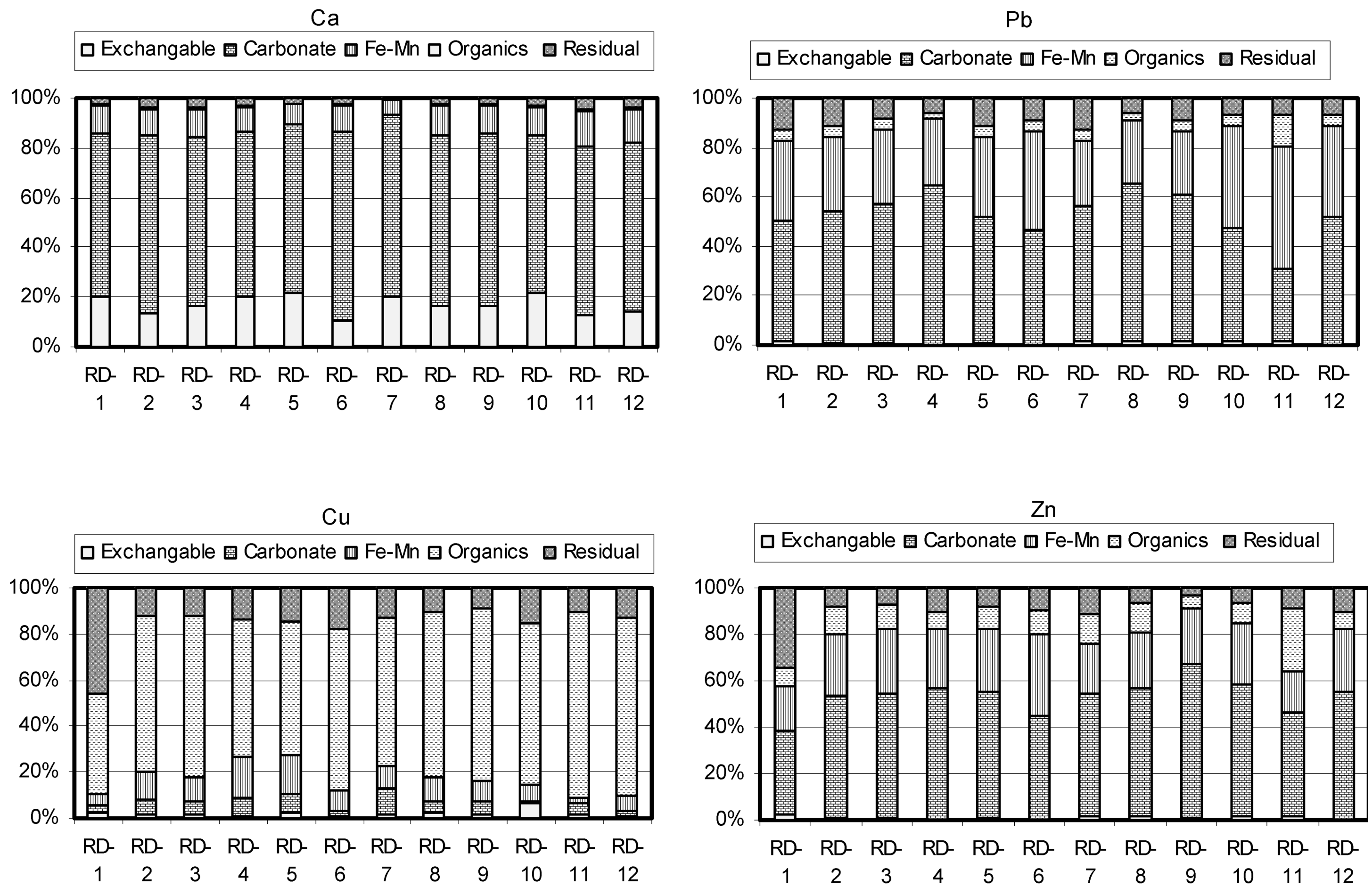

Figure 2. The chemical partitioning patterns of Ca, Cu, Pb, and Zn in the road dust.

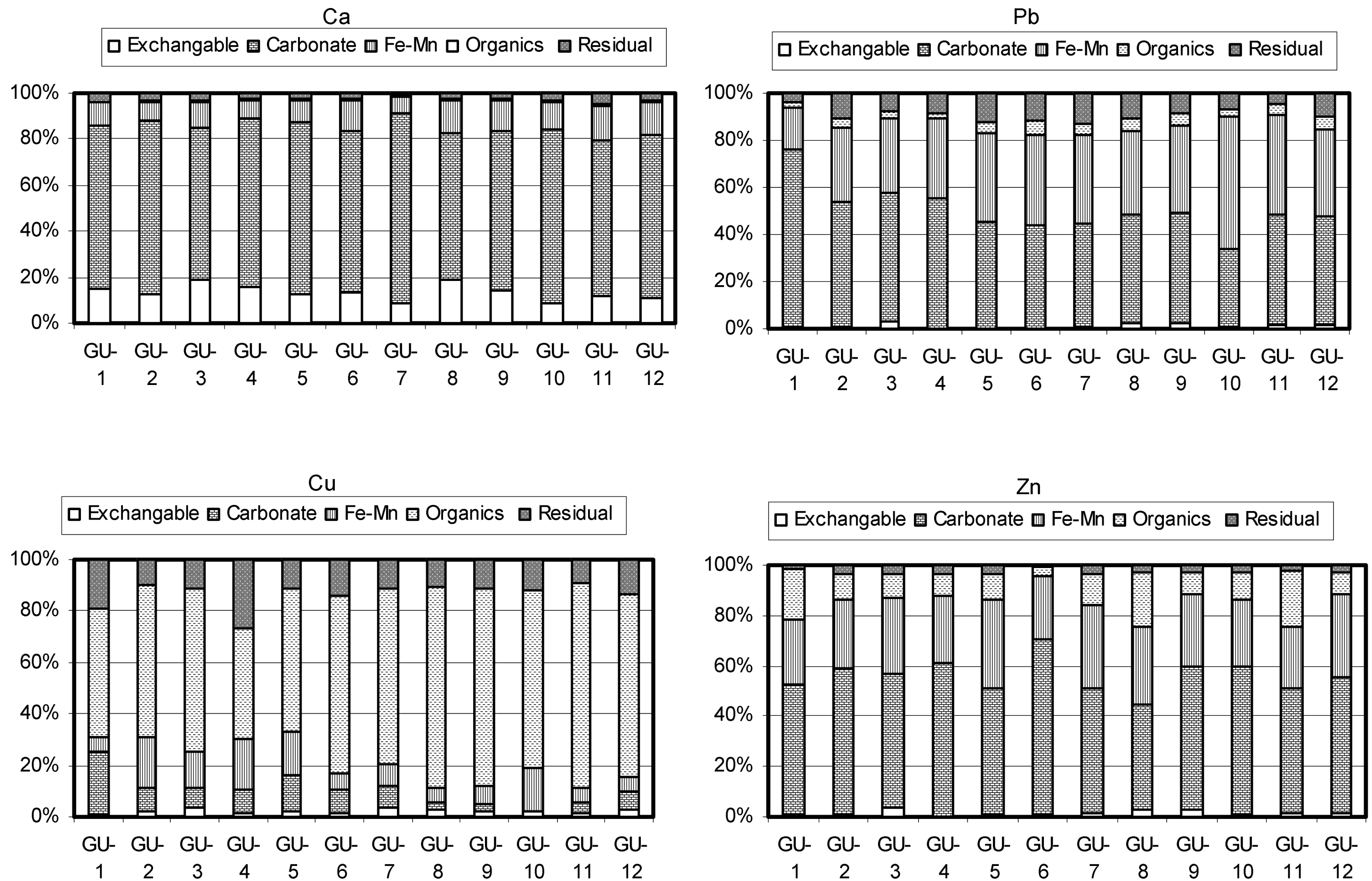

Figure 3. The chemical partitioning patterns of Ca, Cu, Pb, and Zn in the gully sediments.

environment of Guangzhou reflects the characteristics of the anthropogenic activities taking place in a given location, and that traffic- and industrial-related activities are the primary sources of contaminants in the city.

Most previous studies on heavy metal contamination in urban environments in Mainland China were based on urban soils (*e.g.,* Lu *et al.* 2003) or atmospheric particulate matters (*e.g.,* Ning *et al.* 1996). A few recent studies, however, utilized road dusts as sampling media (*e.g.,* Kuang *et al.* 2004). By contrast, road dusts and urban soils have been extensively used to evaluate the level, distribution, and fate of heavy metal contaminants in the surface environment of Hong Kong in the past two decades (Yim and Nau 1987; Li *et al.* 2001; Duzgoren-Aydin *et al.* 2004b). As illustrated in Table 4, heavy metal concentrations in road dusts in Guangzhou were similar to those in Hong Kong reported by Li *et al.* (2001), but noticeably lower than those reported by Yim and Nau (1987). This can be partly attributed to the progressive phase-out of leaded petrol in both Hong Kong and Guangzhou. On the other hand, compared to recent data from other cities such as Birmingham and Coventry, Pb concentrations in Guangzhou were still noticeably higher, whereas Cu and Zn concentrations were comparable. Significantly, although leaded petrol is no longer available in Guangzhou, overall utilization of coal as a major resource of power or production is still widespread both in Guangzhou and elsewhere in mainland China. As coal is a major source of Pb emissions (Adriano 1986), in addition to traffic- and industrial-related sources, the level of Pb contamination is expected to remain high in the region.

Integrated Chemical and Mineralogical Assessment

The data available on the mineralogical compositions of urban deposits worldwide, principally based on road dust samples, is limited. Despite a significant variation in the level of contamination and the differences in urban natural and anthropogenic settings, the major mineral components of the road dusts appear to be similar, and are dominated by quartz and feldspars. Quartz, the most abundant mineral in road dusts and gully sediments in Guangzhou, is biodurable, that is, resistant to decomposition and lacking easily bioavailable contaminants (Plumlee and Ziegler 2004). Its relative abundance would therefore have very little or no effect on the mobility of heavy metals in the urban environment. Feldspar minerals (including plagioclase and K-feldspar) were also common in all urban environments, but may contain trace amounts of heavy metal contaminants in their crystal structures (Sposito 1983). For example, K in feldspar can be substituted by Pb and Cu, whereas Ca in feldspar can be substituted by Pb and Zn. Similarly, during the formation of secondary minerals (such as clay minerals), major cations (K and Ca) can be replaced by trace metal ions (Cu, Pb, and Zn) of the same charge sign and of comparable size. Such co-precipitation requires free diffusion and relatively high structural compatibility (Sposito 1983). More importantly, from an environmental perspective, they do not pose an immediate threat to the receiving ecosystem. The heavy metals captured within the crystal structure of primary or secondary minerals were considered as geogenic and ideally represented by operationally defined residual phase. The residual Cu, Pb, and Zn fractions of urban deposits in Guangzhou were equal or less than 15% (15% for Cu and 10% for Pb and Zn), suggesting their dominantly anthropogenic origin. The type and abundance of urban minerals may, however, play an important role in releasing the heavy metal contaminants into the receiving ecosystem by means of adsorption processes.

Unlike the other urban minerals, carbonate minerals (*e.g.,* calcite) can be at least partly dissolved by weak acids. As a result, heavy metals either captured within the crystal structure or adsorbed to its surface or co-precipitated as heavy metal bearing carbonate minerals (such as $PbCO^3$, $ZnCO^3$) can become easily bioavailable as the ambient pH conditions change. In fact acid rains in the region are common, and their pH values are usually lower than 4.5 (Wang *et al.* 2000), which is low enough to dissolve carbonate minerals at least partially. The lack of calcite in gully sediments (in contrast to corresponding road dusts) can therefore be explained by means of partial dissolution of calcite during transportation from road surfaces to gully pots:

$$CaCO_3(s) + H_2O(aq) — Ca^{+2}(aq) + HCO_3^-(aq) + OH^-(aq) \tag{1}$$

$$CaCO_3(s) + H^+(aq) — Ca^{+2}(aq) + HCO_3^-(aq) \tag{2}$$

The results of the chemical speciation analyses confirmed that Ca was mobile in the surface environment of Guangzhou, as it was mostly associated with the first two operationally defined fractions (>87%). The exchangeable Ca was fairly significant and remained constant (∼17%) in all samples. It probably represented partial dissolution of carbonate fraction rather than ion-exchange processes (cf. Gleyzes *et al.* 2002), particularly in the case of the road dust samples, where most of Ca occurred as calcite. On the other hand, the exact chemical form(s) of Ca in gully sediments was largely unknown, but they were probably a combination of CaO, $Ca(OH)_2$, $CaSO_4$, and $CaCO_3$. However, only the presence of calcite ($CaCO_3$) was confirmed by XRD. Considering that gully sediments were still slightly alkaline, it is likely that they contained a significant amount of $Ca(OH)_2$ together with some $CaCO_3$. As in the exchangeable fraction, the percentage of Ca content recovered from the carbonate/specifically adsorbed phase remained consistent, despite significant differences in actual Ca content and abundance of calcite among the samples. In other words, the overall chemical partitioning of Ca is expected to be similar for the samples from different urban settings (road dusts and gully sediments), disregarding the differences in actual calcite contents, as the extraction process is really heavy on variation in pH condition rather than true dissolution of actual minerals.

It is assumed that the mobility and bioavailability of heavy metals are related to the solubility of chemical forms of the metals and to the order of extraction. In general, heavy metals in the exchangeable fraction tend to be readily soluble and mobile. The carbonate/specifically adsorbed, Fe-Mn oxides and organic fractions, represent the metals that are potentially soluble and mobile. Those in the residual fraction are considered the most immobile and therefore most stable in the environment (Tessier *et al.* 1979; Harrison *et al.* 1981). The relative mobility and bioavailability of Cu, Pb, and Zn in the road dusts and gully sediments of Guangzhou therefore probably decrease in the following order: Pb ∼ Zn > Cu.

The mobility of Pb and Zn was closely associated both with the pH conditions and (to a lesser extent) with the redox potential of the ambient environment. The release of anthropogenic Pb and Zn into the environment is therefore to be expected under mostly acidic conditions. On the other hand, Cu was strongly bound to organic matter and therefore can become easily available under oxidizing conditions.

In addition to the anthropogenic factors, changes in natural conditions, such as increases in the acidity of rainfall and the rate of decomposition of organic matter, can trigger significant mobilization of Pb, Zn, and Cu to the receiving aquatic system. This is of particular concern in subtropical climatic regions where acid rains are common. The ever-increasing accumulation of heavy metals may therefore pose a serious threat both to the environment and to human health in the region.

Finally, the road dusts and corresponding gully sediments in Guangzhou appear to be equally susceptible to variations in environmental conditions, probably because Guangzhou's gullies do not temporarily retain incoming materials due to lack of sedimentation pots (Duzgoren-Aydin *et al.* 2005). Therefore, the gully sediments at least partly represent the direct deposition of atmospheric emission and re-suspended surface material, similar to road dusts. More importantly, however, the lack of sediment pots minimizes the potential processes (including size sorting during sediment mobilization, chemical changes at the solid/solution interface during transport, and interaction with organic matters), which might alter physicochemical (such as pH and Eh) conditions ultimately affecting the solubility of the contaminants (Morrison *et al.* 1995). Therefore, the drainage system of the cities might play an important role in terms of capturing or releasing heavy metal contaminants to the receiving aquatic body. Further studies, however, are required to test this hypothesis.

SUMMARY

- Urban deposits (road dusts and gully sediments) are reflective of a wide range of anthropogenic activities, and are a useful resource for evaluating the level and distribution of heavy metal contaminants in the surface environment.
- This study confirmed that the applied extraction scheme suffers from lack of selectivity of dissolving phases. Similarly, application of a direct instrumental technique (XRD) has its own limitations, such as crystallinity of solid phases. Integrated assessments based on both techniques, however, were complementary and can provide a better understanding of the physicochemical characteristics of the urban system.
- The relative mobility and potential bioavailability of Cu, Pb, and Zn in the urban deposits of Guangzhou were: Pb $\sim$ Zn $>$ Cu. Lead and Zn were expected to be mobile under acidic and less so under reducing conditions, whereas Cu was expected to be released into the environment under oxidizing conditions. In other words, their apparent mobility and bioavailability seemed to be sensitive to variations in the pH and redox potential of their ambient environment. Ever-increasing accumulations of heavy metals in urban settings may therefore pose a threat both to the environment and to human health.

ACKNOWLEDGMENTS

This research was funded by the Dr. S. S. Hui Trust Fund, the University of Hong Kong. We thank Dr. David Wilmshurst (HKU) for his comments on the manuscript.

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