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Assessment of TSP-bound metals through BCR 3- extraction in the urban area of Changsha, China

Chen Lin, Zhai Yun-bo*, Yang Fang, He Yi-de, Peng Wen-feng, and Fu Zong-min
College of Environmental Science & Engineering, Hunan University, Changsha 410082, China

ABSTRACT

In the present study, BCR 3-step sequential extraction procedure was applied to determine the fractionation of heavy metals in TSP samples collected from urban locations in Changsha, China. The average TSP concentration at Changsha in May was 220.7 µg m^{-3} showing that the particle pollution is serious in Changsha. The distributions of heavy metals (Cu, Zn, Mn, Pb, Cd) in different spots were evaluated and the order of average concentrations of heavy metals in Changsha atmospheric air was Zn > Pb > Cu > Mn > Cd. From the percentage distribution of species, approximately 63.3%~89.0%of total Cu present in oxidizable fraction (F3), whereas Mn has the lowest concentration in oxidizable fraction almost below the detecting limits. While Zn and Cd mainly appear in the exchangeable and weak acid soluble fraction (70% and 35%, respectively), Pb prevails in residual fraction (24~43 %). Contamination factors showed Cu, Cd and Zn had higher values indicating a high mobility and Mn and Pb having comparatively low C_f values. Principal component analysis (PCA) was applied to evaluate the analytical results and to identify the possible pollution sources of metals in Changsha.

KEYWORDS: metals, particulate matter, chemical fractionation, BCR sequential extraction, contamination factors

1. INTRODUCTION

Atmospheric total suspended particulate matter (TSP) is still a serious problem that has led to severe deterioration of the urban environment of China [1]. They have adverse environmental and related health consequences as they are vehicles of toxic metals and organic contaminants. Heavy metals are released in to atmosphere through anthropogenic processes such as industrial emissions, fossil fuels burning, garbage incineration and mining activities etc. Metals can accumulate in organism inducing perturbation of the ecosystem and adverse health effects such as cancer, neurotoxicity, immunotoxicity and cardiotoxicity [2, 3, 4]. As the toxic effects of heavy metals are now well recognized in urban places, it is extremely important to control their emissions.

Previous studies in atmospheric particles usually have been based on a total digestion to determine the heavy metals concentrations [5, 6]. Total extracts, however, give no indication of bioavailability, solubility, and mobility of heavy metals. In order to further examine the problems, it is often necessary to quantify specific metallic forms (species) [7, 8], besides, the evaluation of metals toxicity and effects on human health by chemical fractionation are also important when deciding the real activity of metals in the environment.

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*Corresponding author
ybzhai@hnu.edu.cn

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Therefore, the objective of this study is to attain the knowledge of the chemical fractionation of metals in total suspended particles (TSP) in a typical city, influenced mainly by vehicular traffic, also by some industrial focuses. In this paper, the total concentrations of the heavy metals (Cu, Zn, Pb, Cd, Mn) were determined in the samples collected from Gaokai, Jinkai, Kaifu, Maopolin areas of Changsha City which has a typical semi-tropical climate, and the fractionation of each heavy metals was studied by BCR sequential extraction procedure. The bioavailability and eco-toxicity of heavy metals (Cu, Zn, Pb, Cd, Mn) were evaluated by the contamination factors (C_f). Also the principal component analysis (PCA) was used to find the possible origin of heavy metals in the TSP of Changsha.

2. MATERIALS AND METHODS

2.1. Area description

The present study was conducted in urban areas of Changsha, middle-south region of China (Fig. 1). The Changsha City is the capital of Hunan Province, China, located in the eastern part of the province, spanning over 111º53'–114º15'E and 27º51'–28º40'N. Changsha City is a low hilly region with its elevation descending from south to north, varying from 23.5 to 1607.9 m. A subtropical monsoon climate gives Changsha City an annual rainfall of 1483.6 mm, which is mainly from April to July [9].

Twenty TSP filters collected from four stations of the atmospheric monitoring network of Changsha City were analyzed to quantify the content of metals. Sampling sites are presented in Fig. 1, and characteristics of the monitoring stations in Table 1.

2.2. Particulate sampling

The samples were taken from May 7 to May 17 2008 in the summer of Changsha City. They were collected on a pre-heated (4h at 450 °C) fibreglass filters using a medium-volume sampler (TH-150) at a flow rate of 0.1-0.12 m^3min^{-1}. A sampling period of 8h was adopted form 9:00 AM to 5:00 PM. The filters were stored in polyethylene bags at 4 °C. All the procedures were strictly quality controlled to avoid any possible contamination of the samples. The temperature, relative humidity and atmospheric pressure were recorded during the sampling period.

2.3. Instruments and reagents

A Perkin-Elmer (AAnalyst-700) model flame atomic absorption spectrometry (FAAS), a Clifton

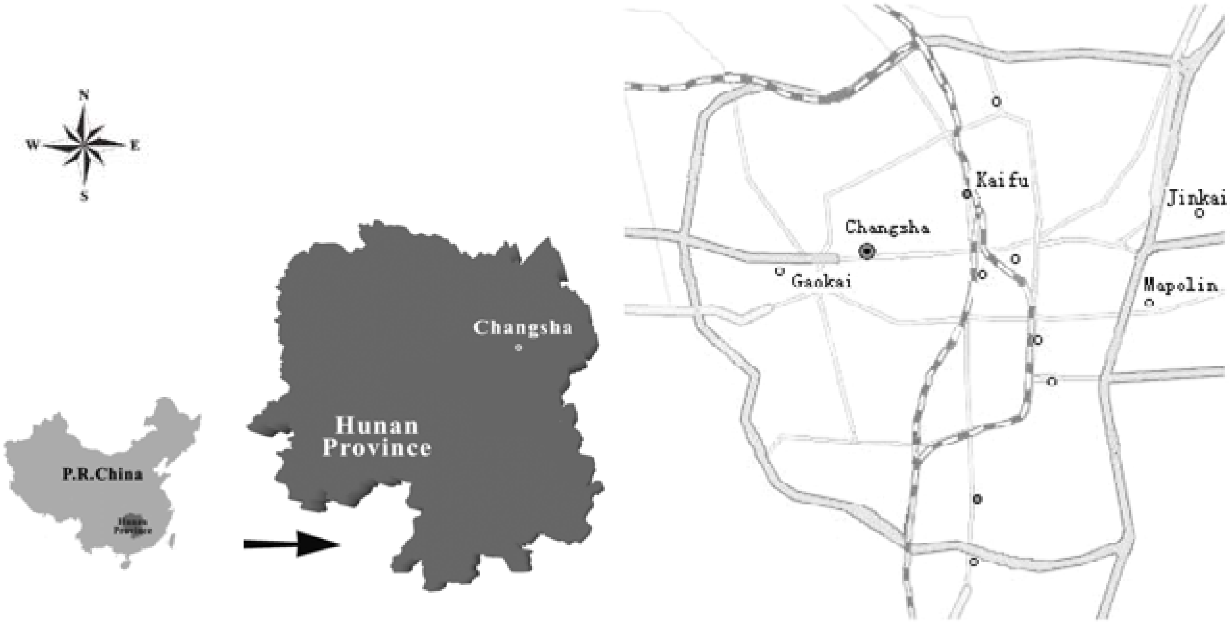


Fig. 1. A geographical map depicting the locations of the four monitoring stations within the city of Changsha, China.

Table 1. Characteristics of monitoring stations.

Stations	Changsha Zone	Characteristics
Gaokai (GK)	Northwest	High-tech industrial area with high traffic
Jinkai (JK)	Northeast	Industrial area with high traffic
Kaifu (KF)	North	Residential and commercial zone with medium traffic
Mapolin (MPL)	East	Living area with low traffic

model shaker, a centrifuge of MLTW54 model and a Jenco 672 model pH-meter were used throughout the analyses. Double-deionized water was used for preparing the solutions and all dilutions. All stock solutions of the metals (1000 mg/L) were prepared from the corresponding pure metals (Tianjin Kermel Reagents Development Centre). The working solutions of metals were used by diluting these stock solutions prior to use. Acetic acid, CH_3COOH; hydroxyl-ammonium chloride, $H_2NOH{\cdot}HCl$; Hydrogen peroxide; ammonium acetate, CH_3COONH_4; HCl and HNO_3 acids were of guaranteed reagent grade. (Tianjin Kermel Reagents Development Centre). All the glassware and plastic vessels were treated by dilute 10% (v/v) HNO_3 acid for 24 h, then rinsed with distilled water and then allowed to air-dry before the use.

2.4. The modified BCR sequential extraction procedure

The modified three-stage procedure recommended by BCR was performed during the sequential extraction on the TSP samples in polythene vessels (50ml volume). The sample filters (including blank sample) were cut into small pieces. The BCR procedure can be described as follows [10]:

Step 1. (Exchangeable and weak acid soluble fraction) each sample was extracted with 20 ml of 0.10 $mol{\cdot}L^{-1}$ acetic acid (Kermel pro-analysis) solution by shaking in a mechanical, end-over-end shaker at 22 ± 5 ºC for 16 h. The extract was separated by centrifugation at 6000 rpm for 15 min, collected in polyethylene bottles and stored at 4ºC until analysis. The residue was washed by shaking for 15 min with 10 ml of doubly deionised water and then centrifuged, reclaiming the supernatant.

Step 2. (Reducible fraction) 20 ml of 0.5 $mol{\cdot}L^{-1}$ hydroxyl-ammonium chloride (Kermel pro-analysis) solution was added to the residue from the first step, and the mixture was shaken at 22 ± 5 ºC for 16 h. The acidification of this reagent is by the addition of a 2.5% (v/v) 2 $mol{\cdot}L^{-1}$ HNO3 solution (prepared by weighing from a suitable concentrated solution). The extract was separated and the residue was washed as in the first step.

Step 3. (Oxidizable fraction) 5 ml of 34% (v/v) hydrogen peroxide (Kermel pro-analysis) solution (adjusted to pH 2.0 with HNO_3) was carefully added to the residue from the second step. The mixture was digested for 1 h at 22 ± 5 ºC and for 1 h at 85 ± 2 ºC, and the volume was reduced to less than 3 ml. A second aliquot of 5 ml 34% of H_2O_2 was added, the mixture was digested for 1 h at 85 ± 2 ºC, and the volume was reduced to about 1 ml. The residue was extracted with 25 ml of 1 $mol{\cdot}L^{-1}$ ammonium acetate (Kermel pro-analysis) solution, adjusted to pH 2.0, shaken at 22 ± 5 ºC for 16 h. The extract was separated and the residue was washed as in previous steps.

Residual from step 3: (Residual fraction) the residue from step 3 was digested with 5 ml aqua regia, followed by microwave digestion (with Telfon—TFM vessel).

2.5. Statistical analysis

The Analytical blanks were almost below the detection limits. The concentration of trace elements measured in the blank filters were subtracted from measuring results and the principal component analysis (PCA) was used to evaluate the analytical data with the aim of finding out the latent relationships between variables and for investigating pollutants (variables) sources. The PCA was applied to the data matrix (18 cases×5 metals and TSP) of pseudo total metal concentrations (the sum of F1 + F2 + F3 + R) to ascertain the possible contributing factors towards the metal concentrations and thereby determine which metals have a common origin.

3. RESULTS AND DISCUSSION

3.1. Total suspended particulate

Concentrations of TSP in the different stations from May 7 to May 17 are given in Table 2 (μg m^{-3}).

It can be seen that the highest value was found at JK area which is the industrial area with many factories and high traffic; although the mean concentration is 269.6 μg m^{-3} below the diurnal arithmetic average of the National Ambient Air Quality Standard (NAAQS), with 300 μg m^{-3} for TSP of level II (GB 3095-1996), the daily maximum concentration exceeds it.

MPL area showed the lowest value probably due to its characteristic of residential area and low traffic. KF area showed the second highest values mostly because of high traffic. It also can be found that GK area had a litter bigger value than the MPL area possibly indicating that high-tech industry brings few particulate matters.

The daily average concentrations of TSP in Changsha were 220.7 ± 42 μg m^{-3} which was comparable with the Chinese standard level II of 300 μg m^{-3} and compared with the limits of the daily average of 200 μg m^{-3} for TSP almost 12% of the daily TSP concentrations was higher than the requirement, showing that the particle pollution is serious in Changsha.

3.2. Total concentrations of airborne trace metals in all study sites

The total concentrations of the heavy metals Cu, Zn, Mn, Pb, and Cd in the four spots are listed in Fig. 2.

Fig. 2 presents concentrations of the five trace elements in air particulate matters of the four spots.

Table 2. Total suspended particulates concentration.

Location	**Maximum**	**Minimum**	**Mean value** (μg m^{-3}, ±SD)
GK	230.4	154.2	185.5±32.6
JK	310.5	197.5	269.6±49.8
KF	308.8	166.2	252.2±56.4
MPL	213.3	143.2	175.3±29.0

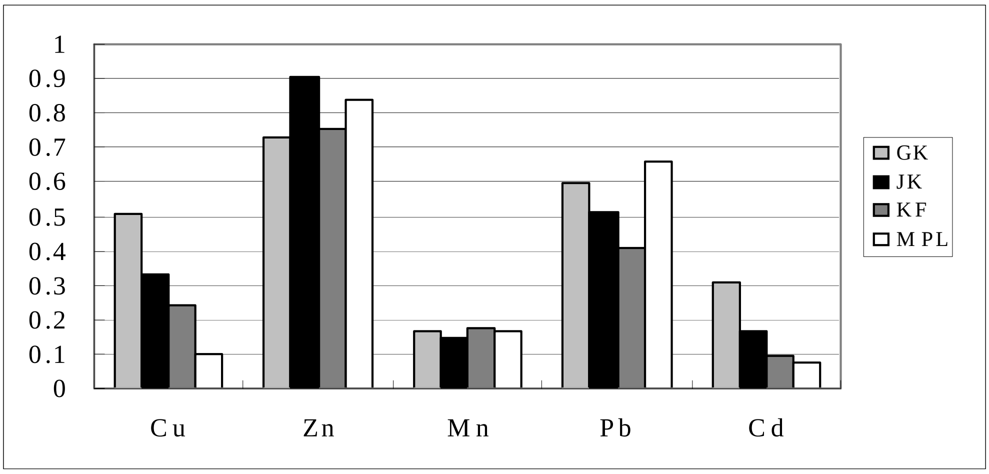


Fig. 2. Total concentrations of selected metals in four spots (μg m^{-3}).

The results are calculated by summing the data of each filter used for BCR extraction to represent the total amount of each trace element. Although GK area has a low TSP concentration, the concentration of Cu and Cd of this spot is higher than other spots indicated that the concentration of TSP and heavy metals has little correlation with each other.

Table 3 shows the analytical results of this study and a comparison to different previous studies [11, 12]. The mean concentrations of all metals in TSP, derived by using the values of each individual site, are: Zn (0.806 μg m^{-3}), Pb (0.544 μg m^{-3}), Cu (0.295 μg m^{-3}), Mn (0.163 μg m^{-3}), Cd (0.161 μg m^{-3}). All the metal concentrations in TSP in Changsha are 1.0~23.5 times higher than those in TSP in Beijing, and 3.2~66.7 times higher compared to those in TSP in the center of Tokyo, Japan. The mean concentrations of all metals can be listed in the following order: Zn > Pb > Cu > Mn > Cd. And the total metals concentration in the four spots can be listed in the following order: GK > JK >KF> MPL, showing that heavy metal contamination in GK is the most serious although along with a low TSP concentration in Changsha City.

3.3. The fractionation of heavy metals in the TSP samples

The bioavailability and eco-toxicity of metals mainly depend on their fractionation in total suspended particulates. Heavy metals that are distributed in acid soluble/exchangeable fraction (F1) and reducible fraction (F2) are readily to be transferred into ecosystem causing pollutions. The oxidizable fraction (F3) in oxidizing condition is also easily mobilized and transformed into acid soluble/exchangeable fraction (F1) or reducible fraction (F2) [13]. So it is important to determine the chemical forms of the studied elements.

The fractionation of Cu, Zn, Pb, Mn, and Cd estimated by BCR procedure represented as percent of total concentrations in TSP is shown in Fig. 3, and the statistical results of each fraction of heavy metals in samples are listed in Table 4.

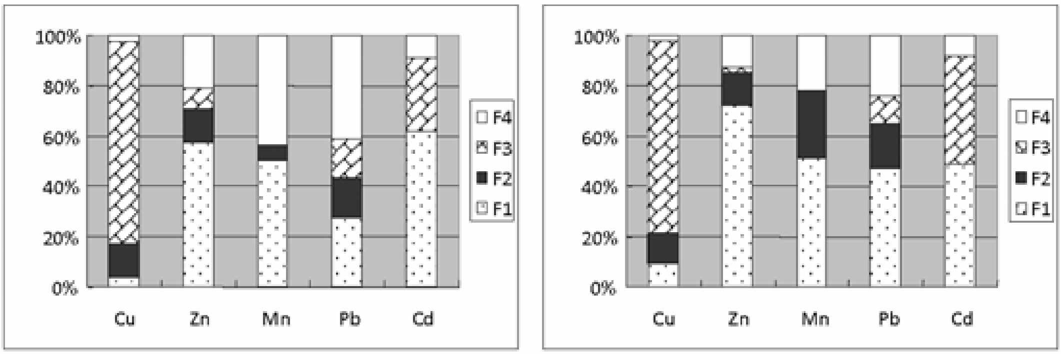
Copper: It is noted that the content of F1, F2 and F4 fraction of copper was low in all the stations, especially residue fraction (F4) low less than 1.3%. 63.3%~89.0% of total Cu present in oxidizable fraction (F3) in the four stations. The obtained results were generally consistent with those reported by other researchers [14]. The presence of Cu in the oxidizable phase indicates that a significant amount of Cu may be sulfidic and/or bound by organic ligands [15]. Although the sequential extraction methods used in each case differed, it does appear that Cu can exhibit varying distributions in PM from different sources and/or locations. Overall, however, the Cu in most of these PM samples did exhibit high environmentally mobile character as well as environmentally immobile character, which may indicate that both anthropogenic and natural sources are significant contributors to Cu [16].

Manganese: On the other hand, Mn has the lowest concentration in oxidizable fraction (F3) and is distributed almost exclusively in the exchangeable

Table 3. The mean trace elemental concentrations of TSP in Changsha and other major cities in the world.

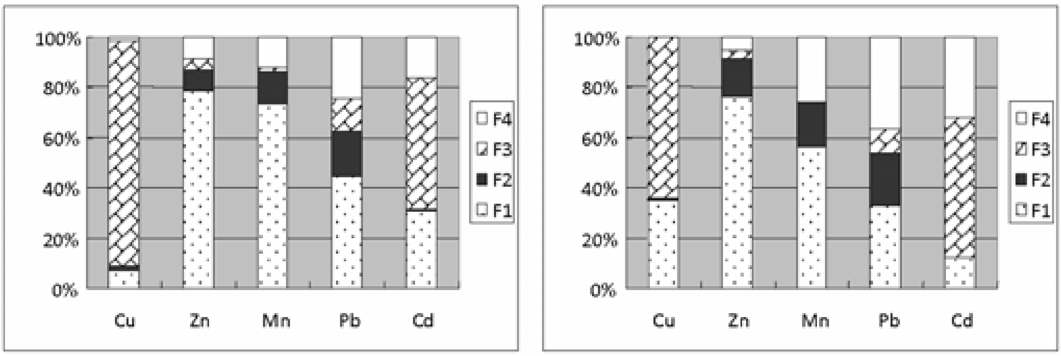
Analyte (μg m^{-3})	Changsha	Beijing	Yokohama (Japan)
	This work	T. Okuda *et al.*[a]	Mizohata *et al.*[b]
Cu	0.295	0.11±0.11	0.07±0.02
Zn	0.806	0.77±0.60	0.25±0.08
Mn	0.163	0.24±0.16	0.04±0.01
Pb	0.544	0.43±0.50	0.08±0.02
Cd	0.161	0.0068±0.00	0.0024±0.00

[a] Okuda *et al.* [11]
[b] Mizohata A *et al.*[12]



(A) Speciation of heavy metals in ST-1

(B) Speciation of heavy metals in ST-2



(C) Speciation of heavy metals in ST-3

(D) Speciation of heavy metals in SB-1

Fig. 3. Speciation of heavy metals in the four spots.

and weak acid soluble fractions (75.9~129.6 ng m^{-3}) and residual fractions (21.6~71.7 ng m^{-3}). Mn having a significant amount of exchangeable and weak acid soluble fraction indicates that a lot of the Mn in these PM samples would be environmentally mobile. Similar mobile character was found in other studies where the distribution of Mn was determined in ambient PM [7].

Zinc: Substantial portions of the total Zn were present in the exchangeable and weak acid soluble fraction (58~80 %), and lesser amounts in the reducible fraction (9~15 %). These first two fractions combined accounted for about 70~91 % of the total Zn content, which indicates that Zn had significant environmentally mobile character in these PM samples, and also suggests that it probably comes largely from anthropogenic sources [14]. The amount of oxidisable Zn is relatively minor (F3) almost less than 10%. The remainder was in the residual fraction, which represented the other significant proportion of Zn in these PM samples (6~21 %). Mostly Zn is produced by melting Zn mineral and smelting ores containing zinciferous impurity. Coal combustion and garbage incineration are also sources of the Zn in the atmosphere.

Lead: Lead in urban and industrial areas is emitted by different sources and each of these industries emits lead with different chemical form [17]. The obtained result showed that Pb is primarily present in the F1 and F4 fractions (70 %~75 %). The result is in good agreement with the reports of other studies [7]. Lead emissions are mainly from traffic and residential heating in urban area. The amount of lead in residual fraction incorporated inside silicates was 24~43 %, resuspension of soil particulate being the main source of these levels. This is in agreement with other studies [7]. It can be concluded that soil dust and traffic are the main source of Pb in urban areas.

Cadmium: Cd distribution into various fractions showed different patterns in each TSP sample.

Table 4. Statistical results of each fraction of heavy metals in samples (ng m^{-3}).

Element	Speciation	ST-1	ST-2	ST-3	SB-1
Cu	F1	19.2±4.4[a]	30.3±6.6	16.5±1.1	34.8±7.7
	F2	68.7±15.4	39.2±4.5	4.8±3.1	1.1±0.3
	F3	408.8±47.3	252.9±15.4	216.0±18.3	63.7±48.0
	F4	12.3±7.5	7.5±5.1	3.1±0.9	BDL[b]
Zn	F1	418.1±4.7	653.7±153.1	591.0±53.5	639.5±149.5
	F2	99.8±5.9	115.9±41.3	62.8±3.8	125.8±124.3
	F3	59.5±17.0	20.1±5.6	33.7±9.0	28.0±7.7
	F4	153.5±1.1	114.3±80.2	64.1±15.2	44.1±4.5
Mn	F1	82.9±9.9	75.9±3.3	129.6±16.6	92.9±12.9
	F2	10.3±3.5	39.9±2.1	22.3±15.1	28.6±31.5
	F3	BDL	BDL	2.1±0.6	0.3
	F4	71.7±21.0	32.6±4.0	21.6±20.3	42.6±18.1
Pb	F1	163.5±17.4	240.3±18.9	183.0±47.8	216.5±41.0
	F2	93.7±14.6	92.4±31.1	71.4±3.3	137.2±14.9
	F3	94.5±24.9	56.4±19.0	54.2±10.3	63.8±2.0
	F4	244.5±18.2	121.7±46.6	99.4±59.6	242.0±11.3
Cd	F1	189.7±11.1	80.9±39.1	30.1±28.9	9.0±7.1
	F2	BDL	BDL	0.7	BDL
	F3	88.4±14.7	71.5±12.3	50.6±4.5	41.5±39.6
	F4	27.8±4.1	13.3±0.8	15.7±5.4	23.6±14.6

[a] Results are expressed as the mean±standard deviations.
[b] BDL means below the detected limits.

Exchangeable and weak acid soluble fraction (F1) was relatively high in samples (9 ng m^{-3} ~ 189.7 ng m^{-3}). Approximately 40% of total Cd in TSP samples was extracted in the first step, showing high bioavailability to environment. This highly mobile character of Cd in urban PM is consistent with data reported by others [17], where this metal appeared to be exclusively in soluble-exchangeable forms, and is often removed mostly in the first step of sequential extractions. This is in agreement with reports that cadmium tends to be more concentrated on the surface of particulate produced by combustion processes, and thus, it would be loosely bound [18]. Cd in reducible fraction (F2) is bellowing the detecting limit indicating that Cd has a relatively higher concentration in oxides than residual fractions.

3.4. Environmental implications

To study HMs retention in TSP samples, the individual contamination factors (C_f) of elements in samples collected from four stations were calculated [19]. In this work, C_f was calculated as the sum of concentrations of metals extracted in the first 3 steps of the sequential extraction divided by the concentration in the residual fraction (extracted with concentrated aqua regia from the residue of the sequential extraction) [20]. The detailed calculations were expressed as follows:

$$C_f = \frac{F1 + F2 + F3}{F4} \tag{1}$$

The calculated contamination factors for each element and sampling site are shown in Table 5.

The experimental results indicated that among the HMs, Cu, Cd and Zn gave the highest C_f values, 40.38~100, 2.14~11.46 and 3.76~17.99 respectively, in all TSP samples collected from different spots of Changsha City, followed by Mn and Pb having comparatively lower C_f values, 1.30~7.13 and 1.44-3.20 respectively, and different metals have different C_f values in different spots. Cu has the highest C_f value in SB-1 showing that Cu almost coming from anthropogenic source and Zn has the same character. Pb and Cd have relatively high C_f values in ST-2 showing that metals having a potential risk of contamination owing to the high bioavailability and toxicity. And in ST-3, Mn has the highest C_f value indicating a higher toxicity.

3.5. Source identification using factor analysis

We have tried to identify and estimate the possible sources of heavy metals using principle component analysis (PCA). PCA was executed by the Varimax Rotated Factor Matrix method, based on orthogonal rotation criterion which maximizes the variance of the squared elements in the column of a factor matrix [21], using a statistical package SPSS 13.0. This method focuses on cleaning up the factors. It produces factors that have high correlations with one smaller set of variables and little or no correlation with another set of variables. The three factor loadings extracted after performing the varimax rotation are given in Table 6.

Three factors accounted for 85.0% of the accumulative variance in Changsha. The highest percentage of variance (41.1%) was explained by a component with high loadings on Mn, Zn and Pb associated with traffic sources and metallurgical and mechanical industries. In fact, Changsha is a modern city with heavy traffic and many automobiles.

The second component accounting for 23.2% of the accumulative variance was related to Cu, Cd. It was associated with industrial sources. The third component explaining 20.7% of the accumulative variance was related to TSP. In conclusion, heavy metals in TSP almost have anthropogenic pollutant sources.

Table 5. Contamination factor of selected elements in particulate matter.

Element	Site			
	ST-1	ST-2	ST-3	SB-1
Cu	40.38	42.99	76.55	100
Zn	3.76	6.91	10.73	17.99
Mn	1.30	3.55	7.13	2.86
Pb	1.44	3.20	3.10	1.73
Cd	10.00	11.46	5.18	2.14

Table 6. Rotated component matrix.

	Principle Component		
	Factor1	Factor2	Factor3
Mn	0.853	-0.052	0.318
Zn	0.885	-0.164	0.292
Cu	0.136	0.898	-0.003
Pb	0.884	0.019	-0.338
Cd	-0.374	0.743	-0.122
TSP	0.119	-0.073	0.963

4. CONCLUSIONS

The applications of metals sequential extraction methods to TSP samples collected from four spots in Changsha provide relevant information about possible toxicity when they are discharged into the environment. The conclusions drawn from this study are as following:

The concentration of TSP in Changsha was 220.7 μg m^{-3} showing that the particle pollution is serious in Changsha. The concentration of TSP in four spots can be listed in the orders: JK > KF > GK > MPL.

The mean concentrations of all metals in TSP, derived by using the values of each individual site, are: Zn (829.6), Pb (565.3), Cu (381.5), Mn (155.4), Cd (160.8 ngm^{-3}) being listed in the following order: Zn > Pb > Cu > Mn > Cd. And the total metals concentration in the four spots can be listed in the following order: JK > MPL > GK > KF.

The distribution of the metals in the target phases of the samples shows similar mobility behaviors, although some differences are present in each extraction stage.

The contamination factors indicated that metal mobility followed the sequence: Cu > Zn > Cd > Pb > Mn.

High pollution levels of the metals in these samples, especially for Cd, Pb, and Zn, can cause important environmental problems and/or risks for human health.

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