Water quality assessment and hydrochemical characteristics of groundwater on the aspect of metals in an old town, Foshan, south China

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The present study is aimed at assessing the water quality and discussing the hydrochemical characteristics and seasonal variation of shallow groundwater on the aspect of metals in the eastern Chancheng district of Foshan city, south China. Multivariate analytical methods such as principal components analysis (PCA) and hierarchical cluster analysis (HCA) were used in this study. The results show that 45% of groundwater in the east-central of study area is not suitable for drinking purpose due to high concentrations of Fe, Pb and Mn. The mean concentrations of Fe, Hg, Cu, Pb, and Mn in dry season are higher than that in wet season. On the contrary, the mean concentrations of Cd, Co, Zn, Ba, Cr, Mo, Ni and Al in wet season are higher than that in dry season. PCA results show that four PCs are responsible for the 78.6% of the total hydrochemical variables in groundwater. Three groups were generated from HCA method. Group 1 reflects the characteristic of wet season and the low ion exchange capacity; group 2 is mainly influenced by the dry season. Reducing environment and high ion exchange capacity are responsible for group 3. The results are useful in addressing future measures in groundwater resource management for local government.

1. Introduction

Foshan of the Guangdong Province in China is an industrial and commercial city. Over the past decades, with the rapid industrialization and urbanization in Foshan city, more water resource for industrial and domestic uses is required. Due to inadequate availability of surface water, to meet the requirement of industrial production and human living, groundwater remains the only option to supplement the ever-increasing demand of water. In another aspect, because it is free of charge, plenty of urban residents in Foshan city depend heavily on groundwater for drinking and domestic purposes (Sun *et al.* 2009). It has been observed that metal contamination of groundwater more often than not goes unnoticed and remains hidden from the public view, especially in urban groundwater due to lack of efficient solid waste disposal systems and sewage treatment plants (Edet *et al.* 2003).

Metals are useful to human beings for the maintenance of health and when a measurable deficit in the diet is allowed, even well-known toxic metals, such as Mo, Co, Cr, Ni, etc. are needed in minute quantities for the normal functioning of cell metabolism (Wang 2004; Pizzol *et al.* 2011).

Keywords. Groundwater; metal; water quality; hydrochemical characteristics; seasonal variation; principal components analysis.

However, these metals are known to cause a wide range of adverse effects on human health in higher doses (Pizzol *et al.* 2011). When metals are discharged into a system, they can migrate or precipitate according to their geochemical mobility and deposit in different components of the systems; unlike organic compounds, they are not degraded, and have the ability to accumulate in the body after getting into human beings.

In recent years, the studies related to metals in groundwater were mainly focused on the hydrochemical assessment and the relationship between metals and other chemical parameters with multivariable statistical analysis (Helena *et al.* 2000; Edet *et al.* 2003; Chen *et al.* 2007; Qian *et al.* 2010, 2011; Zhang *et al.* 2012). A handful of studies discussed the seasonal influence on the metals in groundwater (Leung and Jiao 2006; Buragohain *et al.* 2010). However, to date, not much attention has been paid to discuss the hydrochemical characteristics of metals in groundwater based on the combination of seasonal impact and multivariable statistical analysis, especially in an old town, which has been the primary focus of this study. Furthermore, to date, in the study area, works on metal concentrations have been carried out mainly on the surface water and sediments (Cheung *et al.* 2003; Ouyang *et al.* 2006), but no available data about the metal concentrations in groundwater. Therefore, the objectives of this study are to investigate the distribution and seasonal variation of metal concentration in shallow groundwater of an old town in Foshan, to assess the groundwater quality based on the metal concentrations, and to discuss the sources of metals in groundwater by using multivariate analytical methods. Because the metal composition of groundwater depends not only on natural factors such as the aquifer properties, the quality of recharge waters and the types of interaction between water and rocks, but also on human activities, which can alter these fragile groundwater systems, either by polluting them or by changing the hydrological cycle (Helena *et al.* 2000; Chen *et al.* 2007). Therefore, sophisticated data analysis techniques such as multivariate analytical methods are required to effectively interpret metal data in groundwater. The results will get acquainted with the groundwater quality on the aspect of metals, and will be beneficial to improve the groundwater management for the local government.

2. Materials and methods

2.1 *Study area*

The study area, eastern Chancheng district, is located in the centre of Foshan city and near the Pearl River, south China. It belongs to the coastal area with the deposition of fine particles (silty sand and clay), leading to the slow groundwater flow rate and the formation of stagnant shallow groundwater. Geographically, it is situated between longitudes of 113°01′–113°10′E and latitudes of 22°58′–23°04′N, covers an area of 75.7 km^2, and belongs to the Xijiang River basin. The total population is about 768,700 (Sun *et al.* 2009). The climate is subtropical maritime monsoon climate. The mean annual precipitation is 1777 mm, with 82–85% of precipitation occurring in April to September (Peng and Wang 2004). The average annual temperature is 23.2°C. The average temperature is 13.2°C in January, while the average temperature is 28.5°C in July (Sun *et al.* 2009).

2.2 *Sampling*

In this study, 29 groundwater samples were collected from civil wells at 20 sites of eastern Chancheng district during wet (July–August 2008) and dry (November–December 2008) seasons; among them, samples were collected from 9 sites in both seasons, others in dry season only (figure 1). Samples were collected below water table at the depth of 50 cm by a stainless steel sampler (without corrosion or rust) and filtrated by using 0.45 μm filter membranes, and then stored in clean and sterile 1-L polyethylene bottles which were rinsed at least three times with groundwater before sampling. After collection, each sample was immediately acidified to pH<2 with ultrapure nitric acid and then stored at approximately 4°C before analysis. All probable safety measures were taken at every stage, starting from sample collection, storage, transportation and final analysis of the samples to avoid contamination. *In-situ* measurements of static water table were made using a sonic water-table indicator prior to sampling during dry season.

2.3 *Analytical procedures*

Samples were analyzed at the Institute of Hydrogeology and Environmental Geology and all metal concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin-Elmer Optima 5300 DV, USA). The analytical data quality was ensured through careful standardization, procedural blank measurements, spiked and duplicate samples. The recovery rates of the analyzed metals in the standard reference material (USA NIST SRM 1643d) were >95%. Three replications of each analysis were performed and the mean values were used for calculations.

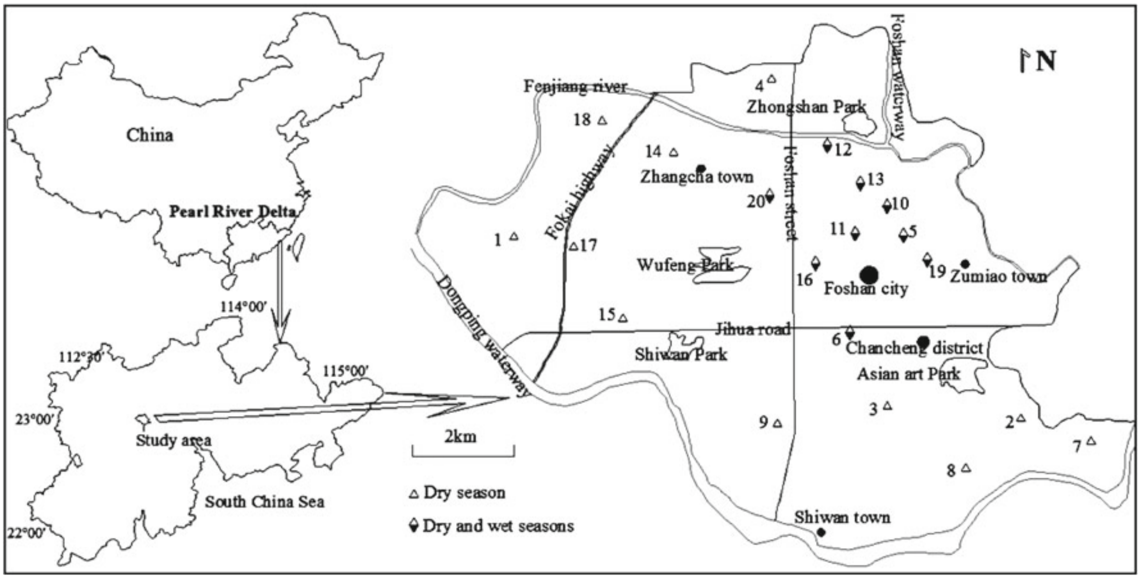

Figure 1. Schematic diagram of the sampling sites in eastern Chancheng district, Foshan, south China.

2.4 *Statistical analysis*

Multivariate analytical methods were used in this study to effectively interpret metal data in groundwater. Hierarchical cluster analysis (HCA) was used in this study to classify samples into different groups based on all the chemical parameters and to indicate the natural associations between samples (Güler *et al.* 2002; Reghunath *et al.* 2002; Chen *et al.* 2007; Zhang *et al.* 2012). Principal components analysis (PCA) is useful in reducing data dimension while retaining important information and representing variables in a form that can be easily interpreted (Singh *et al.* 2005). The statistical software package SPSS 17.0 for windows (SPSS Inc, Chicago, USA) was used for the multivariate statistical calculations. The statistical analysis of HCA and PCA were carried out by the classification and data reduction modules, respectively.

3. Results and discussion

3.1 *Distribution of metals in groundwater*

The minimum, mean, and maximum values of 14 metal concentrations in groundwater of the study area during the dry and wet seasons are shown in table 1 together with the laboratory detection limits (DL), the Chinese drinking water limits (DWL) (Ministry of Land and Resources of the People's Republic of China 2008) and the percentages of samples above the DL and DWL. The concentrations of eight metals (Cu, Ba, Cr, Pb, Mo, Mn, Ni, Al) in all groundwater samples during the dry season are above the DL, while the concentrations of other metals (Be, Cd, Co, Fe, Hg, Zn) in some groundwater samples during the dry season are below the DL, especially for Be which is almost in all of the samples below the DL except in sampling site 13. Most of metal concentrations in all of groundwater samples during dry season are below the DWL except Fe, Pb and Mn. Fe and Pb concentrations in 20% of samples exceed the DWL, and Mn concentration in 40% of samples exceeds the DWL during the dry season. About 45% of groundwater in the study area is not suitable for drinking purpose due to the high concentrations of Fe, Pb and Mn, which is located in the east-central part of the study area, while the groundwater which is suitable for drinking purpose is located in the west and south of the study area except the sampling site 5 (figure 2). The mean metal concentrations in groundwater during the dry season is Fe > Mn > Al > Zn > Ba > Pb > Cr > Cu > Ni > Mo > Co > Cd > Hg > Be.

Nine sites in the study area were sampled not only in dry season but also in wet season in order to examine the seasonal effects on groundwater metal concentrations (figure 1). During the wet season, the concentrations of four metals (Be, Cd, Fe, Hg) in some groundwater samples are below the DL, especially for Be and Hg, the concentrations of which in all of the samples are below the DL, while the concentrations of other metals (Co, Zn, Cu, Ba, Cr, Pb, Mo, Mn, Ni, Al) in all groundwater samples are above the DL. The mean metal concentrations in groundwater during the wet season is Fe > Mn > Al > Zn > Ba > Cr > Cu > Mo > Ni > Pb > Co > Cd > (Hg, Be), which is

Table 1. *Metal concentrations and water quality of groundwater samples during dry and wet seasons.*

Item	Dry season ($n = 20$)								Wet season ($n = 9$)				Difference (%)
	DL (µg/L)	>DL (%)	DWL (µg/L)	>DWL (%)	Min (µg/L)	Max (µg/L)	Mean (µg/L)	SD	Min (µg/L)	Max (µg/L)	Mean (µg/L)	SD	
Be	0.1	5	2	0	BDL	0.2	0.01	0.04	BDL	BDL	BDL		
Cd	0.1	45	5	0	BDL	0.3	0.1	0.1	BDL	1	0.1	0.2	−6.7
Co	0.1	55	50	0	BDL	0.7	0.2	0.2	0.2	1.6	0.7	0.5	−100
Fe	10	70	300	20	BDL	1160	226	353	BDL	1990	357	733	10.8
Hg	0.01	80	1	0	BDL	0.34	0.05	0.08	BDL	BDL	BDL		100
Zn	1	95	1000	0	BDL	210	54	48	17	540	81	172	−1.8
Cu	0.2	100	1000	0	0.8	13.4	3.9	3.3	1.1	18.0	4.5	5.2	13.4
Ba	1	100	700	0	13	120	48	27	20	89	48	24	−16.2
Cr	0.1	100	50	0	1.1	11.3	4.6	2.5	8.0	26.0	16.6	6.0	−54.2
Pb	0.1	100	10	20	0.2	61.0	6.4	13.8	0.3	1.9	0.9	0.4	87.6
Mo	0.1	100	70	0	0.5	8.4	2.5	1.9	2.0	9.8	3.9	2.8	−5.3
Mn	1	100	100	40	3	780	158	216	7	1470	270	456	5.4
Ni	0.1	100	20	0	1.5	5.7	3.3	1.0	1.4	5.9	3.5	1.5	−0.2
Al	1	100	200	0	10	150	73	44	120	260	182	42	−69.7

DL: detection limit, DWL: drinking water limit (Ministry of Land and Resources of the People's Republic of China 2008), BDL: below detection limit, SD: standard deviation. Difference is calculated by the mean metal level by $(\mathrm{Metal}_{\mathrm{dry}} - \mathrm{Metal}_{\mathrm{wet}})/(\mathrm{Metal}_{\mathrm{dry}} + \mathrm{Metal}_{\mathrm{wet}}) * 100\%$.

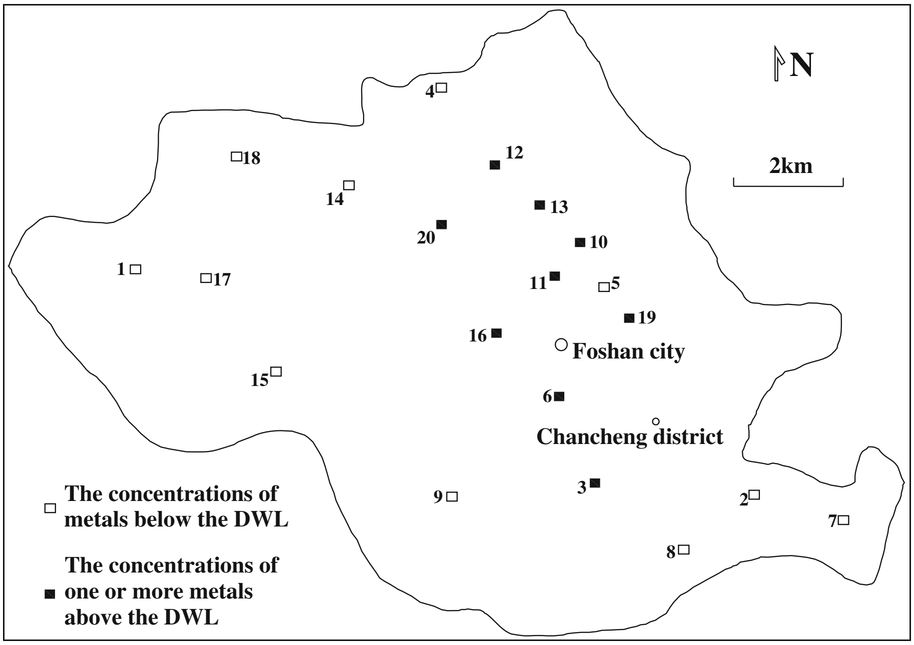

Figure 2. Spatial distribution of metal concentrations in groundwater of the study area during the dry season.

similar to that during the dry season except the Pb. The seasonal comparisons of metal concentrations in the study area are presented in table 1. The mean concentrations of Fe, Hg, Cu, Pb, and Mn in dry season are higher than that in wet season, especially for Hg and Pb, the differences are more than 50%, which is consistent with the results reported by Leung and Jiao (2006) and Buragohain *et al.* (2010) who also observed that the mean concentrations of Fe, Cu and Pb in groundwater in dry season were higher than that in wet season in Hong Kong and Assam of India. One of the possible reasons is that these metals in groundwater of the study area may be controlled by the aquifer itself (Thamdrup 2000; Homoncik *et al.* 2010), because metal concentrations in the aquifer will be diluted in wet season more easily compared with that in dry season due to higher groundwater recharge in wet season (Huang *et al.* 2008). On the contrary, the mean concentrations of Cd, Co, Zn, Ba, Cr, Mo, Ni and Al in wet season are higher than that in dry season, especially for Co, Cr and Al, the differences are also more than 50%. One of the possible reasons pointed out by Leung and Jiao (2006) is that more metals could be leached out from vadose zone into groundwater in the wet season because of the generally higher water table during the wet season. Another explanation is that more metals in groundwater may be recharged from the leakage of sewer pipe during the wet season. For instance, according to our field investigation (Sun *et al.* 2009), plenty of alloy factories such as aluminum alloy and stellite are located in the study area and in the sample sites G6 and G16, generally occur the leakage of sewer pipe during the wet season due to the abundant rainwater and senescent pipes. As a consequence, the Co, Cr and Al concentrations of them in wet season (mean values of 1.4, 23.0 and 235 μg/L) are far higher than that in dry season (mean values of BDL, 5.6 and 33 μg/L). Correspondingly, ammonia nitrogen, as an indicator for sewer, the content of which in G6 and G16 in wet season (mean value of 9.25 mg/L) are also far higher than that in dry season (mean value of 3.02 mg/L) (Huang *et al.* 2013).

As it can be seen from figure 3, the hydrochemical type in wet season is similar to that in dry season. It is shown that, overall, there are more alkaline-earth metal ions than alkaline metal ions; the total concentration of weak acids is higher than that of strong acids; and the carbonate hardness exceeds 50% in the study area. Meanwhile, Ca–HCO_3 is the dominant chemical type in groundwater in both dry and wet seasons (Huang *et al.* 2013).

3.2 *Correlation between variables*

Correlation measures the degree of interrelation between two variables (Edet *et al.* 2003). In this study, Pearson's correlation coefficients (r) between metals were calculated by SPSS 17.0. As far as the selection of variables is concerned, we ruled out Be, Cd, Co and Hg due to the low detection ratios (<60%, see table 1), but retained other

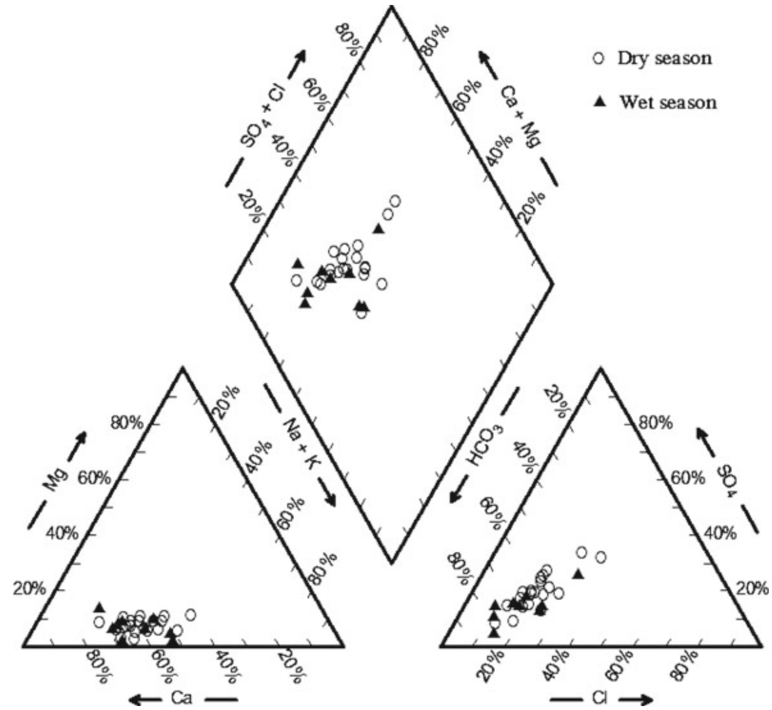

Figure 3. Piper trilinear diagram of the chemical types in groundwater of the study area.

Table 2. *Pearson correlation coefficients for the 10 metals in groundwater of study area.*

Item	Zn	Cu	Ba	Cr	Pb	Mo	Mn	Ni	Al	Fe
Zn	1									
Cu	0.797**	1								
Ba	−0.113	−0.253	1							
Cr	−0.043	−0.058	0.126	1						
Pb	−0.056	0.113	−0.273	−0.209	1					
Mo	−0.049	−0.109	0.242	0.545**	−0.004	1				
Mn	0.019	0.079	0.161	0.386*	0.120	0.673**	1			
Ni	0.200	0.352	0.159	0.319	0.230	0.540**	0.357	1		
Al	−0.032	−0.098	0.333	0.777**	−0.424*	0.234	0.180	0.239	1	
Fe	0.023	0.030	0.233	0.341	−0.058	0.690**	0.718**	0.299	0.096	1

**Correlation is significant at the 0.01 level; *Correlation is significant at the 0.05 level.

10 variables. The correlation matrix (table 2) shows that the metals such as Cr, Mo, Al and Ni which display higher concentrations in wet season than that in dry season are positively correlated with each other (Cr and Mo, $r = 0.545$; Cr and Al, $r = 0.777$; Mo and Ni, $r = 0.54$). Similarly, metals such as Mn and Fe which display lower concentrations in wet season than that in dry season are also positively correlated with each other (Mn and Fe, $r = 0.718$). One interpretation of these observations is that these metals in groundwater have similar hydrochemical characteristics (Chen *et al.* 2007) or sources in the study area as mentioned in section 3.1. In contrast, Al which displays higher concentration in wet season than that in dry season is negatively correlated with Pb which displays lower concentration in wet season than that in dry season (Al and Pb, $r = –0.424$), which may ascribe to the different sources of Pb and Al in groundwater of the study area as mentioned in section 3.1. Cr is positively correlated with Mo ($r = 0.545$), Mn ($r = 0.386$) and Al ($r = 0.777$), Mo is positively correlated with Cr, Mn ($r = 0.673$) and Ni ($r = 0.54$), and Zn is positively correlated with Cu ($r = 0.797$), which may ascribe to the similar chemical behaviour. Because one of the forms of Cr, Mo, Mn, Ni and Al in groundwater generally occur as soluble oxyanions such as CrO_4^{2-}, $Cr_2O_7^{2-}$, MoO_4^{2-}, MnO_4^{2-}, MnO_4^-, NiO_2^- and AlO_2^-, while one of the forms of Zn and Cu in groundwater generally occur as soluble cations such as Zn^{2+} and Cu^{2+}. Mn, positively correlated with Fe

Table 3. *Principal component and varimax rotated component matrix for groundwater samples in the study area (n = 29).*

	Component matrix				Rotated component matrix[a]			
Variables	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
Co	0.884	0.004	−0.295	−0.035	0.432	0.168	0.744	−0.319
Cr	0.833	−0.070	−0.184	−0.051	0.443	0.047	0.675	−0.287
Mo	0.768	0.094	0.422	0.185	0.870	−0.047	0.186	−0.131
Al	0.745	−0.129	−0.484	−0.209	0.142	0.095	0.858	−0.290
Mn	0.622	0.268	0.531	0.075	0.852	0.008	0.079	0.115
Ba	0.559	−0.109	0.076	−0.243	0.356	−0.176	0.482	0.008
Ni	0.540	0.472	0.002	0.498	0.619	0.549	0.017	−0.278
Cu	−0.130	0.871	−0.283	0.153	−0.011	0.896	−0.138	0.238
Cd	0.096	0.839	−0.418	0.080	0.039	0.922	0.120	0.166
Zn	−0.057	0.744	−0.425	0.103	−0.092	0.849	0.022	0.140
Be	−0.190	0.691	0.248	−0.524	0.070	0.296	−0.030	0.869
Hg	−0.357	0.668	0.393	−0.365	0.074	0.246	−0.298	0.841
Fe	0.573	0.323	0.606	−0.201	0.813	−0.064	0.159	0.387
Pb	−0.259	0.087	0.401	0.733	0.262	0.076	−0.789	−0.276
Eigenvalues	4.199	3.389	2.001	1.420	3.146	2.906	2.788	2.169
Variance (%)	29.995	24.206	14.291	10.144	22.471	20.758	19.914	15.492
Cumulative (%)	29.995	54.201	68.492	78.636	22.471	43.230	63.144	78.636

[a]Rotation method: varimax with Kaiser normalization.

($r = 0.718$) in the study area, also indicates similar chemical behaviour. Because the mobility of both Fe and Mn will increase due to the reduction of Fe and Mn from high valence to low valence (Shen *et al.* 1999), the high concentrations of Fe and Mn often occur naturally together in groundwater (Thamdrup 2000; Homoncik *et al.* 2010).

3.3 *Principal component analysis*

Principal component analysis (PCA) is a multivariate data analytic technique. It reduces a large number of variables to a small number of variables, without sacrificing too much of the information. The PCA is used to reduce groundwater chemical parameters (variables) (Davis 1986; Güler *et al.* 2002; Reghunath *et al.* 2002). In this study, the PCA was performed as an eigen-analysis of the correlation matrix and the varimax rotation was adopted to maximize the variation explained by the components (SPSS 17). Four principal components (PC1-4, with eigen-values greater than 1) resulted from the computation, explaining about 78.6% of the variance in the dataset (table 3). The first one is responsible for 22.47% of the total variance and is best represented by Mo, Mn, Ni and Fe. It is known that Mo, Mn and Ni in groundwater generally occur as soluble oxyanions such as MoO_4^{2-}, MnO_4^{2-}, MnO_4^- and NiO_2^-. In addition, it has been reported that the reducing environment is mainly caused by the leakage of sewer pipe network in the study area with the values of dissolved oxygen and redox potential lower than 3 mg/L and 30 mv, respectively (Sun *et al.* 2009; Huang *et al.* 2013), and the reducing environment is one of the main factors for high concentrations of Fe and Mn in groundwater (Huang *et al.* 2008; Liang *et al.* 2009), because the mobility of Fe and Mn will increase due to the reduction of Fe and Mn from high valence to low valence (Shen *et al.* 1999), which leads to the desorption of Fe and Mn from the aquifer medium into the groundwater. Correspondingly, dissolved oxygen is positively correlated with Fe ($r = 0.516$) and Mn ($r = 0.569$) in this study (figure 4). Above discussion implies the co-effect of human activities and natural processes for high concentrations of Fe and Mn in groundwater. Therefore, PC1 can be ascribed to the high anion exchange capacity with high concentrations of Mo, Mn and Ni and reducing environment with high concentrations of Fe and Mn, and characterized by the co-effect of human activities and natural processes. The PC2 explains 20.76% of the total variance and is positively correlated with ion concentration of Cu, Cd and Zn. It is known that Cu, Cd and Zn in groundwater generally occur as soluble cations such as Cu^{2+}, Cd^{2+} and Zn^{2+}, indicating some similar chemical behaviour of them such as canion exchange capacity. Therefore, PC2 may be ascribed to high canion exchange capacity. The PC3 explains 19.91% of the total variance and is mainly participated by Co, Cr, Al and Pb. It has been reported that plenty of alloy factories such as aluminum alloy (Al) and stellite (Co and Cr) are in the study area (Sun

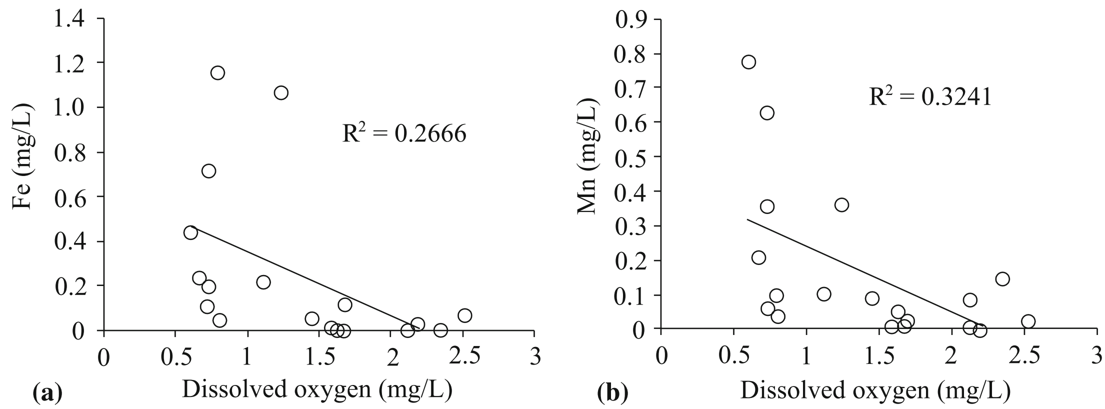

Figure 4. Correlation between the content of dissolved oxygen and Fe and Mn in groundwater of study area during the dry season ((**a**) – dissolved oxygen and Fe, (**b**) – dissolved oxygen and Mn).

et al. 2009), and the waste water from them is discharged into the network of sewer pipe and finally to the treatment plant. During this process, leakage of wastewater to the subsurface is inevitable due to the broken or malfunctioning pipelines (Qian *et al.* 2011), especially in an old town. In this case, more wastewater will enter into the groundwater in the wet season than in the dry season due to the abundant rainwater in wet season, which implies the anthropogenic source for high concentrations of Co, Cr, Al in groundwater of the study area. In contrast, as mentioned in section 3.1, the concentration of Pb in dry season is higher than that in wet season, and the possible reason is that Pb in groundwater of study area may be controlled by the aquifer itself. Therefore, PC3 may be ascribed to the seasonal factor and the anthropogenic source, because PC3 is positively correlated with Co, Cr and Al and negatively correlated with Pb. The PC4 explains 15.49% of the total variance and is best represented by Be and Hg. As mentioned in section 3.1, the concentrations of Be and Hg in the study area are very low (especially in wet season), and both of them are mainly controlled by the natural process such as water–rock interaction and vadose zone leaching (Zhang *et al.* 2011). Therefore, PC4 may be ascribed to the natural process.

3.4 *Hierarchical cluster analysis*

Hierarchical cluster analysis (HCA) is used to test groundwater quality data and determine if samples can be grouped into hydrochemical groups (Anderberg 1973; Davis 1973; Alther 1979; Güler *et al.* 2002; Reghunath *et al.* 2002). In this study, the groundwater samples were classified into different groups by HCA (used the Ward method with Euclidean distance), and three groups were

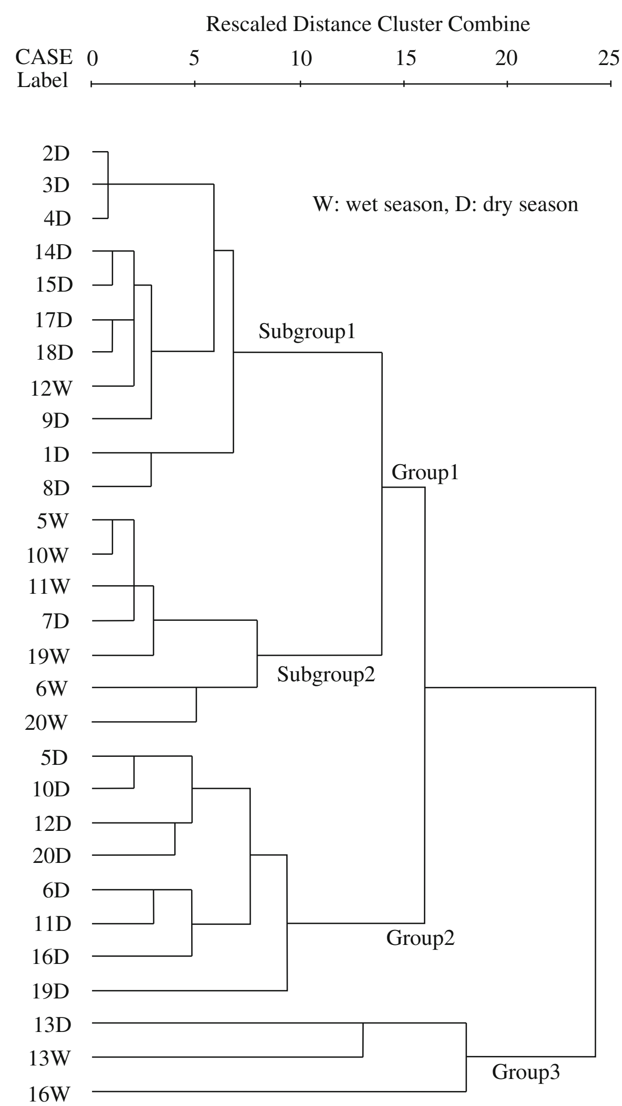

Figure 5. Dendrogram generated from the hierarchical cluster analysis by using the Ward method.

Table 4. *Mean metal concentrations of the groups generated from HCA.*

Group	Subgroup	n	Be	Zn	Cu	Hg	Cd	Ba	Cr	Pb	Co	Mo	Mn	Ni	Al	Fe
	Mean	18	0	30	2.5	0.02	0.05	52	8.9	0.9	0.4	2.3	71	3	132	97
1	1	11	0	27	2.2	0.03	0.05	59	4	0.9	0.3	1.6	57	2.9	106	45
	2	7	0	35	2.9	0	0.04	43	16.8	0.8	0.6	3.4	94	3.3	174	177
2		8	0	61	5	0.05	0.05	35	5	14.7	0	3.7	293	3.5	30	365
3		3	0.1	256	11.4	0.11	0.3	53	13.2	1	0.7	4.5	654	4.6	157	1020

Units: ion concentrations (μg/L).

generated (figure 5). To compare the hydrochemistry difference of three groups, the mean metal concentrations are shown in table 4. Most groundwater samples are classified into group 1 (n = 18), which consists of two subgroups: subgroup 1 with low concentrations of Zn, Cu, Cr, Mo, Mn, Ni reflects the low ion exchange capacity and indicates the opposite of PC1 and PC2, subgroup 2 with high concentrations of Cr and Al and low concentration of Pb reflects the characteristic of wet season and indicates the activity of PC3, which is consistent with the fact that most groundwater samples (5W, 6W, 10W, 11W, 19W, 20W) in subgroup 2 are collected in wet season except the 7D (figure 5). Group 2 consists of eight groundwater samples, with the high value of Pb and low values of Cr, Co and Al, which reflects the characteristic of dry season (as mentioned in section 3.1) and indicates the opposite of PC3. Group 3 consists of three groundwater samples, with the high values of Be, Zn, Cu, Hg, Cd, Mo, Mn, Ni and Fe, which reflects the high ion exchange capacity and reducing environment and indicates the activity of PC1, PC2 and PC4. Correspondingly, sampling sites 13 and 16 which belong to group 3 are located in the old residential area with old and rusty sewage pipes, where leakage of sewage pipes occur frequently (Sun *et al.* 2009). Therefore, the groundwater of sampling sites 13 and 16 are characterized by the reducing environment.

4. Conclusions

This report presents the first hydrochemical characteristics of metals in the Foshan of China by using multivariate analytical methods. The water quality assessment in groundwater on the aspect of metals is also discussed. Forty-five percent of groundwater in the east-central of the study area is not suitable for drinking purpose due to the high concentrations of Fe, Pb or Mn. The mean concentrations of Fe, Hg, Cu, Pb, and Mn in dry season are higher than in wet season. On the contrary, the mean concentrations of Cd, Co, Zn, Ba, Cr, Mo, Ni and Al in wet season are higher than that in dry season.

PCA results show that four PCs are responsible for the hydrochemical variability in the groundwater samples. PC1 can be ascribed to the high anion exchange capacity and reducing environment, and characterized by the co-effect of human activities and natural processes. PC2 represents the high canion exchange capacity. PC3 may be ascribed to the seasonal factor and the anthropogenic source. PC4 represents the natural process such as water–rock interaction.

Three groups and two subgroups were generated from HCA method. Subgroup 1 reflects the low ion exchange capacity. Subgroup 2 is mainly affected by the wet season. Group 2 reflects the characteristic of dry season. Group 3 is mainly influenced by the high ion exchange capacity and reducing environment.

Due to the limits of time and funding, this study still lacks a few important datasets which will be collected in a future study. For instance, lack of some hydrogeological data such as the direction of groundwater flow and the lithology of vadose zone and aquifer. These data are the keys for predicting the variation trend of metals in groundwater of the study area, and these issues will be pursued in future.

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