Arsenic distribution and hydrochemical factors in urban groundwater, Foshan City, South China

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Abstract The distribution of arsenic (As) in shallow groundwater of eastern Chancheng District in Foshan City as a function of season and water table was investigated, and the influence of hydrochemical factors on the As distribution was discussed. The groundwater samples were collected from 20 sites in dry season and 9 sites in wet season. As concentrations in 20% groundwater samples exceeded value of the WHO guideline ($10 \mu g/L$), and the highest As concentration of 23.5 $\mu g/L$ occurred in dry season. It is observed that groundwater As concentration decreased with the increase of depth of water table in dry season, and were generally higher in wet season than that in dry season, indicating that ground surface As might be one of the main sources for shallow groundwater As in study area, especially in wet season. Groundwater As concentration in study area had significantly positive correlated to Eh and K, indicating that reductive dissolution of Fe and Mn (oxy)hydroxides might be one of the main control mechanisms for groundwater As mobilization, while pH and F also played an important role in controlling the groundwater As mobilization in study area.

Key words arsenic; groundwater; hydrochemical factor; seasonal influence; water table

1 Introduction

Groundwater is one of the important sources for industrial and domestic use for a long time in cities of China. It has been observed that groundwater contamination often goes unnoticed and remains hidden from the public view, especially for city shallow groundwater. For instance, arsenic (As) is one of the main toxic contaminants in urban groundwater (Sun et al., 2009). Trace amount of As is common in groundwater, normally does no harm to human health. However, high concentration of As in groundwater can cause adverse effects on human health and make water not potable. For example, World Health Organization (WHO, 2011) regulated that the concentration of As in groundwater should less than 10 µg/L for drinking purpose. At present, many researchers have reported that As is the major toxicant in groundwater of some regions in China such as Xinjiang, Inner Mongolia, Shanxi, Jilin, Guangdong provinces, and so on (Guo et al., 2007; 2010; Huang et al., 2011; Bian et al., 2012).

Foshan of the Guangdong Province in China is an industrial and commercial city. Over the past decades, with the rapid development of industrialization and urbanization in Foshan City, and inadequate availability of surface water, groundwater remains the only option to supplement the ever-increasing demand of water. Therefore, the water quality for drinking is the mostly concerned issue in the city. However, so far the study on the distribution of As in groundwater of Foshan City has not been reported.

The objective of this study were to investigate the change in As concentration as a function of season and groundwater table in shallow aquifer of eastern Chancheng District in Foshan City, and to discuss the influence of hydrochemical factors on the As distribution. The results will be beneficial to improving groundwater management and increasing the availability of good quality groundwater for sustainable

development in Foshan City.

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 slow flow rate and the formation of stagnant shallow groundwater. Geographically, it is situated between 113°01′ E and 113°10′ E and 22°58′ N and 23°04′ N and covers an area of 75.7 km², which belongs to the Xijiang River Basin. The climate of study area belongs to south sub-tropical maritime monsoon climate. The mean annual precipitation is 1600–2300 mm, with 82%–85% of precipitation occurring in April to September (Peng and Wang, 2004). The average annual temperature is 21.7–22.6°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

For the present study, 29 groundwater samples were collected from civil wells at different sites of eastern Chancheng District during wet (July–August 2008) and dry (November–December 2008) seasons. The sampling locations are shown in Fig. 1. Samples were collected below water table at the depth of 50 cm by a stainless steel sampler and filtrated by 0.45 μ m filter membranes, and then stored in clean and sterile 1-L polythene cans. 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.



Fig. 1. Schematic showing the geographical locality of (A) the Pearl River Delta in China; (B) eastern Chancheng District of Foshan City in the Pearl River Delta area; and (C) the sampling sites within eastern Chancheng District.

2.3 Analytical procedures

Electrical conductivity (EC), pH, and Eh were measured by multifunctional portable tester (Multi 340i, German) on site, which was previously calibrated. Potassium (K), Sodium (Na), Calcium (Ca), Magnesium (Mg), Iron (Fe), Manganese (Mn), and Aluminium (Al) analysis of water samples were measured by the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Perkin-Elmer Optima 5300 DV, USA). Ammonical nitrogen (NH₄), Nitrate nitrogen (NO₃), Chloride (Cl), Fluoride (F), Phosphate (PO₄) and Sulphate (SO₄) analysis of water samples were measured by spectrophotometry, bicarbonate (HCO₃) by acid-base titration, chemical oxygen demand (COD) by dichromate reflex method. The analytical data quality was ensured through careful standardization, procedural blank measurements, spiked and duplicate samples. The ionic charge balance of each sample was within $\pm 5\%$. The laboratory also participated in regular national program on analytical quality control.

3 Results and discussion

3.1 As distribution in groundwater

It is observed Fig. 2 that the concentrations of As ranged from below detection limit (BDL) to 23.5 µg/L in dry season. Higher concentrations of As were measured in sites 2-3, 5-13, 16, and 19-20, which distribute in the central and southeast of study area, while relatively lower concentrations of As were measured in sites 1, 4, 14-15, 17-18, which are in the northwest of study area. As concentrations in some samples such as 8, 12, 13, and 16 exceeded WHO guideline value of 0.01 mg/L, that is, 20% of the groundwater samples were exceeded the standards for drinking purpose during the dry season in study area. The highest concentration of As was 23.5 µg/L in sampling site 16 where surrounded by an restaurant in the behind and plenty of domestic sewage. It is observed that the concentration of As decreased with the depth of groundwater table during dry season indicating that As in surface might be one of the main sources for As in shallow groundwater in study area (Fig. 3). However, characterization of more groundwater as well as the surface water and sewage are required to further prove this. This result is in disagreement with the previous study (Munk et al., 2011) who observed that the wells with highest As concentrations draw water from the deeper part of the partially-confined glacial aquifer.

As it can be seen in Fig. 4, patterns within most of sampling sites (except sites 12 and 13) show that the concentrations of As in wet season were higher than that in dry season in study area Similarily, Munk et al. (2011) and Keshavarzi et al. (2011) also observed that the mean concentration of As in groundwater in wet season were higher than that in dry season in Anchorage (USA) and west of Iran. But it is different from the result reported by Buragohain et al. (2010) who observed that overall the concentrations of As in wet season were lower than that in dry season in Dhemaji District, Assam, India. One of the possible reasons pointed out by Munk et al. (2011) that the As was derived from another hydrogeological unit with higher As content that are accessed by groundwater during recharge events in wet season. Furthermore, according to the circumstance of study area, a potential anthropogenic source of As near the surface in study area might be another reason for this phenomenon. For instance, sampling site 16, plenty of sewage which surrounds it might infiltrate into shallow groundwater through recharge events during wet season.

3.2 Hydrochemical factors influence on As distribution

Hydrochemical conditions control the mobilization and transformation of As in groundwater. To identify the main hydrochemical factors influence on the distribution of As in groundwater of study area, correlation coefficients between the concentration of As and other parameters in groundwater during dry season are listed in Table 1. The concentration of As in groundwater of study area had significantly positive correlation with the concentration of Fe, Mn, NH₄, F, and COD, and was positively correlated to pH, but was negatively correlated to Eh and K.

 Table 1
 Correlation coefficients between the concentration of As and other parameters in groundwater during dry season

Item	pH	EC	Eh	K	Na	Ca	Mg	Fe	Mn
As	0.515*	-0.340	-0.533*	-0.520*	-0.226	-0.215	-0.235	0.618**	0.843**
Item	Al	NH_4	HCO ₃	Cl	SO_4	F	NO ₃	PO_4	COD
As	-0.328	0.759**	-0.003	-0.222	-0.410	0.645**	-0.210	-0.058	0.589**

Note: * significance level at the P<0.05; ** significance level at the P<0.01.



Fig. 2. Spatial distribution of As in shallow groundwater of eastern Chancheng District during dry season.

High As concentrations were generally accompanied with high Fe and Mn concentrations of groundwater in study area (Table 1, Fig. 5a–b), indicating As, Fe and Mn in groundwater are leached out from a definite source that is enriched in As, Fe and Mn. Chen (1987) reported that sedimentary stratum near surface contained plenty of Fe and Mn (oxy)hydroxides. Therefore, reductive dissolution of Fe and Mn (oxy)hydroxides might be one of the main processes for As mobilization in groundwater of study area. This process for As mobilization in groundwater was dominant in many other areas such as Bangladesh and Inner Mongolia where natural high As groundwater occurred (Nickson et al., 1998; Guo et al., 2011).



Fig. 3. The relationship between As concentrations and groundwater tables during dry season.

High As concentrations were accompanied with low Eh and high NH_4 and COD concentrations of groundwater in study area (Table 1, Fig. 5c–e). In this study, NH_4 and COD are the anthropogenic factors originating from domestic sewage and industrial waste water which contain plenty of organic matter and nitrogen compounds by the leakage of the drainage network. Under the condition of reductive environment (low Eh), decomposition of organic matter and reduction of nitrogen compounds in the shallow groundwater occurred, which might lead to the reductive dissolution of Fe and Mn (oxy)hydroxides for As-enrichment (Ahmed et al., 2010).



Fig. 4. The concentrations of As in groundwater during wet season and dry season.

The positive correlation between As and pH (Table 1, Fig. 5f) indicated that As distribution in groundwater of study area might be controlled by pH since As had a decrease adsorption onto aquifer mediums such as Fe (oxy)hydroxide mineral with increase pH (Zhu et al., 2011). High As concentrations were generally accompanied with high F concentrations of groundwater in study area (Table 1, Fig. 5g), which is in agreement with the result reported by Paoloni et al. (2005) who also observed that As was positively correlated to F in southeastern Pampa, Argentina, suggesting that the competition for available binding sites in the surface of aquifer mediums lays between F ion and As anions in groundwater of study



Fig. 5. The relationship between As concentrations and other chemical parameters in groundwater during dry season.

area. In this study, no significant relationship can be observed between As and other anions such as HCO_3 , Cl, SO₄, NO₃, and PO₄ (Table 1) indicating that competitive sorption between As and these anions could not explain the elevated As in groundwater of study area (Xie et al., 2012).

4 Conclusions

(1) As concentrations in 20% groundwater samples exceedes the WHO guideline value of 10 μ g/L,

and the highest concentration of As is 23.5 μ g/L during dry season. Higher concentrations of As are discovered in the centre and southeast of study area, while relatively lower concentrations of As are measured in the northwest of study area. It is observed that the concentration of As decreased with the depth of groundwater table during dry season, and the concentrations of As in wet season were generally higher than that in dry season, indicating that As in surface might be one of the main sources for As in shallow groundwater of study area, especially in wet season. (2) The concentration of As in groundwater of study area have significantly positive correlation with the concentration of Fe, Mn, NH₄, F, and COD, and is positively correlated to pH, but negatively correlated to Eh and K, indicating that reductive dissolution of Fe and Mn (oxy)hydroxides might be one of the main processes for As mobilization in groundwater of study area, and pH and F also play important roles in controlling the As mobilization in groundwater of study area.

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