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# Temporal variability of groundwater chemistry and relationship with water-table fluctuation in the Jianghan Plain, central China

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# Abstract

Samples were collected every month from 39 monitoring wells over a period of 1 year and three months (from Jan 2013 to Mar 2014) in the Jianghan alluvial plain in the middle reaches of the Yangtze river, central China, to evaluate the temporal variability of groundwater composition for As and other constituents. The concentrations of K,Na,Ca,Mg in groundwater generally varied less than 30%, whereas concentrations of the redox-sensitive components (Fe,NH<sub>4</sub>-N,S and As) varied greater over time. In wells tapping the confined aquifers with depth of 25m, concentrations of groundwater As were much higher and ranged up to760  $\pm$ 320  $\mu$ g/L seasonally. Higher As concentration were associated with an increasing percentage of As(III) in rainy season and a decrease towards the end of dry season, indicating a reductive mobilization responding to groundwater level fluctuation.

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# 1. Introduction

Naturally arsenic enrichment of groundwater is a subject of great concern, which has been reported from numerous countries worldwide<sup>1-2</sup>. China is one of the most serious waterborne endemic arsenicosis affected area. Typical cases of endemic arsenic poisoning have been reported in two kinds of regions in China<sup>3-4</sup>: Hetao Basin, Huhhot Basin, and Datong Basin were selected as arid inland basins in Northern China; Jianghan Plain is a newly discovered arsenic affected area in Southern China, which is one of the typical humid river deltas. Differences in climate, geological background and anthropogenic activities make investigations of high As groundwater in the

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Jianghan Plain different from those in northern China<sup>5</sup>. Temporal change of As concentrations in groundwater has been reported in Bangladesh and China<sup>6-8</sup>. There is growing evidence that temporal changes of As concentration can be attributed to seasonal fluctuation of water-levels and its effect on redox condition or groundwater flow pattern.

In this paper, we present the results of 15 months groundwater monitoring data, from 39 monitoring wells installed in endemic arsenicosis area in Jianghan Plain. These observations not only fill a gap in our understanding of seasonal variation in groundwater arsenic concentrations, they also help us to figure out the mechanisms of As transformation and the relation to water-level fluctuation during pre-monsoon, monsoon and post-monsoon seasons.

# 2. Materials and methods

#### 2.1. Study area

Jianghan alluvial plain in Central China is located in the middle Reaches of the Yangtze River, formed by Yangtze River and its largest tributary Han River (Fig.1a). It is well known as the beautiful and rich land of fish and rice. It has a sub-tropical monsoonal climate with an annual precipitation and evaporation of about 1200 mm and 1378 mm, respectively. Annual average temperature is 16.8°C. The monitoring field site was constructed in Shahu Original Farm, where the first case of arsenic poisoning was reported in Jianghan Plain<sup>5</sup>. The field site with an area of 10 km<sup>2</sup> lies in the hinterland of eastern Jianghan Plain in Xiantao City, surrounded by Tongshun River, Dongjing River, Kuige River, and Lvfeng River (Fig.1b), and covered by other abundant surface water bodies such as ponds, irrigation channel. The Quaternary groundwater systems can be divided into two groups of aquifers. The first group is composed of late and middle Pleistocence alluvial sediment (medium–coarse sand and gravel, interlaced clay lenses in local area) with the thickness of 30 m, which is the main aquifer for water supply. A total of 39 monitoring wells with three different depths were installed at 13 sites (Fig.1b). At each site, three monitoring wells with 10 m(A), 25 m(B), and 50 m(C) deep tapped shallow aquifers composed of Quaternary deposits.



Fig.1 Maps showing the locations of field monitoring site in Jianghan Plain, as well as the distribution of groundwater and surface water monitoing sites.

### 2.2. Sampling and analysis

Groundwater samples were collected monthly from Jan 2013 to Mar 2014 in Shahu monitoring field site of Jianghan Plain. Temperature, pH, EC, and Eh were measured on site using a portable pH, EC, and Eh meter in situ(HACH HQ40D,USA). NH<sub>4</sub>-N, Fe<sup>2+</sup> and sulfide were measured on site using a portable spectrophotometer

(HACH 2800, USA). Concentrations of HCO<sub>3</sub><sup>-</sup> were measured within 24 hours using acid-base titration methods. The total concentration of dissolved ions (Ca, Mg, Na, K, Fe, and Mn) was determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (IRIS Intrepid II XSP, USA). Anions such as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> were determined using an ion chromatograph (Dionex 2500, USA). Total dissolved As was determined using a hydride generation-atomic fluorescence spectrometer (HG-AFS, 930, Titan, China).

# 3. Results and discussion

### 3.1. Temporal water-level fluctuation and groundwater chemistry variation

Water levels of unconfined aquifer (well A with 10m depth) rose from 21.6 to 23.7 m abl during the wet season (Jun-Sep), drastically declined to 20.1m abl during the dry season (Nov-Mar). Water levels of confined aquifers varied from 21.3-22.3 m abl (well B with 25 m depth) and 21.5-22.3 m abl (well C with 50 m depth) during the wet season to 19.3-21.0 m abl and 19.0-20.9 m abl during the dry season, respectively.

Slight temporal variations in Na, K, Ca, Mg, and HCO<sub>3</sub> concentrations in groundwater were observed, with RSDs less than 30%. In comparison, seasonal variability of the concentrations of redox sensitive constitutes ( $NH_4$ -N,  $S^2$ -, Fe, Mn, SO<sub>4</sub>, As) were much greater (Table 1).

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Index	Well	unit	Pre-monsoon (May, 2013)			Monsoon (Aug, 2013)			Post-monsoon(Nov,2013)		
muex	Depth		Max	Min	Mean	Max	Min	Mean	Max	Min	Mean
	10m		-15.0	-125	-81.7	-132	-170	-153	-62.1	-151	-112
Eh	25m	mV	-46.0	-171	-89.6	-145	-190	-168	-135	-171	-148
	50m		-59.9	-177	-115	-95.5	-211.3	-164	-117	-146	-132
	10m		11.0	0.20	2.64	11.1	0.15	3.45	10.4	0.26	3.22
	25m	17	11.3	0.55	3.11	10.9	0.60	3.75	10.9	0.50	4.03
NH <sub>4</sub> -N	50m	mg/L	3.03	0.85	2.19	2.80	1.05	2.09	2.88	1.13	2.15
	10m		89		15	163	7.0	38.4	44.0	2.00	12.7
a?-	25m	17	121	2	16	62.0	5.0	29.4	34.0	2.00	15.6
S-	50m	μg/L	133	2	34	230	1.0	72.2	258	1.00	88.2
	10m		43.5	4.47	11.0	51.0	4.42	14.4	19.8	< 0.01	8.54
$\mathrm{SO_4}^{2\text{-}}$	25m	mg/L	8.95	4.09	4.74	6.20	4.15	4.64	5.52	< 0.01	4.18
	50m		20.0	4.13	6.40	18.1	4.25	6.52	10.4	< 0.01	5.69
	10m		17.5	0.32	7.86	33.3	3.11	14.1	33.7	1.93	12.5
	25m	17	5.40	1.07	2.97	13.5	1.79	7.62	12.5	0.15	6.30
Fe	50m	mg/L	5.98	0.72	2.43	7.02	2.03	3.70	4.94	1.97	3.49
	10m		5.43	0.54	1.89	5.43	0.57	2.19	4.89	0.26	2.03
	25m	17	5.70	0.60	1.60	6.42	0.29	1.86	6.54	0.17	1.80
Mn	50m	mg/L	4.06	0.17	0.67	3.83	0.19	0.84	3.30	2.57	0.75
	10m		65.5	2.70	20.3	182	23.6	48.0	105	2.57	33.1
	25m	17	122	5.46	48.0	1003	11.1	236	947	10.2	234
As	50m	μg/L	52.7	15.3	31.7	76.6	4.24	46.9	75.4	25.5	49.1

Table 1 Temporal variations of redox-sensitive components in groundwater at different depths at field monitoring site in the Jianghan Plain

#### 3.2. Seasonal variation of arsenic and the relation to water-level fluctuation

Seasonal variation in As concentration was observed in both unconfined aquifer and confined aquifer. Concentrations of total As in groundwaters from 39 wells in the monitoring field site ranged from  $3.6\pm3\mu$ g/L to 760  $\pm320 \mu$ g/L during the monitoring period (Fig.2). Arsenic concentration was generally higher in August than in May. Seasonal variation in redox potential and concentrations of Fe in groundwater was consistent with that in As. Higher As concentration was observed in wells at 25 m. Temproal variations of arsenic concentration related to groundwater levels, with lower concentration corresponding to lower water level (during dry season) and higher concentration corresponding to higher water level (during wet season). Higher As concentration were associated with an increasing percentage of As(III) in rainy season and a decrease towards the end of dry season, indicating a reductive mobilization responding to groundwater level fluctuation. Reductive dissolution of Fe oxides and reductive desorption have been widely accepted as the major mechanisms for As release and mobilization in reducing conditions  $^{2,7-8}$ .



Fig.2 Temporal variation of arsenic concentration in groundwater at different depths in field monitoring site from Jan, 2013 to Mar, 2014.

#### 4. Conclusions

Seasonal variation in As concentration was observed in both unconfined aquifer and confined aquifer in the Jianghan alluvial plain in the middle reaches of the Yangtze river, central China. Concentrations of total As in groundwaters from 39 wells in the monitoring field site ranged from  $3.6\pm3\mu g/L$  to  $760\pm320 \mu g/L$  over a period from Jan 2013 to Mar 2014. Higher As concentration were associated with an increasing percentage of As(III) in rainy season and a decrease towards the end of dry season, indicating a reductive mobilization responding to groundwater level fluctuation.

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