Roles of dissolved organic matter on seasonal arsenic variation in shallow aquifers of the central Yangtze River Basin by EEM-PARAFAC analysis

X.F. Yuan, Y. Deng & Z.J. Lu

Geological Survey, China University of Geosciences, Wuhan, P.R. China

ABSTRACT: Fluorescence excitation-emission matrix (EEM) analysis was applied to characterize seasonal variation of dissolved organic matter (DOM) in arsenic-affected shallow aquifers of the Jiangnan Plain, central China, to better understand the effect of DOM on arsenic transformation during dry season and wet season. It was identified that there are three components of DOM, of which C1 and C3 are fulvic acid-like substances and C2 is humic acid substance, and there is no obvious seasonal variability in C2, and the concentration is slightly higher in the wet season than the dry season. C1 and C3 have the opposite change rules in different seasons, which is mainly reflected in the shallow unconfined water.

1 INTRODUCTION

Naturally arsenic (As) enrichment of groundwater is a subject of great concern, which has been reported from numerous countries worldwide (Keon *et al.*, 2001; Smedley *et al.*, 2002). China is one of the most serious waterborne endemic arsenicosis affected area. Jiangnan Plain is a newly discovered arsenic affected area in Southern China. Fluorescence spectroscopy is a simple, sensitive and nondestructive technique that can provide valuable information regarding the molecular structure of dissolved organic matter (DOM) present in natural waters and generate 3-D excitation emission matrices (EEMs) spectra of DOM. PARAFAC can be applied to decompose fluorescence EEMs into different independent groups of fluorescent components, which can then reduce the interference among fluorescent compounds (Engelen *et al.*, 2009; Chen *et al.*, 2010). In this paper, we reveal the temporal changes of DOM and the relationships among DOM and As.

2 METHODS

2.1 Study area

Jiangnan 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. A total of 39 monitoring wells with three different depths were installed at 13 sites in Shahu monitoring field site of Jiangnan plain. 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.

2.2 Sampling and analysis

Samples were collected in Jan 2016 to Jul 2016 in Shahu monitoring field site of the Jiangnan Plain. Some in-situ parameters including T (°C), EC, DO, Eh, pH, S²⁻, NH₄⁺ and Fe²⁺ were monitored and in-situ measured when sampling. Water samples were also collected for further laboratory analysis, including major and trace elements, dissolved organic carbon (DOC) and 3-D fluorescence spectra analysis. Two multivariate statistical techniques including FA and PARAFAC were applied to hydrochemical variables and EEMs of groundwater, respectively.

3 RESULTS AND DISCUSSION

3.1 Water-level fluctuation and As temporal variation

The water level between the wet and dry season fluctuates about 1 m. Arsenic has a temporal variation in shallow aquifers, and has a relationship with water level, ORP and DOC (Fig. 1).

3.2 Fluorescence characteristics of DOM by PARAFAC analysis

By PARAFAC of samples, it can be identified that there are three components of DOM (Fig. 2), of which C1 and C3 are fulvic acid-like substances and C2 is humic acid substance. The main components of DOM in surface water are C1 and C3, whilst the DOM in groundwater are mostly C1 and C2. C1 and C3 are terrestrial organic matter, the smallest molecule produced in the process of microbial degradation. C2 is the DOM

Figure 1. The generalization of As temporal variation with the water level, ORP and DOC in the aquifer of the Jiangnan Plain, central Yangtze River Basin.

Figure 2. Excitation-emission matrices (EEMs) of groundwater components and spectral characteristics of three-component PARAFAC model validated by split half validation technique.

hybrid component of terrestrial materials, and marine materials and marine organic matter is considered to be the product of microbial utilization. There is no obvious seasonal variability in C2, and the concentration is slightly higher in the wet season than the dry season. C1 and C3 have the opposite change rules in different seasons, which is mainly reflected in the shallow unconfined water. The trend of arsenic concentration changes is the opposite of C1 and C3 (Table 1). The FI index in the sample groundwater is between 1.2 and 1.35, also indicating that the DOM is mainly a terrestrial source, but there is also a mixture of terrestrial source and microbial source, which could come from sediment in the local aquifer.

Table 1. The changes of fluorescence component C1, C2, and C3 in shallow unconfined water and shallow confined water of Fmax value in dry season and wet season.

Monitoring Wells		Dry Season			Wet Season		
		C1	C2	C3	C1	C2	C3
Shallow Unconfined Water	01A	266	126	58	0	140	69
	03A	232	146	70	37	154	96
	05A	132	47	16	121	50	115
	07A	109	33	0	139	54	39
Shallow Confined Water	01B	153	60	42	129	69	119
	03B	151	62	41	130	55	115
	05B	240	119	82	0	113	67
	07B	113	34	0	140	133	88

4 CONCLUSIONS

There is an obvious seasonal variability of As, and its variation has relationship with the water-level, ORP, DOC. There is no obvious seasonal variability in C2, and the concentration is slightly higher in the wet season than the dry season. C1 and C3 have the opposite change rules in different seasons, which is mainly reflected in the 10 m monitoring well.

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