SHORT COMMUNICATIONS

Groundwater Selenium Level and its Enrichment Dynamics in Seawater Intrusion Area along the Northern Coastal Zones of Shandong Province, China

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Abstract—The variation of groundwater properties caused by seawater intrusion, such as OH^- , TDS, SO_4^{2-} , can potentially affect the groundwater Se levels. But there are no researches detailing the mechanism of groundwater selenium characteristics in seawater intrusion areas along coastal zones. Buzhuang town has been selected for study and groundwater is sampled to discuss the behavior of groundwater selenium with the intrusion of seawater. The groundwater Se levels range from 1.43 to 15.60 $\mu\text{g/L}$, with an average of 6.23 $\mu\text{g/L}$. All are within the limit of 10 $\mu\text{g/L}$ except Wanglu village, but the local groundwater Se levels in 8 villages exceed the chronic criterion of 5 $\mu\text{g/L}$, and the Se levels in local groundwater are higher than those in the supplied water which has a non-seawater source. The groundwater Se levels have been shown to be elevated by seawater intrusion. The groundwater Se levels are positively correlated with Cl^- , TDS, Br^- , Na^+ , Mg^{2+} , SO_4^{2-} , Ca^{2+} and Fe and negatively correlated with pH. Ion competition effects and the Na-Mg-sulfate minerals play an important role in the adsorption and desorption for SeO_3^{2-} and SeO_4^{2-} , which are the important dynamic species for groundwater selenium enrichment. However, Ca and Fe ions have less contribution to groundwater Se variation because of the lower affinity for SeO_3^{2-} and SeO_4^{2-} and lesser content in groundwater of seawater intrusion areas.

Keywords: groundwater selenium, seawater intrusion, adsorption and desorption, Shandong province

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INTRODUCTION

Selenium (Se) acts as an important element affecting human health, with a narrow safety range of 40–400 μg per day (Levander and Burk 2006; WHO, 2006). The deficiency or excess of selenium intake causes adverse effects. Selenium deficiency, together with other trace elements as Ca, Fe, Zn, Mn, Cr, has been listed as the possible causes of Kashin-Beck Disease and Keshan Disease although their etiology is till not clear (Ning et al., 2018). The low level in the dietary budget results in dysfunctions of the thyroid gland (Korobova et al., 2014). The excessive intake results in lameness, hair and fingernail loss, cirrhosis of liver, damage to the nervous and circulatory system, and even death (USEPA 2006). Since groundwater has

become an important source of human selenium, groundwater selenium has attracted worldwide attention.

Water-rock (soil) interaction affects the selenium transformation between groundwater and rock (soil) system. The rock affects groundwater Se levels in two aspects: its own Se levels and the dynamic conditions affecting selenium leaching-ability (Fordyce et al., 2005). Selenium can exist in four oxidation states (Se^{2-} , Se^0 , Se^{4+} , Se^{6+}), and the soluble selenium species mainly include selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}), whereas the other forms of Se^{2-} and Se^0 are insoluble and immobile (Bailey, 2017). Hence, the conversion of Se^{2-} and Se^0 into SeO_3^{2-} and SeO_4^{2-} largely determines the groundwater Se levels. A series of physical,

chemical and microbial processes governing Se transformation were reported for groundwater Se enrichment, such as pH, Eh, mineral dissolution, fertilizers/irrigation return flow and so on (Bailey, 2017).

Seawater intrusion, a common process along coastal zones, can potentially change groundwater Se levels by altering groundwater properties. For example, the groundwater becomes alkaline due to seawater intrusion, with the high pH of more than 7.0 (Qi and Qiu, 2011; Ma et al., 2013; Chen et al., 2019), multiple researches documented the Se^{2-} and Se^0 transformation into Se^{4+} and Se^{6+} . Accordingly, the groundwater Se levels should be elevated with the intrusion of seawater (Frost and Griffin, 1977; Bailey, 2017). The more ions (e.g. Fe^{2+} , SO_4^{2-} , Ca^{2+}) in intruded groundwater, the more conducive it is for groundwater Se enrichment since they influence the adsorption/desorption of selenium species (Timpson et al., 1986; Press and Swain, 1990; Gerla et al., 2011). In addition, some properties as high TDS, EC, salinity, which are related to seawater intrusion, are also reported to elevate groundwater Se levels (Crist, 1974; Yi et al., 2014; Wu et al., 2014). However, seawater intrusion is usually not considered when the dynamics of groundwater Se enrichment are discussed, and there is no research detailing the effect of seawater intrusion on groundwater Se levels.

Although there are no direct reports clarifying the relationship between seawater intrusion and groundwater Se levels, the occurrence of high-selenium groundwater in the environment of seawater intrusion can be located in documents. The San Joaquin Valley, USA, a typical area with high-selenium groundwater, is reported to have developed from marine sediments, with soil salinization (Presser and Ohlendorf, 2017). High-selenium groundwater was observed in the Amman Zarqa Basin, Jordan by Mustafa and Ahmad (2010), and Margane et al. (2002) reported that saline water from deep aquifers had intruded here. Therefore, an investigation of groundwater Se levels is necessary for the quality assessment and scientific use of groundwater along coastal zones.

In this research, a typical area of Buzhuang Town, a serious seawater intrusion area in the northern part of Shandong province, was chosen and the groundwater was sampled. The aims of this study are to: (1) clarify the groundwater Se levels in seawater intrusion area along coastal zones; (2) discuss the possible dynamics and the influencing factors of groundwater Se levels along coastal zones by experimental data on the chemical parameters.

STUDIED AREA AND SAMPLING

The Studied Area

The town of Buzhuang is located in the northern section of Shandong province, China. The area is neighbored to the north by the Bohai Sea, and it is a

typical silt-argillaceous coastal plain. The geologic basement is a metamorphic sequence of Jiaodong Formation from the Archeozoic to the Proterozoic era, and Fenzishan Formation and Penglai Formation of the Proterozoic era. The main basement rocks consists of gneiss, schist, granulite, quartzite, slate, marble and so on (Wu et al., 1993). The sedimentary cover consists mainly of the Huangxian Formation of the Eocene, and the Quaternary. There are four main aquifers containing fine to coarse sands and gravels of the Quaternary (Chen et al., 2014).

The area was a piedmont alluvial plain and alluvial marine-deposition plain. The unconsolidated sediments are over 100 m thick. There are several buried layers of brine with the transgression and regression of seawater historically, which have been the sources of salt water intrusion. The local populations are suffering from serious salt-water intrusion since 1980s, and the groundwater tastes a little salty and bitter.

The groundwater in this area is characterized by pore water, with the surrounding loose sediment of Quaternary. The area is classed as low-selenium belt, and the sediments were reported to have low Se levels. According to an agricultural environmental geochemistry survey, the selenium levels of the sediment or soils in this area range from 4 to 247 $\mu\text{g/L}$, with an average of 92 $\mu\text{g/L}$, which is lower than the national Se setting value (200 $\mu\text{g/kg}$) and the background levels of Shandong province (130 $\mu\text{g/kg}$). The sediment or soil Se levels in Gaomi District, a neighbouring area, are documented to be 42.3 ± 12.7 $\mu\text{g/kg}$, but Se in human body appears to be normal levels, with the reported Se levels of 117.4 ± 20 $\mu\text{g/L}$ in blood and 405 ± 90 $\mu\text{g/L}$ in nails, which may be because of the multiple sources of the local diets as seafood (Cao et al., 2007).

Sampling and Analysis

The groundwater was sampled based on the village units, and the locations were shown in Fig. 1. In total, 16 villages were involved. Among which, supplied water in the two villages of Liujia and Bajia was obtained as control samples since the water is from a neighboring area in which there is no seawater.

The water was gathered in pre-cleaned plastic bottles and kept at a low temperature. The groundwater was divided into two parts. One was used for the analysis of pH, TDS, while the other was frozen for the analysis of other ions. pH was determined using PH-3C pH meter. A DDS-320 conductivity meter was used for the TDS analysis. Groundwater Se and Fe levels were determined by ICP-MS, and mixed element standard solutions were used to calibrate the ICP-MS. Cl^- , Br^- , SO_4^{2-} , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} were analyzed using a Dionex ICS-90 Ion Chromatograph.

For quality control, blank water and standard reference water were used. The accuracy of these factors has been verified and estimated by the standard sam-

Fig. 1. The sketch map of the groundwater sample locations.

ples. One sample were repeatedly analyzed every 4–6 samples for reliable performance. The calculated standard deviations for these properties are within the range of 0.1–3%.

RESULTS

Groundwater Selenium Characteristics

The groundwater Se levels and other geochemical properties are listed in Table 1. The pH is neutral-alkaline, varying between 7.31 and 8.26. The TDS range from 0.66 to 2.72 g/L. The anions of Cl^- , Br^- , SO_4^{2-} have levels of 79.35–1105.67, 0.19–1.90 and 33.82–1080.58 mg/L respectively, dominated by Cl^- ions. The cations of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Fe have levels of 114.46–735.96, 4.37–61.64, 2.57–130.57, 0.4–82.07 and 6.09–196.96 $\mu\text{g/L}$ respectively, dominated by Na^+ ions. The local groundwater Se levels range from 1.43 to 15.60 $\mu\text{g/L}$, with an average of 6.23 $\mu\text{g/L}$, while those in the supplied water vary from 1.52 to 1.77 $\mu\text{g/L}$, with an average value of 1.65 $\mu\text{g/L}$.

Different agencies have set different maximum contaminant levels for selenium in drinking-water. The United States Environmental Protection Agency and Health Canada have set it at 50 $\mu\text{g/L}$ (USEPA, 2006), and it is 10 $\mu\text{g/L}$ according to European Union, New Zealand Ministry of Health, Finnish Institute of Drinking Water, Jordanian Institute of Standards and Metrology, World Health Organization (WHO 2006). All the villages are within the limitation of 10 $\mu\text{g/L}$ set by the Ministry of Environmental Protection of China

except Wanglu village. However, the chronic criterion for freshwater aquatic life is suggested to be only 5 $\mu\text{g/L}$ (USEPA 2006), and thus the local groundwater Se levels in 8 villages (accounting for 50%) exceed this threshold.

Groundwater Characteristics and Seawater Intrusion

The groundwater Cl^- , Br^- and TDS change greatly when mixed by seawater. The Cl^- , Br^- and TDS in the local groundwater range from 79.35 to 1105.67 mg/L, from 0.19 to 1.90 mg/L, and from 0.66–2.72 g/L, with the average levels of about 477.03 mg/L, 0.85 mg/L and 1.43 g/L respectively (Table 1). However, the supplied water of Liujia and Bajia villages has Cl^- , Br^- and TDS of 105.52–106.79, 0.15–0.16 and 0.51–0.52 g/L respectively. Clearly, the Cl^- , Br^- and TDS in the local groundwater increased greatly due to seawater mixture.

A standard of seawater intrusion has been set by the China Geological Survey. That is, seawater intrusion is thought to occur when the groundwater exceeds the levels of 250 mg/L Cl^- , or 0.55 mg/L Br^- , or 1.0 g/L TDS. The average of Cl^- , Br^- and TDS in the local groundwater is higher than the recommended levels proposed by the Chinese standards. The Fu'an and Xujiazhuang villages are within safety parameters, and their Se levels are also low. The Br^- and TDS are within the safety range but the Cl^- is more than 250 mg/L in the groundwater of Dahebei village. Despite this, all the local villages have higher groundwa-

Table 1. The groundwater Se levels and other characteristics in Buzhuang Town

Village (depth)	Se	pH	TDS	Cl ⁻	Br ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Fe	SAR
Jinshan (12 m)	9.91	7.51	2.12	665.30	1.15	596.39	541.76	12.26	83.04	49.23	123.12	10.88
Baiyimiao (10 m)	7.61	7.73	1.74	655.41	1.07	304.68	457.69	35.16	91.19	39.76	61.88	9.09
Majia (9 m)	9.14	7.31	2.47	999.55	1.61	760.68	752.26	40.42	124.02	29.24	79.58	13.47
Dongzhao (16 m)	3.39	8.26	1.09	275.66	0.65	33.82	455.39	10.41	2.57	0.40	6.09	57.87
Yaojia (12 m)	5.50	7.89	1.32	504.91	0.83	131.07	430.07	39.18	36.20	23.84	59.31	12.89
Wanglu (10 m)	15.60	7.56	2.72	1105.67	1.90	1080.58	735.96	61.64	130.57	61.63	150.90	12.11
Yingzi (13 m)	3.84	7.64	1.33	317.39	0.80	486.84	340.48	34.64	51.64	26.89	38.15	8.81
Xinsheng (16 m)	5.83	8.24	1.18	438.58	0.61	117.15	432.12	13.23	6.12	4.23	12.90	31.29
Qianlu (13 m)	4.11	8.05	1.13	367.24	0.51	214.70	337.88	39.24	23.78	22.64	40.37	11.77
Xujiazhuang(32 m)	1.35	8.03	0.68	79.35	0.19	251.18	256.72	14.39	5.81	15.56	19.25	14.05
Lyjiazhuang (18 m)	9.35	7.53	0.91	267.45	0.45	157.14	114.46	24.22	64.96	82.07	174.33	2.28
Fu'an (19 m)	1.43	8.17	0.66	126.70	0.27	178.54	252.84	4.37	18.53	21.83	42.75	9.58
Dahebei (30 m)	3.15	8.17	0.98	264.47	0.64	162.12	303.05	8.91	38.72	11.97	21.75	9.53
Liuzhuang (10 m)	6.94	7.44	1.72	610.81	1.16	502.82	416.66	17.73	72.58	65.10	196.96	8.40
Liujia	1.77	7.70	0.51	105.52	0.16	92.20	43.11	1.30	20.60	87.99	222.03	1.07
Bajia	1.52	7.34	0.52	106.79	0.15	90.25	44.16	1.13	20.69	83.63	235.59	1.11

Se and Fe are in µg/L, TDS is in g/L, the others are in mg/L except pH and SAR.

ter Cl⁻, Br⁻ and TDS levels than villages with supplied water, indicating the seawater intrusion in this area.

The SAR (Sodium Adsorption Ratio) is also used as an index of seawater intrusion. It is calculated as follows (Biswas and Mukherjee, 1987):

$$SAR = \frac{Na^+}{\sqrt{Ca^{2+} + Mg^{2+}}}$$

The units are in me/L. It can be seen that the groundwater SARs in all villages exceed the limit of 2.0 from Table 1. In particular, the values in Xujiazhuang, Lyjiazhuang and Fu'an are 14.05, 2.28 and 9.58 respectively. Such results also corroborate the occurrence of seawater intrusion.

The Correlation between Se Levels and Other Geo-chemical Properties

The correlation coefficient matrix of local groundwater characteristics is shown in Table 2. The Se levels are significantly positively correlated ($P < 0.01$) with TDS ($R^2 = 0.847$), Cl⁻ ($R^2 = 0.860$), Br⁻ ($R^2 = 0.832$), SO₄²⁻ ($R^2 = 0.760$), Mg²⁺ ($R^2 = 0.850$), Ca²⁺ ($R^2 = 0.698$), Fe ($R^2 = 0.711$), and positively correlated ($P < 0.05$) with Na⁺ ($R^2 = 0.638$), K⁺ ($R^2 = 0.635$). Also, the selenium levels are significantly negatively ($P < 0.05$) correlated with pH ($R^2 = -0.700$). This can be interrupted to mean that these geochemical characteristics may be responsible for the groundwater Se distribution.

Significant positive correlations exist between TDS and Cl⁻ ($R^2 = 0.978$), Br⁻ ($R^2 = 0.982$), SO₄²⁻ ($R^2 = 0.885$), Na⁺ ($R^2 = 0.907$) and Mg²⁺ ($R^2 = 0.889$). Cl⁻ shows significant positive correlation with Br⁻ ($R^2 =$

0.974), SO₄²⁻ ($R^2 = 0.830$), Na⁺ ($R^2 = 0.903$), K⁺ ($R^2 = 0.642$) and Mg²⁺ ($R^2 = 0.889$). Significant positive correlations are also observed between Br⁻ and SO₄²⁻ ($R^2 = 0.869$), Na⁺ ($R^2 = 0.895$), K⁺ ($R^2 = 0.659$), and Mg²⁺ ($R^2 = 0.889$). This indicates that the groundwater TDS, Cl⁻, Br⁻, SO₄²⁻, Na⁺, Mg²⁺ increase with greater seawater intrusion, and seawater intrusion is the main factor affecting these characteristics in the local groundwater.

DISCUSSION

Freshwater has an average Se level worldwide of about 0.2 µg/L, and the Se level in seawater is lower than that in fresh water, with an average of about 0.1 µg/L. The studies done in the Northwest Pacific Ocean (Aono et al., 1991), the Atlantic Ocean (Cutter and Cutter, 2001), and the South China Sea (Pu, 1990) all reported that seawater had low Se levels. Wu et al. (2014) even illustrated the continental input of dissolved Se from adjacent rivers in the Changjiang (Yangtze) Estuary. Therefore, the Se levels in local groundwater shouldn't be so high if the simple mixing of seawater were to be the only cause. There must be complex physical-chemical interactions to influence the groundwater Se levels.

The groundwater Se levels in this study are attributed to prolonged water-rock interactions. Thus, some Se-bearing rocks, such as marine shale, clay, phosphorite, basalt, and granite, are considered as the sources of high-selenium water (Fordyce et al., 2005). More importantly, the dynamic conditions governing Se transformation between water and rocks, such as pH, Eh, adsorption-desorption processes, biological

Table 2. The correlation coefficient matrix of local groundwater characteristics

	Se	pH	TDS	Cl ⁻	Br ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Fe
Se	1	-.700**	.847**	.860**	.832**	.760**	.638*	.635*	.850**	.698**	.711**
pH	-.700**	1	-.718**	-.671**	-.693**	-.733**	-0.424	-0.5	-.861**	-.783**	-.785**
TDS	.847**	-.718**	1	.978**	.982**	.885**	.907**	.642*	.889**	0.42	0.499
Cl ⁻	.860**	-.671**	.978**	1	.974**	.830**	.903**	.693**	.877**	0.41	0.493
Br ⁻	.832**	-.693**	.982**	.974**	1	.869**	.895**	.659*	.889**	0.415	0.506
SO ₄ ²⁻	.760**	-.733**	.885**	.830**	.869**	1	.746**	.626*	.855**	0.492	.536*
Na ⁺	.638*	-0.424	.907**	.903**	.895**	.746**	1	.541*	.665**	0.033	0.161
K ⁺	.635*	-0.5	.642*	.693**	.659*	.626*	.541*	1	.642*	0.351	0.291
Mg ²⁺	.850**	-.861**	.889**	.877**	.889**	.855**	.665**	.642*	1	.667**	.662**
Ca ²⁺	.698**	-.783**	0.42	0.41	0.415	0.492	0.033	0.351	.667**	1	.955**
Fe	.711**	-.785**	0.499	0.493	0.506	.536*	0.161	0.291	.662**	.955**	1

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

interactions, complexing ability, and reaction kinetics have also been investigated (Korobova et al., 2014; Wu et al., 2014).

The species of groundwater selenium are mainly the soluble SeO_3^{2-} and SeO_4^{2-} , SeO_4^{2-} has a higher solubility than SeO_3^{2-} . The transformation of selenium species into SeO_3^{2-} and SeO_4^{2-} , or that of SeO_3^{2-} into SeO_4^{2-} , can elevate the groundwater Se levels (Afzal et al., 2000). The alkaline condition is helpful for groundwater selenium enrichment by transforming SeO_3^{2-} into SeO_4^{2-} or by decreasing the stability of the SeO_3^{2-} complex with metals (Bailey, 2017). A series of researches indicate that groundwater Se levels are positively correlated with pH, as demonstrated by Frost and Griffin (1977) and Jinadasa and Dissanayake (1992). The pH increases and the alkaline conditions occur due to seawater intrusion, The local groundwater has obviously higher pH values than the supplied water (Table 1). However, the pH does not show any positive correlation with groundwater Se levels, indicating that the transformation of selenium species is not the main dynamic affecting groundwater Se levels in seawater intrusion areas.

The observed fact that the local groundwater Se levels increase with TDS, Cl^- and Br^- (Table 2) implies that the groundwater Se levels are related to seawater intrusion, and the degree of seawater intrusion deeply affects the groundwater Se levels. Previous researches have also documented that groundwater Se levels are positively correlated with Cl^- , TDS, salinity and Br^- (Crist 1974; Mustafa and Ahmad, 2010; Gerla et al., 2011; Presser and Ohlendorf, 2017). Adsorption-desorption processes govern the groundwater Se levels to some extent, and it is estimated that 20% of total

selenium was adsorbed on the rock (soil) surface (Selim and Sparks, 2001). On the other hand, the ion competition effect can reduce the amounts of selenium adsorption on rock (soil) surfaces and release them into groundwater. PO_4^{3-} , NO_3^- , SO_4^{2-} are often documented as competitors (Dhillon and Dhillon, 2000). Balistrieri and Chao (1987) estimated that 50% of selenite oxyanions can be substituted by PO_4^{3-} . Clearly, quantities of such ions are involved in the groundwater when seawater intrudes into groundwater. These ions impede the adsorption of SeO_3^{2-} and SeO_4^{2-} , and even substitute SeO_3^{2-} adsorbed on the rock(soil) surface (Fujii et al., 1988). Furthermore, these ions have been proven to have stronger adsorption capacity than SeO_3^{2-} and SeO_4^{2-} (Balistrieri and Chao, 1987; Neal and Sposito, 1989). The competition ions in local groundwater are several times greater concentration than those in the supplied water (Table 1). Generally, the ion competition effect due to seawater intrusion can cause the release of adsorbed SeO_3^{2-} and SeO_4^{2-} into groundwater and enhance the groundwater Se levels, which should be an important dynamic of groundwater Se enrichment in seawater intrusion areas.

The local groundwater Se levels show good correlations with Na^+ , Mg^{2+} and SO_4^{2-} , which is in agreement with the previous researches by Timpson et al. (1986), and Gerla et al. (2011). These facts suggest that Na-Mg-sulfate minerals may concentrate water-soluble Se. Presser et al. (1990) concluded that structure of these sulfates permits substitution by Se and results in an increase of Se levels characterized by the occurrence of such minerals. Meanwhile, SO_4^{2-} has the same

adsorption mechanism as SeO_3^{2-} and SeO_4^{2-} , and can act as stronger competitors for the adsorption of SeO_3^{2-} and SeO_4^{2-} (Neal and Sposito, 1989). Afzal et al. (2000) also observed the adsorption ability of SeO_3^{2-} and SeO_4^{2-} decreases when SO_4^{2-} is mixed into groundwater. This seems to be corroborated in this work by the relationship between Se levels and Na^+ , Mg^{2+} and SO_4^{2-} , reflecting the increasing role of soluble Na-Mg-sulfate in elevating groundwater Se levels in seawater intrusion areas.

Calcite can be the host phase influencing SeO_3^{2-} activity since the structural similarities between carbonate and selenite oxyanions facilitate the incorporation of amounts of SeO_3^{2-} to the bulk of calcite crystals (Roman-Ross et al., 2006). Lowest Se levels were also detected in water at territories with carbonate loess-like loams (Korobova et al., 2014). Several studies have concluded that Fe adsorbs SeO_3^{2-} and SeO_4^{2-} and removes them from the water environment (Selim and Sparks, 2001). Korobova et al. (2014) even concluded the hydroselenide formed FeSe and precipitated on the reduced barrier in the presence of significant Fe levels, and the elevated Se levels contain lower Fe levels in water. The Ca and Fe ions in the local groundwater show lower levels than those in supplied water (Table 1) probably resulting from the high pH caused by seawater intrusion, which is beneficial for groundwater selenium enrichment. However, there are no decreasing trends of selenium with the increase of Ca and Fe ions in the local groundwater. Instead, positive correlations arise (Table 2). These may be for the following reasons: (1) the limited amounts of calcite crystals contribute less to selenium deposition. Press et al. (1990) also stated Ca ions have less influence on groundwater selenium when compared with Na-Mg-sulfate; (2) The affinity of Fe for SeO_3^{2-} and SeO_4^{2-} adsorption is generally smaller at high pH (Balistrieri and Chao, 1987; Yu, 1997; Su and Suarez, 2000); and (3) The adsorption of SeO_3^{2-} by Fe and other similar metal hydroxides is strongly suppressed by sulfate competition for adsorption sites (Gerla, 2011). The positive correlation may be based on the fact that the more ions mix into the groundwater, the more seawater intrudes. Thus, the contribution of Ca and Fe ions on groundwater Se levels is far less than the ion competition effect in seawater intrusion areas. In fact, the contents of Cl^- , TDS, Br^- , Na^+ , Mg^{2+} , SO_4^{2-} are far higher than those of Ca and Fe ions.

CONCLUSIONS

The groundwater samples in the town of Buzhuang, in Shandong province of China, an area typically characterized by seawater intrusion, were gathered to detect

groundwater Se levels, and to correlate them with the seawater intrusion process. The following findings are revealed:

(1) The groundwater has Se levels of 1.43–15.60 $\mu\text{g/L}$, with an average of 6.23 $\mu\text{g/L}$. Only one village of Wanglu exceeds the limitation of 10 $\mu\text{g/L}$, but the Se levels in 8 villages are above the chronic criterion of 5 $\mu\text{g/L}$. The geochemical indexes of Cl^- , TDS, Br^- and SARs all indicate that the groundwater is intruded. The local groundwater Se levels are obviously elevated by seawater intrusion compared with those in supplied water.

(2) The groundwater Se levels significantly show positive correlations with Cl^- , TDS, Br^- , Na^+ , Mg^{2+} , SO_4^{2-} , indicating an increase of groundwater Se levels with more intrusion of seawater. An ion competition effect and the Na-Mg-sulfate minerals play an important role in the adsorption and desorption of SeO_3^{2-} and SeO_4^{2-} , which seems to be important dynamics of groundwater selenium enrichment. pH is not positively related to groundwater Se levels. Groundwater Se levels do not show negative correlations with Ca and Fe ions, but positive correlations. The lower affinity of Ca and Fe ions for SeO_3^{2-} and SeO_4^{2-} and less contents lead to their less contribution to the groundwater Se variation in seawater intrusion area.

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