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Shallow groundwater quality and associated non-cancer health risk in agricultural areas (Poyang Lake basin, China)

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Abstract Owing to their accessibility, shallow groundwater is an essential source of drinking water in rural areas while usually being used without control by authorities. At the same time, this type of water resource is one of the most vulnerable to pollution, especially in regions with extensive agricultural activity. These factors increase the probability of adverse health effects in the population as a result of the consumption of shallow groundwater. In the present research, shallow groundwater quality in the agricultural areas of Poyang Lake basin was assessed according to world and national standards for drinking water quality. To evaluate non-cancer health risk from drinking groundwater, the hazard quotient from exposure to individual chemicals and hazard index from exposure to multiple chemicals were applied. It was found that, in shallow groundwater, the concentrations of 11 components (NO₃⁻, NH₄⁺, Fe, Mn, As, Al, rare NO₂⁻, Se, Hg, Tl and Pb) exceed the limits referenced in the standards for drinking water. According to the health risk assessment, only five components (NO₃⁻, Fe, As, rare NO₂⁻ and Mn) likely provoke non-cancer effects. The attempt to evaluate

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Z. Sun · B. Gao East China University of Technology, 418 Guanglan Avenue, Nanchang 330013, China the spatial distribution of human health risk from exposure to multiple chemicals shows that the most vulnerable area is associated with territory characterised by low altitude where reducing or near-neutral conditions are formed (lower reaches of Xiushui and Ganjiang Rivers). The largest health risk is associated with the immune system and adverse dermal effects.

 $\label{eq:constraint} \begin{array}{ll} \mbox{Keywords} & \mbox{Water pollution} \cdot \mbox{Non-cancer effects} \cdot \\ \mbox{Health risk assessment} \cdot \mbox{Agrolandscapes} \cdot \mbox{Drinking} \\ \mbox{water} \cdot \mbox{Southeastern China} \end{array}$

Introduction

There is no secret that quality of water resources is an urgent problem in China (Qiu 2010; Yu 2011). According to a survey carried out in 2000–2002 by the Ministry of Water Resources of PRC (People's Republic of China), about 40% of groundwater resources are polluted and not appropriate for drinking purposes, and according to the results of local monitoring in several provinces, this situation continues to get worse (Zhang et al. 2015). The most acute problem of deterioration is for shallow groundwater, which is one of the most important sources of drinking water in rural areas. Shallow depth of occurrence makes it convenient for extraction, but at the same time, it increases vulnerability of this type of water resource to pollution. Shallow groundwater in rural

areas is usually not controlled by authorities because of the lack of a nationwide continuous monitoring of groundwater resources there (Zhang et al. 2015). Zhang et al. (2009) have reported that although 75% of the rural population uses groundwater for drinking, half of which uses decentralised water supplies, and only 5% has water treatment systems.

The residents often have no information about the chemical composition of the water that they are drinking. Such situation is common in the Poyang Lake area, where a rural population prevails. The anthropogenic effect to shallow groundwater in the area is connected basically with extensive agricultural activity, which leads to the spread of nitrate pollution (Sun et al. 2014; Soldatova et al. 2017b). As a result of long-term agricultural activity and growth of fertiliser application (NBSC 2014), nitrate pollution affects many agricultural areas in China (Chen et al. 2007; Zhang et al. 2013, 2015). According to the data from FAO (2002), up to 50% of nitrogen fertilisers volatilise, and about 5-10% penetrate to the subsoil horizon and groundwater. However, nitrates are not the only pollutant of groundwater in the study area. Another potential source of pollution is arsenic as a previous study has shown (Soldatova et al. 2015). The presence of As in groundwater may result from both natural and anthropogenic factors (Wen et al. 2013; Abu Bakar et al. 2015; Liang et al. 2016). This trace element is a serious toxicant which provokes adverse health effects in over 100 million people mainly in Asia (Ravenscroft et al. 2009; Jaishankar et al. 2014). The concentration of Fe in the studied groundwater is also high enough to affect humans. A high content of Fe damages the mitochondria, microsomes and other cellular organelles and affects lipid peroxidation (Albretsen 2006; Jaishankar et al. 2014). Thus, there is a set of reasons to suppose that consumption of shallow groundwater may lead to adverse health effects in the population of the study area. In this case, study of pollutant behaviour and quantitative assessment of human health risk due to consumption of polluted drinking water seem to be an issue of vital importance.

One of the most commonly used methods for health risk assessment was developed by the US Environmental Protection Agency (1989) and adopted in a number of studies (Rasool et al. 2016; Rojas Fabro et al. 2015; Liang et al. 2016; Ihedioha et al. 2017), including the study presented. The aim of the study was to evaluate shallow groundwater quality and assess non-cancer health risk associated with consumption of polluted shallow groundwater in the Poyang Lake area. Non-cancer health risk has been assessed as a risk from exposure to individual components of shallow groundwater and as a cumulative health risk from exposure to multiple components of shallow groundwater on different target systems, organs and processes in humans. Furthermore, the spatial distribution of health risks across the study area and factors affecting the risk distribution were examined for better understanding of the current situation of the quality of the shallow groundwater resources.

Materials and methods

Study area

The study area is located in Jiangxi Province, southeastern China. It covers the northern part of the Poyang Lake basin enclosing Poyang Lake itself. This territory is not only a unique ecosystem and a habitat of rare animal species but also an important agricultural area of Jiangxi Province and China as a whole. The study area has a long history of development, but the main occupation of the residents remains to be agriculture. According to Zhen et al. (2011), arable lands are one of the main land use types in the area surrounding Poyang Lake. Agrolandscapes spread all around the lake (Fig. 1). Wide territories are irrigated for rice, rapeseed, cotton and other crops or occupied by animal farms, including stock and poultry farms and aquaculture ponds. However, crop production prevails.

It is also worth noting that the study area is densely populated. The population density of the counties and districts surrounding Poyang Lake is usually higher than the average population density in Jiangxi Province. The most densely populated area (about 700/km²) is Nanchang prefecture-level city (Thomas Brinkhoff: City Population 2017), which is the administrative centre of the province. Population density affects the ecological state of water resources in the study area along with the large amount of pollutants entering the water from industrial activities. As of 2011, the annual input of pollutants to Poyang Lake reached 269.6 tonnes, of which the volume of total nitrogen and phosphorous amounted to 168.6 and 12.9 tonnes, respectively (Yan et al. 2011).

Climate and hydrogeological settings

The study area has a subtropical monsoon climate with an average annual temperature of 17.5 °C (Ye et al. 2013). The annual precipitation varies from 1400 to 2400 mm (Wang et al. 2014). Distribution of precipitation is irregular in seasons. The rainy season usually lasts from March to June and brings abundant rain and a large amount of surface runoff to the lake. From July to September, the precipitation decreases drastically, and the value of evapotranspiration reaches its maximum (Li and Zhang 2011). The dry season begins approximately mid of September and lasts until February.

Hilly and plain topography is the most widespread in the study area. The lowest part of the area is the mouth of Ganjiang River. The topography of the northern part of the study area is more mountainous. Water-bearing rocks in the region are presented basically by aluminosilicates differing in age and composition. Bedrocks in the mountains are Proterozoic siltstones, mudstones, slates, tuffaceous sandstones, tuffite, hornfels and polymictic conglomerate of fractured rock intruded by granitoids. These ancient rocks are overlaid by Cretaceous, Paleogene and Quaternary red weathering crusts containing kaolinite with Fe hydroxides. In relatively low southern and western areas, there are undefined strata of Cretaceous-Paleogene sandstones, siltstones, mudstones and their conglomerates. The most highly watersaturated sediments are confined to the depression in deltas and channels of the five main rivers feeding the lake, which are filled with Quaternary alluvial and deluvial sediments presented by gravel differing in abrasion, sands, clays and loam (Soldatova et al. 2017b; Shvartsev et al. 2016).

Fresh shallow groundwater, most often used by local people in the rural area for drinking purposes, occurs at a depth of 2–10 m. The rate of subsurface water flow for Poyang Lake basin reaches 20 L/s × km². This value indicates active water exchange in the region (Shvartsev et al. 2016). Previous studies have shown that the main pollutants of shallow groundwater are N-compounds, Cl⁻ and SO₄²⁻, and a minor extent of Na⁺, K⁺, PO₄³⁻ and F⁻ (Soldatova et al. 2017b; Shvartsev et al. 2016; Sun et al. 2014).

Sampling and analytical procedures

During the 3-year period (2013–2015), 67 groundwater samples were collected from wells used by local people for drinking and other domestic purposes in the rural areas of the Poyang Lake basin (Fig. 2). The redox potential (Eh) and pH were measured in situ.

The groundwater samples were stored in 0.6-L precleaned polyethylene bottles for ionic analysis and in 50-mL pre-cleaned polyethylene bottles for analysis of trace elements.

Analysis of water sample composition was performed in the Fundamental Research Laboratory of Hydrogeochemistry of the Research and Education Centre "Water" (Tomsk Polytechnic University (Tomsk, Russia)). The concentrations of SO_4^{2-} , Cl⁻, Ca²⁺, Mg²⁺, Na⁺ and K⁺ were analysed using ICS 1000 ion chromatographs (Dionex, USA). The concentration of HCO_3^- was determined by titration with 0.1 N solution of HCl. The concentrations of NH_4^+ , NO_2^- and NO_3^- were analysed using a spectrophotometer KFK-2 (ZOMZ-Plus, Russia). The concentrations of Si, Fe and trace elements were measured by inductively coupled plasma mass spectrometry (NexION 300D, PerkinElmer, USA). Validation parameters of analytical methods are adduced in Tables 1 and 2.

Methodology of human health risk assessment

To evaluate non-cancer human health risk of the residents of the Poyang Lake area due to the presence of potentially harmful chemicals in shallow ground-water, the hazard quotient (HQ) model derived from US EPA (1989) was applied. Non-cancer human health risk was evaluated for adult men and women separately and for single exposure pathway—chronic oral ingestion intake of potentially harmful components due to consumption of shallow groundwater. The hazard quotient was carried out for 36 individual potentially harmful components of shallow groundwater for which the referent dose (RfD) was determined in accordance with the data from US EPA (2015) and guideline R 2.1.10.1920-04 (2004):

$$HQ = CDI/RfD, (1)$$

where CDI—chronic daily intake, $(mg/kg \times day)$; RfD—referent (safety) dose, $(mg/kg \times day)$.



Fig. 1 Location of the study area and land cover characteristics (State Bureau of Surveying and Mapping 2008; NatGeo 2017)



Fig. 2 Location of the sampling points

Table 1 Valida	ation parameters	of analytica	1 methods
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Component	Measurement range (mg/L)	Validation parameter				
		Repeatability, σ_r (%)	Precision, $\sigma_{\rm R}$ (%)	Accuracy ($p = 0.95$), $\pm \delta$ (%)		
Titration						
HCO_3^-	2.0-10	7	11	25		
	10–100	6	9	20		
	100-3500	3	5	12		
Ion chromatog	graphy					
SO_4^{2-}	0.1–5.0	9	12	25		
	5.0-1000	3	5	10		
Cl⁻	0.1–1.0	11	15	31		
	0.1–10	8	11	23		
	10–500	3	5	10		
Br ⁻	0.05–10	9	12	25		
Ca ²⁺	0.1–5	5	10	23		
	5–150	4	8	18		
Mg^{2+}	0.05–2.5	6	12	26		
	2.5-30	4	8	18		
	30-2500	3	8	11		
Na ⁺	0.05–2	6	12	26		
	2–50	4	8	18		
	50-2000	3	5	11		
K^+	0.1–5	5	10	23		
	5-50	4	8	18		
	50-5000	3	5	11		
Spectrophoton	netry					
NO_2^-	0.02-0.1	17	22	20		
	0.1–3	14	17	14		
NO_3^-	0.1–3	14	20	18		
	3–100	8	14	12		
$\mathrm{NH_4}^+$	0.05–0.1	36	45	39		
	0.1–1	28	42	35		
	1–4	20	22	21		

The average daily intake was assessed according to US EPA (1989, 1992):

 $CDI = (C \times WI \times EF \times ED)/(BW \times AT),$ (2)

where *C*—exposure concentration of chemicals in shallow groundwater (mg/L); WI—water intake (L/day), according to the analysis of the US EPA data (1991, 2014), the target reference value was accepted as 2 L/day; EF—exposure frequency (day/year), accepted value is 350 day/year according to the recommendation of US EPA (1991, 2014) and

guideline R 2.1.10.1920-04 (2004); ED—exposure duration (year), the US EPA (1991, 2014) gives the reference values 30 years for adult resident, taking into account population migration; BW—body weight (kg), accepted values are 66.2 and 57.3 kg for adult men and women, respectively, in accordance with the Chinese residents of nutrition and chronic disease status report (2015); AT—averaging time (days), calculated as ED \times 365 days.

Non-cancer effects are considered possible if the HQ value is equal to or above 1. The risk increases

Components Measurement Error range (p = 0.95), $\pm \Delta$ range (µg/L) $(\mu g/L)$ Ru, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, 0.05 - 2 $\Delta = 0.025 + 0.18 \times C_{\text{metal}}$ Hf, Ta, Re, Au, Tl, Bi, Th, U $\Delta = 0.10 + 0.16 \times C_{\text{metal}}$ 2 - 20 $\Delta = 0.71 + 0.13 \times C_{\text{metal}}$ 20 - 100 $\Delta = 5.6 + 0.08 \times C_{\text{metal}}$ 100-1000 Be, Co, Rb, Y, Ag, Cd, Sb, W 0.1 - 2 $\Delta = 0.025 + 0.18 \times C_{\text{metal}}$ $\Delta = 0.10 + 0.16 \times C_{\text{metal}}$ 2 - 2020-100 $\Delta = 0.71 + 0.13 \times C_{\text{metal}}$ 100-1000 $\Delta = 5.6 + 0.08 \times C_{\text{metal}}$ Li, Mn, Fe, Ga, Ge, Zr, Mo, Sn, Ba, Pb 0.2 - 10 $\Delta = 0.03 + 0.18 \times C_{\text{metal}}$ 10 - 100 $\Delta = 0.55 + 0.14 \times C_{\text{metal}}$ 100-1000 $\Delta = 5.6 + 0.08 \times C_{\text{metal}}$ $\Delta = 0.10 + 0.16 \times C_{\text{metal}}$ B, Al, Si, Sc, Ti, V, Cr, Ni, Cu, Zn, Sr 2 - 2020 - 100 $\Delta = 0.71 + 0.13 \times C_{\text{metal}}$ $\Delta = 5.6 + 0.08 \times C_{\text{metal}}$ 100-1000 As 2 - 200 $\Delta = 0.63 + 0.14 \times C_{As}$ 200-10,000 $\Delta = 15.7 + 0.09 \times C_{\rm As}$ Se $\Delta = 0.63 + 0.14 \times C_{\text{Se}}$ 5 - 200

Table 2 Validation parameters of inductively coupled plasma mass spectrometry

proportionally with the increase in the HQ values above 1. The HQ values below the reference level are not likely to be associated with adverse health effects (US EPA 1989).

To assess the overall potential health risk for noncancer effects from exposure to multiple compounds, the hazard index (HI) approach was used (US EPA 1986, 1989, 2003):

$$HI = \Sigma HQ_i, \tag{3}$$

where ΣHQ_i —sum of HQs for individual chemicals included in a group for cumulative human health risk assessment. Alike the HQ, a hazard index equal or higher than unity is associated with adverse health effects (US EPA 1989).

Chemicals were included in the groups in accordance with the mechanism of their influence to human, its organs, systems and processes (US EPA 1989, R 2.1.10.1920-04, 2004). If the components have a similar mechanism of action in humans, they were included in the same group. Only chemicals with HQ > 0.1 in at least one sampling point were included to cumulative non-cancer health risk assessment, because the HQ values below 0.1 do not contribute significantly to cumulative health risk assessment (US EPA 1998; R 2.1.10.1920-04, 2004). In accordance with these statements, 13 groups of compounds affecting different target organs, systems and processes were formed.

 $\Delta = 15.7 + 0.09 \times C_{Se}$

Mapping of non-cancer human health risk

200-10,000

To evaluate the spatial distribution of potential human health risk, GIS technologies were applied. Implementation of GIS for the study of groundwater chemical composition and health risk assessment allows efficiently managing water resources and protecting water supply sources from pollution; a number of research articles have demonstrated the advantages of this methodology (Hoover et al. 2014; Rojas Fabro et al. 2015; Wu et al. 2017; Li et al. 2017). Health risk maps were constructed in QGIS v.2.14.12 with the application of heat map renderer. For risk mapping, we decided to use the results of the cumulative health risk assessment because the calculation of HI takes into account the overall influence of components contained in shallow groundwater. In some cases, it significantly increases the probability of adverse health effects. Field ranking was carried out considering the maximum value of HI. The field radius

Table 3 Chemical composition of shallow groundwater in the Poyang Lake basin

Component	Concentration (mg/L)			WHO recommendations (2011)	National standard	
	Min Max Average		Average		of PRC (GB5749-2006)	
pН	4.5	7.7	6.23	_	6.5-8.5	
Eh, mV	- 91	382	194	_	_	
HCO ₃ ⁻	2.44	353	50.5	_	_	
SO_4^{2-}	0.14	148	10.4	_	250	
Cl ⁻	0.99	102	14.2	_	250	
NO_2^-	0.01	4.29	0.022	3.0	_	
NO_3^-	0.1	206.3	17.9	50	44.3 ^b	
F ⁻	< 0.05	1.41	0.07	1.5	1.0	
Br ⁻	0.01	0.69	0.05	_	-	
Ca ²⁺	1.7	98.2	19.0	_	-	
Mg^{2+}	0.23	55.2	5.52	_	-	
Na ⁺	1.04	58.3	12.1	_	200	
K^+	0.23	76.0	2.65	_	_	
$\mathrm{NH_4}^+$	< 0.05	6.4	0.1	_	0.64	
TDS	25.1	800.3	183	_	1000	
Li	0.0001	0.0294	0.0011	_	_	
Be	< 0.000003	0.000790	0.000033	_	0.002	
В	0.00125	0.03935	0.00540	2.4	0.5	
Al	0.0003	0.9830	0.0150	_	0.2	
Si	2.20	20.47	6.79	_	_	
Sc	0.00011	0.00111	0.00037	_	_	
Ti	0.000068	0.048	0.00087	_	-	
V	< 0.0001	0.0258	0.0004	_	_	
Cr	0.00007	0.007	0.00088	$0.05^{\rm a}$	0.05^{c}	
Mn	0.0002	4.967	0.0301	_	0.1	
Fe	0.01	64.40	0.07	_	0.3	
Co	0.000004	0.009240	0.000299	_	_	
Ni	< 0.00005	0.00937	0.00078	0.07	0.02	
Cu	< 0.0005	0.0146	0.0003	2.0	1.0	
Zn	< 0.001	0.142	0.006	_	1.0	
Ga	0.000002	0.000980	0.000023	_	_	
Ge	< 0.000001	0.000180	0.000008	_	_	
As	0.00002	0.07912	0.00063	0.01 ^a	0.01	
Se	< 0.0005	0.0272	0.0003	$0.04^{\rm a}$	0.01	
Rb	0.00061	0.03732	0.00476	_	-	
Sr	0.0053	0.9738	0.0897	_	-	
Y	0.00001	0.01275	0.00019	_	-	
Zr	< 0.000005	0.000420	0.000004	_	-	
Mo	< 0.00002	0.00769	0.00018	_	0.07	
Ag	< 0.000005	0.000049	0.000006	_	0.05	
Cd	< 0.000005	0.000973	0.000033	0.003	0.005	
Sn	< 0.000005	0.001230	0.000009	_	-	
Sb	0.000001	0.003140	0.000073	0.02	0.005	

Table 3 continued

Component	Concentration (mg/L)			WHO recommendations (2011)	National standard	
	Min	Max	Average		of PRC (GB5749-2006)	
Cs	< 0.000005	0.002256	0.000050	-	_	
Ba	0.019	0.284	0.070	0.7	0.7	
La	< 0.000005	0.020404	0.000129	_	-	
Ce	< 0.000005	0.036205	0.000190	_	-	
Pr	< 0.0000005	0.0042677	0.0000310	_	-	
Nd	< 0.0000005	0.0160810	0.0001280	_	-	
Sm	< 0.000005	0.003599	0.000025	_	-	
Eu	< 0.000005	0.000796	0.000015	_	-	
Gd	< 0.0000005	0.0033880	0.0000290	_	-	
Tb	< 0.000005	0.000447	0.000004	_	-	
Dy	< 0.000005	0.002430	0.000022	_	-	
Но	< 0.000005	0.000458	0.000005	_	-	
Er	< 0.000005	0.001157	0.000011	_	-	
Tm	< 0.0000005	0.0001441	0.0000021	_	-	
Yb	< 0.0000005	0.0008976	0.0000110	_	-	
Lu	< 0.000005	0.000135	0.000002	_	-	
Hf	< 0.0000005	0.0000200	0.0000006	_	-	
Та	< 0.000005	0.000010	0.000002	_	-	
W	< 0.000005	0.005055	0.000013	_	-	
Re	< 0.000001	0.000360	0.000005	_	-	
Au	< 0.000005	0.000070	0.000002	_	-	
Hg	< 0.000050	0.001400	0.000016	0.006	0.001	
T1	< 0.000005	0.000258	0.000014	_	0.0001	
Pb	< 0.00005	0.02201	0.00020	0.01 ^a	0.01	
Bi	< 0.000003	0.000083	0.000002	_	-	
Th	< 0.000005	0.000699	0.000002	_	-	
U	< 0.000005	0.000903	0.000042	0.03 ^a	-	

-Not available

^aProvisional guideline value (WHO 2011)

^b10 mg/L (measured as N)

^cFor Cr⁶⁺

was defined, taking into account the boundaries of the river watersheds.

Results and discussion

Chemical composition of shallow groundwater and quality assessment

Shallow groundwater has a low salinity, which varies from 17 to 768 mg/L (Table 3). The pH varies

significantly from 4.5 to 7.7, with a mean value of 6.2, but geochemical conditions vary generally from slightly acidic to neutral. It is worth noting that, in accordance with the national standard (GB 5749-2006 2006), two-thirds of the sampling points of shallow groundwater did not meet the standard for drinking water quality in terms of pH (Table 3).

Under natural conditions, shallow groundwater in the study area is HCO₃–Ca and HCO₃–Ca–Na. However, in some cases, the chemical type drastically changes to SO₄–HCO₃–Ca, HCO₃–Ca–K, Cl–Na–Ca







Fig. 4 Distribution of Fe and As concentrations in shallow groundwater in the lower reaches of Ganjiang and Xiushui Rivers

and even Cl–NO₃–Na (Fig. 3) because of the high contents of SO_4^{2-} , Cl⁻, NO₃⁻ and K⁺ (Shvartsev et al. 2016; Sun et al. 2014). Such variations of the chemical composition indicate a complex influence of the natural and anthropogenic factors on the groundwater

origin, the most significant from which are agricultural activity and contamination by domestic sewage (Soldatova et al. 2017b).

The oxidation-reduction potential values vary significantly from -91 to 382 mV, but oxidation conditions with Eh > 100 mV prevail. Reducing and near-neutral conditions with Eh < 100 mV occur mainly to the west of Poyang Lake in the Ganjiang and Xiushui River basins.

Analysis of the chemical composition of shallow groundwater has shown that the groundwater is enriched by nitrogen compounds (Soldatova et al. 2017b). The concentrations of NO_3^- , NO_2^- and NH_4^+ vary from 0.1 to 206.3, 0.01 to 4.29 mg/L and values lower than detection limit (0.05 mg/L) to 6.4 mg/L, respectively (Table 3). Shallow groundwater in more than 20 sampling points did not meet the WHO drinking water quality standards (WHO 2011) and national standards of China (GB 5749-2006 2006) in terms of nitrate-ion concentration. Exceedance of nitrite standards for drinking water is noted at one sampling point (P67). As for NH_4^+ concentrations, in

Component	Hazard quotient (HQ)					
	Men		Women			
	Min	Max	Min	Max		
NO_3^-	0.002	3.7	0.002	4.3		
NO_2^-	0.003	1.2	0.003	1.4		
F ⁻	0.003	0.68	0.004	0.79		
Br ⁻	0.00003	0.02	0.00003	0.023		
Ca^{2+}	0.001	0.069	0.001	0.079		
Mg^{2+}	0.0006	0.145	0.0007	0.168		
Na ⁺	0.0009	0.049	0.001	0.057		
$\mathrm{NH_4}^+$	0.0006	0.189	0.0007	0.219		
Li	0.0002	0.043	0.0002	0.049		
Be	0.00002	0.011	0.00003	0.013		
В	0.0002	0.0057	0.0002	0.0066		
Al	0.000009	0.028	0.000011	0.033		
Ti	0.0000005	0.00035	0.000001	0.00039		
V	0.00013	0.107	0.00015	0.123		
Cr	0.00041	0.041	0.00047	0.048		
Mn	0.000047	1.03	0.000054	1.19		
Fe	0.00085	6.22	0.00098	7.18		
Co	0.000006	0.013	0.000006	0.015		
Ni	0.00004	0.014	0.00004	0.016		
Cu	0.000005	0.0022	0.000006	0.0026		
Zn	0.000041	0.014	0.000047	0.016		
As	0.0016	7.64	0.0019	8.83		
Se	0.00007	0.158	0.00008	0.182		
Sr	0.0003	0.047	0.0003	0.054		
Мо	0.00004	0.045	0.00005	0.051		
Ag	0.000001	0.00029	0.000001	0.00033		
Cd	0.00014	0.056	0.00017	0.065		
Sn	0.00000001	0.00006	0.00000002	0.00007		
Sb	0.00007	0.227	0.00008	0.263		
Ba	0.008	0.118	0.009	0.136		
Dy	0.0000003	0.00035	0.0000003	0.00041		
W	0.0000035	0.0064	0.0000041	0.0074		
Hg	0.000039	0.136	0.000045	0.157		
Tl	0.00033	0.107	0.00038	0.123		
Pb	0.000098	0.185	0.00011	0.211		
U	0.000021	0.015	0.000025	0.017		

 Table 4
 Hazard quotient (HQ) from exposure to individual components in shallow groundwater (calculated for adults)

the guidelines for drinking water quality (WHO 2011), the limit for ammonium concentration is not established. It is only noted that, in natural conditions, the content of $\rm NH_4^+$ rarely exceeds 0.2 mg/L, whereas within the study area, the concentration of $\rm NH_4^+$ is above 0.2 mg/L in more than 20 sampling points. In 10 sampling points, the content of ammonium nitrogen is above the national standards of China (GB 5749-2006 2006). Almost all exceedances of the $\rm NH_4^+$ limit occur in the lower course of Ganjiang and Xiushui Rivers because of reducing conditions with Eh < 0 that results in the accumulation of reduced species in the groundwater (Soldatova et al. 2017a).

Exceedances of the Fe and Mn standards for drinking water (GB 5749-2006 2006) occur in 13 and 22 sampling points, respectively. The high concentrations of Fe and Mn, whose contents vary from 0.01 to 64.4 and 0.0002 to 4.97 mg/L, respectively, are distributed all over the Poyang Lake area; however, the highest content is observed in the area where reducing conditions occur. Reducing conditions lead to accumulation of Fe and Mn in the dissolve phase (Soldatova et al. 2015). Statistical analysis using nonparametric Spearman's rank correlation coefficient has shown a significant correlation ($r_s = 0.65$ at p < 0.05). It confirms that the same factor controls the accumulation of Fe and Mn in shallow groundwater.

High concentrations of Fe in shallow groundwater in the lower reaches of Ganjiang and Xiushui Rivers correlate well with the high concentrations of As (Fig. 4), which is confirmed by the value of the Spearman's rank correlation coefficient ($r_s = 0.68$ at p < 0.05). Concentrations of As exceed the limit for drinking water (0.01 mg/L according to WHO 2011 and GB 5749-2006 2006) in seven sampling points within the study area. Thus, it is concluded that reducing conditions result in mobilisation of As. It is considered that arsenic in the lower course of Ganjiang and Xiushui Rivers presents in trivalent form, rather than As^{5+} (Putilina et al. 2011; ASTDR 2007), because, in reducing or near-neutral conditions, Fe and Mn oxides are dissolved, releasing arsenate that is rapidly reduced to arsenite under these conditions (Gräfe and Sparks 2006). Reduction of iron oxyhydroxides to Fe²⁺ and decomposition of organic matter may also contribute to the reduction of As(V) to As(III) as it has been reported by Chen (2012) and Ahmed et al. (2010). The high content of organic matter in the above-mentioned area may result from a specific combination of natural and anthropogenic factors, such as low-level topography and overuse of organic fertilisers (Soldatova et al. 2017a, b). In the sampling points with Eh < 0 (P2, P14, P15, P16 and P17), As³⁻, which has higher bioavailability (ASTDR 2007), likely dominates over other forms (Putilina et al. 2011). It is also worth noting that the correlation between Mn and As is also significant, but the value of the Spearman's rank correlation coefficient is lower ($r_s = 0.59$ at p < 0.05) in comparison with r_s between Fe and As. It indicates that factors affecting Fe concentration in groundwater have a more obvious influence on As concentrations than factors and processes controlling Mn migration.

In several sampling points, mainly situated in the close proximity to Poyang Lake, the concentrations of Al are slightly above the national standards for drinking water (GB 5749-2006 2006), according to which the Al content must be less than 0.2 mg/L. World Health Organisation does not regulate Al content in drinking water, but in the guideline for drinking water quality (WHO 2011), the suggested value for Al concentration in drinking water is 0.9 mg/L. Occasional minor exceedances of the drinking water quality standards are also observed for Se, Hg, Tl and Pb.

(111) 6

Non-cancer health risk assessment from chronic exposure to individual chemicals in shallow groundwater

Health risk assessment from exposure to individual elements is based on the analysis of HQ (2). Calculation shows that the HQ values exceed the safety value for NO_3^- , NO_2^- , Mn, Fe and As (Table 4). However, for NO_2^- and Mn, the values of HQ slightly above the safety limit occur in only one sampling point for each chemical component: sampling point P67 in Ganjiang and Fuhe Rivers' interfluve for NO_2^- , and sampling point P14 in Ganjiang River mouth for Mn (Fig. 2).

The high probability of non-cancer effects due to the consumption of nitrate-contaminated groundwater occurs in 11 sampling points from the total number of 67 for adult men and in 12 sampling points for adult women. The maximum values of HQ are located in the Ganjiang and Xiushui Rivers' interfluve. However, increased HQ values (> 1) are found throughout the study area. The presence of NO_3^- in groundwater may cause serious haematologic effects, such as

Table 5 Hazard index (HI) from exposure to multiple components in shallow groundwater (calculated for adu	ilts)	
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Target system/organ/process or effects	Exposing components ^a	Hazard index (HI)			
		Men		Women	
		Min	Max	Min	Max
Dermal	Fe, As, V, Se	0.007	10.13	0.008	11.70
Immune	Fe, As, Hg	0.006	10.12	0.006	11.69
Nervous	Mn, As, Hg, Pb	0.003	8.03	0.004	9.28
Cardiovascular	NO3, As, Ba	0.028	7.76	0.031	8.97
Endocrine	As, Hg, Pb	0.003	7.64	0.004	8.83
Gastrointestinal	As, V	0.002	7.64	0.002	8.83
Haematologic	NO ₃ , NO ₂ , Mn, Fe, Pb	0.021	7.25	0.025	8.38
Mucosal tunic	Fe	0.0008	6.22	0.001	7.18
Musculoskeletal	F	0.003	0.68	0.004	0.79
Biochemical	Sb, Tl, Pb	0.001	0.23	0.001	0.27
Hepatic	V, Se, Tl	0.003	0.19	0.004	0.22
Reproductive	Hg, Pb	0.0004	0.19	0.0005	0.21
Urinary	V, Ba, Hg	0.011	0.16	0.013	0.18

^aOnly components with HQ > 0.1 at least in one sampling point were taken into account



Fig. 5 Distribution of health risks of adverse effects for the haematologic system (a for men; b for women)



Fig. 6 Distribution of women health risks of adverse effects for the cardiovascular system





methemoglobinemia, i.e. the increase in level of methemoglobin, which is unable to carry oxygen in blood (ATSDR 2014).

As for arsenic, HQ values higher than unity occur in seven sampling points from the total number of 67 identically for men and women. The areas of adverse health effects from As exposure are located in the lower course of Xiushui and Ganjiang Rivers. It is worth noting that As is characterised by high toxicity and may provoke not only non-cancer effects but also carcinogenic effects (Wu et al. 1989; Hsueh et al. 1998; Smedley and Kinnniburgh 2002; ATSDR 2007).

A high risk of non-cancer effect development due to the consumption of shallow groundwater with a high content of Fe is observed in five sampling points from the total number of 67. It should be noted that the area of adverse health effect distribution almost coincides with the area of the potential risk of adverse health effects from As exposure. It confirms that the same processes affect Fe and As mobilisation in shallow groundwater (Guo et al. 2013).

It is obvious that the distribution of the sampling points with component concentrations higher than the safety limits (WHO 2011; GB 5749-2006 2006) and the location of the sampling points with HQ values higher than unity well coincide in general. However, groundwater quality assessment according to the standards for drinking water quality seems to be stricter and demonstrates exceedance of the safety limits for 11 components (NO₃⁻, NH₄⁺, Fe, Mn, As, Al, rare NO₂⁻, Se, Hg, Tl and Pb), whereas the noncancer human health risk assessment procedure reveals the probability of adverse non-cancer effects





only for five components (NO $_3^-$, Fe, As, rare NO $_2^-$ and Mn).

Non-cancer health risk assessment from chronic exposure to multiple chemicals in shallow groundwater

Cumulative health risk assessment includes the components characterised by HQ > 0.1 at least in one sampling point within the study area. The influence of individual chemicals on particular human organs, systems and processes was also taken into account. Thus, NO₃⁻, NO₂⁻, F⁻, V, Fe, Mn, As, Se, Sb, Ba, Hg, Tl and Pb were chosen as priority components for HI calculation (Table 5). These components of shallow groundwater potentially result in dermal and hepatic effects and affect the immune, nervous, cardiovascular, endocrine, gastrointestinal, haematologic, musculoskeletal, reproductive and urinary systems, as well as mucosal tunic and biochemical processes [R 2.1.10.1920-04 (2004)].

The calculated hazard indexes below unity demonstrate that musculoskeletal, reproductive, urinary, hepatic and biochemical process adverse effects unlikely occur because of the consumption of shallow groundwater.

As for the health risk for the haematologic system, it is identified throughout the study area. Fields with HI > 1 are located in the Xiushui and Ganjiang River basins (Fig. 5); here, the maximum value of HI is also observed. For women, there are two additional fields with HI above 1 located north-east and south-east of Poyang Lake (sampling points P33 and P51) and wider field in the Zhishui and Raohe Rivers' interfluve (Fig. 5b) in comparison with men health risks. It is worth noting that, for other target systems, organs and





processes, there are barely discernible differences between men and women health risk distribution. Thus, only the maps of women health risks will be presented below because, despite the same outline of the border HI = 1, the health risks for women are slightly higher than those for men.

Human health risks concerning diseases of the cardiovascular system (Fig. 6) are connected with the content of NO_3^- , As and Ba in shallow groundwater. They are distributed similarly with women health risk connected with adverse effects for the haematologic system, excluding several additional areas of potential risk of cardiovascular diseases in the northern part of the study area.

Distribution of the risks of adverse effects for mucosal tunic repeats the outlines of the risk distribution from Fe exposure (Fig. 7) because this group consists of solely this element. The health risk areas connected with the development of mucosal tunic diseases are located in the lower reaches of Xiushui and Ganjiang Rivers.

The health risks of the remaining five target systems and organs (dermal, immune, nervous, endocrine and gastrointestinal) are strongly connected mainly with the high content of Fe and/or As in shallow groundwater of the study area (Table 5); other chemical components have only little contribution to the HI values. Thus, the distribution of human health risk is





similar for these systems and organs and reflects the distribution of the risk from Fe and/or As exposure. Areas with HI values above 1 are situated basically in the lower reaches of Xiushui and Ganjiang Rivers (Figs. 8, 9, 10, 11, 12). However, one sampling point (P36) with HI > 1 is to the north-east of Poyang Lake. The largest risk of adverse health effects in the study area is associated with the immune system and integumentary system (dermal effects), for which the maximum values of HI are 10.12 and 10.13, respectively (Table 5).

Conclusion

Shallow groundwater quality assessment according to the limits set up by world and national standards (WHO 2011; GB 5749-2006 2006) demonstrates exceedance of the reference values for 11 components (NO₃⁻, NH₄⁺, Fe, Mn, As, Al, rare NO₂⁻, Se, Hg, Tl and Pb), whereas human health risk assessment from exposure to individual chemicals calculated using the HQ model reveals the probability of non-cancer effects only for five components (NO₃⁻, Fe, As, NO₂⁻ and Mn), with the largest contribution to the



Fig. 11 Distribution of women health risks of adverse effects for the gastrointestinal system

development of non-cancer health effects from NO_3^- , Fe and As. The results of the cumulative non-cancer risk assessment based on HI calculation demonstrate that the most vulnerable area in terms of development of non-cancer effects is allocated in the lower reaches of Xiushui and Ganjiang Rivers. This area is unfavourable with respect to the risk of adverse dermal effects, diseases of the immune, nervous, cardiovascular, endocrine, gastrointestinal and haematologic systems and mucosal tunic diseases, with the largest risk of adverse effects for the immune system and integumentary system (dermal effects). The situation may result from the joint influence of natural and anthropogenic factors favourable for the accumulation of harmful substances in shallow groundwater, such as the major city (Nanchang) in the immediate vicinity of the potential areas at risk, low altitude of these areas, wide spread croplands and farmlands, application of organic fertilisers and livestock waste storage. It is also worth noting that the zones with the increased risk of haematologic and cardiovascular diseases are distributed throughout the Poyang Lake area because the high NO_3^- concentrations are scattered all over the study area. In the current





situation, regular monitoring of shallow groundwater needs to be organised in the study area, especially in the lower course of Xiushui and Ganjiang Rivers. Strategies and measures to reduce the concentrations of potentially hazardous components in shallow groundwater are also required.

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