Hydrochemical characteristics of natural water and selenium-rich water resources in the Northern Daba Mountains, China

Chao Zhao, Kunli Luo, Yajun Du, Yuan Tian, Jie Long, Xiaofeng Zhao and Shixi Zhang

ABSTRACT

The Northern Daba Mountains (NDM) of Shaanxi Province, China, are a well-known selenium (Se)-rich area, and the area is also known for endemic fluorine (F) and arsenic (As) poisoning. In order to study the hydrochemical characteristics and trace element contents of the natural waters of this region, 62 water samples were collected from Lan'gao area in the NDM. The hydrochemical composition was principally characterized by $Ca \cdot Mg \text{-} HCO_3 \cdot SO_4$. F and As concentrations ranged from 0.01 to 0.67 mg/L and from 0.33 to 6.29 μg/L, respectively, lower than Chinese national standard and international guidelines for drinking water quality. One year of monitoring proved that F and As in natural water were not the sources of the local fluorosis and arseniasis in the NDM. The average Se concentration in fissure water was 5.20 μg/L. The average Se content of river water was 2.82 μg/L, 14 times that of the world's surface level (0.2 μg/L). The Se content in eight samples reached the Chinese national standards for mineral drinking water quality (>10 μg/L). Contrasting the water samples of May, July, and September in 2015 shows that the Se content is relatively stable and the increase of humidity might be beneficial to increase the content of selenium and strontium in water.

Key words | Daba Mountains, hydrochemical characteristics, selenium-rich mineral water resources, trace element concentrations

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INTRODUCTION

Trace elements play an important role in human health, especially selenium (Se), arsenic (As), and fluorine (F), and excessive or deficient quantities may cause endemic diseases (Tan *et al.* 2002; Rayman 2006; Selinus *et al.* 2013). Moderate Se intake facilitates thyroid hormone secretion, and has been demonstrated to have an anti-oxidation and anti-cancerous function, as well as improve the human immune system. Conversely, excessive Se intake (>400 μg/d) may lead to selenosis (WHO 2004; Fordyce 2007). Long-term excessive F intake can cause dental as well as skeletal fluorosis. Excessive As exposure can lead to chronic health problems and skin lesions (Selinus *et al.* 2013).

Drinking water is important in the human intake of trace elements (Bleiman & Mishael 2010). Se, F, and As contents in drinking water can have an important effect on human health. Certainly, too low a Se content in drinking water is not good for human health (Fordyce *et al.* 2000). However, Se concentrations in natural water are generally low, rarely exceeding 10 μg/L, with the majority of concentrations below 3 μg/L (Plant *et al.* 2014). The average Se content of global river waters is only 0.2 μg/L (Selinus *et al.* 2013). A high As content in drinking water represents one of the most serious threats to human health. The arsenic content of most natural waters is low (usually <10 μg/L,

with the average $\sim$5 μg/L), but variations in As concentrations between surface water and groundwater are significant ($\sim$0.5–5,000 μg/L) (Selinus *et al.* 2013). Drinking water with F concentrations >1.5 mg/L will probably lead to dental fluorosis, while concentrations >4.0 mg/L may cause skeletal fluorosis and other health problems (Dissanayake 1991). Usually, the F concentration in natural water is 0.1–10 mg/L and <300 μg/L in surface water. It is easy for F to accumulate in groundwater, with the F content in high fluorine groundwaters potentially reaching several hundred mg/L (Selinus *et al.* 2013).

Ankang City, Ziyang County, and Lan'gao County in the Northern Daba Mountains (NDM) in Shaanxi Province, China, are famous for being Se-rich (Combs 2001; Hartikainen 2005). However, the population of this region also suffers from fluorine and arsenic poisoning (Luo 2011; Xu & Luo 2012). The prevalence rate of dental fluorosis in residents of this region is >50% (Chen *et al.* 2003), and even exceeds 90% in some areas (Wen *et al.* 2011). In addition, there is serious arsenic-based pollution of the environment between the Qinling and Daba Mountains. Significant arsenism is found in nine counties, including Pingli, Lan'gao, and Zhenba, affecting more than one million inhabitants (Li *et al.* 2004; Xu *et al.* 2008).

There have been many studies of Se distribution and the provenances of soil and rock in the NDM (Luo *et al.* 1994, 1995, 2001, 2002a; Luo & Jiang 1995; Chen & Luo 1996; Luo 2003, 2011; Li *et al.* 2005; Xu & Luo 2012). Se contents were found to be generally >4.0 mg/kg in the Lower Cambrian and Daguiping Formations of the Silurian, with some even reaching, or exceeding, industrial grade (15 mg/kg). Although more widely Se-enriched strata exhibit contents too low to be mined, they nonetheless enrich crops and the bodies of animals with Se (Luo *et al.* 1994, 1995, 2001, 2002a; Luo & Jiang 1995; Chen & Luo 1996; Luo 2003, 2011; Li *et al.* 2005; Xu & Luo 2012). Further, the Early Paleozoic strata of the Daba region are generally rich in fluorine, with F contents usually >800 mg/kg in the carbonaceous slates, black shales, and phosphate rocks of the Early Cambrian Lujiaping Formation. Fluorine content is approximately several times higher than the average value found in the continental crust (Luo *et al.* 1995; Xu & Luo 2012). Moreover, the As content of the stone-like coals found in this area are as high as 277 mg/kg (Luo 2011),

$\sim$100 times higher than the average As content of the continental crust (Selinus *et al.* 2013). Since we find Se, F, As, and other trace elements in these concentrations in the rocks of the NDM, what are their contents in the area's natural waters? There has, to date, been no systematic investigation of this, and studies of the hydrochemical characteristics and trace element contents of the natural waters of this area are very rare (Luo *et al.* 2002b, 2002c). In particular, there has been a paucity of systematic studies of the trace element content of drinking water in the NDM.

The Qinling-Daba Mountain (QDM) system is not only the water source of the Chinese South-to-North Water Transfer Project (Middle Route), but is also the poorest area of China (Cao *et al.* 2015; Liu *et al.* 2015). Any research into the hydrochemical characteristics and trace element contents of this area therefore is of considerable scientific and practical significance. We collected and analyzed fissure water and river water samples from the NDM to investigate the hydrochemical characteristics and trace element contents of natural waters in this area, and thereby attain a better understanding of the Se, F, and As concentrations found in drinking water in this Se-rich, F- and As-high region. To monitor the stability of content of elements in water, we collected and analyzed fissure and river water samples in May, July, and September, 2015, respectively. Finally, we aimed to quantify, at least approximately, the Se-rich water resources of the NDM.

MATERIALS AND METHODS

Geographical and geological background of the study area

The study area (32 °10′–32 °55′N, 108 °20′–109 °15′E) is located in Lan'gao County, NDM. It has a typical middle elevation, mountainous topography with average altitude ranging from 1,000 m to 1,600 m above sea level (Figure 1(a) and 1(b)). The climate is subtropical humid monsoon. The annual average temperature is $\sim$13–15 °C. Annual precipitation is 900–1,200 mm, mostly concentrated in July and August; annual evaporation is 800–1,200 mm. The warm and humid climate, in combination with the alpine gorge topography, leads to considerable weathering in this area.
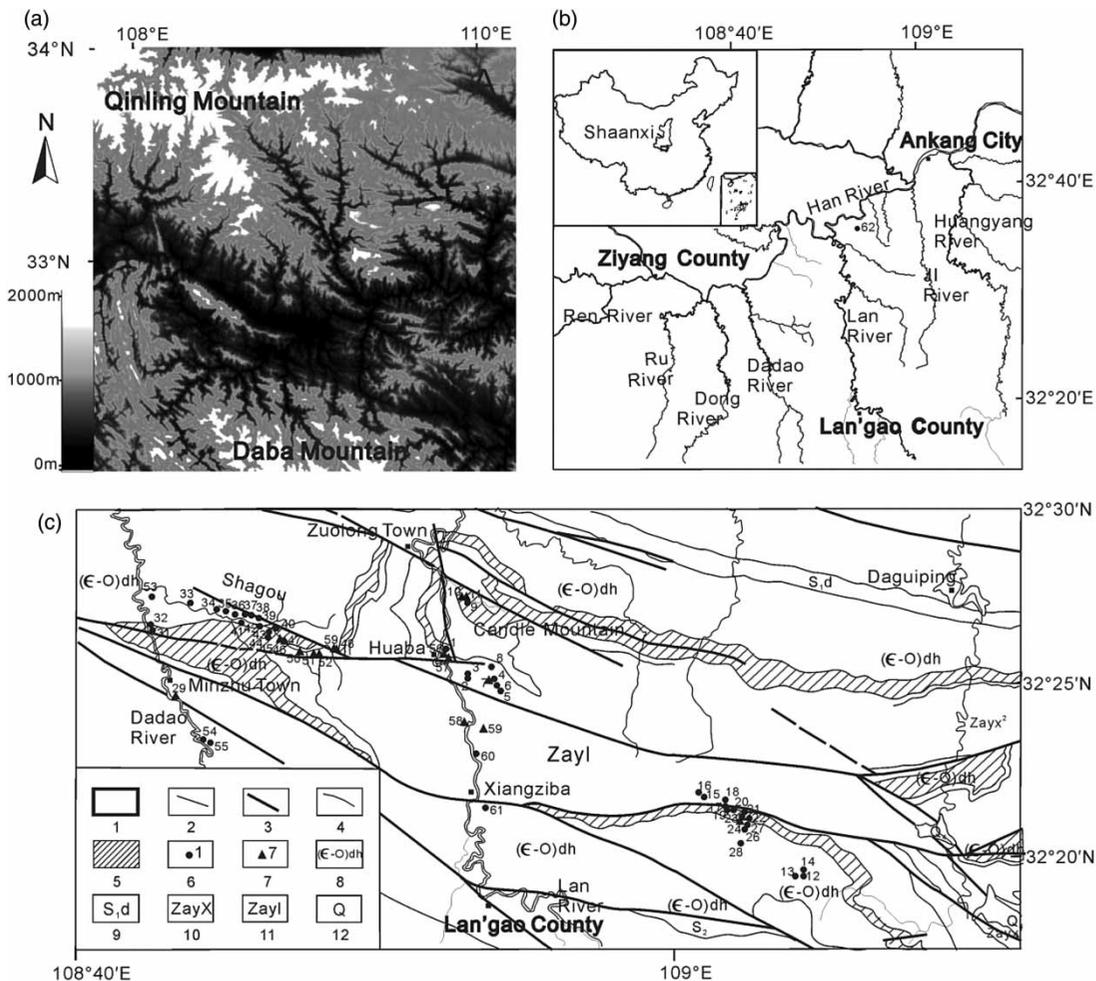
Figure 1 | Location: (a) topographic features of the study area; (b) major cities and the water system; (c) sample locations and geological background of the Daba Fold Zone (GBS 1966). Legend: 1, study area; 2, stratigraphic fault; 3, fault; 4, river; 5, siliceous escarpment; 6, fissure water sample; 7, river water sample; 8, Donghe Formation; 9, Daguiping Formation; 10, Yunxi Group; 11, Yaolinghe Group; 12, Quaternary.

The NDM belongs to the southern margin of the Qinling Fold Belt, covering Ziyang, Lan'gao, and Pingli counties. The strata generally lie in a northwest–southeast direction, with repeated sequences of faults, folds, and strata (Figure 1(c)). The Late Neoproterozoic and Early Paleozoic strata are well developed in this area. The Late Neoproterozoic strata mainly contain volcanic rocks. The Cambrian stratigraphy is dominated by thick carbonaceous strata, containing carbonaceous siliceous slate and carbonate rock, marl, limestone, and anthracite. The Ordovician stratigraphy is composed of carbonaceous argillaceous clastic rocks and carbonate rocks. Carbonaceous slate, sandy slate, and silty fine sandstone dominate the Silurian strata (Luo *et al.* 1994).

Lan'gao County is a fluorosis high-incidence area, and experiences high levels of arsenic poisoning as well as being the focus of local Se poisoning (Luo *et al.* 2004a, 2004b; Li *et al.* 2005). It is also a key region in the Chinese poverty alleviation program (Cao *et al.* 2015). The water system is well-developed in this region (Figure 1(b) and 1(c)). The natural bedrock fissure water and river water are major local sources of drinking water.

Sampling and analytical methods

Sixty-two water samples, comprising 47 fissure water and 15 river water samples, were collected from the NDM in May 2015. Forty-nine (31 fissure water and 18 river water samples) and 61 samples (47 fissure water and 14 river water samples)

were also collected at the same area in July and September 2015, respectively. Residential drinking water at present includes untreated fissure water or river water, so these samples reflected NDM drinking water to some extent (Table S1, available with the online version of this paper).

The collection of samples was conducted in accordance with the Monitoring and Analytical Methods for Water and Waste Water (MEP 2002). Samples were analyzed at the Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences. The pH and total dissolved solids (TDS) were determined using a Switzerland Mettler Toledo pH tester (SevenGo SG2) and a Switzerland Mettler Toledo Ec tester (SevenGo SG3). The total hardness (TH) was calculated using the measured values of Ca^{2+} and Mg^{2+} concentrations. The alkalinity (as HCO_3^-) was measured using acid–base titration (MH 1985; MEP 2002).

Dionex ICS-900 ion chromatography was used to analyze the chloride (Cl^-) and fluoride (F^-) concentrations. Se and As concentrations were determined using a hydride Generation Atomic Fluorescence Spectrometer (MH 1985; MEP 2002). The concentrations of the major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, P, Sr, B, and SiO_2) and the SO_4^{2-} anion were determined using an Elan DRC-e Inductively Coupled Plasma Optical Emission Spectrometer. The analyses of trace elements (Li, Zn, U, Rb, Ba, Bi, Co, Cs, Ga, In, Ti, V, Ag, Al, Be, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, and Tl) were performed by a Perkin-Elmer Optima 5300DV Inductively Coupled Plasma Mass Spectrometry. Parallel samples and repeated measurements were used. The percentage errors in all the samples were relatively low, and mostly $< \pm 5\%$ (Figure S1, available with the online version of this paper).

The box plot was plotted by Origin 8.0 software based on the data of element concentrations in the water. In addition, the 1st, 5th, and 25th percentiles, median, mean, and the 75th, 95th, and 99th percentiles were indicated in each box plot, respectively. The Pearson correlation coefficients analysis was carried out using IBM SPSS 20 software.

RESULTS

Due to the fact that the sampling points of the three times are in the same area, and the main characteristic of the water is consistent, the detailed analysis focused on the May samples.

Hydrochemical characteristics and trace element concentrations

Based on the analysis of 62 water samples collected in May, the pH of water in Lan'gao area ranged from 6.87 to 8.07, with a mean value of 7.58 (Table S2, available with the online version of this paper). The average TDS was 86.13 mg/L, and ranged from 26.6 to 266 mg/L, indicating freshwater with a low SAL (TDS < 500 mg/L). TH was 16.74–295.69 mg/L, and averaged 81.6 mg/L, indicating soft, or very soft, water (Figure 2). The main cation content was $Ca^{2+} > Mg^{2+} > Na^+$; the main anion content was $HCO_3^- > SO_4^{2-} > NO_3^- > Cl^-$ (Figure 3).

Trace element and toxic element concentrations

Concentrations of Li, B, F, Zn, and U in all waters were lower than both the Chinese national standard (CNS) (MH 2006) and international guidelines for drinking water quality (INS) (WHO 2011) (Table 1). F concentrations were in the range of 0.01–0.67 mg/L ($F_{avg} = 0.33$ mg/L). The Ba content of Sample Nos. 36 and 37 exceeded CNS limits (700 μg/L), at 985.27 μ/L and 750.58 μg/L, respectively. The Se content of Sample No. 30 from Minzhu Town, and Sample Nos. 33–37 from Shagou (14.79, 10.16, 23.58, 19.76, 18.18, and 19.48 μg/L, respectively) met Chinese national standards for mineral drinking water quality (CNSM) guidelines (GAQS 2008) (Figure 4). Strontium (Sr) concentrations in Sample Nos. 10, 12, 13, 26, 55, and 61 (0.21, 0.45, 0.44,
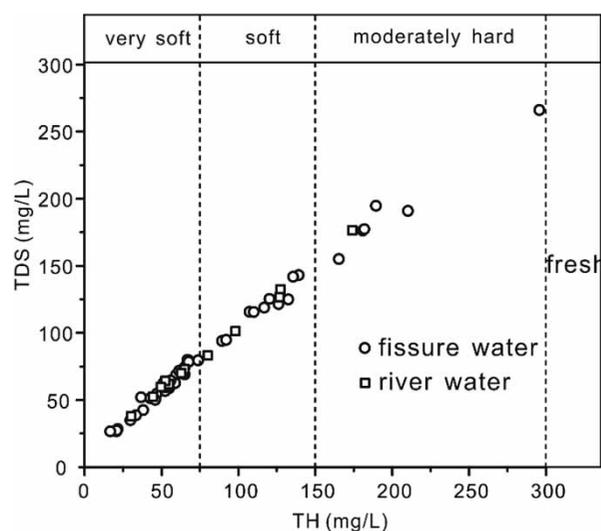

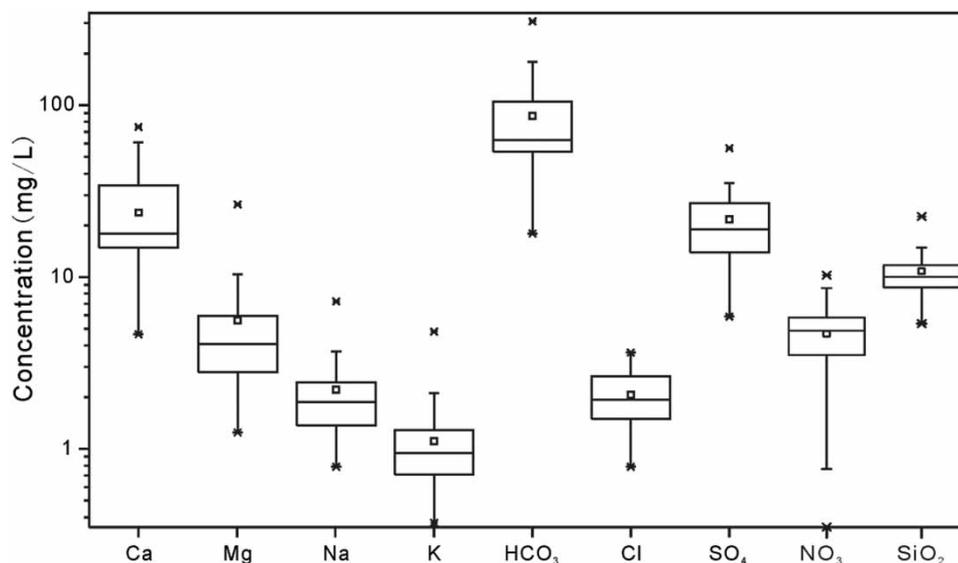**Figure 2** | Natural water characteristics for the Lan'gao area.

Figure 3 │ Box diagram showing the variations in major ion concentrations in natural water samples.

Table 1 │ Concentrations of trace elements in water samples and the test standards

Parameters	Li (μg/L)	B (mg/L)	F (mg/L)	V (μg/L)	Co (μg/L)	Zn (μg/L)	Ga (μg/L)	Se (μg/L)	Rb (μg/L)	Sr (mg/L)	Cs (μg/L)	Ba (μg/L)	U (μg/L)
Min	0.12	0.00	0.01	−5.03	0.03	0.11	0.23	0.21	0.15	0.03	0.00	14.07	0.02
Max	6.18	0.06	0.67	11.46	0.28	94.90	17.14	23.58	5.54	0.45	0.35	958.27	26.00
Mean	0.85	0.01	0.33	−0.19	0.07	15.24	3.54	4.63	0.87	0.13	0.03	192.47	2.36
Median	0.46	0.00	0.35	−2.34	0.05	6.15	2.41	2.64	0.71	0.10	0.01	133.21	0.97
Standard deviation	1.14	0.01	0.19	4.22	0.05	21.93	3.65	5.80	0.82	0.08	0.07	200.52	4.29
Skew	3.47	4.55	−0.05	1.16	2.44	1.99	1.83	1.82	3.38	2.26	4.12	1.89	3.68
CNS (MH 2006)		0.5	1			1,000		10				700	
INS (WHO 2011)		2.4	1.5					40				700	30
CNSM (GAQS 2008)	≥200	<5	<1.5			≥200		≥10		≥0.2		<700	

According to CNSM (GAQS 2008), drinking natural mineral water must have more than one from eight parameters including lithium, strontium, zinc, selenium, iodine, sodium metasilicate, free CO_2, and TDS, that reaches the index limit requirements.

CNS, Chinese national standard for drinking water quality; INS, international guidelines for drinking water quality; CNSM, Chinese national standard for drinking natural mineral water quality.

0.32, 0.21, and 0.39 mg/L, respectively) were also higher than the CNSM limits (Figure 4). The average Se content in fissure water was 5.52 μg/L, with the highest value being 23.58 μg/L; the average content of Se in river water was 2.82 μ/L, with a maximum value of 7.68 μg/L.

With reference to toxic elements, the concentrations of Be, Cr, Mn, Cu, As, Mo, Ag, Sb, Hg, and Pb were lower than both CNS and INS stipulations (Table 2, Figure 4). The arsenic content was in the range of 0.33–6.29 μg/L

($As_{avg} = 2.88$ μg/L). Al concentrations in seven fissure water and two river water samples exceeded CNS limits (200 μg/L). The Fe concentrations of five samples (326.74–484.48 μg/L) were higher than CNS guidelines (300 μg/L). The Ni content of five fissure water samples (20.32–24.58 μg/L) was slightly higher than CNS limits (20 μg/L), but lower than INS guidelines (70 μg/L). Cd content was lower than CNS guidelines, while five fissure water samples (3.37–4.41 μg/L) showed concentrations slightly higher than CNSM limits
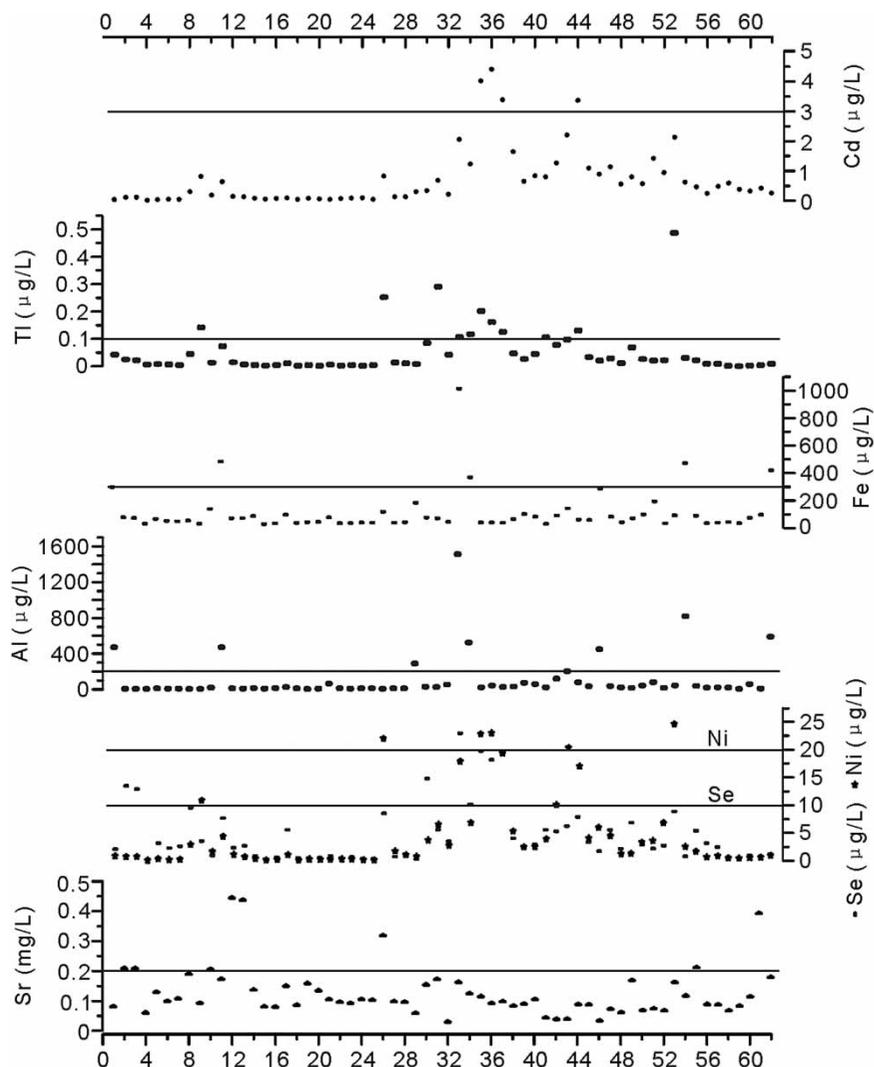
Figure 4 | Concentrations of Se, Sr, and other trace elements in water samples from the Lan'gao area. The dotted lines indicate the legal limits of Se (>10 μg/L) and Sr (>0.2 mg/L).

(3 μg/L). The Tl content of 11 fissure water samples (0.11–0.49 μg/L) was higher than CNS limits (0.1 μg/L) (Table 2, Figure 4).

DISCUSSION

Hydrochemical characteristics of NDM water

The water of the study area was mainly neutral to weakly alkaline. The TDS, TH, and major ion concentrations were lower than the limits outlined by CNS (MH 2006) (Figures 2 and 3, Table 3). The low concentrations of F

and As found in natural water in the study area indicate that these waters are not the source of the region's endemic fluorosis and arsenicosis, and that the water is safe for drinking (Tables 1 and 2).

The Se content of eight samples (10.16–23.58 μg/L) and the Sr concentrations in eight samples (0.21–0.45 mg/L), all met CNSM standards (GAQS 2008) (Table 1, Figure 4). Of these, the Se (13.47 μg/L, 12.89 μg/L) and Sr contents (0.21 mg/L, 0.21 mg/L) of Sample Nos. 2 and 3 from Candle Mountain met the CNSM guidelines (GAQS 2008); their toxic element levels were lower than CNS and INS limits (MH 2006; WHO 2011) (Figure 4).

Table 2 | Concentrations of toxic elements in water samples and the test standards (µg/L)

Parameters	Be	Al	Cr	Mn	Fe	Ni	Cu	As	Se	Mo	Ag	Cd	Sb	Hg	Tl	Pb
Min	−0.25	3.07	0.28	0.01	28.81	0.15	0.15	0.33	0.21	0.13	−0.01	0.03	0.01	0.00	0.00	0.00
Max	0.14	818.71	11.26	6.68	484.48	24.58	14.67	6.29	23.58	52.92	0.14	4.41	4.75	0.02	0.49	0.47
Mean	−0.07	92.89	2.04	0.81	102.37	4.58	2.03	2.88	4.63	8.71	0.01	0.76	0.40	0.00	0.05	0.05
Median	−0.07	22.52	1.04	0.28	68.76	1.36	0.99	2.68	2.64	5.12	0.00	0.36	0.25	0.00	0.02	0.01
Standard deviation	0.09	177.46	2.45	1.37	108.68	6.68	2.89	1.20	5.80	9.83	0.02	1.03	0.64	0.00	0.08	0.10
Skew	0.07	2.53	2.17	2.74	2.34	1.93	2.83	0.75	1.82	2.10	6.54	2.18	5.29	4.11	3.12	2.94
CNS (MH 2006)	2	200	50	100	300	20	1,000	10	10	70	50	5		1	0.1	10
INS (WHO 2011)			50			70	2,000	10	40			3	20	6		10
CNSM (GAQS 2008)			<50	<400		<20	<1,000	<10	<50		<50	<3		<1		<10

CNS, Chinese national standard for drinking water quality; INS, international guidelines for drinking water quality; CNSM, Chinese national standard for drinking natural mineral water quality.

Table 3 | Major element water quality test standards

Unit (mg/L) Parameters	CNS (MH 2006)	INS (WHO 2011)	CNSM (GAQS 2008)
pH	6.5–8.5		
TDS	1,000		≥1,000
TH	450		
Na^+	200		
NO_3^-		50	45
SO_4^{2-}	250		
Cl^-	250		
H_2SiO_3			≥25.0

CNS, Chinese national standard for drinking water quality; INS, international guidelines for drinking water quality; CNSM, Chinese national standard for drinking natural mineral water quality.

Preliminary discussion of the possible causes of variations in water samples

The Gibbs Map is a powerful tool for describing water types, including water from evaporation/crystallization, water dominated by rock type and atmospheric precipitation (Gibbs 1970). Based on the Gibbs map, the hydrochemical composition of water in the Lan'gao area appears to be principally controlled by rock weathering (Figure 5), consistent with the high relative humidity climatic conditions in this subtropical humid monsoon zone.

The percentages of major ions within water determine the water's hydrochemical type; the ratios between the major ions found in water can be clearly shown with a Piper plot (Piper 1944). The main hydrochemical types evident from water samples collected in the Lan'gao area

were as follows: $Ca-Mg-HCO_3-SO_4$ (37 samples); $Ca-HCO_3-SO_4$ (15 samples); $Ca-Mg-HCO_3$ (seven samples); $Ca-HCO_3$ (three samples); $Ca-Mg-Na-HCO_3$ (one sample); and $Ca-Mg-SO_4-HCO_3$ (one sample). The predominant cation and anion in water samples from Lan'gao were Ca^{2+} and HCO_3^-, respectively, indicating that chemical constituents are principally derived from carbonate rock weathering (Figure 6).

Evaluation of Se-rich water resources

The World Health Organization has stated that Se is an indispensable nutrient and essential to human life (WHO 1996). The Chinese Nutrition Society has also listed Se as a vital dietary nutrient (Cheng *et al.* 2009). However, Se is a scarce resource. About 0.5–1 billion people in the world are affected by Se deficiency (Haug *et al.* 2007). Nearly 300 million people in China are affected by a lack of Se in their diet (Yang 1994; Winkel *et al.* 2011; Zhang *et al.* 2014).

Drinking water is crucial for human survival. However, water quality survey data show that Se concentrations are often very low (<1 μg/L) in natural water, and only ∼0.02–10 μg/L in freshwater (Schutz & Turekian 1965; Bowen 1966). For instance, Se content is 0.14 μg/L in the Mississippi River, 0.21 μg/L in the Brazilian Amazon River, and 0.04–5 μg/L in the rivers of China (Wang & Gao 2001).

Europe has the longest commercial mineral water history in the world (Wynn *et al.* 2009). A recent study found that, following European Union legislation, 58.1% of 571
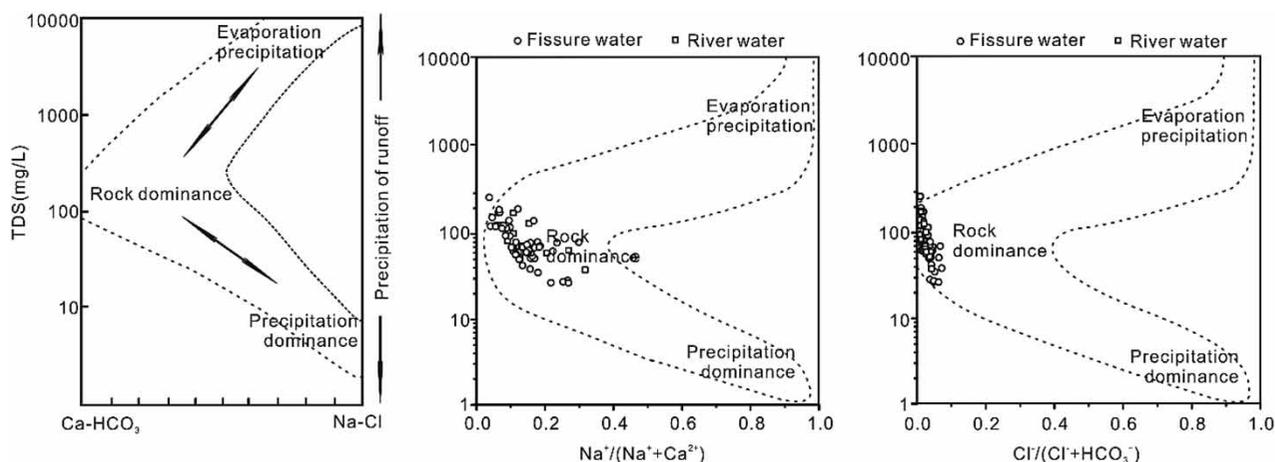
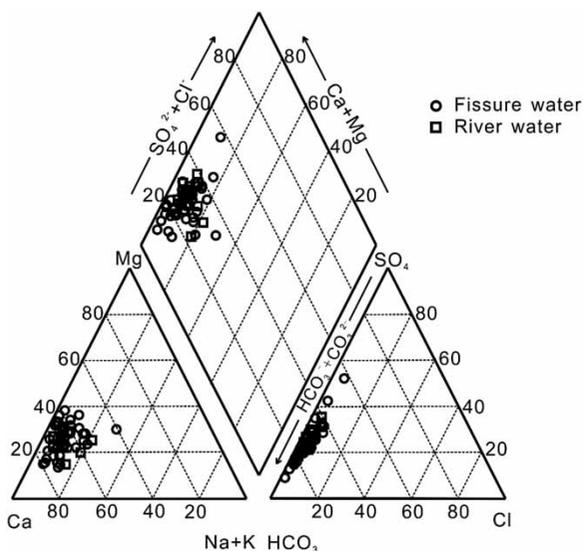**Figure 5** | Gibbs map (boomerang envelope) major ion plots for water in the Lan'gao area.

Figure 6 | Piper diagram showing the concentrations of major cations and anions in NDM water samples.

bottles of mineral water from 23 European countries could be defined as 'suitable for a low-sodium diet', while only 1.2% of the total samples exceeded the Se limit ($>10\,\mu g/L$) (Bertoldi *et al.* 2011). As of February 2015, the total output of the Chinese mineral water market was 5.36 million tons, giving the trade a market value of ¥15.2 billion RMB (DFCMW 2015). However, metasilicate, strontium, and carbonated mineral water types accounted for 90% of that market (Wang 2015). Ninety percent of the remaining categories of mineral water were of lithium, zinc, and iodine types. Se-bearing mineral waters were even rarer (An 1992; Zhang 2009; DFCMW 2015).

CNSM guidelines stipulate that Se content should be $10–50\,\mu g/L$ (GAQS 2008). At present, only one brand of Se-rich mineral water, i.e., 'Rare Water', whose Se content is $>10\,\mu g/L$ (ranging from 25 to $37\,\mu g/L$), has been developed for the Chinese market. Its costs ¥13RMB per 380 mL, which is about ten times the price of ordinary mineral water (¥1–2RMB per 500 mL). The development of natural Se-rich mineral water would clearly have both economic benefits and market prospects. The discovery of high-Se water sources is therefore of important practical significance.

In November 2011, the China Rural Poverty Alleviation and Development Program (2011–2020) was promulgated. This focused on the need for a clear assessment of all ecological assets as well as improvements in ecological and environmental protection work in poverty-stricken areas. The QDM region is typical of such impoverished and underdeveloped areas (Cao *et al.* 2015). Our systematic investigation of high-Se water resources in the QDM region has focused on both the evaluation of ecological assets and poverty alleviation. The results of this study show that Se and Sr concentrations in natural fissure water from the Lan'gao area were moderate in value. The Se content of eight water samples was $10.16–23.58\,\mu g/L$. Of these, the Se ($13.47\,\mu g/L$, $12.89\,\mu g/L$) and Sr contents ($0.21\,mg/L$, $0.21\,mg/L$) of two samples from Candle Mountain, and the Se content ($14.79\,\mu g/L$) of one sample from Minzhu Town met the CNSM guidelines (GAQS 2008), with limited element concentrations lower than both the CNS and INS measures (MH 2006; WHO 2011). The average Se content of river water was $2.82\,\mu g/L$, 14 times higher than that of global surface water ($0.2\,\mu g/L$).

However, the concentrations of some limited elements should be considered during the exploitation of high Se-rich mineral water in the NDM. Cd, Ni, Tl, Fe, and Al concentrations correlated significantly with Se content ($r = 0.73$, 0.71, 0.51, 0.36, and 0.36; $P < 0.01$) (Table 4). Of the eight Se-rich fissure water samples (Se $>10\,\mu g/L$), the Ni content of two samples (22.78, $22.95\,\mu g/L$) and the Tl content of five samples ($0.11–0.2\,\mu g/L$) were slightly higher than the CNS guidelines (Ni $< 20\,\mu g/L$, Tl $< 0.1\,\mu g/L$) (Figure 4), suggesting that the concentrations of these elements in potable water should be taken into account.

Table 4 | Pearson correlation coefficients between Se and Sr, Cd, Ni, Tl, Fe, Al contents in water, Lan'gao area

	Sr	Cd	Ni	Tl	Fe	Al
Se	0.067	0.731*	0.706*	0.514*	0.356*	0.358*
Sr		−0.178	−0.045	0.077	0.062	−0.051
Cd			0.869*	0.571*	0.171	0.219
Ni				0.794*	0.220	0.239
Tl					0.099	0.088
Fe						0.973*

*$P < 0.01$, significant correlation.

Content of trace elements change in response to climate factors

Human activities and climate change have brought about significant changes to water resources and sea level (Xu 2005; Baba *et al.* 2011). However, although some trace elements, such as selenium, are essential for human health and the ecosystem of rivers, few researchers have paid attention to this, which might be due to trace elements in water being difficult or expensive to measure accurately (Selinus *et al.* 2013).

The NDM region remains relatively ecologically intact, with a high forest coverage (70% in the hinterland), no large industrial or mining enterprises, good atmospheric quality, and unpolluted natural soil and biological resources

(Wang 2004; Liu *et al.* 2015). Consequently, element content in the Lan'gao area has been principally affected by natural factors, with relatively weak human influence. Therefore, it is the ideal area to study element content variation and its responses to climate change.

In order to monitor better the stability of Se, Sr, Cd, Ni Tl, Fe, and Al concentrations (beyond the CNS, INS, or CNSM) in water, we collected and analyzed samples of fissure and river water in July and September 2015, respectively (Figures 7 and 8). Water flow quantities were also recorded. Test results showed that Se concentrations in the study area remained stable (Figure 7). For example, Sample No. 33 collected in May 2015 from Minzhu Town exhibited Se contents of 14.79, 22.50, and 27.32 μg/L, in May, July, and September, respectively. Water flow in July
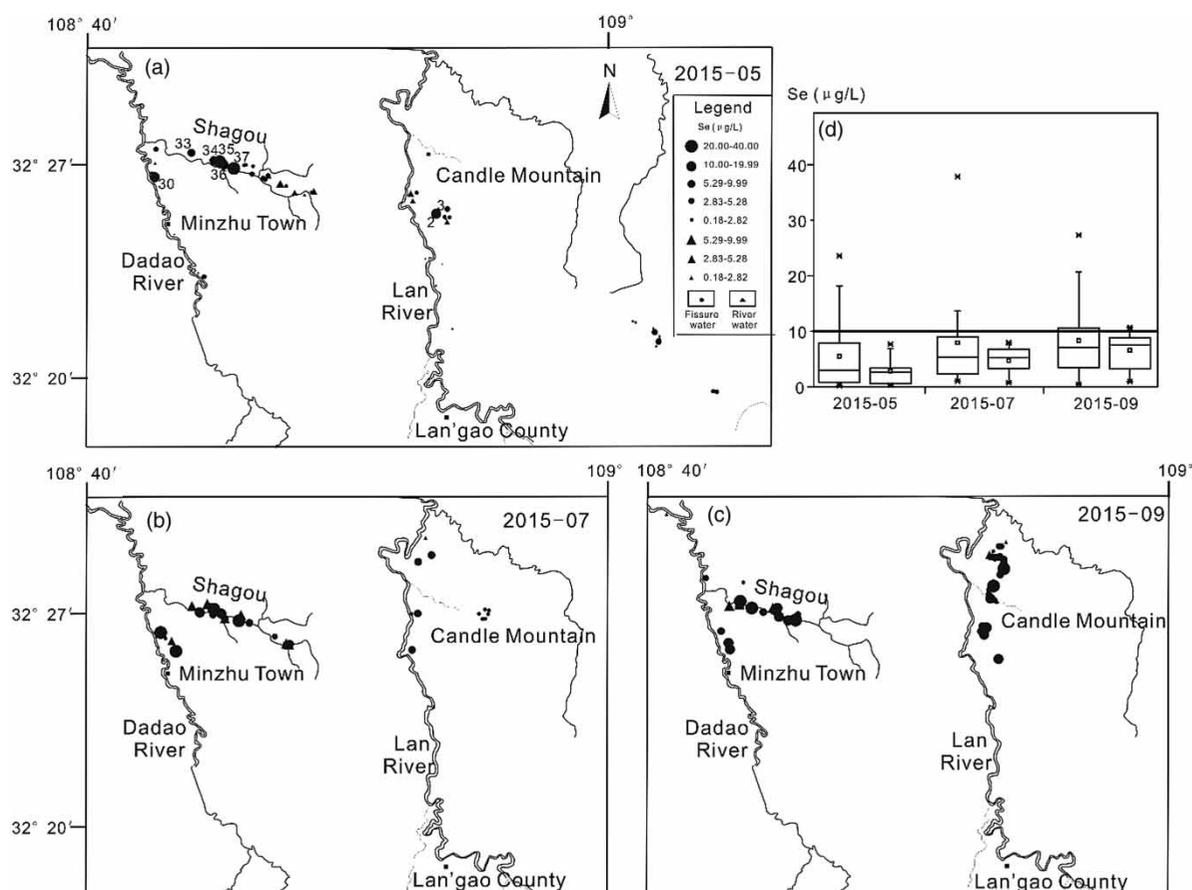

Figure 7 │ The Se content and spatial distribution characteristics of fissure water and river water samples from the Lan'gao area in May, July, and September 2015. (a) 62 samples collected in May 2015; (b) 49 samples collected in July 2015; (c) 61 samples collected in September 2015; (d) box plot showing the Se content of all water samples (from left to right): Se content of 47 fissure water samples and 15 river water samples in May 2015; 31 fissure water samples and 18 river water samples in July 2015; and 47 fissure water samples and 14 river water samples in September 2015. The bold line indicates the legal limit.
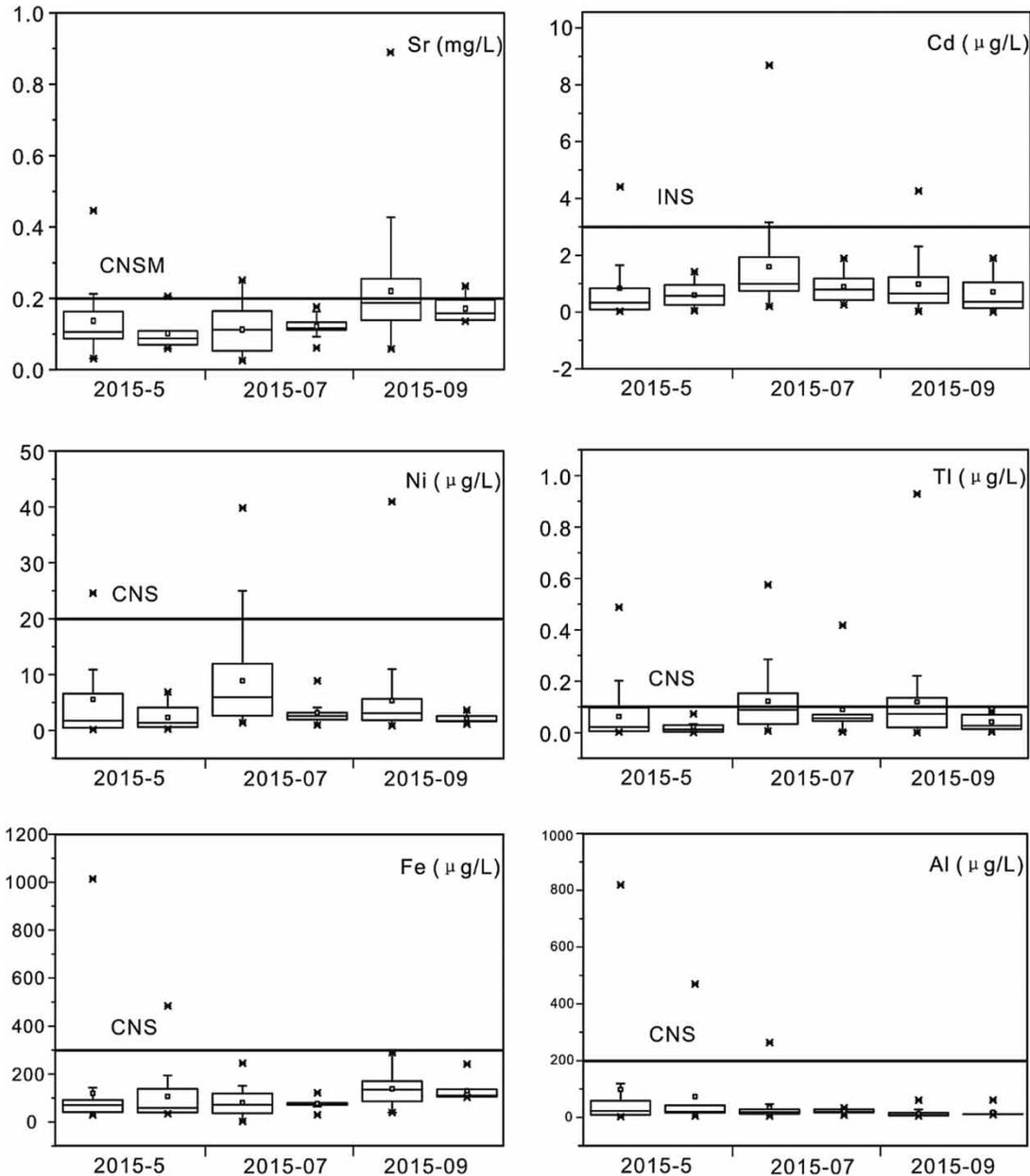
Figure 8 │ The Sr, Cd, Ni, Tl, Fe, and Al contents of water samples from the Lan'gao area. From left to right: 49 fissure water samples and 15 river water samples in May 2015; 31 fissure water samples and 18 river water samples in July 2015; and 47 fissure water samples and 14 river water samples in September 2015. The bold line indicates the legal limit.

($\sim$240 m^3/d) is suited to small-scale mineral water production (Li 2007).

The contents of the limited elements were relatively stable. The Sr concentrations gradually increased from May to September (Figure 8). The mean concentrations of Cd, Ni, Fe, and Al were stable and lower than the INS and CNS (Figure 8). The Tl content was a little higher in

July and September than in May, therefore the long-term toxic impact of Tl in drinking water on the health of local people should be noted.

The change of Se and Sr contents agrees well with the humidity change among the climatic factors in the Lan'gao area (Figure 9). From May to September, the humidity increased slightly, which might contribute to the
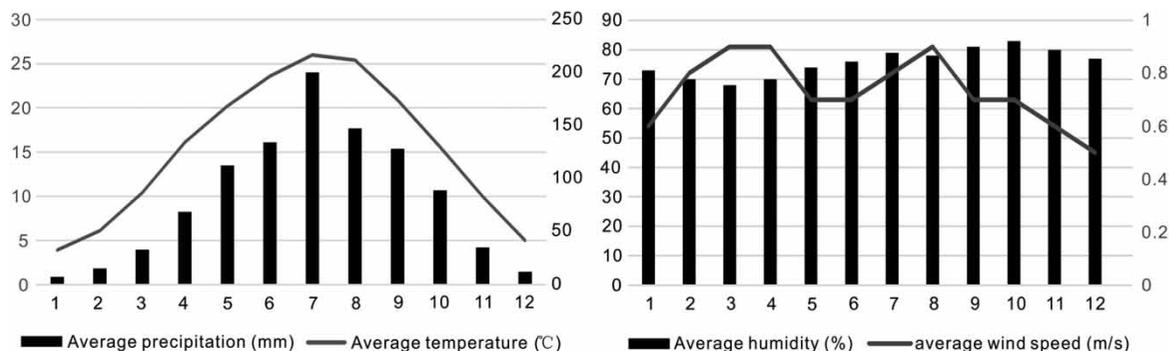
Figure 9 | The climatic factors in the Lan'gao area, including average temperature (°C), humidity (%), precipitation (mm), and wind speed (m/s) (http://data.cma.cn/site/index.html).

interaction between rock and water and is beneficial to the dissolution of Se and Sr elements in water. It is consistent with the Gibbs map showing the hydrochemical composition of water principally controlled by rock weathering (Figure 5) in the high relative humidity climatic conditions. There are similar characteristics during the 1961–1964 selenosis in Enshi, Hubei Province, in China (Yan & Wu 1993). The selenium average content in drinking water was 14.94 μg/L in spring, and 8.14 μg/L in winter, and the seasonal differences might be that warm and humid climate is beneficial to the selenium leaching (Yan & Wu 1993).

Possible sources of endemic fluorosis and arsenism in the NDM

The population of the NDM of Shaanxi Province suffers from endemic fluorine and arsenic poisoning (Luo 2011; Gong *et al.* 2012). Drinking water is one of the important ways of trace element intake for humans (Bleiman & Mishael 2010). In order to verify the stability of fluorine and arsenic contents in water, six field trips were conducted in the study area from May 2015 to March 2016. A total of 218 water samples were collected in May, July, September, October, and December in 2015, and March in 2016 (Tables S3 and S4, available with the online version of this paper). The results indicated that the arsenic and fluoride concentrations in natural water were lower than the CNS and INS standards. Hence, F and As in natural water were not the sources of fluorosis and arseniasis in the NDM.

Stone coal (combustible black shale) is widely used for domestic purposes in the NDM (Luo 2011). The contents of F, As, and Se in the stone coal are about 10–50 times more than in common humic coal (Luo *et al.* 2004a; Zheng *et al.* 2007; Luo 2011; Xu & Luo 2012), and higher than the average contents of the continental crust (Selinus *et al.* 2013). Moreover, F and As emission rates are about 80% and 70%, respectively, during stone coal burning indoors (Ren *et al.* 2006; Yu *et al.* 2009).

There have been some studies of Se, As, and F content, distribution, and occurrence status in rock and soil in the NDM (Luo *et al.* 2004a; Li *et al.* 2005; Xue *et al.* 2010; Gao *et al.* 2011; Xu & Luo 2012; Chen *et al.* 2014). Se-enriched strata are exhibited in the Lower Cambrian and Daguiping Formations of the Silurian (Chen & Luo 1996; Li *et al.* 2005; Luo 2011). Fluorine and arsenic contents of the Early Paleozoic strata, especially in the black shales and phosphate rocks of the Early Cambrian Lujiaping Formation of the Daba region, are approximately several times higher than the average value found in the continental crust (Luo *et al.* 1995; Xu & Luo 2012).

Based on a systematic investigation of the hydrochemical characteristics and trace element contents of fissure and river water in the NDM, this study found that drinking the natural water is not the reason for the endemic fluorine and arsenic poisoning. According to previous research, high fluorine and arsenic content in burning stone coal might be the main explanation of endemic fluorosis and arsenic poisoning in the NDM (Luo 2011; Gong *et al.* 2012). Therefore, to establish the relationship more accurately between indoor combustion of high fluorine and arsenic content in stone coal and the health effect in this region will be the aim of further work.

CONCLUSION

The natural water in the Lan'gao area of the NDM is of relatively good quality and is suitable for drinking. F and As concentrations in natural water were lower than CNS and INS guidelines, indicating that fluorine and arsenic in drinking water are not the source of the area's endemic fluorosis and arsenicosis.

The average Se content in fissure water was 5.52 μg/L. There were eight samples where Se content reached the CNSM guidelines (>10 μg/L). The Sr concentrations of eight samples also met the CNSM guidelines (>0.2 mg/L), with the highest value being 0.45 mg/L. It is noteworthy that the Se (13.47 μg/L, 12.89 μg/L) and Sr contents (0.21 mg/L, 0.21 mg/L) of two samples met the CNSM guidelines, but these limited elements were at the same time lower than both the CNS and INS guidelines.

The Se and Sr contents are relatively stable and reveal an increasing tendency along with the increase of humidity. The high quality low-sodium Se-rich mineral water of the NDM should be able to be commercially exploited, but prior to this, the hydrological geology of this area will require further detailed study.

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REFERENCES

A review of the development and forecast of market prospects of Chinese mineral water industry (DFCMW) 2015 *China Market Report*. Beijing, China (in Chinese).

An, K. S. 1992 Basic types and distribution of natural mineral water resources in China. *Beverage Industry* **A02**, 31–34 (in Chinese).

Baba, A., Tayfur, G., Gündüz, O., Howard, K. W. F., Friedel, M. J. & Chambel, A. 2011 *Climate Change and its Effects on Water Resources*. Springer, Dordrecht, The Netherlands, pp. 547–566.

Bertoldi, D., Bontempo, L., Larcher, R., Nicolini, G., Voerkelius, S., Lorenz, G. D., Ueckermann, H., Froeschl, H., Baxter, M. J., Hoogewerff, J. & Brereton, P. 2011 Survey of the chemical composition of 571 European bottled mineral waters. *Journal of Food Composition and Analysis* **24** (3), 376–385.

Bleiman, N. & Mishael, Y. G. 2010 Selenium removal from drinking water by adsorption to chitosan-clay composites and oxides: batch and columns tests. *Journal of Hazardous Materials* **183** (1–3), 590–595.

Bowen, H. J. 1966 *Trace Element in Biochemistry*. Academic Press, New York, USA.

Cao, S. S., Zhao, W. J. & Duan, F. Z. 2015 Coupling relation analysis between ecological value and economic poverty of contiguous destitute areas in Qinling-Dabashan region. *Acta Geographica Sinica* **34**, 1295–1309.

Chen, D. L. & Luo, K. L. 1996 The selenium content and its environment effect in Early Paleozoic in south of Shaanxi Province. *Shaanxi Environment* **32** (2), 29–31.

Chen, B. Q., Li, Y. L., Bai, G. L., Li, X. Q. & Fan, Z. X. 2003 Progress investigation of coal burning fluorosis areas in Shaanxi Province. *Chinese Journal of Endemiology* **22** (5), 434–436.

Chen, J., Liu, G., Kang, Y., Wu, B., Sun, R., Zhou, C. & Wu, D. 2014 Coal utilization in China: environmental impacts and human health. *Environmental Geochemistry and Health* **36** (4), 735–753.

Cheng, Y., Dibley, M. J., Zhang, X., Zeng, L. & Yan, H. 2009 Assessment of dietary intake among pregnant women in a rural area of western China. *BMC Public Health* **9** (1), 222.

Combs, J. F. 2001 Selenium in global food system. *Brtish Journal of Nutrition* **85** (5), 517–547.

Dissanayake, C. B. 1991 The fluoride problem in the ground water of Sri Lanka – environmental management and health. *International Journal of Environmental Studies* **38** (38), 137–155.

Fordyce, F. 2007 Selenium geochemistry and health. *Ambio* **36** (1), 94–97.

Fordyce, F. M., Zhang, G. D., Green, K. & Liu, X. 2000 Soil, grain and water chemistry and human selenium imbalances in Enshi District, Hubei Province. *China Applied Geochemistry* **15** (1), 117–132.

Gao, J., Yu, J. & Yang, L. 2011 Urinary arsenic metabolites of subjects exposed to elevated arsenic present in coal in Shaanxi Province, China. *International Journal of Environmental Research & Public Health* **8** (6), 1991–2008.

General Administration of Quality Supervision 2008 *Inspection and Quarantine of the People's Republic of China (GAQS) Drinking Natural Mineral Water*. GB 8537-2008 (in Chinese).

Geological Bureau of Shaanxi Province (GBS) 1966 *Geological map of the People's Republic of China. Ziyang, Pingli, Shiquan, Ankang Part*. Ministry of Geology 543 Factory, Changzhi, China (in Chinese).

Gibbs, R. J. 1970 Mechanisms controlling world water chemistry. *Science* **170** (3962), 1088–1090.

Gong, S. Y., Fan, Z. X., Chen, J. G. & Zhang, L. H. 2012 Investigation on the overlapping endemic of fluorosis and arseniasis related with indoor combustion of high fluorine-arsenic content coal in a mountainous township in Southern Shaanxi Province. *Foreign Medical Science Section of Medgeography* **33** (3), 176–180.

Hartikainen, H. 2005 Biogeochemistry of selenium and its impact on food chain quality and human health. *Journal of Trace Elements in Medicine and Biology* **18** (4), 309–318.

Haug, A., Graham, R. D., Christophersen, O. A. & Lyons, G. H. 2007 How to use the world's scarce selenium resources efficiently to increase the selenium concentration in food. *Microbial Ecology in Health and Disease* **19** (4), 209–228.

Li, Z. 2007 The research of the development plan of mineral water industry in Changbai Mountains region. MS Dissertation, University of Jilin, Changchun, China (in Chinese).

Li, Y., Bai, G. L., Zheng, L. Y. & Bai, A. M. 2004 Relation between arsenic in environment and coal burning-borne endemic arsenism in the south of Shaanxi province. *Chinese Journal of Endemiology* **23** (6), 562–565 (in Chinese).

Li, Y. H., Wang, W. Y., Yang, L. S., Luo, K. L. & Li, H. R. 2005 Concentration and environmental significance of water soluble-Se and water soluble-F in soils of south Shaanxi Province. *Environmental Chemistry* **24** (3), 279–283 (in Chinese).

Liu, X. F., Pan, Y. Z., Zhu, X. F. & Li, S. S. 2015 Spatiotemporal variation of vegetation coverage in Qinling-Daba Mountains in relation to environmental factors. *Acta Geographica Sinica* **70**, 705–716.

Luo, K. L. 2003 The age of rock distribution in the selenium region, south Shaanxi Province. *Geological Review* **49** (4), 383–388.

Luo, K. L. 2011 Arsenic and fluorine contents and distribution patterns of Early Paleozoic stonelike coal in the Daba Fold Zone and Yangtze Plate, China. *Energy & Fuel* **25** (25), 4479–4487.

Luo, K. L. & Jiang, J. S. 1995 The Selenium content and enrichment regularity of Lower Cambrian in Ziyang County and Langao County in Shaanxi Province. *Geology-Geochemistry* **1**, 68–71 (in Chinese).

Luo, K. L., Chen, D. L. & Ge, L. M. 1994 *The Black Rock Series and Coal in Paleozoic in Shaanxi Province*. Northwest University Press, Xi'an, China (in Chinese).

Luo, K. L., Zhan, S. Q. & Zhang, M. S. 1995 Enrichment of selenium in stone coal in south Qinling Mountain and its significance. *Journal of Changchun University of Earth Science* **25** (2), 125–130 (in Chinese).

Luo, K. L., Pan, Y. T., Wang, W. Y. & Tan, J. A. 2001 Selenium content and distribution pattern in the Palaeozoic strata in the southern Qinling Mountains. *Geological Review* **47** (2), 211–217 (in Chinese).

Luo, K. L., Tan, J. A., Wang, W. Y., Xiang, L. H. & Li, D. Z. 2002a Chemical mobility of selenium in early Paleozoic rock and stone coal in Daba Mountain, South Qinling. *Acta Scientiae Circumstantiae* **22** (1), 86–91 (in Chinese).

Luo, K. L., Xu, L. R. & Xiang, L. H. 2002b Selenium content in the water of the rivers, springs and wells in the Daba Mountain Area of the south Qinling Mountains. *Acta Geologica Sinica* **76** (3), 389–394 (in Chinese).

Luo, K. L., Xiang, L. H. & Xu, L. R. 2002c Iodine-rich springs discovered in iodine-lacking Ziyang County, South Qinling. *Chinese Journal of Geology* **37** (2), 231–232 (in Chinese).

Luo, K. L., Ren, D. Y., Xu, L. R., Dai, S. F., Cao, D. Y., Feng, F. J. & Tan, J. A. 2004a Fluorine content and distribution pattern in Chinese coals. *International Journal of Coal Geology* **57** (2), 143–149.

Luo, K. L., Xu, L. R., Tan, J. A., Wang, D. H. & Xiang, L. H. 2004b Selenium source in the selenosis area of the Daba region, South Qinling Mountain, China. *Environmental Geology* **45** (3), 426–432.

Ministry of Environment Protection of the People's Republic of China (MEP) 2002 *Methods for Chemical Analysis of Water and Waste Water*, 4th edn. China Environmental Science Press, Beijing, China (in Chinese).

Ministry of Health of the People's Republic of China (MH) 1985 *Standards for Drinking Water Test*. GB575085 (in Chinese).

Ministry of Health of the People's Republic of China (MH) 2006 *Standards for Drinking Water Quality*. GB 5749-2006 (in Chinese).

Piper, A. M. 1944 A graphic procedure in the geochemical interpretation of water analysis. *Transactions of the American Geophysical Union* **25** (6), 914–923.

Plant, J. A., Bone, J., Voulvoulis, N., Kinniburgh, D. G., Smedley, P. L., Fordyce, F. M. & Klinck, B. 2014 11.2 Arsenic and selenium. In: *Treatise on Geochemistry*, 2nd edn (H. D. H. K. Turekian, ed.). Elsevier, Oxford, UK.

Rayman, M. P. 2006 The importance of selenium to human health. *The Lancet* **356** (9225), 233–241.

Ren, D. Y., Zhao, F. H., Dai, S. F. & Luo, K. L. 2006 *Geochemistry of Trace Elements in Coals*. The Science Press, Beijing, China (in Chinese).

Schutz, D. F. & Turekian, K. K. 1965 The investigation of the geographical and vertical distribution of several trace elements in sea water using neutron activation analysis. *Geochimica et Cosmochimica Acta* **29** (4), 259–313.

Selinus, O., Alloway, B., Centeno, J. A., Finkelman, R. B., Fuge, R., Lindh, U. & Smedley, P. 2013 *Essentials of Medical Geology*, revised edn. Springer, London, UK.

Tan, J. A., Zhu, W. Y., Wang, W. Y., Li, R. B., Hou, S. F., Wang, D. C. & Yang, L. S. 2002 Selenium in soil and endemic diseases in China. *Science of the Total Environment* **284** (1), 227–235.

Wang, C. H. 2015 Development conditions and utilization value of natural mineral water resources in China. *Exploration and Development* **2**, 44 (in Chinese).

Wang, C. S. 2004 Study of hydrosphere, atmosphere and biosphere environments in Dabashan Mountain. *Journal of Chongqing*

Technology Business University (Nature Science Edition) **21** (5), 491–496 (in Chinese).

Wang, Z. J. & Gao, Y. X. 2001 Biogeochemical cycling of selenium in Chinese environments. *Applied Geochemistry* **16** (11), 1345–1351.

Wen, X., Deng, B. L., Xue, Y., Yang, T., Meng, L., Wang, P. H. & Duan, X. H. 2011 The epidemiological survey of dental fluorosis in Haoping and Liushui of Ankang area. *Chinese Journal of Conservative Dentistry* **22** (4), 240–243 (in Chinese).

Winkel, L. H. E., Johnson, C. A., Lenz, M., Grundl, T., Leupin, O. X., Amini, M. & Charlet, L. 2011 Environmental selenium research: from microscopic processes to global understanding. *Environmental Science & Technology* **46** (2), 571–579.

World Health Organization and Agriculture Organization of the United Nations (WHO) 2004 *Vitamin and Mineral Requirements in Human Nutrition*, 2nd edn. In: Report of a Joint FAO-WHO Expert Consultation, World Health Organization, Geneva, Switzerland.

World Health Organization (WHO) 2011 *Guidelines for Drinking-water Quality*, 4th edn. World Health Organization, Geneva, Switzerland.

World Health Organization (WHO) Food and Agriculture Organisation and International Atomic Energy Agency Expert Group 1996 *Selenium, trace elements in human nutrition and health*, pp. 105–122.

Wynn, E., Raetz, E. & Burckhardt, P. 2009 The composition of mineral waters sourced from Europe and North America in respect to bone health: composition of mineral water optimal for bone. *British Journal of Nutrition* **101** (8), 1195–1199.

Xu, J. 2005 The water fluxes of the Yellow River to the sea in the past 50 years, in response to climate change and human activities. *Environmental Management* **35** (5), 620–631.

Xu, L. R. & Luo, K. L. 2012 Studies on fluorine distribution in the strata of the Daba region. *Geographical Research* **31** (8), 1503–1511 (in Chinese).

Xu, G. Y., Li, P. A. & Li, X. Q. 2008 Control status of coal-burning fluorosis and arsenism in Shaanxi Province. *Endemic Diseases Bulletin* **23** (1), 49 (in Chinese).

Xue, W., Wang, Z., Chen, Q., Chen, J. H., Yang, H. J. & Xue, S. H. 2010 High selenium status in individuals exposed to arsenic through coal-burning in Shaanxi (PR of China) modulates antioxidant enzymes, heme oxygenase-1 and DNA damage. *Clinica Chimica Acta; International Journal of Clinical Chemistry* **411** (17–18), 1312–1318.

Yan, B. W. & Wu, T. 1993 Department of Endemic Diseases Hubei Anti-Epidemic Station. An investigation of environmental selenium in seleniferous area. *Chinese Journal of Endemiology* **12** (3), 155–158 (in Chinese).

Yang, Z. Y. 1994 Hydrological and geochemical of selenium and its relationship with human health. *Journal of Guilin College of Geology* **14** (2), 192–207.

Yu, J. P., Yang, L. S., Wang, W. Y., Li, Y. & Bai, A. M. 2009 Characteristics of indoor and outdoor air arsenic content as influenced by combustion of high arsenic coal. *Research of Environmental Sciences* **22** (8), 913–917.

Zhang, X. Y. 2009 Water quality characteristic and health significance of natural mineral water in Changbai Mountains. MS Dissertation, Jilin Institute of Architecture and Civil Engineering, Changchun, China (in Chinese).

Zhang, H., Feng, X., Jiang, C. X., Li, Q. H., Liu, Y., Gu, C. H., Shang, L. H., Li, P., Lin, Y. & Larssen, T. 2014 Understanding the paradox of selenium contamination in mercury mining areas: high soil content and low accumulation in rice. *Environmental Pollution* **188** (5), 27–36.

Zheng, B., Wu, D., Wang, B., Liu, X., Wang, M., Wang, A., Xiao, G., Liu, P. & Finkelman, R. B. 2007 Fluorosis caused by indoor coal combustion in China: discovery and progress. *Environmental Geochemistry and Health* **29** (2), 103–108.