

The Genesis Mechanism and Health Risk Assessment of High Boron Water in the Zhaxikang Geothermal Area, South Tibet

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1. The Calculation Steps of Entropy-Weighted Water Quality Index

The unit and magnitude of WQI for different groundwater are frequently different, resulting in wildly different weight calculations. The entropy weight method does not assign weights to evaluation index parameters based on subjective judgment, but rather uses the entropy weight method to standardize each parameter. The subjectivity of indexes can be greatly eliminated by assigning reasonable weights to each index and calculating the comprehensive index according to the information entropy, thus improving the accuracy of WQI [1].

The calculation of EWQI is based on the following steps [2,3]:

1. The selected water quality evaluation indices are normalized using matrix X (Eq. 1), where m and n represent the number of groundwater samples and assessing hydrochemical indices, respectively. The values of m and n in this study are 21 and 13, respectively. Homogenization treatment is carried out based on Eq. (2) and represented by Y_{ij} ;

$$X = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1n} \\ x_{21} & x_{22} & \cdots & x_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ x_{m1} & x_{m2} & \cdots & x_{mn} \end{bmatrix} \quad (1)$$

$$Y_{ij} = \frac{(x_{ij})_{\max}^j - x_{ij}}{(x_{ij})_{\max}^j - (x_{ij})_{\min}^j} \quad (2)$$

2. Calculate information entropy “ E_j ” and entropy weight “ W_j ” using Eqs. (3), (4), and (5). Where P_{ij} represents the ratio of the index j value of sample i .

$$E_j = -\frac{1}{\ln m} \sum_{i=1}^m P_{ij} \times \ln P_{ij} \quad (3)$$

$$P_{ij} = \frac{y_{ij} + 10^{-4}}{\sum_{i=1}^m (y_{ij} + 10^{-4})} \quad (4)$$

$$W_j = -\frac{1 - E_j}{\sum_{j=1}^n (1 - E_j)} \quad (5)$$

3. EWQI can be achieved by Eqs. (6) and (7). “ q_j ” is the quantitative scale of grading for hydrochemical indices and can be calculated by Eq. (7). In this study, C_j represents the content of index j , and S_j represents the standard limit value of drinking water quality index j in China.

$$EWQI = \sum_{j=1}^n W_j \times q_j \quad (6)$$

$$q_j = \frac{C_j}{S_j} \times 100 \quad (7)$$

According to the EWQI, the parameters TDS, pH, SO_4^{2-} , Cl^- , NO_3^- , As, T_{fe}, K^+ , Ca^{2+} , Na^+ , Mg^{2+} , Cd, B were selected for the water quality assessment in Zhaxikang area and the results of entropy weight and water quality class are lists in Table S1 and Table S2, respectively. According to the EWQI results, groundwater is classified into five grades ranging from “high-quality water” to “very poor water.” The classification criteria are shown in Table S3 [1]. The groundwater with ranks 1 and 2 is suitable for drinking purposes.

Table S1. Information entropy and entropy weight of parameters.

Item	TDS	pH	SO_4^{2-}	Cl^-	NO_3^-	As	T _{fe}
E _j	0.9821	0.9658	0.9745	0.9578	0.9831	0.9839	0.9749
W _j	0.0437	0.0835	0.0622	0.1031	0.0413	0.0393	0.0613
Item	K	Ca^{2+}	Mg^{2+}	Na^+	Cd	B	
E _j	0.9722	0.9338	0.9835	0.9710	0.9472	0.9607	
W _j	0.0679	0.1616	0.0403	0.0708	0.1289	0.0960	

Table S2. Assessment results according to the calculated EWQI.

Sample ID	EWQI	Rank	Sample ID	EWQI	Rank
R01	192.69	4	M01	52.22	2
R02	205.15	5	M02	48.42	1
R03	147.16	3	M03	49.84	1
R04	26.92	1	S01	942.01	5
R05	23.59	1	S02	26.98	1
R06	14.75	1	S03	1191.05	5
R07	17.39	1	S04	673.17	5
L01	15.76	1	S05	209.05	5
L02	302.94	5	S06	1373.55	5
L03	75.95	2	S07	1018.70	5
L04	27.39	1			

Table S3. Water quality class based on EWQI.

Range	Rank	Water Quality Type
<50	1	Excellent
50–100	2	Good
100–150	3	Medium
150–200	4	Poor
>200	5	Extremely poor

2. The Calculation Steps of Health Risk Assessment

Health risk assessment is conducive to supporting groundwater quality assessment and environmental management [4].

The exposure dose (DI) for oral ingestion and skin contact could be calculated using the following formulas separately [5,6]:

$$DI_{\text{Ingestion}} = \frac{C_B \times IR \times EF \times ED}{BW \times AT} \quad (8)$$

$$DI_{Dermal} = \frac{SA \times K_p \times ET \times C_B \times CF \times EF \times ED}{BW \times AT} \quad (9)$$

where DI is the daily chronic intake of groundwater (mg/kg/day). C_B is the concentration (mg/L) of the contaminant in the water sample measured by the laboratory. The contaminant in this study is B. The groundwater uptake rate (L/day) is symbolized by IR; the exposure frequency (days/year) is represented by EF, and the exposure duration (year) is denoted by ED. The average weight (kg) is denoted by BW, and the average time (day) is symbolized by AT. SA denotes skin surface area; K_p denotes skin permeability; ET denotes bath exposure time, and CF denotes the unit conversion factor. The values of these parameters are shown in Table S4 [5,6].

Table S4. Model Parameters for the calculation of exposure dose.

Parameters	Unit	Children	Adults
Ingestion rate (IR)	L/day	0.7	2
Exposure frequency (EF)	Days/year	365	365
Exposure duration (ED)	year	12	40
Body weight (BW)	Kg	18	60
Average time (AT)	Days	4380	14600
Surface area (SA)	cm ²	6600	18000
Exposure time (ET)	h/day	0.25	0.25
Skin permeability coefficient (K_p)	cm/h	0.001	0.001
Conversion factor (CF)	L/cm ³	0.001	0.001

The potential hazard for noncarcinogenic risk of Hazard Quotient (HQ) could be calculated using these equations [7]:

$$HQ_{Ingestion} = \frac{DI_{Ingestion}}{RfD} \quad (10)$$

$$HQ_{Dermal} = \frac{DI_{Dermal}}{RfD} \quad (11)$$

where RfD denotes the reference dose of specific contamination. The concentration of B in groundwater samples was found to be high in the study area. According to IRIS database [8], The RfD_B was 0.2 mg/kg/day. The total noncarcinogenic risk was determined as follows [9,10]:

$$HI = HQ_{Ingestion} + HQ_{Dermal} \quad (12)$$

where HI is the hazard index. Values of HQ and HI less than 1 indicate that they are suitable for human health. If the HI and HQ values are greater than 1, the noncarcinogenic risk is unacceptable [11–13].

The noncarcinogenic risk factor for children ranged from 0.002 to 1.844, with an average of 0.375, whereas HQ (Hazard Quotient) for adults ranges from 0.002 to 1.580 (Table S5). Generally, children are at a higher health risk than adults.

Table S5. Assessment results of health risks based on drinking water intake and dermal contact.

Sample ID	HQ _{Ingestion}		HQ _{Dermal}		HI	
	Children	Adults	Children	Adults	Children	Adults
L01	0.004	0.003	9.17E-06	7.50E-06	0.004	0.003
L02	0.008	0.007	1.83E-05	1.50E-05	0.008	0.007
L03	0.047	0.040	1.10E-04	9.00E-05	0.047	0.040
L04	0.004	0.003	9.17E-06	7.50E-06	0.004	0.003
M01	0.193	0.165	4.54E-04	3.71E-04	0.193	0.165
M02	0.014	0.012	3.21E-05	2.63E-05	0.014	0.012
M03	0.181	0.155	4.26E-04	3.49E-04	0.181	0.155
R04	0.002	0.002	4.58E-06	3.75E-06	0.002	0.002
R05	0.002	0.002	4.58E-06	3.75E-06	0.002	0.002
R06	0.002	0.002	4.58E-06	3.75E-06	0.002	0.002
R07	0.010	0.008	2.29E-05	1.88E-05	0.010	0.008
R01	1.221	1.047	4.03E-03	3.30E-03	1.225	1.050
R02	1.839	1.577	4.34E-03	3.55E-03	1.844	1.580
R03	1.709	1.465	2.88E-03	2.36E-03	1.712	1.467

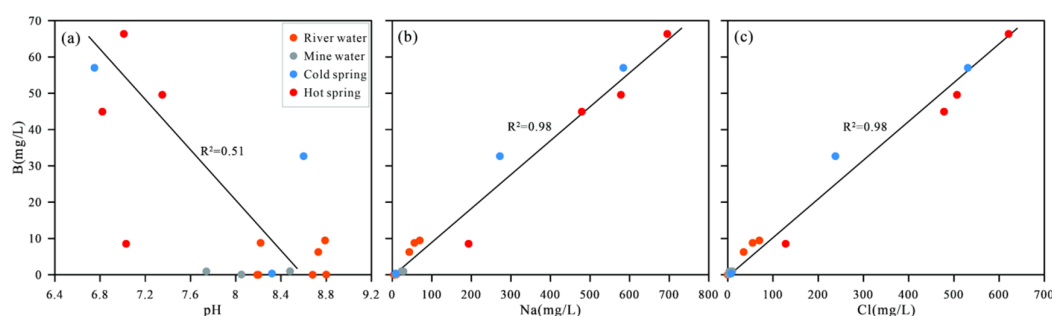
3. Fraction of Spring Water in River Water

Environmental tracer methods often use water chemical parameters [14], soluble components [15,16], and isotopes [17,18] to identify and quantify mixing between two water sources. In study area, the mixing ratio of river water and hot spring water is susceptible to many uncertainties, such as hidden faults in river channels, the number and flow rate of hot springs exposed near rivers, and so on.

Using the equation, the B concentrations in a binary system were used to calculate the fraction (*f*) of spring water in river water samples from Zhaxikang sampling sites. [19]:

$$f = (C_{mix} - C_{rw}) / (C_{sw} - C_{rw}) \quad (13)$$

where *f* is the fraction of spring water, *C_{mix}* is the B concentration (mg/L) of mixed river water downstream(R01), *C_{sw}* is the B concentration (mg/L) of the hot spring(average of S01, S06, and S07), and *C_{rw}* is the B concentration (mg/L) of river water from upstream(R07). The concentration of B is also controlled by pH, as Figure S1a shows that the correlation coefficient between B and pH can reach 0.51. It is clear from the well linear relationship between B, Na, and Cl that B is controlled by adsorption/dissolution in groundwater (Figure S1b & S1c).

**Figure S1.** Relationship of the B concentration with other measured hydrochemical parameters.

Reference

1. Li, P.; Qian, H.; Wu, J. Groundwater Quality Assessment Based on Improved Water Quality Index in Pengyang County, Ningxia,

- Northwest China. *E-Journal of Chemistry*. 2010, 7, 451304. <https://doi.org/10.1155/2010/451304>
2. Adimalla, N. Groundwater quality delineation based on fuzzy comprehensive assessment method (FCAM): a case study. *Arab J Geosci*. 2020, 13, 1-9. <https://doi.org/10.1007/s12517-020-06265-y>
3. Chen, F.; Yao, L.; Mei, G.; Shang, Y.; Xiong, F.; Ding, Z. Groundwater Quality and Potential Human Health Risk Assessment for Drinking and Irrigation Purposes: A Case Study in the Semiarid Region of North China. *Water*, 2021, 13(6). <https://doi.org/10.3390/w13060783>
4. Ugran, V. Groundwater fluoride contamination and its possible health implications in Indi taluk of Vijayapura District (Karnataka State), India. *Environ Geochem Health*, 2017, 39, 1017-1029. <https://doi.org/10.1007/s10653-016-9869-2>
5. Liu, M.; Guo, Q.; Luo, L.; He, T. Environmental impacts of geothermal waters with extremely high boron concentrations: Insight from a case study in Tibet, China. *Journal of Volcanology and Geothermal Research*, 2020, 397. <https://doi.org/10.1016/j.jvolgeores.2020.106887>
6. Sathe, S.; Mahanta, C.; Subbiah, S. Hydrogeochemical Evaluation of Intermittent Alluvial Aquifers Controlling Arsenic and Fluoride Contamination and Corresponding Health Risk Assessment. *Exposure and Health*. 2021. <https://doi.org/10.1007/s12403-021-00411-x>
7. Zhang, Y.; Wu, J.; Xu, B. Human health risk assessment of groundwater nitrogen pollution in Jinghui canal irrigation area of the loess region, northwest China. *Environmental Earth Sciences*, 2018, 77. <https://doi.org/10.1007/s12665-018-7456-9>
8. USEPA. Human health evaluation manual, supplemental guidance: Update of standard default exposure factors, United States Environmental Protection Agency, Washington, DC, 2014.
9. USEPA. Integrated risk information system, United States Environmental Protection Agency, Washington, DC, 2012.
10. Li, P.; Tian, R.; Liu, R. Solute Geochemistry and Multivariate Analysis of Water Quality in the Guohua Phosphorite Mine, Guizhou Province, China. *Exposure and Health*, 2019, 11, 81-94. <https://doi.org/10.1007/s12403-018-0277-y>
11. Wu, J.; Sun, Z. Evaluation of Shallow Groundwater Contamination and Associated Human Health Risk in an Alluvial Plain Impacted by Agricultural and Industrial Activities, Mid-west China. *Exposure and Health*, 2016, 8, 311-329. <https://doi.org/10.1007/s12403-015-0170-x>
12. Adimalla, N.; Qian, H. Groundwater quality evaluation using water quality index (WQI) for drinking purposes and human health risk (HHR) assessment in an agricultural region of Nanganur, south India. *Ecotoxicol Environ Saf*, 2019, 176, 153-161. <https://doi.org/10.1016/j.ecoenv.2019.03.066>
13. Zango, M.; Sunkari, E.; Abu, M.; Lermi, A. Hydrogeochemical controls and human health risk assessment of groundwater fluoride and boron in the semi-arid North East region of Ghana. *Journal of Geochemical Exploration*, 2019, 207. <https://doi.org/10.1016/j.gexplo.2019.106363>
14. Edet, A.; Worden, R. Monitoring of the physical parameters and evaluation of the chemical composition of river and groundwater in Calabar (Southeastern Nigeria). *Environ Monit Assess*, 2009, 157, 243-58. <https://doi.org/10.1007/s10661-008-0532-y>
15. Davis, S.; Whittemore, D.; Fabryka-Martin, J. Uses of Chloride/Bromide Ratios in Studies of Potable Water. *Ground water*, 1998, 36, 338-350. <https://doi.org/10.1111/j.1745-6584.1998.tb01099.x>
16. Rautio, A.; Korkka-Niemi, K. Chemical and isotopic tracers indicating groundwater/surface-water interaction within a boreal lake catchment in Finland. *Hydrogeology Journal*, 2015, 23, 687-705. <https://doi.org/10.1007/s10040-015-1234-5>
17. Dun, Y.; Tang, C.; Shen, Y. Identifying interactions between river water and groundwater in the North China Plain using multiple tracers. *Environmental Earth Sciences*, 2013, 72, 99-110. <https://doi.org/10.1007/s12665-013-2989-4>
18. Lamontagne, S. River infiltration to a subtropical alluvial aquifer inferred using multiple environmental tracers. *Water Resources Research*, 2015, 51, 4532-4549. <https://doi.org/10.1002/2014wr015663>
19. Crandall, C.; Katz, B.; Hirten, J. Hydrochemical evidence for mixing of river water and groundwater during high-flow conditions, lower Suwannee River basin, Florida, USA. *Hydrogeology Journal*, 1999, 7, 454-467. <https://doi.org/10.1007/s100400050218>