**Supplementary Material Cover Sheet**

Hydrochemical characteristics and quality assessment of shallow groundwater in Yangtze River Delta of eastern China

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Number of figures: 7

*Procedures for groundwater sample collection*

Before sample collection, the inside of the well was cleaned by pumping the groundwater for 5–10 mins. Then, the groundwater was collected in a beaker for the next filtration run. The filtered groundwater was preserved in two 50 mL HDPE bottles for ion analysis and one 200 mL HDPE bottle for carbonic acid titration. These HDPE bottles had been cleaned thoroughly to remove impurities based on the method in our previous studies (Peng et al., 2021a; Peng et al., 2021b), and prior to collection, these bottles had been rinsed by filtered groundwater several times. Groundwater in one 50 mL HDPE bottle was acidified to pH < 2 by adding concentrated nitric acid for cation analysis. The groundwater in another 50 mL and 200 mL HDPE bottles was prepared for anion analysis and carbonic acid titration. These bottles were placed in the incubator with ice bags after collection, then transported immediately to the laboratory. All groundwater samples were preserved in the cold room at 4°C for further analysis.

*Water sample measurement*

Since some indicators are sensitive to environmental changes, parameters such as TDS and pH were measured on-site using a portable analyzer (HQ40D). The concentration of anions like F-, Cl-, NO3-, Br- and SO42- were measured by ion chromatography (IC,761COMPACTIC, Metrohm AG) after the groundwater was filtered by 0.22 μm membrane (Sartorius Minisart). Besides, the concentration of CO32- and HCO3- were detected by standard HCl titration using methyl orange and phenolphthalein as indicators. The contents of cations like Ca, Mg, Na, K, As, Cd, Cr, Pb, Fe, Mn, Cu, Zn, Ag, Al, Sr, Se, Ba, Be, B, Li, Mo, Hg, Co, Sb, and Rb were obtained by the inductively coupled plasma emission mass spectrometer (ICP-MS, Agilent 7700, Agilent). In order to guarantee the reliability of the measurement, except for the initial calibration curve, new calibration lines were established after measuring every 10 samples. In addition, the standard solutions (8500-6940, Agilent) were applied to check the accuracy of the measurement. It turned out that the recovery rate of standard solution ranged from 90% to 110%, which indicated that the relative standard deviations of the samples were all < 10%. For further checking and improving the data quality, the charge balance errors of all groundwater samples were within 5%, and the electrical conductivity values of the samples were linearly related to the calculated TDS values. It is worth note that the chemical reagents used in this research were analytical grade.

*Method to calculate the HI*

HI could be obtained by the following Eqs.(1–5) (Dippong et al., 2020; Peng et al., 2021a):

Chronic daily intake by oral ingestion: (1)

Chronic daily intake by dermal absorption: (2)

Non-carcinogenic risk is expressed by hazard quotient: (3)

(4)

(5)

Where and are the health risk caused by oral ingestion and dermal absorption; C is chemical concentration in water; IR is ingestion rate; EF is exposure frequency; ED is exposure duration; BW is body weight; AT is averaging time; SA is skin surface area available for contact; ET is exposure time. CF is the volume conversion factor. KP is the dermal permeability coefficient of a compound in water; RfDo is the reference dose oral; RfDd is the absorbed reference dose. The values of these parameters could be found in Table S4 and Table S5.

**Table S1.** Weight indicator of element i ranging from 1 to 5

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Indicator j | CNS | *P*j | *P*j reference | *w*j1 | *w*j2 | *W*j |
| TH(mg/L) | 450 | 2 | (Xiao et al. 2014; Xiao et al. 2019) | 0.0364 | 0.0891 | 0.0487 |
| TDS(mg/L) | 1000 | 4 | 0.0727 | 0.0638 | 0.0698 |
| Na(mg/L) | 200 | 2 | 0.0364 | 0.0673 | 0.0368 |
| Fe(mg/L) | 0.3 | 4 | 0.0727 | 0.0339 | 0.0371 |
| As(mg/L) | 0.01 | 5 | 0.0909 | 0.0830 | 0.1135 |
| Ni(mg/L) | 0.02 | 1 | 0.0182 | 0.0487 | 0.0133 |
| Cr(mg/L) | 0.05 | 5 | 0.0909 | 0.0585 | 0.0800 |
| B(mg/L) | 0.5 | 3 | 0.0545 | 0.0974 | 0.0799 |
| Al(mg/L) | 0.2 | 2 | 0.0364 | 0.0635 | 0.0347 |
| Cl-(mg/L) | 250 | 3 | 0.0545 | 0.0325 | 0.0267 |
| SO42-(mg/L) | 250 | 4 | 0.0727 | 0.1306 | 0.1429 |
| NO3-(mg/L) | 88.57 | 5 | 0.0909 | 0.0910 | 0.1244 |
| Mn(mg/L) | 0.1 | 5 | 0.0909 | 0.0337 | 0.0461 |
| F-(mg/L) | 1.0 | 5 | 0.0909 | 0.0822 | 0.1124 |
| Se(mg/L) | 0.01 | 5 | (Sahu and Sikdar 2008) | 0.0909 | 0.0246 | 0.0336 |
| Note: CNS is China National Standard for Drinking Water Quality (GB5749-2006) | | | | | | |

**Table S2.** The calculated values of WQI and HI

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample NO. | WQI | HQdermal | HQoral | HI | Sample NO. | WQI | HQdermal | HQoral | HI |
| 1 | 103.59 | 0.0116 | 4.6898 | 4.7014 | 32 | 37.30 | 0.0053 | 1.0074 | 1.0127 |
| 2 | 30.37 | 0.0039 | 0.7369 | 0.7409 | 33 | 32.10 | 0.0030 | 0.4926 | 0.4957 |
| 3 | 36.86 | 0.0080 | 0.5038 | 0.5118 | 34 | 46.45 | 0.0029 | 0.4766 | 0.4795 |
| 4 | 17.42 | 0.0021 | 0.2953 | 0.2974 | 35 | 42.82 | 0.0019 | 0.5361 | 0.5380 |
| 5 | 61.36 | 0.0076 | 2.7948 | 2.8024 | 36 | 110.20 | 0.0204 | 9.5341 | 9.5545 |
| 6 | 23.11 | 0.0062 | 0.2620 | 0.2682 | 37 | 37.90 | 0.0042 | 0.7343 | 0.7385 |
| 7 | 43.29 | 0.0078 | 1.1920 | 1.1998 | 38 | 33.79 | 0.0033 | 0.9589 | 0.9622 |
| 8 | 32.43 | 0.0046 | 0.4999 | 0.5045 | 39 | 67.05 | 0.0074 | 1.4381 | 1.4455 |
| 9 | 140.20 | 0.0403 | 8.9340 | 8.9744 | 40 | 26.54 | 0.0018 | 0.2618 | 0.2637 |
| 10 | 53.94 | 0.0133 | 0.7210 | 0.7344 | 41 | 39.72 | 0.0036 | 0.9733 | 0.9769 |
| 11 | 96.18 | 0.0143 | 3.6184 | 3.6328 | 42 | 42.00 | 0.0032 | 0.8051 | 0.8084 |
| 12 | 24.72 | 0.0042 | 0.5141 | 0.5182 | 43 | 40.36 | 0.0063 | 0.7759 | 0.7822 |
| 13 | 53.86 | 0.0039 | 1.3576 | 1.3614 | 44 | 44.53 | 0.0117 | 0.8268 | 0.8385 |
| 14 | 49.23 | 0.0084 | 1.2543 | 1.2627 | 45 | 42.72 | 0.0056 | 1.6067 | 1.6123 |
| 15 | 88.69 | 0.0120 | 4.7793 | 4.7913 | 46 | 41.25 | 0.0082 | 2.2809 | 2.2891 |
| 16 | 91.59 | 0.0074 | 2.8637 | 2.8711 | 47 | 45.70 | 0.0031 | 1.1541 | 1.1571 |
| 17 | 63.87 | 0.0027 | 0.6781 | 0.6808 | 48 | 48.37 | 0.0017 | 0.6301 | 0.6318 |
| 18 | 38.57 | 0.0069 | 1.4813 | 1.4882 | 49 | 33.61 | 0.0011 | 0.3203 | 0.3214 |
| 19 | 48.12 | 0.0216 | 0.5178 | 0.5394 | 50 | 54.99 | 0.0022 | 0.6461 | 0.6483 |
| 20 | 49.19 | 0.0068 | 0.5938 | 0.6006 | 51 | 59.32 | 0.0095 | 4.0962 | 4.1057 |
| 21 | 50.69 | 0.0053 | 0.6747 | 0.6800 | 52 | 22.11 | 0.0020 | 0.5676 | 0.5696 |
| 22 | 120.01 | 0.0212 | 9.3072 | 9.3284 | 53 | 43.55 | 0.0058 | 2.4451 | 2.4509 |
| 23 | 97.22 | 0.0245 | 1.7751 | 1.7996 | 54 | 64.48 | 0.0122 | 5.2552 | 5.2674 |
| 24 | 72.27 | 0.0067 | 1.5459 | 1.5526 | 55 | 22.72 | 0.0030 | 0.5402 | 0.5431 |
| 25 | 65.49 | 0.0103 | 3.1624 | 3.1727 | 56 | 27.75 | 0.0049 | 1.2219 | 1.2268 |
| 26 | 38.30 | 0.0051 | 0.8627 | 0.8677 | 57 | 54.91 | 0.0036 | 0.9386 | 0.9422 |
| 27 | 30.32 | 0.0045 | 1.3166 | 1.3211 | 58 | 58.58 | 0.0043 | 0.9520 | 0.9564 |
| 28 | 45.45 | 0.0031 | 0.9726 | 0.9757 | 59 | 32.76 | 0.0049 | 0.5240 | 0.5289 |
| 29 | 21.19 | 0.0027 | 0.6846 | 0.6873 | 60 | 35.87 | 0.0018 | 0.3817 | 0.3835 |
| 30 | 83.66 | 0.0120 | 5.2296 | 5.2416 | 61 | 80.71 | 0.0130 | 2.2524 | 2.2654 |
| 31 | 31.68 | 0.0031 | 0.5603 | 0.5634 |  |  |  |  |  |

**Table S3.** Correlation coefficients between element concentrations in groundwater in the study area

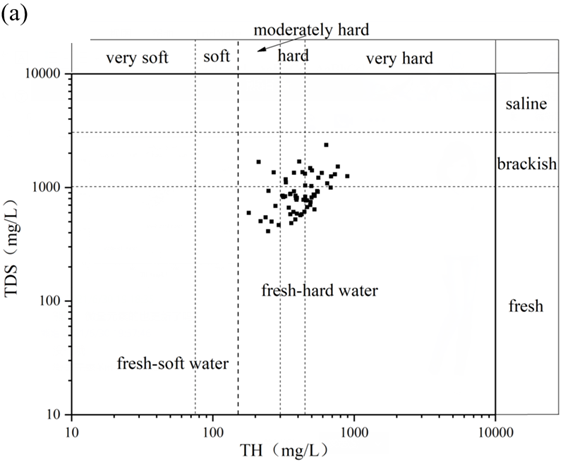
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Na | Mg | K | Ca | Cl- | HCO3- | SO42- | NO3- | Br- | F | B | Sr | Al | Fe | Mn | As | Se | Ni |
| Na | 1.000 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Mg | .432\* | 1.000 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| K | .406\* | .305 | 1.000 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Ca | -.428\* | .065 | -.447\* | 1.000 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Cl- | .830\* | .464\* | .281 | -.125 | 1.000 |  |  |  |  |  |  |  |  |  |  |  |  |  |
| HCO3- | .543\* | .782\* | .328\* | .025 | .481\* | 1.000 |  |  |  |  |  |  |  |  |  |  |  |  |
| SO42- | .197 | .556\* | .065 | .359\* | .321 | .430\* | 1.000 |  |  |  |  |  |  |  |  |  |  |  |
| NO3- | -.043 | .039 | .128 | .308 | .029 | -.027 | .220 | 1.000 |  |  |  |  |  |  |  |  |  |  |
| Br- | .793\* | .594\* | .345\* | -.251 | .816\* | .622\* | .295 | -.019 | 1.000 |  |  |  |  |  |  |  |  |  |
| F- | .425\* | -.228 | .549\* | -.692\* | .180 | -.144 | -.310 | .018 | .241 | 1.000 |  |  |  |  |  |  |  |  |
| B | .776\* | .476\* | .650\* | -.534\* | .578\* | .520\* | .147 | .132 | .761\* | .557\* | 1.000 |  |  |  |  |  |  |  |
| Sr | .058 | .586\* | -.176 | .556\* | .267 | .522\* | .393\* | .007 | .237 | -.568\* | -.099 | 1.000 |  |  |  |  |  |  |
| Al | .200 | .134 | .096 | -.018 | .078 | .209 | .048 | .239 | .099 | .046 | .206 | .030 | 1.000 |  |  |  |  |  |
| Fe | .319 | .477\* | .183 | -.151 | .218 | .383\* | .133 | -.115 | .358\* | -.078 | .346\* | .284 | .410\* | 1.000 |  |  |  |  |
| Mn | .302 | .293 | .128 | -.030 | .273 | .316 | .124 | -.216 | .336\* | -.130 | .180 | .240 | .383\* | .748\* | 1.000 |  |  |  |
| As | .210 | .179 | .139 | -.319 | .265 | .105 | -.173 | -.336\* | .240 | .010 | .235 | .116 | .027 | .416\* | .377\* | 1.000 |  |  |
| Se | .361\* | .225 | .242 | -.274 | .114 | .331\* | -.054 | -.107 | .224 | .213 | .429\* | -.017 | .267 | .408\* | .277 | .282 | 1.000 |  |
| Ni | .197 | -.003 | -.036 | -.052 | .161 | .044 | -.010 | .030 | .189 | .152 | .158 | .041 | .128 | .254 | .178 | .071 | .031 | 1.000 |
| Note: \* means significant correlation at the 0.01 level. | | | | | | | | | | | | | | | | | | |

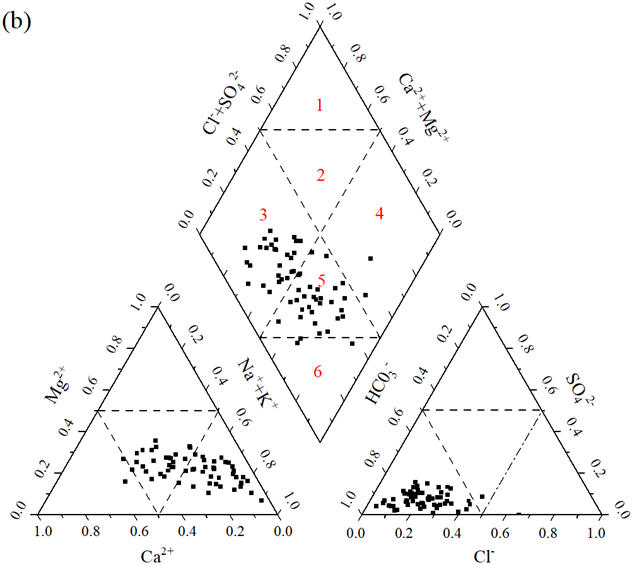
**Table S4.** Parameters for health risk assessment calculation

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | Unit | Value（Children） | References |
| IR (ingestion rate) | L/d | 1.0 | Chinese Ministry of Environment Protection (2013) |
| EF (exposure frequency) | days/year | 350 | USEPA (2004); USEPA (1991) |
| ED (exposure duration) | year | 6 | USEPA (2004); USEPA (1991) |
| BW (body weight) | kg | 26.8 | Chinese Ministry of Environment Protection (2013) |
| AT (average lifespan) | days | AT = ED \*365 d/y | USEPA (1991) |
| ET(exposure time) | h/day | 0.22 | Chinese Ministry of Environment Protection (2013) |
| SA (skin surface area) | cm2 | 9400 | Chinese Ministry of Environment Protection (2013) |

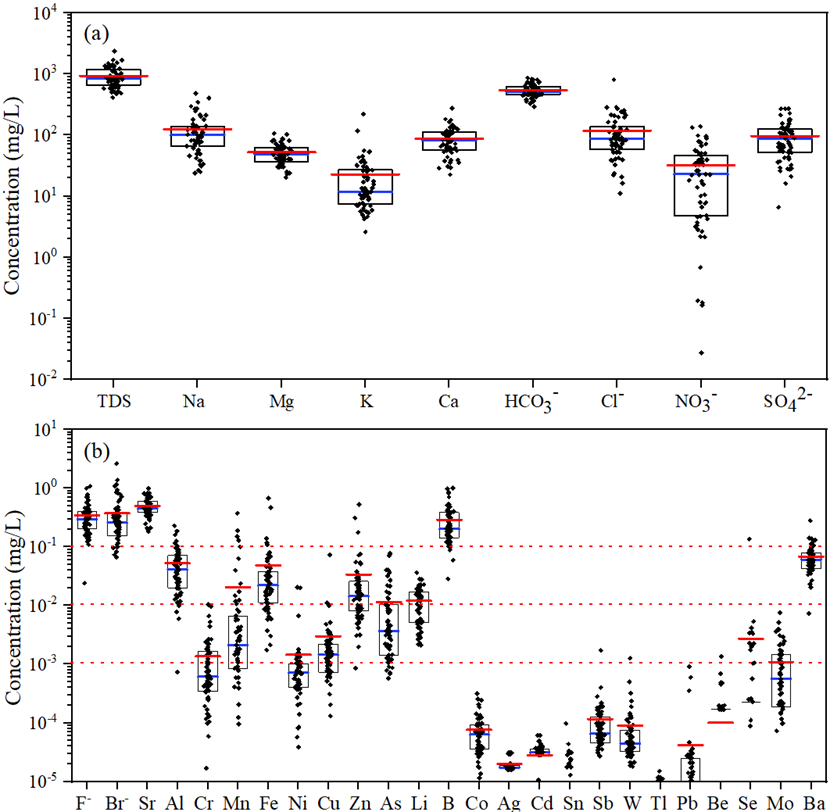
**Table S5.** Values of skin permeability coefficient (Kp) and the reference dose (RfD) of each element

|  |  |  |  |
| --- | --- | --- | --- |
| Element | Kp  (cm/h) | RfDo  (mg/kg/day) | RfDd  (mg/kg/day) |
| Cr | 2×10-3 | 0.003 | 0.000075 |
| As | 1×10-3 | 0.0003 | 0.000285 |
| Cd | 1×10-3 | 0.0005 | 0.000025 |
| Pb | 1×10-4 | 0.0014 | 0.00042 |
| Sr | 1×10-3 | 0.6 | 0.12 |
| Li | 1×10-3 | 0.02 | 0.01 |
| Be | 1×10-3 | 0.002 | 0.001 |
| Al | 1×10-3 | 1 | 0.2 |
| V | 1×10-3 | 0.005 | 0.00001 |
| Mn | 1×10-3 | 0.14 | 0.00096 |
| Fe | 1×10-3 | 0.7 | 0.14 |
| Ni | 2×10-4 | 0.02 | 0.0008 |
| Cu | 1×10-3 | 0.04 | 0.012 |
| Zn | 6×10-4 | 0.3 | 0.06 |
| Se | 1×10-3 | 0.005 | 0.0022 |
| Mo | 1×10-3 | 0.005 | 0.0019 |
| Ba | 1×10-3 | 0.2 | 0.014 |
| B | 1×10-3 | 0.2 | 0.18 |
| Ag | 6×10-4 | 0.005 | 0.0009 |
| Sn | 1×10-3 | 0.6 | 0.06 |
| Sb | 1×10-3 | 0.0004 | 0.000008 |
| Co | 4×10-4 | 0.0003 | 0.00006 |
| Tl | 1×10-3 | 0.00001 | 0.00001 |
| Note: data from USEPA (2004), USEPA (2016), USEPA (2019), Xiao et al. (2019) and Wu et al. (2009) | | | |

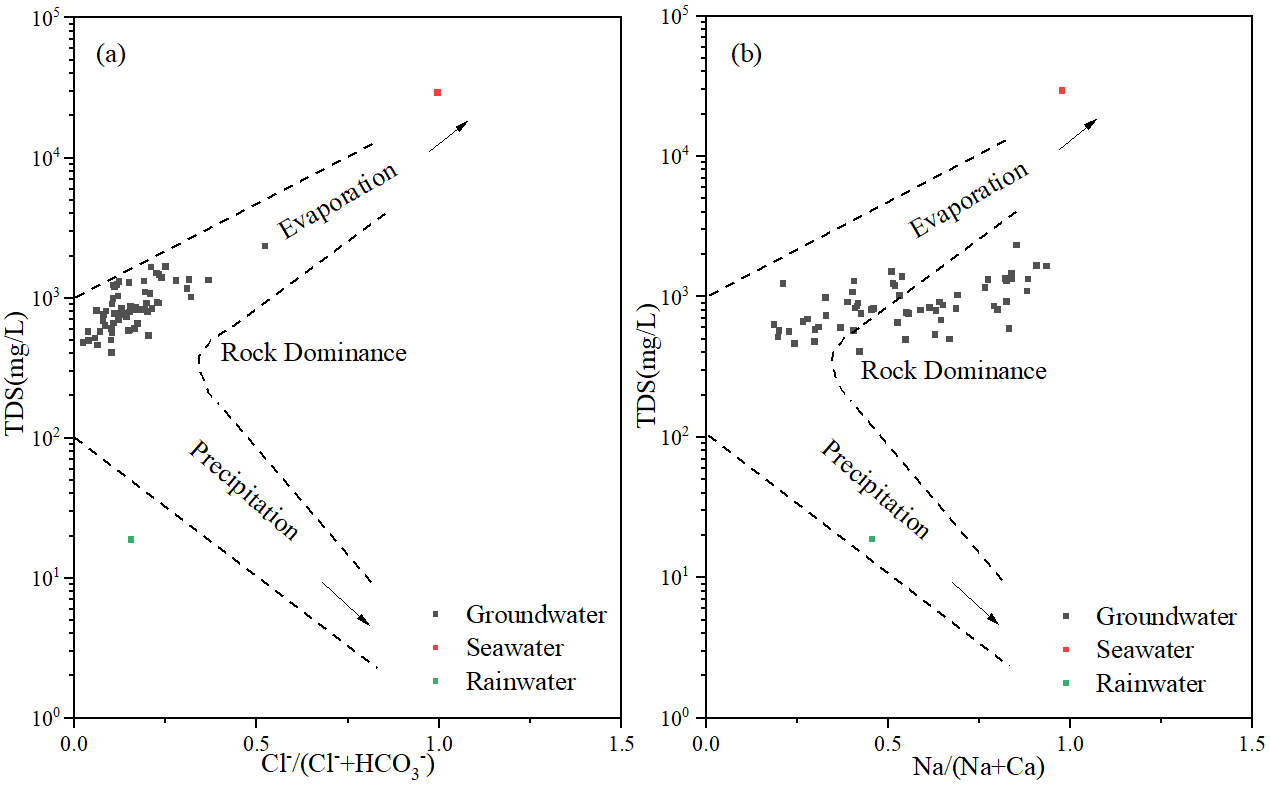




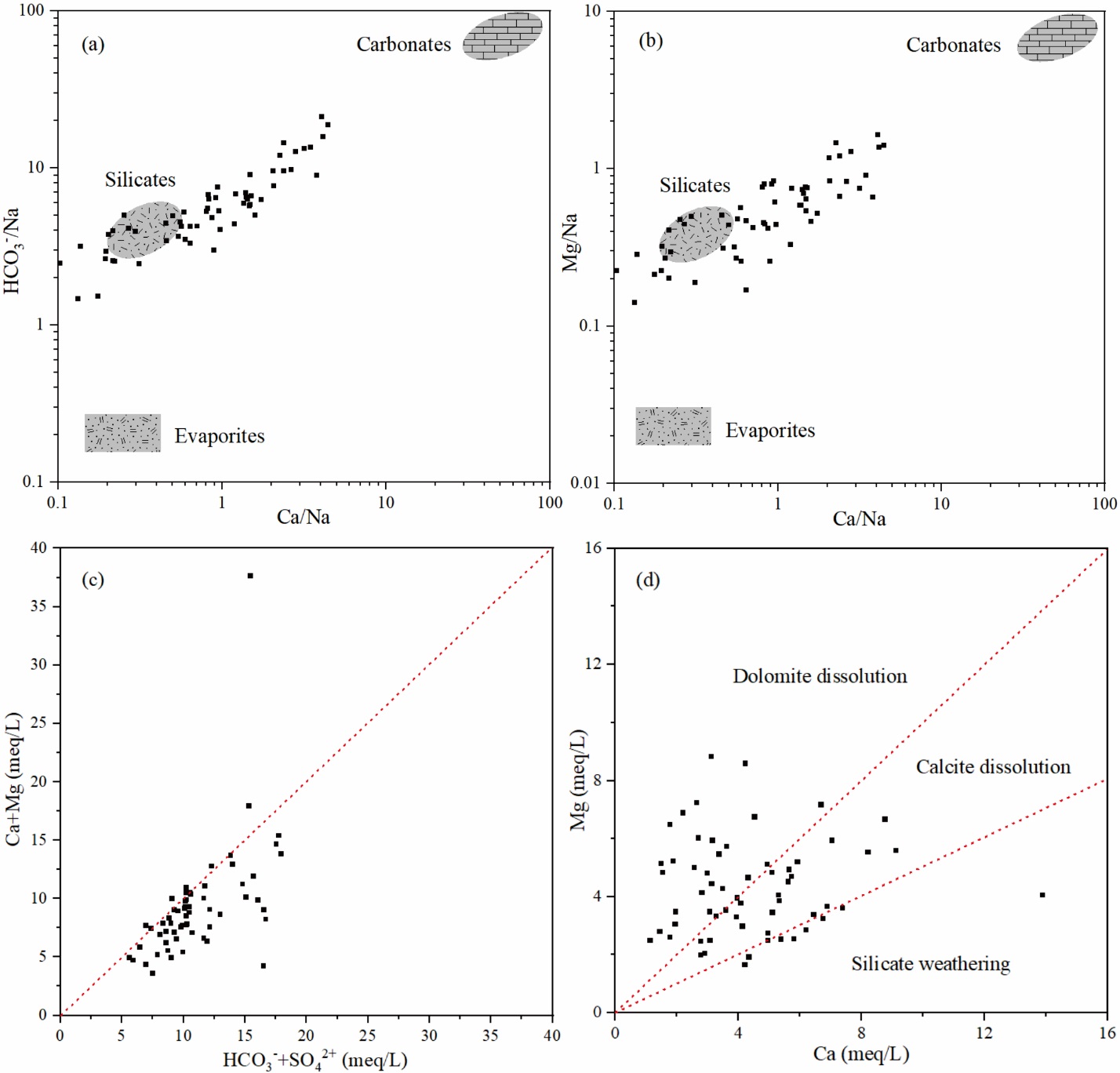
**Fig. S1** (a) The evaluation of groundwater hardness in the study area; (b) Piper diagrams showing proportions among the major chemical components for all water samples. Hydrochemical facies (Piper diagram): 1: Ca-Cl, 2: Ca/Mg-Cl, 3: Ca/Mg-HCO3, 4: Na-Cl, 5: Ca/Na-HCO3, 6: Na-HCO3.



**Fig. S2** Box plots of major elements (a) and trace elements (b).



**Fig. S3** Gibbs diagrams of groundwater in the study area: (a) TDS vs. Cl-/(Cl-+HCO3-); (b) TDS vs. Na/(Na+Ca).

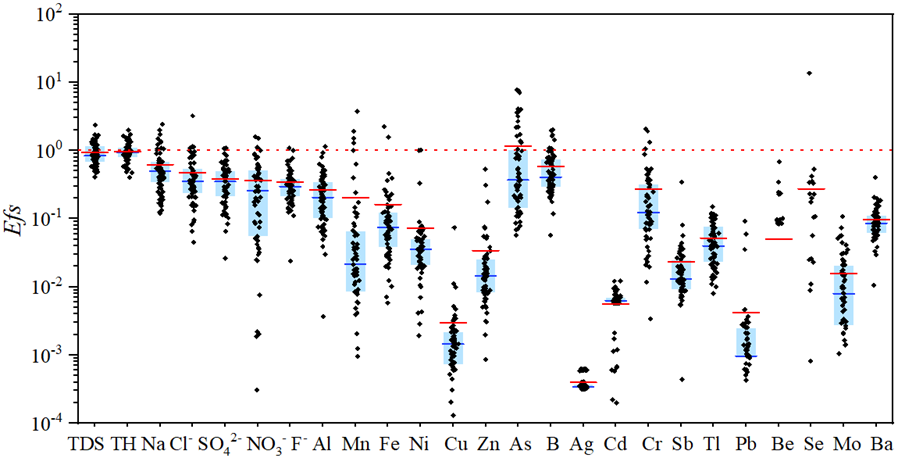


**Fig. S4** Ion ratios in groundwater in the study area: (a) HCO3-/Na vs. Ca/ Na; (b) Mg/Na vs. Ca/Na; (c) (Ca+Mg)/(HCO3-+SO42- ratio; (d) Mg/Ca ratio.

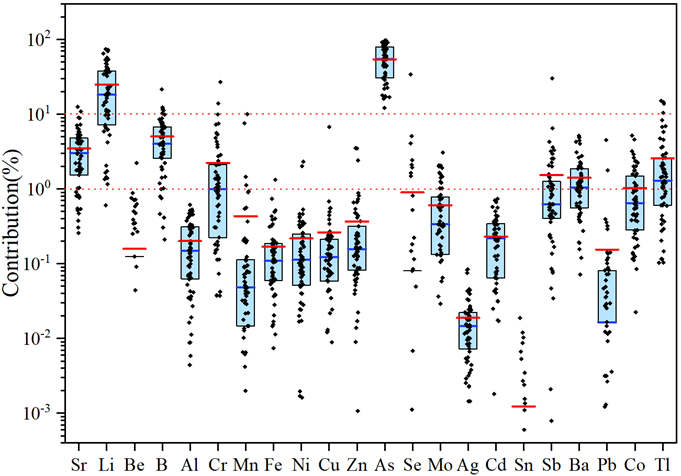
图示

描述已自动生成

**Fig. S5** The spatial distributions of the seawater intrusion fraction in the study area.



**Fig. S6** Enrichment patterns of elements in the groundwater samples in the study area, compared to those in standards for drinking water quality (GB5749-2006). *Efs*=elements of the studied water samples vs. those of the Chinese national standard for drinking water quality.



**Fig. S7** The contribution of trace elements in groundwater samples to the non-carcinogenic risks.

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