

The Human Health Risk Assessment and Countermeasures Study of Groundwater Quality

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1 **The human health risk assessment and countermeasures**
2 **study of groundwater quality**

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16 **Abstract**

17 **Background:** Groundwater serves as the drinking water source, which chemical
18 components directly affect human health. Different regions own their groundwater
19 hydro-chemical characteristics based on various geological, hydro-geological
20 conditions, human activities. From the perspective of human health, it is necessary to
21 select groundwater quality health risk assessment (*GQHR*) factors combined with

22 hydro-chemical characteristics of different regions.

23 **Methods:** In this paper, taking Tongzhou of Beijing,China as the study area,
24 according to the groundwater hydro-chemical characteristics, NO_3^- , NO_2^- , NH_4^+ and
25 F^- were extracted as assessment factors to evaluate the *GQHR*. Based on *GQHR*
26 results, the formation and concentration characteristics of health risk factors and the
27 prominent controlling role of influencing risk distribution were explored from natural
28 and human factors. Furthermore, the targeted measures to prevent the increase of
29 groundwater health risk were put forward.

30 **Results:** Assessment factors: NO_3^- , NO_2^- and NH_4^+ are derived by human factors,
31 such as sewage irrigation, fertilization, and F^- stems from irrigation of geogenic high
32 fluoride groundwater and fertilizer use. Still, their distribution is affected by natural
33 factors (geology, geomorphology, and climate). The *GQHR* follows the order:
34 children > adult females > adult males. The low and medium risk regions are located
35 in upper groundwater, which are mainly controlled by natural factors (groundwater
36 depth, aquifer medium, hydraulic conductivity coefficient, etc.) The measures to
37 prevent the increase of groundwater health risk are to control the pollution sources
38 and reduce the change of groundwater hydrodynamic conditions. The high-risk
39 regions are located in eastern part of the study area, which are affected by both natural
40 and human factors. The preventative measures are to reduce pollution caused by
41 human factors and scientific groundwater resource exploitation and management.

42 **Conclusions:** In this study, corresponding preventative and control measures were

43 proposed for health risks caused by different dominant control effects. Meanwhile, the
44 research results provide a scientific basis for the safety of groundwater supply and
45 environmental exposure in this area. The research ideas and methods can be used as a
46 reference for similar studies.

47 **Key words:** groundwater pollution; human health risk; nature factors; human factors

48 **Background**

49 All over the world, more than 1.5 billion people depend on groundwater for
50 drinking water supply [1]. In China, over 400 among 655 cities (about 61%) rely on
51 groundwater as a drinking water source [2]. According to World Health Organization
52 (WHO), 80% of human diseases are caused by poor water quality [3,4]. With the
53 rapid development of human society, the degree of changes in groundwater quality
54 caused by human activities is gradually increasing [5-7], which significantly affects
55 the hydro-chemical characteristics of groundwater.

56 In the natural environment, groundwater maintains stable material and energy
57 exchange with the surrounding environment, and hydro-chemical components in
58 groundwater maintain balance. However, hydro-chemical components in the natural
59 groundwater are higher in some areas due to their geological conditions [8]. For
60 example, the geogenic high-arsenic groundwater has been found in the United States,
61 Canada, Bangladesh, Vietnam and China [9-12]. With the increasing intervention of
62 human activities on the natural environment, such as the rapid growth of population,
63 frequent agricultural activities, and rapid development of industry, the exchange

64 balance between groundwater and stratigraphic media under natural conditions has
65 been destroyed, leading to changes in the hydro-chemical characteristics of
66 groundwater in some areas [13-15]. In most cases, the evolution of hydro-chemical
67 composition in groundwater will have a deterioration effect on the groundwater
68 environment and lead to groundwater pollution [16-18]. For instance, in the process of
69 agricultural development, excessive use of nitrogen fertilizer caused groundwater
70 pollution. Groundwater in the United States, some parts of Europe, Belgium, France,
71 Spain, Portugal, Greece, and other countries are polluted by nitrate in different
72 degrees [19-22].

73 The hydro-chemical characteristics of groundwater are influenced by both
74 natural and human activities [23]. Different dominant factors lead to different
75 groundwater hydro-chemical characteristics. In order to ensure the safety of
76 groundwater supply, it is essential to clarify the hydro-chemical characteristics of
77 groundwater caused by different dominant factors. Water-rock interaction is an
78 important process of groundwater hydro-chemical origin, and defining its type is very
79 important. In recent years, with the development of numerical simulation techniques,
80 a large number of studies focus on quantitatively analyze the water-rock interaction
81 and sources of pollutants that affect the origin of groundwater by inverse
82 hydrogeochemical simulation [24,25]. For example, PHREEQC was used to
83 quantitatively analyze the hydro-chemical distribution and zonation characteristics of
84 Yinchuan Plain in China [26], and identified the source of fluorine in the groundwater

85 of the North China Plain that mainly came from the dissolution of fluorite in aquifer
86 medium [27].

87 Pollutants entering groundwater can affect groundwater quality and cause
88 varying degrees of hazard to human health [28,29]. Long-term drinking and contact
89 with contaminated groundwater will cause an irreversible impact on human health
90 [30-33]. For example, fluoride is one of the essential trace elements for human health,
91 too high or too low of fluoride intakes will pose a significant health risk to human
92 body, and a high level will lead to fluorosis, a low level will lead to dental caries
93 [34-36]. To clarify the health hazards caused by contaminants in the environment and
94 quantitatively calculate the potential health risk of pollutants to human health. The
95 United States Environmental Protection Agency (USEPA) proposed a health risk
96 assessment model—commonly used for carcinogenic and non-carcinogenic risk
97 assessment of groundwater contamination in 1991[37-39]. Then in 2014, the Ministry
98 of Environmental Protection of China, combined with China's unique humanity,
99 geological and natural conditions, proposed a groundwater quality human health risk
100 assessment (*GQHR*) model [40,41]. The *GQHR* model can be used in any conditions.
101 Still, due to the difference of natural environment and human activities in different
102 regions, the crucial controlling factors of the origin and evolution of groundwater
103 hydro-chemical characteristics are various. Hence, the assessment index should be
104 selected by the characteristic components combined with the actual situation in the
105 health risk assessment.

106 The main objective of this study is to select the *GQHR* assessment factors,
107 combined with hydro-chemical characteristics of groundwater in Tongzhou, a typical
108 area of North China Plain. Based on the assessment results, the natural and human
109 factors affecting the spatial distribution of *GQHR* are analyzed. Then, the targeted
110 countermeasures to prevent the increase of *GQHR* in different level risk areas are put
111 forward. The research results are of great significance to the safety of groundwater
112 supply and the development of economic and social in this area.

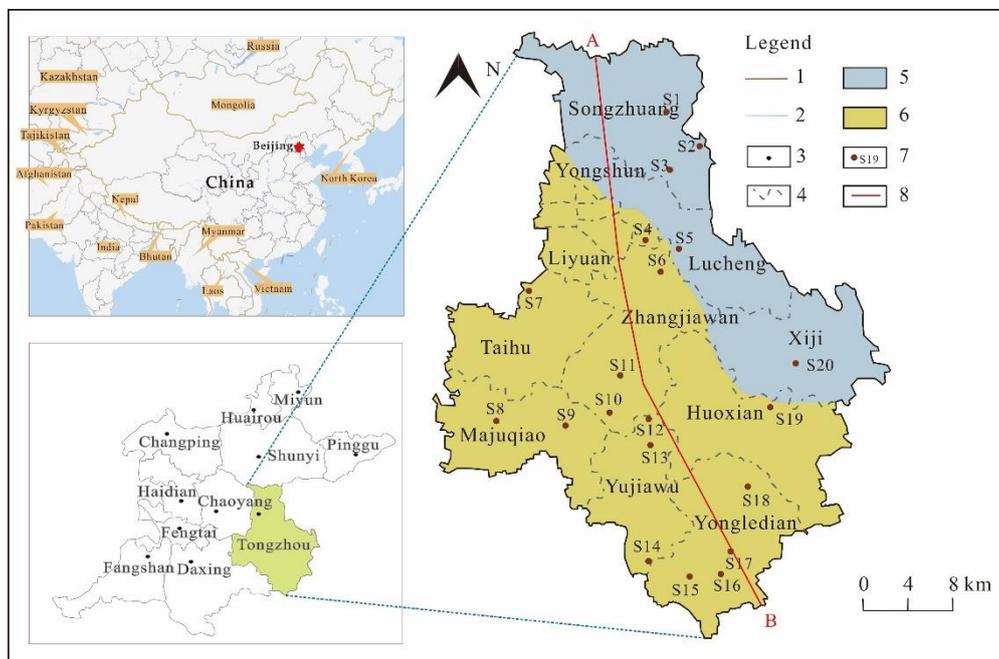
113 **Methods**

114 **Location**

115 Tongzhou District is located in the southeast of Beijing, China, covering an area
116 of 907 km² (Fig. 1). It is situated on the axis of the Beijing-Tianjin Economic Belt.
117 Due to its geographical advantages, Tongzhou has become the base of grain
118 production, vegetable production, non-staple food supply, receiving the evacuated
119 population, and industrial enterprises in Beijing. As one of the critical developing
120 satellite cities of Beijing, groundwater in Tongzhou undertakes the task of water
121 supply for residents. In recent years, groundwater in the study area has been strongly
122 affected by human activities; because of the change of land use type, the accelerated
123 construction of public facilities, and the rapid growth of population.

124 The study area is a continental monsoon climate with an average temperature of
125 11.3 °C. Average annual precipitation of 620 mm, 85% of which is concentrated from
126 June to September. Groundwater flows from northwest to southeast.

127 The terrain in the study area is gentle and slopes from northwest to southeast. In
 128 terms of hydrogeological units, it is located at the fan margin of Chaobai River
 129 alluvial-pluvial fan and Yongding River alluvial-pluvial fan. The surface is covered by
 130 the Quaternary strata, and groundwater mainly exists in it. The aquifer of the
 131 Quaternary aquifer system in the study area is interbedded with sand layers and clay
 132 layers, and the multi-layer arrangement involves thin sand layers divided by
 133 discontinuous heavy silt-and-clay layers. The aquifer is mainly recharged by
 134 precipitation, river infiltration, groundwater lateral runoff, and irrigation return. The
 135 main discharge involves exploitation (for agricultural irrigation) and southeast lateral
 136 runoff. The object of this study is the shallow groundwater with a buried depth of
 137 40~60m.



138
 139 **Fig. 1** Location of Tongzhou and sampling sites. (1) Boundary of Beijing, (2) district boundary, (3)
 140 administrative district, (4) town boundary, (5) Chaobai river alluvial-pluvial fan, (6) Yongding river

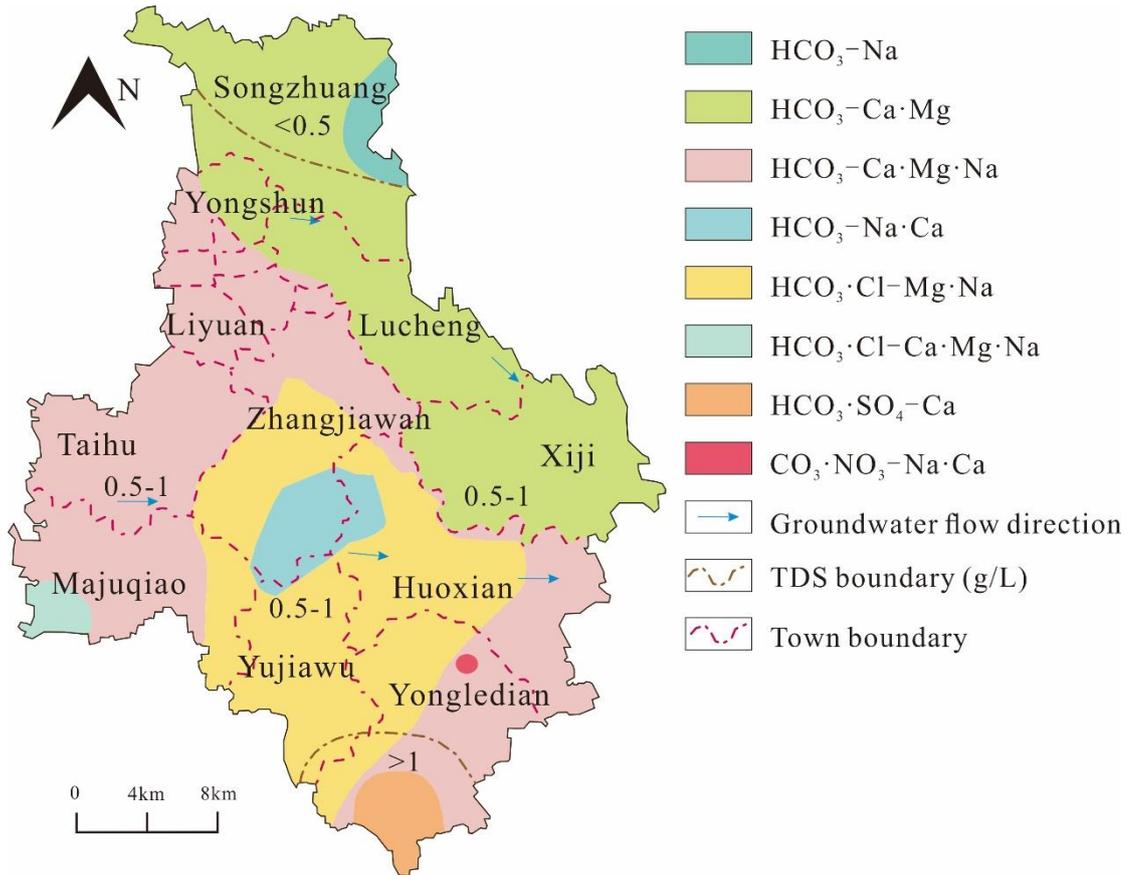
141 alluvial-pluvial fan, (7) groundwater samples, (8) section line.

142

143 **Hydrogeochemical characteristics and selection of risk factors**

144 In June 2017, 20 groundwater samples were collected from wells at a depth of 80
145 meters and used portable GPS to record the location (Fig 1). Samples were collected
146 and analyzed in accordance with the “Technical Specifications for Groundwater
147 Environmental Monitoring” (HJ/T164-2004). pH was measured in the field by a
148 portable water quality analyzer. K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , F^- ,
149 NO_3^- , NO_2^- , NH_4^+ and TDS were analyzed in the laboratory.

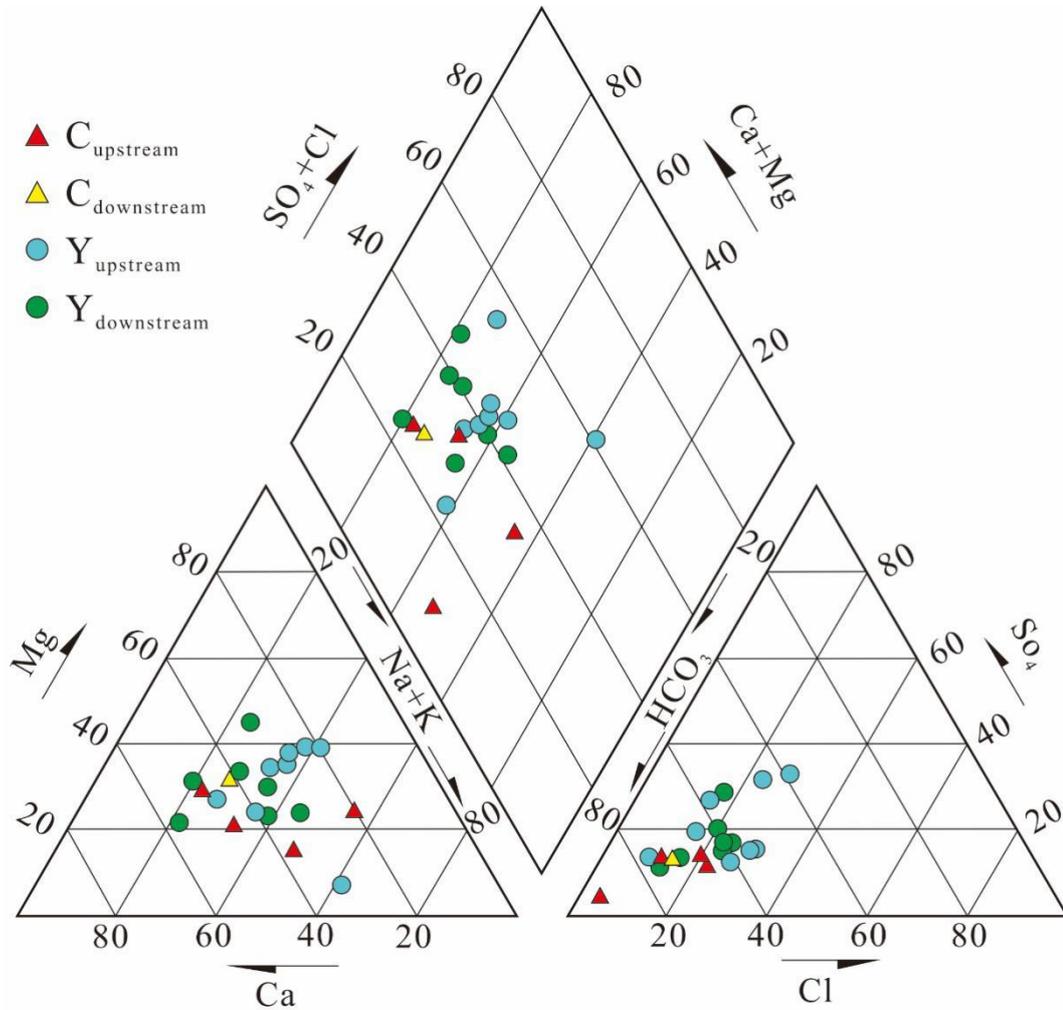
150 The groundwater hydro-chemical types are classified according to the Shukarev
151 classification method and showed in the zoning map (Fig. 2) and Piper diagrams (Fig.
152 3). Two pictures show that the hydro-chemical type of groundwater at the edge of
153 Chaobai River alluvial-pluvial fan is mainly $HCO_3-Ca \cdot Mg$ ($HCO_3-Ca \cdot Na$) type, and
154 HCO_3-Na type water is distributed locally in upper. The groundwater hydro-chemical
155 type at the edge of Yongding River alluvial-pluvial fan is mainly $HCO_3-Ca \cdot Mg \cdot Na$
156 type in upper and changes into $HCO_3-Cl \cdot Mg \cdot Na$ ($HCO_3-Cl \cdot Na \cdot Ca$) type in lower,
157 meanwhile the cations change from $Ca \cdot Mg \cdot Na$ ($Mg \cdot Ca$, $Ca \cdot Mg$) to $Mg \cdot Na$ ($Ca \cdot Na$,
158 $Na \cdot Ca$). The groundwater quality is getting worse with the direction of groundwater
159 flow.



160

161

Fig. 2 Hydro-chemical types zoning map



162

163 **Fig. 3** Piper diagram of groundwater samples. C_{upper}- samples in the upper of Chaobai river
 164 alluvial-pluvial fan; C_{lower}- samples in the lower of Chaobai river alluvial-pluvial fan; Y_{upper}-
 165 samples in the upper of Yongding river alluvial-pluvial fan; Y_{lower}- samples in the lower of
 166 Yongding river alluvial-pluvial fan.

167

168 The ranges of groundwater pH are from 6.97 to 7.84, presenting medium-weak
 169 alkaline. The total dissolved solids (TDS) increases with the direction of groundwater
 170 flow, which changes from <0.5g/L in upper to 0.5~1g/L in lower at the edge of
 171 Chaobai River alluvial-pluvial fan and changing from 0.5~1.0g/L in upper to >1.0 g/L

172 in lower at the edge of Yongding River alluvial-pluvial fan.

173 The results of counting the average content of ions in groundwater according to
 174 geomorphic units are shown in Table 1. (1) The content of each component at the edge
 175 of Chaobai River alluvial-pluvial fan is generally lower than that at the edge of
 176 Yongding River alluvial-pluvial fan. (2) In each geomorphic unit, the ion content
 177 generally increases from upper to lower. (3) The dominance of anions in groundwater
 178 is $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$, and for cations is $\text{Ca}^{2+} > \text{K}^+\text{+Na}^+ > \text{Mg}^{2+}$ ($\text{K}^+\text{+Na}^+$
 179 $> \text{Ca}^{2+} > \text{Mg}^{2+}$) according to their mean values. In general, HCO_3^- and Ca^{2+} are
 180 the dominant components, and $\text{K}^+\text{+Na}^+$ is higher than Ca^{2+} both in the upper of
 181 Chaobai River alluvial-pluvial fan and lower of Yongding River alluvial-pluvial fan.

182 **Table 1** Mean concentrations of ions.

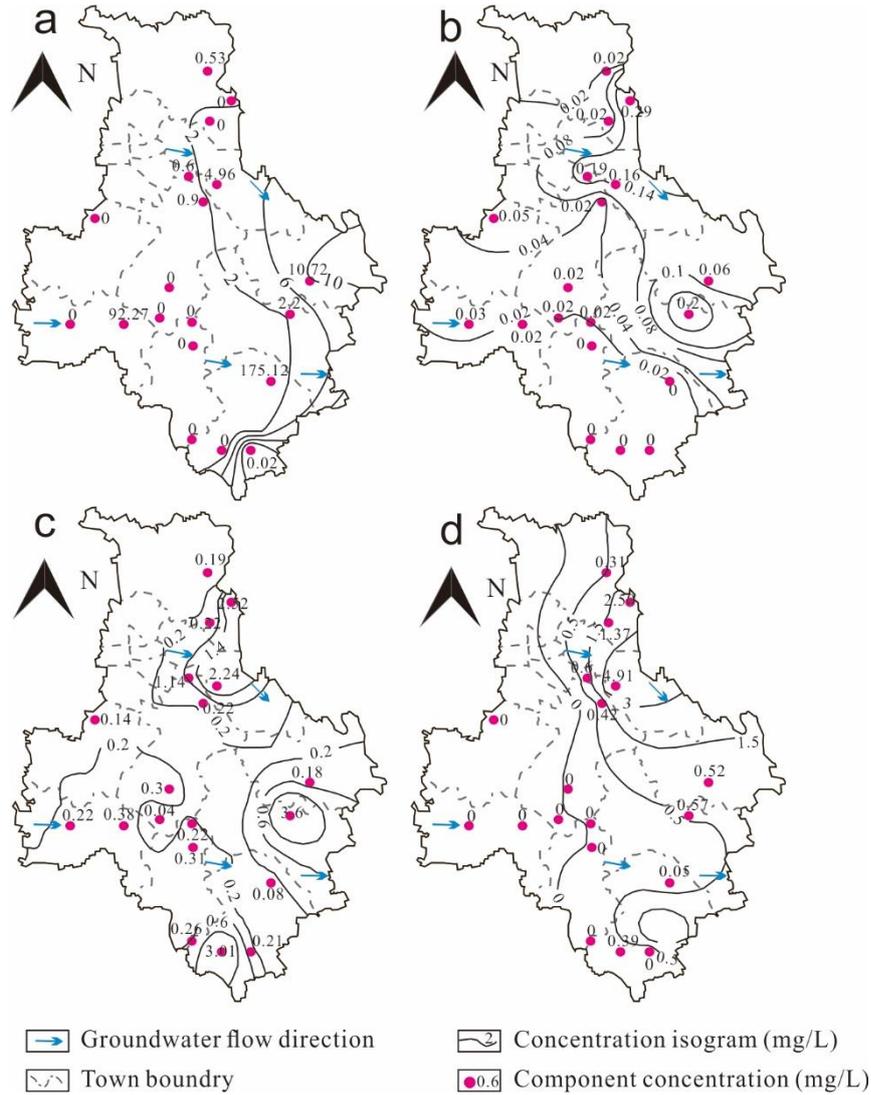
Geomorphic unit	Mean concentration of ions (mg/L)									
	$\text{K}^+\text{+Na}^+$	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	$\text{NO}_3\text{-N}$	$\text{NO}_2\text{-N}$	$\text{NH}_4\text{-N}$	F^-
<i>CRAPFU</i>	70.62	66.08	25.24	32.89	47.32	399.73	2.08	0.12	1.29	2.27
<i>CRAPFD</i>	90.33	112.57	42.09	86.45	83.00	556.23	10.72	0.06	0.18	0.52
<i>YRAPFU</i>	109.02	115.79	58.06	103.65	138.54	614.52	13.40	0.05	0.35	0.15
<i>YRAPFD</i>	160.43	112.86	71.18	142.08	188.76	604.08	25.04	0.03	0.98	0.35

183 **CRAPFU* : upper of Chaobai River alluvial-pluvial fan; *CRAPFD* : lower of Chaobai River
 184 alluvial-pluvial fan; *YRAPFU* : upper of Yongding River alluvial-pluvial fan; *YRAPFD* :lower of
 185 Yongding River alluvial-pluvial fan.

186

187 According to the China Drinking Water Standards ([GB5749-2006](#)) and
 188 concentration isogram distribution maps of nitrate nitrogen ($\text{NO}_3\text{-N}$), nitrite nitrogen

189 (NO₂-N), ammonia nitrogen (NH₄-N) and fluorine (F⁻) (Fig. 4). The concentration of
190 NO₃-N in groundwater ≤20mg/L in most areas and exceeds the standard only in
191 Majuqiao and Yongledian (92.27mg/L and 175.12mg/L, respectively). The
192 concentration of NO₂-N in Tongzhou is all ≤1.00mg/L. The concentration of NH₄-N
193 ≤0.5mg/L in most areas, and exceeded standard areas in Lucheng, Huoxian, and
194 Yongledian southern region, among them, the highest concentration of NH₄-N was
195 3.60mg/L, which was 7.2 times of the standard concentration. F⁻ ups to standard in
196 most areas, excessive points (>1.0mg/L) are mainly distributed at the edge of Chaobai
197 River alluvial-pluvial fan, and the maximum value was 4.91mg/L, which was 5 times
198 of the standard concentration.



199

200 **Fig. 4** Concentration isogram distribution map. (a) Nitrate nitrogen, (b) nitrite nitrogen, (c)
 201 ammonia nitrogen, (d) fluoride.

202 Due to the hydro-chemical characteristics of groundwater and considering that
 203 Tongzhou is a significant agricultural area accompanied by a large amount of use of
 204 nitrogen fertilizer, the *GQHR* factors in this study are selected as $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$,
 205 $\text{NH}_4\text{-N}$, and F.

206 **Groundwater Quality Human Health Risk Assessment**

207 The drinking water source in the study area mainly depends on groundwater, and

208 the most common exposure pathways are oral intake and dermal contact. In this study,
 209 quantified groundwater quality human health risk using (*GQHR*) assessment models
 210 proposed by the Ministry of Environmental Protection of the People's Republic of
 211 China from the above two pathways [41]. The models of oral intake and dermal
 212 contact are as follows.

213 1. oral intake model

$$\text{Intake}_{\text{oral}} = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (1)$$

$$\text{HQ}_{\text{oral}} = \frac{\text{Intake}_{\text{oral}}}{\text{RfD}_{\text{oral}}} \quad (2)$$

214 Where $\text{Intake}_{\text{oral}}$ denotes the daily average exposure dosage through the oral
 215 pathway (drinking water intake) per unit weight (mg/(kg·d)). C indicates the
 216 concentration of the factors tested in the library in groundwater (mg/L). IR implies the
 217 ingestion rate of groundwater (L/d). EF and ED represent the exposure frequency (d/a)
 218 and exposure duration (a), respectively. BW and AT signify the average body weight
 219 (kg) and the mean exposure time (d), respectively. RfD_{oral} denotes the reference
 220 dosage of factors (mg/(kg·d)). HQ_{oral} characterizes the hazard quotient for pollutants
 221 through the oral exposure pathway.

222 2. dermal contact model

$$\text{Intake}_{\text{dermal}} = \frac{DA \times EV \times SA \times EF \times ED}{BW \times AT} \quad (3)$$

$$DA = K \times C \times t \times CF \quad (4)$$

$$SA = 239 \times H^{0.417} \times BW^{0.517} \quad (5)$$

$$\text{HQ}_{\text{dermal}} = \frac{\text{Intake}_{\text{dermal}}}{\text{RfD}_{\text{dermal}}} \quad (6)$$

$$RfD_{\text{dermal}} = RfD_{\text{oral}} \times ABS_{gi} \quad (7)$$

223 In these equations, $Intake_{\text{dermal}}$ represents the daily average exposure dosage
 224 through dermal intake per unit weight (mg/(kg · d)), EV is the daily exposure
 225 frequency of dermal contact, DA signifies the exposure dosage of every single event
 226 (mg/cm²), SA indicates the skin surface area (cm²), K denotes the coefficient of skin
 227 permeability, T implies the contact duration (h/d), CF is a conversion factor, H
 228 represents average resident height (cm), HQ_{dermal} and RfD_{dermal} represent the hazard
 229 quotient and the reference dosage (mg/(kg·d)), respectively.

230 3. total risk model

$$HI_i = HQ_{\text{oral}} + HQ_{\text{dermal}} \quad (8)$$

$$HI_{\text{total}} = \sum_{i=1}^n HI_i \quad (9)$$

231 Where HI_i is the sum of the hazard index of contaminant i from oral intake and
 232 dermal contact, indicating the level of harm to the human body for contaminant i . And
 233 HI_{total} is the total hazard index of all contaminants concerned.

234 RfD_{dermal} is derived from the RfD_{oral} using Eq. (7), where ABS_{gi} is the
 235 gastrointestinal absorption factor which equals 1. Thus, the values of RfD_{dermal} and
 236 RfD_{oral} are equal. As shown in Table 2, common parameters are selected according to
 237 reference manuals of the USEPA and the Ministry of Health of the P.R. China [41,42].

238 **Table 2** Health risk assessment model parameters

Oral intake			Dermal contact		
males	females	children	males	females	children

IR (L/d)	2.7	2.7	1.1	EV	1	1	1
EF (d/a)	365	365	365	K (cm/h)	0.001	0.001	0.001
ED (a)	30	30	6	t (h/d)	0.4	0.4	0.4
BW (kg)	65	55	22	CF	0.001	0.001	0.001
AT (d)	10950	10950	2190	H (cm)	165.3	153.4	99.4

239 Results

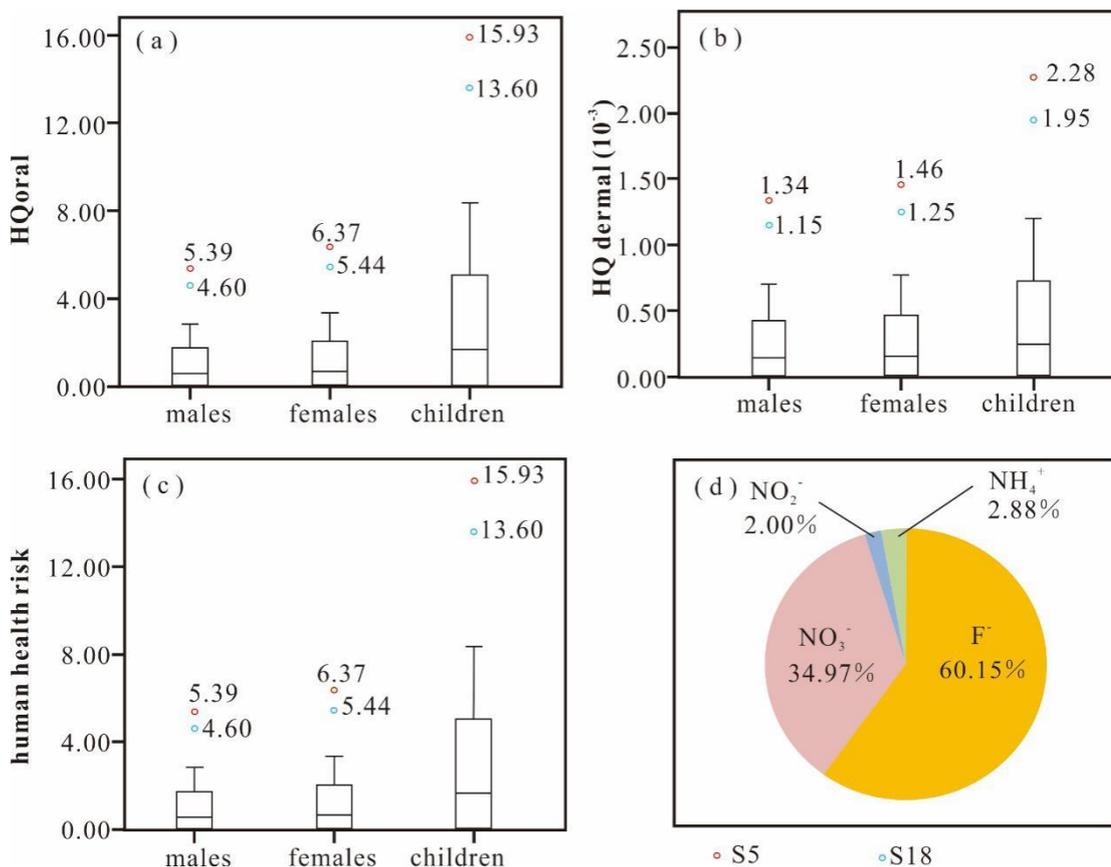
240 The values of RfD_{dermal} and RfD_{oral} both are F^- 0.04 mg/(kg·d), NO_3^- 1.6
241 mg/(kg·d), NO_2^- 0.1 mg/(kg·d) and NH_4^+ 0.97 mg/(kg·d). Figure 5 shows the health
242 risks to adult males, adult females, and children when they are exposed through oral
243 intake and dermal contact

244 For adult males, HQ_{oral} ranges from 0.01 to 5.39, with a mean value of 0.93, and
245 75% of the samples have an HQ_{oral} less than 1. Similarly, for adult females and
246 children, the HQ_{oral} values are 0.01-6.37 and 0.01-15.93, with mean values of 1.37
247 and 3.44, respectively. Besides, 40% of the samples have an HQ_{oral} over than 1 for
248 adult females, and 35% less than 1 for children. And $HQ_{oral} < 1$ indicates that 35% of
249 the groundwater is in a relatively safe condition by the exposure pathway of drinking
250 groundwater in the study area.

251 The hazard quotient through dermal contact (HQ_{dermal}) ranging
252 $2.77 \times 10^{-6} \sim 1.34 \times 10^{-3}$ (adult males), $3.01 \times 10^{-6} \sim 1.46 \times 10^{-3}$ (adult females), and
253 $4.71 \times 10^{-6} \sim 2.28 \times 10^{-3}$ (children), respectively. All values less than 1 signifies that the
254 health risks through dermal contact to the four contaminants are negligible.

255 HI_{total} is basically the same as HQ_{oral} (mean values are 1.16, 1.37, and 3.44,

256 respectively), indicating that the risk of dermal contact to human health is negligible
 257 compared with the risk of oral intake. Still, the values of HQ_{oral} , HQ_{dermal} , and HI_{total}
 258 show the same trend in the same species, all follow the order: males < females < <
 259 children. That is, the influence order is males < females < children through
 260 contaminated groundwater on both exposure pathways and human health risks in the
 261 study area, denoting that children face higher risks than females, which are higher
 262 than males. Because children have the lowest average weight and males have the
 263 highest average weight.

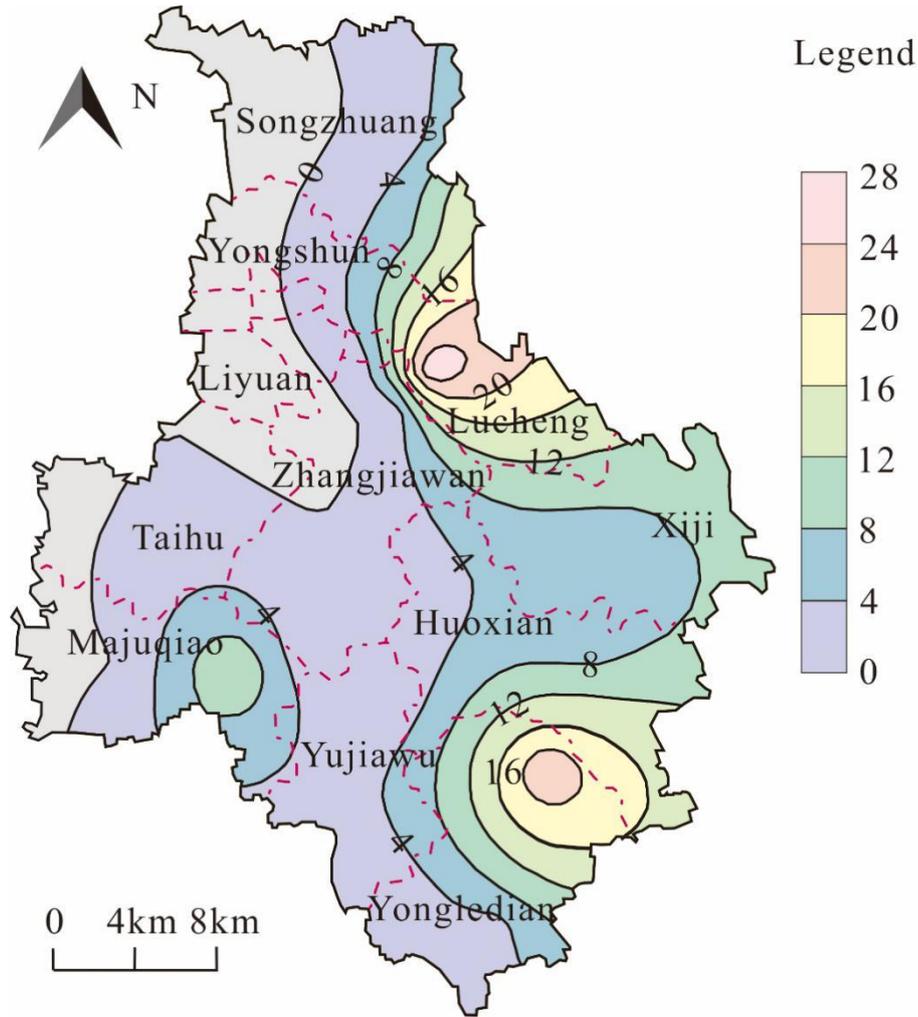


264
 265 **Fig. 5** Boxplots showing the results of groundwater quality human health risks assessment.
 266 (a) Oral intake, (b) dermal contact, (c) total risk, (d) contributive ratios of factors to health risks.

267 S5 and S18 are the groundwater samples.

268 Groundwater quality human health assessment factors contribute differently to
269 *GQHR*. As shown in Fig. 4d, F^- contributes the most to the health risk (60.15%),
270 followed by NO_3^- (34.97%). NO_2^- and NH_4^+ are all less than 3% (2.00% and 2.88%,
271 respectively), which means F^- and NO_3^- are the main factors affecting human health.
272 The abnormal values in Fig. 4a, Fig. 4b, and Fig. 4c are caused by the fact that F^- and
273 NO_3^- in groundwater samples S5 and S18 are significantly higher than other ions,
274 which is consistent with the conclusion obtained in Fig. 4d.

275 Based on HI_{total} , the groundwater quality human health risk distribution map is
276 shown (Fig. 6). It can be seen that the groundwater quality health risk increases from
277 northwest to southeast. Low and medium risk regions are located in the west and
278 middle of the study area, while high-risk regions are mainly located in the east. The
279 highest risk regions are Lucheng (S5) and Yongledian (S18), which are consistent
280 with the polluted distribution of F^- , NO_3^- , NO_2^- and NH_4^+ .



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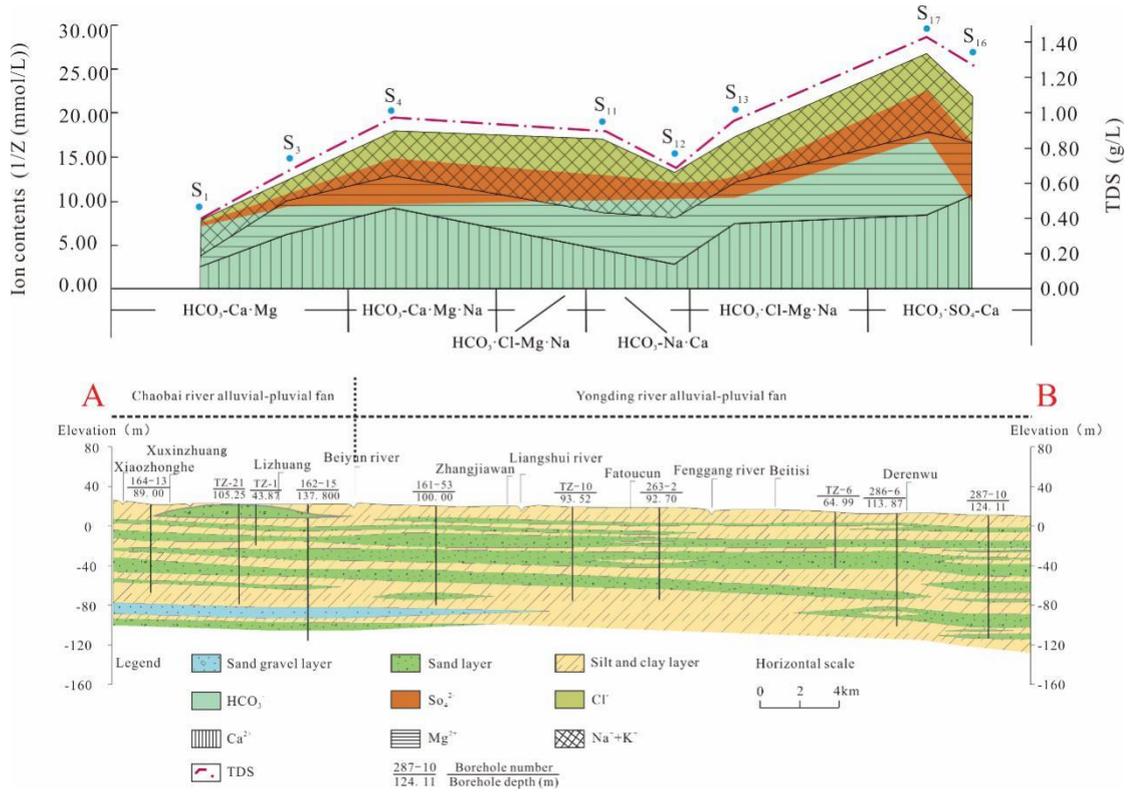
Fig. 6 Groundwater quality human health risks distribution map.

283 Discussion

284 Previous studies [23,43] showed that the sources of groundwater pollutants
 285 (including health risk assessment factors) were mainly affected by human factors, but
 286 their distributions were controlled by natural factors (water-rock interaction,
 287 precipitation infiltration and dilution, evaporation and concentration, etc.).

288 The low and medium risk regions are located in upper groundwater, and the
 289 pollutant load is the lowest in the study area, indicating that human factors play a
 290 small role and natural factors play a leading role.

291 According to the hydrogeological and hydro-chemical profile (Fig. 7), the
292 groundwater depth in the north is deep (5-10m), the hydraulic slope is about 2‰, and
293 the aquifer is dominated by medium-coarse sand and fine sand, which is mainly
294 recharged by meteoric precipitation in flood season. When the recharged groundwater
295 passes through the aquifer, the water-rock interaction mainly occurs by leaching.
296 From the north to the south, the particle size becomes finer, the evaporation and
297 concentration effect is enhanced. The main performance is that the hydraulic slope
298 becomes slower (average value is 1.2‰), the groundwater depth is less than 6m, the
299 material accumulation in groundwater, and the TDS increases (0.5-1g /L). In the south,
300 the groundwater depth becomes shallow (0~5m), the hydraulic slope becomes slow
301 (1‰), and with the combination of evaporation-concentration and human activities,
302 the ionic components continue to accumulate. In the subsequent groundwater
303 management for these regions, the monitoring of pollution sources should be
304 strengthened, such as surface pollution monitoring and river drain contamination
305 management, to prevent river pollution then pollute groundwater. Legitimately
306 regulate the use of groundwater resources, improve people's awareness of resource
307 protection and pollution prevention and control. And controlling individuals to exploit
308 and use groundwater resources in large quantities without permission, so that avoid
309 the increase of runoff and discharge intensity caused by changes in hydrological cycle
310 conditions.



311

312

Fig. 7 Groundwater hydrogeological and hydro-chemical profile map

313

The high-risk regions are mainly located in the eastern part of the groundwater

314

discharge area, which is affected by both natural and human factors. Tongzhou, as an

315

agricultural irrigated area, is principally affected by the use of chemical fertilizers

316

(mainly nitrogen fertilizer), and chemical fertilizers are an important source of health

317

risk assessment factors F⁻, NO₃⁻, NO₂⁻ and NH₄⁺. About 48.05% of the land is used for

318

agriculture, and the average fertilizer application rate is 1172.8 kg/hm². In addition,

319

there is primary high fluoride water in the North China Plain, and the use of high

320

fluoride water irrigation is another important source of fluoride in groundwater. The

321

annual average evaporation is about 3 times the precipitation in the study area, and the

322

groundwater flow rate is slow, reflecting that the hydro-chemical changes of

323

groundwater caused by evaporation exceed the dilution effect of rainfall. So, the

324 groundwater depth plays a decisive role in evaporation. The high-risk regions are
325 located in the discharge area, the groundwater depth changes from 5~10m to 0~5m,
326 evaporation and concentration enhance, so the concentration of F^- , NO_3^- , NO_2^- and
327 NH_4^+ increases.

328 As major agricultural irrigation regions, long-term use of sewage irrigation and
329 chemical fertilizers. Lucheng (S5) and Yongledian (S18) are the areas with the highest
330 risk and located in the discharge area of groundwater. Both human and natural factors
331 lead to high concentrations of F^- and NO_3^- in the chemical indicators of S5 and S18.

332 In the regions where natural and human factors work together, the use of
333 chemical fertilizers should be controlled, organic agriculture should be promoted and
334 farmers' awareness of environmental protection should be raised. It is forbidden to
335 irrigate with sewage and prevent surface soil pollution.

336 We should arrange agricultural irrigation scientifically and reasonably, reduce
337 flood irrigation and promote agricultural pure water sprinkler irrigation. The
338 groundwater pollution caused by human activities should be reduced, and the
339 monitoring of groundwater exploitation should be strengthened to prevent pollutants
340 from infiltrating into groundwater through the surface.

341 **Conclusions**

342 Ensured the hydro-chemical characteristics of the study area by analyzing
343 components in groundwater, and the distribution of groundwater chemical
344 composition is mainly controlled by natural conditions like geology, topography, and

345 hydrogeological conditions, at the same time influenced by human activities.

346 Unlike other *GQHR* assessment studies only consider contamination status or the
347 pollutants in study areas. Our study provides a useful method to select the indexes of
348 *GQHR* assessment model with the characteristics and evolution of groundwater
349 hydrochemistry, and Tongzhou is an agricultural area that means a large use of
350 fertilizer.

351 In terms of the calculated results of *GQHR*, distributed degrees of *GQHR* and
352 identified the dominant control factors. According to various degrees of risk caused by
353 different natural factors and human factors, the targeted countermeasures of reducing
354 the *GQHR* increase were proposed.

355 The research results provide a scientific basis for the safety of groundwater
356 supply and environmental protection in Tongzhou and provide a reference for the
357 same kind of research.

358 **Abbreviations**

359 *GQHR*: groundwater quality human health risk; NO_3^- : nitrate; NO_2^- : nitrite; NH_4^+ :
360 ammonia; $\text{NO}_3\text{-N}$: nitrate nitrogen; $\text{NO}_2\text{-N}$: nitrite nitrogen; $\text{NH}_4\text{-N}$: ammonia
361 nitrogen; F^- : fluorine; K^+ : calcium; Na^+ : sodium; Ca^{2+} : calcium; Mg^{2+} : magnesium;
362 Cl^- : chlorine; SO_4^{2-} : sulfate; HCO_3^- : bicarbonate; CO_3^{2-} : carbonate; TDS: total
363 dissolved solids; WHO: The World Health Organization; USEPA: the United States
364 Environmental Protection Agency; *CRAPFU*: upper of Chaobai River alluvial-pluvial
365 fan; *CRAPFD*: lower of Chaobai River alluvial-pluvial fan; *YRAPFU*: upper of

366 Yongding River alluvial-pluvial fan; *YRAPFD*: lower of Yongding River
367 alluvial-pluvial fan.

368 **Author's contributions**

369 The content of the manuscript was drafted by Tianshan Lan and revised by Yuqing
370 Cao, Shanshan Bao and Fugang Wang. Jinjie Miao, Yaonan Bai and Sida Jia provided
371 the basic data of this paper. All authors provided written feedback and edits on the
372 manuscript and agreed with its content.

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379 **Ethics approval and consent to participate**

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381 **Consent for publication**

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383 **Competing interests**

384 The authors declare that they have no known competing financial interests or personal
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