Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2020.25991

197 (2020) 148–156
September

Spatial distribution, origin, and health risk assessment of manganese contamination in groundwater in a grassland area of Eastern China

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Received 30 August 2019; Accepted 16 April 2020

ABSTRACT

High concentrations of manganese (Mn) in drinking water may have negative effects on human health. This study attempted to better understand the extent of Mn contamination in groundwater by comparing the water quality index with the Chinese drinking water standard limit. In addition, variogram analysis was conducted and the spatial distribution of Mn was determined using Surfer 11 software, and the origin of the Mn in groundwater was discussed. Associated risks for human health for different age groups including infants, children, and adults were assessed using the United States Environmental Protection Agency (USEPA) model. The results showed that the maximum observed Mn concentration was 2.48 mg/L, and the minimum value was below 0.05 mg/L. 76.3% of samples exceeded the Chinese limit (0.1 mg/L). In addition, the maximum value of the water quality index (I_i) was 24.8, indicating that the groundwater in the study area was seriously contaminated by Mn. High Mn concentration (>0.1 mg/L) was distributed in the alluvial plain of the Mo River, while areas with the highest Mn concentrations (>1 mg/L) were distributed in BaYanKuLun country and in hilly areas. The dissolution and leaching of the parent material, redox status, and human activities could raise the concentration of Mn in groundwater. The maximum hazard quotient (HQ) values were 0.770, 0.739, and 0.709 for infants, children, and adults, respectively, with greater HQ values for infants than children and adults due to their lower body weight. At present, groundwater was determined to be safe for humans to drink. However, areas with groundwater Mn concentrations above the Chinese drinking water standard limit (>0.1 mg/L) should be treated to ensure their safety. These findings will be helpful for local authorities when they are determining groundwater management plans and protection measures, as well as beneficial for groundwater protection and utilization in this area. These results can also provide a reference for relevant studies in other regions of the world.

Keywords: Manganese contamination; Groundwater; Spatial distribution; Origin·health risk; Grassland area

1. Introduction

Groundwater is an indispensable component of natural hydrological systems and ecosystems around the world and is often a crucial source of drinking water that can create stable conditions for social development [1]. It is an important water source for domestic consumption, industrial production, and agricultural irrigation in regions in which surface water is scarce [2,3]. Groundwater also plays a vital role in ensuring ecological security in arid

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and semiarid areas [4,5], especially in ecologically fragile areas such as grassland regions in eastern China [6]. Recently, arid regions in China have been facing the double stressors of insufficient water quantity and poor water quality due to both natural factors and human activities [1,7]. To address these stressors, international research has focused on better understanding of the health risks associated with groundwater quality [8–10].

Manganese (Mn) is an important indicator of groundwater quality [11,12]. Mn is abundant in the Earth's crust [13]; it exists in both soil and weathered rocks [14], and as a consequence is ubiquitous in groundwater and other water bodies. Mn is a trace metal needed for human health and is necessary for drinking water at a low concentration [14,15]. In the third edition of the Guidelines for Drinking-Water Quality [16] and Mn concentration of 0.4 mg/L in drinking water was recommended. However, the guideline was discontinued in the fourth edition in 2011 [17]. The World Health Organization (WHO) [18] considered that the concentration of Mn in drinking-water was normally below the guideline [19].

There are many places in the world where drinking water exceeds this limit [20–23] since water treatment is very expensive and treatment facilities are often simple and crude. High concentrations of Mn in drinking water can cause learning disabilities in children [20,24], and can induce Parkinson's disease in adults [25,26]. Despite these serious human health impacts, previous studies have focused more on the effects of other trace metals (e.g. As, Pb, Cd, and Hg) rather than Mn [12,27,28]. Because of this oversight, risk assessment of manganese in groundwater for human health is particularly important.

The Hulunbuir grassland area is located in Hulunbuir City in Inner Mongolia, Eastern China. Grass dominates the surface vegetation and the environment is fragile. Groundwater is one of the main sources of domestic supplies [6]. Increasing amounts of evidence show that Mn concentrations in groundwater in eastern China often exceed the Chinese drinking water standard limit of 0.1 mg/L [23,29]. However, studies on the characteristics, origins, and associated risks to human health of Mn in groundwater in the Hulunbuir grassland areas is scarce. For the Hulunbuir grassland area, the main objectives of this paper are (1) to analyze the spatial distribution characteristics of manganese in groundwater, (2) to identify the primary origin of Mn in groundwater, and (3) to assess the risk to human health associated with ingesting Mn through drinking water. This paper will be helpful for local authorities when they are determining best practices for groundwater management and protection.

2. Materials and methods

2.1. Study area

The study area is in the Hulunbuir grassland area in the northwest of Hulunbuir City, Inner Mongolia, Northeast China, located at 119°08′11″-120°17′04″ E and 49°06′40″-49°41′54″ N. The administrative division belongs to the Chenbar Tiger Banner of Hulunbuir City.

The study area is in the mid-latitude region, which has a mid-temperate continental semi-arid climate. The main climatic characteristics are a long cold winter, short and hot summer, and windy spring and autumn. The average annual precipitation from 2009 to 2019 was 272.8 mm, of which 60% was concentrated in July and August, with average annual evaporation of 1,329.0 mm [6].

The study area belongs to the Erguna River system, which consists of three perennial flowing rivers: the Hailar River, the Mo River and the Yimin River. The annual average discharge of Hailar River was 107 m^3/s, the maximum peak discharge was 1,840 m^3/s (1,958.4.23), and the minimum discharge was zero (1,969.1.8). The average annual discharge of the Mo River was 3.15 m^3/s, the maximum peak discharge was 108 m^3/s (1,977.7.6), and the minimum discharge was zero (1,971.1.1). The average annual discharge of the Yimin River was 36.8 m^3/s. Surface water was one of the main sources for drinking and irrigation in the study area.

There were three types of landforms in the study area: hilly, plain, and high plain regions. Hilly landforms are distributed in the northern part of the study area and have Cretaceous strata (K_1^l) exposed on the surface. Middle Pleistocene alluvial (Q_2^{al}) and Holocene alluvial-pluvial layers (Q_4^{al+pl}) are widely distributed in the alluvial plains of the Hailar and Mo Rivers. In addition, the high plains are covered by Upper Pleistocene ice-water deposits (Q_3^{fgl}) [6]. Groundwater is stored in unconsolidated Quaternary strata and is another main source for drinking and irrigation in the study area.

2.2. Sampling and laboratory analysis

Thirty-eight groundwater samples were collected from the shallow aquifers in the plain and high plain areas in July 2017 (Fig. 1). The exact sampling locations were recorded by a hand-held global positioning system. Before collection, the sample wells were pumped for 2–3 min in order to remove any stale water. All groundwater samples were stored in clean 2 L bottles. Prior to sampling, bottles were washed three times using groundwater from the wells.

All groundwater quality parameters were analyzed using standard procedures [30]. The analyzed water quality indices included sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), nitrate (NO_3^-), and the concentration of Mn. pH and total dissolved solids were measured *in situ* using an SX751 portable electrical conductivity/pH meter (Shanghai Sanxin Company, Shanghai, China). Water samples for cation determination (Na^+, Ca^{2+}, and Mg^{2+}) were filtered with a 0.45 um membrane filter and acidified to a pH < 2. After being filtered, water samples for anion determination were packaged directly into sampling bottles and sent to the laboratory for testing. At the laboratory, sodium (Na^+) and potassium (K^+) were measured using the flame atomic absorption spectrophotometry method. Calcium (Ca^{2+}), and magnesium (Mg^{2+}) were measured using the ethylenediaminetetraacetic acid titrimetric method. Chloride (Cl^-), sulfate (SO_4^{2-}), and nitrate (NO_3^-) were measured using ion chromatography. Bicarbonate (HCO_3^-) was measured using the potentiometric titrimetric method.

The accuracy of the test results was verified by calculating the charge balance error (%CBE) for each sample with the following formula [8,9]:

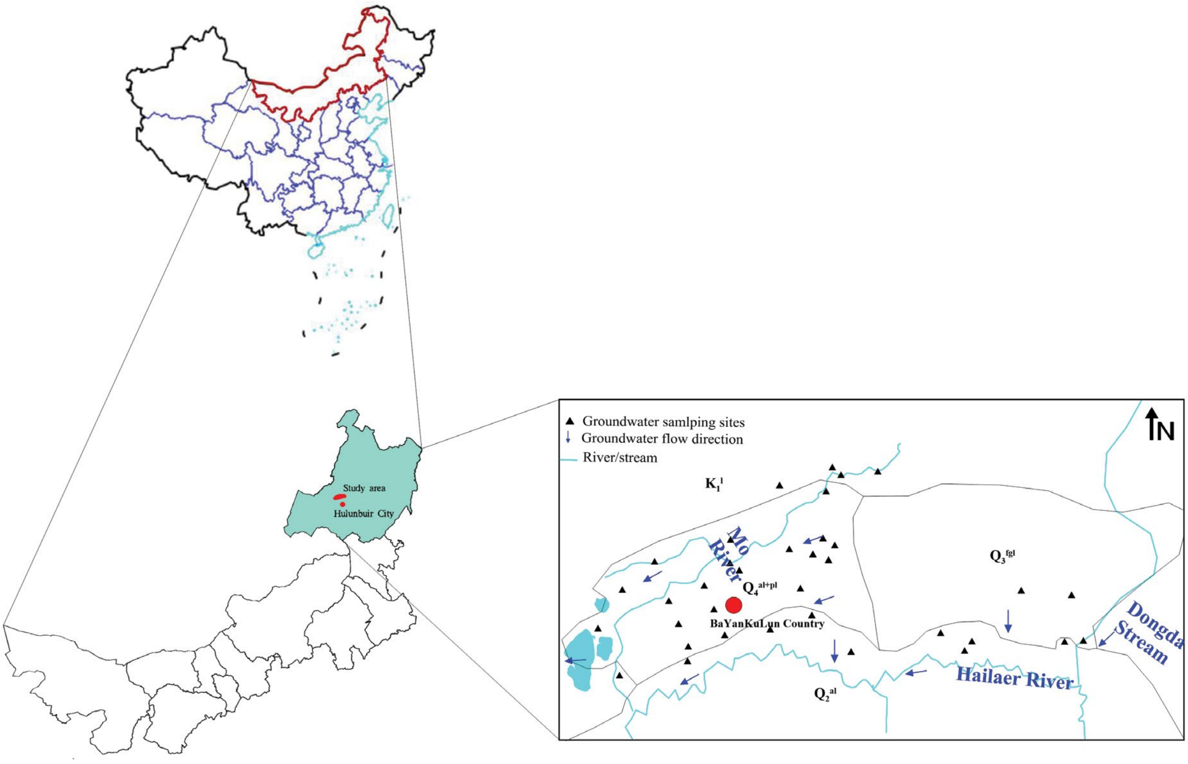

Fig. 1. Map showing the hydrogeology of the study area and sampling locations.

$$\%\text{CBE} = \frac{\sum|\text{cations}| - \sum|\text{anions}|}{\sum|\text{cations}| + \sum|\text{anions}|} \times 100 \quad (1)$$

where all cations and anions are expressed in meq/L. Generally, the %CBE should be within a range of ±10%. The calculated %CBE of all samples were within ±10% in this study.

2.3. Contamination assessment

In this study, the water quality index (I_i) was employed to assess groundwater contamination. The water quality index can be calculated as follows:

$$I_i = \frac{C_i}{C_0} \quad (2)$$

where C_i represents the contaminant concentration in the groundwater, and C_0 is the standard limit of the contaminant for Chinese drinking water [31]. An I_i value greater than 1 indicates that the groundwater is contaminated.

2.4. Geostatistical analysis

To analyze the spatial distribution of the Mn data, the geostatistical analysis was used to draw maps that showed the extent of the pollution for each contaminant [32]. Variogram analysis was conducted in Surfer 11 to determine the spatial variability of Mn. Finally, a spatial distribution map was drawn using the various input parameters with ordinary kriging [33].

2.5. Human health risk assessment

A human health risk assessment evaluates the probability of adverse health impacts on different age groups (infants, children, and adults). In this paper, the oral exposure dose and the non-carcinogenic effects of contaminants were estimated by employing the empirical models proposed by the United States Environmental Protection Agency (USEPA) [34].

The exposure dose (CDI) through drinking water intake can be calculated by the following formula:

$$\text{CDI} = \frac{C_w \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (3)$$

where CDI is the chronic daily intake of groundwater (mg/kg/d); C_w is the concentration of a particular contaminant in the groundwater (mg/L); IR is the ingestion rate of groundwater (L/d); EF is the exposure frequency (d/y); ED is the exposure duration (y); BW is the average body weight (kg); AT represents the average time (days). The parameters in Eq. (3) are given in Table 1.

The potential non-carcinogenic risk of hazard quotient (NCHQ) can be determined by the following equation:

$$\text{NCHQ} = \frac{\text{CDI}}{\text{RfD}} \quad (4)$$

where RfD represents the reference dose of a specific contaminant. The oral reference dose for Mn (0.14 mg/kg/d) was obtained from the Integrated Risk Information System (IRIS) database [35]. When the NCHQ value is larger

Table 1
Parameters used in the exposure dose calculation models

Parameters	Infants	Children	Adults
IR, L/d	0.3	0.78	2.5
EF, d/a	365	365	365
ED, a	1	12	64
BW, kg	6.9	18.7	62.5
AT, d	365	4,380	23,360

than 1, it indicates that the non-carcinogenic risk exceeds the acceptable risk level [8,9,36].

3. Results and discussion

3.1. Characteristics of Mn concentration in groundwater

The statistics of the Mn concentration from the 38 groundwater samples are listed in Table 2. Mn concentration showed a relatively large range, with a maximum value of 2.48 mg/L and a minimum value of below 0.05 mg/L. The maximum value was fifty times larger than the minimum value. The average Mn concentration was 0.74 mg/L, which is 7.4 times larger than the Chinese drinking water standard limit of 0.1 mg/L and nearly twice large than that indicated by the WHO [16] guideline of 0.4 mg/L.

The Mn concentration in 29 of the 38 groundwater samples, or 76.3%, exceeded the Chinese limit, while 50% of the samples exceeded the WHO guideline. The cumulative frequency of Mn concentration in groundwater is shown in Fig. 2. Results showed that most of the groundwater in the study area was not suitable for drinking, according to these standards.

The coefficient of variation (CV) represents the degree of dispersion of the data, which can be divided into three categories: weak (<10%), moderate (10%~100%), and strong (>100%) [37]. In this study, the CV of groundwater was 68.3% or moderate variation. This indicated that a high concentration of Mn was ubiquitous in the groundwater, which may be due to natural conditions (alluvial strata conditions) rather than human activities. Bourg and Bertin [38] and Kim et al. [39] reported that the characteristic of being sensitive to redox conditions common in alluvial aquifers could lead to naturally higher concentrations of Mn, which was consistent with our findings.

Based on the results of the Mn contamination assessment (Table 3), the maximum value of I_i was 24.8 and the average value was 7.4, which indicated that the Mn concentration in groundwater significantly exceeded the national limit and the groundwater in the study area was seriously contaminated by Mn.

3.2. Spatial distribution and origin of Mn in groundwater

To determine suitability for variogram analysis, Mn data were tested using a P–P plot in SPSS 19 (Fig. 3) to confirm whether they conform to a normal distribution before analysis. As shown in Fig. 3, the Mn data were distributed evenly around the theoretical $y = x$ straight line, indicating

Table 2
Statistical parameters of Mn concentration

Contaminant	Manganese (mg/L)
Minimum	–[a]
Maximum	2.48
Average	0.74
CV (%)	68.3
Standard value C_0 (mg/L)	0.1
Exceeding No.	29

[a]The concentration is below the detection limit (0.05 mg/L).

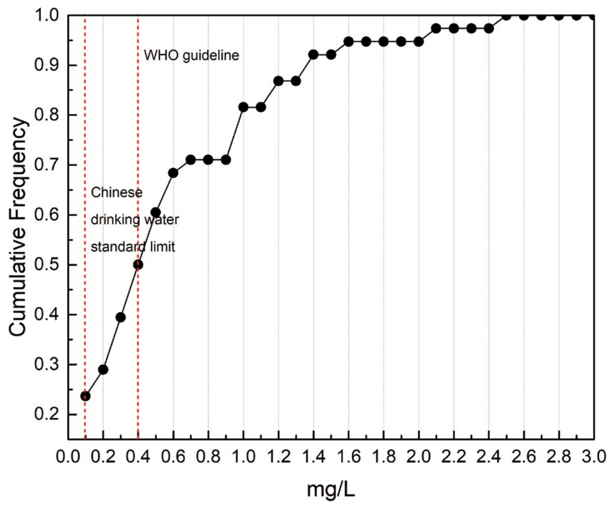

Fig. 2. Cumulative frequency of Mn concentration in groundwater.

Table 3
Results of Mn contamination assessment

Contaminant	Manganese
Water quality index (I_i)	
Minimum	–
Maximum	24.8
Average	7.4
Standard value C_0 (mg/L)	0.1
Exceeding ratio (%)	76.3%

that the data conformed to a normal distribution and could be used for variogram analysis.

Variograms were analyzed at a lag of 22,000 m and a uniform interval of 2,000 m using Surfer 11. Four theoretical models were applied to determine the best fit (exponential, spherical, power, and Gaussian), with the exponential model demonstrating the best fit ($R^2 = 0.587$) (Fig. 4). The exponential model can be expressed by:

$$\gamma(h) = C_0 + C\left(1 - \exp\left(\frac{-3h}{a}\right)\right) \quad (5)$$

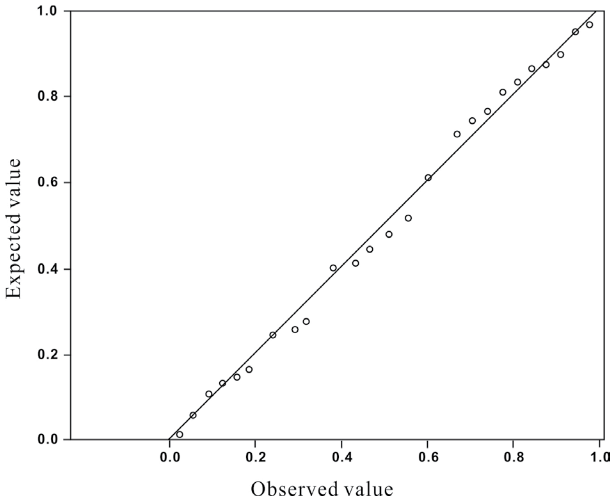

Fig. 3. Normal P–P plot of Mn.

where C_0 is the nugget variance, C is the sill, h is the lag interval, and a is a range parameter [32].

Based on the exponential model, the spatial distribution of Mn concentration in groundwater was obtained using Surfer 11 via Kriging (Fig. 5). As shown in Fig. 5, an area with high Mn concentration (>0.1 mg/L) was distributed mainly in the alluvial plain of the Mo River, while the highest Mn concentrations (>1 mg/L) were distributed in BaYanKuLun country and hilly areas.

Under natural conditions, Mn in groundwater occurs in sediments and soils, primarily originating from the dissolution and leaching of the parent material [32,40]. In addition, Mn concentration is affected by redox status and human activities [11,12,32].

In the study area, the Quaternary alluvial aquifer is made of fine sand and clay, which contains a large amount of manganese nodules [41]. While the dissolution and leaching of manganese-bearing minerals increased the concentration of Mn [32], dynamic groundwater conditions meant that

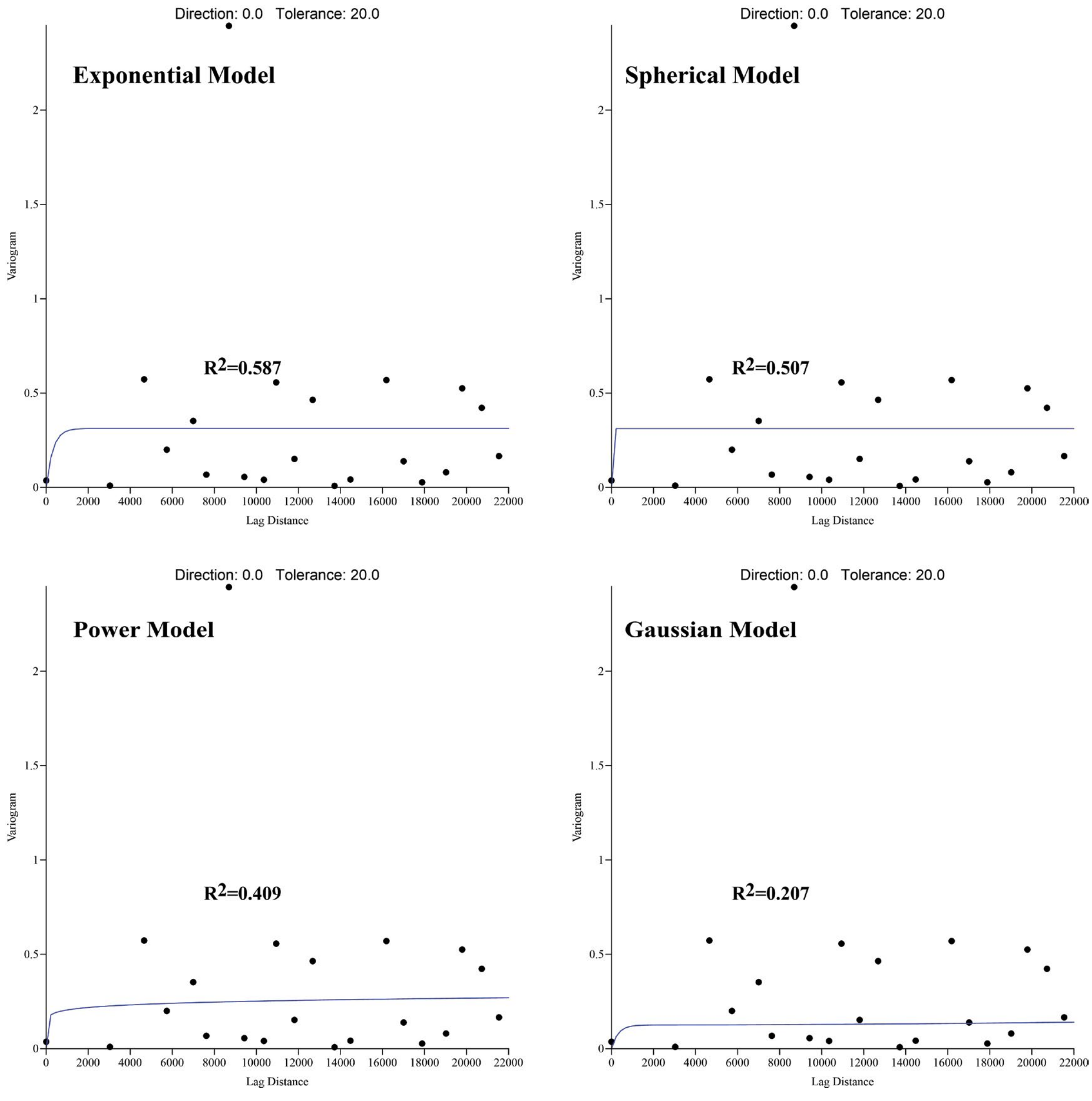

Fig. 4. Fitting charts for different models (a) exponential, (b) spherical, (c) power, and (d) Gaussian models.

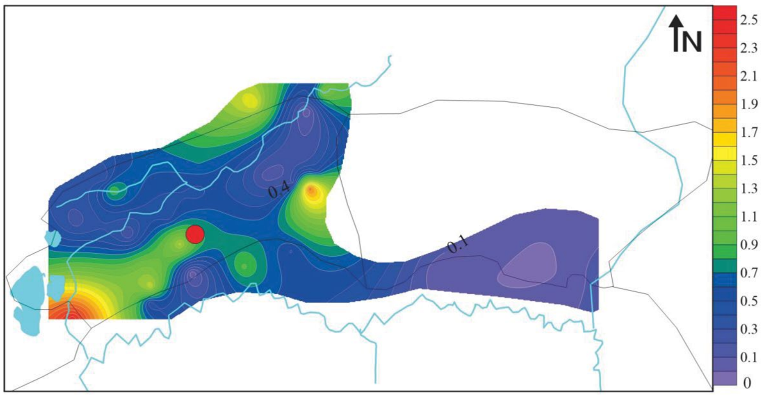

Fig. 5. Spatial distribution map of Mn concentration.

circulation was fast, which accelerated the dissolution of the manganese-bearing minerals [6]. This combination of effects explains the area of high Mn concentration (>0.1 mg/L) distributed in the alluvial plain of the Mo River. In addition, the groundwater level was deep in hilly areas and the reduction environment was conducive to the dissolution of manganese-bearing minerals [14], causing the Mn concentration to be relatively high (>1 mg/L). Intense human activities in the area such as cattle and sheep husbandry and sewage discharge also raised the Mn concentration in soils and elevated the Mn content in groundwater in the BaYanKuLun area and the region downstream. All these characteristics in alluvial aquifers raised the concentration of Mn in groundwater in the study area.

3.3. Human health risk assessment

The above discussions have already shown that the groundwater in the study area was polluted by high levels of Mn. It was essential to assess the risk to human health in the study area since groundwater is one of the main drinking water sources for local residents. The hazard quotient (HQ) plays a vital role in evaluating the non-carcinogenic health risk of Mn for different age groups such as infants, children, and adults in the region [9].

Results of the human health risk assessment for Mn pollution for different age groups through drinking water intake in the study area are presented in Fig. 6 and Table 4. As shown in Fig. 6 and Table 4, the maximum HQ values were 0.770, 0.739, and 0.709 for infants, children, and adults, respectively. If HQ values exceed 1, the groundwater is considered unsafe for human consumption [1,36]. In the study area, HQ values were less than 1 for all groundwater samples for infants, children, and adults, indicating that the groundwater was safe for human domestic use. However, HQ values for infants were greater than those for children and adults, suggesting that infants face higher health risks than children and adults due to their lower body weight [1,42].

The groundwater was classified as unsuitable for drinking, although the HQ values for infants, children, and adults were less than 1, due to the Mn concentrations (>0.1 mg/L) exceeding the Chinese drinking water standard limit.

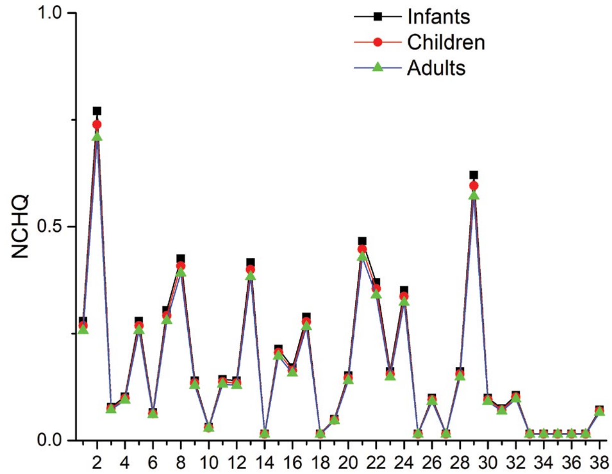

Fig. 6. Non-carcinogenic hazard quotient of different age groups.

Therefore, prior to drinking, groundwater should be treated to ensure its safety. A groundwater monitoring network should be set up to better understand groundwater quality in real-time and better predict and manage impacts on the health of communities and ecosystems [8].

3.4. Uncertainty analysis

In this paper, the characteristics and spatial distribution of Mn concentration were analyzed using geostatistical methods, and the associated human health risk was assessed employing the model recommended by the USEPA. The results are helpful and meaningful for groundwater management and the protection of both people and ecosystems. However, there are still several uncertainties.

One uncertainty stems from the application of geostatistical methods in the determined variogram. The accuracy in calculating the parameters of the variogram largely depends on the number and the representativeness of the groundwater samples [43,44]. More representation and a larger quantity of groundwater samples should be collected to reduce the uncertainty in results.

Table 4
Calculated human health risk for different age groups

No.	Concentration (mg/L)	HQ		
		Infants	Children	Adults
G1	0.90	0.280	0.268	0.257
G2	2.48	0.770	0.739	0.709
G3	0.25	0.078	0.074	0.071
G4	0.33	0.102	0.098	0.094
G5	0.90	0.280	0.268	0.257
G6	0.21	0.065	0.063	0.060
G7	0.98	0.304	0.292	0.280
G8	1.37	0.425	0.408	0.391
G9	0.45	0.140	0.134	0.129
G10	0.10	0.031	0.030	0.029
G11	0.46	0.143	0.137	0.131
G12	0.45	0.140	0.134	0.129
G13	1.34	0.416	0.399	0.383
G14	–	–	–	–
G15	0.69	0.214	0.206	0.197
G16	0.55	0.171	0.164	0.157
G17	0.93	0.289	0.277	0.266
G18	–	–	–	–
G19	0.16	0.050	0.048	0.046
G20	0.49	0.152	0.146	0.140
G21	1.50	0.466	0.447	0.429
G22	1.19	0.370	0.355	0.340
G23	0.52	0.161	0.155	0.149
G24	1.13	0.351	0.337	0.323
G25	–	–	–	–
G26	0.32	0.099	0.095	0.091
G27	–	–	–	–
G28	0.52	0.161	0.155	0.149
G29	2.00	0.621	0.596	0.571
G30	0.32	0.099	0.095	0.091
G31	0.24	0.075	0.072	0.069
G32	0.34	0.106	0.101	0.097
G33	–	–	–	–
G34	–	–	–	–
G35	–	–	–	–
G36	–	–	–	–
G37	–	–	–	–
G38	0.23	0.071	0.069	0.066
Minimum	–	–	–	–
Maximum	2.48	0.770	0.739	0.709
Average	0.74	0.229	0.219	0.210

Another uncertainty is from the calculation of the HQ when applying the USEPA model. The parameters in the human health risk assessment model are empirical values or average values from regions. However, gender differences in the exposed population are ignored in this study, which may cause some uncertainty [45]. To improve the accuracy of the results, basic research on health risks of Mn should be carried out to provide suitable parameters for the Chinese population and to provide a scientific basis for regional groundwater quality health and safety management.

4. Conclusion

In this study, 38 groundwater samples were collected from the Hulunbuir grassland area in eastern China. The Mn contamination in groundwater was evaluated using the water quality index and by comparing samples with the Chinese drinking water standard limit. In addition, variogram analysis was conducted and the spatial distribution of Mn was determined using Surfer 11 software. The potential origin of Mn in the groundwater was also discussed. Moreover, the possible risk to human health risk was assessed and the uncertainties were discussed. The following conclusions can be summarized.

- The maximum Mn concentration was 2.48 mg/L and the minimum value was below 0.05 mg/L. 76.3% of the groundwater samples exceeded the Chinese standard limit. In addition, the maximum value of I_i was 24.8, indicating that the groundwater in the study area was seriously contaminated by Mn.
- The Mn data were best represented by the exponential model. An area of high Mn concentration (>0.1 mg/L) was distributed mainly in the alluvial plain of the Mo River, while the highest Mn concentrations (>1 mg/L) were distributed in BaYanKuLun country and hilly areas. The dissolution and leaching of the parent material, redox status, and intensity of human activities could raise the concentration of Mn in groundwater.
- The maximum HQ values were 0.770, 0.739, and 0.709 for infants, children, and adults, respectively. HQ values for infants were greater than children and adults. The groundwater was classified as safe for drinking. However, due to the concentrations of Mn (>0.1 mg/L) that are higher than the Chinese drinking water standard limit, the groundwater should be treated to ensure its safety before drinking.

Acknowledgments

This research was financially supported by the National Key R&D Program of China (Grant Nos. 2016YFC0501104 and 2017YFC0804100), the State Key Laboratory of Water Resource Protection and Utilization in coal mining (Grant No. SHJT-16–30.10), Tiandi Science and Technology Co. Ltd. Science and Technology Innovation Venture Capital Special Project (2018-TD-MS073) and the National Natural Science Foundation of China (Grant No. 41302214).

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