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Elevated Fe and Mn Concentrations in Groundwater in the Songnen Plain, Northeast China, and the Factors and Mechanisms Involved

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Abstract: Groundwater is an essential source of drinking and irrigation water. However, elevated Fe and Mn concentrations in groundwater have been found in recent decades, which can adversely affect human health and decrease crop quality and yields. The roles of hydrogeochemical changes and groundwater pollution (exogenous reductive material inputs) in this have not been studied adequately. We determined the distribution of Fe and Mn concentrations in groundwater in the Songnen Plain, northeast China, which is known for elevated Fe and Mn concentrations, and investigated the factors and mechanisms involved in causing the elevated concentrations. Chemical and statistical analyses indicated that the Fe and Mn concentrations in groundwater significantly correlated with climate parameters (precipitation and temperature), surface features (altitude, distance from a river, soil type, soil texture, and land use type) and hydrogeochemical characteristics (chemical oxygen demand and NH_4^+, NO_3^-, and P concentrations). In particular, the Fe and Mn concentrations in groundwater are higher in areas containing paddy fields and water bodies than other land use type areas. Areas with groundwater containing ultra-high Fe and Mn concentrations have almost all of the favorable factors. The main reasons for the elevated Fe and Mn concentrations in groundwater in the study area are the Fe/Mn mineral-rich strata and soil with abundant organic matter acting as sources of Fe and Mn to the groundwater and the reductive environment in the lower terrain and areas containing water bodies favoring Fe and Mn dissolution in the groundwater. Inputs of pollutants from agricultural activities have caused the Fe and Mn concentrations in groundwater to increase. Future studies should be performed to study interactions between pollutants from agricultural activities and Fe and Mn in groundwater and develop environmental management strategies for preventing future increases in Fe and Mn concentrations and promoting sustainable development of agriculture.

Keywords: Fe; Mn; hydrogeochemistry; environmental pollution; Songnen Plain

1. Introduction

Groundwater is a very important source of water for humans. However, with the intensification of human activities, groundwater pollution has become a global problem of concern [1,2]. High concentrations of iron and manganese are an important factor affecting groundwater quality. Anthropogenic pollutants, such as dissolved organic carbon [3] and ammonia [4], can cause high Fe and Mn concentrations in groundwater, as can geogenic contamination, which is widespread and presents as regional distribution [5]. High Fe and Mn concentrations in groundwater have prevented the utilization of groundwater resources.

Fe and Mn are widely distributed in soil and sediment and are redox active [6], which is the main reason high Fe and Mn concentrations in groundwater can be caused by geogenic contamination. Fe in groundwater is mainly present as Fe(II) and Fe(III) that often form complexes with organic compounds. Fe in sediment is often present as ferrous minerals such as pyrite and siderite, Fe oxides/hydroxides (hematite, magnetite, goethite, and limonite), and silicate minerals such as biotite and pyroxene. Mn in groundwater is often present as Mn(II), which is mainly supplied by Mn-bearing minerals such as psilomelane, manganite, and pyrolusite [7]. Minerals containing divalent Mn as a minor constituent in igneous and metamorphic rocks can also act as sources of Mn to groundwater [8].

High Fe and Mn concentrations have been found in groundwater around the world, including in the USA [4,9], European countries [10], India [11], and China [12]. High Fe and Mn concentrations in water can adversely affect human health and decrease crop quality and yields [13,14]. A threshold of 0.3 mg/L for Fe in water has been set in the US Environmental Protection Agency Safe Drinking Water Act [15]. The European Union has provided parametric values of 0.2 mg/L and 0.05 mg/L for Fe and Mn, respectively [16]. The World Health Organization has recommended a threshold of 0.4 mg/L for Mn in water [17]. However, it has been found that Mn at a concentration of 0.1 mg/L in water can affect the health of children [18]. The Chinese groundwater quality standard limit for Mn is 0.1 mg/L, and elevated Fe and Mn concentrations in groundwater are defined as concentrations >0.3 mg/L and >0.1 mg/L, respectively [19].

Dissolved Fe and Mn concentrations in groundwater are controlled by the redox conditions and pH. Solubility drives the mobilities of Fe and Mn in acidic conditions. In neutral environments, Fe and Mn mainly enter groundwater after reductive dissolution of Fe and Mn minerals [4,20]. The mobilities of Fe and Mn in groundwater are affected by many factors, including the groundwater age [9], groundwater table depth [4], climate [21], fluctuations in the groundwater level [22], and salinity [21].

Songnen Plain, an important area for grain growing in China [23], is a typical area with elevated Fe and Mn concentrations in groundwater. However, groundwater is an essential source of drinking and irrigation water in the Songnen Plain [24]. Numerous studies of groundwater in the Songnen Plain have been focused on regional hydrogeochemical characteristics [25], local hydrogeochemical characteristics [26], and the genesis of groundwater containing elevated Fe and Mn concentrations in particular areas [21,27,28]. However, few studies of the various factors and mechanisms involved in causing elevated Fe and Mn concentrations in groundwater at the regional scale have been performed. The sources and mechanisms involved in the mobilization of Fe and Mn in groundwater are not well understood, and the effects of human activities on Fe and Mn concentrations in groundwater at the regional scale need to be investigated. The aims of this study were to: (1) assess the distribution of groundwater containing elevated Fe and Mn concentrations in the Songnen Plain; (2) identify the factors (natural and related to human activities) affecting Fe and Mn concentrations in groundwater using statistical methods, and (3) identify the mechanisms involved in causing groundwater in the Songnen Plain to contain elevated Fe and Mn concentrations.

2. Study Area

The study area, Songnen Plain, is at 121°21′ E–128°12′ E, 43°36′ N–49°45′ N. The Songnen Plain is bounded to the east, north, and west by the Zhangguangcai Range, the Lesser Khingan Mountains, and the Greater Khingan Mountains, respectively (Figure 1). The boundary between the Songnen Plain and Liaohe Plain is to the south. The study area is vast and contains fertile soil. There are well-developed industrial zones and large agricultural areas. The industrial activities mainly include mechanical and electrical industry, heavy duty machinery, petrochemical industry, textiles, and papermaking [29]. The Songnen Plain has a continental monsoon climate and is in the mid-temperate zone. The annual average temperature is −4.0 to 5.5 °C, annual precipitation is 400–500 mm, and potential evaporation is 1900 mm [30]. The Second Songhua River, which originates in the Changbai Mountains, and the Nenjiang River, which originates in the Greater Khingan Range, flow into the Songhua River and through the study area west to east.

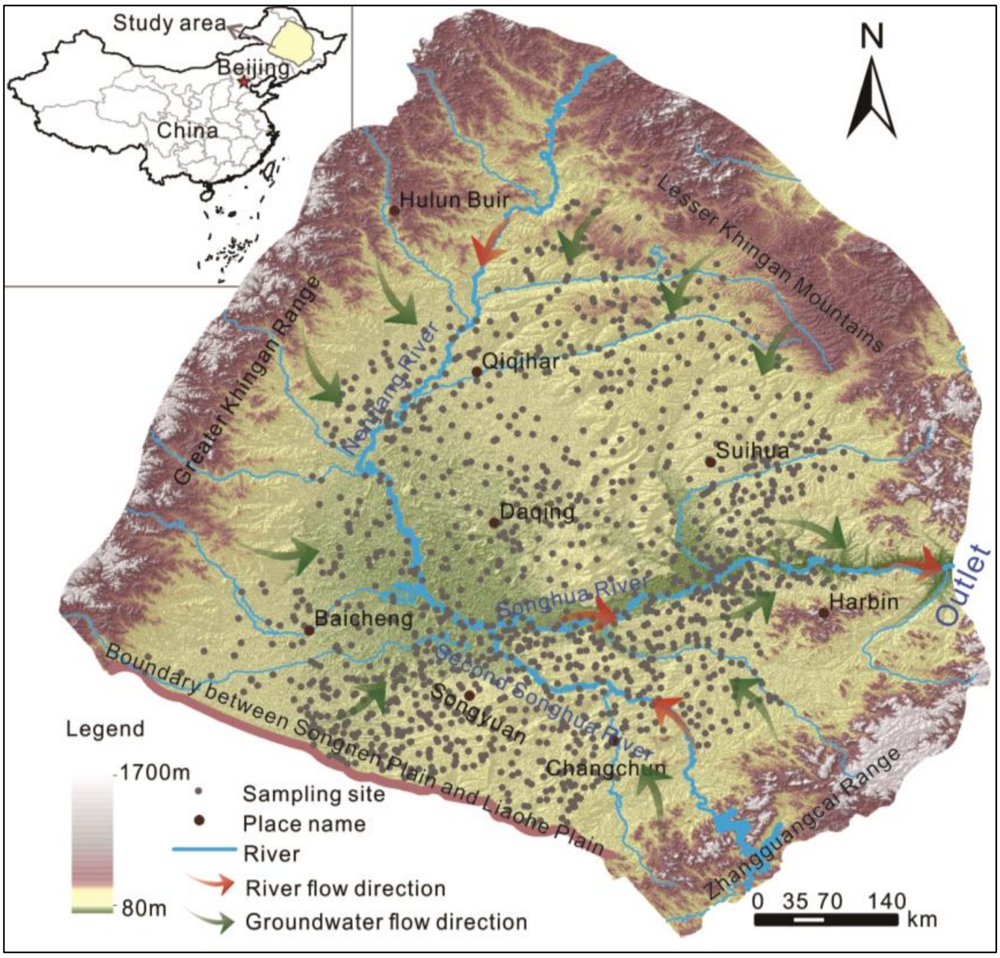


Figure 1. Location of the Songnen Plain and the sampling site locations.

The Songnen Plain can be divided into an eastern high plain, a central low plain, a western piedmont plain, and a river valley plain. The eastern high plain is mainly composed of middle Pleistocene loess-like silty clay and sand with Cretaceous bedrock underneath. The upper part of the central low plain is upper Pleistocene loess-like sandy loam and fine-silty sand, and the middle part is gray–black mucky silty clay sand with a middle Pleistocene sand layer, with Tertiary sandstone and shale beneath. The western piedmont plain is mainly pebble gravel and sandy gravel.

The topographic characteristics of the Songnen Plain give the area a relatively independent aquifer system that includes porous aquifers and fractured aquifers in Cretaceous, Tertiary, and Quaternary formations. There are regional, intermediate, and local groundwater flow systems in the east-west direction. Groundwater is recharged by precipitation, river water, irrigation water, and lateral runoff, and discharged through evaporation, discharges to rivers, lateral runoff, and artificial exploitation. Groundwater flowing from the northern, eastern, and western mountains and northern boundary form a discharge center at the junction of the Second Songhua River and Nenjiang River. Eventually, the groundwater flows out of the study area in the Songhua River or through lateral runoff [26].

3. Materials and Methods

3.1. Data Acquisition

Samples were collected between 2013 and 2015 from 1332 groundwater sampling sites evenly distributed across the study area. A map of the study area with the sampling sites marked is shown in Figure 1. Several groundwater samples were collected from one sampling site for the testing of different parameters. Most of the groundwater samples were collected from wells in residential areas (e.g., villages). Such wells do not generally have anti-seepage structures. The well tubes are made of PVC or cement and 100–200 mm in diameter. The water table depth is less than 20 m. A well was pumped with a pumping rate of 0.3–1 m^3/h for ~3 min before a fresh groundwater sample was collected. The sampling bottle was washed three times with groundwater before a sample was collected. Each sample was passed through a 0.22 μm membrane filter. HNO_3 and H_2SO_4 were added to samples for metal ion analysis and NH_4^+ analysis, respectively. Each sample was transported to the laboratory immediately after being sealed, and was then stored at 4 °C and analyzed as soon as possible. A total of 18 parameters (chemical oxygen demand (COD_{Mn}), pH, total dissolved solid (TDS), total hardness (TH), and K, Ca, Na, Mg, Fe, Mn, As, total phosphorus (TP), HCO_3^-, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-, and NO_2^-) were analyzed (Table S1).

3.2. Study Methods

The Fe and Mn concentration distributions in groundwater were analyzed using the kriging concentration interpolation module in ArcGIS 10.2 software. The altitudes of each sampling site were measured data. Annual meteorological precipitation, average meteorological temperature, soil type, and land use type for each sampling site were extracted from relevant maps (Table S2). The distance of each sampling site from the nearest river was calculated using ArcGIS 10.2 software using a river distribution map. Significant differences between values for groups of influencing factors were identified by performing Mann–Whitney and Kruskal–Wallis tests [31]. The relationships between concentrations of various indicators were assessed by performing Spearman correlation analyses [32]. A concentration below the detection limit was set to half the detection limit before a statistical test was performed. The statistical analyses were performed using SPSS 18 software.

4. Results and Discussion

4.1. Distributions of Elevated Fe and Mn Concentrations

Elevated Fe (0.3 mg/L) and Mn (0.1 mg/L) concentrations were found in 52.3% and 58.3%, respectively, of the groundwater samples from the study area (Table S3) [19], and the sites from which samples containing elevated Fe and Mn concentrations were collected were very broadly spread over the study area (Figure 2). Spatial variations were larger for the Fe concentrations than the Mn concentrations in the groundwater (the standard deviations of the Fe and Mn concentrations were 4.71 mg/L and 0.86 mg/L, respectively), and the Fe concentrations were higher than the Mn concentrations, which was mainly attributed to the differences of Fe and Mn contents in sediments. Significant variation of Fe concentrations may be due to the variation of reactivity of different Fe oxides [5]. However, the spatial distributions of groundwater containing elevated Fe and Mn concentrations were similar. Groundwater with elevated Fe and Mn concentrations was mainly found in the groundwater runoff and discharge areas in the middle of the Songnen Plain. Elevated Fe and Mn concentrations were found in 80.4% and 82.0%, respectively, of the groundwater samples collected below 140 m elevation (Table S4). Groundwater containing ultra-high Fe and Mn concentrations were clearly from sites along the river. The Fe concentrations were all >2.5 mg/L and in some samples were 25–50 mg/L, and the Mn concentrations were generally >0.5 mg/L.

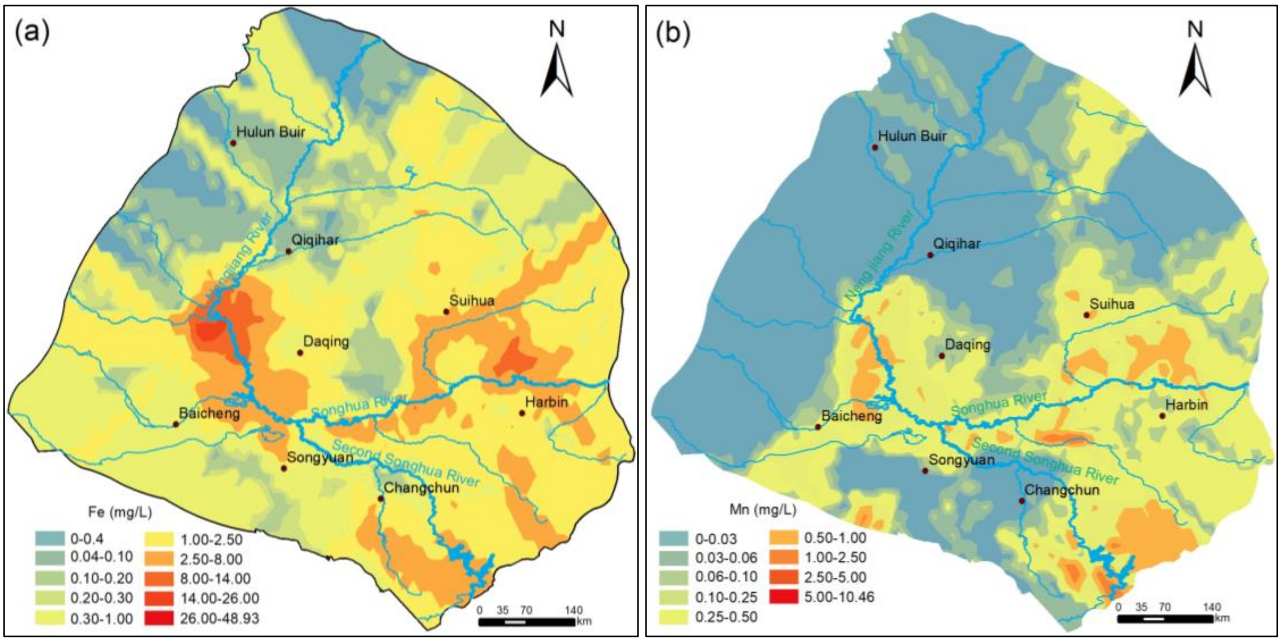


Figure 2. Distributions of (**a**) Fe and (**b**) Mn in groundwater in the Songnen Plain.

Interestingly, Daqing, an area with groundwater containing low Fe and Mn concentrations, is between areas with groundwater containing elevated Fe and Mn concentrations. Daqing is an industrial city. Large-scale exploitation of groundwater in the Quaternary Lindian formation, Taikang formation, and confined water in Cretaceous in Daqing have caused a cone of depression [33]. Artificial exploitation of groundwater could disturb the redox conditions of an aquifer, increase the dissolved oxygen concentration in the groundwater, and cause dissolved Fe and Mn in groundwater to be oxidized. The presence of Fe minerals can promote oxidation of ferrous Fe [22]. In addition, the groundwater level correlates well with the Fe and Mn concentrations in groundwater under natural conditions. The Fe and Mn concentrations in groundwater increase as the groundwater level rises [21]. This may be because the Eh (oxidation-reduction potential) of groundwater will decrease as the groundwater level increases and the increased reducing nature of the aquifer will cause more Fe and Mn to dissolve [34].

4.2. Factors Causing Elevated Fe and Mn Concentrations

4.2.1. Effects of Climate

There were significant differences between the Fe ($p < 0.05$) and Mn ($p < 0.001$) concentrations in groundwater from areas with different annual meteorological precipitation (Table 1). Significantly higher Fe concentrations and Mn concentrations were found in groundwater from areas with annual meteorological precipitation > 500 mm than in groundwater from areas with annual meteorological precipitation $\leq$ 500 mm (Figure 3). Higher Mn concentrations have also been found in groundwater from areas with humid climates (mean annual precipitation > 500 mm) than in groundwater from areas with arid climates [4]. This is because anoxic groundwater is more likely in an area with a humid climate than an arid climate and anoxic groundwater is conducive to reductive dissolution of Fe and Mn oxides.

Table 1. Summary of the results grouped by the influencing factors of Fe and Mn concentrations in the groundwater.

Influencing Factors		Groups (n = Number of Samples)				p-Values	
						Fe	Mn
Climate	Precipitation(mm)	(300,400] (n = 99)	(300,500] (n = 516)	(500,600] (n = 678)	(600,700] (n = 39)	$p < 0.05$	$p < 0.001$
	Temperature (°C)	(1,3] (n = 75)	(3,5] (n = 304)	(5,6] (n = 471)	(6,7] (n = 482)	$p < 0.001$	$p < 0.001$
Surface features	Altitude (m)	(0,140] (n = 250)	(140,160] (n = 414)	(160,180] (n = 224)	(180,400] (n = 444)	$p < 0.001$	$p < 0.001$
	Distance to the nearest river (km)	(0,5] (n = 252)	(5,10] (n = 199)	(10,40] (n = 533)	(40,150] (n = 348)	$p < 0.001$	$p < 0.001$
	Soil type	Dark-brown earths (n = 14)	Black soils (n = 263)	Chernozems (n = 343)	Castanozems (n = 19)	$p = 0.306$	$p < 0.05$
		Aeolian sandy soils (n = 150)	Meadow soils (n = 444)	Bog soils (n = 24)	Solonchaks (n = 11)		
		Solonetzs (n = 29)	Paddy soils (n = 15)	Water body (n = 16)	/		
	Soil texture	Sand (n = 72)	Loam (n = 407)	Clay (n = 849)	/	$p < 0.05$	$p < 0.001$
	Land use type	Paddy field (n = 92)	Dryland (n = 782)	Forest land (n = 37)	Grassland (n = 113)	$p < 0.05$	$p = 0.144$
		Water body (n = 73)	Construction land (n = 58)	Unutilized land (n = 175)	/		
Hydrochemical characteristics	COD_{Mn} (mg/L)	$\leq$1 (n = 475)	1–2 (n = 467)	>2 (n = 390)	/	$p < 0.001$	$p < 0.001$
	NH_4^+ (mg/L)	$\leq$0.5 (n = 1082)	0.5–1 (n = 130)	>1 (n = 118)	/	$p < 0.001$	$p < 0.001$
	NO_3^- (mg/L)	$\leq$1 (n = 393)	1–10 (n = 351)	10–50 (n = 213)	>50 (n = 375)	$p < 0.001$	$p < 0.001$
	TP (mg/L)	$\leq$0.02 (n = 163)	0.02–0.1 (n = 202)	0.1–0.4 (n = 190)	>0.4 (n = 174)	$p < 0.001$	$p < 0.001$

The p-values were calculated using Kruskal–Wallis tests and a p-value of less than 0.05 indicates there are significant differences among the Fe/Mn concentrations in groundwater from different groups of one influencing factor.

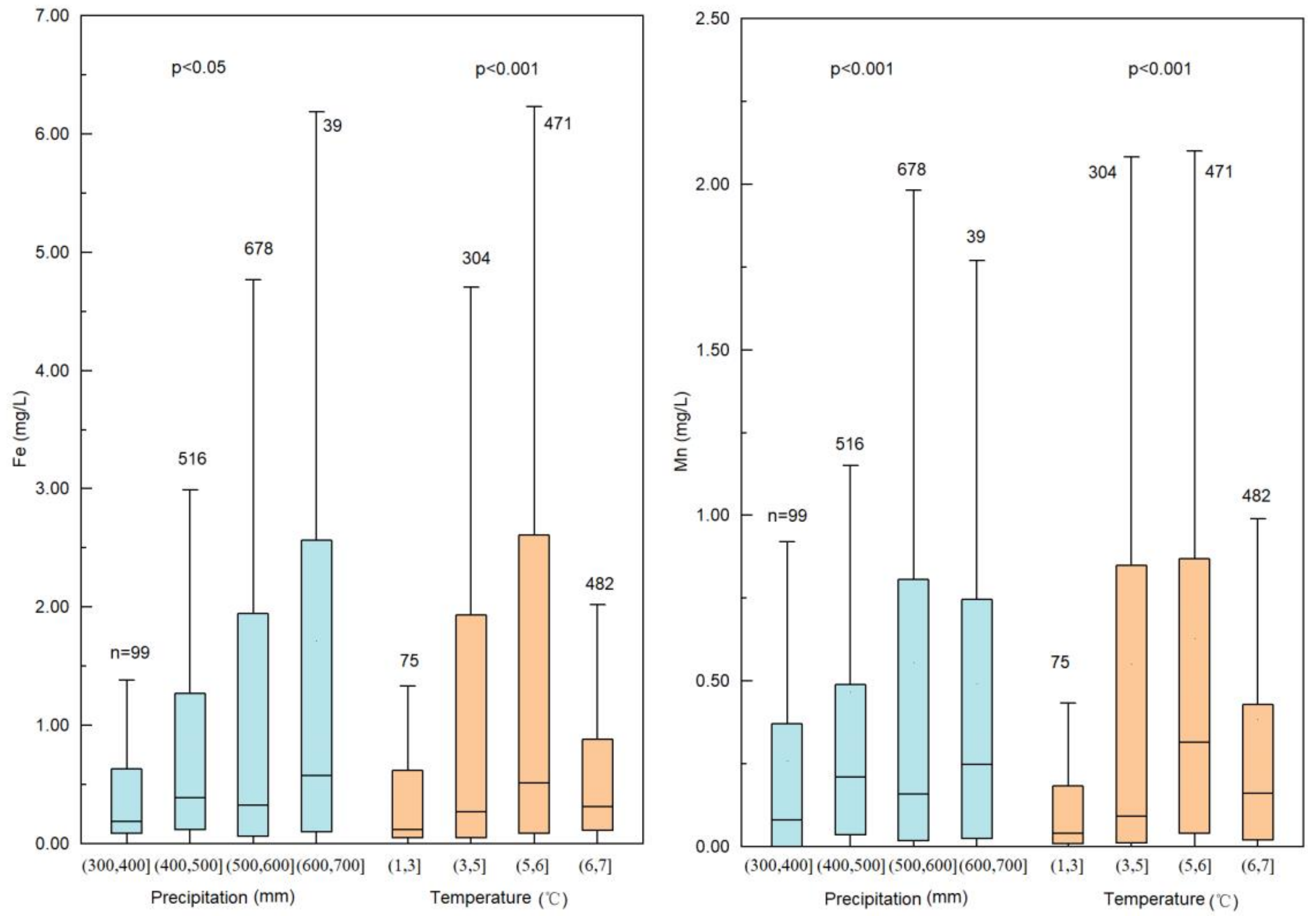


Figure 3. Fe and Mn distributions in groundwater from areas with different climates. 'Precipitation' and 'temperature' mean annual meteorological precipitation and annual average meteorological temperature, respectively, in 2015. The p-values are for Kruskal–Wallis tests. A p-value of less than 0.05 indicates there are significant differences among the Fe/Mn concentrations in groundwater from different groups of one influencing factor. n is the number of samples.

There were also significant differences ($p < 0.001$) between the Fe and Mn concentrations in groundwater from areas with different annual average meteorological temperatures (Table 1). Interestingly, the Fe and Mn concentrations in groundwater first increased and then decreased as the annual average meteorological temperature increased (Figure 3). The Fe and Mn concentrations in groundwater were highest at 5–6 °C, and elevated Fe and Mn concentrations in groundwater are 59.4% and 66.5%, respectively (Table S4). There is a positive correlation between groundwater temperature and land surface temperature in shallow groundwater (<30 m) [35]. The relationships between Fe and Mn concentrations and annual average meteorological temperature may therefore have been related to temperature-related biogeochemical processes. The redox state [36] and biological processes [37] can be affected by the temperature. It has previously been found that the pH and oxygen saturation of groundwater decrease as the temperature increases. High temperatures can affect microbial respiration, which can deplete oxygen in groundwater and make the conditions more reducing [38]. Microbe-mediated Fe and Mn redox cycles coexist in nature [39]. The temperature can affect the activities of Fe and Mn reducing and oxidizing bacteria. Sand column research showed that the temperature strongly affects the removal ratios of Fe and Mn in groundwater. As the temperature increases, the Fe and Mn removal ratios first increase and then decrease [40]. The variations in Fe and Mn concentrations in groundwater with temperature that we found may therefore have been caused by complex chemical and biological processes.

4.2.2. Effects of Surface Features

Altitude

The Fe and Mn concentrations in groundwater increased as the altitude decreased (Figure 4a), and there were significant differences between the Fe and Mn concentrations in groundwater from areas at four different altitudes (Table 1). Pore water in Quaternary formations in the study area was mainly controlled by the topography and geomorphology and formed a local groundwater flow system [29]. The high terrain area is therefore a groundwater recharge area with good runoff conditions. Oxygen is supplied to groundwater when precipitation and surface water recharge the groundwater. This brings the groundwater environment into a partially oxidized state and causes Fe to be present as oxides [30]. Moreover, the shorter residence time causes dissolved Fe and Mn in groundwater to migrate and not be accumulated. The aquifer in the lower terrain gradually becomes a reducing environment with a longer groundwater residence time, which is beneficial to the reductive dissolution of Fe and Mn oxides [27]. Furthermore, the Fe and Mn concentrations in the groundwater also increase because of evaporation. Low Fe and Mn concentrations have also been found in recharge areas in other regions, such as Xinjiang [41] and the Hetao Basin [12]. The Mn concentration increased, then decreased, and then increased again as the altitude decreased from the recharge area to the discharge area. Once dissolved oxygen and NO_3^- have been reduced, Mn oxides will be reduced [42], so the Mn concentration will increase at the beginning of the reduction. The released Mn will be absorbed by iron minerals with high adsorption capacities. Thus, the Mn distribution that we found may therefore have been caused by a combination of reduction and adsorption/co-precipitation processes. Similar results have been found for the Hetao Basin [12].

Distance to the Nearest River

The distance to the nearest river significantly ($p < 0.001$) affected the Fe and Mn concentrations in groundwater (Table 1). The Fe and Mn concentrations in groundwater were high in areas close to rivers. Elevated Fe and Mn concentrations have been found in groundwater in river valleys in other studies [43]. Under natural conditions, Fe and Mn are likely to become enriched on river floodplains, in lacustrine sediments, and in oxbow lakes. Such sediment will contain abundant active organic carbon, which can promote the development of a reductive environment in an aquifer [5,44]. Organic compounds can act as ligands for Fe, so the reductive dissolution of Fe oxides can be promoted at high organic carbon concentrations. In addition, the river valley in the study area generally has a dual structure. There is a layer of cohesive soil with 2–4 m depth in the upper part, which makes the lower gravel aquifer present a more closed reduction environment [29]. In addition, infiltration of river water containing a high dissolved organic carbon concentration can increase the Fe and Mn concentrations in shallow groundwater [5]. The COD_{Mn} in the main stream of the Songhua River is generally >4 mg/L [45]. The mean and median COD_{Mn}s in the groundwater samples were 1.90 and 1.3 mg/L, respectively. The COD_{Mn} is generally higher for river water (>4 mg/L) than groundwater, and groundwater is recharged by rivers in the rainy season [46]. Recharging with river water will therefore indirectly increase the Fe and Mn concentrations in groundwater.

Soil Type

The soil type can affect the Fe and Mn concentrations in groundwater [47], because different types of soil can have very different types and contents of Fe and Mn oxides and organic matter [48]. It can be seen that elevated Mn concentrations in groundwater (Figure 2) mainly occur in black soil and chernozem areas (Figure 5a) but elevated Fe concentrations in groundwater occur widely across the study area (the soil calcification scheme can be seen in [49]). Significant differences ($p < 0.05$) were found between the Mn concentrations in groundwater from areas with different soil types (Table 1), which indicates soil type can affect Mn concentrations in groundwater. No significant differences were found between the Fe concentrations in groundwater from areas with different soil types, but the distribution of the Fe concentrations in groundwater from areas with different soil types is shown as a box plot (Figure 4b). The Fe and Mn concentrations were higher in groundwater from areas with black soils, chernozems, meadow soil, bog soils and water body than that in other soil types, and the proportion of groundwater samples with elevated iron and manganese in these areas is more than 50% (Table S4).

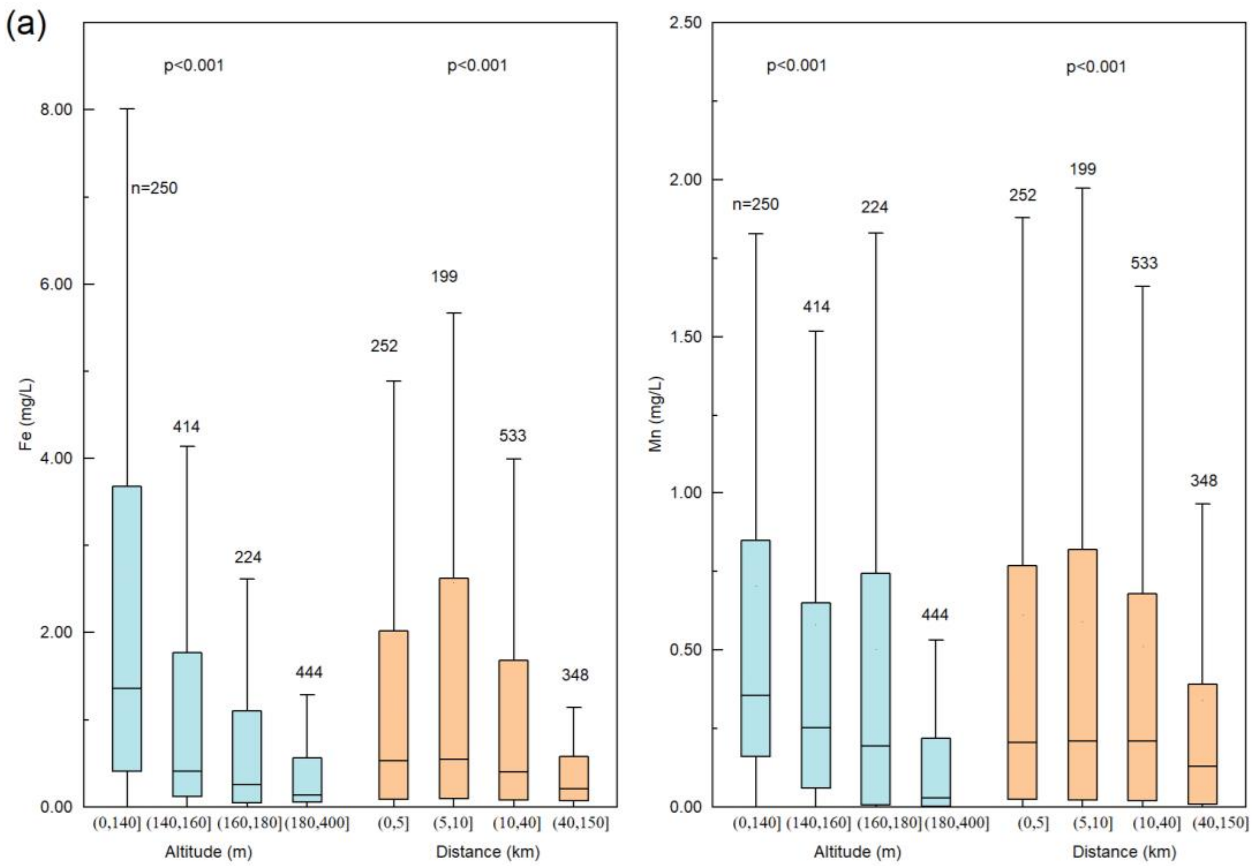
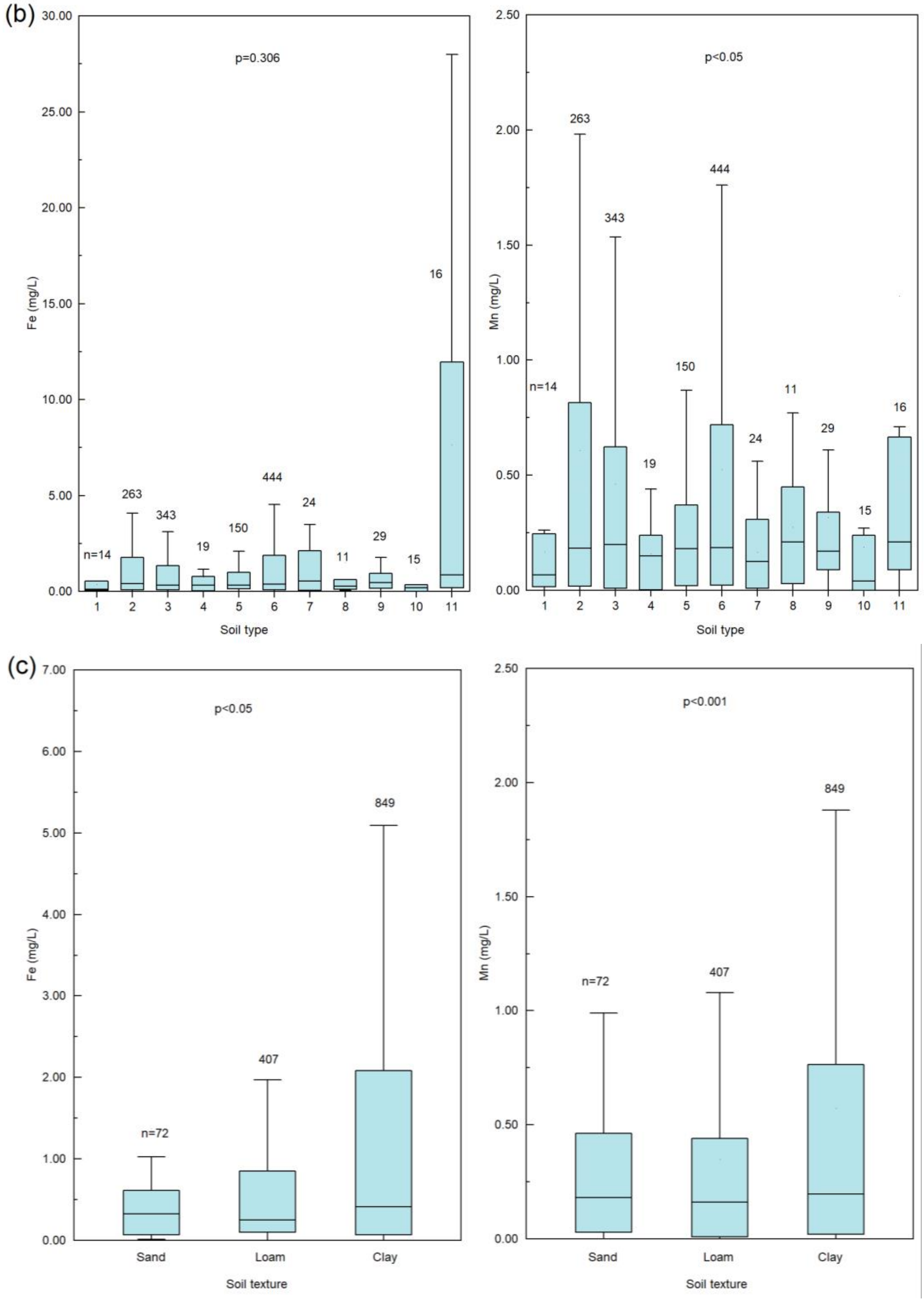


Figure 4. *Cont.*



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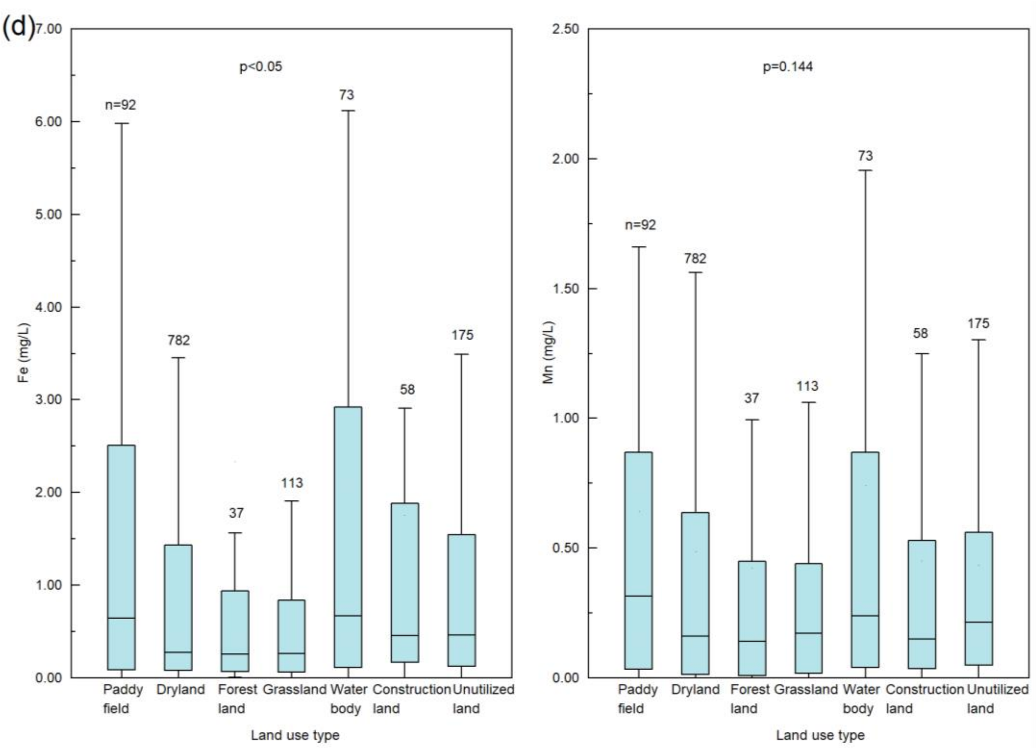

Figure 4. Fe and Mn distributions in groundwater from areas with various types of surface features. (**a**) Altitudes of the sampling sites and distances between the sampling sites and the nearest river. (**b**) Soil type (1–11 mean, in order, dark-brown earths, black soils, chernozems, castanozems, aeolian sandy soils, meadow soils, bog soils, solonchaks, solonetzs, paddy soils, and water body). (**c**) Soil texture. (**d**) Land use type. The *p*-values were calculated using Kruskal–Wallis tests and *p*-value of less than 0.05 indicates there are significant differences among the Fe/Mn concentrations in groundwater from different groups of one influencing factor. *n* is the number of samples.

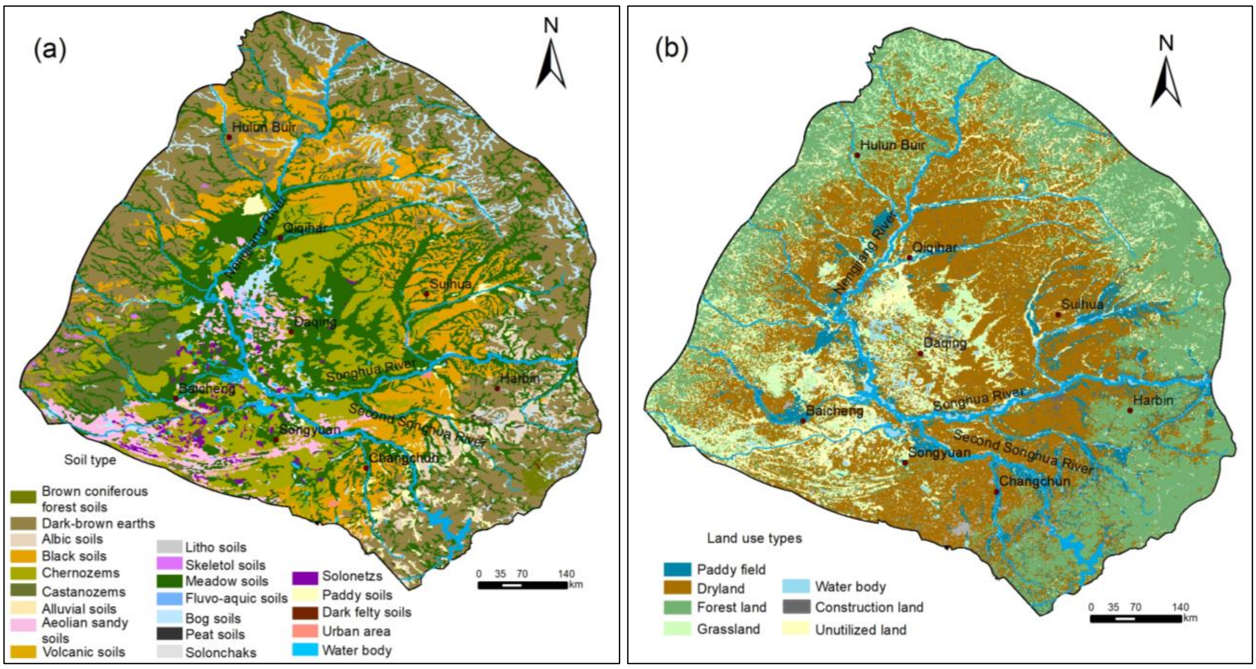

Figure 5. (**a**) Soil types and (**b**) land use types in the study area (data source can be seen in Table S2).

Black soils are mainly found in the northern and eastern parts of the study area, where the terrain is slightly higher than elsewhere (Figure 5a). The main minerals in black soils are illite and montmorillonite, and there are small amounts of chlorite, hematite, and limonite. The organic matter content of black soil is quite high. Humic acids are the main types of humic substances in black soils. The illuvial horizon contains many yellow or brown Fe and Mn rust spots and nodules. These rust spots are generally goethite [50]. Mn is often adsorbed onto the surfaces of Fe oxides or is present as Mn oxides and hydroxides in the solid phase. Mn will be released when Fe oxides are reduced [4].

Low valency dissolved Fe and Mn in soil can be generated through several processes. (1) With large amounts of organic matter (to donate electrons) present, abiotic reduction and dissimilatory microbial reduction of Fe(III) and Mn(III,IV) oxides can occur and promote Fe and Mn mobility [51]. (2) The abiotic reductive dissolution reaction rate can be accelerated in the presence of ligand–reducing pairs [20]. Complexes formed between organic matter and Mn can hinder Mn adsorption by clay minerals and increase Mn mobility [52]. (3) Light can markedly affect the Fe(III) reduction rate [53] and may contribute to Fe(III) reduction at the soil surface. (4) Under aerobic conditions, the presence of organic matter can greatly decrease the rate and degree of Mn(II) oxidation by oxygen that occurs on goethite surfaces [51]. Favorable environmental conditions and the various mechanisms through which Fe and Mn can be released mean that dissolved Fe and Mn in soil can enter groundwater through the infiltration of precipitation.

Chernozem occurs in large parts of the study area, mainly in the central low plain. The clay minerals in chernozem are dominated by montmorillonite. Chernozem contains large amounts of Fe oxides and organic matter but has a lower humic substance content and a thinner humus layer than black soil [50]. The mechanisms through which Fe and Mn are released are similar for chernozem and black soil. In the study area, the Fe and Mn concentrations in groundwater were therefore higher in areas with black soil than in areas with chernozem (Figure 4b).

In the study area, meadow soils are mainly in the river valley. The organic matter content of meadow soil is high and there is a thick humus layer. Humic acid is the main type of humus. There are obvious rusty spots, grey spots, and Fe-Mn nodules in meadow soil [50]. Therefore, precipitation and river water infiltration leach Fe and Mn ions and transfer them to the groundwater and increase the Fe and Mn concentrations in the groundwater.

The Fe concentrations in groundwater in areas with bog soil were also high. Bog soils are generally found in low-lying areas and are covered by long-term or seasonal surface water. The high groundwater level, long-term immersion, and lack of oxygen cause the redox potential of the soil to be low. Large amounts of reducing substances (e.g., H_2, H_2S, and CH_4) and organic acids are therefore produced through organic matter decomposition. The Eh of bog soil is generally <250 mV [50]. Fe and Mn oxides in soil are reduced to soluble low valency Fe and Mn [54]. The causes of elevated Fe and Mn concentrations in groundwater under water bodies classified by soil type and land use type are described in the section "Distance to the nearest river".

Soil Texture

There were significant differences between the Fe and Mn concentrations in areas with different soil textures (Table 1). The Fe and Mn concentrations in groundwater were highest in areas with clay soil (Figure 4c). The main clay minerals in clay are layered aluminosilicates containing Fe and Mn. Fe–Mn nodules also occur in clay [47,55]. and are sources of Fe and Mn to groundwater [27]. Clay soil contains fine particles and small interparticle pores and is poorly ventilated and permeable, making it readily able to become a reducing environment conducive to the reductive dissolution of solid Fe and Mn. The Fe and Mn concentrations in groundwater in the plain area increased as the overlying clay thickness increased [47].

Land Use Type

There were seven land use types in the study area (Figure 5b). Significant differences were found between the Fe concentrations in groundwater from areas with different land use types (Table 1), indicating that the land use type affects the Fe concentration in groundwater. The Fe concentrations in groundwater were highest in areas containing paddy fields and water bodies (Figure 4d). The Fe concentrations in groundwater from land with other land use types decreased in the order construction land > unutilized land (including saline–alkali land) > dryland > forest land > grassland. No significant differences were found between the Mn concentrations in groundwater from areas with different land use types, but the Mn concentrations decreased in a similar order to the Fe concentrations. Paddy fields are conducive to reducing environments developing because of the presence of surface water. Moreover, NH_4^+ generated by the application of N fertilizers during agricultural activities can promote the reduction of Fe–Mn oxides and cause Fe and Mn to be released into the water (see the section "Distance to the nearest river").

4.2.3. Effects of Hydrochemical Characteristics

pH

The Fe and Mn concentrations in the groundwater samples did not obviously correlate with the pH. The pH of samples was 5.7–10.3 and the mean and median were both 7.4, indicating that the groundwater environment in the study area is weakly alkaline. The samples at pH $\geq$ 7 accounted for 76.2% of the 328 samples with elevated Fe concentrations and pH data. The samples at pH $\geq$ 7 accounted for 77.3% of the 375 samples with elevated Mn concentrations and pH data. Generally, Fe and Mn concentrations in groundwater are controlled by the redox conditions and pH, and the solubility of Fe and Mn is higher at low pH [56]. This indicated that the elevated Fe and Mn concentrations in groundwater were mainly affected by reductive dissolution in the study area. This has also been found for other parts of the Songnen Plain [27].

NH_4^+

The Fe and Mn concentrations in the groundwater samples with different NH_4^+ concentrations were markedly different (Table 1). The Fe and Mn concentrations in groundwater were high when the NH_4^+ concentration was high (Figure 6). For the groundwater samples with NH_4^+ concentrations >1 mg/L, >90% of the groundwater samples contained elevated Fe and Mn concentrations (Table S4). Naturally generated NH_4^+ is mainly related to a reducing environment. Organic carbon is dominant in a reducing environment, and natural organic carbon often contains N-containing compounds. Decomposition of these compounds causes a reducing environment to develop and NH_4^+ to be produced. NH_4^+ is therefore a good indicator of the organic carbon degradation intensity [57]. It is therefore common for Fe, Mn, and NH_4^+ to coexist [5,27]. It has previously been found that NH_4^+ pollution caused by human activities, such as the release of sewage and agricultural and industrial waste, can cause the Fe and Mn concentrations in groundwater to increase [41,58].

COD_{Mn}

The Fe and Mn concentrations in groundwater increased markedly as the COD_{Mn} increased (Figure 6). Elevated Fe and Mn concentrations were found in >70% of the groundwater samples with COD_{Mn} >2 mg/L (Table S4). The COD_{Mn} is an important indicator of the organic matter concentration in water. The larger the COD_{Mn}, the more serious the organic pollution and the more reducing the environment is. Organic matter has been found to promote the release of Fe and Mn in aquifers in field studies [4] and laboratory experiments [3]. Reductive dissolution of Fe and Mn oxides mediated by microorganisms is an important mechanism that increases Fe and Mn concentrations in groundwater. Exogenous organic carbon replenishment can stimulate rapid responses of indigenous microorganisms and transfer Fe and Mn to groundwater [59]. At the same time, sediment rich in Fe and Mn oxides can promote organic matter degradation [60], which could alleviate organic matter pollution of groundwater.

NO_3^-

Significant negative correlations were found between the NO_3^- concentration and Fe and Mn concentrations in the groundwater samples (Figure 6). Elevated Fe and Mn concentrations were found in only 26.7% and 29.3%, respectively, of the groundwater samples with NO_3^- concentrations >50 mg/L (Table S4). NO_3^- reduction occurs before Fe and Mn oxides are reduced, according to the redox sequence [42]. Groundwater containing a high NO_3^- concentration will usually remain sufficiently oxidative to prevent reductive dissolution of Fe and Mn oxides [61]. Agricultural activities in the study area have caused large amounts of NO_3^- to enter groundwater [25,62]. NO_3^- can act as a strong oxidant in a relatively reductive environment. Under the action of microorganisms, Fe(II) and Mn(II) could be used as electron donors during denitrification to produce Fe(III) and Mn(IV), respectively, and therefore decrease the Fe and Mn concentrations in the groundwater [21]. At low NO_3^- concentrations, microbe-mediated Mn reduction may dominate [4].

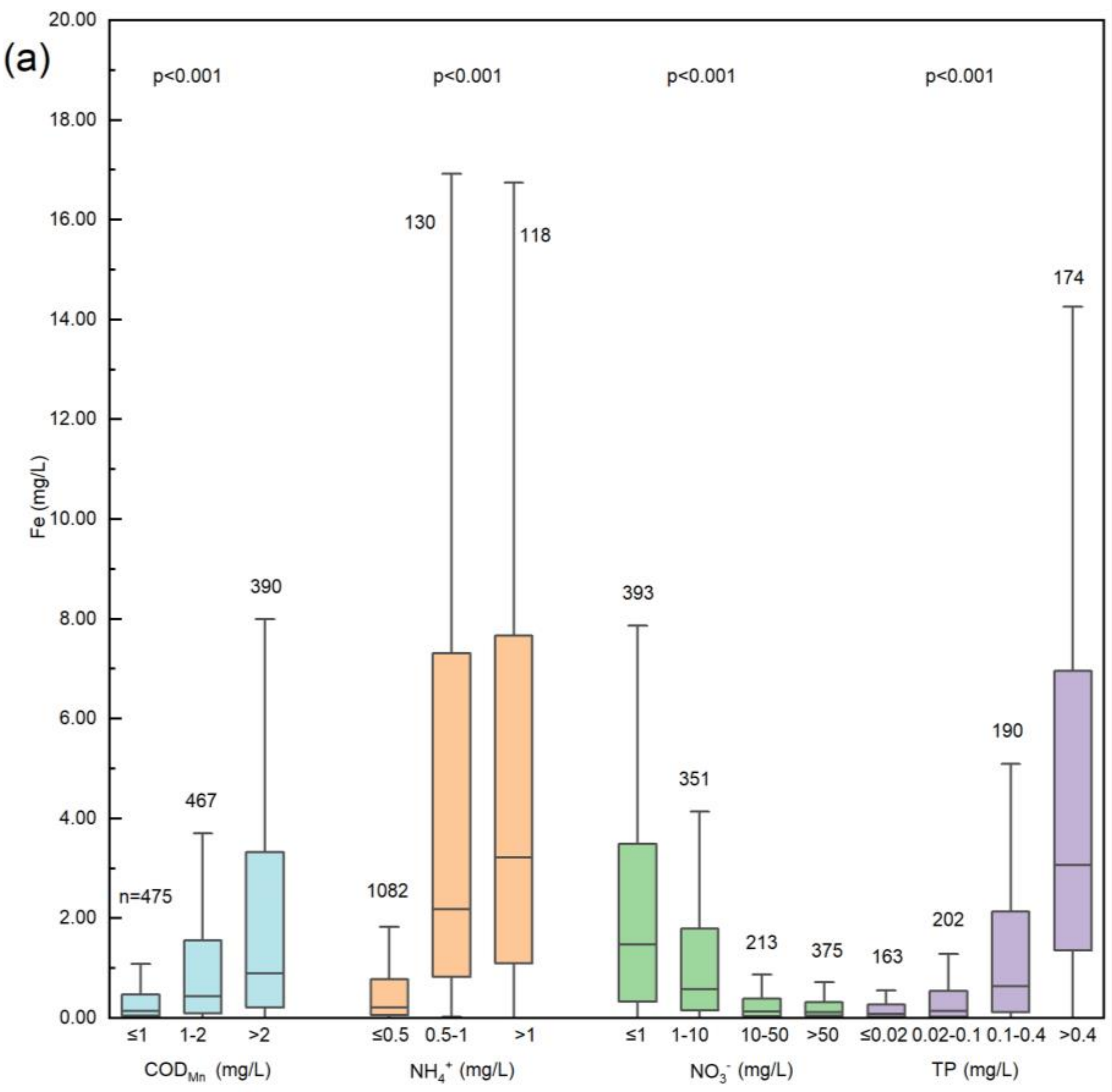

Figure 6. *Cont.*

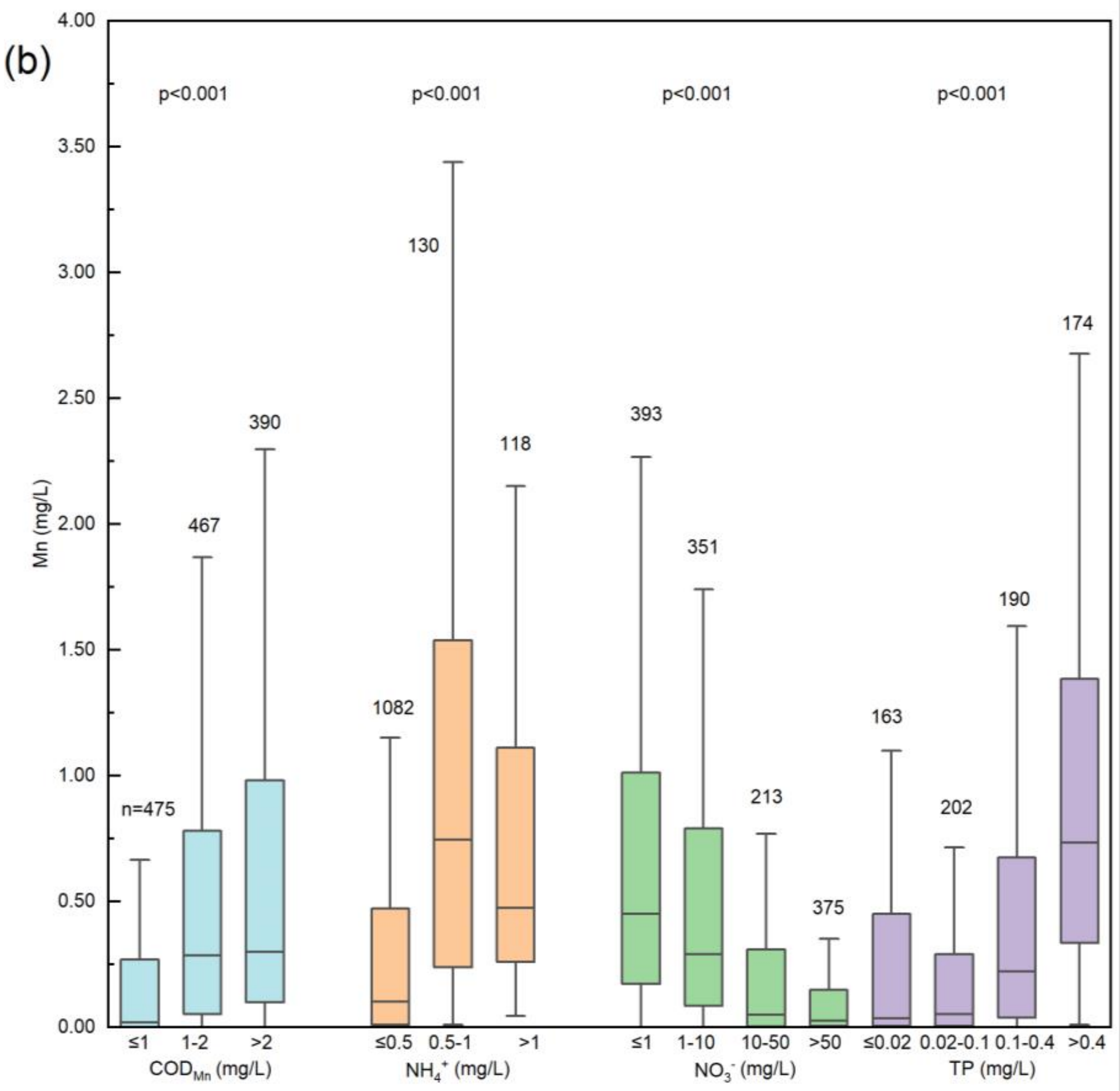

Figure 6. (**a**) Fe and (**b**) Mn distributions in groundwater in areas with different hydrochemical characteristics. The *p*-values were calculated using Kruskal–Wallis tests. *n* is the number of samples.

TP

The TP concentrations in the groundwater samples were very high. The mean concentration was 0.3 mg/L, which was higher than the relevant environmental quality standard for surface water (0.2 mg/L) [63]. The minimum and maximum were below detection limit and 7.12 mg/L, respectively. The TP concentration significantly positively correlated with the Fe and Mn concentrations, the correlation coefficients being 0.546 and 0.424, respectively (Table 2). The Fe and Mn concentrations were much higher in the groundwater samples with TP concentrations >0.4 mg/L than in the other samples (Figure 6). N and P pollution are mainly caused by agricultural activities [64,65], so N and P pollution may occur simultaneously. Excessive use of phosphate fertilizers occurs in the study area [66]. We therefore speculated that the TP concentration probably represented the effects of human activities. The NH_4^+ and NO_3^- concentrations significantly correlated with the TP concentration ($p < 0.01$), and the correlation coefficients were 0.561 and −0.502, respectively. This indicated that the high TP concentrations in groundwater in the study area may have been caused by agricultural pollution. Markedly higher TP contents have previously been found for agricultural land than other land use types in the study area [67]. The NH_4^+ concentration, TP concentration, and COD_{Mn} in the groundwater samples were therefore grouped by land use types (Figure S1), and it was found that these three indicators that may be affected by human activities were significantly different for different land use types.

Table 2. Spearman correlation results.

Variables		Mn	As	NH_4^+	NO_3^-	COD_{Mn}	TP
Fe	Correlation coefficient (r)	0.600 **	0.423 **	0.545 **	−0.450 **	0.357 **	0.546 **
	n	1332	1332	1332	1332	1332	729
Mn	Correlation coefficient (r)	1.000 **	0.481 **	0.515 **	−0.426 **	0.388 **	0.424 **
	n	1332	1332	1332	1332	1332	729

TP: total phosphorus; **: there is a significant difference at 0.01 level; *n*: number of samples.

The Fe and Mn distributions in groundwater from areas with different land use types were compared with the NH_4^+, TP, and COD_{Mn} distributions, and it was found that the distribution characteristics are similar. The Fe and Mn concentrations in groundwater were highest in areas with paddy fields and water bodies, and the NH_4^+ concentration, TP concentration, and COD_{Mn} in groundwater were also highest in areas with paddy fields and water bodies. This indirectly indicated that human activities have strongly affected the Fe and Mn concentrations in groundwater in the study area. Our hypothesis was tested further by superimposing the sampling sites with high NH_4^+ concentrations (>0.5 mg/L), high *p* concentrations (>0.2 mg/L), and high COD_{Mn}s (>1.0 mg/L) on the land use types map (Figure S2) and map of the distributions of the Fe and Mn concentrations in groundwater (Figure S3). The sampling sites with high NH_4^+ concentrations, TP concentrations, and COD_{Mn}s in groundwater were mostly in areas with large amounts of agricultural land and water bodies and matched closely the distributions of elevated Fe and Mn concentrations.

The results were compared with the results of a study of the vulnerability of aquifers in the Songnen Plain [25], and it was found that the Fe and Mn distributions were similar to the aquifer vulnerability index distribution. The Fe and Mn concentrations in groundwater were high in areas with high vulnerability indices. The vulnerability of an aquifer represents the difficulty with which the groundwater could become polluted, which can indirectly reflect the influences of human activities on Fe and Mn concentrations in groundwater.

Positive Correlations between the Fe, Mn, and As Concentrations

The Fe and Mn concentrations were significantly positively correlated (r = 0.6) (Table 1). High Fe and Mn concentrations in groundwater may have simultaneously occurred because of partial overlaps in the redox conditions during the reduction of Fe and Mn oxides [18]. The Fe and Mn concentrations in groundwater significantly positively correlated with the As concentration (r > 0.4 for both). The main active form of As in sediment is As bound to Fe/Mn oxides. This form of As will be released during the reductive dissolution of Fe/Mn oxides under moderately reducing conditions [30,42]. However, adsorption of As by Fe/Mn oxides means that the Fe, Mn, and As concentrations will not necessarily significantly positively correlate [61]. The results we found may have been caused by Fe oxides being reductively dissolved to the degree that the remaining fractions could no longer adsorb all of the released As [68].

4.3. Formation of Groundwater with Elevated Fe and Mn Concentrations

Groundwater with elevated Fe and Mn concentrations may form in the study area because of the presence of Fe and Mn sources, environmental conditions being favorable, and external stimulation occurring. Under suitable climate conditions and in a reducing environment, Fe and Mn in rocks rich in Fe/Mn minerals in mountainous areas around the plain and overlying soils will enter groundwater and accumulate through long-term leaching. Reducing substances introduced through human activities can promote the release of Fe and Mn into groundwater and increase the Fe and Mn concentrations.

The Fe and Mn concentrations in Quaternary confined water in the study area are low, while that in Quaternary phreatic water are high [33]. However, the lithologic conditions of them are similar, and the confined water is in a more reducing environment. Therefore, this study also indicates that Fe and Mn concentrations in shallow groundwater are largely affected by shallow characteristics such as surface features and the vadose zone. Similar conclusions have been drawn in many other studies [4,18].

Groundwater containing ultra-high Fe and Mn concentrations was mainly found at sites in the river valley, which has almost all of the favorable factors mentioned above. The annual meteorological precipitation is >500 mm in most parts of the study area (Figure S4), and the annual average meteorological temperature is 5–6 °C (Figure S5). The soil is mostly meadow soil, and the main land use types are paddy fields and water bodies. Lots of agricultural activities occur, and the aquifers are very vulnerable. Inputs of exogenous reducing substances can stimulate the reductive dissolution of Fe and Mn oxides. The terrain is low and the area is in the regional groundwater discharge area, which will be conducive to Fe and Mn enrichment.

4.4. Implications for Environmental Management

The wide distributions of groundwater containing elevated Fe and Mn concentrations in the study area mean that large numbers of people are affected. It is therefore necessary to suggest that residents of affected areas take appropriate measures to treat the water before consumption or to construct centralized drinking water sources using appropriately selected aquifer locations, considering many people in rural areas still drink untreated groundwater from private domestic wells. Geological processes are the main reasons for the elevated Fe and Mn concentrations in groundwater in the study area, but it is necessary to be alert to further increases in Fe and Mn concentrations in groundwater that may be caused by NH_4^+ and organic pollution caused by human activities. Meanwhile, anthropogenic pollutants could be degraded when the Fe and Mn concentrations in the groundwater increase. Regulating the biochemical reactions of primary chemical components and pollutants in aquifers may allow pollution of groundwater to be controlled and remediated.

5. Conclusions

Groundwater containing elevated Fe and Mn concentrations is widely distributed in the Songnen Plain, and the Fe and Mn distribution characteristics are similar. Groundwater containing ultra-high Fe and Mn concentrations was found along the river that runs through the study area. The Fe and Mn concentrations in groundwater significantly correlated with climate parameters, surface features, and hydrogeochemical characteristics. The Fe and Mn concentrations in groundwater increase as annual meteorological precipitation increases, and first increase and then decrease as the annual average meteorological temperature increases. The Fe and Mn concentrations are higher in the groundwater discharge area than in the groundwater recharge area. The Fe and Mn concentrations in groundwater are higher in areas close to the river than elsewhere. The Fe and Mn concentrations in groundwater are higher in areas with black soils, chernozems, meadow soils, and water bodies than in areas with other soil types. The finer the soil particles are, the higher the Fe and Mn concentrations are in groundwater. The Fe and Mn concentrations in groundwater are significantly higher in areas with paddy fields and water bodies than in areas with other land use types. The COD_{Mn}, NH_4^+ concentration, and TP concentration positively correlated with the Fe and Mn concentrations in groundwater. This reflects the common influences of natural conditions and human activities on the Fe and Mn concentrations in groundwater. Areas with groundwater containing ultra-high Fe and Mn concentrations have almost all of the favorable factors.

In summary, the distributions of elevated Fe and Mn concentrations in groundwater in the Songnen Plain are caused by Fe and Mn minerals in strata and soil and the favorable reducing environment in the aquifers. Exogenous reductive material inputs (COD_{Mn}, NH_4^+) caused by human activities could increase Fe and Mn concentrations in groundwater further. It is important to determine how further increases in the Fe and Mn concentrations in groundwater could be prevented and the current situation improved.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/agronomy11122392/s1, Figure S1: NH_4^+ concentrations, total phosphorus (TP) concentrations, and chemical oxygen demand (COD_{Mn}) compared with the Fe and Mn concentrations in groundwater in areas with different land use types, Figure S2: Overlay of the sampling points with high NH_4^+ concentrations, total phosphorus (TP) concentrations, and chemical oxygen demand (COD_{Mn}) in groundwater on a land use map, Figure S3: Overlay of the sampling points with high NH4+ concentrations, total phosphorus (TP) concentrations, and chemical oxygen demand (CODMn) in groundwater on a map of the distributions of the Fe and Mn concentrations in groundwater, Figure S4: Annual meteorological precipitation in 2015 in the study area, Figure S5: Annual average meteorological temperature in 2015 in the study area, Table S1: Methods for determining water quality indicators and the corresponding detection limits, Table S2: Data sources used in the study, Table S3: Statistical data for the Fe and Mn concentrations in the groundwater samples, Table S4: Summary of the Fe and Mn concentrations in the groundwater samples. grouped by the influencing factors.

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