

Article

Distribution and Origins of Hardness in Shallow and Deep Groundwaters of the Hebei Plain, China

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Abstract: Elevated hardness concentrations in groundwater have become a noteworthy concern in recent decades because long-term drinking of groundwater with high levels of hardness is an important factor resulting in chronic kidney diseases. In this study, the distribution and origins of groundwater total hardness (TH) in various sub-plains and different land-use areas of the Hebei Plain (HBP) were investigated. A total of 445 groundwater samples in the HBP were collected once in 2021, and twelve chemical parameters, including TH in groundwater, were analyzed. Results showed that TH-rich (>450 mg/L) shallow groundwater in both the central and littoral plains was more than twice that in the Piedmont plain. Similarly, TH-rich deep groundwater accounted for about 18% in the central plain but was negligible in the Piedmont plain. In the Piedmont plain, TH-rich shallow groundwater in urban areas was twice or more than in other land use types. By contrast, both TH-rich shallow and deep groundwaters in agricultural areas in the central plain were higher than those in rural areas. This was opposite to TH-rich shallow groundwater in the littoral plain. In the Piedmont plain, TH-rich shallow groundwater was mainly attributed to water-rock interaction, groundwater over-extraction, and the infiltration of domestic sewage and animal waste. In the central plain, both TH-rich shallow and deep groundwaters likely ascribed to the evaporite dissolution and seawater intrusion. By contrast, the leaching of agricultural fertilizers resulting in the dissolution of Ca-rich and Mg-rich minerals in the vadose zone was mainly responsible for the occurrence of TH-rich shallow groundwater in the littoral plain. Therefore, in order to limit elevated hardness concentrations in groundwater in the HBP, limiting shallow groundwater extraction and strengthening the supervision of the domestic sewage and animal waste in the Piedmont plain are recommended. Besides, restricting the use of nitrogenous fertilizers in the littoral plain is also recommended.

Keywords: total hardness; TH-rich shallow groundwater; groundwater over-extraction; evaporites dissolution; agricultural areas; Hebei plain



Citation: Qian, Y.; Zhen, S.; Yue, C.; Cui, X. Distribution and Origins of Hardness in Shallow and Deep Groundwaters of the Hebei Plain, China. *Water* **2024**, *16*, 310. <https://doi.org/10.3390/w16020310>

Academic Editor: Fernando António Leal Pacheco

Received: 12 December 2023

Revised: 5 January 2024

Accepted: 10 January 2024

Published: 17 January 2024



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1. Introduction

Groundwater is important for food security, human health, and ecosystems. Globally, groundwater is the main source of drinking water for more than 2.5 billion people, and about 70% of groundwater abstraction is used for agricultural irrigation [1]. Especially in areas with insufficient surface water, such as the Hebei Plain (HBP) and islands, groundwater is often the major water resource for drinking and irrigation purposes [2,3]. For example, groundwater accounted for more than 52% of the total water supply in the Hebei Province of China in 2019 [4]. However, the use of groundwater is always limited by its water quality, which is always controlled by kinds of natural and anthropogenic factors [5,6] because poor quality groundwater is often harmful to human beings and/or unsuitable for irrigation and industrial purposes [7–10]. For example, long-term drinking of groundwater with high levels of hardness is an important factor resulting in chronic kidney diseases that are

associated with reduced glomerular filtration rate and/or increased albumin excretion [11]. In addition, elevated hardness groundwater is also unfit for agricultural irrigation because it can render salinity and alkali hazards to soil [12]. Unfortunately, one publication in recent reported that elevated hardness was one of the major indicators for poor quality groundwater in the HBP; more than half of groundwater in phreatic aquifers and about 5% of groundwater in confined aquifers in the HBP showed that total hardness concentration above the allowable limit (450 mg/L) recommended by China [13].

To date, the origins of elevated hardness groundwater in many areas have already been investigated globally. A couple of studies reported that the infiltration of wastewater/leachate with high levels of hardness was often mainly responsible for elevated hardness in groundwater in industrial areas and landfills [14,15]. Similarly, the release of Ca^{2+} and Mg^{2+} from sediments via the ion exchange process under the condition of sewage irrigation was generally the major driving force for increasing groundwater hardness in irrigation areas [16,17]. By contrast, Cloutier et al. pointed out that groundwater with elevated hardness in a sedimentary rock aquifer system in Québec of Canada, was likely attributed to geogenic sources such as the dissolution of dolostone [18]. In addition, Cucchi et al. revealed that the occurrence of elevated hardness groundwater in plains aquifers of northeastern Italy probably ascribed to the over-extraction of groundwater [19]. This was also the main factor for elevated hardness groundwater in the HBP in the last century [20]. Besides, some researchers revealed hydrochemical characteristics related to groundwater hardness via different hydrogeochemical zones in the HBP during 1975–2010 [21,22]. For example, Zhan et al. reported that average concentrations of Ca^{2+} , Mg^{2+} , and total hardness in shallow groundwater in the Piedmont alluvial fan-recharge zone of the HBP during 1975–2005 increased by 42.6%, 40.5%, and 20.6%, respectively; meanwhile, from the piedmont alluvial fan-recharge zone to the coast plain-discharge zone, total hardness concentration in shallow groundwater in the HBP was from less than 450 mg/L increased to more than 900 mg/L [22]. However, human activities in the HBP accompanied by urbanization have intensified in recent decades [23]. This may affect spatial distribution and origins of groundwater hardness in the HBP. Recently, Li et al. investigated groundwater quality in the Hutuo river alluvial plain of the HBP and showed that about 26% of shallow groundwater and 20% of deep groundwater were characterized by high levels of total hardness (>450 mg/L) [24]. Bai et al. investigated groundwater chemistry in Yongqing County in the northern part of the HBP and reported that groundwater total hardness concentration in phreatic aquifers was up to 840 mg/L [25]. Guo et al. surveyed groundwater quality in the Bazhou irrigation district of the HBP and found that the total hardness concentration was up to 1483 mg/L in shallow groundwater but less than 90 mg/L in deep groundwater [26]. However, knowledge of the distribution and origins of hardness-rich shallow and deep groundwaters in the whole HBP is still limited.

Therefore, this study aims to depict the current spatial distribution of groundwater hardness in different land use types in the HBP and discuss the origins of elevated hardness in both shallow and deep groundwaters. Results will be beneficial for groundwater resource management in the HBP.

2. Study Area

2.1. Geographical Conditions

The HBP is part of the North China Plain and occupies an area of about 7.3×10^4 km². It is bounded by Henan province and Bohai Bay in the south and east and bounded by Taihang and Yanshan mountains in the west and north, respectively (Figure 1A). It has deep soil, abundant sunshine, and very flat topography [22]. The mean annual precipitation of the HBP is 500–600 mm and about 60–70% concentrated between June and August, whereas the mean annual evaporation rate is in the order of 1000–1300 mm [27,28]. The HBP is dominant in agriculture, with agricultural land more than 70% of the total area, and groundwater is the main water resource for agricultural irrigation [29]. With the

development of urbanization, the construction land in the HBP increased by more than 20% during the period of 2010–2020, which was mainly transformed from agricultural land [23].

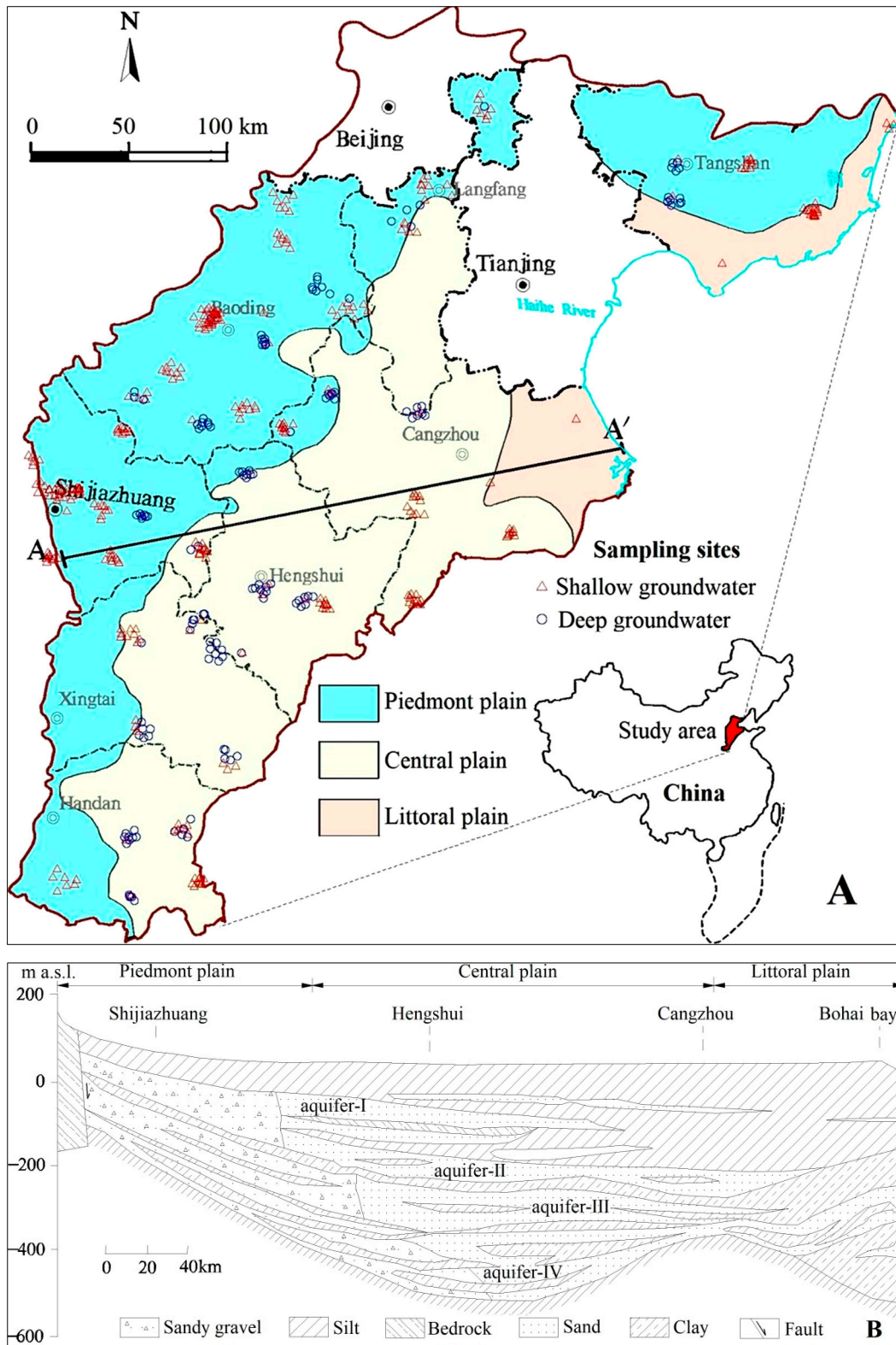


Figure 1. Hydrogeological setting and sampling sites in the Hebei Plain. (A) sampling sites, (B) cross section.

2.2. Geological and Hydrogeological Conditions

The HBP is a large sedimentary basin. Quaternary sediments originate from the middle and lower reaches of the Yellow River, the Haihe River, the Luanhe River, and their tributaries. Its thickness is approximately 150–500 m. It can be divided into the Piedmont Plain (PP), the Central Plain (CP), and the Littoral Plain (LP) from west to east [30]. They consist of fluvial deposits, alluvial and lacustrine deposits, and alluvial deposits with interbedded marine deposits, respectively. The PP has more plentiful groundwater resources in comparison with CP and LP because it has more recharge sources [31]. The HBP has four aquifer groups (Figure 1B). The aquifer-I at the top of the HBP is formed in the Holocene and a range of 10–50 m below land surface (BLS), with coarse-grained sand in the PP to fine-grained sand in the LP. The aquifer-II is formed in the upper Pleistocene with a range of 120–170 m BLS, with sandy gravel and medium to fine sand [21]. Groundwater in the above two aquifers is denoted as shallow groundwater and is a major water resource for agricultural irrigation. The aquifer-III is formed in the middle Pleistocene with a range of 170–350 m BLS. It consists of sandy gravel in the PP and medium to fine sand in the CP and LP [21]. While the aquifer-IV is formed in the lower Pleistocene and >350 m BLS, it consists of cemented sandy gravel and thin layers of weathered sand. Groundwater in these two aquifers is denoted as deep groundwater [32,33]. Groundwater was mainly recharged by lateral flow from mountain areas and vertical infiltration from rivers and irrigation return [21,33]. On a regional scale, groundwater flows are from the west to the east or the northeast. The groundwater flow velocity is 0.013–0.26 m/d in the PP and decreases to 0.002–0.10 m/d in the CP [34]. Recently, deep groundwater levels in urban areas increased significantly but still decreased in agricultural areas, which are often recharged by the leakage of overlying shallow groundwater [22,35].

3. Materials and Methods

3.1. Groundwater Sampling

A total of 306 shallow groundwater samples and 139 deep groundwater samples in the HBP were collected from July to September 2021. Among them, 202 shallow samples and 61 deep groundwater samples were collected from the PP, 84 shallow samples and 78 deep groundwater samples were collected from the CP, and 20 shallow samples were collected from the LP, respectively. In order to ensure samples representing the in-situ conditions, they were collected after pumping at least 3 well volumes or 30 min. Samples were filtered through 0.45 µm membrane filters to remove suspended solids in the field. All samples were stored at 4 °C until laboratory procedures could be performed.

3.2. Analytical Techniques

The pH was measured in the field by a multi-parameter portable meter (HANNA, HI 98121, Shanghai, China). HCO_3^- , CO_3^{2-} , and the total dissolved solids (TDS) were determined by volumetric and gravimetric methods, respectively. Other major anions (NO_3^- , SO_4^{2-} , Cl^-) were carried out on IC (Shimadzu LC-10ADvp, Kyoto, Japan). Chemical oxygen demand (COD) and total hardness (TH) were determined by potassium dichromate and EDTA titration methods, respectively. Major cations (Ca^{2+} , Na^+ , K^+ , Mg^{2+}) were measured by ICP-AES (ICAP6300, Thermo, New York, NY, USA). To assure data quality for indicators, each groundwater sample was analyzed in triplicate, sample batches were regularly interspersed with standards and blanks, and all data were corrected for instrument drift. The relative errors were $\leq \pm 5\%$ for all analyzed indicators.

3.3. Principal Components Analysis (PCA)

The PCA reduces high dimensional space into a smaller number of dimensions called principal components (PCs) by linearly combining measurements [36–38]. In this study, the PCA was used to extract the PCs that control the TH in shallow and deep groundwaters in various plains from 12 groundwater chemical parameters [39–41]. The units of these parameters were mg/L, except for pH. Log-transformed data and a standardized data

matrix were used in the PCA to give each variable equal weight in the multivariate statistical analysis. Rotation of the PCs was conducted using the Varimax method [42,43]. The number of PCs to keep was based on the Kaiser criterion (eigenvalues > 1). The terms “strong”, “moderate”, and “weak” (as applied to PC loadings) referred to the absolute loading values of >0.75, 0.75–0.5 and 0.5–0.3, respectively [8]. The software SPSS® Version 23.0 (SPSS Inc., Chicago, IL, USA) was used for the PCA in this study.

4. Results and Discussion

4.1. Characteristics of Groundwater Chemistry

Statistics for hydrochemical parameters in shallow and deep groundwaters in various sub-plains of the HBP are shown in Table 1. Median pH values in both shallow and deep groundwater in various sub-plains of the HBP were approximately 7.3–8.1, indicating that both shallow and deep groundwaters in the HBP were near neutral to weak alkaline. Moreover, deep groundwater showed a little bit more alkaline than shallow groundwater in both PP and CP according to their median pH values. From the PP to the LP, the median COD concentration in shallow groundwater increased gradually, indicating that shallow groundwater towards reducing environments from the PP to the LP. This is likely ascribed to the decrease of shallow groundwater flow velocity from the PP to the LP and the coarse-grained sand in the PP to fine-grained sand in the LP [21,34,37]. Moreover, deep groundwater showed a more oxidizing environment in comparison with shallow groundwater because median COD concentrations in shallow groundwater in both PP and CP were higher than those in deep groundwater. This probably ascribes to the more frequent reductive contamination (e.g., ammonium consuming dissolved oxygen) in shallow groundwater than in deep groundwater in the HBP [13,44]. Median concentrations of TDS and some major ions, such as Na^+ , Cl^- , and SO_4^{2-} , in shallow groundwater in both CP and LP were more than twice that in the PP. This likely ascribes to the stronger water-rock interaction and evaporation and the occurrence of seawater intrusion in the latter two sub-plains [13]. These are also likely responsible for the higher median concentrations of K^+ , Ca^{2+} , Mg^{2+} , and HCO_3^- in shallow groundwater in the latter two sub-plains than in the PP. In both of PP and CP, median values of TDS and most major ions (excluding K^+ and Na^+) in shallow groundwater were more than 1.5 times that in deep groundwater. This is likely due to the more frequent salt contamination in shallow groundwater than in deep groundwater because salt-contaminated groundwater was commonly characterized by high levels of TDS, Cl^- , and SO_4^{2-} [36,44–46]. By contrast, median concentrations of K^+ and Na^+ in shallow groundwater in the PP were lower than those in deep groundwater. This is likely because of the cation exchange in vadose zones that adsorbed Ca^{2+} and Mg^{2+} are replaced by K^+ and Na^+ [13]. Unlike the above major ions, the median value of NO_3^- in shallow groundwater in the PP was more than twice that in CP and LP. This indicates that shallow groundwater NO_3^- contamination was more often in the PP than in the other two sub-plains because shallow groundwater in the PP was characterized by stronger oxidizing environments and lower COD levels in comparison with that in the other two sub-plains [10,13,47]. This is also probably responsible for the higher median concentration of NO_3^- in deep groundwater in the PP than in the CP. Moreover, in the PP, the median NO_3^- concentration in shallow groundwater was 7 times that in deep groundwater, indicating that shallow groundwater in the PP was more vulnerable to NO_3^- contamination in comparison with deep groundwater.

4.2. Distribution of Groundwater Total Hardness

Groundwater TH concentrations in various sub-plains in the HBP are shown in Figure 2. Shallow groundwater TH concentrations in the PP ranged widely from 15 to 1411 mg/L with a median value of 343 mg/L. Median concentrations of shallow groundwater TH in CP and LP were 2.3 times and 1.8 times that in the PP, respectively. This is probably attributed to the stronger water-rock interaction and evaporation process in CP and LP than in the PP because shallow groundwater in the former two sub-plains presents

slower flow velocity and shallower groundwater levels than in the PP [13,34]. This is also likely responsible for the higher median concentration of TH in deep groundwater in the PP than in the CP. In both PP and CP, median concentrations of TH in shallow groundwater were more than twice that in deep groundwater. This is probably due to the cation exchange that adsorbed Ca^{2+} and Mg^{2+} in vadose zones replaced by Na^+ and/or K^+ , and finally infiltrating into shallow groundwater rather than deep groundwater via the water flow [13,48,49]. In addition, groundwater TH concentrations in areas with different land uses in the HBP were also investigated. In the PP, the median concentration of shallow groundwater TH in urban areas was more than 1.5 times that in rural and agricultural areas. In contrast, median concentrations of deep groundwater TH in rural and agricultural areas were 1.3 times and 1.1 times that in urban areas. Moreover, median TH concentrations in shallow groundwater in urban, rural, and agricultural areas were 4.1 times, 2.1 times, and 2.4 times those in deep groundwater, respectively. These likely indicate that anthropogenic inputs of TH in urban areas were stronger than those in rural and agricultural areas, and anthropogenic inputs of TH had contributed to shallow groundwater rather than deep groundwater because the intensity of human activities in urban areas was commonly stronger than that in other areas [39,43]. Besides, in the CP, median TH concentrations in both shallow and deep groundwaters in rural areas were lower than those in agricultural areas. By contrast, in the LP, the median TH concentration in shallow groundwater in rural areas was approximately twice that in agricultural areas.

Table 1. Descriptive statistics of chemical parameters in shallow and deep groundwaters in the Hebei Plain.

Items	Shallow Groundwater									Deep Groundwater					
	Piedmont Plain			Central Plain			Littoral Plain			Piedmont Plain			Central Plain		
	Min.	Med.	Max.	Min.	Med.	Max.	Min.	Med.	Max.	Min.	Med.	Max.	Min.	Med.	Max.
pH	5.0	7.5	13.4	6.2	7.4	8.2	6.7	7.3	9.2	6.2	7.8	10.3	7.1	8.1	8.3
COD	0.3	0.7	8.4	0.3	1.4	2.8	0.5	1.6	14.1	0.2	0.6	2.0	0.4	0.8	4.0
TDS	140	507	3688	224	1857	12,180	284	1116	23,550	185	324	1857	325	714	9570
K^+	0.3	1.4	13.8	0.4	1.8	12.4	0.6	5.0	51.0	0.3	1.5	3.8	0.3	1.2	7.5
Na^+	6	33	724	35	384	2670	53	100	6465	7	52	489	74	206	1940
Ca^{2+}	5	82	257	9	111	509	32	147	571	4	34	166	5	32	282
Mg^{2+}	1	33	217	5	131	833	6	55	1219	1	13	135	2	24	759
SO_4^{2-}	4	61	1999	30	438	5967	21	178	3665	5	37	804	46	179	3964
CO_3^{2-}	<DL	<DL	18	<DL	<DL	12	<DL	<DL	59	<DL	<DL	12	<DL	<DL	30
HCO_3^-	109	319	915	135	651	1118	227	449	604	103	229	877	57	226	1172
Cl^-	6	51	966	19	342	2040	21	213	13,830	2	19	466	12	132	2066
NO_3^- -N	<DL	5.6	44.5	<DL	0.4	36.2	<DL	2.0	70.1	<DL	0.8	23.5	<DL	0.4	6.3

Note: pH without the unit while other parameters with the unit of mg/L; <DL: below detection limits.

Compared to the allowable limit (450 mg/L) of TH in groundwater recommended by China [50], about 33.2% of shallow groundwater in the PP exceeded the allowable limit of TH and is denoted as TH-rich groundwater in this study. TH-rich shallow groundwater in CP and LP were 2.4 times and 2.1 times that in the PP, respectively. Similarly, TH-rich deep groundwater in the CP was 11.2 times that in the PP. Moreover, TH-rich shallow groundwater in PP and CP was 20.8 times and 4.4 times TH-rich deep groundwater, respectively. In the PP, the proportion of TH-rich shallow groundwater in urban areas was 72%, and was 2.0 times and 2.7 times that in rural and agricultural areas. By contrast, TH-rich deep groundwater in the PP only occurred in agricultural areas rather than urban and rural areas. In the CP, both TH-rich shallow and deep groundwaters in agricultural areas were higher than those in rural areas. In contrast, TH-rich shallow groundwater in rural areas in the LP was 100% and was 1.4 times that in agricultural areas.

As shown in Figure 3, TH-rich shallow groundwater in the PP was commonly dominated by Ca^{2+} in cations and HCO_3^- in anions, respectively, and Ca- HCO_3 facies accounted for 80.6% of TH-rich shallow groundwater in the PP. By contrast, in the CP, TH-rich shallow groundwater was generally dominated by Na^+ in cations, and Na- SO_4 facies (36.4%), Na- HCO_3 facies (24.2%), and Na-Cl facies (19.7%) were major hydrochemical facies in TH-rich shallow groundwater. Similarly, TH-rich deep groundwater in the CP was also

dominated by Na^+ in cations, and Na-Cl facies (42.9%) and Na-SO_4 facies (35.7%) were major hydrochemical facies. In the LP, TH-rich shallow groundwater was commonly dominated by Ca^{2+} in cations and Cl^- in anions, respectively, and Ca-HCO_3 facies (42.9%) and Na-Cl facies (28.6%) were major hydrochemical facies in TH-rich shallow groundwater. In addition, in the PP, TH-rich shallow groundwater dominated by Mg^{2+} in urban, rural, and agricultural areas was 0%, 10.3%, and 40%, respectively. In both CP and LP, TH-rich shallow groundwater dominated by Mg^{2+} in agricultural areas accounted for 21.0% and 11.1%, respectively, but none in rural areas. Besides, TH-rich deep groundwater dominated by Mg^{2+} only occurred in agricultural areas (7.7%) in the CP.

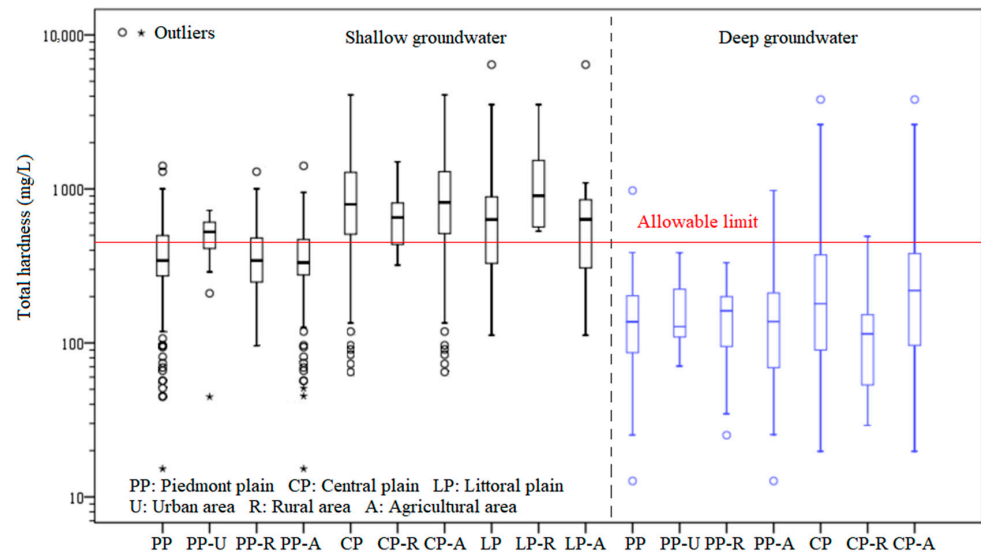


Figure 2. Distributions of total hardness in shallow and deep groundwaters in various sub-plains and different land-use types in the Hebei Plain.

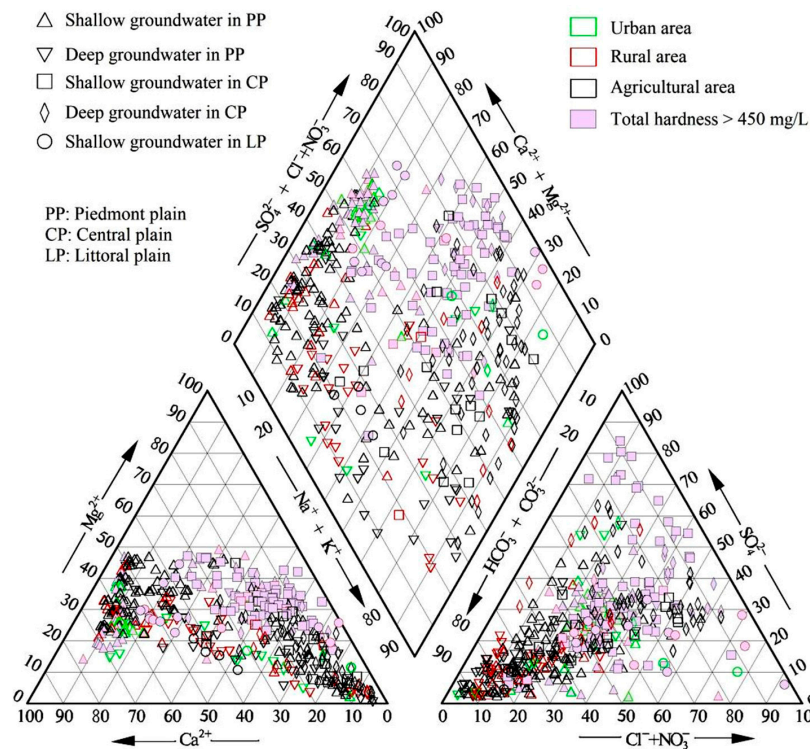


Figure 3. Hydrochemical facies in shallow and deep groundwaters in various sub-plains and areas with different land use in the Hebei Plain.

4.3. Origins of Groundwater Total Hardness

4.3.1. Gibbs Diagram

In this study, the Gibbs Diagram was used to analyze hydrogeochemical processes that control groundwater TH levels in the HBP. As seen in Figure 4, Na/(Na + Ca) ratios in 75.7% of shallow groundwater and 83.6% of TH-rich shallow groundwater in the PP were below 0.5 and accompanied by low levels of TDS (<1200 mg/L). This indicates that rock weathering was the dominant hydrochemical process for TH-rich shallow groundwater in the PP [49]. In the PP, the mean TDS concentration in TH-rich shallow groundwater with Na/(Na + Ca) ratios < 0.5 was more than twice that in shallow groundwater with TH < 450 mg/L and Na/(Na + Ca) ratios < 0.5. This indicates that the salinisation with cation exchange was probably another important hydrochemical process for TH-rich shallow groundwater in the PP [51]. On the other hand, the vadose zone thickness covering shallow groundwater in the PP was thicker because shallow groundwater in the PP was over-extracted, and its water table has been deeper continuously for the past 40 years [52]. In this case, more Ca²⁺ and Mg²⁺ would be released from the vadose zone into shallow groundwater by the cation exchange of Na⁺ and/or K⁺ via water flow and finally result in elevated TH and TDS concentrations in shallow groundwater [19,20]. This inference was supported by the evidence that shallow groundwater TH concentrations in the PP had a significantly positive correlation with the depth of the shallow groundwater table (Figure 5). Therefore, it can be concluded that the hydrochemical process of TH-rich shallow groundwater in the PP was mainly controlled by both rock weathering and salinisation with cation exchange resulting from groundwater over-extraction. By contrast, TH-rich shallow groundwater in the other two sub-plains was unaffected by the salinisation with cation exchange because the over-extraction of shallow groundwater in these two sub-plains was insignificant, and their shallow groundwater TH concentrations had insignificant correlations with the depth of shallow groundwater table (Figure 5).

In the CP, Na/(Na + Ca) ratios and TDS concentrations in TH-rich shallow groundwater were higher in comparison with that in the PP. For instance, Na/(Na + Ca) ratios in 89.4% of TH-rich shallow groundwater in the CP were above 0.5, with a mean TDS concentration of 3013 mg/L (Figure 4). This infers that the dissolution of evaporites with cation exchange and/or the evaporation process was probably mainly controlled by hydrochemistry of TH-rich shallow groundwater in the CP [51] because shallow groundwater in the CP was shown shallower depth of water table and longer residence time in comparison with that in the PP [33]. However, the depth of the shallow groundwater table in the CP was generally deeper than 3 m [44]. This indicates that the evaporation process had little influence on the hydrochemistry of TH-rich shallow groundwater in the CP because groundwater evaporation is negligible when the groundwater table is deeper than 3 m [52]. Thus, evaporite dissolution rather than the evaporation process was likely the major hydrochemical process for TH-rich shallow groundwater in the CP. It was also probably the major hydrochemical process for TH-rich deep groundwater in the CP because Na/(Na + Ca) ratios in 92.9% of TH-rich shallow groundwater in the CP were above 0.5 with a mean TDS concentration of 2937 mg/L (Figure 4). In addition, about 16.7% of TH-rich shallow groundwater and 21.4% of TH-rich deep groundwater in the CP were characterized by Na/(Na + Ca) ratios > 0.8 and TDS concentrations > 3000 mg/L (Figure 4). This indicates that seawater intrusion was likely another important factor controlling the hydrochemistry of TH-rich shallow and deep groundwaters in the CP [44]. As a consequence, evaporite dissolution and seawater intrusion were two major hydrochemical processes controlling both TH-rich shallow and deep groundwaters in the CP.

In the LP, more than 70% of TH-rich shallow groundwater was characterized by Na/(Na + Ca) ratios < 0.5 and TDS concentrations < 1500 mg/L (Figure 4). This indicates that rock weathering was likely the major factor for TH-rich shallow groundwater in the LP [53]. Besides, about 21.4% of TH-rich shallow groundwater in the LP was characterized by Na/(Na + Ca) ratios > 0.9 and TDS concentrations > 7000 mg/L (Figure 4), indicating that seawater intrusion was another important factor controlling hydrochemistry of TH-rich

shallow groundwater in the LP. Thus, rock weathering and seawater intrusion were two major hydrochemical processes controlling TH-rich shallow groundwater in the LP.

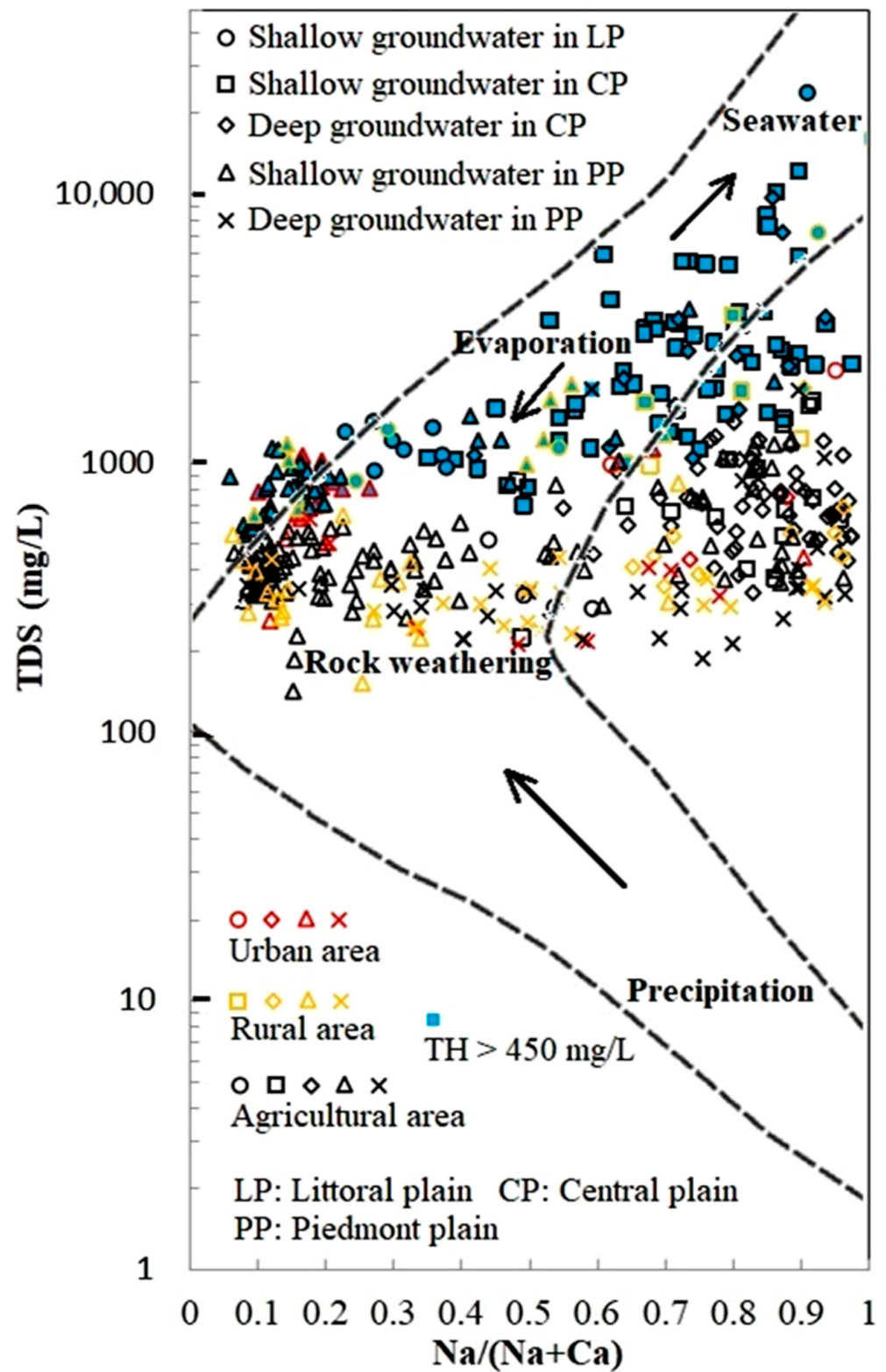


Figure 4. Gibbs diagram of shallow and deep groundwaters in various sub-plains and areas with different land use in the Hebei Plain.

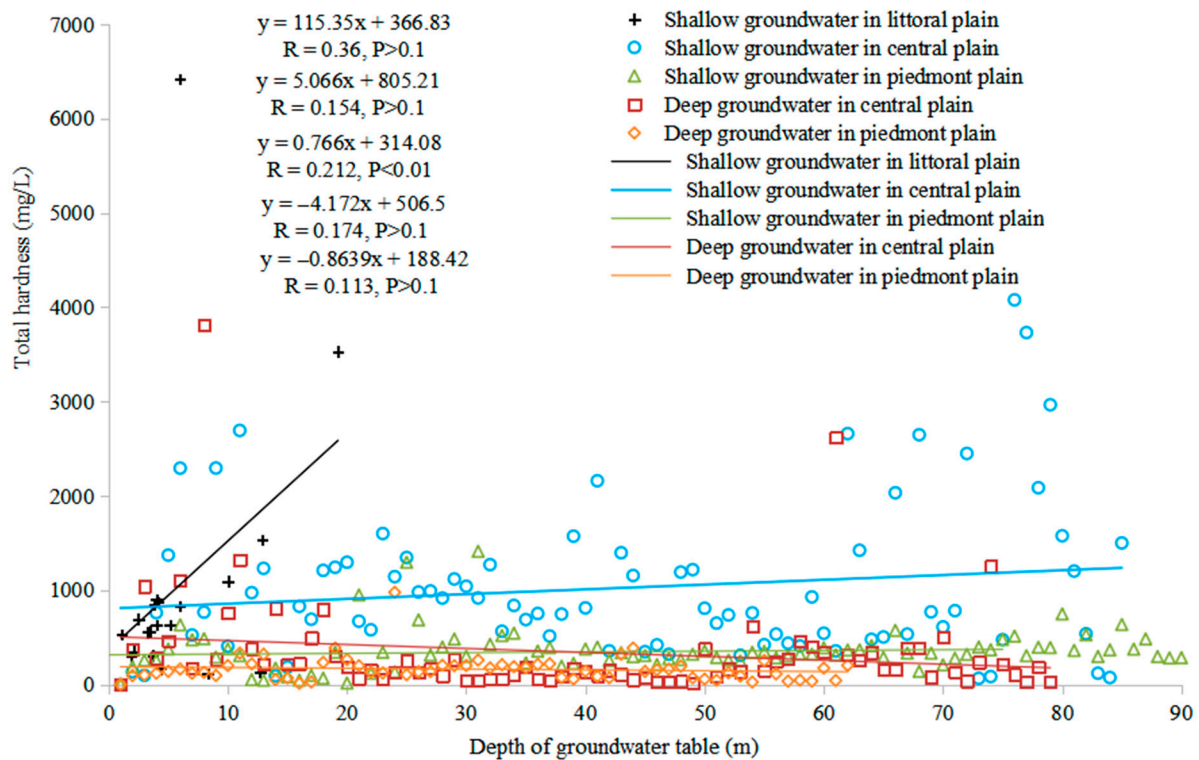


Figure 5. Relationships between total hardness concentrations and groundwater tables in shallow and deep groundwaters in various sub-plains in the Hebei Plain.

4.3.2. Principal Components Analysis

In this study, factors (PCs) controlling groundwater chemistry in various sub-plains of the HBP, where TH-rich groundwater often occurs, were extracted by the PCA. As shown in Table 2, shallow groundwater chemistry in the PP was mainly controlled by four factors. PC1 was shown strong positive loadings (SPL) (>0.75) of TDS, Na^+ , SO_4^{2-} , and Mg^{2+} , and moderate positive loadings (MPL) (0.5–0.75) of Cl^- and TH. This indicates that the PC1 was likely indicative of the water-rock interaction and salinisation (resulted from groundwater over-extraction), because TH-rich shallow groundwater in the PP was mainly controlled by rock weathering and salinisation (as mentioned previously) that resulted in elevated TDS, Na^+ , SO_4^{2-} , Mg^{2+} , Cl^- , and TH concentrations in shallow groundwater in the PP [13,20]. Besides, TH-rich shallow groundwater in the PP was also affected by another factor (PC2) because it also had a MPL of TH. Specifically, the PC2 had SPL of NO_3^- and Ca^{2+} and MPL of K^+ and TH. This factor probably represented the dissolution of Ca-rich minerals accompanied by the infiltration of domestic sewage and animal waste because domestic sewage and animal waste are an enrichment of N and K and are main sources for high levels of NO_3^- and K^+ in shallow groundwater in the PP [10,36,47], and NO_3^- contamination results in the dissolution of calcium-rich minerals in vadose zone via water flow [44]. As a consequence, water-rock interaction, groundwater over-extraction (salinisation), and the infiltration of domestic sewage and animal waste (dissolution of calcium-rich minerals) were mainly responsible for the occurrence of TH-rich shallow groundwater in the PP.

In the CP, shallow groundwater chemistry was mainly controlled by two PCs. PC1 showed SPL of TDS, TH, Mg^{2+} , SO_4^{2-} , Na^+ , Cl^- , and Ca^{2+} . This indicates that TH-rich shallow groundwater in the CP was likely attributed to the evaporite dissolution and seawater intrusion because they were two major factors controlling TH-rich shallow groundwater in the CP (as mentioned above), and the dissolution of evaporites (e.g., dolomite and bitter salt) would enrich shallow groundwater TDS, TH, Mg^{2+} , SO_4^{2-} , and Ca^{2+} concentrations [46], besides, seawater intrusion would result in high levels of TDS, Na^+ , and Cl^- in shallow groundwater [36,45]. Similarly, they were also mainly responsible for the

occurrence of TH-rich deep groundwater in the CP, because PC1 in deep groundwater in the CP also had SPL of TDS, Mg²⁺, SO₄²⁻, TH, Na⁺, Cl⁻, and Ca²⁺, and a MPL of HCO₃⁻ (Table 2).

Table 2. Principal component (PC) loadings for chemical parameters in shallow and deep groundwaters in various sub-plains in the Hebei Plain.

Items	SG in PP				Items	SG in CP		Items	SG in LP			Items	DG in CP		
	PC1	PC2	PC3	PC4		PC1	PC2		PC1	PC2	PC3		PC1	PC2	PC3
TDS	0.94	0.25	0.17	0.11	TDS	0.98	0.09	Mg ²⁺	0.99	-0.06	-0.04	TDS	1.00	0.04	-0.03
Na ⁺	0.86	-0.35	-0.13	0.13	TH	0.97	0.18	TDS	0.99	-0.08	-0.06	Mg ²⁺	0.98	0.06	-0.01
SO ₄ ²⁻	0.84	0.23	-0.13	-0.01	Mg ²⁺	0.97	0.16	Cl ⁻	0.99	0.02	-0.07	SO ₄ ²⁻	0.98	0.03	0.01
Mg ²⁺	0.77	0.15	0.49	0.10	SO ₄ ²⁻	0.94	-0.06	TH	0.99	0.07	0.02	TH	0.98	0.11	0.00
Cl ⁻	0.71	-0.01	0.17	0.01	Na ⁺	0.94	0.08	Na ⁺	0.99	-0.11	-0.10	Na ⁺	0.97	-0.03	-0.07
TH	0.62	0.60	0.46	0.06	Cl ⁻	0.82	0.12	COD	0.95	0.24	-0.03	Cl ⁻	0.95	0.10	-0.03
NO ₃ ⁻	-0.03	0.88	0.07	0.00	Ca ²⁺	0.77	0.16	K ⁺	0.85	-0.02	-0.08	Ca ²⁺	0.84	0.28	0.04
Ca ²⁺	0.31	0.84	0.31	-0.01	K ⁺	0.34	-0.32	SO ₄ ²⁻	0.70	-0.56	-0.08	HCO ₃ ⁻	0.68	-0.13	-0.17
K ⁺	-0.14	0.65	-0.17	0.59	HCO ₃ ⁻	0.08	0.81	pH	0.24	-0.86	-0.21	K ⁺	0.13	0.92	-0.01
pH	0.06	-0.23	-0.78	0.03	pH	-0.14	-0.78	HCO ₃ ⁻	0.14	0.74	-0.18	COD	0.17	0.88	-0.16
HCO ₃ ⁻	0.50	-0.10	0.63	0.33	COD	0.24	0.72	Ca ²⁺	0.66	0.67	0.32	NO ₃ ⁻	-0.07	0.33	0.12
COD	0.17	-0.01	0.13	0.91	NO ₃ ⁻	0.01	0.42	NO ₃ ⁻	-0.10	0.04	0.98	pH	-0.03	0.03	0.98
Eigenvalue	4.2	2.6	1.7	1.3		6.1	2.2		7.5	2.1	1.2		7.0	1.8	1.0
EV (%)	35.2	21.5	14.1	11.1		50.6	18.1		62.7	17.7	9.7		58.0	15.4	8.6
CV (%)	35.2	56.7	70.8	81.9		50.6	68.7		62.7	80.3	90.1		58.0	73.3	81.9

Notes: SG: Shallow groundwater; DG: Deep groundwater; PP: Piedmont plain; CP: Central plain; LP: Littoral plain; EV: Explained variance; CV: Cumulative variance; Bold and italics numbers: maximum absolute PC loading of one parameter.

By contrast, in the LP, shallow groundwater chemistry was mainly controlled by three PCs. PC2 showed SPL of Ca²⁺, TH, and NO₃⁻, and a MPL of Mg²⁺ (Table 2). This was likely indicative of the dissolution of Ca-rich and Mg-rich minerals (e.g., dolomite) resulting from the NO₃⁻ contamination due to agricultural fertilizers because the mean concentration of shallow groundwater NO₃⁻ in agricultural areas in the LP was more than twice that in urban and rural areas, and NO₃⁻ contamination results in the dissolution of Ca-rich and Mg-rich minerals in vadose zone via water flow [44]. Therefore, the occurrence of TH-rich shallow groundwater in the LP is mainly ascribed to the leaching of agricultural fertilizers.

5. Conclusions

In this study, distributions of TH in shallow and deep groundwaters in various sub-plains in the HBP were investigated. Elevated groundwater TH concentrations in both CP and LP were more severe than that in the PP because TH-rich shallow groundwater in both CP and LP was more than twice that in the PP, and TH-rich deep groundwater accounted for about 18% in the CP but was negligible in the PP. Besides, TH-rich groundwater in the CP occurred more frequently in agricultural areas than in rural areas. This was opposite to TH-rich shallow groundwater in the LP. By contrast, TH-rich shallow groundwater in the PP was more frequent in urban areas than in other land use types.

In addition, the origins of TH-rich shallow and deep groundwaters in various sub-plains in the HBP were also investigated by the Gibbs diagram and PCA. In the PP, TH-rich shallow groundwater was mainly attributed to water-rock interaction, groundwater over-extraction (salinisation), and the infiltration of domestic sewage and animal waste (dissolution of calcium-rich minerals). In the CP, both TH-rich shallow and deep groundwaters likely ascribed to the evaporite dissolution and seawater intrusion. By contrast, the leaching of agricultural fertilizers resulting in the dissolution of Ca-rich and Mg-rich minerals in the vadose zone was mainly responsible for the occurrence of TH-rich shallow groundwater in the LP.

Therefore, in the PP, local governments should limit shallow groundwater extraction and strengthen the supervision of domestic sewage and animal waste to restrict shallow groundwater TH concentrations. Besides, in the LP, they should strengthen the supervision of the use of N-fertilizers in agricultural activities.

Author Contributions: Conceptualization, X.C.; Methodology, S.Z.; Software, C.Y.; Validation, C.Y.; Investigation, S.Z. and X.C.; Writing—original draft, Y.Q.; Writing—review & editing, Y.Q. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by National Geological Survey Project (DD20230423) and Hebei Province High level Talent Team Construction Project (225A4204D).

Data Availability Statement: The datasets generated and/or analyzed during the current study are not publicly available.

Conflicts of Interest: The authors declare no conflict of interest.

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