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Hydrogeochemical Characteristics and Groundwater Quality in Phreatic and Confined Aquifers of the Hebei Plain, China

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Abstract: This study aims to investigate hydrogeochemical characteristics and groundwater quality in the Hebei Plain and to discuss factors controlling the groundwater quality. A total of 54 groundwater samples were collected and analyzed for 31 hydrogeochemical parameters, and a fuzzy synthetic evaluation (FSE) method was used for assessing groundwater quality. Results show groundwater total hardness, total dissolved solids (TDS), and major ions excluding K^+ in phreatic aquifers higher than that in confined aquifers. From the Piedmont plain to the littoral plain, phreatic aquifers towards the reducing environment, and the enhancement of water–rock interaction, ion exchange process, and evaporation probably resulted in the increase in groundwater TDS, major ions (excluding HCO_3^- and SO_4^{2-}), B, and Mn concentrations. Moreover, phreatic groundwater chemistry was mainly controlled by rock weathering changing into evaporite dissolution and seawater intrusion from the Piedmont plain to the littoral plain, according to the Gibbs diagram. The proportion of drinkable groundwater in confined aquifers was 1.6 times that in phreatic aquifers. In phreatic aquifers, the proportion of drinkable groundwater in the Piedmont plain was as high as 68%, but none of the drinkable groundwater occurred in the central and littoral plains. Groundwater quality in phreatic aquifers was mainly controlled by five factors, including the water–rock interaction, the marine geogenic sources, the agricultural pollution, the acidification, and the reductive environment. By contrast, groundwater quality in confined aquifers was mainly controlled by three factors, including the water–rock interaction and redox processes, agricultural pollution, and the input of external water. Therefore, in the Hebei Plain, groundwater in confined aquifers is more suitable for drinking purposes than in phreatic aquifers. Additionally, phreatic groundwater in the Piedmont plain should be protected.

Keywords: hydrogeochemical characteristics; groundwater quality; Hebei Plain; phreatic aquifer; confined aquifer

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1. Introduction

Groundwater is one of the major freshwater resources for human beings in coastal plains. It plays an important role in drinking, industrial, and domestic purposes in urbanizing areas, as well as irrigation purposes in agricultural areas, especially in plains (e.g., Hebei Plain) where surface water is short [1]. For instance, Huan et al. reported that groundwater supplied more than 70% of drinking water in the Hebei Plain [2]. However, many intense human activities such as urbanization, industrialization, mining activities, and agricultural intensification have impacted regional groundwater quality in recent decades on a global scale [3–7]. For example, Gan et al. reported that domestic sewage and animal waste were major sources of groundwater nitrate pollution in several alluvial-pluvial fans in the Hebei Plain due to urbanization and agricultural activities [8]. Therefore, it is necessary to understand the current status of hydrogeochemical characteristics and groundwater quality for groundwater management in the Hebei Plain because various human activities likely have already changed hydrogeochemical conditions and water quality in the groundwater of this area [9].

To date, many studies have already investigated hydrogeochemical characteristics and groundwater quality in part areas within the Hebei Plain. For instance, Xing et al. investigated hydrogeochemical characteristics in the Hebei Plain by using two groundwater flow paths [10]. Zhang et al. assessed the natural background levels of chemical components in the groundwater of the Hutuo River catchment area within the Hebei Plain [11]. Zhang et al. revealed the spatial distribution of iodine in groundwater in the Hebei Plain via a groundwater section [12]. Zhang et al. reported the spatial distribution of groundwater chemistry and quality in the southern Hebei Plain [13]. Liu et al. revealed factors controlling groundwater chemical evolution under reduced exploitation in the Heilongjiang region within the Hebei Plain [14]. Hao et al. recently reported the annual variability of fluoride concentrations in deep groundwater of a land subsidence plain in Cangzhou within the Hebei Plain [15]. By contrast, the Hebei Plain is a large-scale geological unit, and few studies focused on the spatial distribution of hydrogeochemical characteristics and groundwater quality in this entire area [16]. Especially in recent decades, the intensity of human activities in the groundwater of this area has increased [9].

Therefore, the present study aims to investigate the current status of hydrogeochemical characteristics and groundwater quality in the whole Hebei Plain, where human activities strengthen and discuss factors controlling groundwater quality in this entire area. In this study, 54 groundwater samples were collected from both phreatic and confined aquifers. The Piper and Gibbs diagrams were used for analyzing hydrogeochemical characteristics in various aquifers and land use types and a fuzzy synthetic evaluation (FSE) method was used for assessing groundwater quality in different aquifers and land use types [17–19]. In addition, a principal components analysis (PCA) was used to extract major factors that control groundwater chemistry and quality in the study area [20]. The conclusions will enhance the groundwater management level for sustainable development in the Hebei Plain.

2. Study Area

2.1. Geographical Conditions

The Hebei Plain includes the entire plains of Beijing, Tianjin, and Hebei Province, with a total area of approximately 9.25×10^4 km^2 (Figure 1A). It is bounded by mountains in the West and North and adjacent to Bohai Bay in the east. The topography generally inclines eastward from an altitude of about 100 m above sea level (ASL) in the west to about 2 m ASL in the east [16]. The climate is typically continental semiarid with a mean annual temperature of 11.3 °C and a mean annual precipitation of approximately 500 mm/year, and the summer monsoon generally contributes more than 70% of the annual precipitation from June to September [21]. It is one of the major granaries of China. Croplands in the Hebei Plain, including 17 large irrigation districts and many small-scale irrigated farms, account for 72% of the total area, and approximately 70% of the total water supply for grain production is supported by groundwater [22].

2.2. Geological and Hydrogeological Conditions

The Hebei Plain is a large Mesozoic and Cenozoic sedimentary basin with a basement of the Sinian bedrock. Alluvial and fluvial sediments originated from the middle and lower reaches of the Yellow River, the Haihe River, the Luanhe River, and their tributaries and formed sedimentary aquifers in this basin. The sediment thickness of Quaternary deposits is about 150–500 m. The Quaternary sediments consist of fluvial deposits in the Piedmont plain, alluvial and lacustrine deposits in the central plain, and alluvial deposits with interbedded marine deposits in the littoral plain [23]. The Piedmont plain has more plentiful groundwater resources than the central and littoral plains due to the mountain-front recharge, waterbody leakage from reservoirs, and groundwater lateral flow [24].

Aquifers in the Hebei Plain can be divided into four groups according to hydrodynamic conditions and the distribution of aquifers and aquitards (Figure 1B). From the top to the bottom, the first aquifer group (aquifer-I) consists of phreatic aquifers in a range of 10–50 m below land surface (BLS) with coarse-grained sand in the Piedmont plain to fine-grained sand in the littoral plain. The second aquifer group (aquifer-II) is composed of multiple semi-confined aquifers with buried depths of 120–210 m BLS, while the third aquifer group (aquifer-III) consists of confined aquifers and has the lower boundary between 170 and 350 m BLS, both of them are dominated by sandy gravel in the Piedmont plain and by medium to fine sand in the central and littoral plains. The fourth aquifer group (aquifer-IV) also consists of confined aquifers with cemented sandy gravel and weathered sand in the Piedmont plain, medium to fine sand in the central plain, and fine sand in the littoral plain, lies below 350 m BLS with a thickness of 50–60 m [25,26]. In recent decades, groundwater recharge from rivers, lakes, and wetlands has reduced significantly because surface water flow to the Hebei Plain is often cut off by reservoirs built upstream, especially during the dry seasons [24]. Groundwater flow velocity ranged from 0.013 to 0.26 m/d in the Piedmont plain and from 0.002 to 0.10 m/d in the central plain [27]. Groundwater flows regionally from the west to the east or the northeast; in other words, it flows from the Piedmont plain via the central plain to the littoral plain [10].

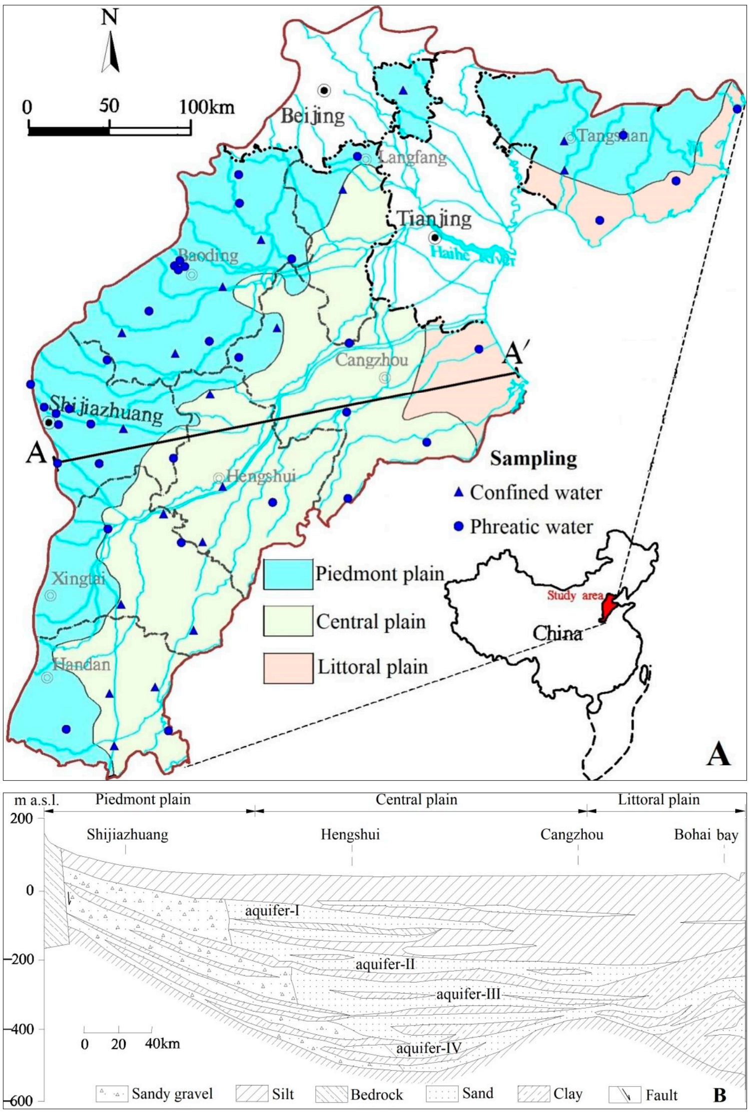

Figure 1. Hydrogeological setting and sampling sites in the Hebei Plain. (**A**) sampling sites, (**B**) cross section.

3. Materials and Methods

3.1. Groundwater Sampling

A total of 54 groundwater samples in the Hebei Plain were collected once in August 2021. Among them, 31 samples, 19 samples, and 4 samples were collected from the Piedmont plain, the central plain, and the littoral plain, respectively. In the Piedmont plain, 22 and 9 samples were collected from phreatic and confined aquifers, respectively. In the central plain, 9 and 10 samples were collected from phreatic and confined aquifers, respectively. In the littoral plain, all samples were collected from phreatic aquifers. In order to ensure samples representing the in-situ conditions 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. Three bottles were used to store groundwater for the analysis of chemical components. Groundwater in a 200-mL brown glass bottle was used to analyze sulfide (S^{2-}), while two 500-mL polyethylene bottles were used to store groundwater for the analysis of trace elements and other inorganic chemicals. One bottle used for trace elements analysis was acidified with nitric acid to a pH of less than 2. All samples were stored at 4 °C until laboratory procedures could be performed.

3.2. Analytical Techniques

All analyses were carried out at the Groundwater Mineral Water and Environmental Monitoring Center of the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences. A multi-parameter portable meter (HANNA, HI 98121, Shanghai, SH, China) was used to measure pH in the field. HCO_3^-, CO_3^{2-}, and the total dissolved solids (TDS) were measured using volumetric and gravimetric methods, respectively. Total hardness (TH) and chemical oxygen demand (COD) were measured by EDTA and potassium dichromate titration methods, respectively. Major cations, Fe, Al, and Mn, were determined by ICP-AES (ICAP6300, Thermo, New York, NY, USA). As, Pb, Hg, Cd, Cr(VI), Se, Ni, Ba, Zn, and B were measured by ICP-MS (Agilent 7500ce ICP-MS, Tokyo, Japan). S^{2-} was measured by the iodometric method. NH_4^+ and other anions (NO_3^-, SO_4^{2-}, Cl^-, NO_2^-, F^-, I^-) were carried out on IC (Shimadzu LC-10ADvp, Kyoto, Japan). 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 less than ±5% for all analyzed indicators.

3.3. Fuzzy Synthetic Evaluation (FSE) Method

In this study, we used a fuzzy membership function with the groundwater quality standards of China (Table 1) to evaluate groundwater quality [28]. Linear membership functions are in the Equation (1).

$$r_{ij} = \begin{cases} 0,\ (C_i \le S_{ij-1} \text{ or } C_i \ge S_{ij-1}) \\ \frac{C_i - S_{ij-1}}{S_{ij} - S_{ij-1}},\ (S_{ij-1} < C_i < S_{ij}) \\ \frac{S_{ij+1} - C_i}{S_{ij+1} - S_{ij}},\ (S_{ij} < C_i < S_{ij+1}) \\ 1,\ (C_i = S_i) \end{cases} \tag{1}$$

where r_{ij} indicates the fuzzy membership of indicator i to class j; every indicator is characterized by five classes (I, II, III, IV, V) according to the groundwater quality standards of China [28]. C_i stands for the analytical value of groundwater quality indicator i, and S_{ij} stands for the allowable value of groundwater quality indicator. The fuzzy membership matrix R consists of groundwater quality indicators and classes.

The weight of groundwater quality indicator is expressed as

$$W_i = \frac{C_i}{S_i} \tag{2}$$

where W_i is the weight of groundwater quality indicator i, C_i is the analytical value of groundwater quality indicator i, and S_i is the arithmetic mean of allowable values of each class.

Table 1. Groundwater quality standards of China for drinking and irrigation.

Items	Class I	Class II	Class III	Class IV	Class V
pH	6.5–8.5	6.5–8.5	6.5–8.5	5.5–6.5 and 8.5–9.0	<5.5 and >9.0
TH (mg/L)	≤150	≤300	≤450	≤650	>650
TDS (mg/L)	≤300	≤500	≤1000	≤2000	>2000
COD (mg/L)	≤1	≤2	≤3	≤10	>10
Cl^- (mg/L)	≤50	≤150	≤250	≤350	>350
NO_3^- (as N, mg/L)	≤2	≤5	≤20	≤30	>30
SO_4^{2-} (mg/L)	≤50	≤150	≤250	≤350	>350
F^- (mg/L)	≤1	≤1	≤1	≤2	>2
NO_2^- (as N, mg/L)	≤0.01	≤0.1	≤1	≤4.8	>4.8
I^- (μg/L)	≤40	≤40	≤80	≤500	>500
S^{2-} (mg/L)	≤0.005	≤0.01	≤0.02	≤0.1	>0.1
NH_4^+ (as N, mg/L)	≤0.02	≤0.1	≤0.5	≤1.5	>1.5
Na^+ (mg/L)	≤100	≤150	≤200	≤400	>400
B (mg/L)	≤0.02	≤0.1	≤0.5	≤2	>2
Al (mg/L)	≤0.01	≤0.05	≤0.2	≤0.5	>0.5
Fe (mg/L)	≤0.1	≤0.2	≤0.3	≤2	>2
Mn (mg/L)	≤0.05	≤0.05	≤0.1	≤1.5	>1.5
Ba (mg/L)	≤0.01	≤0.1	≤0.7	≤4	>4
Zn (mg/L)	≤0.05	≤0.5	≤1	≤5	>5
Pb (μg/L)	≤5	≤5	≤10	≤100	>100
As (μg/L)	≤1	≤1	≤10	≤50	>50
Se (μg/L)	≤10	≤10	≤10	≤100	>100
Ni (μg/L)	≤2	≤2	≤20	≤100	>100
Cd (μg/L)	≤0.1	≤1	≤5	≤10	>10
Cr(VI) (μg/L)	≤5	≤10	≤50	≤100	>100
Hg (μg/L)	≤0.1	≤0.1	≤1	≤2	>2
Suitability	Drinking, Irrigation	Drinking, Irrigation	Drinking, Irrigation	Irrigation	Not suitable

Note: data from reference [28].

The normalized weight of each indicator is calculated by the formula:

$$a_i = \frac{C_i}{S_i} / \sum_{i=1}^{m} \frac{C_i}{S_i} = W_i / \sum_{i=1}^{n} W_i \tag{3}$$

where a_i is the normalized weight of indicator i and W_i is the sum of the weight of all groundwater quality indicators. The fuzzy A consists of the weight of each groundwater quality indicator.

The water quality assessment by fuzzy membership is based on the matrix B,

$$B = A \times R \tag{4}$$

The fuzzy B is the matrix of membership to each groundwater quality class. Groundwater sample is classified into the class with the maximum membership [29].

3.4. Principal Components Analysis (PCA)

The PCA is a useful tool for reducing a large number of variables to a small number of principal components (PCs) by linearly combining measurements [30,31]. In this study, the PCA was used to reduce variables and extract the main impact indicators that are responsible for the poor-quality groundwater. In addition, it was also used to extract related variables and infer the underlying natural and/or anthropogenic processes that control the groundwater quality [32]. Rotation of the PCs was conducted using the Varimax method. PCs with eigenvalues > 1 were retained for analyses. The PCA was operated by the SPSS® release 23.0 version.

4. Results and Discussion

4.1. Characteristics of Groundwater Chemistry

As shown in Table 2, groundwater pH in both phreatic and confined aquifers was predominantly near neutral to weak alkaline in the Hebei Plain. Similarly, the median values of groundwater pH in southern Hebei Plain from 2018 to 2020 were 7.6–7.8 [13]. This indicates that groundwater pH in the Hebei Plain in recent years was shown to be stable. Groundwater COD concentrations were a wide range of 0.31–14.11 mg/L in phreatic aquifers but a narrow range of 0.3–1.39 mg/L in confined aquifers. Both groundwater TH and TDS concentrations in phreatic and confined aquifers were shown wide ranges, and their median values in phreatic aquifers were 3.4 times and 1.5 times those in confined aquifers, respectively. Similarly, in the North China Plain containing the Hebei Plain, the median TDS value in shallow groundwater was also approximately 1.5 times that in deep groundwater from 2006 to 2008 [33]. This is probably attributed to anthropogenic inputs and/or the infiltration of minerals dissolution in the vadose zone via the water flow because wastewater with high concentrations of TDS often infiltrates into phreatic aquifers rather than confined aquifers [16,17]. Major ions except NO_3^- and K^+ in phreatic and confined aquifers were shown wide range concentrations. Generally, groundwater major anions concentrations in both phreatic and confined aquifers were orders of $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$, and median concentrations of groundwater HCO_3^-, SO_4^{2-}, Cl^-, and NO_3^- in phreatic aquifers were 1.7 times, 2.1 times, 1.3 times, and 8 times of those in confined aquifers, respectively. This is probably due to the anthropogenic inputs of these anions and the infiltration of dissolution of related minerals (e.g., calcite, dolomite, gypsum, and halite) in the vadose zone for phreatic aquifers rather than for confined aquifers [8,16]. Unlike major anions, median values of groundwater major cations in phreatic aquifers were shown in an order of $Ca^{2+} > Na^+ > Mg^{2+} > K^+$, but those in confined aquifers presented an order of $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. Median concentrations of groundwater Ca^{2+}, Mg^{2+}, and K^+ in phreatic aquifers were 4.0 times, 3.1 times, and 1.4 times those in confined aquifers, respectively. By contrast, the median value of groundwater Na^+ in phreatic aquifers was approximately half of that in confined aquifers. These are likely not only due to the anthropogenic input of K^+ and the infiltration of dissolutions of Ca and Mg-containing minerals (e.g., calcite, dolomite) in the vadose zone for phreatic aquifers but also because of the stronger ion exchange process of "Na in sediments replaced by Ca and Mg" in confined aquifers than in phreatic aquifers [9,10]. Median concentrations of trace metal(lion)s including B, Mn, Al, Fe, and Ba in groundwater in both phreatic and confined aquifers were higher than detection limits, while that of others including Zn, Ni, Cd, Pb, As, Se, Hg, and Cr(VI) in groundwater of phreatic and/or confined aquifers were lower than detection limits. Median values of groundwater Al and Ba in phreatic aquifers were approximately double those in confined aquifers. This indicates that groundwater Al and Ba in the Hebei Plain mainly originated from the anthropogenic inputs and/or the infiltration of dissolution of Al- and Ba-containing minerals in the vadose zone [32,34]. By contrast, the median concentration of groundwater F^- in phreatic aquifers was 0.8 times that in confined aquifers. This is consistent with the distribution of groundwater pH in the study area; the median pH value in phreatic aquifers was 0.9 times that in confined aquifers (Table 2). These indicate that geogenic factors such as alkaline conditions likely control the distribution of groundwater F^- in the Hebei Plain because alkalization is in favor of the desorption and dissolution of fluorinated minerals [13,35]. In addition, other chemical components, including I^-, NO_2^-, NH_4^+, and S^{2-} in groundwater of phreatic and/or confined aquifers, were also shown to have median values lower than detection limits.

Table 2. Descriptive statistics of groundwater chemical parameters in phreatic and confined aquifers.

Items	**Phreatic Aquifers**			**Confined Aquifers**		
	Min.	**Med.**	**Max.**	**Min.**	**Med.**	**Max.**
pH	6.75	7.49	8.22	7.17	8.21	8.82
COD	0.31	0.81	14.11	0.3	0.63	1.39
TH	69.2	469.5	6415	41.5	136.9	3808
TDS	256	686	23,550	185	463	9570
CO_3^{2-}	<DL	<DL	5.9	<DL	5.9	29.7
HCO_3^-	108.7	388.8	1009	73.1	228.9	845.7
Cl^-	9	82.3	13,830	2.5	61.6	2066
NO_3^--N	<DL	3.2	23.9	<DL	0.4	16.9
SO_4^{2-}	7	147.1	2736	6.1	70.3	3964
K^+	0.4	1.9	51	0.4	1.4	3.2
Na^+	5.9	62.5	6465	24	111.4	1940
Ca^{2+}	18.3	98.3	570.8	7.5	24.4	281.8
Mg^{2+}	6.3	41.7	1219	5.4	13.6	759
I^-	<DL	<DL	0.906	<DL	<DL	0.665
NO_2^--N	<DL	<DL	0.223	<DL	<DL	0.081
NH_4^+-N	<DL	<DL	1.02	<DL	<DL	0.37
S^{2-}	<DL	<DL	0.19	<DL	0.005	0.217
F^-	0.16	0.47	2.57	0.15	0.6	2.11
B	<DL	0.06	1.31	0.02	0.06	0.95
Mn	<DL	0.03	3.89	<DL	0.02	0.77
Al	<DL	0.07	0.54	0.01	0.03	0.15
Fe	<DL	0.06	78.31	<DL	0.07	2.94
Ba	0.01	0.07	0.41	0.01	0.04	0.19
Zn	<DL	<DL	36.11	<DL	0.01	2.26
Ni	<DL	0.001	0.007	<DL	<DL	0.006
Cd	<DL	<DL	<DL	<DL	<DL	<DL
Pb	<DL	<DL	0.001	<DL	<DL	0.003
Se	<DL	<DL	0.016	<DL	<DL	0.002
Hg	<DL	<DL	<DL	<DL	<DL	<DL
As	<DL	<DL	0.009	<DL	<DL	0.008
Cr(VI)	<DL	<DL	0.006	<DL	<DL	0.008

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

Statistics for concentrations of groundwater chemical parameters in phreatic aquifers in Piedmont, central, and littoral plains are present in Table 3. Groundwater pH in phreatic aquifers in all three plains was near neutral to weak alkaline. The median concentration of groundwater COD in phreatic aquifers increased gradually from the Piedmont plain to the littoral plain. This indicates that the groundwater environment from the Piedmont plain to the littoral plain is reducing environment because of the decrease in groundwater flow velocity from the Piedmont plain to the littoral plain [27]. As median and mean concentrations are concerned, TDS and most major ions, including Cl^-, K^+, Na^+, Ca^{2+}, and Mg^{2+} in groundwater in phreatic aquifers, increased gradually from the Piedmont plain to the littoral plain. This is probably attributed to the change in water–rock interaction and evaporation from the Piedmont plain to the littoral plain and the frequent occurrence of seawater intrusion in the littoral plain because ion exchange and evaporation processes for groundwater chemistry from the Piedmont plain to the littoral plain in the Hebei Plain become stronger [10,16,17,36]. For example, Zhan et al. have already pointed out that Ca- and Mg-containing minerals (e.g., calcite, dolomite, and gypsum) in groundwater in the Piedmont plain were shown less negative saturation indices than those in central and littoral plains, and resulting in concentrations of groundwater TDS accompanied by Ca and Mg from the Piedmont plain to the littoral plain increased [16]. In addition, median and mean concentrations of B and Mn in groundwater in phreatic aquifers also increased gradually from the Piedmont plain to the littoral plain. This likely ascribes to the enhancement of the ion exchange process and reductive dissolution from the Piedmont plain to the littoral plain in the Hebei Plain because the enrichment of B in groundwater is commonly accompanied by ion exchange that depletes Ca and enriches Na in groundwater [37], and the reductive dissolution of Mn containing minerals is in favor of the enrichment of Mn in groundwater [38]. By contrast, median and mean concentrations of groundwater HCO_3^-, F^-, Fe, and Zn in phreatic aquifers in the central plain were higher than those in the other two plains. In addition, median and mean concentrations of groundwater NO_3^- in phreatic aquifers in the Piedmont plain were higher than those in other two plains. This indicates that groundwater NO_3^- contamination was more often in the Piedmont plain than in the other two plains because the groundwater environment in the Piedmont plain was more oxidizing than that in the other two plains [9].

Table 3. Descriptive statistics of groundwater chemical parameters in phreatic aquifers in Piedmont, central, and littoral plains.

Items	**Piedmont Plain**				**Central Plain**				**Littoral Plain**			
	Min.	**Med.**	**Mean**	**Max.**	**Min.**	**Med.**	**Mean**	**Max.**	**Min.**	**Med.**	**Mean**	**Max.**
pH	7.03	7.53	7.52	8.22	6.75	7.34	7.38	7.88	7.22	7.45	7.53	7.99
COD	0.31	0.58	0.70	1.52	0.69	1.48	1.61	2.82	1.57	2.20	5.02	14.11
TH	69	391	386	662	356	980	1211	2619	297	920	2138	6415
TDS	256	555	575	1118	1394	2356	3109	7110	511	4646	8338	23,550
HCO_3^-	109	311	339	610	296	754	710	1009	293	485	442	507
Cl^-	9	58	61	160	135	464	545	1551	51	2143	4542	13,830
NO_3^--N	<DL	7.1	8.0	19.7	<DL	0.4	2.9	23.9	<DL	0.8	1.2	3.2
SO_4^{2-}	7	66	94	249	302	477	995	2736	21	634	629	1229
K^+	0.4	1.6	1.7	3.0	0.7	1.8	1.8	3.1	6.2	19.5	24.1	51.0
Na^+	6	32	48	200	323	530	648	1565	76	1358	2314	6465
Ca^{2+}	18	91	98	207	41	103	135	326	32	114	208	571
Mg^{2+}	6	34	36	80	57	143	215	523	25	166	394	1219
I^-	<DL	<DL	0.02	0.34	0.04	0.19	0.23	0.45	<DL	0.11	0.28	0.91
NO_2^--N	<DL	<DL	0.01	0.22	<DL	<DL	0.02	0.11	<DL	0.01	0.04	0.15
NH_4^+-N	<DL	<DL	0.01	0.14	<DL	0.06	0.19	1.02	<DL	0.17	0.18	0.37
S^{2-}	<DL	<DL	<DL	0.010	<DL	<DL	0.042	0.190	<DL	0.008	0.014	0.040
F^-	0.16	0.35	0.45	1.92	0.39	0.87	1.13	2.57	0.47	0.83	0.86	1.30
B	<DL	0.04	0.05	0.25	0.16	0.48	0.59	1.31	0.06	0.76	0.60	0.82
Mn	<DL	<DL	0.07	1.11	0.12	0.27	0.49	1.43	0.34	0.42	1.27	3.89
Al	<DL	0.07	0.07	0.16	0.03	0.09	0.15	0.54	0.03	0.09	0.09	0.15
Fe	<DL	0.03	0.10	0.61	0.04	0.76	10.11	78.31	<DL	0.64	0.65	1.33
Ba	0.01	0.09	0.12	0.41	0.01	0.02	0.03	0.07	0.02	0.08	0.11	0.25
Zn	<DL	<DL	0.01	0.09	<DL	0.01	4.02	36.11	<DL	<DL	0.01	0.03
Ni	<DL	<DL	0.001	0.004	<DL	0.003	0.003	0.004	<DL	0.002	0.003	0.007
Cd	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Pb	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.001	<DL	<DL	<DL	<DL
Se	<DL	<DL	0.001	0.005	<DL	<DL	0.002	0.016	<DL	<DL	<DL	<DL
Hg	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
As	<DL	<DL	<DL	0.005	<DL	<DL	0.002	0.009	0.002	0.003	0.003	0.004
Cr(VI)	<DL	<DL	0.001	0.006	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL

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

As seen in Figure 2, groundwater anions were generally dominated by HCO_3^- in both phreatic and confined aquifers in the Hebei Plain. By contrast, groundwater cations in phreatic aquifers were dominated by Ca^{2+} and Na^+, but confined aquifers, they were almost dominated by Na^+. The numbers of hydrogeochemical facies for groundwater in phreatic and confined aquifers were 18 and 13, respectively. Hydrogeochemical facies of groundwater in phreatic and confined aquifers were dominated by Ca·Mg-HCO_3 facies (25.7%) and Na-HCO_3 facies (15.8%), respectively. In phreatic aquifers, groundwater cations in residential areas were dominated by Ca·Mg facies, which in uncultivated lands were dominated by Na·Mg facies and Na facies, but in agricultural areas were dominated by Ca·Mg facies and Na·Mg facies. On the other hand, groundwater anions in both residential and agricultural areas were dominated by HCO_3 facies and $HCO_3{\cdot}SO_4$ facies, while in uncultivated lands they were dominated by Cl facies and HCO_3 facies. These likely hint that hydrogeochemical facies in residential areas were mainly controlled by geogenic factors, while in uncultivated and agricultural lands they were controlled by both geogenic and anthropogenic factors. Because shallow groundwater in the study area is dominated by Na facies and Cl facies, often ascribed to anthropogenic inputs, while that dominated by Ca facies, Ca·Mg facies, HCO_3 facies, and $HCO_3{\cdot}SO_4$ facies is generally attributed to geogenic sources [11,16]. Unlike in other coastal areas, such as the Pearl River Delta [39], no NO_3 facies groundwater occurred in the Hebei Plain. It is worth mentioning that all groundwater samples with the concentration of NO_3^- accounted for >10% of total major anions concentration (meq) were located in agricultural and residential areas. This indicates that groundwater NO_3^- contamination in the Hebei Plain likely originated from agricultural activities and human wastes [8].

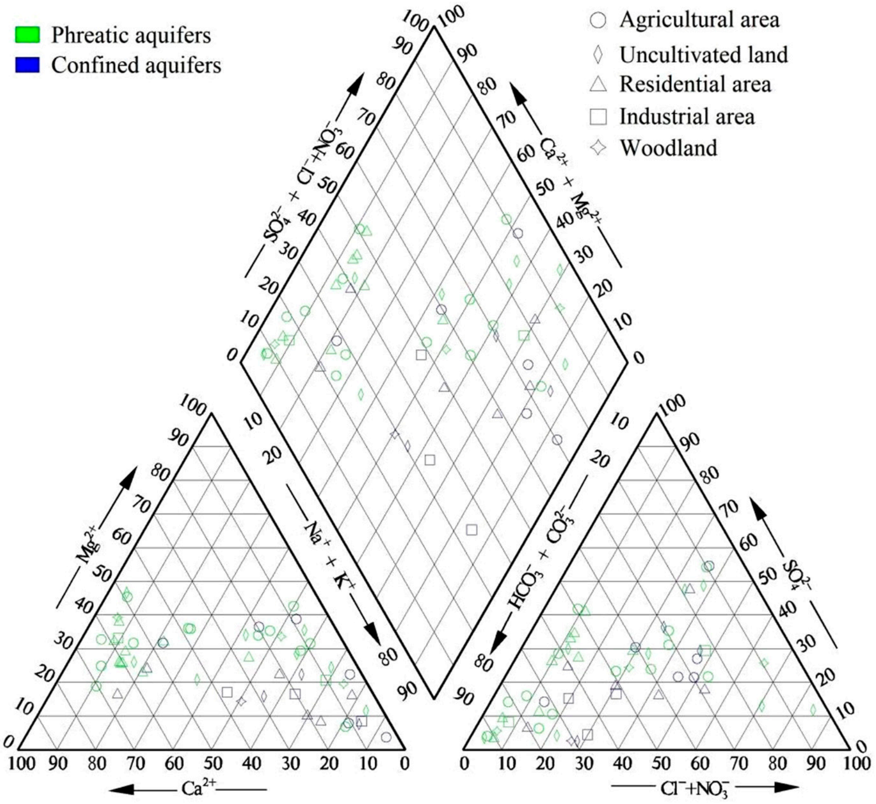

Figure 2. Hydrogeochemical facies of groundwater in phreatic and confined aquifers in the Hebei Plain.

In this study, the Gibbs Diagram was applied to analyze groundwater chemistry in the Hebei Plain. As shown in Figure 3, Na/(Na + Ca) ratios in 86.4% of phreatic groundwaters in the Piedmont plain were less than 0.5 and accompanied by low levels of TDS (<1000 mg/L). This indicates that rock weathering was the dominant mechanism for phreatic groundwater chemistry in the Piedmont plain [18]. By contrast, the confined groundwater in the Piedmont plain was also accompanied by low levels of TDS (<1000 mg/L) but commonly showed higher Na/(Na + Ca) ratios than that in phreatic groundwaters, approximately 67% of confined groundwaters in the Piedmont plain were characterized by Na/(Na + Ca) ratios > 0.5. This infers both rock weathering and ion exchange processes controlling groundwater chemistry in confined aquifers in the Piedmont plain because longer residence times for groundwater in confined aquifers than in phreatic aquifers is in favor of the ion exchange process of sediments adsorbed Na replaced by groundwater Ca [23,26,40]. Compared to the Piedmont plain, Na/(Na + Ca) ratios and

TDS concentrations in both phreatic and confined groundwaters in the central plain were higher. This implies that the evaporation process and/or the dissolution of evaporites with cation exchange for groundwater chemistry in the central plain were likely more important than that in the Piedmont plain because the depth of groundwater level in the central plain was shallower than that in the Piedmont plain and the residence time for groundwater in the central plain was longer than that in the Piedmont plain [26,41]. On the other hand, the depth of groundwater level in the central plain in both phreatic and confined aquifers was generally deeper than 3 m [9,21], indicating that the impact of the evaporation process on groundwater chemistry in the central plain was negligible because evaporation from groundwater is often little when the groundwater level deeper than a few meters [42]. Therefore, evaporite dissolution with cation exchange mainly controlled groundwater chemistry in the central plain. Additionally, in the central plain, the median concentration of TDS in phreatic groundwater was more than three times that in confined groundwater. This indicates that evaporite dissolution for groundwater chemistry in phreatic aquifers in the central plain was more important than confined aquifers [18]. In phreatic aquifers, groundwater Na/(Na + Ca) ratios and TDS concentrations in the littoral plain were commonly higher than in Piedmont and central plains. This is likely attributed to strong evaporite dissolution and the occurrence of seawater intrusion in the littoral plain [9,43].

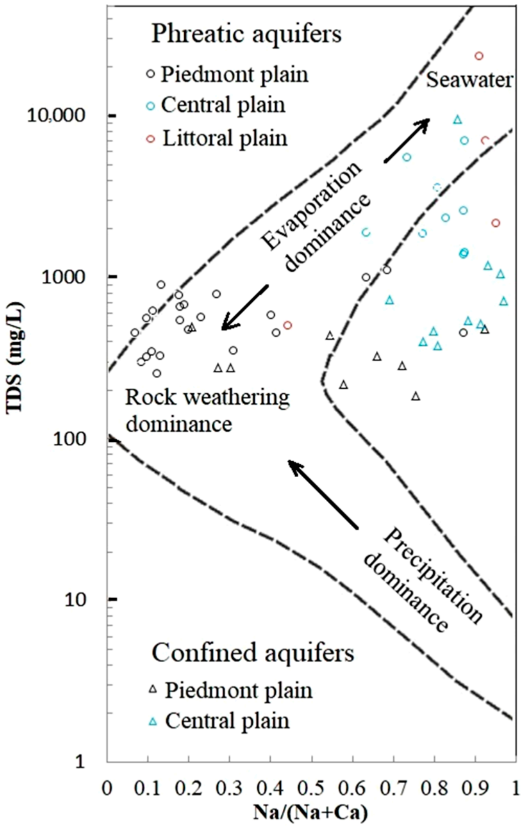

Figure 3. Gibbs diagram of groundwater samples in the Hebei Plain.

4.2. Distribution of Groundwater Quality

Compared to standards for groundwater quality in China [28], proportions of groundwater samples with concentrations of chemical components exceeded allowable limits (PEAL) for drinking purposes are shown in Table 4. In the Hebei Plain, TH was shown the highest PEAL of 54.3% in phreatic aquifers, followed by ten components (Mn, TDS, Na^+, Fe, Cl^-, SO_4^{2-}, I^-, B, F^-, and S^{2-}) with their PEALs > 10% and six components (Al, COD, NO_3^-, NH_4^+, Zn, and Se) with their PEALs of 2–10%, while the PEALs of other nine components in phreatic aquifers were zero. By contrast, in confined aquifers, S^{2-} was shown the highest PEAL of 31.6%, followed by seven components (F^-, Na^+, Mn, TDS, Fe, Cl^-, and I^-) with their PEALs > 10% and five components (TH, SO_4^{2-}, B, Zn, and pH) with their PEALs of 5.3%, while other 13 components with their PEALs of zero. Among them, the PEALs of TH, SO_4^{2-}, and B in phreatic aquifers were more than 10 times, 5 times, and 3 times those in confined aquifers. The PEALs of Mn, TDS, Na^+, Fe, Cl^-, and I^- in phreatic aquifers were 2–3 times those in confined aquifers. In addition, the PEALs of Al, COD, NO_3^-, NH_4^+, and Se in phreatic aquifers were also higher than those in confined aquifers. In contrast, the PEALs of S^{2-}, F^-, pH, and Zn in phreatic aquifers were lower than those in confined aquifers. Within phreatic aquifers, seven components including TH, Mn, Fe, TDS, Na^+, F^-, and I^- in the Piedmont plain showed their PEALs > 0; by contrast, 17 components including Mn, TDS, Na^+, Cl^-, SO_4^{2-}, TH, I^-, Fe, B, F^-, S^{2-}, Al, Zn, COD, Se, NO_3^-, and NH_4^+ in central and littoral plains showed their PEALs > 0. Moreover, PEALs of all these 17 components in central and littoral plains in phreatic aquifers were much higher than those in the Piedmont plain. For example, PEALs of Mn, TDS, Na^+, Fe, I^-, and F^- in central and littoral plains in phreatic aquifers were much more than 7 times, 10 times, 20 times, 5 times, 17 times, and 8 times those in the Piedmont plain, respectively. These indicate that groundwater quality in the Piedmont plain within phreatic aquifers was better than in central and littoral plains.

Table 4. Statistics for proportions of groundwaters with chemical concentrations exceeded allowable limits.

Items	Allowable Limits	Phreatic Aquifers	Confined Aquifers	Piedmont Plain	Central and Littoral Plains
TH	<450 mg/L	54.3%	5.3%	40.9%	76.9%
Mn	<0.1 mg/L	45.7%	15.8%	13.6%	100%
TDS	<1000 mg/L	40.0%	15.8%	9.1%	92.3%
Na^+	<200 mg/L	37.1%	21.1%	4.5%	92.3%
Fe	<0.3 mg/L	34.3%	15.8%	13.6%	69.2%
Cl^-	<250 mg/L	31.4%	15.8%	0	84.6%
I^-	<0.08 mg/L	31.4%	15.8%	4.5%	76.9%
SO_4^{2-}	<250 mg/L	31.4%	5.3%	0	84.6%
B	<0.5 mg/L	20.0%	5.3%	0	53.8%
F^-	<1 mg/L	17.1%	26.3%	4.5%	38.5%
S^{2-}	<0.02 mg/L	14.3%	31.6%	0	38.5%
Al	<0.2 mg/L	5.7%	0	0	15.4%
Zn	<1 mg/L	2.9%	5.3%	0	7.7%
COD	<3 mg/L	2.9%	0	0	7.7%
NO_3^--N	<20 mg/L	2.9%	0	0	7.7%
NH_4^+-N	<0.5 mg/L	2.9%	0	0	7.7%
Se	<0.01 mg/L	2.9%	0	0	7.7%
pH	6.5–8.5	0	5.3%	0	0
NO_2^--N	<1 mg/L	0	0	0	0
Ba	<0.7 mg/L	0	0	0	0
Ni	<0.02 mg/L	0	0	0	0
Cd	<0.005 mg/L	0	0	0	0
Pb	<0.01 mg/L	0	0	0	0
Hg	<0.001 mg/L	0	0	0	0
As	<0.01 mg/L	0	0	0	0
Cr(VI)	<0.05 mg/L	0	0	0	0

Notes: PEAL = proportion of groundwater samples with the concentration of one component exceeded the allowable limit; data of allowable limits are from reference [28].

The groundwater quality (5 classes) of the Hebei Plain was assessed by the FSE method and shown in Figure 4. In phreatic aquifers, the percentages of classes II, III, IV, and V of groundwater samples were 17.2%, 25.7%, 25.7%, and 31.4%, respectively. In other words, 43% and 57% of groundwater samples in phreatic aquifers were good-quality (drinkable, classes I to III) and poor-quality (undrinkable, classes IV and V), respectively. By contrast, the percentages of classes I, II, III, IV, and V groundwater samples in confined aquifers were 15.8%, 21.0%, 31.6%, 15.8%, and 15.8%, respectively. The proportion of drinkable groundwater in confined aquifers was 1.6 times that in phreatic aquifers. In phreatic aquifers, the proportion of drinkable groundwater in the Piedmont plain was as high as 68%, but none of drinkable groundwater occurred in the central and littoral plains. In addition, the proportions of drinkable groundwater in phreatic aquifers in different land use types were in the order of residential area (55.5%) > agricultural area (53.9%) > industrial area (50%) > woodland (33.3%) > uncultivated land (12.5%). This indicates that groundwater quality in phreatic aquifers in the Hebei Plain was probably controlled by natural factors rather than anthropogenic factors because groundwater pollution was generally more frequent in three former land use types than in two latter ones [44].

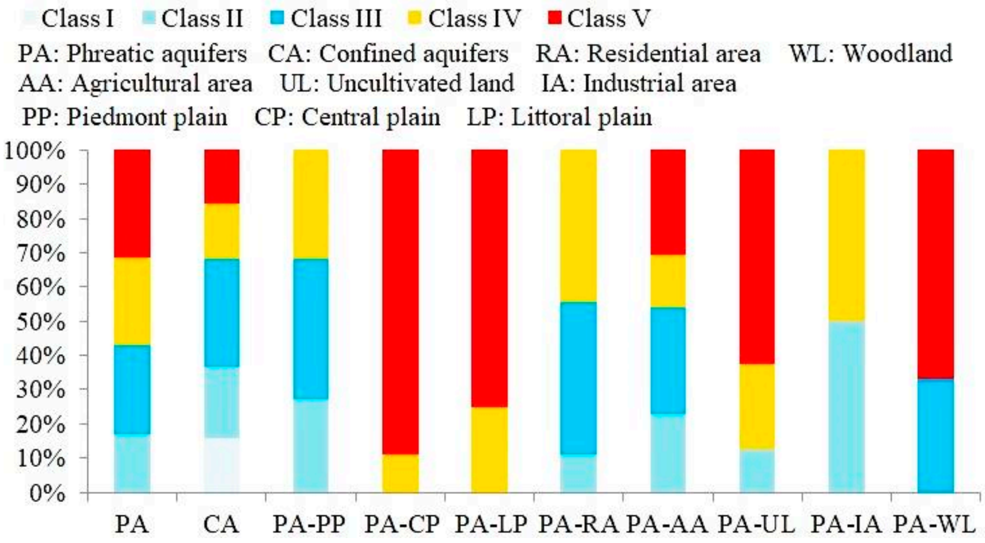

Figure 4. Groundwater quality in various aquifers and different land use types in the Hebei Plain.

4.3. Factors Controlling Groundwater Quality

In this study, the PCA was used to analyze the factors controlling groundwater quality in phreatic and confined aquifers in the Hebei Plain. Here, parameters in the PCA include pH, major ions, and exceeding indicators that concentrations in one or more groundwater samples are higher than their allowable limits. As shown in Table 5, groundwater quality in phreatic aquifers was mainly controlled by five factors. PC1 (factor 1) had strong positive loadings with Cl^-, COD, Na^+, TDS, Mn, TH, Mg^{2+}, K^+, and Ca^{2+}, indicating that the PC1 was indicative of the water–rock interaction (e.g., minerals dissolution, ion exchange) because the dissolution of (evaporate) minerals and the ion exchange process were mainly responsible for enrichments of Cl^-, Na^+, TDS, Mn, TH, Mg^{2+}, K^+, and Ca^{2+} in phreatic groundwater (Figure 3) [16]. PC2 (factor 2) showed high positive loadings of I^-, HCO_3^-, and B and moderate positive loadings of SO_4^{2-} and F^-. This was likely representative of the marine geogenic sources because groundwater SO_4^{2-} and B often originated from the oxidation of pyrite and the dissolution of glauconite in carbonate rocks in marine sediments [45], and the enrichment of groundwater I^- and HCO_3^- accompanied with alkalization (in favor of groundwater F^- enrichment) is often resulted from the mineralization of organic iodine in marine sediments in coastal areas [33,46–48]. PC3 (factor 3) explained 11.6% of the total variance with strong to moderate positive loadings of Se, Zn, and NO_3^-. This probably represented the agricultural pollution because groundwater with high levels of NO_3^- and Zn in phreatic aquifers in the Hebei Plain was generally distributed in agricultural areas (Figure 2) [8], and NO_3^- inputs were in favor of groundwater Se enrichment via the oxidation of reduced Se in sediments [34]. PC4 (factor 4) had a strong negative loading with pH and a moderate positive loading with Fe, indicating that the PC4 likely represented the acidification because the acidification elevates the mobilization of Fe in sediments [49]. PC5 (factor 5) showed a high positive loading of NH_4^+ and weak positive loadings of S^{2-} and Al. This was likely indicative of the reductive environment because the reductive environment is in favor of the enrichment of NH_4^+ and S^{2-} in groundwater [3,50].

Table 5. Principal component (PC) loadings for groundwater chemical parameters in phreatic and confined aquifers in the Hebei Plain.

Items	Phreatic Aquifers					Items	Confined Aquifers		
	PC1	PC2	PC3	PC4	PC5		PC1	PC2	PC3
Cl^-	**0.976**	0.063	−0.045	−0.064	−0.079	TDS	**0.991**	0.015	0.083
COD	**0.976**	0.065	0.000	0.025	0.024	Cl^-	**0.991**	0.058	0.033
Na^+	**0.969**	0.215	−0.018	−0.004	−0.016	Na^+	**0.986**	0.072	0.008
TDS	**0.964**	0.242	0.001	0.065	0.009	Mg^{2+}	**0.985**	−0.018	0.139
Mn	**0.932**	0.183	−0.111	0.089	0.069	TH	**0.982**	−0.054	0.158
TH	**0.931**	0.262	0.012	0.217	0.053	SO_4^{2-}	**0.981**	−0.010	0.131
Mg^{2+}	**0.924**	0.312	−0.006	0.161	0.047	Mn	**0.969**	−0.056	0.100
K^+	**0.889**	−0.124	−0.058	−0.198	0.052	B	**0.950**	0.223	−0.131
Ca^{2+}	**0.857**	0.048	0.090	0.416	0.071	HCO_3^-	**0.945**	−0.105	−0.055
I^-	0.161	**0.826**	−0.221	−0.020	0.029	Fe	**0.943**	0.225	0.142
HCO_3^-	0.100	**0.806**	0.123	0.224	0.073	I^-	**0.915**	0.249	−0.086
B	0.479	**0.759**	0.184	−0.063	0.215	Ca^{2+}	**0.914**	−0.210	0.239
SO_4^{2-}	0.424	**0.680**	0.180	0.297	0.199	COD	**0.686**	0.298	−0.328
F^-	0.041	**0.574**	−0.082	−0.557	0.144	Zn	0.024	**0.925**	−0.033
Se	−0.034	0.066	**0.955**	0.031	−0.008	S^{2-}	0.611	**0.771**	−0.091
Zn	0.022	0.184	**0.935**	−0.075	0.109	pH	−0.501	**0.648**	−0.253
NO_3^-	−0.098	−0.323	**0.706**	0.173	−0.276	K^+	0.220	0.074	**0.832**
pH	−0.191	−0.281	−0.052	**−0.800**	−0.066	F^-	0.089	0.289	**−0.805**
Fe	0.078	0.106	−0.101	**0.617**	0.499	Eigenvalue	12.3	2.3	1.7
NH_4^+	0.032	0.025	−0.056	0.072	**0.853**	Explained variance (%)	68.2	12.7	9.5
S^{2-}	−0.009	0.349	0.256	0.221	**0.487**	Cumulative % of variance	68.2	80.9	90.4
Al	0.000	0.260	−0.155	−0.354	**0.435**				
Eigenvalue	8.4	3.5	2.6	2.0	1.6				
Explained variance (%)	38.1	15.7	11.6	9.1	7.4				
Cumulative % of variance	38.1	53.8	65.4	74.5	81.9				

Note: Bold numbers = maximum absolute PC loading of one parameter.

By contrast, groundwater quality in confined aquifers was mainly controlled by three factors. PC1 (factor 1) had strong positive loadings with TDS, Cl^-, Na^+, Mg^{2+}, TH, SO_4^{2-}, Mn, B, HCO_3^-, Fe, I^-, and Ca^{2+}, and a moderate positive loading with COD. As mentioned previously, the water–rock interaction, such as minerals dissolution and ion exchange, was mainly responsible for the enrichment of TDS, Cl^-, Na^+, Mg^{2+}, TH, SO_4^{2-}, HCO_3^-, and Ca^{2+} in confined groundwater (Figure 3). Additionally, the reductive dissolution of Fe/Mn (hydroxy)oxides loaded with I^- in the reductive environment was mainly responsible for the enrichment of groundwater Mn, Fe, and I^- in the Hebei Plain [46]. Therefore, the PC1 was assumed to be representative of the water–rock interaction and redox processes. PC2 (factor 2) showed strong positive loadings with Zn and S^{2-} and a moderate positive loading with pH, indicating that the PC2 was not a natural factor because groundwater zinc generally presents in low concentrations in the presence of sulfide [51]. On the other hand, groundwater with high values of Zn, S^{2-}, and pH in confined aquifers was distributed in the agricultural area. Therefore, it can be concluded that the PC2 was likely indicative of agricultural pollution. PC3 (factor 3) had strong positive and negative loadings with K^+ and F^-, respectively. This likely represented the input of external water because the input of external water, such as the ecological water with low levels of F^- occurred in the Hebei Plain in recent years [15].

5. Conclusions

Hydrogeochemical characteristics and groundwater quality in phreatic and confined aquifers of the Hebei Plain were investigated. Anthropogenic inputs and/or the infiltration of minerals dissolution in the vadose zone resulted in groundwater TH, TDS, Al, Ba, and major ions excluding K^+ in phreatic aquifers higher than in confined aquifers. By contrast, more alkaline conditions were likely responsible for higher concentrations of groundwater F^- in confined aquifers than in phreatic aquifers. From the Piedmont plain to the littoral plain, phreatic aquifers towards the reducing environment, and the enhancement of water–rock interaction, ion exchange process, and evaporation probably resulted in the increase of groundwater TDS, major ions (excluding HCO_3^- and SO_4^{2-}), B, and Mn concentrations. Moreover, the phreatic groundwater chemistry was mainly controlled by rock weathering changing into evaporite dissolution and seawater intrusion from the Piedmont plain to the littoral plain, according to the Gibbs diagram.

In the Hebei Plain, groundwater in confined aquifers is more suitable to be developed for drinking purposes than in phreatic aquifers because the proportion of drinkable groundwater in confined aquifers was 1.6 times that in phreatic aquifers according to this investigation. For phreatic aquifers, groundwater in the Piedmont plain should be protected because of the much higher proportion of drinkable groundwater in the Piedmont plain than in the other two plains. Groundwater quality in phreatic aquifers was mainly controlled by five factors, including the water–rock interaction, the marine geogenic sources, the agricultural pollution, the acidification, and the reductive environment. By contrast, groundwater quality in confined aquifers was mainly controlled by three factors, including the water–rock interaction and redox processes, agricultural pollution, and the input of external water.

This is the first time to depict the distribution of groundwater chemistry and quality in the whole Hebei Plain in recent years. However, knowledge of the origins of various poor-quality groundwaters in this area is still limited. Thus, in the future, we will focus on sources, driving forces, and treatment of poor-quality groundwater in this area.

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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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