*Article*

# Key Factors Dominating the Groundwater Chemical Composition in a Grain Production Base: A Case Study of Muling–Xingkai Plain, Northeast China

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**Abstract:** Groundwater quality in the Muling–Xingkai Plain (MXP) is closely related to food security and human health. The chemical composition of groundwater in MXP has attracted great attention. A total of 168 groundwater samples were collected in MXP, and principal component analysis, chemical ion analysis and stable isotopic analysis were used to explore key factors affecting the chemical composition and hydrochemical evolution process of groundwater. Results show sources of chemical ions in groundwater are silicate minerals, carbonate minerals and domestic sewage. Domestic sewage is responsible for groundwater with high levels of $Cl^-$, $SO_4^{2-}$ and $NO_3^-$, but a reduction environment can lead to groundwater with a high level of $NH_4^+$ due to nitrification. Human activity and soil media together influence groundwater chemical composition. Groundwater with a high level of chemical ions is mainly collected from wells near river channels, where coarse-textured soils are overlying aquifers. The black soil far away from river channels can retard the infiltration of wastewater. Agricultural activities do not directly lead to deterioration of groundwater qualities, and agricultural non-point-source pollution does not occur in MXP. Nearly 70% of the population in MXP is living in the southern plain, where the influence of sewage on groundwater chemical composition is obvious. Thus, shallow groundwater far away from river channels is the best choice for irrigation. Some measures should be implemented to control the discharge of domestic sewage for the protection of groundwater. In addition, it is necessary to avoid the transformation of the redox environment of groundwater in the northern plain.

**Keywords:** groundwater; hydrochemistry; human activities; agricultural area; Muling–Xingkai Plain

## 1. Introduction

Groundwater is one of the most valuable natural resources in the world, and it can support nearly all kinds of human activities [1–5]. Generally, the development and utilization of groundwater resources are closely related to the chemical composition and qualities of groundwater. The chemical composition of groundwater can be influenced by natural processes (such as hydrogeological conditions, redox conditions and interaction of groundwater with minerals) and human activities (e.g., exploitation, sewage discharge and fertilizer application). Many important physicochemical and ecological processes are disrupted by changes in groundwater qualities, and even the rational utilization of groundwater resources is influenced by high levels of chemical ions [6–8]. It is necessary to ensure the safety of groundwater quality. The issues of groundwater chemical characteristics and their dominating factors have attracted more attention in the world. Relevant studies have been conducted in coastal areas, arid or semi-arid areas, karst areas and even

rapidly urbanized areas [9–12]. At present, agricultural activities have become a critical cause and a source of groundwater pollution. Irrigation return flow water with chemical pollutants can lead to the groundwater and surface water being unsuitable or less valuable for other water uses [13–16]. Therefore, groundwater chemical characteristics under the influence of human activities in agricultural areas have become a research focus [17–21]. It is of great significance to identify the key factors influencing the chemical composition and hydrochemical evolution process of groundwater for rational utilization of water resources and food security in agricultural areas [22–24].

Muling–Xingkai Plain (MXP) is one of the biggest and most important grain production bases in NE China, where plants and crops grow in rich, dark soil. A great deal of pesticides and fertilizer is frequently applied, which could lead to deterioration of water quality. However, black soils with weak infiltration capacity can retard the infiltration of irrigation water and other surface water. Human activities coupled with special soil conditions result in a complex chemical evolution process of groundwater in MXP. Previous studies showed that agricultural activities have influenced groundwater qualities in local areas [25]. Recent studies show domestic sewage in residential zones is the source of contamination of groundwater [26,27]. Food security and human health in MXP are closely related to groundwater qualities. It is necessary to perform a thorough analysis to understand the chemical characteristics of groundwater and to distinguish the main factors affecting the chemical composition of groundwater in MXP.

Chemical ion analysis and multivariate statistical analysis have been widely applied to assess hydrochemical processes and geochemical evolution in complex systems [28–30]. These methods coupled with isotopic analysis were effectively applied to delineate the hydrochemical evolution process and to distinguish the source of chemical ions in groundwater [31–34]. Generally, correlation among chemical variables is the basis of chemical ion analysis [35]. Multivariate analysis is mainly applied to classify samples and to further identify the principal components. These methods are effective ways to distinguish the key factors influencing groundwater chemical composition [36,37].

The chemical evolution process of groundwater and dominant factors affecting chemical composition under the anthropogenic influence and special soil conditions are investigated using chemical ion analysis and multivariate statistical analysis in MXP. The aims are to (1) show the chemical composition of groundwater, (2) identify the chemical evolution process of groundwater, (3) distinguish various factors affecting the chemical composition of groundwater and (4) provide some implications for the protection of groundwater. The results will be beneficial for groundwater resource management in agricultural areas with similar geological or hydrogeological conditions.

## 2. Description of Study Area

### 2.1. Geographical Conditions

MXP occupies an area of about 10,000 km$^2$ in NE China, extending between longitudes of 131°30′–133°40′ E and latitudes of 45°05′–46°17′ N. Wandashan Mountain is found along the north side and west side of the study area. The east and south boundaries of the study area are Wusuli River and Xingkai Lake, respectively. Abuqing River, Qihulin River and Muling River are three major rivers (Figure 1), and rivers flow through the plain from west to east. The annual average air temperature is 1.9 degrees centigrade, and the temperature is highest in July (21 °C) and lowest in January (−21 °C). Mean annual rainfall is 540–680 mm, with June to September accounting for about 70% of it.
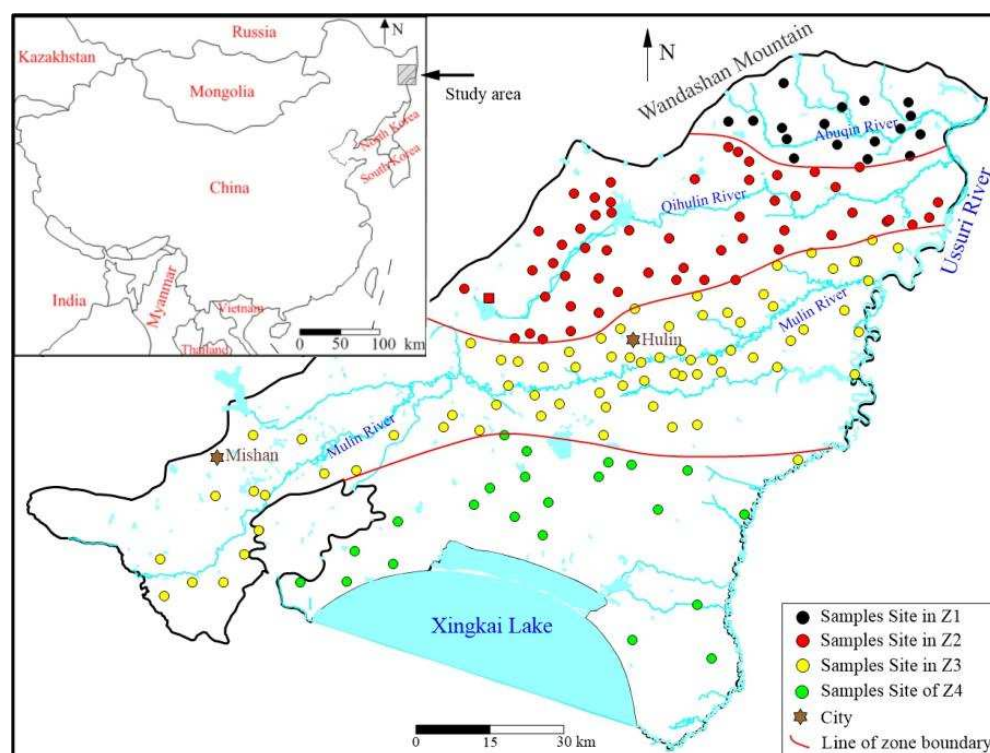
**Figure 1.** Study area and sampled sites.

*2.2. Hydrogeological Setting*

Four hydrogeologic subdivisions are divided based on rivers and lakes in the plain. Abuqin zone (Z1) and Qihulin zone (Z2) are located in the northern plain, and Muling zone (Z3) and Xingkai zone (Z4) are distributed in the middle and southern part (Figure 1).

Aquifers principally consist of Quaternary alluvial and lacustrine deposits and Neogene sediments. The thickness of the aquifer is 50–200 m, and the depth to groundwater is 2–20 m. Phreatic aquifers are widely overlain by thick black clay layers with small infiltration coefficients, especially the aquifer in Z4. Sandy sediments are mainly distributed along river channels. Groundwater flows from west to east, similar to the flow direction of rivers in MXP.

Recharge sources of groundwater are atmospheric precipitation, surface water and irrigation water. Groundwater is principally discharged by evaporation, artificial extraction and lateral outflow into river channels.

*2.3. Land Uses and Human Activities*

Large areas of natural grasslands and wetlands in the MXP have been exploited and turned into croplands since 1950s. In addition, large areas of gardens and woodland were turned into croplands, and many dry farmlands distributed in piedmont zones were turned into rice fields recently. The farmlands are widely distributed in MXP.

Groundwater is the main irrigation water in Z1, Z2 and Z3. Rice fields in Z4 are mainly irrigated by surface water abstracted from Xingkai Lake. A large amount of agricultural effluents has seeped underground, which may lead to a change in groundwater quality. Meanwhile, the quality and yield of crops may be influenced by groundwater quality. Mishan city and Hulin city are located in Z3, and villages are distributed widely in MXP. Domestic sewage in the rural area is discharged into leak channels, and it poses a threat to groundwater quality.

## 3. Materials and Methods

This study was conducted based on 164 groundwater samples collected in 2016–2018, and the numbers of samples in Z1, Z2, Z3 and Z4 are 17, 54, 71 and 22, respectively (Figure 1). Samples were filtrated by using 0.45 μm filter membranes and then stored under a temperature of 4 °C. Field parameters pH, temperature (T), electrical conductivity (EC) and redox potential (Eh) were measured on-site.

All analyses were carried out at the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences. Analyses for total concentrations of four major cations ($K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$) were measured by inductively coupled plasma mass spectrometry. $NO_3^-$, $Cl^-$, $Br^-$ and $SO_4^{2-}$ analyses of water samples were measured by spectrophotometry. $HCO_3^-$ was measured by acid–base titration. Total dissolved solids (TDS) were measured gravimetrically. The relative error was less than 3% for all analyzed elements.

In this study, chemical ion analysis was carried out based on the molar ratio or milliequivalent ratio among chemical ions. It can suggest the source of the chemical ions, water–rock interaction and even the influence of human activities. Principal component analysis (PCA) was applied to analyze possible processes influencing the chemical composition of groundwater using the IBM SPSS program (version 19, 2010, SPSS Inc. Chicago, IL, USA). Parameters Eh and EC were eliminated for samples in Z1, Z2 and Z3 due to more than 50% of data values being missing (Table 1). In addition, nearly half of the samples were below the detection limit value for $NH_4^+$, and the values were replaced by 0.5 times the detection limit. Rotation of principal components was carried out in PCA, and the expressions "strong", "moderate", and "weak" were applied to describe the factor loading values of >0.75, 0.75–0.50 and 0.50–0.30, respectively [38].

**Table 1.** Statistics of groundwater chemistry data in four zones of Muling–Xingkai Plain (MXP).

| Parameter | Unit | Z1 (*n* = 17) | | | | | Z2 (*n* = 54) | | | | | Z3 (*n* = 75) | | | | | Z4 (*n* = 22) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Min. | Max. | Mean | SD | CV (%) | Min. | Max. | Mean | SD | CV (%) | Min. | Max. | Mean | SD | CV (%) | Min. | Max. | Mean | SD | CV (%) |
| PH | Standard | 5.87 | 7.80 | 6.63 | 0.52 | 8 | 6.09 | 7.60 | 6.74 | 0.38 | 6 | 5.92 | 7.46 | 6.74 | 0.31 | 5 | 6.38 | 7.15 | 6.77 | 0.23 | 3 |
| TDS | $mg·L^{-1}$ | 64.70 | 442.40 | 195.48 | 93.35 | 48 | 84.59 | 746.10 | 243.40 | 122.94 | 51 | 90.05 | 1179.00 | 248.20 | 154.13 | 62 | 106.00 | 1154.00 | 278.58 | 208.11 | 75 |
| $K^+$ | $mg·L^{-1}$ | 0.52 | 2.61 | 1.45 | 0.60 | 41 | 0.22 | 49.69 | 3.09 | 7.50 | 243 | 0.33 | 22.92 | 2.87 | 3.96 | 138 | 0.48 | 42.57 | 4.29 | 8.54 | 199 |
| $Na^+$ | $mg·L^{-1}$ | 5.40 | 52.17 | 17.37 | 11.46 | 66 | 8.42 | 63.79 | 20.27 | 12.36 | 61 | 3.75 | 96.68 | 20.07 | 13.32 | 66 | 6.21 | 79.05 | 27.50 | 16.17 | 59 |
| $Ca^{2+}$ | $mg·L^{-1}$ | 6.01 | 79.08 | 29.87 | 17.57 | 59 | 10.07 | 120.40 | 38.87 | 25.36 | 65 | 8.79 | 167.20 | 36.17 | 22.15 | 61 | 12.65 | 191.40 | 38.09 | 36.05 | 95 |
| $Mg^{2+}$ | $mg·L^{-1}$ | 2.78 | 29.10 | 11.84 | 7.34 | 62 | 4.37 | 44.26 | 12.81 | 7.89 | 62 | 4.27 | 55.84 | 12.44 | 8.14 | 65 | 3.72 | 81.35 | 13.90 | 15.36 | 111 |
| $Cl^-$ | $mg·L^{-1}$ | – | 64.93 | 7.76 | 15.41 | 198 | 0.35 | 59.72 | 11.51 | 14.91 | 129 | – | 184.30 | 20.03 | 29.04 | 145 | 0.35 | 308.90 | 37.09 | 66.53 | 179 |
| $SO_4^{2-}$ | $mg·L^{-1}$ | 1.61 | 28.21 | 6.90 | 6.24 | 90 | 1.62 | 74.18 | 22.91 | 21.07 | 92 | 1.70 | 181.30 | 24.24 | 31.56 | 130 | 1.64 | 125.80 | 23.59 | 33.24 | 141 |
| $HCO_3^-$ | $mg·L^{-1}$ | 18.23 | 504.40 | 174.93 | 125.42 | 72 | 33.63 | 642.00 | 183.49 | 115.47 | 63 | 24.46 | 354.60 | 133.93 | 72.41 | 54 | 66.03 | 550.30 | 153.16 | 104.06 | 68 |
| $NH_4^+$ | $mg·L^{-1}$ | 0.02 | 7.70 | 1.53 | 2.52 | 165 | 0.01 | 7.00 | 1.00 | 1.63 | 163 | 0.02 | 5.30 | 0.66 | 1.31 | 198 | 0.02 | 3.90 | 0.69 | 1.27 | 185 |
| $NO_3^-$ | $mg·L^{-1}$ | 1.75 | 104.30 | 9.58 | 23.83 | 249 | 0.20 | 147.70 | 9.74 | 24.17 | 248 | 1.75 | 399.00 | 32.61 | 68.66 | 211 | 1.78 | 95.68 | 21.24 | 29.95 | 141 |
| EC | $ms·cm^{-1}$ | | | | | | | | | | | | | | | | 0.13 | 2.05 | 0.50 | 0.40 | 80 |
| Eh | mv | | | | | | | | | | | | | | | | −164.00 | 135.00 | 10.58 | 80.16 | 758 |

Note: SD: standard deviation; CV: coefficient of variation; –: below detectable limit.

## 4. Results and Discussion

### *4.1. Chemical Characteristics*

#### 4.1.1. General Chemistry

The descriptive statistics of groundwater chemistry data in four zones are presented in Table 1 and Figure 2. pH is predominantly slightly acidic to near neutral with TDS 64.7–1179 mg/L, and ionic composition is dominated by $Ca^{2+}$ (6.01–191.4 mg·$L^{-1}$), $Na^+$ (3.75–96.68 mg·$L^{-1}$) and $HCO_3^-$ (18.23–642 mg·$L^{-1}$). The order of abundance of cations is $Ca^{2+} > Na^+ > Mg^{2+} > K^+ > NH_4^+$, and anions follow the order of $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$. The differences in chemical ion concentrations in the four zones are obvious. Samples in Z1 have the lowest levels of $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $Cl^-$ and $SO_4^{2-}$ but the highest level of $HCO_3^-$. The ion concentrations of samples in Z4 are highest, except $NH_4^+$. Concentrations of chemical ions in Z2 are nearly identical to those in Z3, except $NO_3^-$ and $NH_4^+$. Nearly all of the chemical parameters in the four zones are characterized by a high coefficient of variation. The groundwater chemical composition is influenced by multiple factors.
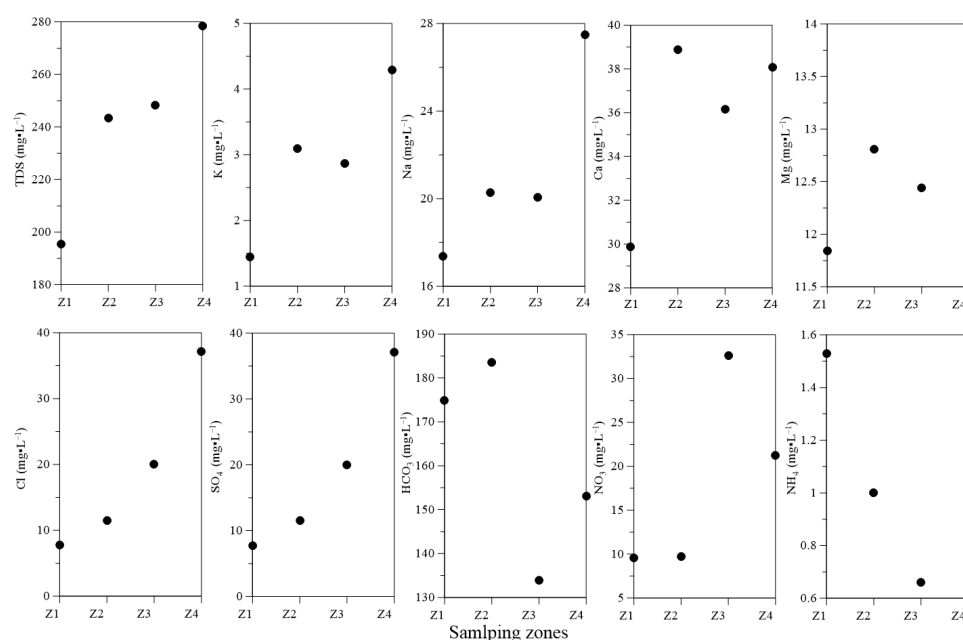


**Figure 2.** Concentration of chemical parameters in four zones.

#### 4.1.2. Groundwater Types

With respect to cations, most samples are scattered in zone B in the lower-left triangle, indicating a mixed type. Only a few samples in Z3 and Z4 are Ca-type (Figure 3). With respect to anions, most groundwater samples are plotted in zone E in the lower-right triangle. Most groundwater samples are $HCO_3$-type.

As shown in the central diamond plot in Figure 3, more than half of the samples are scattered in zone 1, which indicates that alkaline earth elements and bicarbonate are the most common in groundwater chemistry. A large number of samples in Z1 and Z2 are scattered in zone 1, but more than half of the samples in Z3 and Z4 are scattered in zone 4. Zone 4 means samples are mixed chemical types. The chemical composition of samples in the southern part of MXP is significantly influenced by multiple factors.

The water type of groundwater samples in MXP is predominantly Ca-$HCO_3$. However, samples with water types of Ca·Mg·Na-$HCO_3$, Ca·Mg-$HCO_3$, Ca·Mg-$HCO_3$·$SO_4$ and Ca·Na-$HCO_3$ are widely distributed in the study area. At present, some samples are characterized by the water type of $SO_4$, even $NO_3$, which hardly occurred before 1963 [27]. The chemical composition of groundwater in MXP is influenced by human activities.
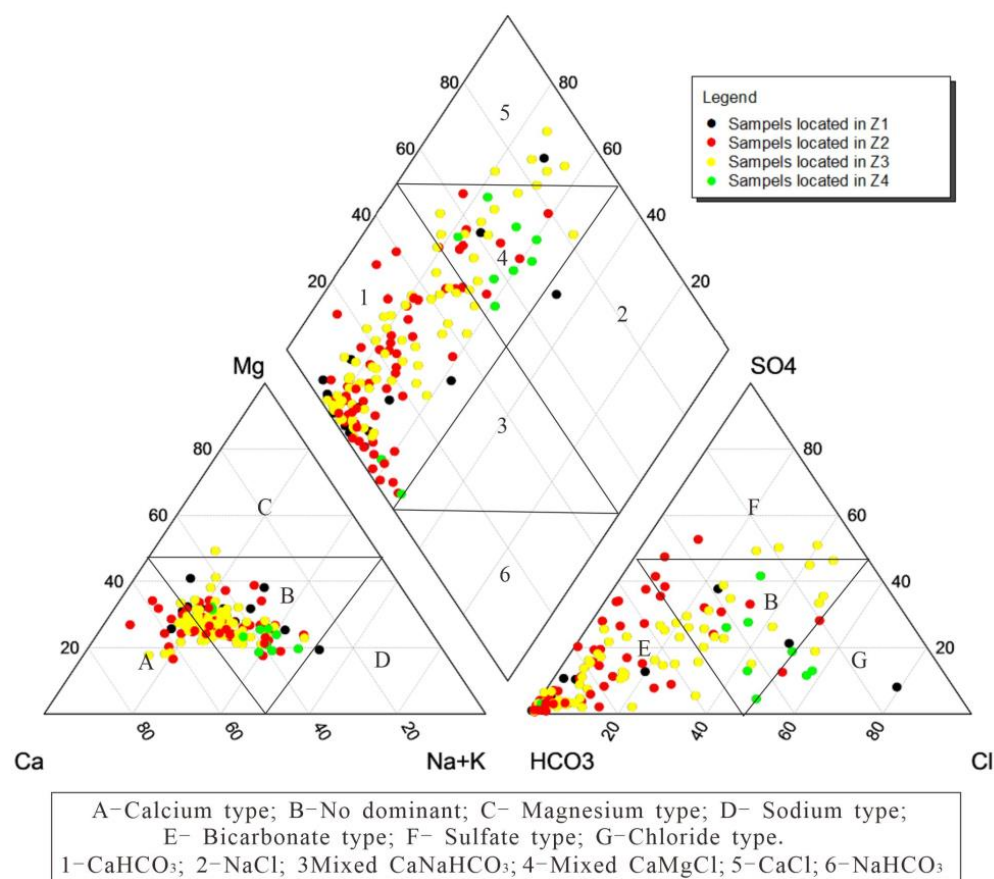
**Figure 3.** Piper third-line diagram of groundwater samples in MXP.

*4.2. Hydrochemical Evolution Process*

4.2.1. Chemical Ion Analysis

(1)    Gibbs Plot

Gibbs diagram can be used to detect the primary formation mechanism of the water chemistry [39]. The weight ratios of $Na^+/(Na^++Ca^{2+})$ and $Cl^-/(Cl^-+HCO_3^-)$ of most samples are less than 0.5, with TDS 200–500 mg/L (Figure 4). Rock dissolution is the predominant mechanism controlling the groundwater chemistry [40]. However, many groundwater samples do not fall in the banana-shaped area in the Gibbs diagram (Figure 4). The chemical composition is influenced by other factors, such as human activities and cation exchange reactions. Samples in and out of the banana-shaped area are defined as the "general samples" and the "special samples" in this paper, respectively. Only a few special samples were collected from wells in Z1 and Z2 (Table 2), suggesting the slight effect of external factors on the chemical compositions of groundwater in the northern plain.

**Table 2.** The number of the special samples in four zones.

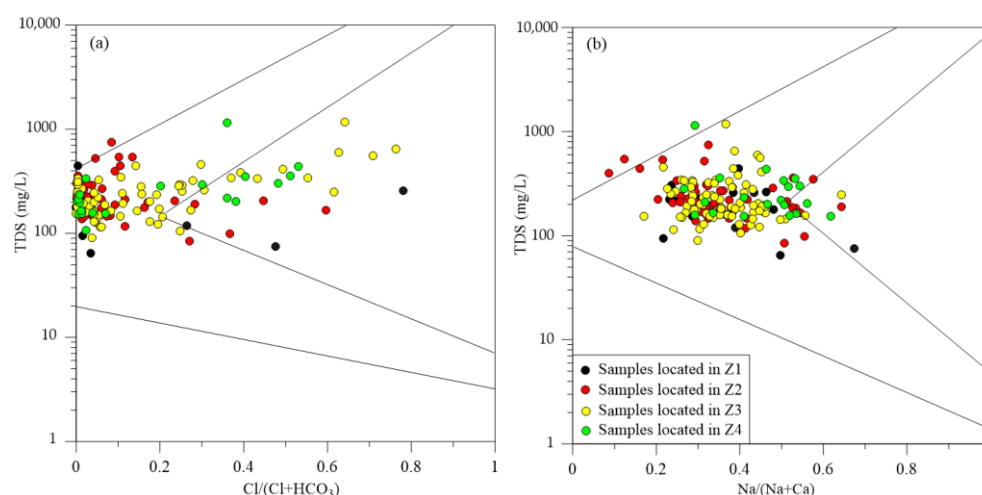| Zones | Total Samples | Number of Special Samples | C (%) |
|---|---|---|---|
| Z1 | 17 | 3 | 17.65 |
| Z2 | 54 | 9 | 16.67 |
| Z3 | 71 | 16 | 22.53 |
| Z4 | 22 | 10 | 45.45 |

Note: C: ratio of the number of special samples to total samples.

**Figure 4.** Gibbs plot of water samples in MXP: total dissolved solids (TDS) as a function of weight ratios of (**a**) (Cl/Cl+HCO$_3$) and (**b**) Na/(Na+Ca).

(2)    Mixing diagram

A mixing diagram can be used to analyze the origin of chemical ions produced by the dissolution of different minerals [41]. Na$^+$ normalized molar ratios are usually depicted in the diagram based on three representative lithologies (Figure 5).
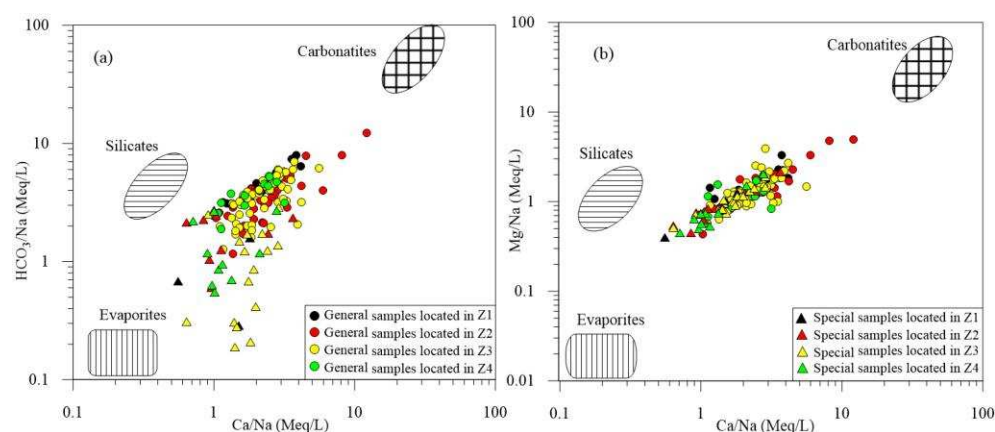


**Figure 5.** Bivariate diagrams of (**a**) (HCO$_3$/Na) versus (Ca/Na), (**b**) (Mg/Na) versus (Ca/Na).

Most general samples are close to the end-member of silicate and end-member of carbonatites (Figure 5) but far away from the end-member of evaporite. Chemical compositions of general samples are dominated by silicate dissolution and carbonate dissolution to different degrees [42]. The special samples lie close to the end-member of evaporates, suggesting the major contribution of evaporite (NaCl) dissolution to chemical composition.

Generally, a natural source of chloride in groundwater far from seas is the weathering of chloride-bearing evaporate deposits. However, mineralogical analysis on samples of rock debris and water-bearing units shows the compositions are quartz (52%), plagioclase (21%), clay mineral (16%), potassium feldspar (10%) and carbonates (1%). Halite and gypsum minerals are not the main components of rock and stratum. The study area is far away from the coastline, so the source of Cl$^-$ is not seawater. The chemical composition of special samples may be influenced by other factors. Cl$^-$ is one of the major anthropogenic components in groundwater [43]. Human activities are severely influencing the chemical composition of groundwater in local areas.

(3)    Ionic ratios

The specific hydrogeochemical processes can be further shown by milliequivalent ratios of chemical parameters. Sediments in MXP are characterized by sand and fine clay with adsorbed $Na^+$. Therefore, $Ca^{2+}$ and $Mg^{2+}$ in the groundwater can exchange with $Na^+$ absorbed on the surface of clay minerals as shown in Equation (1).

$$2Na \text{ (Clay)} + (Ca^{2+} + Mg^{2+}) \text{ (Groundwater)} \leftrightarrow (Ca + Mg) \text{ (Clay)} + 2Na^+ \text{ (Groundwater)} \tag{1}$$
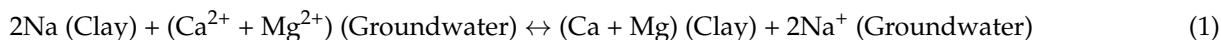
Does cation exchange lead to the special samples falling out of the banana-shaped area in the Gibbs diagram? As shown in Figure 6a, the special samples are not linearly related. The cation exchange process of $Na^+$ for $Ca^{2+}$ in aquifers is not shown. The general samples lie along the 1:1 line, indicating the occurrence of the cation exchange process. However, concentrations of $\rho(Na^+ + K^+ - Cl^-)$ only vary from 0 to 1 meq/L. Cation exchange processes do not predominate the concentrations of $Ca^{2+}$, $Mg^{2+}$ and $Na^+$ in groundwater.
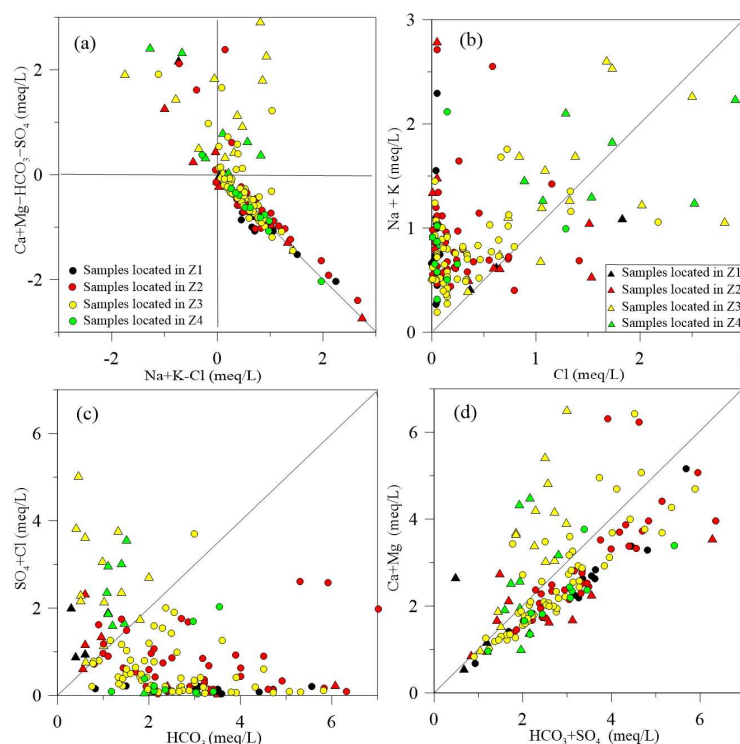


**Figure 6.** Bivariate diagrams of (**a**) ($Ca+Mg-HCO_3-SO_4$) versus ($Na+K-Cl$), (**b**) ($Na+K$) versus $Cl$, (**c**) ($SO_4+Cl$) versus $HCO_3$, (**d**) ($Ca+Mg$) versus ($HCO_3+SO_4$).

Sources of $Ca^{2+}$ and $Mg^{2+}$ can be inferred from milliequivalent ratios of $\rho(Ca^{2+} + Mg^{2+})/\rho(HCO_3^- + SO_4^{2-})$ (Figure 6d). Nearly all the general samples lie under the 1:1 line, so the dissolution of silicate minerals is controlling the concentration of $Ca^{2+}$, $Mg^{2+}$ and $HCO_3^-$ in groundwater [44]. In addition, the dissolution process of silicate minerals also can be shown by the ratios of $\rho(SO_4^{2-} + Cl^-)/\rho HCO_3^-$ and $\rho(Na^+ + K^+)/\rho Cl^-$ (Figure 6b,c). The dissolution of silicate minerals is a key geochemical process controlling chemical composition in groundwater. Special samples in Figure 6, especially the special samples in Z3 and Z4, are far away from general samples. Groundwater qualities in the southern plain have been seriously affected by human activities.

### 4.2.2. Stable Isotope Analysis

The combined utilization of stable isotopes and chemical parameters can identify possible groundwater contamination. When rock–water interaction controls the concentration of chemical ions in groundwater, continued dissolution of rocks can elevate the concentration of related ions in groundwater with a slight fluctuation in the stable isotopic value, for the low isotopic fraction. In addition, a linear relationship will exist between the

chemical ion concentration and the stable isotopic value under the effect of evaporation [45]. When some chemical ions increase sharply without dissolution of related minerals, but stable isotopic values of groundwater stay rather constant, the wastewater from human activities may be the principal cause of the high level of related chemical ions.

Figure 7 illustrates the relationships between the concentration of chemical variables ($Cl^-$, $SO_4^{2-}$, $NO_3^-$, $Na^+$, $Mg^{2+}$ and $Ca^{2+}$) and the $\delta^{18}O$ value of groundwater. The elevation of chemical ions for most general samples results from evaporation and mineral dissolution. However, concentrations of chemical ions for special samples increase sharply with little modifications in stable isotopic values, especially for $Cl^-$, $SO_4^{2-}$ and $NO_3^-$. Major anthropogenic components in the groundwater include $Cl^-$ and $NO_3^-$, as well as $SO_4^{2-}$. The chemical composition of special samples is influenced severely by human activities. The result of stable isotope analysis is consistent with the results discussed above.
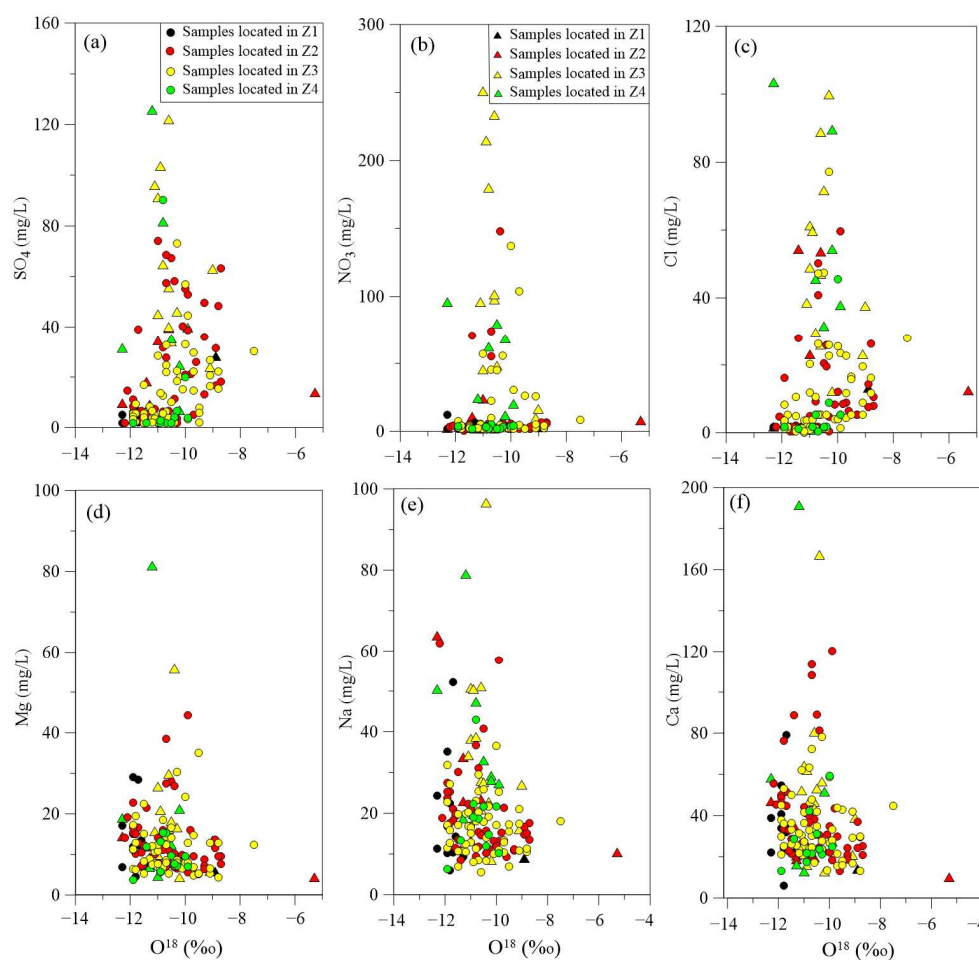


**Figure 7.** Variations of (**a**) $SO_4$, (**b**) $NO_3$, (**c**) Cl, (**d**) Mg, (**e**) Na, (**f**) Ca with the $\delta^{18}O$ value of groundwater.

### 4.2.3. PCA

PCA is used to further discuss the key factors dominating the chemical composition of groundwater in four zones, and the results are shown in Table 3.

(1)　Z1

The chemical composition of groundwater samples in Z1 is controlled by a three-factor model, and the cumulative variance of the three PCs is 87.81%. PC1 comprises strong loading of $Ca^{2+}$, TDS, $Mg^{2+}$, $HCO_3^-$, $Na^+$ and PH, and TDS values increase with the concentrations of $HCO_3^-$, $Ca^{2+}$, $Na^+$ and $Mg^{2+}$. Water–rock interactions are responsible for their occurrence. Based on the chemical analysis mentioned above, the dissolution of silicate and carbonate minerals is responsible for the chemical composition of groundwater.

Potassic fertilizers and urea fertilizers are widely applied in MXP. When the topsoil with high permeability occurs in farmlands, a clear correlation between $K^+$ and $NH_4^+$ will be indicated in groundwater. Thus, PC3 is the indication of agricultural activities.

Potential sources of $Cl^-$ in groundwater include natural sources (dissolution of minerals), agricultural chemicals, animal waste and septic effluent. In PC2, no clear correlation is observed between $Cl^-$ and $K^+$. Thus, fertilizer is not the main source of $Cl^-$. In addition, a high level of $Cl^-$ cannot result from the dissolution of minerals as discussed above. $Cl^-$ and $NO_3^-$ are the major components of domestic sewage [43]. Previous studies showed that the discharge of domestic sewage in MXP had resulted in a high level of $NO_3^-$. Chemical parameters $Cl^-$ and $NO_3^-$ associated with factor 2 imply the influence process of domestic sewage.

(2)　Z2

A three-factor model can be used to explain the chemical composition of groundwater samples in Z2, and the cumulative variance of three PCs is 79.83%. As in the analysis of Z1, PC1 is the indication of water–rock interaction. PC2 with high positive loading of $Cl^-$ and $SO_4^{2-}$ and moderate loading of $NO_3^-$ indicates that domestic sewage is responsible for groundwater chemistry. PC3 with moderate positive loading of $NH_4^+$ and $K^+$ suggests groundwater quality is affected by agricultural production.

(3)　Z3

Groundwater chemistry in Z3 is controlled by a three-factor model, and the cumulative variance of the three PCs is 88.74%.

PC1 comprises strong loading of TDS, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2+}$, $Cl^-$ and $NO_3^-$ and moderate loading of $K^+$. The strong correlations among TDS, $Na^+$, $Ca^{2+}$, $Mg^{2+}$ and $K^+$ show that water–rock interaction is responsible for chemical composition. However, strong correlations among $NO_3^-$, $Cl^-$ and $SO_4^{2-}$ are mainly caused by human activities. The TDS value is increased with concentrations of $SO_4^{2-}$, $Cl^-$ and $NO_3^-$, which suggests that infiltration of domestic sewage is responsible for its high concentrations in groundwater. Thus, the chemical compositions of groundwater are dominated by water–rock interaction and domestic sewage.

PC2, which comprises strong loading of PH and $HCO_3^-$ and positive loading of $Ca^{2+}$ and $Mg^{2+}$, indicates the slight dissolution process of carbonate minerals [7].

PC3, which only comprises strong loading of $NH_4^+$ and weak loading of $NO_3^-$, indicates reduction conditions.

(4)　Z4

Groundwater chemical composition in Z4 is controlled by a two-factor model, and the cumulative variance of the two PCs is 83.08%.

PC1, which comprises strong loading of TDS, $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2+}$, $Cl^-$, $HCO_3^-$ and EC, implies water–rock interactions are responsible for chemical composition.

Halite and gypsum minerals are not the main constituents of rock and stratum. Chlorine-bearing fertilizers are not applied frequently. Thus, the high concentration of $Cl^-$ and $SO_4^{2-}$ cannot be attributed to the dissolution of minerals. Domestic wastewater is the main source of $Cl^-$ and $SO_4$. PC1 indicates that water–rock interaction and domestic sewage control groundwater chemical composition.

PC2 comprises strong positive loading of PH and $NH_4^+$ and negative loading of $NO_3^-$ and EH. Redox conditions may dominate the content of $NH_4^+$ and $NO_3^-$. Other ions do not show a significant correlation with $NH_4^+$ and $NO_3^-$, which implies that organic matter decomposition is dominating the concentration of nitrogen species. PC2 can be regarded as "natural reduction conditions". Large areas of natural grasslands and wetlands were exploited and turned into croplands in the last few decades in MXP. Abundant herbaceous plants were buried underground. The organic matter decomposition has produced plenty of $NH_3$-N. Thus, redox conditions can influence the content of nitrogen species.

**Table 3.** Principal component loading for groundwater samples in four zones.

| Chemical Parameter | Z1 | | | Z2 | | | Z3 | | | Z4 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | PC1 | PC2 | PC3 | PC1 | PC2 | PC3 | PC1 | PC2 | PC3 | PC1 | PC2 |
| PH | **0.820** | −0.390 | −0.037 | **0.860** | −0.272 | −0.301 | −0.115 | **0.957** | −0.084 | 0.228 | **0.775** |
| TDS | **0.965** | 0.140 | 0.131 | **0.819** | 0.559 | 0.036 | **0.995** | −0.011 | 0.029 | **0.996** | −0.040 |
| K$^+$ | −0.210 | −0.108 | **0.913** | 0.482 | 0.448 | **0.589** | **0.684** | −0.211 | 0.016 | **0.943** | 0.213 |
| Na$^+$ | **0.845** | 0.136 | −0.271 | **0.771** | −0.069 | 0.215 | **0.935** | −0.069 | −0.044 | **0.881** | −0.253 |
| Ca$^{2+}$ | **0.969** | 0.000 | 0.108 | **0.777** | 0.563 | −0.111 | **0.943** | 0.185 | 0.096 | **0.982** | 0.049 |
| Mg$^{2+}$ | **0.952** | −0.033 | −0.003 | **0.779** | 0.576 | −0.046 | **0.922** | 0.228 | 0.068 | **0.978** | 0.063 |
| HCO$_3^-$ | **0.920** | −0.350 | 0.136 | **0.969** | 0.114 | 0.180 | −0.015 | **0.760** | 0.420 | **0.783** | 0.587 |
| SO$_4^{2-}$ | −0.428 | 0.128 | −0.624 | −0.075 | **0.826** | 0.026 | **0.866** | −0.331 | −0.273 | **0.823** | −0.140 |
| Cl$^-$ | −0.117 | **0.953** | −0.234 | 0.129 | **0.804** | 0.018 | **0.861** | −0.212 | −0.232 | **0.944** | −0.235 |
| NH$_4^+$ | 0.016 | −0.091 | **0.892** | 0.037 | 0.019 | **0.700** | −0.068 | −0.003 | **0.979** | −0.012 | **0.669** |
| NO$_3^-$ | 0.019 | **0.976** | −0.060 | 0.177 | **0.566** | −0.042 | **0.896** | −0.253 | −0.476 | 0.262 | **−0.835** |
| EC | | | | | | | | | | **0.981** | −0.014 |
| Eh | | | | | | | | | | 0.127 | **−0.812** |
| Eigenvalue | 5.25 | 2.21 | 2.20 | 4.44 | 2.90 | 1.44 | 6.39 | 1.85 | 1.53 | 7.86 | 2.94 |
| Explained variance (%) | 47.74 | 20.09 | 19.98 | 40.38 | 26.40 | 13.05 | 58.06 | 16.80 | 13.88 | 60.45 | 22.63 |
| Cumulative % of variance | 47.74 | 67.83 | 87.81 | 40.38 | 66.77 | 79.83 | 58.06 | 74.86 | 88.74 | 60.45 | 83.08 |

### 4.3. Factors Dominating the Groundwater Chemical Characteristics

As the discussion above mentioned, water–rock interaction, infiltration of domestic sewage, agricultural activities and redox conditions are the main factors dominating the chemical composition of groundwater in MXP (Figure 8).
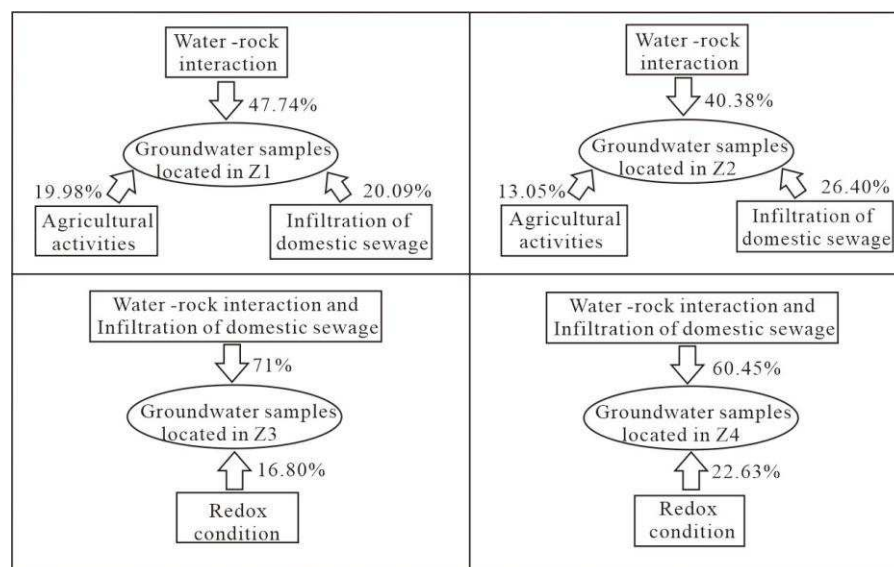


**Figure 8.** Factors dominating the groundwater chemical characteristics in different zones in MXP.

Agricultural activities only slightly influence the chemical composition of groundwater in the northern plain (Z1 and Z2). The redox environment of groundwater in the southern plain (Z3 and Z4) is a key factor influencing the concentration of NO$_3^-$ and NH$_4^+$. The thick silt layer overlaying aquifers can lead to a reduction condition. Organic matter decomposition can produce plenty of NH$_3$-N. A high level of NO$_3^-$ is closely related to nitrification.

Nearly all the special samples were collected from wells near river channels, where coarse-textured sediments are overlying aquifers (Figure 9). Coarse-textured sediments mainly consist of sand and gravel, and they can allow water to infiltrate downwards easily. Most villages in MXP lack sewage disposal systems, and domestic sewage is discharged

into a seepage pit directly. Thus, the discharge of domestic sewage in the rural areas near the rivers often leads to abnormal groundwater types.
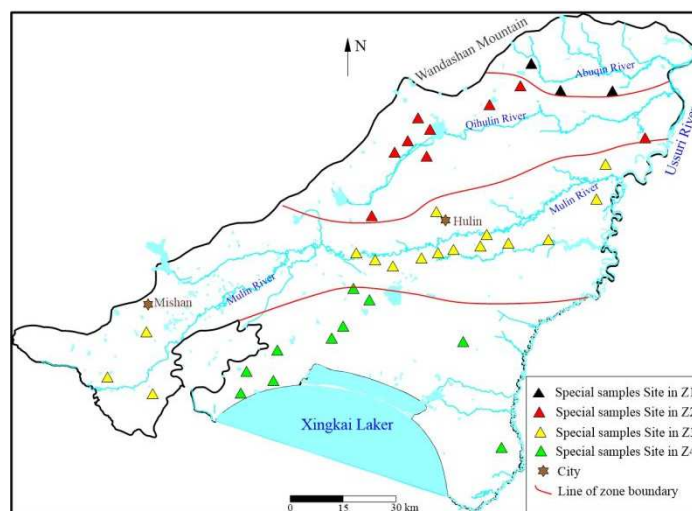


**Figure 9.** The distribution of the special samples in four zones.

Most of the plants grow in rich, black soil in MXP. Black soils can deter or retard the downward infiltration of water. Thus, agricultural activities do not influence the chemical composition of groundwater significantly due to the weak permeability of black soil. The dissolution of silicate minerals and carbonate minerals is the original source of groundwater. It is the most important factor dominating the chemical composition of groundwater in MXP. The saturation index (SI) data show that calcite, dolomite, gypsum and halite are in an unsaturated state (Table 4). The dissolution of minerals is the critical factor dominating the chemical composition of groundwater.

**Table 4.** Saturation index of groundwater samples in four zones.

| Saturation Index | Z1 | | | Z2 | | | Z3 | | | Z4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Max** | **Min** | **Mean** | **Max** | **Min** | **Mean** | **Max** | **Min** | **Mean** | **Max** | **Min** | **Mean** |
| SI (Calcite) | 0.37 | −3.34 | −1.95 | 0.26 | −2.49 | −1.25 | 0.08 | −2.79 | −1.56 | 0.44 | −1.78 | −1.45 |
| SI (Dolomite) | 0.58 | −5.52 | −2.24 | 0.29 | −5.2 | −2.64 | −0.15 | −4.52 | −3.02 | 0.75 | −3.84 | −2.56 |
| SI (Gypsum) | 2.61 | −3.75 | −3.23 | −0.61 | −3.65 | −2.74 | −1.91 | −3.56 | −2.75 | −1.31 | −3.85 | −2.85 |
| SI (Halite) | −7.25 | −9.62 | −8.35 | −7.29 | −9.68 | −8.89 | −6.91 | −9.54 | −8.51 | −6.23 | −9.7 | −8.88 |

Domestic sewage from rural areas near rivers is a significant factor affecting the chemical composition of groundwater in local areas. Nearly 70% of the population in MXP is living in the southern plain. That is why most of the special samples are located in Z3 and Z4.

Though MXP is an important grain production base in China, agricultural activities do not lead to the deterioration of groundwater quality. Thick black soil layers deter the infiltration of wastewater. Soil media are an important natural factor influencing the chemical composition.

## 5. Suggestions for Groundwater Management

Agricultural activities do not directly lead to deterioration of groundwater qualities, and agricultural non-point-source pollution does not occur in MXP. However, the discharge of domestic sewage has led to the abnormity of groundwater quality near river channels. Therefore, shallow groundwater far away from river channels and residential zones can be used as irrigation water based on food safety and human health.

The sampling depth of special samples usually ranges from 4 to 30 m. Chemical compositions of deep groundwater with a depth of more than 80 m are relatively stable (Figure 10), and major chemical ion concentrations hardly exceed the drinking water standard. Deep groundwater is the best choice for water supply.
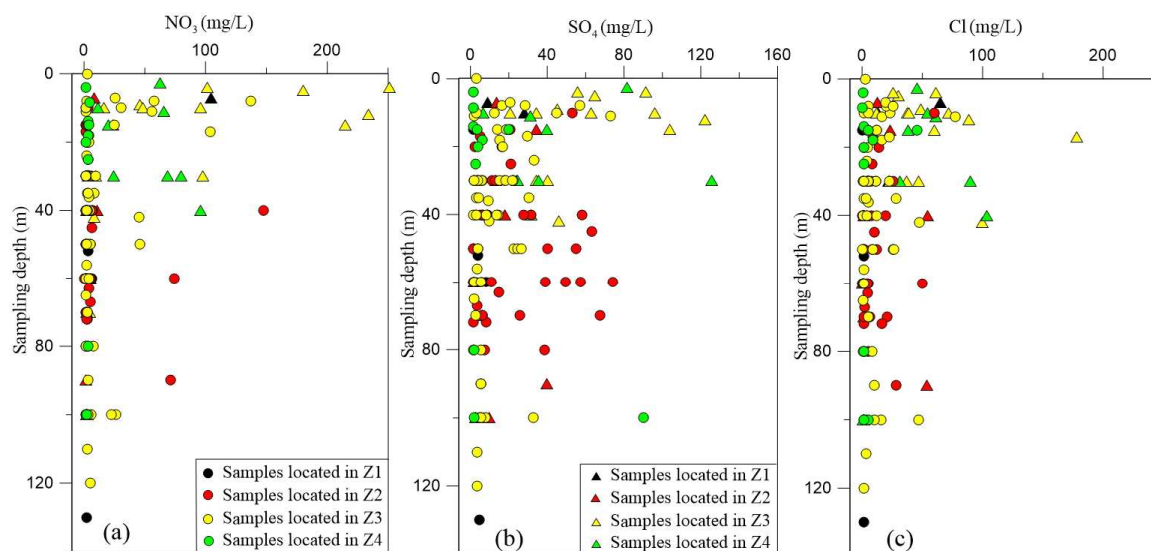


**Figure 10.** Variations of (**a**) $NO_3$, (**b**) $SO_4^{2-}$, (**c**) Cl with sampling depth (well depth).

Nitrification has led to the transformation of $NH_4^+$ into $NO_3^-$. Thus, samples in Z3 and Z4 are characterized by a low level of $NH_4^+$. However, samples in Z1 and Z2 are characterized by a high level of $NH_4^+$. Human activities, such as digging many wells and overpumping, can increase dissolved oxygen in groundwater and accelerate nitrification. Such activities may increase the concentration of $NO_3^-$ in groundwater.

To avoid the deterioration of groundwater quality and protect groundwater resources, local governmental should (1) construct sewage disposal systems immediately in rural areas, (2) supervise the indiscriminate discharge of various wastewaters, (3) impose control on the construction of wells and groundwater pumping and (4) protect the thick black soil layer to retard the infiltration of wastewater.

## 6. Conclusions

(1) Dissolution of silicate minerals and carbonate minerals is the most important factor dominating the chemical composition of groundwater in MXP. Groundwater in MXP is predominantly Ca-HCO$_3$ in composition. Human activities have significantly influenced the chemical composition of groundwater in the residential zone near rivers. Thus, the NO$_3$ type and SO$_4$ type exist.

(2) Agricultural activities only slightly influence the chemical composition of groundwater in the northern plain, and human activities have significantly influenced the chemical composition of groundwater in the southern area. Groundwater in the southern plain is characterized by a high level of $NH_4^+$, which is related to the decomposition of organic matters in a reduction condition. The samples in the northern plain are characterized by a high level of $NH_4^+$, and it is necessary to avoid the transformation of a reduction condition into an oxidation environment.

(3) Due to the widespread distribution of thick black soils in MXP, agricultural non-point-source pollution does not occur. The discharge of domestic sewage mainly influenced the chemical composition of shallow groundwater. So, deep groundwater with a depth of more than 80 m is the best choice for water supply. In addition, shallow groundwater far away from river channels should be used as irrigation water.

(4) Government agencies should adopt some strategies to protect groundwater resources. These strategies include regulating the amount and type of fertilizers applied to

farmland, constructing sewage disposal systems in rural areas, and strengthening the supervision of the discharge of wastewater and construction of deep wells.

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