HYDROCHEMISTRY CHARACTERISTICS OF GROUNDWATER IN AGRICULTURAL OASIS AREAS, NORTHWEST CHINA

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ABSTRACT
Hydrochemistry of groundwater provides new insight to studying on water evolution in arid and semi-arid regions. The chemical properties of sixty-three groundwater samples were assessed from oasis areas in the middle reaches of Heihe River Basin of northwest China, with the aiming of evaluating natural and anthropogenic factors controlling groundwater quality. Results of the study showed that: The 55.6% groundwater samples were non-salinized whereas 33.3% slightly salinized and 11.1% moderately salinized existed. The major ions of the groundwater were dominated by Na+, Ca²⁺, HCO₃⁻, SO₄²⁻, and Cl⁻. The 34.9% of the samples showed NO₃⁻ more than the human affected value. The major anthropogenic inputs into the groundwater contain nitrate, phosphate, potassium and chloride, with Cl⁻ and NO₃⁻, which were the major contributors to groundwater pollution resources in the study area. Elevated knowledge of geochemical evolution of groundwater in agricultural oasis areas of northwest China could generally improve understanding of hydro-chemical systems in arid and semi-arid regions of China; further maintain sustainable development and effective management of groundwater resource.

KEY WORDS
Hydrochemistry, Shallow groundwater, Irrigation, Human inputs, in agricultural oasis areas, Sustainable development.

1. Introduction
Water shortages have become an increasingly serious problem all over the world, especially in the arid and semi-arid regions, where water is commonly of critical economical, social and ecosystem significance. Groundwater, as the major source of water supply in the middle reaches of the Heihe River Basin, located in an agricultural oasis in the arid region of northwest China, has been the focus of attention due to recognition of the increasing stress in water resources and of the serious environmental degradation. Intensive oasis agricultural activities in the middle reaches of Heihe River Basin have caused a high demand on groundwater resources while also putting these resources at serious risk to environmental pollution. And, the frequency application of chemical nitrogen fertilizers in widespread agricultural practices poses a serious threat on groundwater pollution.

Elevated concentration of NO₃⁻ in groundwater from intensive agriculture in the middle reaches of Heihe River Basin has raised concern over possible contamination of drinking water supplies in recent years (Yang and Liu, 2010).

Regardless of utmost importance of the hydro-chemical evolution of groundwater in the middle reaches of Heihe River Basin, very little research has been investigated about the phenomena (especially in anthropogenic input) to identify the chemical composition of groundwater or factors that presently influence them. This paper attempted to systematically analyze the natural process of hydro-chemical characteristics and the influencing factors of the anthropogenic activities based on the relationship between cations and anions in the middle reaches of Heihe River Basin in a typical small-scale agricultural oasis area. Thus, the objectives of this work were to (1) investigate the origin, hydro-chemical characteristics of the shallow groundwater; (2) identify the influence of anthropogenic activities on the hydro-chemistry of groundwater in agricultural oasis areas, in the middle reaches of Heihe River Basin, of northwest China.

2. Materials and methods

2.1 Study area
The study area is located in Linze County, Zhangye District, the typical agricultural oasis areas, Gansu Province, in the middle reaches of Heihe River Basin, northwest China. The average elevation for the study area is 1400 m (a.s.l). This region has a typical desert climate and characterized by cold winters and dry hot summers with a mean annual precipitation of 117 mm. Mean annual evaporation is 2390 mm. Average annual temperature is 7.6. The zonal soil in marginal oasis is Calci-Orthic Aridosols derived from diluvial-alluvial materials according to Chinese Soil Taxonomy, which is equivalent to the Calciorthids in terms of USDA soil taxonomy classification. Due to long-term encroachment of drift sand from Badanjilin Desert and deposition of aeolian sand, Psamments developed in some areas and sandy lands formed. Grain crops, particularly seed maize, are densely cultivated in the agricultural area of the Oasis, sustained by the continuous application of chemical nitrogen fertilizers (mainly urea and salvolatile). Intensive
agricultural practices (application of fertilizers, irrigation practices) led to environmental pollution. Cultivated area is 3715 ha², Grain crops, particularly seed maize, sustained mainly by the continuous application of chemical nitrogen fertilizers. Recently, the total amount of nitrogen fertilizers applied on the maize fields was more than 450 kg ha⁻¹ year⁻¹ (Shu et al., 2007).

2.2 Methods

2.2.1 Sample collection

Fig.1 Maps showing the locations of study area and sampling sites

2.2.2 Field measurements

In the field, we measured concentrations of HCO₃⁻ through titrimetric method electrical conductivity (EC), pH and temperature using the Model 63 Handheld pH, Conductivity, Salinity and Temperature System (YSI Company, Yellow Springs, Ohio, USA). Filtered samples were used for analysis of the major cations and anions.

2.2.3 Laboratory measurements

Major cations (Ca²⁺, Na⁺, Mg²⁺, and K⁺) were analyzed using a DX-100 ion chromatograph (Dionex Corporation, Sunnyvale, CA, USA). And anions (SO₄²⁻, Cl⁻, and NO₃⁻) were analyzed using an ICS-2500 ion chromatograph. The precision of the analyses, all of ions were measured in the key laboratory of ice core in Cold and Arid Regions Environmental and Engineering Research Institute of Chinese Academy of Science. With each measurement repeated three times to estimate the error (Freeze and Cherry, 1979) was within ±1% for all samples.

3. Results and discussion

3.1 Groundwater chemistry

The total of groundwater salinity is presented according to the classification of Robinove (Robinove et al., 1958), fresh water (<1000 mg/l), slightly salinized (1000-3000 mg/l), moderately salinized (3000-10000 mg/l), extremely salinized (10000-35000 mg/l) and brine water (35000 mg/l). The results showed that 55.6% groundwater samples were non-salinized while 33.3% slightly salinized and 11.1% moderately salinized were occurred in the study area.

The statistical parameters, such as the minimum, maximum, mean and standard deviations of chemical compositions of the groundwater samples were analyzed and the results are listed in Table 1. The major ions of groundwater are dominated by Na⁺, Ca²⁺, and HCO₃⁻, SO₄²⁻, and Cl⁻, which represent (on average) 74% and more than 80% of total cations and anions, respectively. The concentrations of Na⁺, Ca²⁺, Mg²⁺, and K⁺ account for on average 44.0%, 30.3%, 24.1% and 1.6% of all the cations, respectively. The most of the K⁺ are not abundant. The source of K⁺ may be due to weathering of potash silicate, use of potash fertilizer (Ranjan et al., 2013). The relative abundance of the major anions follow the trend HCO₃⁻ > SO₄²⁻ > Cl⁻ > NO₃⁻, contributing on average, respectively, 48.9%, 33.6%, 15.6% and 1.9% of the total anions.

The WHO’s (World Health Organization) drinking water guideline limits for NO₃⁻ is 50 mg/l (WHO, 1993), a total of six samples (9.5%) showed higher concentrations. Based on study results of Eckhardt (1995), Groundwater with NO₃⁻ concentration above 13 mg/l of NO₃⁻ is so-called the human affected value due to anthropogenic activities. The 34.9% of groundwater samples showed NO₃⁻ above the human affected value was contamination. According to a NO₃⁻-N concentration standard of drinking water issued by China in 1986 used by Liu was used to assess groundwater quality (Liu et al., 2005). Groundwater quality was divided into: fine quality groundwater (NO₃⁻-N concentrations range from 0 to 2 mg/l), fair quality groundwater (Nitrate-N concentrations fall between 2 and 5 mg/l), and qualifying groundwater (Nitrate-N concentrations range from 5 to 10 mg/l). The result showed that NO₃⁻ concentrations in 31.7% of samples (20) were more than 20 mg/l (Fig. 2). This was an undoubted fact that the content of NO₃⁻ was slightly greater at the study area, which is due to the overuse of fertilizers and manure on agricultural fields.
concentration (Böhm et al., 2008; Jalali, 2005). On the other hand, the cation exchange between magnesium (Mg\(^{2+}\)) and Na\(^{+}\) ions. The SAR values for each water sample were calculated by the following equation (Richter, 1954).

\[
SAR = Na^+/\sqrt{(Ca^2+ + Mg^{2+})/2}
\]

Where the concentrations are milliequivalents per litre (meq/l).

The SAR value of groundwater in the study area is less than 10 suggesting nature of groundwater within the permissible irrigation activity, whereas the SAR value of groundwater is more than 10, indicating salinity hazard. That is to say, it has been occurred the decrease of Ca\(^{2+}\) and Mg\(^{2+}\) and increase of Na\(^{+}\) in groundwater, causing soil sodicity. On the other hand, the cation exchange between Ca\(^{2+}\) or Mg\(^{2+}\) and Na\(^{+}\) may also explain the excess Na\(^{+}\) concentration (Böhm et al., 2008; Jalali, 2005). The result showed in Table 1 that the SAR values of 11 groundwater samples (accounted for 17.5%) were above 10, indicated that elevated Na\(^{+}\) concentration was mainly contributed to high concentration of TDS. And it also suggested that the groundwater posed a serious salinity hazard threat of the environment.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Range</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAR</td>
<td>&lt;10</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>11-17</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>18-26</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td>&gt;26</td>
<td>Very high</td>
</tr>
<tr>
<td>Salinity hazard (EC) (µs/cm)</td>
<td>&lt;250</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>250-750</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>750-2250</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td>&gt;2250</td>
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<tr>
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<td>Excellent</td>
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<tr>
<td></td>
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<td></td>
<td>40-60</td>
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<td></td>
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<td></td>
<td>&gt;80</td>
<td>Unsuitable</td>
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<tr>
<td>RSC</td>
<td>&lt;1.25</td>
<td>Good</td>
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<tr>
<td></td>
<td>1.25-2.50</td>
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</tr>
<tr>
<td></td>
<td>&gt;2.50</td>
<td>Unsuitable</td>
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### 3.2.2 Residual sodium carbonate

According to Eaton (Eaton, 1957), the excess sum of carbonate is denoted by ‘Residual sodium carbonate’ (RSC), a high value of RSC in water leads to an increase in the adsorption of sodium in soil. Water with high RSC has high pH affect the suitability of groundwater for irrigation. RSC can be calculated as using the formula (Raghunath, 1987):

\[
RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+})
\]

Where samples are in milliequivalents per liter (meq/l). Almost One-third samples show low RSC values exhibiting good quality of groundwater. 30% of the locations show doubtful to unsuitable nature for irrigation purposes in shallow groundwater (Table 2). We can concluded that continued high RSC waters use to irrigation will lead to the loss of crop yields (Vasanthavigar et al., 2012a; Vasanthavigar et al., 2012b).

### 3.2.3 Sodium percentage (Na%)

Sodium concentration in classifying irrigation water was emphasized due to affecting structure and aeration of soil, which further affected plant growth and soil permeability (Karanth, 1987). The sodium percentage (Na%) using the below formula:

\[
Na\% = (Na^+ + K^+)/ (Ca^{2+} + Mg^{2+} + Na^+ + K^+) \times 100
\]

The diagram is divided into 4 groups with increase in salinity hazard and 4 groups with increase in SAR (Fig. 3). The plot of analytical data on the Wilcox diagram
(Wilcox, 1955) shows that almost one-third of the locations in shallow groundwater is in permissible quality to doubtful range and may be used for irrigation purposes (Fig. 3).

In order to further clarify the change of the water quality, we use the study result to compare with the previous study results (Wen et al., 2008) in the similar area. It can be seen from figure 4 the content of major ion in the present study is higher than that in previous year. This indicate that shallow groundwater salinity hazard became more and more serious due to the increasing use of fertilizer and groundwater development, which should be paid more attention.

3.3 Water-rock interaction

Rainwater, water-rock interaction and human activities is generally responsible for Changes in overall chemical properties (Richard, 1954). The mechanisms that assess the properties of groundwater can be identified from Gibbs plot (Richard, 1954). As illustrated in the Gibbs plot of log TDS versus Na/(Na+Ca) and Cl/(Cl+HCO₃) in figure 5 (Gibbs, 1970; Gibbs, 1971), evaporation and precipitation are the dominant processes attributing to the chemistry processes of groundwater. The plot of log TDS versus Na/(Na+Ca) (Fig. 5A) shows that evaporation and weathering of rocks are the most influencing factors in the development of the chemistry properties of the groundwater at the study area.

Fig. 3 Water classification

Evaporation concentrates the remaining water in the unsaturated zone and caused precipitation and deposition of evaporate that are eventually leached into the saturated zone and changed the chemistry composition of groundwater (Gillardet et al., 1999). This source of groundwater salinity is amplified in the study area.
log TDS verse Cl/(Cl+HCO₃⁻) plot (Fig. 5B) clearly also suggests that the evaporation and the rock weathering are the controlling factors for the chemistry composition of groundwater samples.

3.4 Anthropogenic contamination

With the increasing of agricultural activities, anthropogenic activities was also a major factor for salinization of groundwater and further water quality degradation in agricultural oasis, in the middle reaches of Heihe River Basin. Since it is well known that nitrate, phosphate, potassium and chloride are mostly originated from agricultural fertilizers and animals waste. As pointed out by previous researches, variation in total dissolved solids (TDS) in groundwater may be related to land use and also to pollution (Gillardet et al., 1999; Ellaway et al., 1999); thus, it is necessary to use ionic verses TDS plots such as Cl against TDS to identify the influence of human activities on the water chemistry properties of groundwater (Jacks and Rajagopalan, 1996). Scatter graphs for groundwater at the study area showed in figure 6A-F. The significant correlation between TDS and Ca²⁺(r=0.75) (Fig. 6A) existed, A general positive relationship between TDS and Na⁺ (r=0.58) (Fig. 6B), TDS and Mg²⁺(r=0.65) (Fig. 6C), TDS and NO₃⁻(r=0.41) (Fig. 6F). Moreover, there is strongly correlation with both TDS and Cl⁻(r=0.83) (Fig. 6D), SO₄²⁻(r=0.91) (Fig. 6E), indicating that groundwater have received significant anthropogenic activities. There were similar results in arid and semi-arid region (Jalali, 2009; Shanyengana et al., 2004). Moreover, making use of this salinized groundwater for irrigation practise causes increased contamination of environment through the annual crop plant, irrigation practice and evapotranspiration cycles.

NO₃⁻-N pollution sources in integrated water quality management have been growing concern worldwide recently. NO₃⁻-N resulted generally from land use system (Böhm et al., 2008), application of N fertilizers (Malali, 2005), atmospheric input (including biological emissions, combustion products from burning vegetation and soil dust) (Stallard et al., 1981), and also from nitrification of organic N and NH₄⁺ (Jeong, 2001). There is a positive relationship between Ca²⁺ and NO₃⁻(r=0.50) in figure 7a. The adverse trend exists between pH and SO₄²⁻ in figure 7b (r=0.79), this strongly suggests that part of the source of sulphate could be origin from biochemical reactions(Xiao et al., 2002). Another indication of sulphate source is that NO₃⁻ is linearly correlated with SO₄²⁻(r=0.58) (Fig. 7c), this strongly indicated the same as or similar to those of source of NO₃⁻, and hence could be anthropogenic activity, since NO₃⁻ is most likely of anthropogenic origin (Han and Liu, 2004). These two ions would rapidly infiltrate downward to the groundwater along with irrigation water after irrigation. Based on the above analysed, we suggest that the enrichment of sulphate and nitrate ions in groundwater mainly derived from agricultural activities. This is in line with previous studies (Gallardo and Tase, 2007; Malali, 2005). Gallardo and Tase carried out hydrogeology and geochemical character of groundwater in a typical small-scale agricultural area of Japan. They found there was a strong positive relation(r=0.75) between NO₃⁻ and SO₄²⁻, And Jalali studied geochemistry characterization of groundwater in an agricultural area, in Iran. He also observed a strong positive correlation(r=0.58) between NO₃⁻ and SO₄²⁻. These also attributed it to the applied overused fertilizers.

![Fig.6 Relationship graphs among TDS and ions in groundwater at the study area](image)

4. Conclusion

Chemical properties of groundwater in the middle reaches of Heihe River Basin, northwest of China, are controlled by both natural geochemical processes and anthropogenic activities. The chemical composition of groundwater is dominated by Na⁺, Ca²⁺, HCO₃⁻, SO₄²⁻, and Cl⁻. The substantial amounts of NO₃⁻ and SO₄²⁻ detected in groundwater are a consequence of fertilizer application and its mobilization. Salinity and sodium hazard are the principal groundwater quality concerns in the study area. High sodium concentration and salinity of shallow groundwater leads to deterioration of soil matrix from high RSC, Na % versus EC plot and SAR versus EC plot. The study shows that shallow groundwater is unsuitable at few locations. In summary, proper management strategies are very necessary to protect groundwater resource and environment in the study area. Some measurements such
as water-saving irrigation was used to decrease irrigation percolation and prevent spreading of the pollution, and which mitigate the sustainable development of agriculture in the transit zone and save of groundwater.

Fig.7 Relationship between A Ca$^{2+}$ and NO$_3^-$, B SO$_4^{2-}$ and pH, and C SO$_4^{2-}$ and NO$_3^-$ in groundwater of the study area

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References


