Abstract—Groundwater is the main source of water supply in the Guanzhong Basin, China. To investigate the quality of groundwater for agricultural purposes in Jiaokou Irrigation District located in the east of the Guanzhong Basin, 141 groundwater samples were collected for analysis of major ions (K⁺, Na⁺, Mg²⁺, Ca²⁺, SO₄²⁻, Cl⁻, HCO₃⁻, and CO₃²⁻), pH, and total dissolved solids (TDS). Sodium percentage (Na%), residual sodium carbonate (RSC), magnesium hazard (MH), and potential salinity (PS) were applied for irrigation water quality assessment. In addition, multivariate statistical techniques were used to identify the underlying hydrogeochemical processes. Results show that the content of TDS mainly depends on Ca²⁺, Na⁺, Mg²⁺, and SO₄²⁻, and the HCO₃⁻ content is generally high except for the eastern sand area. These are responsible for complex hydrogeochemical processes, such as dissolution of carbonate minerals (dolomite and calcite), gypsum, halite, and silicate minerals, the cation exchange, as well as evaporation and concentration. The average evaluation levels of Na%, RSC, MH, and PS for irrigation water quality are doubtful, good, unsuitable, and injurious to unsatisfactory, respectively. Therefore, it is necessary for decision makers to comprehensively consider the indicators and thus reasonably evaluate the irrigation water quality.

Keywords—Irrigation water quality, multivariate statistical analysis, groundwater, hydrogeochemical process.

I. INTRODUCTION

GROUNDWATER is the most precious resource for various purposes in support of domestic, agricultural, and industrial development all over the globe [1], [2]. The Guanzhong Basin has fertile soil with a long history of irrigation, so the quality demand for irrigation water is high. However, it is located in a semi-arid area lacking surface irrigation, so the quality demand for irrigation water is high. Therefore, it is necessary for deciding on how to use groundwater for agricultural purposes in support of domestic, agricultural, and industrial development all over the globe [1], [2]. The Guanzhong Basin has fertile soil with a long history of irrigation, so the quality demand for irrigation water is high. However, it is located in a semi-arid area lacking surface irrigation, so the quality demand for irrigation water is high. Therefore, it is necessary for decision makers to comprehensively consider the indicators and thus reasonably evaluate the irrigation water quality.

In order to evaluate irrigation water quality, many indices have been put forward and widely used in groundwater, such as Na, sodium adsorption ratio (SAR), RSC, MH, permeability index (PI), Kelley’s ratio (KR), and PS [2]-[5]. Multivariate statistical techniques, such as Pearson’s correlation analysis, cluster analysis (CA), and principal components analysis (PCA) are effective tools for assessing groundwater quality, and interpreting the hydrogeochemical processes [6]-[9]. Jiaokou Irrigation District is a typical irrigation area in Guanzhong Basin; therefore, to assess the water quality for irrigation purpose and to disclose the underlying hydrogeochemical processes, this study investigated the groundwater of Jiaokou Irrigation District using the multivariate statistical methods. The findings of this study can provide reasonable guidance for the groundwater irrigation in this area.

II. STUDY AREA

The Jiaokou Irrigation District (34°30′7″–34°52′37″N, 109°12′40″–110°10′1″E), surrounded by Shichuan River in the west, Luo River in the east, and Wei River in the south, is located in the east of the Guanzhong Basin, Shaanxi province, China. The topography of Jiaokou Irrigation District is divided into floodplain, first terrace, and second terrace of the Wei River, loess plateau, and sand belt (Fig. 1). The climate is classified as warm temperate and semi-arid monsoon. Mean annual temperature and precipitation are 13.4 °C and 548.5 mm, respectively [10]. The groundwater flows from northwest to southeast in this area. The land use throughout majority of this area is for agricultural purpose [10], [11].

III. MATERIALS AND METHODS

A. Sampling and Analysis

Totally, 141 groundwater samples were collected in the Jiaokou Irrigation District. The sampling sites are presented in Fig. 1. The pH and TDS of groundwater samples were measured using portable devices in the field. The SO₄²⁻ and Cl⁻ were tested by ion chromatography, and HCO₃⁻ was tested by alkalinity titration. Ca²⁺ and Mg²⁺ were analysed by the EDTA titrimetric method. The concentrations of K⁺ and Na⁺ were determined by flame atomic absorption spectrophotometry. To ensure accuracy in the analysis, the charge balance error (CBE) for the water samples should be controlled within the acceptable range of ± 5% [2], [4], [10], [12], [13].

\[
CBE = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \times 100\% \tag{1}
\]

where, all cations and anions were expressed in meq/L.

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B. Indicators for Irrigation Water Quality

Four indicators, Na, RSC, MH, and PS were selected to evaluate the groundwater for irrigation purposes. They were calculated using (2)-(5) [2].

\[
\text{Na\%} = \frac{\left(\text{Na}^+ + \text{K}^+\right) \times 100}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+} \tag{2}
\]

\[
\text{RSC} = \left(\text{CO}_3^{2-} + \text{HCO}_3^-\right) - \left(\text{Ca}^{2+} + \text{Mg}^{2+}\right) \tag{3}
\]

\[
\text{MH} = \frac{\text{Mg}^{2+}}{\text{Ca}^{2+} + \text{Mg}^{2+}} \times 100 \tag{4}
\]

\[
\text{PS} = \frac{1}{2} \text{SO}_4^{2-} \tag{5}
\]

where, all ionic concentrations are expressed in meq/L.

C. Multivariate Statistical Analysis

In this study, the Pearson’s correlation analysis was used to find potential relationships among the irrigation quality indices and hydrochemical parameters of groundwater samples. Coefficient values of 0.7 and 0.3 are the threshold for strong, medium, and weak correlation [10], [14]. The hierarchical cluster analysis (HCA) was conducted by using a metric of Euclidean distance to classify the irrigation quality indices and hydrochemical parameters and to identify their pattern of associations. These analyses were performed using the Statistical Package for Social Sciences software (SPSS. 20).

IV. RESULTS AND DISCUSSION

A. Groundwater Hydrochemical Parameters

The geographical spatial distribution of all the groundwater parameters was obtained using a geographic information system (GIS) interpolation technique, and shown in Fig. 2. The distribution of TDS is similar to that of Cl\textsuperscript{-}, Na\textsuperscript{+}, Mg\textsuperscript{2+}, and SO\textsubscript{4}\textsuperscript{2-}, indicating that these ions mainly determine the TDS. The contents of these components are high in the center of this area, with the low groundwater level, suggesting that the evaporation concentration plays an important role [10]. In addition, probably due to the good permeability and strong water circulation of sand, the TDS content of the groundwater in the sand belt is low (Fig. 2). The other ions also have low contents in the sandy areas. Except for the sand area in the east, the HCO\textsubscript{3}^- content is generally high in the whole region, which may be related to widespread carbonate minerals such as calcite and dolomite.

B. Irrigation Water Quality

Too high Na% will destroy soil structure and reduce irrigation effect [2]. From Table I, Na% ranges from 13.04\% to 88.09\%, with a mean of 60.63\%, indicating that the average level of irrigation water quality is doubtful. The water with high RSC easily leads to the deposition of sodium carbonate and makes the soil barren [15]. Table I shows that RSC has a range between -33.47 meq/L and 20.23 meq/L (mean of -1.62 meq/L), indicating that the average level of irrigation water quality is good. More Mg\textsuperscript{2+} in water would result in the alkaline soil, which can reduce the permeability of soil and thus adversely affect crop yields [16]. MH has a range of 31.01-91.34\%, with a mean of 74.45\%. This indicates overall irrigation water quality level is unsuitable. In addition, PS ranges between 0.19 and 93.63 meq/L (mean = 17.20 meq/L), suggesting that the average irrigation level of groundwater is injurious to unsatisfactory.
C. Multivariate Statistical Analyses

From Table II, it is seen that Na% has a moderate relationship with HCO₃⁻ (R = 0.61) and Na⁺ (R = 0.54). RSC has a strong negative relationship with Ca²⁺ (R = -0.74) and Mg²⁺ (R = -0.81). These results can be explained by exchange and adsorption which consumes the Ca²⁺ and Mg²⁺ provided by the carbonate dissolution, thus producing HCO₃⁻ and Na⁺. MH has a medium positive correlation with HCO₃⁻ (R = 0.60) and Na⁺ (R = 0.50), which also indicates the existence of cation exchange, especially the substitution of Ca²⁺ for Na⁺. PS has a strong positive relationship with Cl⁻ (R = 0.99), and SO₄²⁻ (R = 0.96) also has a strong correlation with TDS (R = 0.95), Na⁺ (R = 0.93), and Mg²⁺ (R = 0.78), indicating that TDS mainly depends on Na⁺, Mg²⁺, Cl⁻, and SO₄²⁻ (Table II). These also reflect that the main hydrogeochemical processes may be dissolution of silicate minerals (K-, Na-, and Ca-
feldspar), carbonate minerals (dolomite and calcite), gypsum, and halite, the cation exchange, as well as evaporation and concentration.

Based on the cut-off at the smallest distance (12.5) [17], the irrigation quality indices and hydrochemical parameters of groundwater samples can be divided into two main clusters in the dendrogram (Fig. 3). In cluster 1, it can be found that PS, Na⁺, Mg²⁺, Cl⁻, and SO₄²⁻ are first grouped together, which verifies the conclusion of the correlation analysis, namely, the TDS is greatly influenced by the dissolution of gypsum and halite, as well as evaporation and concentration. Meanwhile, the RSC, Ca²⁺, and K⁺ are also first grouped together, suggesting the dissolution of carbonate and cation exchange. In cluster 2, it includes HCO₃⁻, CO₃²⁻, Na%, and MH, which also indicates the occurrence of carbonate dissolution and exchange and adsorption. The carbonate dissolution provides the HCO₃⁻, CO₃²⁻, Ca²⁺, and Mg²⁺, while Ca²⁺ and Mg²⁺ are consumed by cation exchange along with producing K⁺ and Na⁺, as well as promoting the dissolution of carbonate minerals such as calcite and dolomite.

### Table I

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Unit</th>
<th>Range</th>
<th>Water quality</th>
<th>Maximum</th>
<th>Minimum</th>
<th>Mean</th>
</tr>
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<tbody>
<tr>
<td>Na%</td>
<td>%</td>
<td>&lt;20</td>
<td>Excellent</td>
<td>88.09</td>
<td>13.04</td>
<td>60.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20-40</td>
<td>Good</td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td>Doubtful</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;80</td>
<td>Unsuitable</td>
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<tr>
<td>RSC</td>
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<td>20.23</td>
<td>-33.47</td>
<td>-1.62</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;2.50</td>
<td>Unsuitable</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>MH</td>
<td>%</td>
<td>&lt;50</td>
<td>Suitable</td>
<td>91.34</td>
<td>31.01</td>
<td>74.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;50</td>
<td>Unsuitable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>meq/L</td>
<td>&lt;3.0</td>
<td>Excellent to good</td>
<td>93.63</td>
<td>0.19</td>
<td>17.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0-5.0</td>
<td>Good to injurious</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;5.0</td>
<td>Injurious to unsatisfactory</td>
<td></td>
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</table>

### Table II

<table>
<thead>
<tr>
<th>R</th>
<th>Na%</th>
<th>RSC</th>
<th>MH</th>
<th>PS</th>
<th>K</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>CO₃²⁻</th>
<th>HCO₃⁻</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
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<tbody>
<tr>
<td>Na%</td>
<td>1</td>
<td>0.42**</td>
<td>1</td>
<td>0.64**</td>
<td>0.09</td>
<td>1</td>
<td>0.30**</td>
<td>-0.59**</td>
<td>0.30**</td>
<td>0.30**</td>
<td>0.43**</td>
<td>0.30**</td>
</tr>
<tr>
<td>RSC</td>
<td>0.42**</td>
<td>1</td>
<td>0.30**</td>
<td>-0.62**</td>
<td>0.35**</td>
<td>1</td>
<td>0.04</td>
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<td>0.04</td>
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<tr>
<td>MH</td>
<td>0.64**</td>
<td>0.30**</td>
<td>0.09</td>
<td>1</td>
<td>0.14</td>
<td>0.22**</td>
<td>1</td>
<td>0.12</td>
<td>0.03**</td>
<td>0.60**</td>
<td>0.07</td>
<td>0.16</td>
</tr>
<tr>
<td>PS</td>
<td>0.64**</td>
<td>0.30**</td>
<td>1</td>
<td>0.59**</td>
<td>0.09</td>
<td>0.93**</td>
<td>0.12</td>
<td>0.91</td>
<td>0.25**</td>
<td>0.29**</td>
<td>0.07</td>
<td>0.96</td>
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<tr>
<td>K⁺</td>
<td>0.30**</td>
<td>-0.62**</td>
<td>0.35**</td>
<td>1</td>
<td>0.14</td>
<td>0.12</td>
<td>1</td>
<td>0.30**</td>
<td>0.43**</td>
<td>0.30**</td>
<td>0.25**</td>
<td>0.30**</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.43**</td>
<td>0.25**</td>
<td>0.37**</td>
<td>1</td>
<td>0.13</td>
<td>0.11</td>
<td>0.29**</td>
<td>-0.07</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.33**</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.61**</td>
<td>0.31**</td>
<td>0.60**</td>
<td>0.21</td>
<td>0.07</td>
<td>0.45**</td>
<td>0.15</td>
<td>0.26**</td>
<td>0.59**</td>
<td>0.13</td>
<td>0.22**</td>
<td>0.43**</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.27**</td>
<td>-0.63**</td>
<td>0.35**</td>
<td>0.99**</td>
<td>0.25**</td>
<td>0.89**</td>
<td>0.40**</td>
<td>0.79**</td>
<td>0.13</td>
<td>0.22**</td>
<td>0.43**</td>
<td></td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>0.30**</td>
<td>0.30**</td>
<td>0.57**</td>
<td>0.33**</td>
<td>0.96</td>
<td>0.16</td>
<td>0.92**</td>
<td>0.33**</td>
<td>0.33**</td>
<td>0.18</td>
<td>0.90**</td>
<td>0.30**</td>
</tr>
</tbody>
</table>

Notes: R is the Pearson's correlation coefficient; ** Significant at the 0.01 level (2-tailed); * Significant at the 0.05 level (2-tailed).

### V. Conclusions

To reveal the water quality status for irrigation purpose, to explore the relationship between irrigation indicators and hydrogeochemical parameters of groundwater and to disclose the underlying hydrogeochemical processes, this study provides an investigation of groundwater of Jiaokou Irrigation District, using the multivariate statistical analysis methods. The geographical spatial distribution of TDS is similar to that Cl⁻, Na⁺, Mg²⁺, and SO₄²⁻, indicating the content of TDS mainly depends on these ions. The HCO₃⁻ content is generally high except for the eastern sand area, which may be related to widespread carbonate minerals. Based on the Na%, RSC, MH, and PS, the average irrigation level is doubtful, good, unsuitable, and injurious to unsatisfactory, respectively. The evaluation results are not completely consistent, mainly due to the influence of complex hydrogeochemical processes, including the dissolution of carbonate minerals (dolomite and calcite), gypsum, halite, and silicate minerals, the cation exchange, as well as evaporation and concentration. Therefore, it is necessary to consider the indexes...
comprehensively to evaluate the irrigation water quality reasonably.

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REFERENCES