Assessing the source of nitrate and heavy metals in groundwater resources of Abarkooh plain, central Iran

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Abstract: Abarkooh alluvial aquifer is located in southwest of Yazd city at the center of Iran. Groundwater is the main source for irrigation and domestic uses. These activities are also considered as the potential causes of the groundwater contamination in this plain. The study was carried out to assess hydrogeochemical properties of groundwater with the aim to find probable sources of major contaminants including nitrate and heavy metals. In this regard 37 water samples were collected and analyzed for major ions (Ca, Mg, Na, K, Cl, HCO₃ and SO₄), nitrate and heavy metals with environmental priority including arsenic (As), lead (Pb) and cadmium (Cd). Values of electrical conductivity (EC) increase from recharge area at the west to the eastern discharging parts where the playa is present. The abundance of cations and anions vary in the order of Na³⁺>>Mg²⁺>Ca²⁺>K⁺ and Cl⁻>>SO₄²⁻>HCO₃⁻, respectively. The highest values of Na and Cl are observed at the east where the saline water intrusion is probable due to the intensive abstraction of groundwater which reverses the groundwater flow direction. Pb and Cd are highly correlated with Na, Cl and EC, confirm their geogenic source due to saline water intrusion. Nitrate is high at the west where the un-managed application of fertilizers in agricultural lands is so dominant. A geogenic source for As was proposed based on the results of principal component analysis (PCA). The study confirms the main role of anthropogenic processes in contamination of Abarkooh aquifer generally resulted from over-exploitation of the aquifer and agricultural activities.

Key words: nitrate, heavy metal, geogenic, anthropogenic, Abarkooh, Iran

1. INTRODUCTION

The water is the major key in sustainable development, so it is necessary to be managed and conserved (UNESCO, IHP 2014). In this regard the groundwater resources need more attention especially in arid areas, where the surface waters are not generally available. Chemical composition of groundwater is mainly controlled by natural or geogenic factors (Fig. 1) including chemistry of recharge water, soil processes, aquifer mineralogy, as well as the man-made contaminant (Davidson and Wilson 2011).

Geology of the groundwater basin and the materials in contact with the water, as well as the process and reactions that occur from recharge to discharge points affect the quality of groundwater (Gannon et al. 2012). The chemical quality of groundwater is evolved as the residence time of groundwater in contact with geological materials is increased (Environment Southland, 2010). Agricultural, industrial and mining activities are the main man-made causes threatening or degrading the quality of the aquifers. Irrigation is the main use of water in arid region, known as the major diffuse source of groundwater pollution, as well (Todd and Mays 2005).

Abarkooh plain, located in southwest of Yazd province at central Iran, is important for agriculture and industry development. The main activity is agriculture, as the irrigated lands cover about 11000 hectare of the plain area. The Alluvial aquifer of Abarkooh is being discharged by 730 wells, 30 qanats and 1 spring with the total discharge annual rate of 178 million cubic meters (Pourab Consulting Engineers, 2012). The plain groundwater hydrograph shows decrease in water table with an average rate of 0.6 m/year, which is mainly due to reduction in rainfall recharge, as well as, over-exploitation of the aquifer. The mean annual precipitation is 59 mm (Pourab
Consulting Engineers, 2012). Low rate of aquifer recharge and over-drafting the aquifer for agricultural uses increase the potentials for aquifer contamination. Therefore, this study was aimed to assess the chemical quality of the aquifer and to find probable sources of the contaminant in the groundwater, especially those important from environmental viewpoint such as nitrate and heavy metals.

2. STUDY AREA DESCRIPTION

The study area is located in central Iran, 140 km far from the Yazd city (Fig. 2). The alluvial aquifer of the Abarkooh plain is unconfined, which is recharged from the western boundaries. The general groundwater flow direction is from west to the east. The aquifer is surrounded by carbonate rocks in the west and north and evaporate sediments in a playa at the east (Fig. 3).

Exploitation of groundwater mainly for agricultural use changes the flow direction and creates a depression in water table. Concentration of groundwater flow lines toward the depression reverses the flow direction, enhancing the contamination of the aquifer by saline water intrusion.

3. MATERIALS AND METHODS

A total of 37 groundwater samples were collected in a systematic random way in April 2016.
Figure 3 shows the location of the sampling points in Abarkooh aquifer. Electrical conductivity (EC) and pH were measured in the field. Two polyethylene bottles were field in each location after they were rinsed with water twice before sampling. The samples for measuring heavy metals were filtered (0.45 µm cellulose filter) and acidified by nitric acid to a pH lower than 2. Sampling and chemical analysis were performed based on APHA (2005). Calcium, magnesium, chloride and bicarbonate were determined by titration, sodium and potassium by flame photometer and sulfate and nitrate by spectrophotometer. Environmental high priority heavy metals including Cd and Pb measured by GF-AAS* and As by HG-AAS†. The accuracy of the chemical analysis was checked by the ion balance approach. The error was less than 5% for most of the samples (80%). In some samples with EC greater than 6000 µS/cm, the calculated error was less than 10%, confirming the accuracy of the chemical analyses (Hounslow 1995; Montcoudiol et al. 2014).

4. RESULTS AND DISCUSSION

4.1 Descriptive analyses and correlation coefficients

A summary of descriptive statistics of the chemical parameters including major ions, nitrate and selected heavy metals is presented in Table 1. Except for pH and nitrate with a normal distribution, the other parameters with skewness greater 1, having abnormal distribution (Montcoudiol et al. 2014). So, the correlation coefficients (Table 2) were calculated based on spearman method (Thilagavathi et al. 2012). The highest correlation coefficient was found between Cl, Na and EC, which is significant at the 0.01 level. The lowest one is related to As showing no-dependent on the other parameters.

Table 1. The statistical summary of the hydrochemical parameters in Abarkooh aquifer.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>Std. Deviation</th>
<th>Skewness</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.16</td>
<td>7.32</td>
<td>7.21</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>EC µS/cm</td>
<td>13300</td>
<td>11920</td>
<td>10675.3</td>
<td>3631.78</td>
<td>1.88</td>
</tr>
<tr>
<td>TH mg/L</td>
<td>2760</td>
<td>3250</td>
<td>3305</td>
<td>62.24</td>
<td>1.24</td>
</tr>
<tr>
<td>TDS mg/L</td>
<td>7726.0</td>
<td>10740.5</td>
<td>10770.54</td>
<td>10374.44</td>
<td>1.83</td>
</tr>
<tr>
<td>Cl (mg/L)</td>
<td>6423.0</td>
<td>1199.0</td>
<td>1070.53</td>
<td>1456.14</td>
<td>2.13</td>
</tr>
<tr>
<td>NO3 (mg/L)</td>
<td>124.0</td>
<td>124.57</td>
<td>249.20</td>
<td>193.61</td>
<td>1.04</td>
</tr>
<tr>
<td>HCO3 (mg/L)</td>
<td>400.00</td>
<td>104.00</td>
<td>172.65</td>
<td>78.74</td>
<td>2.18</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>49.90</td>
<td>5.37</td>
<td>21.69</td>
<td>12.62</td>
<td>0.62</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>29.00</td>
<td>1.01</td>
<td>1.20</td>
<td>445.04</td>
<td>419.57</td>
</tr>
<tr>
<td>SO4 (mg/L)</td>
<td>58.00</td>
<td>1.30</td>
<td>8.31</td>
<td>8.59</td>
<td>2.00</td>
</tr>
<tr>
<td>NO2 (mg/L)</td>
<td>820.51</td>
<td>30.00</td>
<td>169.11</td>
<td>104.90</td>
<td>1.31</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>12.72</td>
<td>0.30</td>
<td>2.53</td>
<td>2.08</td>
<td>2.40</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>7.20</td>
<td>0.09</td>
<td>0.30</td>
<td>1.45</td>
<td>2.75</td>
</tr>
<tr>
<td>Pb (µg/L)</td>
<td>16.43</td>
<td>0.03</td>
<td>2.56</td>
<td>3.81</td>
<td>2.92</td>
</tr>
</tbody>
</table>

n= 37 samples, TH as CaCO3

Table 2. Correlation matrix between various parameters in Abarkooh aquifer.

4.2 Spatial variations of pH and EC

The pH of the groundwater samples varies from 6.9 to 7.8, which is in the range (6.5-8.5) for the

* Graphite Furnace-Atomic Absorption Spectrometry
† Hydride Generation-Atomic Absorption Spectrometry
natural waters (Stumm and Morgan 1996; WHO 2011; EPA 2012). Spatial variations of pH in Abarkooh aquifer (Fig. 4) shows the pH values are generally more than 7, due to buffering effects as a result of the high salinity of the groundwater (Isa et al. 2013).

The variations of EC in the Abarkooh aquifer are presented in Figure 4. It ranges from 1000 to 15000 µs/cm with an increasing trend from recharge area at the west to the east where the playa is existed. Iso-potential map of the aquifer (Fig. 8) shows the general groundwater flow direction is from west to the east. A depression in water-table is observed at the east where the discharging wells are concentrated. So, the saline water intrusion is probably occurred at this part of aquifer.

4.3 Spatial variations of major ions and hydrochemical facies

Figure 5 shows the statistics for major ions analyses. The highest coefficient of variation and standard deviation is observed for Cl⁻ and Na⁺. Concentrations of the major ions are ordered as the following sequence: Cl⁻>>SO₄²⁻>HCO₃⁻, Na⁺>>Mg²⁺>Ca²⁺>K⁺.

Spatial variations of the dominant ions of Na⁺ and Cl⁻ are displayed in Fig. 6. The highest concentrations are observed at the east, where the probable saline water intrusion is occurred. This is in coincidence with the increase in EC, as it was mentioned before.

Plotting chemical analysis on Piper diagram (Fig. 7) confirms the dominant water type is Na-Cl (67% of the water samples). Other water types such as Mg-Cl (22%), Ca-Cl (8%) and Ca-SO₄ (3%)
are also observed. Distribution of water types in Abarkooh aquifer (Fig. 8) shows change in type of water as the groundwater flows in the aquifer. The dominant water type at the recharge area at the west is Ca-Cl where the limestone and dolomite rocks are presented (Fig. 3).

Figure 6. Spatial variations of Na and Cl in Abarkooh aquifer.

Figure 7. Piper diagram and water type of the groundwater samples from Abarkooh aquifer.

Figure 8. Spatial distribution of water types in Abarkooh aquifer.

Figure 9. Scatter diagram of (Ca + Mg) − (SO4 + HCO3) versus (Na − Cl)

The water types change to Na-Cl at the east. The Mg-Cl water types are also presented locally at the east near the Mehrdasht village. This is probably related to ion-exchange process. The scatter diagram Na-Cl versus (Ca+Mg)-(HCO3+SO4) in Figure 9 shows most of the samples (about 80%)
locate near the zero, confirming the congruent dissolution of calcite, dolomite and gypsum as the likely processes in the Abarkooh aquifer. The other samples are scattered along the line with the slope of -1, stating occurrence of the ion exchange process in the aquifer (Marie et al. 2001; Tlili-Zrelli et al. 2012).

4.4 Spatial variations of the nitrate ion

Changes in the nitrate concentrations in Abarkooh aquifer are displayed in Figure 10. The nitrate concentrations range from 5.6 to 50 mg/l. The average concentration is about 22 mg/l which is lower than the drinking standard of 50 mg/l (WHO 2011). The natural limit for nitrate is lower than 10 to 15 mg/l (CDPH, 2010) and the values greater suggest the anthropogenic contamination of the groundwater (Multer 1995). More than 85% of groundwater samples from Abarkooh aquifer have nitrate concentrations greater than 10 mg/l as most of them locate at the western part of the aquifer. Lowest depths to water table, coarse grained sediments of the aquifer and development of orchards enhance the potentials for agricultural contaminations in this area. Correlations between nitrate and other ions (Table 2) show the highest coefficient with Ca and SO$_4$, as these ions are also concentrated in western part of the aquifer.

4.5 Spatial variations of heavy metals

In this study, environmental high priority heavy metals consisting As, Cd and Pb were measured and analyzed. Spatial changes of As in Abarkooh aquifer are illustrated in Figure 11. Arsenic is relatively high at the north-east of the aquifer, where the concentrations exceeding standard limits of 10 ppb (WHO, 2011) in two samples. The concentration of As in fresh non-contaminated waters is usually less than 1 ppb. Increase in water salinity enhances the concentration to about 2-3 ppb. Arsenic concentrations more than 10 to 30 ppb are found in polluted waters by pesticides and fertilizers used in agriculture (Moore and Ramamoorthy 1984).

![Figure 10. Spatial variations of nitrate in Abarkooh aquifer.](image1)

![Figure 11. Spatial variations of As in Abarkooh aquifer.](image2)

The concentrations of Pb and Cd are more than detection limit of 1 and 0.1 ppb, respectively, in 10 groundwater samples. The spatial changes in concentration of Pb and Cd are presented in Figure 12. A good correlation is found between these two heavy metals, as well as the EC (Fig. 13). The concentrations of Pb and Cd increase more than 5-16 ppb and 1-7 ppb, respectively, at the east and southeast of the aquifer. The concentrations are exceeding maximum contaminant level (MCL) of WHO, which is 10 ppb for Pb and 3 ppb for Cd. The increase in concentration of Pb and Cd in this part of the aquifer is probably related to saline water intrusion which is more expectable in this area where the groundwater flow direction is reversed due to the concentrated discharge of the aquifer by the wells.
4.6. Source of nitrate and heavy metals

In this research principle component analysis (PCA) was performed to identify origin of the elements in groundwater from Abarkooh aquifer. The rotated component matrix by Varimax method (Table 3) shows the parameters classified in 3 main groups (Fig. 14). In each component the parameters with loading rate more than 0.5 are considered (Miller and Miller 2000). The first component with the highest variance is composed of Cl, EC, Na, Ca, Mg, Cd and Pb. This is the main factor enhancing the salinity of the Abarkooh aquifer. As it was mentioned before it is mainly resulted from saline water intrusion which increases the major ions as well as the heavy metals (Pb, Cd) at the east and the southeast of the aquifer. The second component composed of As, HCO$_3$, SO$_4$ and pH probably identifies a geogenic source such as dissolution or weathering of pyrite. The process increases the concentration of As, HCO$_3$ and SO$_4$ simultaneously. It decreases the pH which is confirmed by the negative loading rate of pH. The third component is only comprised of NO$_3$ which confirms its anthropogenic source from agricultural activities. The SO$_4$ with the high loading rate in this component in accordance with the high correlation coefficient between NO$_3$ and SO$_4$ (Table 2) confirm the impact of agriculture on enhancement of the contaminants in the groundwater resources.

5. CONCLUSION

Hydrochemical characteristics of Abarkooh aquifer in central Iran show the major role of human impacts on contamination of the groundwater resources. The EC, major ions and heavy metals
including Pb and Cd are increased at the east and the southeast where the saline water intrusion is occurred in response to the over-exploitation of groundwater by deep wells. It reverses the groundwater flow direction, causing intrusion of saline groundwater from playa located outside the aquifer boundary. Based on the results the source of As in the northeast of the aquifer is probably related to the geology. The nitrate ion with highest concentrations at the west of the aquifer is mainly resulted from agricultural activities. The spatial variations of the elements which approved by PCA fairly confirm the ideas.

**Table 3. Rotated component matrix.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Component 1</th>
<th>Component 2</th>
<th>Component 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>0.965</td>
<td>0.124</td>
<td>-0.791</td>
</tr>
<tr>
<td>Cl</td>
<td>0.986</td>
<td>0.003</td>
<td>-0.119</td>
</tr>
<tr>
<td>SO4</td>
<td>0.170</td>
<td>0.712</td>
<td>0.468</td>
</tr>
<tr>
<td>NO3</td>
<td>-0.146</td>
<td>0.107</td>
<td>0.946</td>
</tr>
<tr>
<td>HCO3</td>
<td>0.641</td>
<td>0.731</td>
<td>0.031</td>
</tr>
<tr>
<td>Na</td>
<td>0.951</td>
<td>0.057</td>
<td>-0.040</td>
</tr>
<tr>
<td>Mg</td>
<td>0.645</td>
<td>0.131</td>
<td>0.312</td>
</tr>
<tr>
<td>Ca</td>
<td>0.857</td>
<td>0.357</td>
<td>0.270</td>
</tr>
<tr>
<td>As</td>
<td>0.140</td>
<td>0.758</td>
<td>-0.106</td>
</tr>
<tr>
<td>Cd</td>
<td>0.664</td>
<td>0.072</td>
<td>0.006</td>
</tr>
<tr>
<td>Pb</td>
<td>0.206</td>
<td>0.029</td>
<td>-0.004</td>
</tr>
<tr>
<td>pH</td>
<td>-0.385</td>
<td>-0.721</td>
<td>0.124</td>
</tr>
</tbody>
</table>

**Figure 14. Component plot in rotated space.**

## ACKNOWLEDGMENTS

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## REFERENCES


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