

The Investigation of Groundwater Pollutions around Ramhormoz City in Khuzestan Province, IranMahdi Rahmanian¹, Hossein Sedghi¹, Mohammad Nakhaei², Mohammad Manshouri³

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Abstract: Meidavood, located in the northeastern part of Khuzestan, and one of the environs of Ramhormoz, is located between latitude 31° 10' to 31° 25' north and longitude 49° 10' to 50° 10' east. This region consists of two stratum water units : a) the Karsti unit consisting Asmari and Gachsaran formations, b)the alluvial unit or the Eidavood-Daloon plain. The underground water in unit b, feeds through precipitations and lateral seepage from the water leaking through leakages from adjacent formations and the water flows mostly from east to the west of the unit. In order to investigate the quality of the underground water in this region, water sampling was conducted by standard methods of EPA 2001. The results of the titrated measurement and flame photometry showed the main components of these bodies of water which, due to the dissolution of the Gachsaraan formation, the dominant facies is the calcium-phosphate. Also, the results of the ICO-OES analysis of the underground water showed that the concentration of Arsenic is more than the permissible global ones (10 bbp) in almost 81% of deep wells and the concentration of iron, manganese, nickel, and vanadium is high in those wells. The results of the XRE analysis of the surrounding geological formations and the aquifer sediments suggested that the original source of Arsenic can be attributed to the Asmari and Gachsaran formations. It seems that the key process responsible for the release of Arsenic in the Meidavd-Daloon alluvium aquifer deep wells is biological disintegration of organic materials associated with oil hydrocarbons. This process causes the dissolution of arsenic oxy-hydroxides of iron and manganese and, as a result, iron and nickel in organic materials enter underground water. Given the oxidation-reducing conditions, the Meidavood-Daloon alluvium aquifer can be categorized into 4 regions:1)partly reducing, medium- reducing, and highly - reducing. In this aquifer, the arsenic-contaminated wells are located in highly and medium reducing parts.

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Introduction

Hydrogeology, which is the study of underground waters, is growing very fast using four essential elements governing underground waters, namely geology, physics, chemistry, and biology. Although in dealing with the quality of underground waters, a comprehensive and simultaneous investigation of these four elements is not possible due to scientific and economic limitations, the qualitative investigation of these waters without considering the interactions of these elements is complicated and sometimes impossible. Despite qualitative and quantitative limitations in sampling underground water, chemical analysis, and data interpretation, since the chemistry of water reflects geological, physical, and biological conditions and changes in underground waters, underground water geologists focus their attention primarily on the chemical composition of these waters, in such a way that in most underground water studies, traces of water chemistry can be seen. If we consider the ground as a system, the quality of the output water coming out of this system relies on the quality of the

input water, the physical and chemical features of the system, the length of the passing or stopping of water, physical, chemical,

and biological reactions between the system and the water throughout the path and entering and mixing of other waters with the system. Since the system is made up of geological materials, the geological specification of the system and its water is essential to restring the conditions of the system and determining the quality of the water in different parts of the system. This study tries to investigate the drinking quality of the underground waters in Meidavood (northeastern part of Khuzestan), taking into consideration the primary ions and some secondary and water soluble ions, based on geological and geochemical features of these waters.

Geographical features of the region

The region under the study is located northeast of Ramhormoz, which is of Baghmalek environs. It is located in the longitude 49° and 50' to eastern 49° and 56' and the latitude 31° 12' to northern 31° 19'(X : 388159 to 396020) and Y: 3455000 to 3475000). The

main road to leading to the region is the asphalted road from Ramhormoz to Baghmalek. The region can be divided to two parts: the mountainous part and the alluvial one. The most important mountainous part is the Kuh Sefid anticline which is 80 km long and the general trend is 120-130 N (west eastern – southeastern). It has a plunge toward Meidavood and in the southeast is limited to the Daloon – Meidavod plain. This plain has a 36-kilometer area with the Talkh River (the southern border) and the A'la River (northern part) as the most important rivers in this plain.

Geological features

Stratigraphy

The region is located in stratified Zagros, and the outcrop formations related to underground water can be categorized into two classes: calcic formations (Asmari) and gypsum- marl formations (Gachsaran formation). The Kuh-Sefid anticline is mainly made up of the Asmari formation and the debris left from its landslides.

Structural geology

Since the region is a part of the stratified Zagros, the main geological structure is can be divided into anticlines (e.g. the Kuh Sefid anticline), clines (the Meidavood-Daloon cline), faults, crevices, and fractures. The Kuh-Sefid anticline is a simple one with a cylinder base which seems to have a semi-straight axis. It is 80-km long and due to lateral faults, is partially curved. The degree of fracture and crevice is high and is evident in longitudinal, latitudinal and transverse forms. There is a left-lateral strike-slip fault on the northwestern hillside, running along the axis of the anticline from northwest to southeast. Furthermore, there are two faults perpendicular to the anticline axis. One of these faults has caused a great decomposition of the Asmari lime and some small springs in the northwestern hillside, and the second fault, which is near the nose of the anticline, has created a shear area. Also, a reverse fault has been detected which makes some layers of the Asmari formation lie on the layers of the Gachsaran formation, and the hydraulic connection between the plain and the calcic formation of Asmari are possible through transverse fractures.

Hydrogeology

Hydro- geologically, the region can be divided into two hydro-stratum units. The first one is the hard formation (Karsti hydro-stratum unit) which is mainly created in Asmari and Gachsaran units, and the other one is the alluvial hydro-stratum unit which is the result of water storage in residual alluvial layers in the alluvial plain of Meidavood-Daloon.

Investigation processes

This study was conducted in 3 investigation processes which are as follows:

- 1) Library research

- 2) Field study
- 3) Laboratory research

Library research

In this phase, the researchers tried to achieve a thorough understanding of the region, studying previous studies and hydrogeological, geological and topographical maps so that the field study could be planned. The general setting, the geographical location, linking roads were studied, and the best places for sampling ground-level and underground water as well as sampling the rocks, sediments, and other geological materials were located. In addition, the faults and their main fractures and crevices were located by studying geological maps, aerial photographs with 1/40000 scales, and satellite photos (38-165 , 38-164 rows) and the relationship of these structural phenomena with underground water resources coming out of the hard formations (Asmari and Gachsaran) was investigated.

Field study

Sampling water resources

Since the main objective of this study was to investigate the factors affecting the quality of underground water in Meidavood, and since the main focus was placed on location-driven changes in the quality of the water, the sampling was conducted with good dispersion in July 2009, which is a good indicator of dry seasons in the region. At this time of the year, the amount of precipitation is low and since the underground water is not fed by these precipitations, there is a good balance between the aquifer and the underground water and possible ground-level contaminations could be detected more easily. During the sampling process, all underground and ground-level resources were sampled, which, hydro logically, could be classified into the following classes:

- 1) Hard formation water samples: the SP₁ and SP₆ samples (taken from Gachsaran formation output springs), SP₂, SP₃, SP₄, and SP₅ (taken from output springs of Asmari formation) and the W_K sample (taken from the Karsti well of MohammadAbad drinking water which was dug in Asmari formatin).
- 2) The samples taken from shallow wells (12 meters deep on average) including WL₁ to WL₆ samples
- 3) The samples taken from deep wells (83.5 meters deep on average) including W₁ to W₁₆ samples.
- 4) Samples taken from ponds formed in rice farms including the pond₁ to pond₈ samples and samples taken from A'la (Ri₁) and Talkh(Ri₂) rivers.

In order to sample the water resources in the region, 250-ml polypropylene containers were used. Sampling was conducted using standard methods of

EPA 2006. Each container was cleansed with normal citric acid 1, and rinsed with deionized water. Sampling was conducted 20 minutes after pumping, when the PH values, temperature, and electrical conductivity (EC) had been stable. At least 15 samples were taken doubly, so that the accuracy of laboratory analyses was guaranteed. After sampling, the values of temperature, pH, Eh, TDS, and EC were measured and samples were classified into three categories: the first group included samples taken for measuring primary anions and cations (Ca^{+2} , Mg^{+2} , Na^+ , K^+ , Cl^- , SO_4^{-2} , and HCO_3^-), the second group included samples for measuring secondary anions (Br^- and I^-), and the third group included samples for measuring rare elements (arsenic, iron, manganese, nickel, and vanadium).

Laboratory research

Measuring primary anions and cations:

In order to measure the density of primary anions and cations, different flame photometric and titration methods were used.

A) Measuring the density of calcium (Ca^+): in order to measure the density of calcium, the volume titration method and the titration material Ethylene Diamine Tetra acetic Acid were used, and to finish the reaction, calkon carbokyclic acid was used.

B) Measuring the concentration of magnesium (Mg^+): the solutions produced from calcium titration in the previous stage, were neutralized by normal hydrochloric acid 1, and the amount of magnesium was measured using the equation 1:

$$(1) \quad Mg(mg / lit) = \frac{a \times 2.43 \times 1000}{V}$$

In this equation, a represents the amount of titrating material in liters, and V is the volume of the sample. In this experiment, 1 ml of 1% M of the titrating material equals 2.431mg of Mg^{2+} and 4.031 mg of MgO.

c) measuring the concentration of sodium (Na^+) and potassium (K^+): in order to measure the concentration of these elements, the JENWAY flame photometry device, model PFF7 was used. Prior to measuring these ions, the water samples were passed through the Ashless filters so that the materials which could potentially affect the measurement process were filtered.

d) Measuring the concentration of bicarbonate (HC_3): it was measured by titration using the methyl orange and normal hydrochloric 1.

e) Measuring the concentration of sulfate (SO_4^{2-}): in order to measure the concentration of this anion, first, the water samples were passed through strong cation filters to gain the associated acids, then, the barium chloride solution was added to deposit sulfate, and

finally, in the presence of magnesium ions and the titration solution with EDTA, the amount of remaining barium was measured and the concentration of sulfate was calculated.

f) measuring the amount of chloride (Cl^-): to measure this anion, the Mohr – Winkler method was used. In this method, silver nitrate and the chloride ions deposit mercury chloride in the neutral or partly alkali environment. In the presence of potassium chromate, when silver nitrate had mixed with all chloride ions, the first additional drop of nitrate mixed with potassium chromate and produced mercury chromate with brick red color.

Measuring the accuracy of hydro-chemical data

Since the concentration of the main elements in this study was measured using titration and flame photometry which are not highly accurate, the resulting data were tested for accuracy using the following method:

a) The reaction error: r the balance error which is calculated by equation (2)

$$(2) \quad Error = \frac{\sum Cation - \sum Anion}{\sum Cation + \sum Anion} \times 100$$

The reaction error value must not be greater than 10%.

b) EC graphs against the sum of anions and the sum of cations.

c) The graph of the sum of anions against the sum of cations

Using the methods in (b) and (c), irrelevant data could be identified and excluded. The determination coefficient for the best goodness of fit line in these graphs must approach 1 and digression from this value indicates a measuring error or lack of thorough measurement of all ions.

EDS and EC values

In order to control and examine the accuracy of EC and TDS data, these methods were used:

a) Designing the graph of field-measured TDS relative to lab-measured TDS

b) Designing the graph of field-measured EC relative to lab-measured EC

Comparing the concentration of rare elements in ground and underground water samples

a) According to the standards of WHO (2004), 81% of deep wells (except for W_{15} , W_5 , and W_3), 42% of output water of hard formations (SP_6 , SP_3 , and SP_1), 16% of shallow wells and 37% of ground-level waters contain arsenic levels higher than the allowed amount for drinking (10ppb).

b) according to the secondary standard of IUCN(2007), nearly 44% of deep wells, 28% of water going out of hard formations, and 10% of ground-level water

contain a higher level of manganese than the allowed one (50bbp)

c) According to the secondary standard of the IUCN (2007), nearly 31% of deep wells in the region contain higher levels of iron than the allowed one.

d) In most samples, iron has a greater concentration compared to other elements. This could be attributed to a high degree of iron minerals (especially oxide ones) in sedimentary environments.

e) the concentration of rare elements, especially iron, manganese, and arsenic in deep wells (group 1) is higher than the others. This could be attributed to reducing conditions in these wells.

Findings

- 1- Most ground-level and underground water taken from the region is of calcium-sulfate type, which is due to the dissolution of gypsums in the Gachsaran formation the mixing of the water in this formation with other water in the region.
- 2- There is not a specific evolutionary trend in the chemical quality of the water in the Meidavood-Daloon alluvial aquifer. The dominant hydro-geochemical facies in this plain is a calcium-sulfate one and the amount of calcium and sulfate increases with the flow of water from feeding zones (east and northeast) to discharge or stop zones.
- 3- Local entering of brines from the Gachsaran formation to W₁₁ and W₁₂ wells increases the amount of TDS, EC, chloride and sodium around these wells.
- 4- The place distributions of calcium and sulfate in deep wells of Meidavood-Daloon aquifer are very similar. There is an increasing trend toward W₁₁ and W₁₂ (due to local entering of Gachsaran brines) and W₂ and W₁₃ wells (due to stopping of water in the aquifer).
- 5- The comparison of rare elements in the water samples shows that the concentration of rare elements especially iron, manganese, and arsenic is the highest in deep wells. This could be attributed to the reducing environment in these wells. In addition, in all four groups, the changes in arsenic and iron are similar, which indicates a strong hydro-geochemical bond between these two elements.
- 6- The dispersion graphs of the concentration of rare elements compared to the Eh of water show a high determination coefficient, especially for deep wells. This indicates that Eh is a controlling factor in the concentration of these elements.
- 7- The concentration of arsenic in Meidavood-Daloon deep wells indicates a close relationship between the saturation of iron and manganese minerals (especially Fe(OH)₃, hasmanite, hematite, pyrolignite, and magnetite). This shows that these mineral could function as arsenic absorbents.
- 8- The place distributions of iron, manganese, arsenic, nickel, and vanadium in Meidavood-Daloon deep wells are similar and there is an increasing trend in the amount of these elements toward the northeastern part of the plain and in the area of W₁, W₁₀, and W₁₆ wells, which is toward the concentration place of minerals related to oil hydrocarbons.
- 9- Based on the place distributions of Eh and place changes of rare elements in Meidavood-Daloon deep wells, this aquifer could be hydro-geologically mapped as follows:
 - Partly reducing zone: the areas surrounding W₃, W₄, W₅, W₆, W₇ and W₈ wells
 - Medium-reducing zone: the areas surrounding W₂, W₁₁, W₁₂ and W₁₃ wells
 - Reducing zone: the areas surrounding W₁, W₁₀ and W₁₆ wells
 - Highly reducing zone: the areas surrounding W₉
- 10- The arsenic source of the Asmari formation water is probably the oxidation of pyrite impurities in its lime formations. This is evident in wells near this formation such as W₃, W₄ and W₅.
- 11- The arsenic source of the Gachsaran formation is the arsenic absorbed by iron oxides in red marnes. Creating a reducing environment (due to organic materials related to oil hydrocarbons) could release arsenic.
- 12- Investigating the quality of ground-level and underground water in terms of drinking indicates that most water taken from the region is not drinkable due to the sulfate anion, and some samples contain higher levels of chloride than standard levels.
- 13- Based on the standards of WHO (2004), 80% of deep wells, 42% of water coming out of hard formations, 16% of shallow wells, and 37% of ground-level water are contaminated with arsenic (over 10ppb).
- 14- Based on the standards of the IUCN (2007), nearly 31% of deep wells contain iron more than the allowed level for drinking (300ppb) and the other resources are not contaminated.
- 15- Based on the standards of IUCN (2007), nearly 44% of deep wells, 28% of output water from hard formations, and 10% of

ground level water contain higher levels of magnesium than the allowed levels for drinking (50bbp).

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