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Groundwater for Sustainable Development

journal homepage: www.elsevier.com/locate/gsd

Geochemistry of soil and groundwater in arid regions: Qatar as a case study



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ARTICLE INFO

Article history:

Received 18 June 2015

Received in revised form

23 November 2015

Accepted 29 December 2015

Available online 31 December 2015

Keywords:

Soil and groundwater geochemistry

Natural and anthropogenic inputs

Harsh environment

ABSTRACT

This study aims to merge the findings of soil and groundwater geochemistry analyses for the same locations, and to investigate the natural and anthropogenic factors affecting the interaction and, inter-linkages among different parameters (with special care to contaminants that may affect environment), and human health. A broad spectrum of physicochemical parameters, including anions, cations, heavy metals, and rare earth elements have been analyzed for the first time on this scale of sampling campaigns using state-of-the-art laboratories inside Qatar. The results of 250 groundwater samples and 310 topsoil samples showed a very strong correlation for major cations (Ca, Mg, Na and K) and common heavy metals (Pb, Fe, Mn, Zn and Co) in both water and soil. One big challenge in studying soil geochemistry in Qatar is the importation of fertile soils from Asia to the agricultural areas. The harsh arid environment and naturally occurring sand/dust storms and soil erosion increase the complexity. More studies on soil mineralogy and geochemistry are needed to identify the exact sources of elevated parameters in groundwater and soil. The findings of the study are important to the region and for countries worldwide that have similar conditions of aridity, water scarcity, and human development. Additionally, a good understanding of groundwater geochemistry should be coupled with soil geochemistry. Such coupling gives powerful tools to plan both land use and water management strategies.

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1. Introduction

1.1. Groundwater and soil in arid regions

The origin, hydrochemical evolution, and age of groundwater in arid lands can be understood through comprehensive and integrated approaches of soil/water investigation. The studies should include soil mineralogy and chemistry, aquifer matrix, water biogeochemistry, and chemical and isotopic analyses of groundwater. Special care is given to the groundwater studies – the only natural water resource – where surface water is limited or absent. Management of groundwater requires a dynamic understanding of the aquifer systems, water chemistry, contaminant transport, hydrology, hydrogeology, geochemistry, and exploitation and recharge (Lange and Leibundgut, 1999; Cudennec et al., 2007). Although water resources are very limited in the arid regions, the quality of the groundwater – as the major or the only source – is determined by the interaction with the rocks and soil profiles. Different processes at surface and deep layers affect the quality of the groundwater. Lack of recharge leads to deterioration of the groundwater quality and quantity, and allows external

contamination sources (e.g. seawater intrusion) to spoil the limited water resources in the arid and coastal areas. Additionally, within the arid areas, the chemical composition of groundwater is strongly affected by the evaporation of the shallow groundwater, and this leads to dissolution of mainly halite and gypsum during precipitation seasons and recharge. Soil salinization has become a global ecological problem under the influence of increasingly prominent climate change (Jianguo et al., 2014). Generally, poor soils are located above deteriorated groundwater aquifers and the salty soils are linked to the salty groundwater. It is well known that soils are excellent filters; however rich soils (nutrients, minerals, organic matter, etc.) are associated with good and renewed groundwater quality. Most of the elevated contaminants naturally occurred in drinking water (e.g. fluoride and arsenic) that cause documented diseases come from dissolution of their minerals in groundwater (Shomar et al., 2004; Xiaojing et al., 2014).

1.2. Groundwater and soil geochemistry in Qatar

Anthropogenic and natural stresses are limiting factors for sustainable water management strategies and action plans in Qatar. As Qatar depends > 99% on desalinated water, the groundwater in Qatar is used for seasonal agricultural activities. The aquifers are depleted and degraded due to over-exploitation,

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seawater intrusion, and minimum recharge (Shomar et al., 2014). The chemistry of soil in Qatar is affected by natural and anthropogenic influences. Clear examples are the continuous soil erosion, regular sand and dust storms, negligible amounts of precipitation, and very high evaporation associated with extensive urbanization and industrialization. Details of these influences are described in Shomar et al. (2013) and Shomar and Dare (2015). Shallow groundwater in Qatar is transferred into the vadose zone and to the atmosphere via evaporation, limited transpiration, and diffuse seepage. The dissolved constituents are projected to precipitate and accumulate as minerals such as calcite and gypsum in the deep vadose zone. The recent study of Kuiper et al. (2015) gives extensive information and data on the groundwater situation of Qatar: the locations of the aquifers, physical and chemical characteristics of groundwater quality, and elevated molybdenum (Mo) in the groundwater. In general, the groundwater in Qatar is brackish and concentrated in the northern areas of the country.

2. Scientific challenges and new additives in this study

The main objectives of the study are to integrate the results of groundwater and soil geochemistry of Qatar as an arid country, and to highlight the most natural and anthropogenic sources of the elevated parameters including the chemical contaminants. The deterioration of soil quality is not limited to the misuse and abuse of soil for different applications.

Salinity does not only affect the macro-scale (major anions and cations) of the soil/water chemistry but also the occurrence and mobility of heavy metals. The study of Acosta et al. (2011) showed very strong correlation between the elevated salinity of soil and mobility of heavy metals. The mobile metals will find their way in the groundwater. That study looked at major salts of CaCl_2 , MgCl_2 , NaCl , and Na_2SO_4 and their impacts on the mobility of four heavy metals Cu, Cd, Pb, and Zn. A study by Kadkhodaie et al. (2012) found that the total amount of heavy metals (Cd, Pb, Ni) decreased in soil as salinity increased. The explanation of such behavior is the formation of mobile forms of the metals: the Cu-sulfate, followed by competition with cations ($\text{Mg} > \text{Ca}$) and chloride then Zn and Ca^{2+} competition for sorption sites with sulfate. Water geochemistry is linked to the cation-exchange and weathering of different minerals such as aluminosilicates, the most abundant minerals of the earth crust.

The water associated with oil and gas is known as produced water (PW) or coproduced water. In most cases, the water associated with oil production is very salty ($> 50,000 \text{ mgCl/l}$) and contains cocktails of organic and inorganic residues. Within the production processes, PW is injected alone or mixed with seawater-which is less salty-to enhance well recovery. Most PW is considered as waste and is disposed with or without treatment. Disposal of PW associated with oil and gas production to the sea or by injection to the deep aquifer is practiced worldwide; however, both disposal to the sea and injection into deep aquifers can have severe and serious environmental consequences. Depending on the chemistry of the injected water and rock structure and mineralogy, different reactions and outcomes occur. The study of Puntervold and Austad (2008) provides a very good example of an aquifer in the USA where PW mixed with seawater was injected. The chalk formation of the aquifer was significantly affected by the chemistry of the injected produced water. For this study, the existing aquifer water contained various amounts of divalent cations like Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} . Injection of PW to the aquifer changed the composition due to the interaction between PW/seawater and the chalk formation. The fluid-rock interaction involved dissolution of CaCO_3 , substitution of Ca^{2+} by Mg^{2+} at the chalk surface, and precipitation of CaSO_4 , SrSO_4 and BaSO_4 ,

depending on the reservoir temperature. Actual chemical equilibrium reactions in the chalk matrix could be achieved in relation to variation in temperature during continuous injection of seawater. The injection process may lead to wettability modification, irreversible thermodynamics, and impact on the mechanical strength of the chalk matrix.

3. Study area, sampling and analysis

The study area, the sampling and analysis procedures are given in detail in Shomar et al. (2013) and Kuiper et al. (2015). Briefly, groundwater ($n=205$) samples were collected from the Northern shallow aquifer (40–80 m deep) of Qatar. Physical parameters (pH, EC, TDS and DO) have been taken during the sampling campaigns using portable kits. Samples were stored in clean polyethylene (PE) bottles and stored at 4 °C. Anions (Cl^- , F^- , Br^- , NO_3^- and SO_4^{2-}) were analyzed by ion chromatograph (Dionex ICS-1100). Groundwater samples were acidified upon return to labs with HNO_3 (Normaton for trace analysis) to $\text{pH} < 2$. Cations (Ca^{2+} , K^+ , Mg^{2+} and Na^+) and total As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, U, V, Zn and rare earth elements (REE) were analyzed using Finnigan Element HR/ICP/MS. HCO_3^- and TOC were analyzed with TOC-V_{CPH} Analyzer (Shimadzu).

Composite soil samples were collected at the same time and location of groundwater samples.

Approximately 0.5 kg of topsoil were placed into polyethylene (PE) cups and stored at 4 °C. The coordinates of each sample were recorded by a GPS. In the lab, soil samples were manually ground and sieved through a 20- μm sieve and ground to a very fine powder by using a sand mill (FRITSCH-Labor Planeten Mühle, Pulverisette 5). Approximately 0.5–1.0 g of each homogenized sample was dissolved in 10.5 ml of concentrated HCl (37%) and 3.5 ml of concentrated HNO_3 (65%) in 50 ml retorts. The samples were degassed (12 h) then heated to 160 °C on a sand bath until a complete extraction had taken place (3 h). After cooling, the solutions were diluted with distilled water in 50 ml volumetric flasks and kept in 100 ml polyethylene bottles for cations and trace element analyses by the HR/ICP/MS. Mercury was analyzed by an advanced mercury analyzer (AMA) 254 solid phase Hg-Analyzer (LECO). Total C and S contents were determined in dried samples by a Carbon-Sulfur Determinator (Leco CS-225).

Figs. 1 and 2 show the locations of groundwater wells and of soils collected in 2013 and 2014. The two studies explained in detail the method of soil and water sampling and preservation, instrument calibration, and the methods of quality assurance and quality control (QA/QC). This study focuses on the common and shared parameters between groundwater and top soils.

4. Results and discussion

The results of this study are limited to the major statistical values for groundwater (Table 1) and soil samples (Table 2). Table 3 shows the average concentrations of major elements in the upper crust and lower crust according to Turekian and Wedepohl. (1961). Details of the results for both soil and groundwater can be found in Shomar et al. (2013) and Kuiper et al. (2015). Advanced statistical approaches such as multivariate analysis (PCA, CA etc.) can be used to confirm the findings and correlations. Due to the inter-linkages between groundwater and soil geochemistry, the following sections treat water and soil separately but without ignoring such strong relationships.

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