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# Assessing the hydrogeochemical processes affecting groundwater pollution in arid areas using an integration of geochemical equilibrium and multivariate statistical techniques\*

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#### ABSTRACT

Rapid economic expansion poses serious problems for groundwater resources in arid areas, which typically have high rates of groundwater depletion. In this study, integration of hydrochemical investigations involving chemical and statistical analyses are conducted to assess the factors controlling hydrochemistry and potential pollution in an arid region. Fifty-four groundwater samples were collected from the Dhurma aquifer in Saudi Arabia, and twenty-one physicochemical variables were examined for each sample. Spatial patterns of salinity and nitrate were mapped using fitted variograms. The nitrate spatial distribution shows that nitrate pollution is a persistent problem affecting a wide area of the aquifer. The hydrochemical investigations and cluster analysis reveal four significant clusters of groundwater zones. Five main factors were extracted, which explain >77% of the total data variance. These factors indicated that the chemical characteristics of the groundwater were influenced by rock -water interactions and anthropogenic factors. The identified clusters and factors were validated with hydrochemical investigations. The geogenic factors include the dissolution of various minerals (calcite, aragonite, gypsum, anhydrite, halite and fluorite) and ion exchange processes. The anthropogenic factors include the impact of irrigation return flows and the application of potassium, nitrate, and phosphate fertilizers. Over time, these anthropogenic factors will most likely contribute to further declines in groundwater quality.

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#### 1. Introduction

Groundwater is one of the most precious natural resources in arid areas because of the scarcity of rainfall and negligible surface water resources. In such areas, groundwater is often characterized by significant spatio-temporal variability (El Alfy and Merkel, 2006; Metwaly et al., 2014; Gemail et al., 2017). A Common source of natural pollutants in groundwater is the dissolution of minerals in some aquifers under certain pH and redox conditions (Rasool et al.,

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http://dx.doi.org/10.1016/j.envpol.2017.05.052 0269-7491/© 2017 Elsevier Ltd. All rights reserved. 2015; Singh and Mukherjee, 2015). Population growth and rising living standards are increasing the demand for water in arid areas, and this demand has put great stress on the limited water resources (Moosavirad et al., 2013). The overexploitation of groundwater coupled with minimal recharge results in overall groundwater degradation and depletion (Kulmatov et al., 2015; Mirlas et al., 2015). Furthermore, increased use of fertilizers to improve agricultural yields can increase groundwater pollution (Bouzourra et al., 2015; El Alfy and Faraj, 2016; Milhome et al., 2015).

Aquifer systems are influenced by the spatial and temporal variability of natural and anthropogenic factors. The relationships and spatio-temporal variations of these factors, as well as the limits and hierarchy of their interactions between the components, can be statistically demonstrated (Dragon, 2006; El Alfy, 2013; Kolsi et al.,

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2013; Machiwal and Jha, 2015). Geostatistics is useful for modeling spatial distribution, variograms are used to measure spatial correlation, and the kriging variance is a function of the geometric configuration. The kriging estimation variances are independent and are related to model variogram and the spatial arrangement of the sample data. Kriging interpolation is used to provide the best variable closeness value of an estimate in relation to the actual value using the least squares technique (Bradai et al., 2016; Kitanidis, 1997).

Multivariate statistical methods have been used to draw meaningful information from large volumes of environmental data, and these techniques have often been used in exploratory data analysis as tools to classify samples and identify pollution sources (Panagopoulos et al., 2016; Reghunath et al., 2002; Srivastava et al., 2012). Factor and cluster multivariate statistical analyses can help in interpreting large numbers of parameters to achieve a better understanding of the hydrochemical processes involved. To improve management of water resources on a regional scale, the aim of this study is to identify and evaluate the interfering natural and anthropogenic factors affecting groundwater hydrochemistry in an arid area.

Because of the complex interactions between anthropogenic and geogenic factors affecting groundwater hydrochemistry, this study is unique in its application of an integrated approach with hydrochemical investigation, geostatistics, and multivariate statistical analyses in an arid region. Thus, this study was conducted to overcome the interference of various hydrochemical problems that affect shallow aquifers in arid areas. To conserve and sustain the rapidly depleting groundwater resources in arid areas, advanced assessment tools are needed to better understand the relationships between land-use and natural and anthropogenic sources of contamination.

#### 2. Study area

#### 2.1. Climate

The study area, which covers 1060 km<sup>2</sup>, is located approximately 60 km southwest of Riyadh, Saudi Arabia (Fig. 1). This area's climate is affected by a sub-tropical high pressure belt. The deep depressions of the eastern Mediterranean system in the spring and fall seasons cause a number of sandstorms, which are typically followed by rainfall (Hasanean and Almazroui, 2015). The most distinctive features of these convective rainfall events are their local distributions, short durations, and high intensity. The study area is characterized by its dry climate, with a mean high temperature of 35 °C, mean low relative humidity of 28%, and high evaporation rates (GIZ, 2015). The total mean annual potential evaporation is more than 3600 mm with a monthly average of about 295 mm. There are frequent flash floods, where their frequencies and magnitudes are controlled by the interaction of several different variables including rainfall, antecedent catchment conditions, and land-use distribution. The high-relief area acts as a recharge area, with surface water flow directed downward to the low-lying areas in the east (Fig. 2).

#### 2.2. Geomorphological setting

The study area is characterized by west-facing cuestas that developed from variably resistant layers of Paleozoic to Neogene sedimentary rocks (Alsharhan and Nairn, 1997). This plateau is dissected by numerous ephemeral streams with courses that follow tectonic structures, and several isolated hills are present (Fig. 2). The terrain is characterized by highly variable relief, with ridges and mountain ranges in the east and with relative lowlands in the

west. From the western to south eastern parts of the study area, there is a low-lying plain, with a typical slope of  $<5^{\circ}$ . Toward the north and northeast, the terrain is high and undulating with dramatic slopes that reach up to 70°. Almost 85% of the area has low relief and is covered with sand dunes, sand sheets, and alluvium. The resistant limestone of the Tuwaiq Mountains form cliffs, scree slopes, and steep erosional features. Wadi Dhurma and its tributaries have steep-walled valleys, which are eroded and can be up to 100 m deep; these valleys contain alluvium up to 50 m in thickness. The wadi systems that are still active today originated during the Miocene, under the prevailing arid conditions, and only minor geomorphological modifications are observed (GIZ, 2015). For instance, the western part of the study area is covered by the Ounyfidah sand dunes and sheets and Pediplains (Fig. 2). Ephemeral streams of wadi Dhurma and its tributaries form an alluvial plain, which is sporadically active during intense rain storms and are important recharge sources.

#### 2.3. Geological and hydrogeological setting

There are three main geological units of Early (Toarcian-Aalenian) to Middle Jurassic (Bajocian—Callovian) age in the study area. The Dhurma Formation overlies the Marrat Formation and underlies the Tuwaiq Formation (Fig. 1S). These Jurassic rock units are overlain by alluvium deposits, which are classified into the following two types: recent deposits in active wadis and older deposits in inactive channels and hanging terraces. These sediments are deposited in the deeply incised Wadi Dhurma and its tributaries, which cut deeply into the bedrock. At the base of this succession, the Marrat Formation consists of limestone and shale, with subordinate siltstone and sandstone (Fig. 1S). This formation is an aguitard with low hydraulic conductivity, and separates the Minjur and Dhurma aquifers. The Dhurma Formation consists mostly of carbonates and shales with a total thickness of 100–200 m and an eastward dip of 1–2° eastward dip (Sogreah, 1968). Because of dissolution, this fractured limestone represents a secondary aquifer with low to moderate hydraulic conductivity and a moderate to high storage coefficient. Groundwater pumping has been practiced over the years to provide an adequate water supply for agricultural and residential uses. The water level of the Dhruma aquifer is tested and varies from 623 to 695 m (a.s.l.) and the groundwater flows from west to southeast with a hydraulic gradient that ranges between 0.11 and 0.23% (Fig. 1S). The hydraulic conductivity of the Dhurma aquifer varies between 10<sup>-4</sup> and  $2.2 \times 10^{-4}$  m/s, with an average value of  $1.6 \times 10^{-4}$  m/s. Its transmissivity values vary between  $1.5 \times 10^{-3}$  and  $2.9 \times 10^{-3}$  m<sup>2</sup>/s, with an average value of  $2.2 \times 10^{-3}$  m<sup>2</sup>/s, the storage coefficient averages  $2.9 \times 10^{-3}$  and the specific storage is  $9.24 \times 10^{-5}$  m<sup>-1</sup> (GIZ, 2015).

#### 2.4. Land-use/Land-cover

Figs. 2 and 3 show that there is a belt of circular farms that extend from the northwestern to the southeastern parts of the study area. The city of Al-Muzahimiyah is located in the southeast, and other smaller urban areas exist in the central and southern parts of the region (Dhurma, Hajoufah, and Mashaalah). The northeast consists predominantly of rural areas located along the water divide of the Tuwaiq Mountains. Some of the most problematic pollution sources in the study area are related to unsewered rural and urban regions, and sewage contamination has likely had long-term influence on groundwater resources. Pollution sources associated with farming are mainly related to intensive livestock farms and unwise applications of fertilizers and pesticides.

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