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Hydrochemistry of groundwater salinity sources in the shallow aquifer: Case of Annaba plain (Ne Algeria)

A. Benchaib*, L. Djabri, A. Hani, H. Chaffai, N. Boughrira

Water Resources and Sustainable Developpement Laboratory, Badji Mokhtar Annaba University, Annaba, Algeria

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Abstract

The growth of population and expanding agricultural and industrial sectors in the recent years, have created an increase in demand. However the overexploitation of the coastal aquifer of Annaba Gulf (North-East Algeria). These heavy demands have caused a degradation of groundwater hydrochemical quality (salinization). To identify the origin of groundwater salinity; hydrochimical and physical parameters information has been examined and to interpret the processes of the mineralization. Electrical conductivity values varied between 838 and 10600 μ S/cm. Chloride concentration attained 1850mg/L and the proportion of seawater intrusion in the extreme north of the plain was 8.58% calculated by seawater fraction formal, showing the intense seawater intrusion. Cation-exchange reactions and water–rock interactions related to the dissolution of evaporitic formation and calcite occurred by ionic relationships during seawater intrusion. Nitrate values ranged from o to 11.4mg/L under the drinking water standards. Therefore, the main origin of groundwater salinization was attributed to seawater intrusion with the contribution of anthropogenic pollution.

*Corresponding Author: A. Benchaib 🖂 wahidhydro@gmail.com

Introduction

A general feature of coastal areas is their large water demand, because of the fact that they are usually densely populated and subject to intensive agriculture and tourism. The intensive exploitation of coastal aquifers in an attempt to satisfy this demand may generate problems. One of these problems is presented in our case study as a degradation of the groundwater hydrochimistry by salinization in Annaba Gulf. Groundwater salinization in coastal areas occurs in many aquifers around the world (Barlow, P.M., 2003; Bear, J., Cheng, A.H.-D et al., 1999) and in numerous Mediterranean countries (Benavente, J., Larabi, A et al., 2004; Cost Environment Action 621, 2005). Understanding the spatial variations in the chemical composition of groundwater is helpful to identify the different pollution sources (Mahesha, A., Nagaraja, SH., 1996), delimit and fight it, in order to preserve for future generations. In the previous studies, seawater intrusion is presented as the major cause and origin of groundwater quality degradation (Xiao, G., Yang, J et al., 2014; Zhang, B., Song, X et al., 2013), which observed in the case of unconfined aquifer connected to the sea where a strong demand in water resources induced a decrease of piezometric level (Veronique de Montety *et al.*, 2008).

Farmland, factories and tourist areas are located on the coastal area, where the economy is developing rapidly. Agriculture depends on intensive irrigation and fertilization to improve the soil efficiency. However excessive amounts of fertilizers infiltrate into the groundwater with the irrigation return flow. Waste water emissions from factories can cause deterioration of the groundwater. Also, domestic sewage makes a contribution to groundwater salinization. These anthropogenic contaminations may result in high nitrate concentrations in the groundwater (Xianfang Song et al., 2016). Summer is the period of water ressources scarcity. Furthermore; the cultivated crops in this saison are mainly tomatoes, melon and water melon. These crops need intense irrigation that causes an increased request for groundwater. To satisfy water demand, farmers intensifly pump water from wells and drillings which imbalances freshwater–saltwater interface (Larbi Djabri *et al.*, 2013). The objective of this study is to determine the salinization sources (seawater intrusion; anthropogenic sources) in the shallow coastal aquifer depending on groundwater hydrochemical characteristics.

Material and methods

Geographic and geological situation

The studied region is located in the North-East of Algeria (Fig.1). It is bordered by the Mediterranean Sea from the North, by Drean town from the South, by Mafragh River from the East and by Fetzara Lake from the West. The plain is supplied from the West by the river coming from the Edough mount, and from the South by the upstreams coming from Ain Berda and Guelma mounts. The studied area is characterized by the outcrop of a sedimentary and a metamorphic formations (Fig.2). These formations date from the Paleozoic to the Quaternary. The metamorphic formations which outcrop in the western part date from the Paleozoic. They form the Edough, Belilieta and Boukhadra massif, constituted mainly of gneiss. The sedimentary formations age go from the Mesozoic to the Quaternary. This latter is constituted of alluvial sediments forming the reservoir rock. We distinguish the old Quaternary (high terraces) containing the alluvial aquifer, where the material is made of sand, clay and gravels. The recent Quaternary correspond to the low and the average terraces. The actual Quaternary: the alluvial fans are actual bed deposits of the river; they are formed of sand and gravels. (Larbi Djabri et al., 2013).

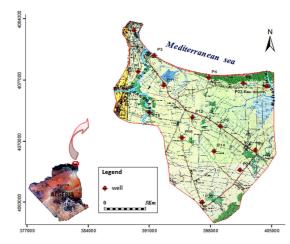


Fig. 1. Location of the study area and sampling sites.



Fig. 2. Geologic characteristics of the study area.

Hydrogeology

The ground of Annaba plain receive an important aquifer possibilities, where two hydrogeologic layers are superposed the upper one called free, in which the wells are implanted, and the deep one is captive becomes free in its southern part (Drean region) (Fig.3) (Larbi Djabri *et al.*, 2013).

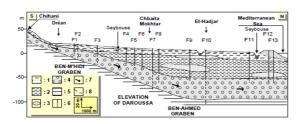


Fig. 3. geological cross section through the aquifer system.

1: clayey sand (shallow aquifer); 2: detritic clay; 3: sand; 4: stons and gravels (deep aquifer); 5: numidian clay; 6: borehole; 7: flow line; 8: piezometric level of the deep aquifer.

Sample collection and treatment

Fifteen groundwater samples were taken from domestic wells, and one seawater sample from the Mediterranean sea in the periode of November2016. Wells location (Fig.1) and piezometric level were recorded when sampled. Electrical conductivity (EC), pH and water temperature (T) were measured in situ via (WTW Multiparameter device). The major ions of the water samples were treated and analyzed in the physical and chemical analysis laboratory.

Seawater fraction

The seawater fraction in groundwater was estimated using chloride concentration as this ion has been considered as a conservative tracer (Custodio, E., Bruggeman, GA., 1987), not affected by ion exchange. It is calculated as follows (Appelo, CAJ., Postma, D., 2005):

fsea = (Ccl, sample - Ccl, fresh)/(Ccl, sea - Ccl, fresh)

Where *fsea* is the seawater fraction, *Ccl*, *sample* is the chloride concentration of the sample, *Ccl*, *sea* is the chloride concentration of the Medeterranean sea, and *Ccl*, *fresh* represents the chloride concentration of the freshwater. The freshwater sample was chosen considering the lowest measured value of the electrical conductivity (EC) (Slama, F., Bouhlila, R *et al.*, 2010). The only inputs are either from the aquifer matrix salts or from a salinization source like seawater intrusion.

Ionic deltas

Based on the seawater fraction, the theoretical concentration of each ion i resulting from the conservative mixing of seawater and freshwater was calculated using:

 $Ci, mix = fsea \times Ci, sea + (1 - fsea) \times Ci, fresh$

where *Ci*, *sea* and *Ci*, *fresh* are the concentration of the ion i of the seawater and freshwater respectively. For each ion i, the difference between the concentration of the conservative mixing *Ci*, *mix* and the measured one *Ci*, *sample* simply represents the ionic deltas resulting from any chemical reaction occurring with mixing:

 $\Delta Ci = Ci, sample - Ci, mix$

When ΔCi is positive, groundwater is getting enriched for ion i, whereas a negative value of ΔCi indicates a depletion of the ion i compared to the theoretical mixing (Andersen, MS., Nyvang, V *et al.*, 2005).

Results and discussion

Interpretation of piezometric map (November 2016) The groundwater map (Fig. 4) shows that there is a general south—north flow. However, at the Daroussa mount we notice a change of the flow direction. This latter is from the sea to the continent. This tendency with the high depressions localized on the central and southern part of the map; pointing out probably a penetration of seawater. The map shows also an interlink between the sea, rivers and aquifer. These elements certainly affect the water chemistry (Larbi Djabri *et al.*, 2013).

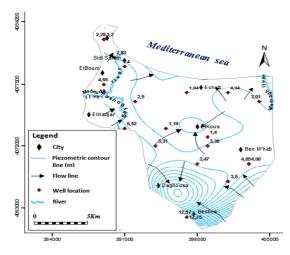


Fig. 4. Piezometric map of the shallow aquifer (November 2016).

The characteristics of groundwater salinity

The salinity of the groundwater is determined by EC (Bouchaou, L et al., 2008; Gime'nez, E., Morell, I., 1997). which was chosen as an index to evaluate the extent of groundwater salinity (Fig.5). The main contributors to the groundwater salinity are Cl-, Na+, Mg²⁺, Ca²⁺, K⁺, SO₄²⁻, HCO₃⁻ and NO₃⁻. EC values in the groundwater ranged from 838 to 10600µS/cm, with an average of 5916.86µS/cm. The highest values were measured in the area extended from northwest southest of the plain. Where the high to concentrations are possibly the results of seawater intrusion into the aquifer system, and the other high ones inside the plain either from human activities such as agriculture, industry or from the developement of seawater-freshwater interface.

Seawater intrusion processes

The extent of seawater intrusion is shown in (Fig.6 a,b). The trend of the chloride distribution is consistent with the seawater fraction. The most serious seawater intrusion area is located in the line where the cities ELBouni, ELHadjar on the Est to ELKous and south of Ben M'hidi; with a highest chloride concentration of 1850mg/L and a seawater proportion of 8.58%.

The drawdown from overexploitation of groundwater has caused seawater intrusion.

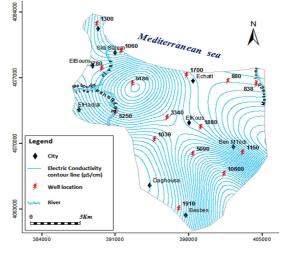


Fig. 5. Spatial distribution of electric conductivity (EC).

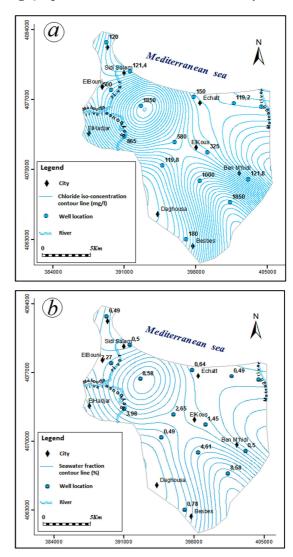


Fig. 6. Spatial distribution of chloride concentration (a) and seawater percentage (b).

The bivariate diagram (Fig.7a) reveals good correlation for most samples between the electrical conductivity and the chloride concentration. All of the samples are located in the chloride-depleted domain (above the mixing line). The mixing line join seawater sample with freshwater sample. (Fig.7 b) shows the relationship between sodium and chloride. The samples distribute around the mixing line. A few of samples are adjusting the mixing line and under it. But the majority of samples are located in the chloride-depleted domaine indicate that sodium is enriched in the aquifer. However, a big part of samples (Fig.7c) concentrated in the chloridedepleted domain, means that calcium enriched in the groundwater, generally samples scatter near the mixing line. When a good correlation observed between magnisium and chloride (Fig.7d). According to (Fig.7a,b,c,d), the enrichment of sodium and the depletion of calcium and magnisium at some wells

suggests that there is a possibility of salinization from the processes of the evaporitic formations dissolution. Furthermore (Fig.7e), shows the sulfate enrichment of the half sampls. In order to completely understand the processes that the theoretical content variation indicates, and to find out more about the behavior of the cations, the ionic delta was plotted for sodium, calcium, magnesium and sulphate (Xianfang Song et al., 2016), (Fig.7 f). The great majority of the samples are enriched in calcium and magnisium, a few of samples depleted in sulphite when a big part of sampls are depleted in sodium. This suggests that the probability of seawater intrusion is insufisant (El Yaouti, F., El Mandour A et al., 2009). However, the excess of calcium, magnisium and sulfite, indicates the existence of other sources contributing to the enrichment of groundwater. Fertilizers can be considered as potential sources of Ca2+, Mg2+ and SO42- (Milnes, E., Renard, P., 2004).

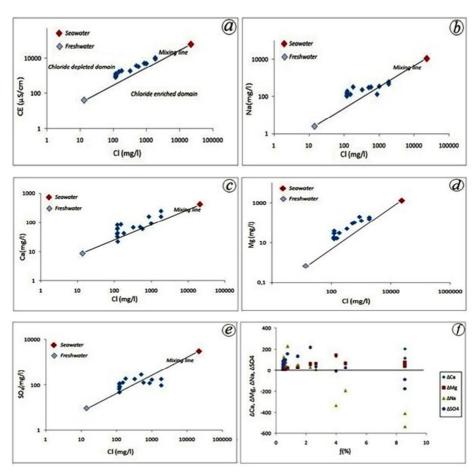


Fig. 7. The bivariate diagram of (a): electrical conductivity/Cl relationship; (b): Na/Cl relationship; (c): Ca/Cl relationships; (d): Mg/Cl relationships; (e): SO4/ Cl relationships; (f): Δ (Na, Ca, Mg and SO4) versus seawater percentage of groundwater samples.

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Pollution by human activities

Due to the joint development of industry and agriculture, groundwater is under enormous pressure in the study area. Contamination by nitrate occurred. The spatial distribution of the nitrate pollution is shown in (Fig. 8). Nitrate concentrations range between 0 and11.4 mg/L. Then all samples are under the drinking water standard (50 mg/L).

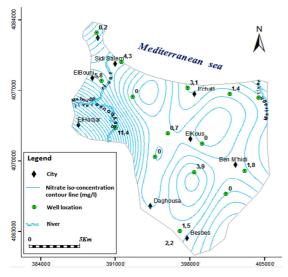


Fig. 8. Spatial distributions of nitrate (NO3).

The relationship between nitrate contamination and seawater intrusion is shown in (Fig.9), which reveals high nitrate concentrations at low seawater fraction. This indicates that the nitrate contamination has no relation to seawater intrusion. Instead, nitrate contamination can be attributed to human activities including abuse of fertilizers, industrial wastewater and domestic sewage.

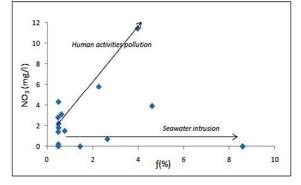


Fig. 9. The bivariate diagram of seawater fraction versus NO₃.

Conclusion

The study method used reveals that electrical conductivity values varied between 838 and 10600 μ S/cm. Chloride concentration attained 1850 mg/l and the proportion of seawater intrusion in the extreme north of the plain was 8.54%, showing the intense seawater intrusion. Nitrate values ranged from 0 to 11.4 mg/l which it is the drinking water standards 50 mg/l; where there is very low possibility of anthropogenic pollution. Therefore, the main origin of groundwater salinization was attributed to seawater intrusion with the contribution of anthropogenic pollution.

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