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RESEARCH PAPER

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Geochemical and isotope study of groundwater of anthropogenic coastal aquifer: Meboudja and Low seybouse Plain, Annaba (Ne Algeria)

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Abstract

The coastal plain aquifer of Meboudja and low Seybouse close to Annaba in Algeria (P precipitation = 700mm/y) is composed of a detrital fluvial Plio-Quaternary basin, bordred by a mountainous relief, the Mediterranean Sea and a marshy area. During recent decades, the urbanization of the plain, the development of the agricultural and industrials activities and the succession of dry years have led to a water-level lowering and groundwater quality degradation. Preliminary results from a geochemical and isotopic (¹⁸O, ²H and ³H) study show different origins of groundwater with different geochemical characteristics indicating various possible origins in the acquisition of the mineralization. The degradation of water quality is larger in the most irrigated areas marked by high nitrate contents. The tritium data show a recent groundwater renewal with two different recharge modes: fast recharge due to the infiltration of irrigation water and runoff water, and diffuse recharge by direct infiltration of precipitation.

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Introduction

In recent decades, human activity and climate change have largely altered hydrological cycles, particularly in coastal areas, occupied by about 50% of the world's population (Custodio & Bruggeman, 1987). In Algeria, more than 70% of the population is urban and is mainly located in coastal towns.

The Mediterranean basin is an area where the abundance of water, the fertility of the land and the mild climate on the coasts have led to continued migration to coastal areas. This increase in population has led to a change in land use and above all to intensive pumping of groundwater in order to satisfy ever-increasing domestic demand, but above all, increasingly important water needs in the industrial and agricultural fields. This demand is due to the extension of cultivated land and particularly to the development of irrigated crops (messadi *et al.*, 2001). This situation procreate serious consequences for water resources, especially phreatic water, marked by a drop in groundwater levels, which can locally be

materialized by marine intrusion processes and more generally by the degradation of water quality (Kherici N. 1993). This is the case for the aquifers on the east coast of Algeria, which have been experiencing a quantitative and qualitative deterioration of water for several years, mainly due to the strong pressure on the resource to satisfy a constantly increasing demand.

The phreatic aquifer of the Meboudja and the low Seybouse plain is the subject of this study, is an example of a coastal aquifer subjected to severe climatic and anthropic constraints.

Material and methods

Environmental data

The coastal plain of Annaba is located in NE Algerian, about 2km east of Annaba and 60km north of Tarf. It is bounded on the west by a metamorphic basement (Edough, 140m) in the southwest (Fetzara lake), and on the east by the Mafragh aquifer system on the north by the Mediterranean sea (Fig. 1).



Fig. 1. Geographical situation of the study area.

The climate in Annaba is warm and temperate according to the Köppen-Geiger climate classification. The average temperature in Annaba is 18.4°C. The average annual rainfall is 712mm. The strong contrast of rainfall and temperature between a mild and humid winter and a hot and dry summer, is mitigated by the proximity of the sea.

The study area is a part of the Wadi Seybouse watershed NE Algerian, that was generated during the important subsidence during the Mio-Pliocene. On the edged reliefs that correspond to very tectonized structures, sandy-clay and sandstone formations attributed to the Mio-Pliocene are exposed (Larbi djabri, 1996). Limited to the West by a metamorphosed crystalline massif (the Edough). The lower Seybouse area corresponds to an alluvial plain filled by recent Seybouse stream deposits following the retreat of the sea (Fig.2). the Geophysical works and recent studies have shown that it is a synclinal structure generally consisting of detrital alluvia (sandy-clay and silty) of upper Pliocene to Quaternary age, whose thickness varies from 7 to 20m. These recent deposits constitute a favorable hydrogeological reservoir in which the groundwaters of the Meboudja and the lower Seybouse plain circulate.



Fig. 2. Extract from a geological map of Annaba region. (J.M Villa 1980).

The plain is characterized by low altitudes that rarely exceed 20m at the foot of the mountains, which oscillate in the center of the plain around 5m, reaching only a few decimetres near the sea.

These weak topographical slopes have favored the extension of wetlands and swamps in the eastern part around wadi Seybouse and the salines area. Vegetable growing under irrigation dominates agricultural practices. However, arboriculture and cereals are the majority in piedmonts zone. Cultivated land is sometimes greatly reduced by the growing urbanization of local agglomerations (El Hadjar, Sidi Ammar, Chaiba and Sidi Salem) due to the phenomenon of periurbanization developing in areas close to the sea. Whatever, the type of land use, the pressure on water resources has increased considerably, especially on groundwater materialized by an ever increasing number of wells. (Débieche 2002, Djorfi 2008).

Hydrogeology

The superficial aquifer of the Meboudja and the lower Seybouse is presented in synclinal structure filled with thick layers of sandy-clayey and loamy detritic deposits of Plio-Quaternary age resulting from successive defluviations of the lower Seybouse Valley (djidel .2004). In the west area of Annaba town (between Edough Mountain and Mafragh) where the width of the study area exceeds several hundred meters; The phreatic aquifer is found in alluvial formations (Fig. 03). It is fed from the direct infiltration of rainwater and the centralized runoff in the wadis descending from the border reliefs towards the plain including wadis Seybouse and Meboudja. The overall flow of groundwater is from south to north.



Fig. 3. Aquifer system of the Annaba plain. (In Djidel.2004).

The low zone crossed by the Seybouse is the natural outlet for groundwater and surface water (Fig. 4). The static level of the aquifer is between 7 to 10m deep in the upper zones at the foothills of the mountss and passes to less than one meter in low zones of the plain notably on the edges of the sea. The permeability varies between 10^{-4} and 10^{-6} m / s (Boughrira *et al.* 2015), transmissivities

vary between 4.8×10^{-3} to 4.5×10^{-2} m² / s due to the fine lithology (abundance of clay and silts).

The highest exploitation is in the region of El Hadjar and the sallines where we observe the greatest concentration of wells, most of which are equipped with motor pumps.



Fig. 4. Piezometric map of the study area (October 2014).

In recent years, the noticeable increase in salinization of groundwater could be a limiting factor for their use and could also lead to a degradation of soil quality. Overexploitation of resources could also lead to an invasion of marine waters on coastal portions. In order to investigate the main causes of groundwater salinization, a sampling campaign was undertaken between October 2014 and December 2015 on 46 water points in three repetitions, which were the subject of geochemical analyzes (major elements and some trace elements) and isotopic (¹⁸O, ²H and ³H):

- 21 sampling points including (two industrial discharges, 5 stations and 14 wells in October 2014)
- 6 sampling points including (2 stations and 4 wells in April 2015)
- 19 sampling points including (3 stations, two industrial discharges and 14 wells in December 2015)

the major elements (Na⁺, Mg^{+ 2}, Ca^{+ 2}, K⁺, Cl⁻, SO₄⁻², HCO₃⁻ and NO₃⁻) were analyzed by high performance ionic liquid chromatography (HPILC) equipped with IC / Pak TM CM / D for the cations, using EDTA and nitric acid as the elutint, and on a Metrohm chromatograph equipped with CI SUPER-SEP columns for anions, using phthalic acid and acetonitrile as the eluent. The overall detection limit for the ions was 0.04 mg L⁻¹. The concentrations of CO_3^{-2} and HCO_3^{-} were analyzed in the laboratory by titration using 0.1 N HCl. The ionic balance for all

samples was less than 5%. Stable isotope analyzes (^{18}O / ^{16}O and ^{2}H / 1H) were performed using the LGR DLT 100 Laser Absorption Spectrometer (Penna *et al.*, 2010). The results are reported in the V-SMOW standard. 21 samples were selected for tritium analyzes using electrolyte enrichment technology and the liquid scintillation technique (Taylor, 1976). The concentration of ³H is expressed in tritium units (TU). A TU is defined as the isotope ratio ³H / ¹H ¹/₄ 10¹⁸.

Results and discussion

Water quality and chemical facies

The electrical conductivity (EC) of the water shows wide variations, more than 60% of the samples taken have values higher than 2mS / cm. Geographically we can distinguish two areas (Fig.05):

- A first zone (A) located in the south of El Hadjar city, where EC oscillates between 3 and 5.5mS / cm. In this area near the ARCELOR complex and marked by intense agricultural activity, the aquifer is formed by alluvial detrital formations. The piezometric level is close to the surface of the ground.
- A second zone (B) between El Hadjar city in the south and the sea in the North: This is the most cultivated region especially in low areas where shallow depth (less than 5 m) of the piezometric level facilitates its exploitation, EC values are between 2 and 3 mS / cm. for the surface waters the EC values are between 0.6 and 2mS / cm.



Fig. 5. Distribution of EC μs / cm in the study area.

The Piper diagram of sampling data (Fig. 06) differentiates evolution from hydrogynocarbonate sodium and sulphate-calcium facies in the upper parts of the plain to a characteristic sodium chloride facies in the lower zone of the plain near the Mediterranean Sea.



Fig. 6. Piper diagram of analyzed water samples.

The chemical facies observed are in direct relation with the lithology of the reservoir and the proximity of the wells to the sea or the wadis. The return of irrigation water to highly cultivated lowland areas (piezometric level less than 5m) is also an important factor conditioning the quality of groundwater locally. The correlations established between EC and major element concentrations show a good correlation with Cl- and Na + (r^2 respectively is 0.93 and 0.77) dominant elements that control the saline load (Fig. 07). The high presence of Cl- and Na + in the charged waters of coastal areas and in the lower part of the plain at the edge of the sea is the result of the combination of two important factors characterizing the study area: the effect of sea spray and dry deposition stores on the ground and the return of irrigation water to the aquifer, direct marine intrusion being unlikely, the level of the waterin coastrel aquifer remaining higher than the sea level.



Surface water

Fig. 7a. Na mg /l according to CE µs /cm and b: Cl mg /l according to CEµs/cm.

Origin of salts in groundwater

In Mediterranean areas, the salts deposited in the unsaturated zone following the evaporation of rainwater and especially those used for irrigation, are resumed by dissolution during the following rainy episodes, reaching the aquifer, this leads to an increase in the salinity of groundwater. In the study area, the return of irrigation water is also confirmed by the abundance of nitrates at high concentrations, in the lower part of the plain, 40 to 81mg / l. (81mg / l at well 12).

This is the result of the intensive use of fertilizers of chemical and animal origins in the cultivation of vegetables highly practiced on these regions (Mariotti A. 1994). The discharge of domestic wastewater into septic tank badly sealed also contributes contamination in the lowest areas where the piezometric level is close to the ground surface. The high concentrations of dissolved salts featured the zones where the static level of the aquifer is less than 5m because of the more intensive agricultural activities (Fig. 8).



Fig. 8. Map of the distribution of nitrates in the study area.

In areas near the sea, a large amount of salts rich in Na⁺ / Cl⁻ are deposited on the surface of the soil in the form of sea spray or even dry deposition. In addition to the other processes described above, these deposits can be leached to the aquifer, all the more easily because of the shallow depth of the aquifer and the sandy-clay nature of the soils that promote rapid circulation of water. The marine origin of the salts is confirmed by the Br/Cl ratio (18 × 10⁻³), measured in the water of the wells near the coast in the lower zone of the plain (Youssef H *et al.*, 1999).

Couple SO42- / Cl- and Conductivity

The influence of these two elements on the electrical conductivity of the water was checked at graph 6. It is noted that the conductivity is influenced by chlorides only by sulphates. The graphical representation shows that 80% of points have a ratio of less than 1, indicating a dominance of chloride ions (marine influence) compared to gypsum ions (Fig. 09). It is also important to note that the high concentrations of sulphate ions are deposited in the surface waters due to the leaching of triassic formations crossed by the wadis before arriving to the plain.



Fig. 9. SO_4^{-2} according to Cl⁻ and SO_4^{-2}/Cl^- according to EC μ s/cm.

Isotopic study

Stable isotopic analysis data ¹⁸O and ²H deuterium (estimation error 0.05 and 0.08 ‰), from 46 water points over three different periods are analyzed at LRAE of Sfax "Tunisia", show a range of stable isotope contents varying between -5.42 and -3.12‰ for ¹⁸O and -31.52 and -21.25‰ for 2H. The average contents are - 4.53 and -27.37‰ for ¹⁸O and 2H respectively. The tritium (3H) analyzed with Sfax's LRAE, in addition, allows by its presence to identify the recent to very recent waters with respect to its natural atmospheric level (salines station, 3.5 UT) and with respect to the anthropogenic atmospheric peak resulting to the nuclear tests in the open air between 1950 and 1963, mainly located in the northern hemisphere, United States, Russia and Algeria.

In detail, the isotopic composition of the phreatic aquifer water makes it possible to distinguish two types of origins plus the origin of surface water (Fig. 10):

- Water from a direct infiltration of rainwater (group G1) whose isotopic composition varies between - 5.42 and -4.56 ‰ for ¹⁸O and -33.52 and -27.78 ‰ for ²H. On the diagram ¹⁸O vs ²H the representative points of this type of water are placed on and around the local meteorological line (d = 10) showing no significant evaporation with a deuterium excess generally greater than 10 (celle Jeanton *et al.*, 2001).

- These waters characterize samples from wells located in the central zone of the plain east of the city of Annaba. The low tritium values (greater than 1.5 TU) observed for these waters indicate, according to the age model used, that they came from a recent recharge after the 1950s (Craig, H. 1961).
- Evaporated water from a refill by return irrigation water (Group G2). This type of water, whose isotopic composition varies between -4.56 and -3.72‰ for ¹⁸O and -26.9 and -31.2‰ for ²H, characterizes the water points located in the downstream zone of the plain where the piezometric level of the aquifer is very low close to the ground surface.



Fig. 10. The meteoric line of the waters in the Meboudja and the low Seybouse plain.



Fig. 11. Histogram of tritium concentrations in groundwater and surface water of Meboudja and low Seybouse plain.

The tritium contents of this type of water vary between 1.9 and 3.1 UT. Evidence of a recent component (post-1980) and indicating current recharge from rainwater:

- A water of isotopic composition, -4.03 to -3.12 for ¹⁸O and -21.2 to -24.03 ²H, highly compared to those of the two preceding groups "group G3". This type of water characterizes the surface waters. Tritium contents have values ranging from 3UT to 3.9 UT. The five water points sampled at the wadis (M1, M2, M3, S1, and S2) show the highest tritium contents (between 3 and 3.9UT). (Fig. 11).

Conclusion

The geochemical and isotopic study of the phreatic aquifer water of Meboudja and the lower Seybouse plain made it possible to identify the different possible origins of the waters feeding the aquifer and to explain the effect of the intense anthropization observed in the study area.

It has been shown that the deterioration of groundwater quality is a direct result of contamination caused by intense agricultural activity that consumes a lot of water. The return of irrigation water into the aquifer causes salinization of water by chemical and organic fertilizers used by local farmers, marked by high levels of nitrates, especially in the central part of the highly exploited plain and in the surface water. Another fraction of the salts measured in the waters of the aquifer would result from the leaching of marine aerosols by rainwater.

In addition, the isotopic study made it possible to identify the current recharge areas of the aquifer and distinguish between different types of water with recent and old transfer.

To improve the understanding of the salinization mechanisms, to control and evaluate the origins of the salts, specific trace elements could be used, and for a more precise dating of the water, the use of anthropogenic markers like dissolved gases (CFC or SF6 or 85K), would allow a use more rational groundwater resource.

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