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GEOCHEMICAL AND ISOTOPIC INVESTIGATION OF SURFACE AND GROUNDWATER QUALITY IN THE PLAIN OF MEBOUDJA. ANNABA. N-E OF ALGERIA

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Abstract— An in-depth hydrogeological study of surface and groundwater resources using chemical and isotopic methods has been recently carried out in the Meboudja plain, Annaba (north-eastern Algeria). In this sector, the surface waters of rivers are permanent and therefore groundwater in mio-plio-quaternary formations is the source of water reserves used in domestic and agricultural domains.

The strong mineralizations are recorded in the wells located near the industrial discharges and on the edge of the Meboudja Wadi. Therefore Meboudja acts as a contaminants diffuse source throughout its stream.

A considerable concentration of tritium in underground water allowed a qualitative identification of the current component (^{3}H). It is assumed that this component is provided by recent rainfall at the plio-quaternary outcrop of the studied area.

The data deduced from the ^{18}O isotopes and the deuterium isotopes in the groundwater samples indicate a recharge with current precipitation. Water with lower ^{18}O and ^{2}H values is interpreted as being recharged by non-evaporated precipitation from higher-altitude Mediterranean air masses. However, it is believed that the water containing relatively enriched δ^{18}O and δ^2H contents reflects the presence of an evaporation process related to the long-term practice of flood irrigation.

Key-Words- *Meboudja plain. hydrochemical characteristics, stable isotope, industrial pollution, recharge of aquifers, Northeast of Algeria.*

I- INTRODUCTION

The area under study is located in eastern Algeria and it is part of the Annaba Plain. characterized by an average annual precipitation of 700 mm / year. It is drained in its western part by Meboudja stream, a canal drained the Fetzara lake of 14 km in length. The western border is characterized by metamorphic reliefs of the Edough mountain (1000m) and the down stream part is occupied by the Seybouse wadi. As in many other North African regions, water resources are limited in this eara.

The contamination of this resource by chemical fertilizers, pesticides, industrial and urban discharges. has been so intense that in certain sectors, particularly at the confluence of the two streams Meboudja and Seybouse, the environment has become hazardous to the fauna, flora and human health. In this sector, the Meboudja stream serves like an open seweage. Water, whether soft, salty, rainwater, groundwater or surface water, can be spoiled by materials that can make it harmful. It causes various diseases and can seriously alter health and the physical environment [1]. The aim of this study, therefore, is to determine the influence of pollutants on the aquatic environment (surface water and underground water).

II-Materials and methods

1. General settings

The Meboudja plain constitutes part of Annaba plain (NE, Algeria). It is bordered to the west by the dominant Edouch massif of Annaba, to the north by the Mediterranean Sea, to the east by the swamps of Mekrada and by the lake of Fetzara to the southwest. It is bounded on the south by the eastern prolongation of the Numidian chain (Fig.1)

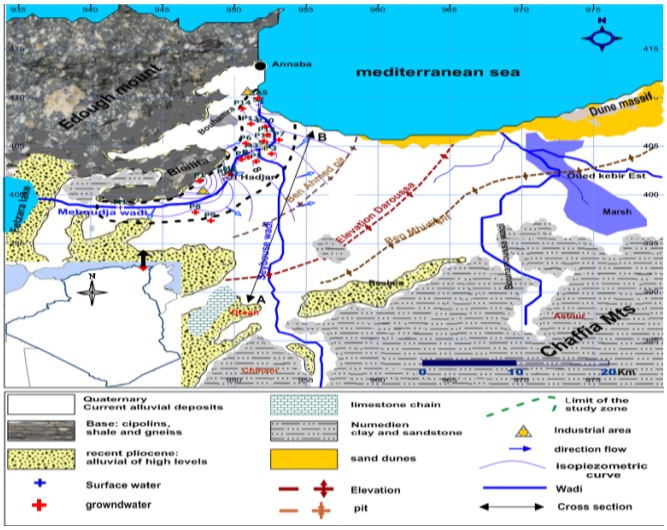

Fig.01 : geological map of Annaba.

The geology of the western boundary is characterized by the presence of a polycyclic metamorphic base (Edough mountain 1000m) covered by a Meso-Cenozoic tectonic roof and intersected by various magmatic rocks: peraluminous leucogranites in the Upper Burdigalian; sub-alkaline microgranites and peraluminous rhyolites in Langhien, [2]. To the south, we find the alluvial deposits of Lake Fetzara and the Numidian chain of the Chaffia Mountains. To the south-east, the Numidian flysch is set up during the Oligocene. Consisting of thick sandstone levels with 90-97% of quartz, the latter is based on pale-colored clays and all are covered by supra-Numidian clays [3]. (fig.1).

2. sampling and analysis procedure

Samples of the groundwater and surface water in the study area were collected intermittently in different seasons (October 2014, April 2015, and December 2015) to observe spatial and temporal variations in geochemical and isotopic parameters. the major elements (Na^+, Mg^{+2}, Ca^{+2}, K^+, Cl^-, SO_4^{-2}, HCO_3^- and NO_3^-) 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. 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 conducted using the LGR DLT 100 Laser Absorption Spectrometer [4]. The results are reported in the V-SMOW standard.

III- Results and discussion

1. Physico-chemical data

The physical and chemical characteristics of the groundwater samples show significant variations attributed to the spatial distribution of the geological facies in the studied plain. The total dissolved solids (TDS) values in surface water ranged from 663 mg / L to 1515 mg / L. The lowest TDS values are recorded in samples taken in October 2014 along the Meboudja stream from the SNS located upstream of the Meboudja to the confluence of the Meboudja and the Seybouse which is located downstream of the complex and the city of El Hadjar.

Surface water and groundwater reflect a great spatial variability of hydrochemical facies. The wide range of hydrochimical types indicates the variability of the chemical processes leading to the observed groundwater mineralization where the surface water represent Mg-Ca-HCO_3 and Ca-SO_4 and the water of the Meboudja plain is dominated by Ca^{+2} and SO_4^{-2}. This water is enriched with sulphate ions following the dissolution of the evaporite material present in the gypsum deposits, limestone and dolomitic limestone of Miocene outcrops. In addition, the surface water of the Meboudja and Seybouse wadis is classified as Mg-Na-Cl-SO_4.

The points on the Ca^{+2} curve with respect to SO_4^{-2} (Fig. 2b) can be grouped into 2 groups where

The first represents sampling points near the 1: 1 line (gypsum dissolution line) and showing a simultaneous increase in calcium and sulphate ions; this model indicates the same origin of the ions mentioned, which is the probable dissolution of gypsum and / or anhydrite. This process can be clearly confirmed by the linear evolution of gypsum and anhydrite saturation indices that are

calculated using the PHREEQC program and the sum of calcium and sulphate (Fig.2(b, d)).

The second group is formed by the phreatic aquifer samples (P11, P12, P6) and has a more pronounced excess of Ca^{2+} on the SO_4^{2-} ions; we believe that the origin came from the dissolution of carbonate minerals. As shown in (Fig. 2a), the points representing the upper aquifer samples fall either on or just above the 1:1 line of stoichiometric equilibrium.

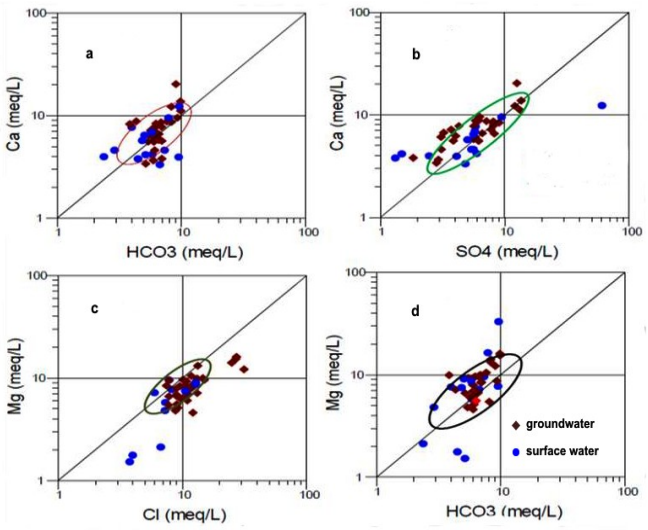

Fig.2 (a,b,c,d): Relationships between the various major elements : a- (Ca, HCO_3), b- (Ca, SO_4), c- (Mg, Cl) and d- (Mg, HCO_3).

The abundance of carbonate rocks (calcareous and dolomitic limestone) and erosion rates in the upstream zone of the plain suggest that the dissolution of carbonate minerals can potentially add significant quantities of Ca^{+2} and Mg^{+2} to the groundwater of the phreatic aquifer. The Mg^{+2} / Ca^{+2} ratios in this groundwater are maintained around 0.4 and 2.23. This model is compatible with an equilibrium control governed by calcite and dolomite minerals [5].

2. Isotopic study

Isotopic geochemistry techniques are valuable tools for studying many problems of hydrological and hydrogeological evaluation and the mechanisms of hydrochemical control in any groundwater system.

2.1 Isotopic composition of surface water

The values of $\delta^{18}O$ and $\delta^{2}H$ of the samples of the Meboudja and Seybouse streams vary from -3.49 to -4.03 and from -22.1 to -24.02 respectively. Seasonal differences in isotopic content in streams water can be determined by several factors, including moisture sources, amount of precipitation, weather conditions during evaporation, condensation and precipitation [6]-[7].

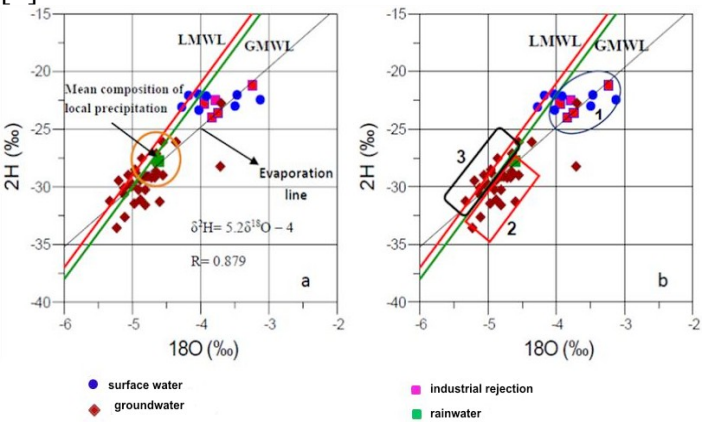

Fig.3 (a, b): meteoric line of surface and groundwater in Meboudja plain.

2.2 Isotopic Composition of groundwater

The average isotopic composition of groundwater is similar to the local precipitation recorded in the saline station (-5.02 for $\delta^{18}O$ and -30.1 for $\delta^{2}H$). This similarity in the isotopic composition between the majority of groundwater and local precipitation, indicates that groundwater has been recharged under similar climatic conditions as presently, prevailing in the region [7].

This in turn suggests that the groundwater of the studied plain is recharged at higher altitudes than the elevation of the local rainfall station (E = 10 m.a.l.). If we consider the $\delta^{18}O$ altitudinal gradient (G) 0.4‰/100 m [8], the aquifer recharge altitude (RA) is estimated according to the following equation:

RA = E + 100 × ($\delta^{18}O$ mean local rainfall- $\delta^{18}O$ Groundwater) / G.

The calculated values, between (3 m) and (167 m) m.a.s.l, coincide with the elevation of aquifer outcrops in the study area.

2.3. Tritium

The concentration of tritium in groundwater depends mainly on the initial atmospheric concentration at the time of recharge and the

radioactive decay that has occurred since in infiltration process [9].

The ^{3}H concentrations in the plain waters were measured during a sampling season. In October 2014, ^{3}H values varied between 1.6 TU and 3.8 TU while in April 2015 they varied between 1.8 and 3.2 TU. These data confirm that the storage and ground surface area have seasonal variations of the tritium content. It is therefore important to note that the isotopic signature of groundwater is obviously influenced by seasonality. It is largely controlled by atmospheric processes (precipitation, evaporation) and the Mediterranean Sea.

IV- Conclusion

In Annaba region (North-East of Algeria) a thorough hydrogeological investigation is required in order to determine the concentration of the major elements encountered in underground water and in surface water. Stable isotopes ($\delta\,^{18}O$, $\delta\,^{2}H$) and radiogenic (^{3}H) were used to provide basic information on groundwater chemistry control processes and to derive the recharge mechanism of the Méboudja plain.

The spatial distribution of salinity indicates that the salinity of underground water is somehow controlled by the different geological facies of the basin. The hydrochemical study shows the predominance of water type Ca, Mg, Cl, SO_4 in underground water and $CaSO_4$ in surface water resulting mainly from the interaction of rock water such as the dissolution of evaporate and carbonate minerals, cation exchange and silicate-feldspar-participating reactions.

Stable isotopic signatures indicate that most samples of underground water have a meteoric origin and are recharged under modern climatic conditions. Groundwater evaporated with relatively lower contents of $\delta^{18}O$ and $\delta^{2}H$ reflecting reflux at higher altitudes and evaporated water with heavy isotope enrichment demonstrate the appearance of a process of evaporation of the front surface or after infiltration into the unsaturated zone and groundwater. The samples taken from the surface water rivers show an $\delta\,^{18}O$ and ^{2}H enrichment, typical of water subjected to open surface evaporation in a Mediterranean region and revealing a significant seasonal evolution.

The tritium data confirm the modern recharge of water in the plain; this recharge is considered to have taken place in the mio-plio-quaternary alluvial overlays in the region of the lateral valley. The age estimates using stable isotope techniques corroborate the recent origin of groundwater in the basin.

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