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## Water Rock Interaction [WRI 14]

# Impact of rock weathering on the chemical composition of groundwater determined by inverse modeling in large sedimentary basins

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### Abstract

This study focuses on the geochemistry of groundwater in large Eocene aquifers sedimentary system with the main goals of investigating the influence of rock weathering and quantifying the inputs from each of several end-members (i.e silicate, carbonate, evaporite) by using an inverse method approach of budget equations. We report here the results obtained on 42 groundwater samples collected in a large aquifer (The) in the Adour-Garonne district (SW France). Mass budget equations solved using an inverse method allowed to estimate the contribution of the different sources among which, carbonate inputs dominate, evaporites often plays the second role, and silicate inputs may be important.

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### 1. Introduction

This study is part of ongoing research based mainly on the major element composition of groundwater from the sedimentary Eocene aquifer system in the Adour-Garonne district of southwest France. This aquifer covers an area of 116 000 km<sup>2</sup> and represents 1/5 of the French territory [1]. It is limited by the Massif Central to the east, by the Armorican Massif to the north, by the Pyrenees to the south and by the Atlantic Ocean to the west (Fig. 1). The Eocene aquifer system constitutes a series of major aquifers used

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for drinking water, agriculture irrigation, thermo-mineral water resource and gas storage. The Eocene aquifer, composed of sandy Tertiary sediments alternating with carbonate deposits, is a multi-layer aquifer being artesian to the west of the district and confined with piezometric levels around 250 m depth to the east of the district. The Eocene aquifer system is characterized by a high permeability and a thickness of several tens to a hundred meters, and is made up of at least five aquifers: Paleocene (P), Eocene Infra-Molassic Sands (IMS), Early Eocene (EI), Middle Eocene (EM), Late Eocene (ES). The deposit sequences characterizing the Eocene aquifer system are progradational westward, from detrital deposits to carbonates with evaporites domes. Groundwater recharge may occur to the east at the edge of the Massif Central, to the south at the edge of the Pyrenees and by inflow from the Paleocene aquifer. The mineralogy of the sand deposits is very simple, consisting mainly of quartz augmented with calcite and at places dolomite and K-feldspars.

The potentiometric surface is characterized by a trough in the north of the Aquitaine Basin due to extensive long-term groundwater abstraction. The historical decline of the potentiometric surface has been roughly one meter per year in the center of the basin. In the south, this surface shows a decline of the water table in the IMS Eocene and in the Paleocene aquifer, which is less of a decline than in the north (around half meter per year). In some areas of Eocene or Paleocene outcrops a rainfall influence inducing direct aquifer recharge can be seen in the water table evolution (P-4). The main flows in the ISM aquifer are from East to North-West and from the North Pyrenean Front to the North and from the South-East to the North-West for the Paleocene flow. Anthropogenic activities such as agricultural practices does not influence the chemical composition (no nitrates, residence time of the water > 5ka). This study complements previous investigations using isotopes [1-3] that revealed three main weathering end-members (evaporate dissolution, weathering of silicate minerals, and input from carbonates) plus rainwater input. This study aims at quantifying the inputs from each of these end-members by applying the inverse technique to optimize the estimation of the different sources [4]. A total of 42 groundwater samples were collected from borewells in the Eocene sands water body (Fig. 1, [1, 2]). The water samples were chemically analysed by analysed by ionic chromatography (Cl, SO<sub>4</sub>, NO<sub>3</sub>), induced coupled plasma atomic emission spectrometry (Ca, Na, Mg, K) and inductively coupled plasma mass spectrometry (Sr).

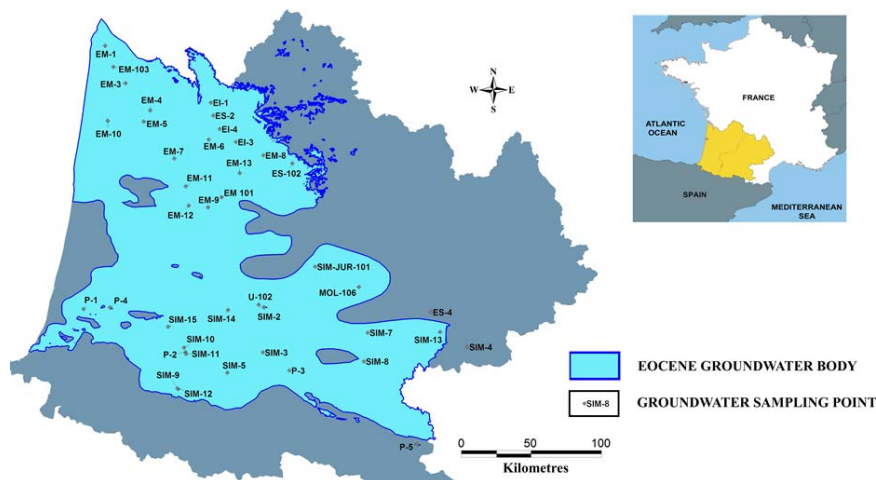


Fig. 1: Hydrogeologic framework of the Eocene aquifer in the Bassin d'Aquitaine, groundwater sampling points.

## 2. Geochemical data

### 2.1. Salinity of the groundwater and water types

The Total Dissolved Solids (TDS, the total mineralization of water calculated by summing cations and anions) have large variations between 74 (P-3) and 2513 mg/l (SIM-8). Variations within the same aquifer are also significant, from 74 up to 1253 mg/l in the Paleocene aquifer; from 255 up to 1033 mg/l in the middle Eocene aquifer and from 230 up to 2513 mg/l in the Eocene infra-molassic sand (IMS). The highest mineralization is generally encountered in water draining evaporite formations (gypsum and/or halite) as evidenced in the southern part of the aquifer. The spatial distribution of the TDS values indicates several places having salinities > 1000 mg/l, the highest being observed in the southeast part of the basin. Waters from the Eocene sands aquifer are mostly calcium bicarbonate type but sodium bicarbonate, sodium chloride and sodium sulphate waters can be observed in several locations. For example, in the Eocene infra-molassic sand, the calcium bicarbonate type is predominantly observed, changing eastward to sodium chloride and then to sodium bicarbonate. These water types reflect the geology of the basin, from silicates to carbonates and evaporites deposits (west and north of the basin).

## 3. Contribution of rain and rock weathering to ground water chemical compositions

For a given lithology, depending on the residence time, water fluxes, water-rock interactions and possible dilution/evaporation effects, a range of concentrations in dissolved element concentrations are reached. In order to compensate for the variable influence of these effects, concentrations of dissolved elements are commonly normalized to Na concentrations [4, 5]. Mg/Na versus Ca/Na molar ratios of groundwater are reported in Fig. 2a in which mixing between two end-members is represented by a straight line, as illustrated for the calculated relationship between the carbonate and evaporite end-members. In addition to the clear trend observed between Mg/Na and Ca/Na molar ratios, some sampling points (SIM-7, 8 and SIM-13) cannot be explained by the general mixing scheme. The main trend observed in Fig. 2 corresponds to the evolution between halite dissolution and partial silicate dissolution (low Mg/Na and Ca/Na molar ratios) and carbonate dissolution (high Mg/Na and Ca/Na molar ratios). Cyclic salts [5] inputs as represented by seawater play a weak role in the origin of the groundwater compositions [3]. The 4 samples plotting outside the mixing field may be impacted by carbonate precipitation as Ca contents are among the lowest (<0.4 mmol L<sup>-1</sup>) and groundwaters are oversaturated with respect to calcite and dolomite [2, 3]. As a complementary approach to determining chemical sources, the Sr isotope and Ca/Sr compositions of the groundwaters allow additional constraint on the different end-members as shown by Négrel et al. [3]. Sr isotopes are particularly useful for identifying the weathering of evaporite formations (as their <sup>87</sup>Sr/<sup>86</sup>Sr ratio of around 0.7075 is that of Eocene marine evaporites), the weathering of carbonates (as the increase in the Ca/Sr ratio suggests) and the weathering of silicate (as the more radiogenic value of around 0.715 refers to). Variations of boron isotopes confirm this mixing by coupling with the observed lithologies in the boreholes plus the rainwater inputs [1] ( $\delta^{11}\text{B}$  around 0‰ for silicate, 20‰ for carbonate and evaporites ([B] around 10 and 2000  $\mu\text{g/L}$ , respectively).

Having constrained the end-members, we formalize the mixing model for the major ions, constrain the source reservoirs that correspond to the identified end members in the groundwater, and we test this model using an inversion scheme similar to that presented by Négrel et al. [4]. Details on the mixing model equations, the inverse method of resolution and choice of the end-member ratios are given in [4] and [5]. The model presented above was applied to the groundwaters and allowed to calculate the proportions of major ions (Na, Ca, Mg...) derived from rain and from silicate, carbonate and evaporite weathering. From the mass balance point of view, the global contribution of each end-member was

obtained by summing the individual contribution of each element. The inversion results are illustrated in Fig 2b for some selected groundwater samples identified in Fig.2a: EM9 from the mid Eocene, SIM 2, 4, 15 from the Eocene Infra-Molassic Sands aquifer; carbonate inputs dominate the groundwater chemistry with regards to major ions, particularly for SIM2 (>90%) and evaporite often plays the second major role as in EM9 (around 27%). Rainwater inputs are always negligible. Silicate inputs may be important as in SIM15 (around 11%).

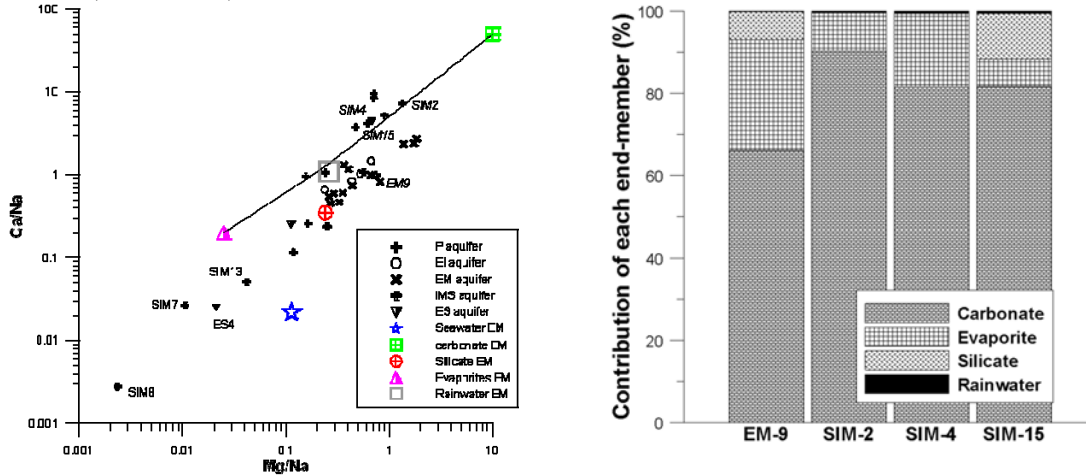


Fig. 2: (a) Mixing diagrams using Na-normalized molar ratios in the groundwaters; (b) illustration of the contribution of the end-members for selected groundwater samples

This work highlights the potential use of the inversion scheme previously defined and largely used in river basins [4, 5]. The inverse method constituted of several mass budget equations and solved using the best set of values for the parameters among those that verify the equations is particularly adapted for the purpose of this study where we want to extract the rock components (carbonate, evaporites and silicate) from the groundwater.. Further work will concern extension of the technique to the whole Aquitanian Basin, as well as other large basin like the Parisian Basin.

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