

Dynamic of Sea Water Interface using Hydrochemical Facies Evolution Diagram

by Elena Giménez-Forcada

Abstract

This paper analyzes the results of a theoretical simulation of sea water intrusion and its dynamics. The assignment of hydrochemical facies identifies whether the aquifer is in the phase of sea water intrusion or freshening, indicating the status of the aquifer in terms of the advance or regression of the saline front. A new multi-rectangular diagram is proposed that aids interpretation of these important processes through the representation and evolution of hydrochemical facies (hydrochemical facies evolution diagram, HFE-D). As an example, the HEF-D is applied to an alluvial aquifer in the Vinaroz-Peñíscola Plain (Spain), where Ca-Cl facies characterize the sea water intrusion phase, while Na-MixHCO₃/MixSO₄ facies characterize a freshening stage.

Introduction

In coastal aquifers it is important to realize that sea water intrusion is a dynamic, not a static, process that depends on the periodic changes in the recharge-discharge balance of the aquifer. Any influence, direct or indirect, on the aquifer's water balance affects the position and movement of the sea water interface and chemistry of the groundwater.

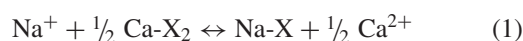
The relationship between the dynamic movement of the sea water interface and the hydrochemistry of groundwater suggests that a study of the chemical variations will allow the phase of sea water intrusion of the aquifer to be identified as well as the evolution and dynamics of the saline front (phases of sea water intrusion or freshening) within the aquifer.

The aims of this paper are to identify the hydrochemical facies that characterize each stage of intrusion and freshening, and to introduce a new type of diagram

that aids identification of the processes occurring and the evolution of the hydrochemical facies, which taking into account the dynamic character of sea water intrusion.

Cation Exchange Reactions and Dynamics of Sea Water Intrusion

Ion exchange processes are useful in the study of the dynamic of sea water intrusion occurring in coastal alluvial aquifers. The following cation exchange reaction takes place (Appelo and Postma 2006):



During sea water intrusion, reverse cation exchange occurs (Na\Ca) (\rightarrow), while direct cation exchange (Ca\Na) moves in the opposite direction (\leftarrow). The Ca-Cl facies is recognized as the clearest feature of the advance inland of the saline wedge, while the Na-HCO₃ facies characterizes the freshening phase.

Appelo and Willemssen (1987), Appelo et al. (1990), Beekman (1991), Boluda (1994), and Lambrakis and Kallergis (2001), among others, have studied this type of situation using laboratory simulations, based on the principles of ion chromatography and/or geochemical modeling. Appelo and Willemssen (1987) simulated the intrusion process using a geochemical model based on experimental chromatographic studies, using dilute sea

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water. Boluda (1994) also simulated this phenomena with nondiluted sea water and verified the increase in concentration of Cl^- , SO_4^{2-} , Na^+ , K^+ , and Mg^{2+} to reach the concentration in sea water, as well as different behaviors of Ca^{2+} , whose concentration initially experienced a spectacular, sharp increase resulting from the Na/Ca ion exchange. This feature was also linked to the precipitation of gypsum (Boluda 1994, Gomis et al. 1996, Gomis-Yagües et al. 2000).

In the freshening stage, experiments by Beekman (1991) offer a model that simulates the recovery of the aquifer. The $\text{Ca}-\text{HCO}_3$ fresh water displaces the saline water with which the aquifer had been in equilibrium. The process entails a series of reactions that sequentially cede Na^+ (and Mg^{2+}) to the solution, in exchange for Ca^{2+} , which is retained in the exchange complex.

Using geochemical simulation models, Lambrakis and Kallergis (2001) studied the multicomponent ion exchange process and freshening time under natural recharge conditions (in this case, $\text{Ca}, \text{Mg}-\text{HCO}_3$ water). They detected an exchange process involving $\text{Ca}, \text{Mg}/\text{Na}$ in which the $\text{Ca}, \text{Mg}-\text{HCO}_3$ water is converted into water dominated by $\text{Na}-\text{HCO}_3$. They concluded that partial restoration can be achieved, resulting in water similar to the recharge water, but that complete restoration of the aquifer is practically impossible due to the long time period required. Indeed, it is uncommon for an aquifer to reach the final phase of intrusion or recovery; more commonly, there is an alternation of incomplete periods of both processes.

In general terms, the results of both simulations indicate that Na/Ca and Ca/Na exchange, as well as the equilibria with the carbonate and sulfate minerals (calcite and gypsum) are the principal processes that control the composition of groundwater in a coastal alluvial aquifer affected by sea water intrusion.

Hydrochemical Facies in the Sea Water Intrusion and Freshening Stages

The methodology of classification proposed in the current study takes into account the one proposed by Stuyfzand (1993). Although this study does not change the basic criteria, it proposes a classification that has regard only to the percentages of major ions implicated in the hydrochemical processes that are related to the dynamics of sea water intrusion (Ca^{2+} , Na^+ , HCO_3^- , SO_4^{2-} , and Cl^-).

The facies is determined as a function of the percentage of Ca^{2+} and Na^+ cations, and HCO_3^- (or SO_4^{2-}) and Cl^- anions with respect to the sum of cations and anions, respectively. The facies are identified using the term *Mix* to indicate that the percentage of the cation or anion is less than 50%, but at the same time it is more than the percentage of any of the other cations and anions considered.

When complex processes are simplified it is inevitable that certain lower order considerations are sacrificed. This occurs when the discussion does not take into account the

ions occupying a secondary position in the two end members (fresh water and sea water), as is the case for SO_4^{2-} , Mg^{2+} , and K^+ . The $\%\text{SO}_4^{2-}$ is considered an alternative to $\%\text{HCO}_3^-$ because both can represent the principal anion in the recharge water (fresh water). The Mg^{2+} ion has an irregular behavior in exchange reactions and for this reason $\%\text{Mg}^{2+}$ is not taken into account in the exchange processes. Lastly, the percentage sodium incorporates the percentage of potassium, as the concentration of K^+ is generally much lower than that of Na^+ .

Diagram to Identify Hydrochemical Facies Evolution (HFE) in the Intrusion and Freshening Stages

Among the popular graphical representations of water, chemistry and hydrochemical facies are triangle diagrams, which show concentrations as percentage meq/L of the total anions and cations; water with different chemical composition is represented by a point at a different position in each triangle. Until now, when a single diagram is needed to represent the cationic and anionic facies (e.g., the piper diagram) the right and top vertices (Cl^- and SO_4^{2-}) from the right-hand triangle (anions) and the left and upper (Ca^{2+} and Mg^{2+}) vertices of the left-hand triangle (cations) must be grouped together. The sum is represented in the central field ($\%\text{Cl}^- + \%\text{SO}_4^{2-}$) against $\%\text{HCO}_3^-$, and the sum ($\%\text{Ca}^{2+} + \%\text{Mg}^{2+}$) against ($\%\text{Na}^+ + \%\text{K}^+$). It is not simply that a single point represents a unique facies, but that the point also takes on the corresponding interpretation, so that the sum or representation of the two ions in the same field of the diagram implies a similar behavior of both water types, or the value of a parameter in the interpretation of a process is reinforced.

In the current study, an alternative diagram is introduced to solve this problem. In some aspects, it is similar to the multi-rectangular diagram (MRD) proposed by Ahmad et al. (2003) and in other aspects to the piper trilinear diagram in rectangular coordinates, proposed by Ray and Mukherjee (2008). This new diagram can also be used to represent the main processes that intervene in a coastal aquifer and so allow the stages of saline advance or withdrawal to be recognized by studying the evolution of the hydrochemical facies.

In the proposed diagram (Figure 1), the abscissae represent, separately, the percentages of Na^+ and Ca^{2+} in meq/L, reproducing the base-exchange reactions. If water contains a percentage Ca^{2+} greater than that of Na^+ , then the percentage Ca^{2+} is represented; while if the opposite occurs, the percentage of Na^+ is plotted. The values are calculated using the total sum of cations (including Mg^{2+}).

The ordinates represent the percentages of anions: the percentage of chloride represents sea water and the percentage of bicarbonate or sulfate (depending on the dominant anion in fresh water) characterizes the recharge water. In other words, the percentages of SO_4^{2-} and

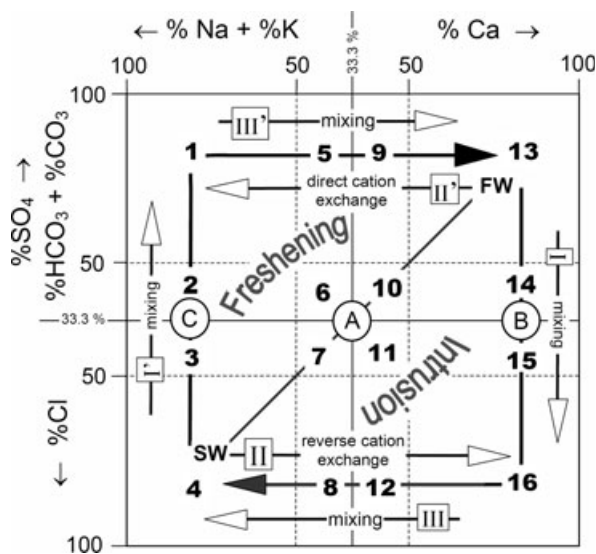


Figure 1. HFE-D showing the main processes occurring in intrusion and freshening stages. In order to draw the lines of evolution of facies, it was decided to eliminate the values of calcium and sodium percentages between 0% and 33.3%. In a sample where the %Ca is less than 33% the point would be represented in the quadrant corresponding to the %Na. 1: Na-HCO₃/SO₄, 2: Na-MixHCO₃/MixSO₄, 3: Na-MixCl, 4: Na-Cl, 5: MixNa-HCO₃/SO₄, 6: MixNa-MixHCO₃/MixSO₄, 7: MixNa-MixCl, 8: MixNa-Cl, 9: MixCa-HCO₃/SO₄, 10: MixCa-MixHCO₃/MixSO₄, 11: MixCa-MixCl, 12: MixCa-Cl, 13: Ca-HCO₃/SO₄, 14: Ca-MixHCO₃/MixSO₄, 15: Ca-MixCl, 16: Ca-Cl. (A) Mixing between end members: fresh water-sea water; (B) HFE evolution in intrusion period; (C) HFE evolution in freshening period. (I) and (I') initial process of mixing in intrusion and freshening stages; (II) and (II') reverse and direct base-exchange reactions; (III) and (III') mixing during the later stages of each process until reaching equilibrium with the chemical facies of the dominant flow.

HCO₃⁻ are not summed, but rather are represented by choosing the ion present in higher percentage (e.g., the Na-HCO₃/SO₄ facies can represent both the Na-HCO₃ facies and the Na-SO₄ facies). If there is water of both facies then the sample will be represented using the percentage of bicarbonate (if %HCO₃⁻ > %SO₄²⁻) or sulfate (if %SO₄²⁻ > %HCO₃⁻), and this will be indicated in the center of the diagram using different symbols. The result is a representation of 4 heterotopic facies (Na-HCO₃, Na-Cl, Ca-HCO₃, and Ca-Cl) out of 16 facies (or 6 out of 24 facies if one takes into account that sulfate and bicarbonate water can coexist).

The hydrochemical facies evolution diagram (HFE-D) was applied to the data from an alluvial aquifer on the East Coast of Spain (Vinaroz-Peñíscola Plain; Figures 2a and 2b) where samples were taken in both summer and winter. The samples collected in summer generally correspond to hydrochemical facies that indicate a generalized sea water intrusion through the aquifer, while the winter samples indicate that certain parts of the aquifer are in a phase of recovery related to the recharge water. The presence of water with a sulfate facies indicates that the recharge water can be either bicarbonate or sulfate type.

During the intrusion phase, the exchange reactions are more evident, while during the recovery phase, the water samples are positioned close to the trend line that represents simple binary mixing between fresh water and sea water (although one can recognize facies typical of this new stage by incipient reactions of direct ion exchange).

Plotting the samples on a piper diagram (Figure 2c) and integrating the interpretation of the phases of freshening and intrusion (Al-Agha and El-Nakhal 2004) confirms that in the central diamond-shaped field there is an evolutionary trend for each stage of the process (intrusion and freshening), but it is difficult to recognize the sequence of facies in detail and therefore the succession and interpretation of processes. In contrast, this is possible using the HFE-D.

Samples collected in Vinaroz-Peñíscola Plain are represented in Figure 2a. The fresh water corresponds to the facies Ca-HCO₃/SO₄ (13), while the sea water belongs to the Na-Cl facies (4). The succession of facies along the line of mixing (A) (4-7-10-13) (Figure 1) indicates simple binary mixing with little or no intervention of base-exchange reactions. During the phase of sea water intrusion, to the right and beneath line (A), there is an initial increase in salinity and a rapid and marked reverse exchange of Na/Ca, which is recognized by the characteristic Ca-Cl facies (16) (evolution 13-14-15-16). Finally, this type of water evolves toward facies that are closer to sea water (Na-Cl) (4) (evolution 16-12-8-4). In the freshening stage, to the left and above the line (A), direct exchange processes occur more slowly; the water gain Na⁺ and cede Ca²⁺ until Na-HCO₃/SO₄ (1) facies is achieved (evolution 4-3-2-1). In Vinaroz-Peñíscola Plain only the facies Na-MixHCO₃/MixSO₄ (2) is reached. Later, the water evolves toward types that are closer to recharge freshwater (13) (evolution 1-5-9-13).

As general argumentation (see Figure 1), in the case of intrusion the water will first increase in salinity (line I) and this triggers, almost simultaneously, the development of reverse exchange reactions (line II), resulting in the characteristic composition CaCl; finally, the water evolves along line (III), which represents the final mixture and the trend of the water composition toward that of sea water (NaCl). Something similarly occurs in the case of freshening: the change in chemical composition causes the onset of direct ion exchange reactions (lines I' and II'). In the last stage of the process, the trend toward the composition of the recharge water that participates in the recovery of the aquifer causes the water to evolve along line III', which represents the ultimate stages of this phase.

Conclusions

The proposed classification of water by hydrochemical facies employs the percentage content of the principal major ions. Representation of the percentages of Ca²⁺ and Na⁺ identifies the direct and reverse ion exchange reactions, as well as water mixing. Representation of the percentage of anions such as %Cl⁻ (sea water), %HCO₃⁻,

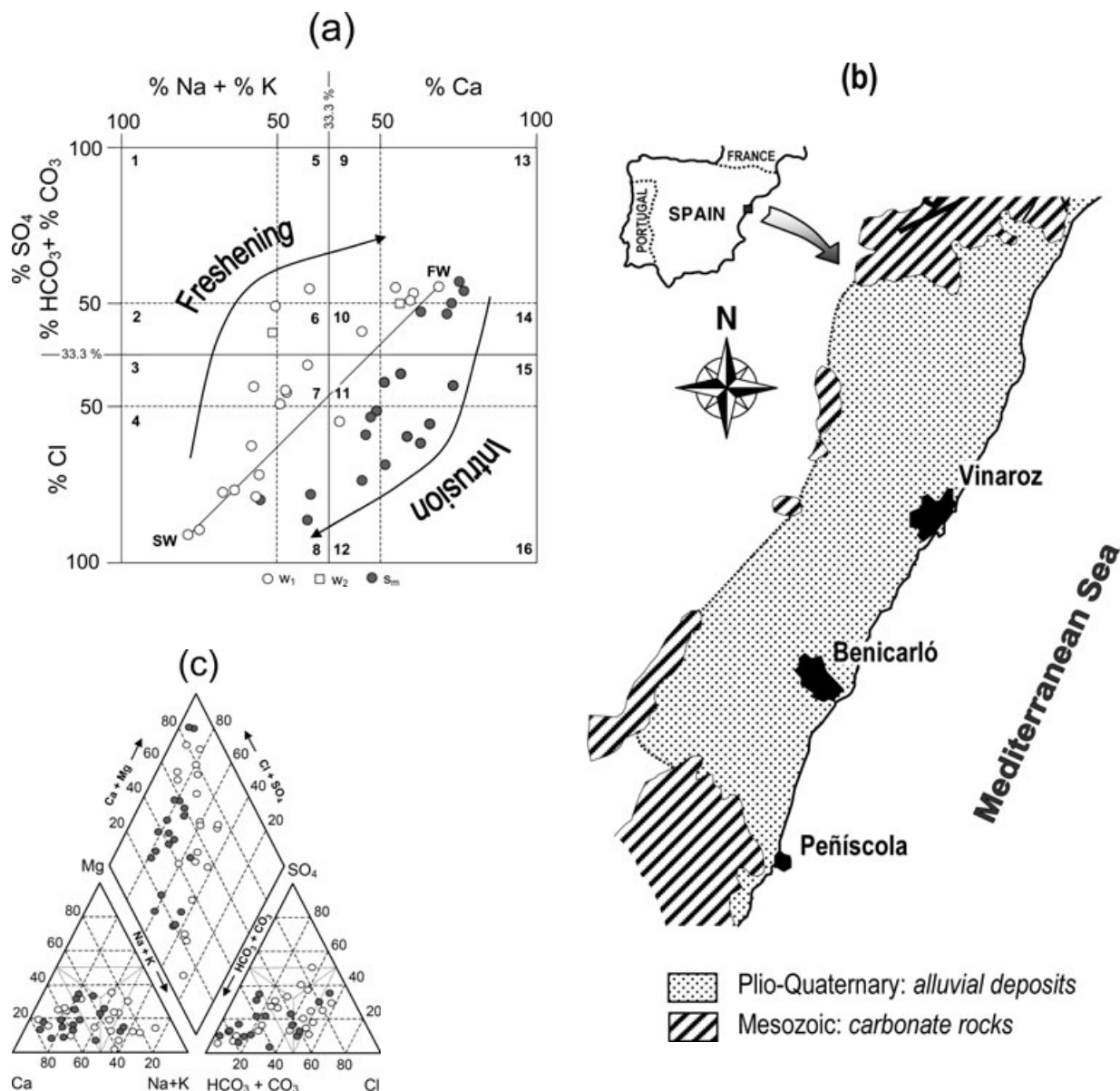


Figure 2. Application of HFE-D to the coastal aquifer of Vinaroz-Peñíscola Plain. (a) The winter samples are located in the area associated with the freshening stage (HCO_3 water [W_1] and SO_4 water [W_2]), while the samples taken in summer (S_m) are represented mainly in the part corresponding to the intrusion stage. (b) The map (top right) shows the location of the Vinaroz-Peñíscola Plain. (c) The piper diagram (bottom right) shows the summer and winter samples, and their evolution in each phase. The concentrations of NO_3 were not considered in the calculation of the percentages of anions. FW, fresh water; SW, sea water.

or SO_4^{2-} (recharge water) identifies the mixing processes occurring.

One of the advantages of the HFE-D is that it can be modified and adapted to each case; that is, it does not require that the behavior of one ion be linked to that of any other, but rather it permits the choice of which ions are represented and/or the way in which they are grouped together. In the case detailed here, the HFE-D identifies the sequence of facies and the processes identified in theoretical and experimental simulations of the movement of the sea water front in the intrusion and freshening phases. The HFE-D is another complementary tool that can be applied in the analysis and discussion of similar situations.

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