Methods Note

Dynamic of Seawater Interface using Hydrochemical Facies Evolution Diagram (HFE-D)

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Abstract
This paper analyses the results of a theoretical simulation of seawater intrusion and its dynamics. The assignment of hydrochemical facies identifies whether the aquifer is in the phase of seawater 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 example, the HEF-Diagram has been applied to Vinaroz-Peñíscola Plain (Spain) and good results have been obtained.

Key words: Salt water intrusion

Introduction
In coastal aquifers it is important to realise that seawater 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 seawater interface and the chemistry of the groundwater.

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

The aims of this paper are to identify the hydrochemical facies that characterise 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 takes the dynamic character of seawater intrusion into account.

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

\[ \text{Na}^+ + \frac{1}{2} \text{Ca-X}_2 \leftrightarrow \text{Na-X} + \frac{1}{2} \text{Ca}^{2+} \]
During seawater intrusion, reverse cation exchange occurs (Na\Ca) (→), whilst direct cation exchange (Ca\Na) moves in opposite direction (←). The Ca-Cl facies is recognised as the clearest feature of the advance inland of the saline wedge, while the Na-HCO₃ facies characterises the freshening phase.

Several authors such as Appelo and Willemsen (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 modelling.

Appelo and Willemsen (1987) simulated the intrusion process using a geochemical model based on experimental chromatographic studies, using dilute seawater. Boluda (1994) simulated also this phenomena with non diluted seawater and verified the increase of concentration of Cl⁻, SO₄²⁻, Na⁺, K⁺ and Mg²⁺ until to reach the concentration in seawater, as well as the different behaviour of Ca²⁺, whose concentration initially experimented 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 Ca-HCO₃ 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 Mg²⁺) to the solution, in exchange for Ca²⁺, 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, Ca,Mg-HCO₃ waters). They detected an exchange process involving Ca,Mg\Na and in which the Ca,Mg-HCO₃ waters are converted into Na-HCO₃ ones. 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 the two 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 sulphate minerals (calcite and gypsum) are the principal processes that control the composition of the groundwater in a coastal alluvial aquifer affected by seawater intrusion.

**Hydrochemical facies in the seawater 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 seawater intrusion (Ca²⁺, Na⁺, HCO₃⁻, (SO₄²⁻) and Cl⁻).

The facies is determined as a function of the percentage of Ca²⁺ and Na⁺ cations, and HCO₃⁻ (or SO₄²⁻) and Cl⁻ anions with respect to the sum of cations and anions, respectively. The facies can use the term Mix to indicate that the percentage of the cation or anion is less than 50% but at the same time greater 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 (freshwater and seawater), as is the case for SO₄²⁻, Mg²⁺ and K⁺. The %SO₄²⁻ is considered as an alternative to %HCO₃⁻ because both can
represent the principal anion in the recharge water (freshwater). The Mg\(^{2+}\) ion has an irregular behaviour in exchange reactions and for this reason %Mg\(^{2+}\) is not taken into account in the exchange processes. Lastly, the percentage sodium incorporates the percentage of potassium, since 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**

Various types of graphical representations of water chemistry and hydrochemical facies exist. Triangle diagrams show concentrations as percentage meq/L of the total anions and cations, in which waters with different chemical composition are represented by a point at a different position in the 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 (%Cl\(^-\) %SO\(_4^{2-}\)) against %HCO\(_3^-\), and the sum (%Ca\(^{2+}\) %Mg\(^{2+}\)) against (%Na\(^+\) %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 behaviour 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 Rajan 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 recognised by studying the evolution of the hydrochemical facies.

In the diagram proposed in the current paper (Figure 1), the abcissae represent, separately, the percentages of Na\(^+\) and Ca\(^{2+}\) in meq/L, reproducing the base exchange reactions. If the water contains a percentage Ca\(^{2+}\) greater than that of Na\(^+\), then the percentage Ca\(^{2+}\) is represented; whilst 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 seawater and the percentage of bicarbonate or sulphate (depending on the dominant anion in freshwater) characterises the recharge water. In other words, the percentages of SO\(_4^{2-}\) and HCO\(_3^-\) are not summed, but rather are represented by choosing the ion present in higher percentage (e.g. the Na-HCO\(_3\)/SO\(_4\) facies can represent both the Na-HCO\(_3\) facies and the Na-SO\(_4\) facies). If there are waters of both facies then the sample will be represented using the percentage of bicarbonate (if %HCO\(_3^-\) > %SO\(_4^{2-}\)) or sulphate (if %SO\(_4^{2-}\) > %HCO\(_3^-\)), and this will be indicated in the centre of the diagram using different symbols.

The result is a representation of four heterotopic facies out (Na-HCO\(_3\), Na-Cl, Ca-HCO\(_3\) and Ca-Cl) of a total of sixteen facies (or 6 out of 24 facies if one takes into account that sulphate and bicarbonate waters can coexist).

The HFE-D was applied to data from a alluvial aquifer on the eastern coast of Spain (Vinaroz-Peñíscola Plain; Figures 2a, 2b) where samples were taken in both summer and winter periods. The samples collected in summer generally correspond to hydrochemical facies that indicate a generalised seawater intrusion through the aquifer, whilst 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 sulphate facies indicates that the recharge waters can be either bicarbonate or sulphate 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 freshwater and seawater (although one can recognise 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 (see 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 recognise the sequence of the facies in detail and therefore the succession and interpretation of processes. In contrast, this is possible using the HFE-D.

![Figure 1](image_url)

**Figure 1.** Hydrochemical Facies Evolution Diagram (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%. It must be borne in mind that 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/MixSO₄, 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: freshwater-seawater; (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.

In figure 2a, samples collected in Vinaroz-Peñíscola Plain are represented. The fresh water correspond to the facies Ca-HCO₃/SO₄ (13), whilst the seawater belongs to Na-Cl facies (4). The succession of facies along the line of mixing (A) (4-7-10-13) indicates simple binary mixing with little or no intervention of base exchange reactions.
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 (HCO3 waters (w1) and SO4 water (w2)), while the samples taken in summer (Sm) 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 NO3 have not been considered in the calculation of the percentages of anions.

FW: freshwater; SW: seawater.
During the phase of seawater 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 recognised by the characteristic Ca-Cl facies (16) (evolution 13-14-15-16). Finally, this type of water evolves towards facies that are closer to seawater (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 waters gain Na⁺ and cede Ca²⁺ until Na-HCO₃/SO₄ (1) facies is achieved (evolution 4-3-2-1). In Vinaroz–Peñíscola Plain only it is reached the facies Na-MixHCO₃/MixSO₄ (2). Later, the waters evolves towards type 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 (evolutive line I) and this triggers, almost simultaneously, the development of reverse exchange reactions (evolutive line II), resulting in the characteristic CaCl; finally, the evolutive line (III) develops, which represents the final mixture and the trend of the water composition towards that of seawater (NaCl). Something similar occurs in the case of freshening: the change in chemical composition causes the onset of direct ion exchange reactions (evolutive lines I' and II'). In the last stage of the process, the trend towards the composition of the recharge water that participates in the recovery of the aquifer causes the production of the facies evolution (III'), which represents the ultimate stages of this phase.

**Conclusions**

The proposes classification of the 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⁻ (seawater), %HCO₃⁻ or %SO₄²⁻ (recharge water) identifies the mixing processes occurring.

One of the advantages of the HFE-Diagram is that it can be modified and adapted to each case; i.e., it does not oblige that the behaviour of one ion be linked to that of any other, but rather is permits the choice of which ions are represented and/or the way in which they are grouped together in the representation.

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 seawater front in the intrusion and freshening phases. It should be borne in mind that, in any case, the HFE-D must be considered as another complementary tool that can be applied in the analysis and discussion of similar situations.

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**References**


