Methods Note

An Excel Macro to plot the HFE-Diagram to identify seawater intrusion phases

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Abstract

A Hydrochemical Facies Evolution Diagram (HFE-Diagram) is a multi-rectangular diagram, which is a useful tool in the interpretation of seawater intrusion processes. This method note describes a simple method for generating an HFE-D plot using the spreadsheet software package, Microsoft Excel. The code was applied to groundwater from the alluvial coastal plain of Grosseto (Tuscany, Italy), which is characterized by a complex salinization process in which seawater mixes with sulphate or bicarbonate recharge water.

Key words: HFE-Diagram, Excel macro, Hydrochemistry, Seawater intrusion, Grosseto Plain, Italy

Introduction

The salinization of coastal aquifers due to seawater intrusion can be summarized as the mixing between the recharge water or freshwater (usually calcium bicarbonate facies) and seawater (sodium chloride facies), considered alongside the capacity of the aquifer to alter groundwater chemistry through chemical reactions. The dynamics of seawater intrusion, with its alternating freshening and seawater intrusion, can be recognized by the evolution of the chemistry of the major ions over time. In this note, a simple method to generate a Hydrochemical Facies Evolution Diagram (HFE-Diagram) is described, which can assist in the interpretation of marine intrusion processes through the representation of the evolution of hydrochemical facies (Giménez-Forcada 2010; Giménez-Forcada 2014).

An HFE-Diagram considers the percentage of the four most significant ions and their relationships, giving sixteen possible hydrochemical facies (thirty two if Mg^{2+} and SO_4^{2-} participate with HCO_3^- and Ca^{2+}) (Figure 1).
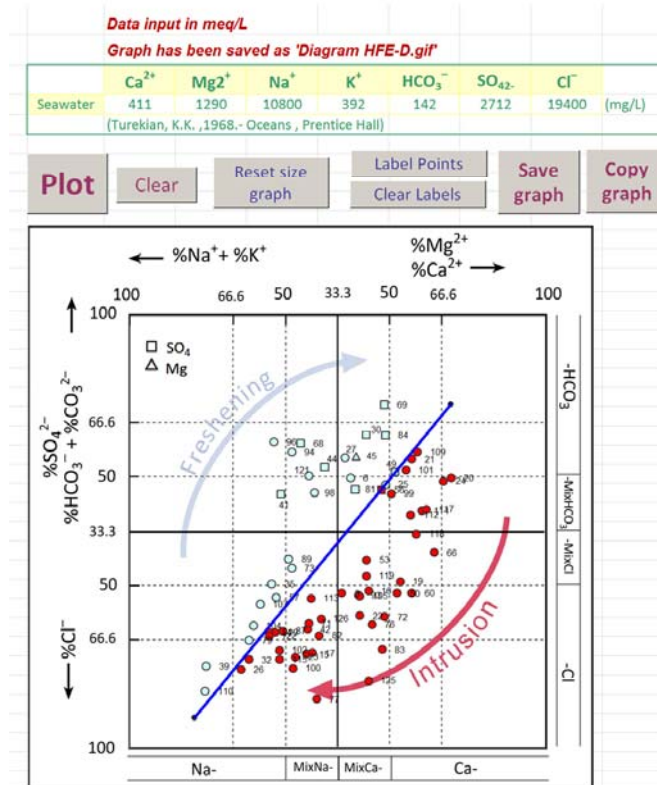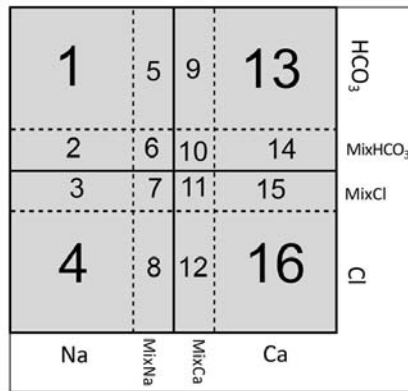
Figure 1. HFE-D showing the sixteen facies. 1: Na-HCO$_3$, 2: Na-MixHCO$_3$, 3: Na-MixCl, 4: Na-Cl, 5: MixNa-HCO$_3$, 6: MixNa-MixHCO$_3$, 7: MixNa-MixCl, 8: MixNa-Cl, 9: MixCa-HCO$_3$, 10: MixCa-MixHCO$_3$, 11: MixCa-MixCl, 12: MixCa-Cl, 13: Ca-HCO$_3$, 14: Ca-MixHCO$_3$, 15: Ca-MixCl, 16: Ca-Cl. FW: freshwater; SW: seawater. Below, screenshot of the HFE-Diagram plot for several samples collected in the coastal aquifer of Grosseto (Tuscany, Italy), together with the buttons used for calculating the code. The symbols for Mg and SO$_4$ waters have been changed manually.

The ordinates of the HFE-Diagram represent the mixing phenomena in terms of the relative percentages of anions; thus the %Cl indicates the seawater end member, while %HCO$_3$ or %SO$_4$ reveals the dominant anion in the fresh groundwater. The abscissas identify base-exchange reactions according the percentages of (Na$^+$+K$^+$) and Ca^{2+}. The percentages

are calculated from the total cation or anion content, including those not expressly represented (usually Mg^{2+} or SO_4^{2-}).

The diagram shows the line of conservative mixing between seawater and freshwater. For seawater, the composition given by Turekian (1968) is used as a default, while freshwater composition is selected by the program once the set of waters has been introduced. These two points determine the position of the mixing line, which in turn determines the fields of intrusion and freshening phases.

Alongside the mixing line, two arrows are shown. The freshening arrow points from the most salinized water towards the freshwater facies (the Na-HCO3 facies) and symbolizes mixing processes and direct exchange reactions. The intrusion arrow represents mixing between seawater and freshwater and reverse exchange processes. It points from freshwater to more saline waters and its characteristic facies is Ca-Cl.

The HFE-Diagram is a useful tool to determine the dynamics of the saline front, namely seawater intrusion or freshening. However, its application can be complex when conventional methods are used to represent sample points because two different coordinates are used: the coordinates shown in the diagram represent the percentage values, while the real coordinates of each point which must be calculated by applying simple but cumbersome corrections.

The purpose of this method note is to provide a method for generating the HFE-D plot using a computer spreadsheet. The HFE-D plot macro can be used for any four-component data where each component is represented as a percentage.

Method

The program is written in VBA (Visual Basic for Applications) and can be embedded in any version of Microsoft Excel. The advantage is that no installation is required, merely the support of Excel or other spreadsheet. It is possible that Excel will refuse to open the Macro Excel document if the security setting is high but this is resolved with the proper security setting (intermediate) or simply by the user enabling the macro.

The code is linked to the button option provided to the user (Figure 1). The _Plot_ button code performs basic calculations for drawing the points on the diagram. The other buttons are associated with short codes that perform the tasks indicated, and which do not require further explanation.

Before implementing the program, the graph is empty: no points are shown, nor is the line of freshwater - seawater mixing represented (because the corresponding cells are empty).

The HFE-D _Plot_ button code consists of the following phases (see Figure 2):
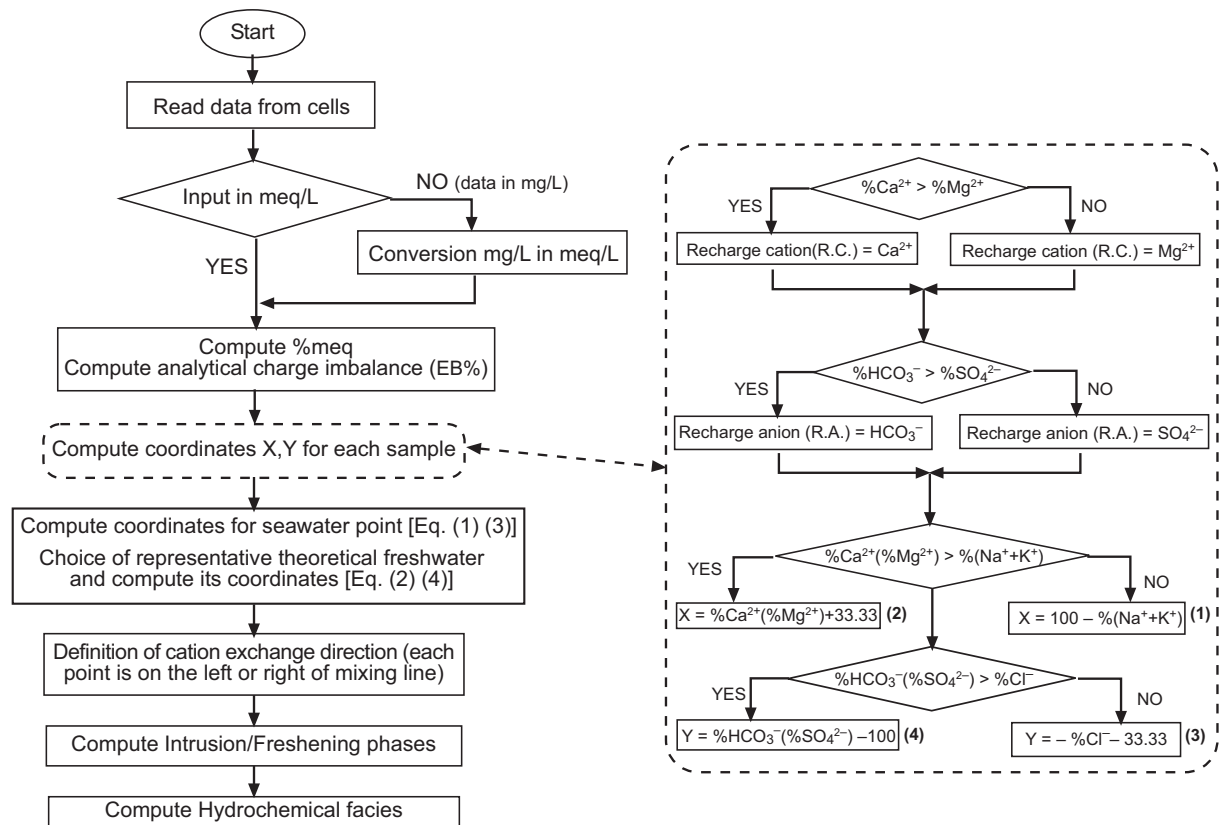
Figure 2. Flowchart showing the computational procedure. Numbers in square brackets indicate formulas in the text.

Step I: Reading the data entered by the user in the Excel sheet.

The data of major ion concentrations are introduced in mg/L or meq/L units. If the input data units are in mg/L, the program performs the conversion of data to meq/L units. The units used for data input are displayed in cell P2, sited above the HFE-D plot (Figure 1).

The electrical charge imbalances, as well as percentage of each ion, anions and cations, are calculated. These data can be consulted on the spreadsheet called *Percentages*.

Step II: Calculating the coordinates of the corresponding point on the graph.

This phase appears more developed on the right side of the flowchart (Fig. 2):

For each sample, the cation and anion representative of freshwater is selected. For the cations, either Ca^{2+} or Mg^{2+} is selected, according to which has the highest percentage. For anion recharge, either HCO_3^- or SO_4^{2-} is chosen, depending on which has the highest percentage. For ease of explanation in the following formulas, we have assumed a sample of fresh water (recharge) where the most abundant ions are Ca^{2+} and HCO_3^- (calcium bicarbonate facies).

The calculations for the corresponding point coordinates are as follows:

$$\text{If } \%(Na^+ + K^+) > \%Ca^{2+} : X = 100 - \%(Na^+ + K^+) \qquad [1]$$

$$\text{If } \%Ca^{2+} > \%(Na^+ + K^+) : X = Ca^{2+} + 33.33 \qquad [2]$$

$$\text{If } \% Cl^- > \% HCO_3^- : Y = 100 - \%(Na^+ + K^+) \qquad [3]$$

$$\text{If } \% HCO_3^- > \%Cl^- : Y = HCO_3^- - 100 \qquad [4]$$

If the anion in the recharge water is sulphate, % sulphate simply replaces % bicarbonate. Similarly, if the most abundant cation in the recharge water is magnesium, it is sufficient to replace calcium by magnesium.

Step III: Calculation of the mixing line

To delineate the seawater-freshwater mixing line, the coordinates for both endpoints need to be calculated. The default composition of seawater corresponds to data provided by Turekian (1968), which are displayed in cells P5-V5, in the *Diagram* sheet. The coordinates for the seawater endpoint are calculated using formulas [1] and [3].

The theoretical freshwater is selected according to which water has the highest percentage of cation recharge (Ca^{2+} or Mg^{2+}) and anion recharge (HCO_3^- or SO_4^{2-}). The program searches through all the waters and determines the highest cation and anion percentages for a theoretical freshwater. The position of the freshwater endpoint is calculated using equations [2] and [4], and its coordinates are written in the corresponding cells in the *Data* sheet.

These two coordinates are then used to plot the mixing line, for which they represent the endpoints.

Step IV: Definition of the direction of cation exchange and whether the phase is intrusion or freshening

For each sample, the direction of cation exchange is calculated according the position of the point relative to the mixing line. Points to the left of the line represent direct exchange, while points to the right represent reverse exchange. The coordinates for each point are written to different columns in the *Data* sheet, according to whether they reflect a freshening or an intrusion stage. Points positioned to the left of the mixing line (direct exchange) are written in columns E and F, while those to the right (reverse exchange) are written in columns G and H; thus the graph constitutes two distinct series. The intrusion or freshening phase is defined in column K of the first sheet (*Diagram*), where each sample appears either in blue (freshening phase) or red (intrusion phase). On this sheet, the hydrochemical facies of all samples are displayed in columns L and M, according to criteria defined by Giménez-Forcada (2010).

Step V: Compute hydrochemical facies

In columns K and L of the first sheet, the hydrochemical facies – according to Gimenez-Forcada (2010) – are displayed. If the cation percentage (%Ca or %Mg) in the recharge water is higher than that of %Na, the facies will be 'Ca' or 'Mg', provided that %Ca(%Mg)>50%;

otherwise, the facies will be 'MixCa' or 'MixMg'. Likewise, if the recharge anion (%HCO$_3$ or %SO$_4$) is higher than %Cl, the facies will be 'HCO$_3$' or 'SO$_4$', whenever %HCO$_3$(%SO$_4$)>50%, otherwise, the facies will be 'MixHCO$_3$' or 'MixSO$_4$'.

Using the code is very simple. The user must type or 'copy & paste' the values corresponding to the composition of their samples in columns B to I, then click the *Plot* button. When the user introduces data for major ion concentrations, the results of the calculations are shown in three sheets of the Excel Macro.

In the *Diagram* sheet, the phase of every water sample is given in column K using different colours: blue for freshening and red for intrusion. Columns L and M display the hydrochemical facies of the sample (Figure 3).

In the *Data* sheet, the coordinates of the sample on the HFE-Diagram are presented. Columns E-F contain data for the freshening phase, while columns G-H show data corresponding to the intrusion phase (although this information is not of interest to the user). In columns C and D, the coordinates corresponding to freshwater/recharge water and seawater are indicated.

The Macro code compares the real value of %Ca (or %Mg) in calcic waters, or of %(Na+K) in sodic waters, against the theoretical value indicated by the line of mixing on the graph. Any minor discrepancy between these values – even a difference of one percent or decimals of a percentage point – is interpreted by the program as freshening (plotted in blue) or intrusion (plotted in red). A peculiarity occurs when an actual water sample coincides with the theoretical fresh water identified by the code (maximum %HCO3 and maximum %Ca in a recharge water with a calcium bicarbonate facies). In this case, even though the water does not belong to either phase, the program forces a colour to be shown; this must be accepted as a limitation of the code.

In the *Percentages* sheet, major ion percentages are displayed in columns B-H, and the sum totals of cations and anions are shown in columns J and K. Column M presents the imbalance in electrical charge.

Below, some necessary and useful advice for the user is detailed.

The array of data entered by the user must include a sample in each line, and the ions must be entered in the same order as indicated at the head of the table. The data can be introduced in mg/L or meq/L. At the start of execution, a box asking for units of data is displayed, and the user must select the appropriate units (mg/L or meq/L).

There can be no blank intermediate lines. If the user decides to delete a sample point from the diagram, it is necessary to move up the lines beneath it to avoid a blank line. This is because the program reads line by line until it encounters an empty value for Ca^{2+}, which it interprets as the end of the input data. On the other hand, if any information is missing for a particular sample (e.g. no data on K$^+$ or NO$_3^-$), the program proceeds without any problem, performing calculations using just the data provided.

An alphanumeric reference code for each sample can be entered in column A of the *Diagram* sheet. This column is used only by the program to label points on the diagram, if

that option is subsequently chosen by the user. Otherwise, it is not necessary to fill these cells.

The default chemical composition of seawater can be changed in cells P5-V5, on the *Diagram* sheet (always in mg/L).

(a)

Ref.	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	Phase	Facies	
Hydrochemical Facies Evolution Diagram HFE-D											
Giménez-Forcada (2010). GROUND WATER, Vol. 48, No. 2–(pages 212–216)											
3	3,91	3,5	3,87	0,06	4,6	0,62	5,7		Intrus.	MixCa	Cl
6	3,61	3,02	3,05	0,05	4,74	0,93	3,85		Fresh.	MixCa	MixHCO3
15	7,8	4,04	9,06	0,25	3,05	2,71	14		Intrus.	MixNa	Cl
16	10,23	5,05	8,48	0,19	9,21	2,39	12,25		Intrus.	MixCa	Cl
17	7,58	4,83	8,85	0,29	3,84	2,5	15,17		Intrus.	MixNa	Cl
19	8,7	4,14	3,52	0,13	5,05	3,33	7,88		Intrus.	Ca	MixCl
20	5,49	1,1	1,33	0,1	3,92	2,4	1,55		Intrus.	Ca	MixHCO3
21	4,73	1,76	1,81	0,09	4,42	1,46	2,07		Intrus.	Ca	HCO3
22	9,48	5,54	8,43	2,53	6,34	3,54	14,3		Intrus.	MixCa	Cl

(b)

		Freshening			Intrusion	
	X	Y	X	Y	X	Y
This sheet is not for the user. It contains data used by the program						
Seawater	20,90	-123,61			68,0	-85,5
Recharge water	102,65	-27,68	70,6	-50,2	56,7	-104,2
					76,4	-84,7
Number of data: 69					58,4	-103,9
					86,5	-81,8
					102,7	-50,2
					90,3	-44,4
					73,8	-92,5
					53,1	-105,0
					100,2	-51,1
			81,8	-52,1		
					35,7	-108,9

(c)

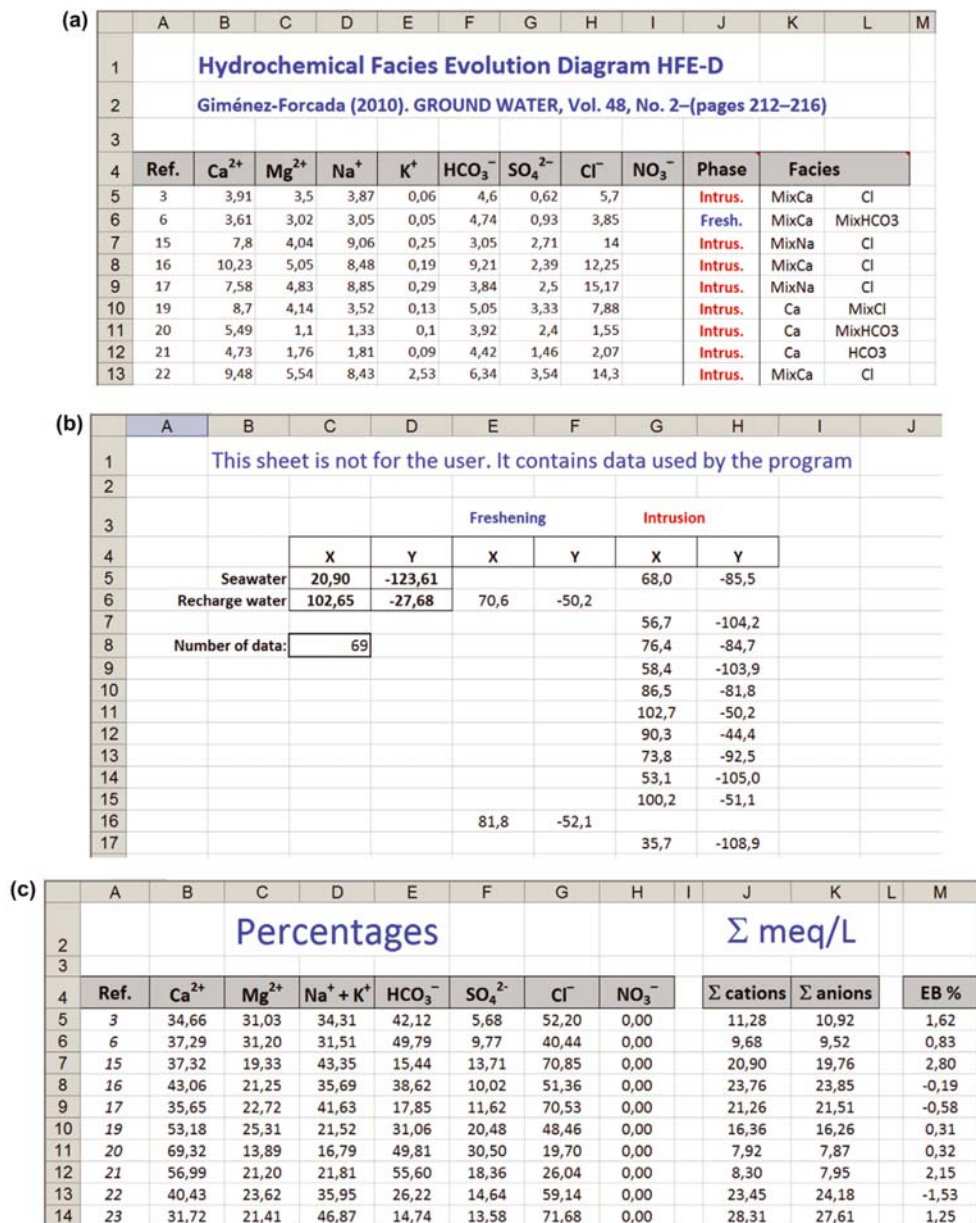| | | Percentages | | | | | | | Σ meq/L | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ref. | Ca^{2+} | Mg^{2+} | $Na^+ + K^+$ | HCO_3^- | SO_4^{2-} | Cl^- | NO_3^- | | Σ cations | Σ anions | EB % |
| 3 | 34,66 | 31,03 | 34,31 | 42,12 | 5,68 | 52,20 | 0,00 | | 11,28 | 10,92 | 1,62 |
| 6 | 37,29 | 31,20 | 31,51 | 49,79 | 9,77 | 40,44 | 0,00 | | 9,68 | 9,52 | 0,83 |
| 15 | 37,32 | 19,33 | 43,35 | 15,44 | 13,71 | 70,85 | 0,00 | | 20,90 | 19,76 | 2,80 |
| 16 | 43,06 | 21,25 | 35,69 | 38,62 | 10,02 | 51,36 | 0,00 | | 23,76 | 23,85 | -0,19 |
| 17 | 35,65 | 22,72 | 41,63 | 17,85 | 11,62 | 70,53 | 0,00 | | 21,26 | 21,51 | -0,58 |
| 19 | 53,18 | 25,31 | 21,52 | 31,06 | 20,48 | 48,46 | 0,00 | | 16,36 | 16,26 | 0,31 |
| 20 | 69,32 | 13,89 | 16,79 | 49,81 | 30,50 | 19,70 | 0,00 | | 7,92 | 7,87 | 0,32 |
| 21 | 56,99 | 21,20 | 21,81 | 55,60 | 18,36 | 26,04 | 0,00 | | 8,30 | 7,95 | 2,15 |
| 22 | 40,43 | 23,62 | 35,95 | 26,22 | 14,64 | 59,14 | 0,00 | | 23,45 | 24,18 | -1,53 |
| 23 | 31,72 | 21,41 | 46,87 | 14,74 | 13,58 | 71,68 | 0,00 | | 28,31 | 27,61 | 1,25 |

Figure 3. Three screenshots of Excel spreadsheets from the HFE-Diagram Macro, showing example calculations.

The *Clear* button removes all data written by the execution of Plot, so leaving an empty graph. It is not strictly necessary to do this since, if the user wants to make a second graph using data from another family of sample data, clicking the *Plot* button will clear any previous graph before plotting the new one.

The *Reset Graph Size* button redraws the diagram with the number of pixels specified by the user (this number refers to the graph itself, excluding the peripheral axis legends). Resizing can be done manually (as in any Excel chart) but since the chart should be exactly square, which is difficult to ensure by eye, the *Reset Graph Size* is helpful.

The *Label Points* button writes the reference code on the diagram – to the right of each point – as indicated by the user in the first column (column A in *Diagram* sheet). The font size must first be provided.

As in any Excel document, the user can freely change font type and size; likewise, the shape, size and colour of the two sets of points on the graph. However, it will not be possible to insert rows or columns because the program expects the first sample line to be in row 5, with its corresponding analytical data occupying columns B through I.

Once the HFE-D has been drawn, the graph can be copied into other documents using 'copy and paste'. The graph can be saved by clicking the *Save graph* button. It will be saved in the 'Documents' folder as 'Diagram HFE-D.gif'. Each time a new graph is saved, it replaces the previous one. In cell P3, the message 'Graph has been saved as 'Diagram HFE-D.gif'' is displayed.

The HFE-Diagram can also be useful for investigating mixing processes other than marine intrusion, provided the evolution of hydrochemical facies is identified. In this case, the points could be represented in the HFE-Diagram without the symbols linked to marine intrusion processes (freshening and intrusion arrows, freshwater and seawater, and mixing line), in a *generic HFE-D*.

Results

The code was applied to the groundwater of the alluvial plain of Grosseto, a coastal plain on the Tyrrhenian Coast of Italy, which is characterized by a complex salinization process in which recharge waters with a sulphate or bicarbonate facies mix with seawater as a result of marine intrusion. The high salinity values are related to seawater intrusion in the coastal zones (Bencini and Pranzini 1993; Pranzini and Bencini 1996), but the composition of the Grosseto waters is mostly a result of a three-part mixing between seawater and two recharge waters with sulphate and bicarbonate facies, respectively (Giménez-Forcada et al. 2001). Figure 1 represents the composition of water samples in an HFE-Diagram, which was drawn using the code described in this paper. It takes account of the major ion composition (excluding nitrate concentrations).

Twenty-two facies types are identified, namely Ca-Cl, Ca-HCO$_3$, Ca-MixCl, Ca-MixHCO$_3$, Ca-MixSO$_4$, Ca-SO$_4$, MixCa-Cl, MixCa-HCO$_3$, MixCa-MixCl, MixCa-MixHCO$_3$, MixCa-MixSO$_4$, MixCa-SO$_4$, MixMg-SO$_4$, MixNa-Cl, MixNa-HCO$_3$, MixNa-MixCl, MixNa-MixHCO$_3$, MixNa-SO$_4$, Na-Cl, Na-HCO$_3$, Na-MixCl, and Na-MixSO$_4$ (Figure 1). The number of facies types is high because four separate components participate in the recharge waters: for anions HCO$_3^-$ and SO$_4^{2-}$, and for cations, Ca^{2+} and Mg^{2+}. To symbolize sulphate and magnesium facies, different symbols are selected manually, as indicated in the figure 1.

From figure 1, it can be seen that the majority of samples belong to an intrusion phase, but there is also very clear evidence of freshening stages. For example, the Na-SO$_4$ facies represents the state of aquifer after washing by calcium sulphate recharge water once direct exchange reactions have taken place.

Thus, representation of the samples in the HFE-Diagram corroborates the hypotheses about the salinization of this aquifer developed in previous studies, greatly simplifying hydrochemical analysis overall.

Conclusions

The HFE-D macro code is a user-friendly application designed to represent a set of hydrochemical data in an HFE-D plot, by calculating a new set of coordinates, (X,Y), which are based on the percentages of major cations and anions. Furthermore, the application calculates the relationship between each sample point and the theoretical line of mixing, and this relationship characterizes each dataset for any aquifer. This relationship is read in terms of the direction of cation exchange, direct (freshening) or reverse (intrusion).

The main feature of the HFE-D macro code is the facility to plot hydrochemical data in this new diagram, using any version of Microsoft Excel. As a result, it offers the advantage of requiring no installation, but simply spreadsheet support. Moreover, the application provides additional information regarding the percentages of major ions, electrical charge imbalance, and assignment of hydrochemical facies.

When applied to the Grosseto coastal plain aquifer, the HFE-D Excel Macro revealed itself as a useful tool for identifying the most important processes involved in the salinization of this coastal aquifer.

Software Availability

The software is available free, either on request to the authors at javisan@usal.es or e.gimenez@igme.es, or by downloading the Excel Macro directly from http://hidrologia.usal.es/HFE-D.htm or http://www.igme.es/HFE-D/HFE-D.htm.

Acknowledgements

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