Chapter 27
“MODELAGUA”: An Interactive Program of Inverse Mass-Balance Model for Geochemical Study: An Example of its Application in Aguascalientes, Mexico

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Abstract With the reference of interactive programs such as BALANCE NETPATH and PHREEQCI, for modelling net geochemical mass-balance reactions between an initial and final water along a hydrologic flow path, which also computes the mixing proportion of two initial waters and net geochemical reactions that can account for the observed composition of a final water, an interactive program of inverse model has been developed (MODELAGUA) that not only allows starting from well-known data of the chemical composition of the water and the rock to identify in a quantitative way the geochemical reactions that give origin to this composition, but also allow an analysis of mixture of waters and net geochemical reactions that can account for the observed composition of a final water, making use of a natural tracer whose geochemical behavior allows them to be used as conservative ions. In this work MODELAGUA is presented, as an interactive program of inverse model mass-balance and an example of its application.

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27.1 Introduction

The geochemical models consist of the application of physical-chemical principles to the interpretation of hydrogeochemical systems. This methodology has been developed according to two approaches: (a) the inverse one (mass-balance) that uses a well-known data of the composition of the waters and the rocks with the objective of identifying in a quantitative way the geochemical reactions that give origin to this composition; and (b) the direct one that in the basis of some well-known initial conditions on the rock-water system, it predicts the characteristics of the resulting solution of the performance of some hypothetical reactions. Both approaches have some uses and intrinsic limitations that force their use under the most appropriate conditions (Gimeno and Peña 1994; Martínez et al. 2000).

For systems with appropriate chemical, isotopic, and mineralogical data, the inverse approach of speciation and mass-balance provides the most direct means to determine models of geochemical reaction quantitatively. For systems with inadequate or nonexistent data, the model of reaction rules provides a method, in the beginning, of prediction of geochemical reactions. In some cases it is useful to combine both simulation types.

BALANCE (Parkhurst et al. 1982) is a program to calculate mass transfer for reactions in groundwater. It defines and quantifies reactions between groundwater and minerals; calculates the mass transfer necessary to account for a change in composition between two water samples; and also models the mixing of waters, redox reactions and isotopic composition. The program NETPATH (Plummer et al. 1991, 1994) is an interactive program for modelling net geochemical mass-balance reactions between an initial and final water along a hydrologic flow path, very similar to BALANCE. The main advantage of the system is that every possible geochemical mass-balance reaction model is examined between selected evolutionary waters for a set of chemical and isotopic constraints, and a set of plausible phases in the system (Parkhurst et al. 1982; Plummer et al. (1991)). On the other hand PHREEQCI expands on previous approaches by the inclusion of a more set of mole-balance equations and the additional of inequality constrain that allow for uncertainties in the analytical data (Parkhurst 1997).

An interactive program of inverse model has been developed (MODELAGUA) that not only allows starting from well-known data of the chemical composition of the water and the rock to identify in a quantitative way the geochemical reactions that give origin to this composition, but also allows the analysis of mixture of waters and net geochemical reactions that can account for the observed composition of a final water, making use of natural tracer whose geochemical behavior allows them to be used as conservative ions. In this work is presented MODELAGUA, as an interactive program of inverse model mass-balance and an example of its application.

27.2 Description of the MODELAGUA

27.2.1 Modelling Procedure

The program MODELAGUA has the objective to determine the geochemical processes that originate the chemical composition of natural waters, by means of mass-balance models and mixture analysis, also allowing the realization of Stiff graphics and the determination of hydrogeochemical patrons for the classification and determination of the type of water.

Due to these limitations to make the mass-balance correctly, it is necessary to know the lithology type to which the aquifer belongs, to select only the reactions that are logical from the geochemical point of view and to revise the validity of the results with kinetic and thermodynamic approaches.

The pattern of mass balance allows to relate a study sample with a reference and to establish the geochemical processes that have taken place. As it was already pointed out, the samples selected as references and samples should correspond with the same flow line in the aquifer; therefore, the difference of mass between both samples will be due to the geochemical processes in the region.

As the data correspond to concentration values and not to mass values, it is necessary to keep in mind the variation that can be due to concentration phenomenon, for example, the plant evapotranspiration. For this reason the concepts of concentration factor and preservative ion are introduced.

- ***Conservative ion:*** Compound that does not participate in any geochemical processes. Generally, the ion chloride can be used as a preservative ion.
- ***Concentration factor:*** Factor that quantifies the concentration processes can be determined easily starting from the selection of a preservative ion. If this factor is similar to 1, it means that there are no concentration phenomena taking place.

In comparison with commercial programs that are based on mass-balance models such as BALANCE, NETPATH and PHREEQC, MODELAGUA has the advantage of being supported on Windows which provides greater speed and easiness of operation; the data may be entered within the MODELAGUA environment or can be imported in other formats (dbf, txt, excel and mdb), and the incorporation of a new method of recognition of hydrogeochemical patrons, as well as the optimization of the calculation algorithm in the mass-balance, and in the mixture analysis through the use of natural tracers whose geochemical behavior allows them to be used as preservative ions.

27.2.2 Calculation of Hydrochemical Patterns

The classification by means of hydrochemical patron is of great utility because it allows the grouping of samples with different chemical composition and to analyze possible relationships among them; it also provides qualitative information of the processes that can influence the composition of the waters.

For these reasons it is included in the program MODELAGUA, intending as the first step in the treatment of the data, as it constitutes an important guide for the selection of the reactions when carrying out the model by means of mass balance or mixture analysis.

For the determination of the hydrochemical patterns corresponding to a study sample, the program makes the comparison of its chemical composition with each one of the values of the different present patterns. For this it takes a distance approach, the sum of the quadratic difference among the value of concentration of each ion (Ci) and the concentration value corresponding to this ion in the pattern that is analyzing (Cpi), according to the expression (Eq. 27.1):

$$D_p = \Sigma_i\left(\left(C_i - C_{pi}\right)^2\right) \tag{27.1}$$

where Ci and Cpi are expressed in part by ten of meqv/L, i takes values from 1 until the number of majority ions and p takes values from 1 until the number of existent patterns. The calculation is carried out for each patron ***p*** and one is selected with minor distance to the (Dp). The values of part by 10 of meqv/L of the different patterns do not need to be extracted of a chart; however, they are generated in their own program by means of iterative cycles.

27.2.3 Mass Balance

If two waters are connected in one line of flow, it should be expected that both possess the same chemical composition. If it is not in this way, it is clear that during the trajectory of the first sample up to the second, geochemical processes that modified their composition, have occurred. This composition difference or Ionic Delta can be used to determine the processes that take place in the region. The program MODELAGUA also considers the possibility that during the trajectory of the waters, concentration variations occurred, for example, by means of the evapotranspiration phenomenon, which is the reason why the concentration factor, the variable ***F*** is introduced. This way the calculation of the ionic delta for each compound will be (Eq. 27.2):

$$\Delta C_i = C_{i(\text{sample water})} - F * C_{i(\text{references samples water})} \tag{27.2}$$

To determine ***F***, a preservative ion can be used (q), an ion that does not participate in any interaction water-rock process, where (Eq. 27.3):

$$F = C_{q(\text{sample water})} / C_{q(\text{references samples water})} \tag{27.3}$$

This way (Eq. 27.3) the program calculates ***F*** according to the selected preservative ion and substituting in Eq. 27.2, it calculates the ionic delta for the rest of the ions.

Once the value of the ionic delta well known, it can be done to the mass balance for the determination of the geochemical processes. The algorithm of calculation of the mass balance, traditionally, is based on the solution of the Eq. (27.4) system:

$$\Delta \mathrm{C_i} = \Sigma_\mathrm{k}(\mathrm{a_k} * \ \mathrm{b_{ik}}) \tag{27.4}$$

(ΔCi: ionic delta; a_k: Mass transferred in each k process (value to calculate); b_{ik}: estequiometric coefficient of each component ***i*** in each reaction k).

The program MODELAGUA adds a process of optimization to the equations system (Eq. 27.4); it introduces a new variable E_i: error made in the adjustment of each equation ***i***, this way (Eq. 27.5):

$$\Delta \mathrm{C_i} = \Sigma_\mathrm{k}(\mathrm{a_k} * \ \mathrm{b_{ik}}) + \mathrm{E_i} \tag{27.5}$$

Then defining the total error of the balance (Et) as (Eq. 27.6):

$$\mathrm{E_t} = \Sigma_\mathrm{i}\left(\mathrm{E_i}^2\right) \tag{27.6}$$

It is obtained (Eq. 27.7):

$$\mathrm{Et} = \Sigma_\mathrm{i}\left([\Delta \mathrm{C_i} - \Sigma_\mathrm{k}(\mathrm{a_k} * \ \mathrm{b_{ik}})]^2\right) \tag{27.7}$$

With the objective of finding the solution for which the error of the balance is minimum, the process of optimization of this function is carried out deriving partially regarding to each variable to calculate (a_k) and equaling to zero the obtained equations. This way the following system of equations is obtained (Eq. 27.8):

$$\partial \mathrm{E_t}/\partial \mathrm{a_k} = \Sigma_\mathrm{i}(\mathrm{b_{ik}}) * \ [\Delta \mathrm{C_i} - \Sigma_\mathrm{k}(\mathrm{a_k} * \mathrm{b_{ik}})] = 0 \tag{27.8}$$

This is then the system of equations that is solved by the program MODELAGUA. This process of optimization contributes to the advantages of the program that allows systems to solve that do not possess the exact solution and also the system of Eq. 27.8. It does not present the restriction that the number of selected processes ***k*** have to be similar to the number of ions ***i***, as it happens with the equation system (Eq. 27.4); and for this reason the program can always offer the most approximate solution for any number of reactions and compounds that are selected.

27.2.4 Mixture Analysis

For the case to be modeled, the study sample as the result of the mixture of two reference samples is necessary to determine the mixture percentage previously for each reference. In a similar way to the concentration factor, the mixture percentage can be calculated starting from the selection of a preservative ion, an ion that only owes its difference of mass to the effect of the mixture when not participating in any geochemical process. In the case it is studied, the composition of a sample as a result of the mixture of two waters, the calculation of the Ionic Delta is different, as it is necessary to know the mixture proportion, which can be calculated starting from a preservative ion.

For a preservative ion (q), the resulting composition (CR) of the mixture of two waters of composition (CA) and (CB) will be given by the Eq. 27.9:

$$\mathrm{CR_q} = \mathrm{x}\left(\mathrm{CA_q}\right) + (1 - \mathrm{x})\left(\mathrm{CB_q}\right) \tag{27.9}$$

Where (x) is the fraction of compound ***q*** in mixture from the sample A and (1 − x), the corresponding for the component ***q*** in mixture from the sample B.

Obtaining ***x*** from Eq. 27.9 and multiplying by 100, the mixture percent can be determined (Eq. 27.10):

$$\mathrm{x} * 100 = 100 \ * \ \left(\mathrm{CR_q} - \mathrm{CB_q}\right)/\left(\mathrm{CA_q} - \mathrm{CB_q}\right) \tag{27.10}$$

Therefore, the difference between the two members of Eq. 27.9 will be indicative of the processes that take place, and the values in this case are taken as ionic delta (ΔCi). This way (Eq. 27.11):

$$\Delta \mathrm{C_i} = \mathrm{CR_i} - [\mathrm{x}(\mathrm{CA_i}) + (1 - \mathrm{x})(\mathrm{CB_i})] \tag{27.11}$$

Once calculated, the mixture percent $(\mathrm{x} * 100)$ according to Eq. 27.10 for the selected preservative ion, the ionic delta can be calculated for the rest of the ions substituting the value of ***x*** in Eq. 27.11.

Once the value of the ionic delta (ΔCi) is well known, the rest of the calculation is the same as in the case of the mass balance, by means of the equation system (Eq. 27.8). To carry out the calculations, the program needs that the analytic data corresponding to the concentration of major cations and anions are introduced as study sample water or as two reference samples: Study sample water – sample of water taken in the point where the geochemical processes wanted to be determined; and References sample water–sample of water taken in points located in the same line of flow as that of the study sample. Two reference samples are only needed in the case that is desired to model to the study sample as the result of the mixture of two types of different waters.

27.3 Application

The area studied corresponds to the called Aguascalientes Valley or Graben. This area constitutes a rectangle with coordinated UTM 2′390,000–2′490,000 N and 760,000–800,000 E (Fig. 27.1). The Aguascalientes Valley or Graben is a topographical depression of about 80 km with 20 km of maximum width in their northern and southern ends, and about 10 km of minimum width in their central part. It is flanked to the east and the west by horsts or tectonic pillars that form NW-SE and NE-SW system of fractures. The filler of The Aguascalientes Valley or Graben constitute alluviums

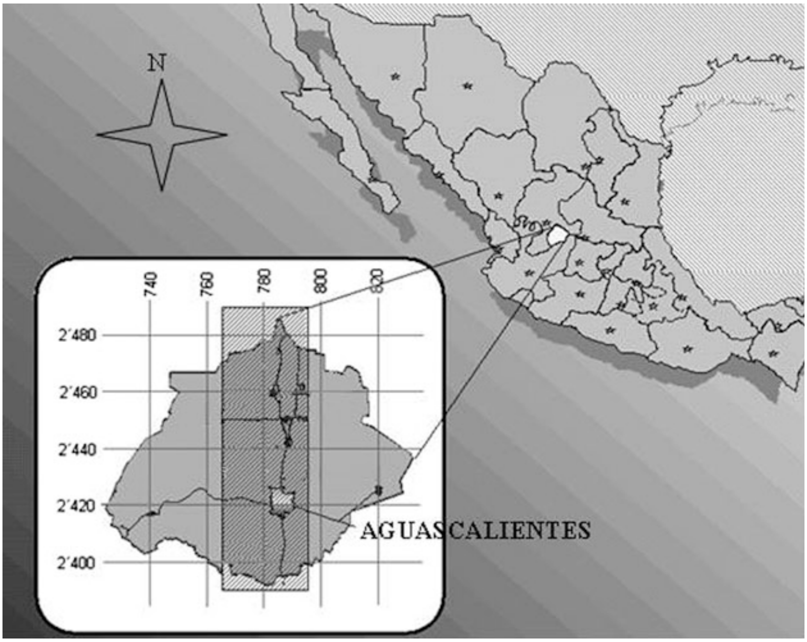

Fig. 27.1 Localization of area the study

formed by sedimentary material not consolidated. The recent alluvial material is compound, mainly, for gravels, sands and not well classified clays, which does not present stratification and in general it is not consolidated. Filler material consists of gravels and sand products of the erosion of the underlying units; in general this type of deposits stuffs the valleys and it is located in the piedmont (INAGUA-UAQ-UNAM technician report 2003).

The most important aquifer of the Aguascalientes Valley supplies a demand of almost 500 million m^3/year. The aquifer of the Valley of Aguascalientes has had an intensive exploitation in such a way that the rate of average depression 3.0 m/year, in the last decades in the urban area of Aguascalientes. Establishment problems and cracking of the land have also been related to the exploitation of the aquifer. The main areas of recharge of the aquifer of the Aguascalientes Valley or Graben come from the oriental flank and from the northern area of the Graben.

Aguascalientes aquifer is conformed in its upper part by detritus sedimentary rocks formed by alluvial materials (carried silts and deposited by the rivers and streams of the region); these alluvial materials are not consolidated, and for its grain they are of the type gravels, sands, limes and clays (Lutites) that form layers of strata of variable geometry whose thickness varies from some meters in the limits of the valley, up to 200 m in its center. According to these features, the minerals that can be found in these rocks are: Clays of kaolinite type ($Al_2Si_2O_5(OH)_4$), montmorillonite, alkaline feldspars ($NaAlSi_3O_8$, $KAlSi_3O_8$), quartz (SiO_2).

Table 27.1 Hydrogeochemical inverse mass-balance model obtained from **MODELAGUA**. Distribution of the mineral mass transformed by water-rock interaction

Name	Cl^-	HCO_3^-	SO_4^{2-}	Na^{2+}	Ca^{2+}	Mg^+	K^+
Sample AG-9	0.590	11.000	0.803	6.413	2.025	0.014	0.599
Rain water	0.160	0.200	0.000	0.210	0.040	0.038	0.010
Concentration factor	3.7						
IONIC DELTA	0.000	10.223	0.803	5.637	1.877	0.003	0.562
PROCESSES							
Albite-kaolinite	0.000	5.637	0.000	5.637	0.000	0.000	0.000
Anorthite-kaolinite	0.000	3.754	0.000	0.000	1.877	0.000	0.000
Microcline-kaolinite	0.000	0.562	0.000	0.000	0.000	0.000	0.562
Pirita-hemetite	0.000	0.000	0.803	0.000	0.000	0.000	0.000
CO_2-HCO_3^-	0.000	0.271	0.000	0.000	0.000	0.000	0.000
TOTAL	0.000	10.223	0.803	5.637	1.877	0.000	0.562
ERROR	0.000	0.000	0.000	0.000	0.000	0.003	0.000

Under the alluvial silts there are conglomerates and fractured igneous rocks. The conglomerates and the igneous rocks have a thickness from 200 to 300 m and they constitute the lower part of the aquifer. Minerals such as quartz (SiO_2), alkaline feldspars ($NaAlSi_3O_8$, $KAlSi_3O_8$), calcic plagioclases ($Ca_2Al_2Si_2O_8$), muscovite ($KAl_2[AlSi_3O_{10}][OH]_2$), micas of lithium of the lepidolite group ($KLi_{1.5}Al_{1.5}[Si_3AlO_{10}][FOH]_2$) are present. All these minerals are very insoluble, that is why the waters that drain the same one is, in general, of very low mineralization. However, some samples of the study area present high TSS, like it is the case of sample AG-9 (Beautiful Hill; Well 70), with TSS of the order of 1,085 mg/L, which is given by the high temperature (26 °C) and pH 6.50. Considering you like thermal waters because their temperature is more than 4° above the half temperature of the area (17 °C). The sample AG-9 probably originates from the deepest aquifer layer. Taking all this in consideration, the geochemical model through MODELAGUA is carried out that allows starting from the concentrations of the majority ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, CL^-; in these samples the concentration of SiO_2 were not determined) of the sample water (in this case the AG-9) and of the representative rain water of the area to obtain the following results (Table 27.1).

The principal geochemical processes that originate the chemical composition for water sample AG-9.

$$\underset{\textbf{Albite}}{5.64\ NaAlSi_3O_8} + 5.64\ CO_2 + 31.02\ H_2O \leftrightarrow \underset{\textbf{Kaolinite}}{2.82\ Al_2Si_2O_5(OH)_4} + 5.64\ Na^+ + 5.64\ HCO_3^- + 11.28\ H_4SiO_4$$

$$\underset{\textbf{Anorthite}}{1.88\ CaAl_2Si_2O_8} + 3.75\ CO_2 + 5.63\ H_2O \leftrightarrow \underset{\textbf{Kaolinite}}{1.88\ Al_2Si_2O_5(OH)_4} + 1.88\ Ca^{2+} + 3.75\ HCO_3^-$$

$$0.56\,KAlSi_3O_8 + 0.56\ CO_2 + 3.08\ H_2O \leftrightarrow 0.28\,Al_2Si_2O_5(OH)_4 + 0.56\ K^+ + 0.56\ HCO_3{}^- + 1.12H_4SiO_4$$

Microcline **Kaolinite**

$$0.40\,FeS_2 + 1.5\,O_2 + 3.0\,H_2O \leftrightarrow 0.40\,Fe(OH)_3 + 0.80\,SO_4{}^{2-} + 1.6\,H_3O^+$$

Pirite **Hematite**

$$0.27\ CO_2 + 0.14\ H_2O + 0.07\ O_2 = 0.27\ HCO_3{}^-$$

27.4 Conclusions

MODELAGUA by means of an inverse mass-balance model allows the establishment of the main geochemical processes responsible for the chemical composition of the water sample, AG-9, which is the weathering of the minerals Albite and Anorthite which are abundant in the deepest aquifer layer in Aguascalientes.

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