

"MODELAGUA": a new interactive program of inverse mass-balance model for geochemical study"-- an example of its application in Aguascalientes, Mexico.

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Abstract

The geochemical model consists on 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 chemical composition of the water and the rock 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 of the water-rock system, it predicts the characteristics of the resulting solution of the performance of hypothetical chemical reactions. With the reference of interactive programs such as BALANCE and NETPATH, 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 allow 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 allow to do 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 a new interactive program of inverse model mass-balance and an example of its application.

Keywords: Geochemical models; mass-balance models; MODELAGUA

1. Introduction

The geochemical models consist on 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 us to use them under the most appropriate conditions (Gimeno and Peña, 1994, Martinez, et al., 2000).

For systems with appropriate chemical, isotopic, and mineralogical data, the inverse approach of speciation and mass-balance, provides the most direct mean 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 geochemicals reactions. In some cases it is useful to combine both simulation types. The results of the inverse, although very useful models for systems with enough

information, are only partially restricted by thermodynamic approaches. The direct models can be used to check the thermodynamic consistency of the result of the mass-balance and to predict the quality of the water in the points in that the information is insufficient. **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. Also models mixing of waters, redox reactions and isotopic composition. Runs as a batch program requiring input files prepared with the pre-processor BALNINPT, or a text editor. The pre-processor automatically accesses a chemical reaction data base, BALNINPT.DAT, included with the software. BALANCE is no longer maintained by the developers; it has been replaced by the program NETPATH (Plummer et al., 1991; 1994), which 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)).

An interactive program of inverse model has been developed (MODELAGUA) that not only allow 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 allow to do 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 a new interactive program of inverse model mass-balance and an example of its application.

2. Description of the MODELAGUA

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 belongs the aquifer, 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 reference and sample 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 doesn't participate in the geochemical processes in the region and therefore the difference of mass among its value in the sample and the one present in the reference is only owed to concentration processes. It can be used, generally, the ion chloride as 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 not concentration phenomena taking place.

In comparison with commercial programs that are based on mass-balance models such as BALANCE and NETPATH, MODELAGUA has the advantage of being supported on Windows what provides it bigger 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 to use them as preservative ions.

2.2. Calculation of Hydrochemical Patterns

The classification by means of hydrochemical patron is of great utility because it allows to group samples with different chemical composition and to analyze possible relationships among them, it also provides a qualitative information of the processes that can be influencing on 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, since 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 is taken as distance approach, the sum of the quadratic difference among the value of concentration of each ion (C_i) and the concentration value corresponding to this ion in the pattern that is analyzing (C_{pi}), according to the expression:

$$D_p = \sum_i ((C_i - C_{pi})^2) \quad (1)$$

Where C_i and C_{pi} 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 it is selected the one with minor distance to the real values (D_p). The values of part by ten of meqv/L of the different patterns don't need to be extracted of a chart but they are generated in the own program by means of iterative cycles.

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 happened. 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, it have happened concentration variations, for example, by means of the evapotranspiration phenomenon, reason why as concentration factor, the variable F is introduced. This way the calculation of the ionic delta for each compound will be:

$$\Delta C_i = C_{i(\text{sample water})} - F * C_{i(\text{references samples water})} \quad (2)$$

To determine F , a preservative ion it can be used (q), an ion that doesn't participate in any interaction water-rock process, were:

$$F = C_{q(\text{sample water})} / C_{q(\text{references samples water})} \quad (3)$$

This way (Eq. 3) the program calculates F according to the selected preservative ion and substituting in equation 2 it calculates the ionic delta for the rest of the ions.

Once well-known the value of the Ionic Delta it can be done 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 equation system:

$$\Delta C_i = \sum_k (a_k * b_{ik}) \quad (4)$$

(ΔC_i : 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. 4), it introduces a new variable E_i : error made in the adjustment of each equation i , this way:

$$\Delta C_i = \sum_k (a_k * b_{ik}) + E_i \quad (5)$$

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

$$E_t = \sum_i (E_i^2) \quad (6)$$

It is obtained:

$$E_t = \sum_i ([\Delta C_i - \sum_k (a_k * b_{ik})]^2) \quad (7)$$

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

$$\partial E_t / \partial a_k = \sum_i (b_{ik}) * [\Delta C_i - \sum_k (a_k * b_{ik})] = 0 \quad (8)$$

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 to solve systems that don't possess exact solution and also the system of equations 8, it doesn't 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. 4); and for this reason the program can always offer the most approximate solution for any number of reactions and compound that are selected.

2.5. Mixture Analysis

For the case in that we want to model the study sample as the result of the mixture of two reference samples, it 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, since 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), it will be given by the equation:

$$CR_q = x(CA_q) + (1 - x)(CB_q) \quad (9)$$

Where (x) it 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 equation 9 and multiplying by 100, the mixture percent can be determined:

$$x * 100 = 100 * (CR_q - CB_q) / (CA_q - CB_q) \quad (10)$$

Therefore, the difference between the two members of the equation (VI) it will be indicative of the processes that take place, and the values in this case, are taken as ionic delta (ΔC_i). This way:

$$\Delta C_i = CR_i - [x(CA_i) + (1 - x)(CB_i)] \quad (11)$$

Once calculated the mixture percent ($x * 100$) according to the equation 10 for the selected preservative ion, the ionic delta can be calculated for the rest of the ions substituting the value of x in the equation 11.

Once well-known the value of the ionic delta (ΔC_i), the rest of the calculation is the same as in the case of the mass balance, by means of the equation system (Eq. 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.
- References samples water: Sample of water taken in points located in the same line of flow that the study sample.

Two reference samples are only needed in the case that is wanted to model to the study sample as the result of the mixture of two types of different waters.

3. Application

The area studied corresponds to the called Aguascalientes Valley or Graben. This area constitutes a rectangle with coordinated UTM 2'390,000 to 2'490,000 N and 760,000 to 800,000 E (Fig. 1).

The Aguascalientes Valley or Graben is a topographical depression of about 80 kilometers with 20 kms of maximum width in their northern and southern ends, and of about 10 kms 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 formed by sedimentary material not consolidated. The recent alluvial material is compound, mainly, for gravels, sands and not well classified clays, which doesn't present stratification and in general it is not consolidated. Filler material, consists of gravels and sands product 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 m³/year. The aquifer of the Valley of Aguascalientes has had an intensive exploitation, in such a way that the rhythm 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 north area of the Graben. The occident flank has little impact in the recharge of the aquifer because the basement works as waterproof barrier and it is little depth in this flank, in occasions in the surface.

In summary, Aguascalientes aquifer is conformed in its upper part by detrital sedimentary rocks formed by alluvial materials (carried silts and deposited by the rivers and streams of the region); these alluvial materials are not consolidated (they are not hardened as a rock), and for its grain they are of the type gravels, sands, slimes 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 meters in its center. According to these features, the minerals we can find in these rocks are: Clays of kaolinite type (Al₂Si₂O₅(OH)₄), montmorillonite, alkaline feldspars (NaAlSi₃O₈, KAlSi₃O₈), quartz (SiO₂).

Under the alluvial silts there are conglomerates and fractured igneous rocks. The conglomerates are also materials of sedimentary origin, but they are already hardened, this is, they are already transformed into rocks because their permeability is given by fracturamiento and not by porosity. The conglomerates and the igneous rocks have thickness from 200 to 300 meters and they constitute the lower part of the aquifer. Minerals such as quartz (SiO₂), alkaline feldspars (NaAlSi₃O₈, KAlSi₃O₈), calcic plagioclases (Ca₂Al₂Si₂O₈), muscovite (KAl₂[AlSi₃O₁₀][OH]₂), micas of lithium of the lepidolite group (KLi_{1.5}Al_{1.5}[Si₃AlO₁₀][FOH]₂) are present.

All these minerals are very insoluble, it that's 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 1 085 mg/L, that which comes given by the high temperature (26 °C) and to the first floor pH (6.50) that presents.

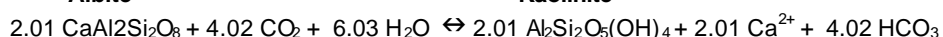
Considering you like thermal water because their temperature is more than 4 degrees above the half temperature of the area (17°C). Taking all this in consideration, it is carried out the geochemical model through MODELAGUA that allows us, starting from the concentrations of the majority ions (Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, SO₄²⁻, CL) of the sample water (in this case the AG-9) and of the representative rain water of the area, to obtain the following results (Tab. 1 and 2; Fig. 2):

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



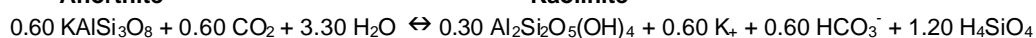
Albite

Kaolinite



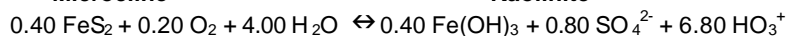
Anorthite

Kaolinite



Microcline

Kaolinite



Pirite

Hematite

4. Conclusions

MODELAGUA by means of an inverse mass-balance model allows to establish that the main geochemical processes responsible for the chemical composition of the water sample AG-9, is the weathering of the mineral Albite and Microcline which are abundant in the detritic sedimentary rocks of igneous origin.

5. References

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Figure captions

Figure 1. Localization of area the study.

Figura 2. Stiff graphics of sample AG-9, calculate for MODELAGUA.

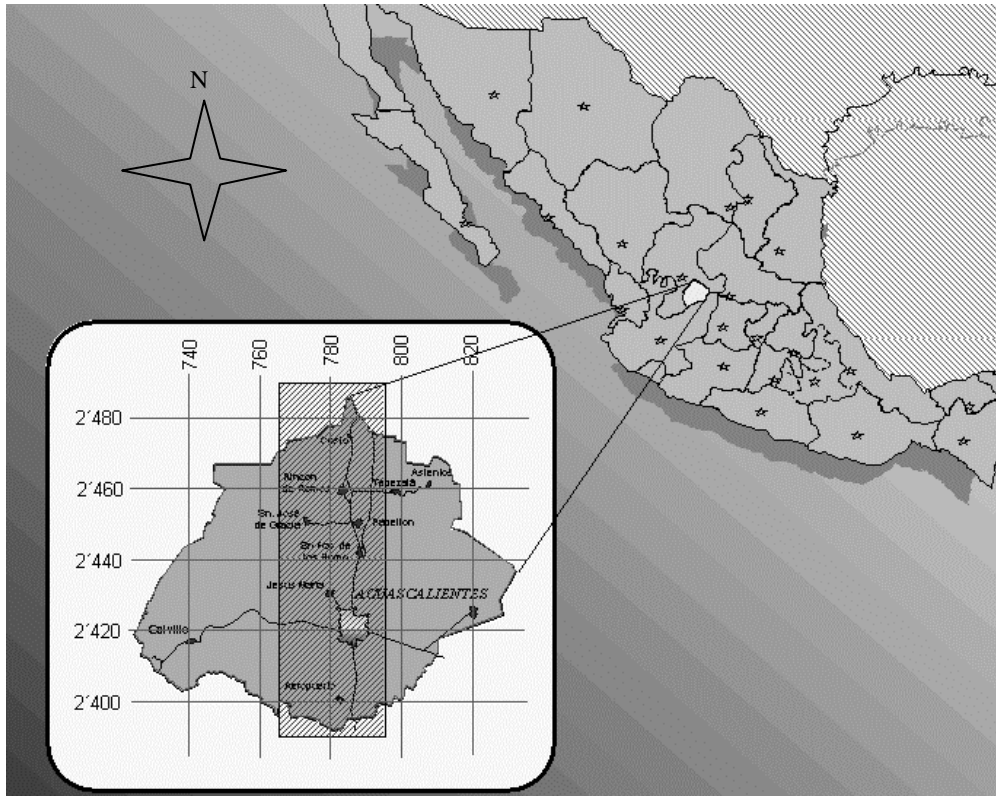


Figure 1.

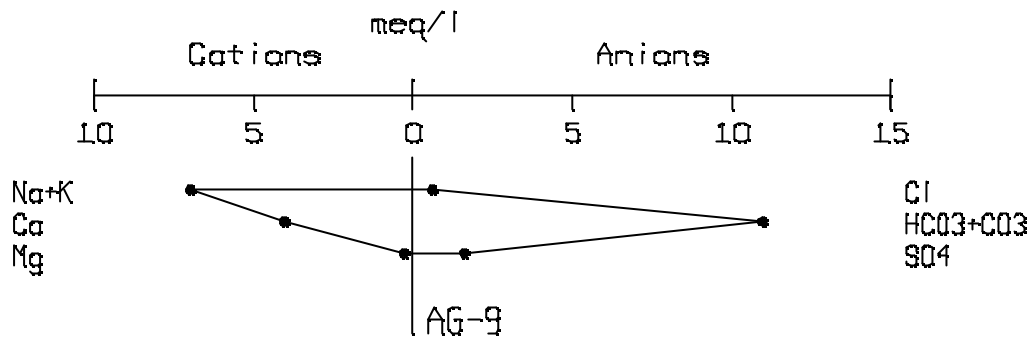


Figure 2.

Table captions

Table 1. Hydrogeochemical Inverse Mass-Balance Model obtained from **MODELAGUA** Distribution of the mineral mass transformed by water-rock interaction:

Table 2. Distribution of the mineral mass transformed by water-rock interaction:

Table 1.

Name	Cl⁻	HCO₃⁻	SO₄²⁻	Na²⁺	Ca²⁺	Mg⁺	K⁺
Sample AG-9	0.059	11.000	0.803	6.413	2.025	0.014	0.599
Rain Water	0.160	0.200	0.000	0.210	0.040	0.030	0.010
IONIC DELTA	0.000	10.926	0.803	6.335	2.010	0.000	0.596
PROCESSES:							
Albite -Kaolinite	0.000	6.335	0.000	6.335	0.000	0.000	0.000
Anorthite-Kaolinite	0.000	4.020	0.000	0.000	2.010	0.000	0.000
Microcline-Kaolinite	0.000	0.600	0.000	0.000	0.000	0.000	0.600
Pirita - Hemetite	0.000	0.000	0.803	0.000	0.000	0.000	0.000
TOTAL:	0.000	10.926	0.803	6.335	2.010	0.000	0.596
ERROR:	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 2.

	mmol/L	mg/L	%
Albite	6.33	1 658	68.25
Anorthite	0.08	166	6.84
Microcline	0.60	558	22.97
Pirite	0.40	47	1.94
		2 429	100