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Sensitivity and uncertainty analysis of mixing and mass balance calculations with standard and PCA-based geochemical codes

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Abstract

One of the most important observations that can be obtained from the study of an aquifer system dominated by mixing is the contribution of each end-member water to the chemical composition of every water parcel in the aquifer. Once the first-order effect of mixing has been taken into account via the mixing proportions, water–rock interaction can be used to explain the remaining variability. There are many sources of uncertainty that can prevent the accurate calculation of the mixing proportions of a mixing-dominated system, but the type and intensity of the chemical reactions that have taken place as a consequence of mixing is one of the most critical. Here the uncertainty in the computed mixing proportions of samples from a "synthetic" aquifer system derived from the actuation of different chemical reactions are assessed (always remembering that the chemical reactions are a second-order effect). These uncertainties are explored using two different geochemical codes in order to infer the limits of both methodological approaches: PHREEQC, as an example of a standard geochemical code; and M3, as an example of a Principal Component-based geochemical code. Several synthetic water samples are created with the direct approach of PHREEQC, both by pure mixing and including different types of chemical reactions. Together with the chemical information of the end-member waters, these samples are then fed into PHREEQC (inverse modelling) and M3 and the mixing proportions and mineral mass transfers are computed. PHREEQC calculations give a reasonable estimate of the real mixing proportions and the chemistry of the groundwaters. However, similar mixing proportions and mass transfers can be obtained using different sets of reactions, indicating a source of uncertainty that should be overcome with additional chemical information. For M3, where synthetic samples have been included in a real data set of groundwater samples from the Scandinavian Shield, mixing proportions are only mildly affected either by the number of compositional variables or the number of samples used for the Principal Component Analysis (PCA). However, the robustness of the output is quite sensitive to whether only conservative compositional variables are used or both conservative and non-conservative compositional variables. Mass balance calculations in M3 are much more sensitive to non-conservative compositional variables and the recommendation here is not to use non-conservative variables with PCA-based codes if any information about reactions is to be obtained.
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1. Introduction

The mixing of different water types is a common and potentially important process in many natural and artificial systems (Vázquez-Suñé et al., 1997; Laaksoharju et al., 1999c; Suk and Lee, 1999; Douglas et al., 2000; Carrera et al., 2004; Rueedi et al., 2005). Knowledge of the composition of the initial waters that become mixed to give a final mixed water allows, in principle, for the calculation, via a mass balance analysis, of the percentage of each end-member water in the final mixture *and* the changes in hydrochemistry due to chemical reactions (e.g., Parkhurst and Appelo, 1999; Appelo and Postma, 2005).

The aquifer system in the Laxemar and Forsmark areas, situated on the Baltic coast of Sweden, is composed of intrusive igneous rocks (granites, granodiorites and tonalites). Apart from some younger granite, pegmatitic granite and pegmatite, most rocks are 1.85–1.90 Ga old and are affected, to a variable extent, by penetrative ductile deformation (SKB, 2005a,b). This deformation is associated with recrystallization under amphibolite-facies (>500–550 °C) metamorphic conditions at depths probably greater than 15 km. Apart from the ductile deformation, all rocks are affected by brittle deformation, which gives rise to a dense network of fractures, both impermeable and water-bearing. Most water circulates through these high-permeability channels, although matrix blocks between main fractures also contain water. Many of these fractures are coated with fracture-filling minerals.

The chemical characteristics of groundwaters in the Laxemar and Forsmark areas are the result of a complex mixing process driven by the input of different recharge waters since the last glaciation (Laaksoharju and Wallin, 1997; Laaksoharju et al., 1999c, 2005). The successive penetration at different depths of dilute glacial melt-waters and Littorina Sea marine waters has triggered complex, density and hydraulically driven flows that have mixed them with old (long residence time) highly saline waters (brines) present in the fractures and the rock matrix. The recent infiltration of meteoric and Baltic Sea marine waters has only affected the shallowest part of the aquifer system, above 200 m depth.

Geochemical study of the Forsmark and Laxemar groundwaters, both with simple conservative elements (Smellie et al., 1995; Laaksoharju and Wallin, 1997; Laaksoharju et al., 1999c, 2004a,b)

and with more refined isotopic techniques (Peterman and Wallin, 1999; Louvat et al., 1999; Negrel and Casanova, 2005) has confirmed the existence of at least four end-member waters: a brine, a marine water (ancient Littorina Sea), a modern meteoric water and an old glacial melt-water. As a result, from a purely geochemical viewpoint, mixing can be considered the prime irreversible process responsible for the chemical evolution of the Forsmark and Laxemar groundwater systems. The successive disequilibrium states resulting from mixing have completely conditioned the subsequent water–rock interaction processes and hence the re-equilibration pathways of the mixed groundwaters. Thus, knowledge of the contribution of each end-member water to the observed present groundwaters (i.e., their *mixing proportions*) can give important clues to the dynamic evolution of the aquifer systems at Forsmark and Laxemar in particular, and to any mixing-dominated aquifer system in general.

The quantitative assessment of mixing (and reaction) in groundwaters can be approached by inverse modelling with standard geochemical codes like NETPATH (Plummer et al., 1994) or PHREEQC (Parkhurst and Appelo, 1999), and with PCA-based codes such as M3 (e.g., Laaksoharju et al., 1999c, 2008). In both cases a correct selection of the end-member waters is critical for the approach to work. Besides the first-order process of mixing, the inclusion of water–rock chemical reactions represents an additional source of uncertainty that must be addressed when analysing the sensitivity of the computed mixing proportions to variable mineral mass transfers.

Thus, any mixing calculation performed on a real, complex groundwater system has several sources of uncertainty that contribute to the final accuracy of the computed mixing proportions. Among these sources, the most important are (1) the number and compositions of the water end-members that contribute to the chemical composition of the groundwater, as stated above; (2) the spatial and/or temporal chemical variability of each end-member (end-member waters need not be spatially homogeneous nor temporally constant); (3) the possible chemical reactions that could contribute to the evolution of the groundwater system after each mixing event, which also dictates the conservative versus non-conservative behaviour of specific elements during mixing; and (4) analytical uncertainties.

In this paper, only uncertainties derived from case (3) are dealt with in detail. In order to minimise the effect of the other types of uncertainties, *synthetic* samples have been created by mixing specific and perfectly known end-member waters, therefore avoiding the first two sources of uncertainty. Type-1 uncertainties have been extensively studied by Luukkonen (2001), Bath and Jackson (2002), Laaksoharju (2004) and Laaksoharju et al. (2004a,b) in the context of the Scandinavian Shield, where the reader is referred for details. The basic conclusion drawn from these studies is that a correct identification of the end-member waters is *critical* for a successful prediction of the mixing proportions. Type-2 uncertainties have also been analysed by Laaksoharju (2006) in the context of the Scandinavian Shield groundwaters. Type-4 uncertainties are much smaller than Type-2 uncertainties and therefore can be ignored in a first approximation. However, when calculating mixing proportions with PHREEQC, this type of uncertainty has been taken into account and this is briefly explained below.

In summary, this paper, which has a clear methodological flavour, assesses the uncertainty in the calculated mixing proportions introduced by chemical reactions (second-order effect) in a mixing-dominated (first-order effect) "synthetic" groundwater system. This is explored using the standard geochemical code PHREEQC, and the PCA-based code M3 by means of a mass balance inverse modelling calculation. As the aim is to gauge the impact of chemical reactions on the computed mixed proportions, uncertainties due to poor knowledge of the end-members are eliminated by using synthetic samples created from known end-member waters. Section 2 explains how these synthetic waters are created with the direct modelling capabilities of PHREEQC, and also briefly introduces the two different geochemical codes PHREEQC and M3 used in the rest of the paper. In total, 10 different synthetic water samples are created by mixing four end-member waters, five of them saline and five brackish, with compositions similar to many real groundwaters from the Scandinavian Shield. These synthetic samples differ in the type and intensity of the chemical reactions that have been imposed on them after the mixing step.

Section 3 summarises the results obtained with the inverse modelling capabilities of PHREEQC and M3 for the 10 different synthetic samples. The principal stress falls on how the chemical reactions affect the computed mixing proportions, and less

on how the chemical reactions themselves can be identified. The results obtained with PHREEQC are evaluated first, and then those obtained with M3. The section is organised from the less complex samples (only mixing) to the most complex (mixing and several chemical reactions acting together).

Finally, Section 4 is a discussion on the assessment of the uncertainties in view of the results presented in Section 3. It is concluded that PHREEQC can predict the correct mixing proportions in most cases, provided a guess at the chemical reactions that have taken place is made. M3 can also correctly predict the mixing proportions for most synthetic samples, more so when only conservative elements are used as input variables. As for the chemical reactions, an indeterminacy is always present, which is inherent to any inverse modelling in the presence of external uncertainties. That means that different sets of chemical reactions can give the same final chemical composition for a specific water sample. In this respect, an independent assessment of which chemical reactions are most likely is an indispensable ingredient to a successful application of this methodology.

Before closing the Introduction, it is important to stress again that this methodology is useful only when the system under consideration is dominated by mixing. If mixing is the first-order effect, reactions would only be of secondary importance, and their impact on the final composition of a water sample would be small compared to the overwhelming impact of mixing (except for physicochemical parameters like pH and Eh, whose behaviour during mixing is highly nonlinear). If reactions are so important as to completely modify the composition of the mixed water, an alternative methodology should be used.

2. Modelling methodology

2.1. PHREEQC and M3 approaches

PHREEQC, an example of a well known standard geochemical code, can solve multi-end-member mixing and reaction problems by forward and inverse modelling (Parkhurst and Appelo, 1999). When dealing with forward modelling, PHREEQC computes the chemical composition of a mixed water knowing the chemical composition of each initial water *and* the mixing proportions. Additionally, on the final mixed water several equilibrium constraints can be imposed representing chemical

reactions that modify the water composition computed only by mixing.

The inverse modelling approach of PHREEQC starts from the chemical composition of the final mixed water, the chemical composition of each selected initial water, and the stoichiometry of a set of feasible phases (minerals that dissolve and/or precipitate, exchangeable phases, gases, etc., representing heterogeneous chemical reactions) and computes from there the proportion of each end-member and the mineral mass transfers that best explain the chemical composition of the final mixed water. For that purpose, PHREEQC minimises the sums of the residuals of all variables in the mixing problem, including those that take part in reactions.

Because of this, the output of the calculation is *not* a unique set of mixing proportions and of mineral mass transfers due to reactions. PHREEQC will usually output many different sets of mixing proportions and mineral mass transfers. In the jargon, each combination of a set of mixing proportions and a set of mineral mass transfers is called a *model*. Accordingly, the result of each inverse calculation is a set of models, and it will be said that PHREEQC has "found" different models meaning that the output of PHREEQC consists of many sets of mixing proportions + mineral mass transfers. Usually all these models (anything between 2 and several hundred) can be grouped by similitude of mixing proportions and mineral mass transfers into a small number of *really* different combinations.

The fact that the output of PHREEQC consists of many different models makes the use of this classical methodology very difficult and tedious when applied to a large groundwater dataset. Previous knowledge of the results given by a PCA-based code can be of inestimable help in selecting a smaller set of models (ideally only one) from the PHREEQC output.

M3 is a Principal Component Analysis code that approaches the modelling of mixing and mass balance from a purely geometrical perspective (Laaksoharju et al., 1999a,b; Gómez et al., 2006). As opposed to standard geochemical codes, M3 tries first to explain the chemical composition of a water by pure mixing, and only then are deviations from the pure mixing model interpreted as chemical reactions.

The M3 multivariate approach uses several chemical and physicochemical variables (conservative and non-conservative) to construct an ideal linear mixing model of the groundwater system. This is done by performing a Principal Component rotation of a $n \times n$ covariance matrix, where n is the number of chemical and physicochemical variables (e.g., Gershenfeld, 1999). Each element of the covariance matrix expresses the degree of correlation of a pair of variables. Graphically this is equivalent to the rotation of a reference frame composed of n orthogonal axes (one axis for every variable) until one axis, the first principal component, points in the direction of the maximum variability of the data set; another axis, the second principal component, points in the perpendicular direction with the second-largest variability; and so on for the other axes. Once the samples *and* the end-members have been expressed in the Principal Component co-ordinates, mixing proportions are calculated in a straightforward way as the *local* co-ordinates of each sample in a hyper-tetrahedron whose vertices are the end-members (Laaksoharju, 2005). This hyper-tetrahedron is a simplex and therefore always has as many dimensions as end-members minus one. Because there is one co-ordinate (i.e., one axis) for each input variable, at least as many input variables as end-members minus one are needed to obtain the mixing proportions (e.g., if three input variables are being used, say the concentration of Cl, Br, and ^{18}O, it would be possible to give mixing proportions between two, three or a maximum of four end-member waters).

Actually, M3 can calculate the mixing proportions with two different algorithms, called "Two principal component mixing" (see Laaksoharju et al., 2008) and "*n*-principal component mixing". The first algorithm uses only the information stored in the first two principal components to compute the mixing proportions (geometrically, it works on the 2-dimensional plane defined by the first two principal components), whereas the second one uses all principal components to compute the mixing proportions (geometrically, it works in an *n*-dimensional space, where *n* is the number of input compositional variables, Laaksoharju, 2005). All the calculations reported in this paper have been carried out with the *n*-principal component mixing algorithm.

Once the mixing proportions are calculated, the constituents that cannot be described by mixing are described using reactions by simple elemental mass balance supported by independent knowledge of the system. Reactions are inferred heuristically (by inspection) from the difference, for each sample, between the actual value of an input variable and

the value computed by M3 assuming pure mixing. For example, if there is a deficit of both Ca and HCO_3^- in the computed composition compared with the actual Ca and HCO_3^- contents, it could be inferred that calcite has precipitated. There is no rigorous statistical test to decide whether a deviation between the computed and the analysed concentration of an element in a sample is sufficient to invoke a reaction.

2.2. Generation of synthetic waters

In order to work with a dataset where uncertainties due to a poor knowledge of the number and exact composition of the end-members are kept at a minimum, several synthetic waters chemically similar to those in the Scandinavian Shield have been created. This procedure was carried out with the direct approach implemented in PHREEQC.

To create the synthetic waters with PHREEQC, four end-members have been used: Brine (Br), Littorina (Lit), Glacial (Gl) and Precipitation (P). The composition of each end-member is reported in Table 1. The following two mixing proportions have been used:

SALINE : 60%Br + 10%Lit + 30%Gl + 0%P

BRACKISH : 1.6%Br + 50.8%Lit + 24.4%Gl + 23.2%P

The chemical composition obtained with these mixing proportions is shown in Tables 2 and 3. The chemical characteristics of Sample SALINE are similar to the deepest and more saline groundwaters found in the Laxemar area. The chemical composition of Sample BRACKISH is similar to many brackish, Littorina-bearing groundwaters found in different areas of the Scandinavian Shield.

The chemical composition of these two waters, as obtained by conservative mixing of the four mentioned end-members, has been further modified by imposing three different sets of reactions (at 25 °C, using the WATEQ4F thermodynamic database):

- **Set A**: equilibrium with calcite, illite and chlorite;
- **Set B**: ionic exchange involving Na, Ca, K and Mg, plus calcite equilibrium;
- **Set C**: ionic exchange involving Na, Ca, K and Mg, plus calcite equilibrium plus SO_4-reduction;

Each of these three sets of reactions give rise to a different water type.

2.2.1. Type-A waters

The effects of equilibrium with phases like calcite, albite, adularia and kaolinite on the composition of the groundwaters have been evaluated by Laaksoharju et al. (2004a, 2005) and, in most cases, the amount of mass transfer and the corresponding chemical changes are very small. From these minerals, the most important phase is calcite and has been included in the calculations.

Alongside calcite, illite and chlorite (two of the most common phyllosicates found in fracture fillings in the Forsmark and Laxemar areas) were also selected for the equilibrium calculations. The chemical composition of type-A waters, obtained as a result of superimposing these reactions on samples SALINE and BRACKISH are shown in Tables 2 and 3 under columns "SALINE-A" and "BRACKISH-A", respectively. Compared with the original mixed waters, the chemical composition in these re-equilibrated waters barely changes.

2.2.2. Type-B waters

As no cation exchange capacity data of fracture-filling materials for the Forsmark and Laxemar boreholes are available, some indirect estimations (Viani and Bruton, 1997) have been used for the calculations with PHREEQC. The final chemical composition of the waters affected by cation exchange is shown in Tables 2 and 3 under the headings "SALINE -B" and "BRACKISH-B", respectively. Columns B1 and B2 show the resultant composition considering two different cation exchange capacity (CEC) constants: 0.1 mol/kg H_2O (column B1)

Table 1
Composition of the end-members used in this work (from Laaksoharju, 2005)

End-member	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	HCO$_3$ (mg/L)	Cl (mg/L)	SO$_4$ (mg/L)	Br (mg/L)	^{2}H (dev)	^{3}H (TU)	^{18}O (dev)
Brine	8500	45.5	19,300	2.12	14.1	47,200	906	323.6	−44.9	0.00	−8.9
Glacial	0.17	0.4	0.18	0.1	0.12	0.5	0.5	0.0	−158	0.00	−21
Littorina	3674	134	151	448	93	6500	890	22.2	−38	0.00	−4.7
Precipitation	0.4	0.29	0.24	0.1	12.2	0.23	1.4	0.0	−80	168	−10.5

Table 2
Chemical and isotopic composition of the SALINE synthetic samples

SALINE samples: 60% Br + 10% Lit + 30% Gl + 0% P

	SALINE	SALINE-A	SALINE-B		SALINE-C
	Only mixing	Mixing + equilibrium (calcite, illite, chlorite)	Mixing + cation exchange (CE) + calcite eq.		Mixing + CE + calcite eq. + SO_4-reduction
			B1: CEC = 0.1 mol/kg H_2O	B2: CEC = 0.2 mol/kg H_2O	
pH	7.16	7.99	6.97	6.97	6.28
Na	5894.58	5894.58	5991.13	6073.90	6476.21
K	43.24	42.62	40.70	25.25	40.11
Ca	12557.06	12545.04	12488.90	12440.80	12064.08
Mg	46.74	50.48	42.78	39.57	39.93
HCO_3^-	18.61	2.92	18.01	17.49	85.66
Cl	31326.30	31326.30	31326.30	31326.30	31326.30
SO_4^{2-}	678.84	678.84	678.84	678.84	582.78
Br	212.56	212.56	212.56	212.56	212.56
d^2H (per mil)	−78.14	−78.14	−78.14	−78.14	−78.14
$d^{18}O$ (per mil)	−12.11	−12.11	−12.11	−12.11	−12.11
Tritium (^3H)	0	0	0	0	0

Concentrations in mg/L.

Table 3
Chemical and isotopic composition of the BRACKISH synthetic samples

BRACKISH samples: 1.6% Br + 50.8% Lit + 24.4% Gl + 23.2% P

	BRACKISH	BRACKISH-A	BRACKISH-B		BRACKISH-C
	Only mixing	Mixing + equilibrium (calcite, illite, chlorite)	Mixing + cation exchange (CE) + calcite eq.		Mixing + CE + calcite eq. + SO_4-reduction
			B1: CEC = 0.1 mol/kg H_2O	B2: CEC = 0.2 mol/kg H_2O	
pH	7.41	7.63	7.38	7.34	7.14
Na	2036.20	2036.20	1853.43	1769.06	2236.20
K	69.83	68.97	53.99	51.61	50.79
Ca	412.02	408.82	658.51	742.68	369.46
Mg	230.34	231.53	183.74	178.32	152.85
HCO_3^-	50.92	46.13	50.64	50.03	147.05
Cl	4158.60	4158.60	4158.60	4158.60	4158.60
SO_4^{2-}	473.66	473.66	473.66	473.66	377.60
Br	17.02	17.02	17.02	17.02	17.02
δ^2H (per mil)	−77.13	−77.13	−77.13	−77.13	−77.13
$\delta^{18}O$ (per mil)	−10.09	−10.09	−10.09	−10.09	−10.09
Tritium (^3H)	39	39	39	39	39

Concentrations in mg/L.

and 0.2 mol/kg H_2O (column B2). In contrast with type-A waters, the chemical variation introduced by cation exchange (Na, K, Ca and Mg) is considerably bigger.

2.2.3. Type-C waters

The SO_4-reduction process has been defined in PHREEQC by the reaction

$$SO_4^{2-} + 2CH_2O + OH^-$$
$$\rightarrow HS^- + 2HCO_3^- + H_2O \qquad (1)$$
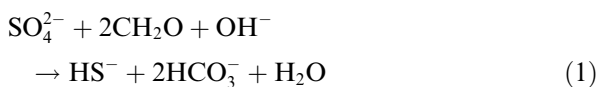
using a reaction progress of 1 mmol. The effect of this simple reaction on the SO_4 and carbonate concentrations in waters is consistent with the ranges found in groundwaters affected by SO_4-reduction (Laaksoharju and Wallin, 1997). This reaction has been combined with cation exchange (CEC = 0.2 mol/kg H_2O) and calcite equilibrium in order to create type-C samples SALINE-C and BRACKISH-C.

Summarising, for each of the two selected mixing proportions, SALINE and BRACKISH, there are five synthetic samples with which the inverse approach implemented in PHREEQC and in M3

have been checked: only mixing (one sample); mixing + Set-A reactions (one sample); mixing + Set-B reactions (two samples); and mixing + Set-C reactions (one sample).

In what follows, waters SALINE and BRACKISH without a suffixed letter are waters affected only by mixing, whereas waters with a suffixed letter are affected by mixing *and* the specific set of reactions designated by the corresponding letter (A: equilibrium with calcite, chlorite and illite; B: cation exchange and calcite equilibrium; C: cation exchange, calcite equilibrium and SO_4-reduction).

3. Results

3.1. Inverse modelling with PHREEQC

This approach allows the calculation of all the possible mixing proportions (with respect to several selected end-members) and mass transfers (with respect to a set of selected chemical reactions) that can justify the chemistry of a specific water sample.

In the present case, the justifying waters (called "final waters" in the calculation procedure) are the synthetic waters presented in the previous Section, and the end-members (called "initial waters" in PHREEQC terminology) Brine, Littorina, Glacial and Precipitation, are the same used in the direct modelling to create the synthetic waters. This is so because it is necessary to concentrate on the uncertainty derived from an incomplete knowledge of the chemical reactions, not on an incomplete knowledge of the end-member waters.

Four sets of mineral phases (reactions) have been considered in the mass balance calculations, similar to those used to create the synthetic waters:

- **Set 1**: calcite, illite and chlorite (used to create the synthetic waters of type A).
- **Set 2**: calcite and exchangers CaX_2, NaX, MgX_2 and KX (used to create the synthetic waters of type B).
- **Set 3**: Set 2 plus the SO_4-reduction reaction.
- **Set 4**: Set 1 plus the SO_4-reduction reaction.

The chemical parameters used in the calculations (termed "constraints" in the terminology of the approach) are pH, Na, K, Ca, Mg, HCO_3, SO_4, Cl, Br, δ^2H and $\delta^{18}O$. Bromide has been included, together with Cl, δ^2H, $\delta^{18}O$ and SO_4 (only when SO_4-reduction is negligible), as conservative elements during mixing. These elements are essential

parameters in determining the mixing proportions because their concentration in the final water only depends on the end-member mixing proportions. Calculations were repeated by deleting some of these conservative elements (Br or SO_4) and the results did not change very much in most cases, indicating that there is redundant information in the conservative elements (however, keeping as many conservative elements as possible is always advantageous because results are more robust with redundant information). All other chemical parameters included in the calculations are subject to mass transfer and they are dissolved/precipitated from/to reacting phases to satisfy the calculation constrains (chemical concentrations of the elements).

Inverse modelling in PHREEQC also allows the treatment of analytical uncertainties, including both chemical and isotopic uncertainties. The uncertainty used is 0.05 units for pH, 0.1‰ for $\delta^{18}O$, 1‰ for δ^2H and 5% for the rest of the elements.

The mass balance results for the different types of samples follows here.

3.1.1. Pure mixing

These synthetic samples are the result of conservative mixing between end-members in the proportions indicated in Tables 2 and 3. Therefore, in principle, the inverse method of PHREEQC should only need the end members as initial waters to obtain these final waters (no mineral phases needed). However, in order to avoid errors in the resolution algorithm the definition of a feasible set of phases (reactions) is required. When doing this, and independently of the phases, PHREEQC obtains several models, the first of which is always the pure mixing model which consistently reproduces the original mixing proportions, as Table 4 shows. For these models, propagating the assumed analytical uncertainties in order to maximize their impact on the mixing proportions (by selecting the models with more extreme mixing proportions), an uncertainty of 5% in the calculated mixing proportions is obtained.

The other models found by PHREEQC involve mass transfers with respect to the selected set of phases. These transfers are negligible and only produce a variation of the order of 0.1% in the mixing proportions, well inside the assumed analytical uncertainties.

These results indicate that PHREEQC is able to detect with high precision the existence of a conservative mixing process. This seems obvious, as the

Table 4
Mixing proportions obtained by inverse modelling with PHREEQC for samples created by pure mixing with the direct approach

		Sample SALINE		Sample BRACKISH	
		Synthetic data (PHREEQC direct approach)	Inverse approach results without mass transfer	Synthetic data (PHREEQC direct approach)	Inverse approach results without mass transfer
% Mixing	Brine	60	59.41	1.6	1.61
	Littorina	10	10.55	50.8	51.18
	Glacial	30	30.03	24.4	24.60
	Precipitation	0	0.00	23.2	24.61

synthetic waters have been created with the same code. However, the mathematical algorithm used for the inverse modelling is completely different to the one used in the direct method. The inverse method implemented in PHREEQC uses linear equalities and inequality constraints to compute at the same time the mixing proportions and the mineral mass transfers, taking into account analytical uncertainties. Because this set of equations and inequalities is different from the one used in the direct approach, one can in principle create a sample with the direct algorithm and then be unable to recover the correct mixing proportions and mass transfers with the inverse approach if a different set of reactions is used. With two end-members the verification of this two-way procedure is difficult and time-consuming. With three or more end-members, it is simply a nightmare.

3.1.2. Mixing + equilibrium with calcite, illite, and chlorite

Type-A samples were created assuming mixing and equilibrium with calcite, illite and chlorite. As was shown in Tables 2 and 3, the effect of these reactions on the dissolved concentration of the selected elements is minimal, smaller in most cases than the analytical uncertainty considered in the calculations.

When the inverse modelling is carried out with Set 1 (column "Set 1" in Table 5) the same set of reactions used for the creation of these waters, the obtained models reproduce with high accuracy the original mixing proportions *and* also the (very low) mass transfers. Some models are even able to justify the final waters with no mass transfers. This means that type-A waters can be explained just by conservative mixing, which is reasonable considering that the chemical changes produced by the reactions are inside the assumed analytical uncertainty limits. Taking into account these input uncertainties, maximum variations in the mixing proportions are of the order of $\pm 2\%$.

When a set of reactions different to the one used to create the samples is included (column "Set 2" in Table 5, ionic exchange), PHREEQC obtains again some models just by mixing, which reproduce almost perfectly the original mixing proportions. The rest of the models, with higher mass transfers than in type-A waters, produce more variable mixing proportions, although always close to the original ones, because mass transfers associated with the exchange reactions represent only a minor percentage of the dissolved concentrations. A closer look at Table 5 shows that Set-2 tends to overestimate the proportion of the brine end-member. This is due to the exchange of Na between the water and

Table 5
Mixing proportions obtained by inverse modelling with PHREEQC for samples SALINE-A and BRACKISH-A (mixing + equilibrium with calcite, illite, and chlorite)

	Sample SALINE-A				Sample BRACKISH-A			
	Synthetic data (direct approach)	Inverse approach			Synthetic data (direct approach)	Inverse approach		
		Set 1	Set 2			Set 1	Set 2	
			No mass transfer	With mass transfer			No mass transfer	With mass transfer
% Brine	60	59.02	59.07	63–65	1.6	1.65	1.60	1.6–1.9
% Littorina	10	10.9	10.88	7.4–10.9	50.8	50.48	50.55	47.6–50.9
% Glacial	30	30.07	30.05	25.4–31.1	24.4	24.23	24.27	22.7–24.5
% Precipitation	0	0.0	0.0	0.0–8.7	23.2	23.64	23.53	22.9–27.8

the exchanger, which is compensated (to give the correct concentration of Cl^-) with a lower concentration of Littorina (to subtract Cl^- from the water) and a higher one of Precipitation (to dilute the final water, thus further lowering the Cl^- content).

These results show that uncertainties related to a poor knowledge of the reacting phases can increase the final uncertainty in the mixing proportions up to a maximum of 9%.

3.1.3. Mixing + cation exchange + calcite equilibrium

In type-B samples ionic exchange processes and calcite equilibrium introduce stronger chemical changes in the waters. When the inverse modelling is performed with Set 2 ("Set 2" column in Table 6), which is the same set of reactions used to generate the B1 waters, several models are obtained. Some of them reproduce exactly the original mixing proportions and mass transfers. Table 6 gives the range of mixing proportions taking into account all the models found by PHREEQC. Variations are most important in the Precipitation end-member, although these are always smaller than 10%.

Inverse modelling the chemistry of the waters with Set 1 ("Set 1" column in Table 6; mineral equilibrium), the number of models found by PHREEQC and the variation in mixing proportions are smaller than with Set 2. Mixing proportions for Sample SALINE-B agree very well with the original proportions. As for Sample BRACKISH-B, differences between original and calculated mixing proportions are lower than 8%, being highest for the Precipitation end-member. Mass transfers (of the order of 0.1 mmol) and direction of reactions (dissolution or precipitation) are both reasonable in the context of this methodology. The narrower range of mixing proportions in the SALINE sample is due to the higher content of the Brine end-member

in this sample, which fixes the proportion of Brine very strictly (no other end-member can provided so much Na^+ and Cl^-) and thus the proportion of the other end-members.

These results indicate that mixing proportions can be well reproduced, with no important effects from reactions. However, as different sets of reactions can reproduce the chemistry of the final waters, an independent assessment of the feasible reactions that have possibly taken place in the system must be carried out beforehand. In other words, if the aim is mixing proportions, the results are reliable; on the other hand, if the main interest is reactions, then the intrinsic underdetermination inherent to the inverse modelling shows up and should be corrected by independent means.

3.1.4. Mixing + cation exchange + calcite equilibrium + sulphate-reduction

These samples represent the combined effects of ionic exchange, calcite equilibrium and SO_4-reduction. Sulphate-reduction affects dissolved SO_4^{2-} content, and this has very high concentrations in the two sets of synthetic waters, SALINE and BRACKISH. As both Littorina and Brine end-members have high SO_4^{2-} contents, SO_4^{2-} in the final water can come from either source and this introduces a source of uncertainty in the mixing proportions of Littorina and Brine, depending on whether SO_4^{2-} is treated as conservative or non conservative.

When using Set 3 for the inverse modelling (the original set of phases), a fairly high variation in mixing proportions is obtained, especially for the Precipitation end-member (column "Set 3" in Table 7). Although these variations could be considered acceptable in most cases, it casts some doubts on the results, indicating the need of independently checking with additional data (Fe and sulphide con-

Table 6
Mixing proportion results obtained by inverse modelling with PHREEQC samples SALINE-B and BRACKISH-B (mixing + equilibrium with calcite + cation exchange)

	Sample SALINE-B			Sample BRACKISH-B		
	Synthetic data (direct approach)	Inverse approach		Synthetic data (direct approach)	Inverse approach	
		Set 2 (low mass transfer)	Set 1		Set 2 (low mass transfer)	Set 1
% Brine	60	57.6–63.3	59.50	1.6	0.0–3.0	3.0
% Littorina	10	8.5–12.5	10.45	50.8	44.0–58.0	44.6
% Glacial	30	28.1–30.1	30.03	24.4	20.9–28.3	31.2
% Precipitation	0	0.5–7.5	0.0	23.2	13.0–31.0	21.2

Table 7
Mixing proportion results obtained by inverse modelling with PHREEQC for Samples SALINE-C and BRACKISH-C (mixing + ionic exchange, calcite equilibrium and SO_4-reduction)

	Sample SALINE-C			Sample BRACKISH-C		
	Synthetic data (direct approach)	Inverse approach		Synthetic data (direct approach)	Inverse approach	
		Set 3 (range)	Set 4 (range)		Set 3 (range)	Set 4 (range)
% Brine	60	62.6–68.4	64.0–64.5	1.6	0.8–2.1	1.1–1.2
% Littorina	10	0.0–8.0	6.0–8.0	50.8	45.6–58.6	50.6–56.5
% Glacial	30	25.0–29.5	28.2–28.9	24.4	21.6–33.1	24.3–27.4
% Precipitation	0	0.0–11.3	0.0	23.2	12.0–30.7	15.0–23.9

centrations, S isotope data, etc.) the extent of the SO_4-reduction process.

When using Set 4 for the inverse modelling (column "Set 4" in Table 7), consisting of SO_4^{2-}-reduction and equilibrium with calcite, illite and chlorite, mixing proportions are closer to the original ones and their variability smaller. These results indicate, again, that similar mixing proportions can be obtained using different sets of reactions.

3.2. M3 mixing and mass balance calculations

The same synthetic waters created in Section 2.2 with the direct modelling approach of PHREEQC have been used for verifying M3 performance, with the exception of the water affected by SO_4^{2-} reaction, that in this case has no cation exchange nor equilibrium with calcite in order to better appreciate changes in the concentration of SO_4^{2-} and HCO_3^-. Ideally M3 should provide mixing proportions as close as possible to the original ones, independent of the variability introduced by the added chemical reactions (because M3 tries first to account for mixing, and only the unexplained part of the chemical composition is then attributed to water–rock interaction). *In principle*, the chemical differences between the synthetic water and the water obtained from the M3-calculated mixing proportions, could be used, via a mass balance step, to determine the reactions that have taken place.

In order to verify this assumption, the two sets of synthetic waters (SALINE and BRACKISH, with and without reactions) have been included in a real groundwater dataset from the Laxemar area consisting of 158 samples. This is a necessary step as M3 uses a multivariate approach, Principal Components Analysis, for which a large number of samples is required. Actually, for few samples PHREEQC

would be a simpler and better option. The strong point of M3 is precisely the ability to work with thousands of samples at the same time.

Mixing proportions have been calculated with M3 considering end-members Brine, Glacial, Littorina and Precipitation as before. The input compositional variables used for these calculations are Na, K, Ca, Mg, HCO_3, SO_4, Cl, δ^2H, $\delta^{18}O$ and ^3H. Bromide has not been used in these first runs because not all samples in the Laxemar dataset report the concentration of this constituent. The results obtained for the different synthetic samples are shown below. The *n*-principal components algorithm implemented in the new version of M3 has been used in all calculations (Laaksoharju, 2005).

3.2.1. Samples representative of pure mixing

Here, the synthetic waters created by conservative mixing (SALINE and BRACKISH) and by mixing and equilibrium (SALINE-A and BRACKISH-A) are included (Table 8).

Table 8 shows that M3 reproduces very well the mixing proportions for all samples. This result is important in itself, as it demonstrates that the *n*-dimensional generalization of the PCA analysis implemented in M3 is able to correctly evaluate simple mixing processes in waters.

In this and the following tables the upper part (Mixing) contains the calculated mixing proportions. The lower part (Mass Balance) shows the mass balance calculated by M3 for the three conservative constituents Cl, δ^2H and $\delta^{18}O$. Results of mass balance for conservative constituents are calculated as

$$\frac{|C_{sample} - C_{predicted}|}{C_{sample}} \times 100,$$

where C_{sample} is the real concentration and $C_{predicted}$ is the predicted concentration.

Table 8
M3 results for the synthetic waters created by pure mixing (samples SALINE and BRACKISH) and by mixing and equilibrium with calcite (samples SALINE-A and BRACKISH-A)

		SALINE samples			BRACKISH samples		
		Synthetic data (PHREEQC)	M3 results		Synthetic data (PHREEQC)	M3 results	
			SALINE Pure mixing	SALINE-A Mixing + mineral eq.		BRACKISH Pure mixing	BRACKISH-A Mixing + mineral eq.
Mixing	Brine	60	60.0	58.2	1.6	1.4	1.3
	Littorina	10	11.5	12.4	50.8	51.7	51.8
	Glacial	30	28.5	29.4	24.4	24.4	24.9
	Precipitation	0	0.0	0.0	23.2	22.5	21.9
Mass Bal, %	Cl		7.2	9.7		3.1	4.02
	δ^2H		2.3	3.0		0.4	0.01
	$\delta^{18}O$		1.7	3.0		0.0	0.00

The ability to identify pure mixing processes (in which all the elements behave as conservative) allows checking the actual non-conservative behaviour of the chemical elements included in the PCA. In M3 methodology (but not in PHREEQC), constituents participating in chemical reactions are treated on exactly the same footing as the non-reactive ones and therefore the reacting constituents also influence the computed mixing proportions of every water sample. This problem is further explored in the last Section.

3.2.2. Samples with mixing, ionic exchange and equilibrium with calcite

M3 results for synthetic samples created by mixing, ionic exchange and calcite equilibrium (samples SALINE-B and BRACKISH-B) show differences in the mixing proportions with respect to the original ones. These differences depend on the type of sample (Table 9): small variations for SALINE waters and bigger variations for BRACKISH waters.

For samples SALINE-B1 and SALINE-B2 (B1 samples are obtained with a cation exchange capacity of 0.1 mol/kg H_2O, and samples B2 with a value of 0.2 mol/kg H_2O), M3 mixing proportions have an uncertainty of 7% for Littorina and lower for the rest of the end-members (especially for Glacial). The predicted concentration of the conservative constituents (Cl, δ^2H, $\delta^{18}O$) is in very good agreement with the original ones, and always with uncertainties below 6%.

For BRACKISH-B1 and B2 samples (with Littorina as the main end-member) M3 results are well away from the original mixing proportions, especially for Brine and Littorina end-members (Table 9). Mass balances show differences of around 50% (for Cl) with respect to the synthetic sample.

These results are particularly important when checking the reliability of the mixing proportions provided by M3. In fact, they indicate that the effects of the chemical reactions propagate into the calculated mixing proportions and, therefore, M3

Table 9
M3 results for the synthetic waters created by mixing, ionic exchange and calcite equilibrium (samples SALINE-B and BRACKISH-B)

		SALINE samples			BRACKISH samples		
		Synthetic data (PHREEQC)	M3 results CEC increase		Synthetic data (PHREEQC)	M3 results CEC increase	
			SALINE-B1	SALINE-B2		BRACKISH-B1	BRACKISH-B2
Mixing	Brine	60	61.24	65.89	1.6	8.1	8.5
	Littorina	10	9.94	2.94	50.8	36.6	35.3
	Glacial	30	28.82	31.17	24.4	23.8	24.1
	Precipitation	0	0.00	0.00	23.2	31.4	32.1
Mass Bal, %	Cl		5.7	0.1		49.9	55.9
	δ^2H		1.7	2.2		4.2	4.8
	$\delta^{18}O$		0.8	3.3		6.0	6.9

Table 10
Composition of sample SALINE-SR, affected by SO$_4$-reduction (no ion exchange nor equilibrium with calcite)

	SALINE samples		BRACKISH samples	
	Only mixing	Mixing + sulphate-reduction (SALINE-SR)	Only mixing	Mixing + SR (BRACKISH-SR)
pH	7.16	7.25	7.41	7.65
Na	5894.58	5894.58	2036.20	2036.20
K	43.24	43.24	69.83	69.83
Ca	12557.06	12557.06	412.02	412.02
Mg	46.74	46.74	230.34	230.34
HCO$_3^-$	18.61	122.03	50.92	168.16
Cl	31326.30	31326.30	4158.60	4158.60
SO$_4^{2-}$	678.84	582.78	473.66	377.60
Br	212.56	212.56	17.02	17.02
d^{2}H (per mil)	−78.14	−78.14	−77.13	−77.13
d^{18}O (per mil)	−12.11	−12.11	−10.09	−10.09
Tritium (^{3}H)	0	0	39	39

mixing proportions can not be used to calculate the mass balance of the non-conservative elements. This is obvious when looking at Cl$^-$ mass balances in Table 9. Chloride is a conservative constituent and its calculated concentration should be in perfect agreement with the concentration in the synthetic water.

The noise introduced by chemical reactions in the mixing proportions computed by M3 is non-lineal and depends on the chemical characteristics of the sample. While in some cases (SALINE samples) the variation in the mixing proportions is low and acceptable, in others (BRAKISH samples) the variation is high and the discrepancies are large.

3.2.3. Samples with mixing and sulphate-reduction

The effect of SO$_4$-reduction on the chemical variables included in the analysis carried out with M3 is only visible in the concentrations of SO$_4^{2-}$ and HCO$_3^-$. Sulphate-reduction is thus a reaction with relatively simple effects on only two parameters, as

can be clearly seen in Table 10 comparing the concentrations in sample SALINE-SR with those in sample SALINE: only SO$_4^{2-}$ and HCO$_3^-$ change. Note, however, that pH also changes, but that this variable is not used as an input to M3.

M3 results depend again on the type of sample (Table 11). For the SALINE samples the calculated mixing proportions are close to the original ones; however, for the BRACKISH samples the discrepancies are large. Mass balance calculations for the conservative constituents are very useful (again) to detect this problem: while in the first case the deviation in Cl$^-$ content is <5%, in the second case it is around 80%.

3.2.4. Calculations only with conservative elements

From all the previous results, it is clear that modifications introduced on some elements by the chemical reactions produce deviations in the mixing proportions calculated by M3. These deviations can be more or less important depending on the type

Table 11
M3 results for the synthetic waters created by mixing and SO$_4$-reduction (samples SALINE-SR and BRACKISH-SR)

		SALINE samples		BRACKISH samples	
		Synthetic data (PHREEQC)	M3 results	Synthetic data (PHREEQC)	M3 results
			SALINE-SR (SO$_4$-reduction)		BRACKISH-SR (SO$_4$-reduction)
Mixing	Brine	60	64.4	1.6	12.6
	Littorina	10	4.5	50.8	22.7
	Glacial	30	23.6	24.4	13.7
	Precipitation	0	7.5	23.2	51.0
Mass Bal, %	Cl		2.0		78.5
	δ^2H		5.4		0.5
	δ^{18}O		3.3		3.0

Table 12
M3 results for the synthetic waters created by pure mixing using only conservative constituents (Cl, Br, δ^2H and $\delta^{18}O$)

		Sample SALINE			Sample BRACKISH		
		Synthetic data (PHREEQC)	M3 results		Synthetic data (PHREEQC)	M3 results	
			All elements (considered conservative)	Only conservative elements		All elements (considered conservative)	Only conservative elements
Mixing	Brine	60	60.0	59.3	1.6	1.4	1.9
	Littorina	10	11.5	10.6	50.8	51.7	49.5
	Glacial	30	28.5	30.0	24.4	24.4	23.9
	Precipitation	0	0.0	0.0	23.2	22.5	24.7
Mass Bal, %	Cl		7.2	0.9		3.1	0.07
	δ^2H		2.3	0.001		0.4	0.001
	$\delta^{18}O$		1.7	0.008		0.0	0.0

and extent of reactions, and the type of water involved, all subject to uncertainty in a study with real water samples.

A possible solution to this problem could be to limit the PCA analysis to constituents behaving conservatively in the system. Among all the constituents considered in the calculations (Na, K, Ca, Mg, HCO$_3$, SO$_4$, Cl, δ^2H and $\delta^{18}O$) only three of them (Cl, δ^2H and $\delta^{18}O$) have an *a priori* conservative behaviour. M3 needs at least three input compositional variables to compute the mixing proportions of four end-members. But these input compositional variables should give independent information, and δ^2H and $\delta^{18}O$ are highly correlated ($r = -0.98$). Due to working with four end-members (Brine, Glacial, Littorina and Precipitation), an additional conservative element is required. For this purpose, Br$^-$ has been selected as the fourth conservative element, although not all water samples in Laxemar have been analysed for Br.

In order to verify this approach, the previous M3 calculations have been repeated using four input variables, Cl, Br, δ^2H and $\delta^{18}O$. Only the two synthetic samples not affected by reaction, samples SALINE and BRACKISH, are used for this test in order to assess the importance of the number of input compositional variables in the computed mixing proportions.

M3 results are shown in Table 12 together with previous results as obtained with conservative and non-conservative elements (taken from Table 8). It can be seen that M3 correctly reproduces the original mixing proportions indicating that the decrease in the number of input parameters does not reduce the precision with which mixing proportions are estimated when waters are the result of pure mixing.

This is of course only true if there is no uncertainty in the end-members (Rueedi et al., 2005).

More importantly, the differences in mass balances for the conservative constituents are very small, as it should be for conservative constituents, certainly much smaller than working with conservative and non-conservative constituents at the same time. For example, Cl reduces its imbalance from 7.2% to 0.9% in Sample SALINE and from 3.1% to 0.07% in Sample BRACKISH. The reduction in the ^2H and ^{18}O imbalance is even more pronounced (a factor of 100).

This results can be generalised to waters affected by mixing *and* reaction (i.e., to real groundwaters) as this method is based only on conservative constituents which, by definition, are not affected by reactions.

A more comprehensive verification of these results is needed (with a wider range of synthetic samples), but nevertheless the use of conservative elements in M3 to compute mixing proportions can be an important methodological improvement as it seems to be able to avoid the noise produced by the non-conservative constituents therefore extending the qualitative interpretation of the mass balances to a more quantitative basis.

4. Discussion and conclusions

4.1. PHREEQC

Mixing and mass balance calculations performed with PHREEQC give a reasonable estimate of the real mixing proportions. The use of four conservative constituents (Cl, Br, δ^2H, $\delta^{18}O$) seems to provide extra robustness to the calculated proportions

independent of the reactions (phases) included in the calculations.

This last statement must be explained. First, all the inverse modelling results presented here have been obtained using exactly the same end-members selected to create the synthetic samples, assuring that way that the differences in the original mixing proportions *really* are due to chemical reactions. The effects of a different selection of end-members have already checked elsewhere and can dramatically modify mixing proportions and mass transfers (Laaksoharju, 1999, 2004; Luukkonen, 2001; Laaksoharju et al., 2004a,b).

Second, SO_4-reduction in waters with high SO_4 contents (similar to the ones used in this work) produces additional variations due to the presence of two end-members which supply this component to the waters (Brine and Littorina). Therefore, the actual operation of this process must be clearly established before the mass balance calculations are performed. Alternatively, the inclusion of a higher number of parameters in the model should be taken into account.

Finally, with the input compositional variables used in the mass balance calculations, the chemistry of the groundwaters can be explained invoking different sets of reactions, mainly ionic exchange and equilibrium with different mineral phases (aluminosilicates and calcite) without important modifications in the calculated mixing proportions. This non-uniqueness of the set of reactions that can explain the composition of a water sample is in itself a source of uncertainty for the mineral mass transfers (not so much for the mixing proportions) that can be overcome with additional chemical information (e.g. Al concentration) and, of course, with a detailed knowledge of the mineralogy (rock matrix and fracture fillings) of the flow system. However, the lack of Al data in the studied groundwaters and of exchange capacity constants in the fracture-filling minerals are two important limitations, both in assessing the feasibility and extent of these processes before the mass balance calculations are carried out, and in the overall performance of the approach.

4.2. M3

The uncertainty and sensitivity analysis performed in this paper has demonstrated that the PCA analysis implemented in M3 is able to reproduce, with high accuracy, the mixing proportions

of synthetic waters created only by conservative mixing of several end-members (i.e., all the elements behave conservatively).

This capability has allowed assessing the errors produced by this methodology on real samples in which the components can behave non-conservatively (affected by chemical reactions). When chemical reactions only produce slight variations with respect to the chemical composition of the conservative mixing (lower than 2%), M3 gives mixing proportions in very good agreement with the real ones.

When chemical reactions produce an important compositional change (higher than 10% for the studied samples) M3 mixing proportions do not reproduce the original values, and the departure depends on the chemical reaction and/or the type of water. For example, the effect of a simple reaction like SO_4-reduction (only affecting two of the components included as input variables in the calculations, SO_4^{2-} and HCO_3), can be responsible for important deviations in the calculated mixing proportions. The noise produced by the non-conservative components in this kind of statistical analysis propagates directly to the mixing proportions calculated by the code.

These findings have important consequences on the use of M3 when conservative and non-conservative components are included. The noise introduced by the reactions in any study with real waters may be unknown *a priori* and therefore, its effects on the calculated mixing proportions would also be unknown. Therefore, M3 mixing proportions should not be used without first checking its accuracy with the mass balance of the conservative components: if the imbalance is small, then the mixing proportions are reliable. The conservative behaviour of a component is not known *a priori*, but can easily be demonstrated with suitable ion–ion plots or other simple geochemical tools.

Nevertheless, once the mixing proportions are calculated, mass balances, also provided by the code (with respect to the conservative components, especially Cl^-), can easily detect those samples in which reactions have produced a distortion of the calculated mixing proportions. An analysis of this sort is shown in Fig. 1, where 1088 samples from the Laxemar area have been analysed by M3 using a set of input compositional variables with conservative and non-conservative elements. Brine, Littorina, Glacial and Precipitation were used as end-members. The figure is a plot of the first two principal components, which together accumulate more
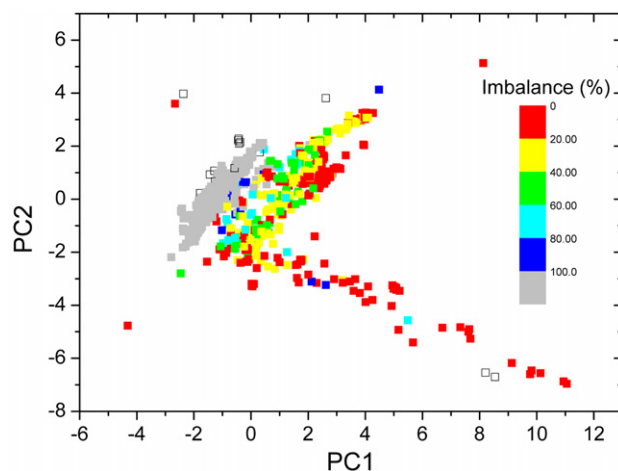
Fig. 1. Chlorine imbalance (measured as an absolute percent deviation from the real Cl content) for a set of groundwaters from the Laxemar area consisting of 1088 samples. Grey samples have Cl imbalance greater than 100% and correspond to superficial waters with very low Cl content. Open squares are samples not explained by mixing. The loadings of the first principal component, PC1, are $0.418 \times Na + 0.3494 \times K + 0.3264 \times Ca + 0.3197 \times Mg - 0.1469 \times HCO_3 + 0.3793 \times Cl + 0.4032 \times SO_4 + 0.3002 \times {}^2H - 0.08537 \times {}^3H + 0.2627 \times {}^{18}O$; the loadings of the second principal component, PC2, are $-0.2846 \times Na + 0.3125 \times K - 0.4291 \times Ca + 0.3309 \times Mg + 0.1808 \times HCO_3 - 0.3771 \times Cl + 0.04698 \times SO_4 + 0.3387 \times {}^2H + 0.229 \times {}^3H + 0.4283 \times {}^{18}O$.

than 80% of the compositional variance. Samples are colour-coded with respect to Cl imbalance, calculated as (Cl in sample – Computed Cl)/Cl in sample × 100. Only those waters with an imbalance smaller than 20% should be considered for modelling purposes. A plot like the one shown in Fig. 1 should be considered a basic preliminary tool when assessing the reliability of the calculated mixing proportions. If most samples have large deviation for the conservative components, that would mean that the aquifer system is probably dominated by reactions, not by mixing, and a different approach should be used (e.g. inverse modelling with PHRE-EQC or another classical geochemical code). On the other hand, if deviations are small, mixing is probably the dominating process and further modelling with M3 should be pursued.

The most obvious alternative in this case, as shown here, is the use of M3 only with really conservative components in each system. Once the mixing proportions have been calculated with the conservative components, the deviation with respect to the non-conservative components can be used to infer chemical reactions. The scoping calculations performed with this methodology indicate that the calculated mixing proportions agree very well with the synthetic ones and are not affected by the reduction in the number of input compositional variables (only four conservative components have been used, instead of the 10

input compositional variables of the other runs). This approach can be inadequate depending on the number of end-members and the availability of conservative components in each case study. Nevertheless, it offers the possibility of obtaining quantitative and reliable mixing proportions and its use, combined with additional methodologies (eg. classical mass balance and inverse modelling with PHREEQC or similar codes), would be further explored. In fact, the use of M3 to obtain reliable mixing proportions for a large number of samples should be the first step in the methodology, which would then be completed with the mass transfer calculations with PHREEQC starting with already known mixing proportions for the initial waters.

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