**MINERAL WEATHERING RATES CALCULATED FROM SPRING WATER DATA:
A CASE STUDY IN AN AREA WITH INTENSIVE AGRICULTURE,
THE MORAIS MASSIF, NE PORTUGAL.**

Running Head: Mineral Weathering Rates Calculated From Spring Water Data

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ABSTRACT

This study identifies and quantifies the water–rock interactions responsible for the composition of twenty-five spring waters, and derives the weathering rates of rock-forming minerals in a complex of petrologic units containing ultramafics, amphibolites, augengneisses and micaschists. Bulk chemical analyses were used to calculate the mineralogical composition of these rocks; the composition of the rock-forming minerals were determined by microprobe analyses. The soils developed on augengneisses and micaschists contain predominantly halloysite or mixtures of halloysite and smectites (the other units). The mineralogical and chemical data on rocks and soils are essential for writing the proper weathering reactions and for solving mole balances between the amounts of weathered primary minerals and secondary products formed (soils and solutes in groundwater). Ground waters emanating in springs were collected in three consecutive seasons, namely late Summer, Winter and Spring, and analyzed for major components. Using an algorithm based on mole and charge balance equations, we linked the average concentrations of the solutes with a combination of possible weathering reactions. To sort out the best match of weathering reactions and the concomitantly generated water composition, we checked the results against the boundary condition of similarity between the predicted and actual clay mineral abundance in the soils. Having selected the best-fit weathering reactions, we also could calculate the mineral weathering rates by combining the median discharge rates and recharge areas of the springs and normalizing the rates by the mineral abundance. For the one case—plagioclase—for which comparison with published results was possible, our results compare favorably with rates calculated by other groups. For the most abundant primary minerals we found the following order of decreasing weathering rates (in moles/(ha·y·% mineral)): forsterite (485) > clinozoisite (114) > chlorite (49) > plagioclase (45) > amphibole (28). Insofar this order differs from commonly used orders of weatherability, this has to be due to differences in the hydrologic regime within this area and between this and other case studies.

As additional objective, we wanted to explain the effects of contributions by sources other than water-rock interactions. The latter processes are coupled with acquisition of carbonate alkalinity and dissolved silica. Contributions by sources other than water-rock interactions are manifest by the chloride, sulphate and nitrate concentrations. We could approximate the contribution of atmospheric deposition. More importantly, knowledge of the application and composition of fertilizers enabled us to assess the effects of farming on the composition of ground waters emanating in the springs. We also could estimate how selective uptake of nutrients and cations by vegetation as well as ion-exchange processes in the soil modified the spring water composition.

Using this rather holistic approach, we can satisfactorily explain how spring waters, in this petrologically and agriculturally diverse area, acquired their composition.

INTRODUCTION

During the time interval between disappearance into the soil and emanation in a spring, water has been subject to many processes which can be briefly summarized as uptake or release of components in interactions with biota and minerals. The benchmark study of Garrels and Mackenzie (1967) demonstrated how a spring water composition could be related to water–mineral interactions in the soil. However, in many places on the globe, the biota—including man—plays an important if not major role in controlling the chemistry of shallow groundwater. To [resolve](#) the problem of assessment of the role of the various participants in this interplay between water and (in)organic [phases](#), mass balance studies in small drainage basins have become instrumental. In this context, we may refer to the pioneering studies on the Hubbard Brook watershed–ecosystem (Likens and Bormann, 1995, and references therein; Likens et al., 1998) and to the work of Velbel (1985ab, 1986, 1992, 1993, 1995). These studies [ignore](#) the influences of industrial and agricultural activities, other than their expression as atmospheric input. However, direct introduction of chemicals has also to be taken into account [in many watersheds](#) (Paces, 1986; Pacheco and Van der Weijden, 1996; Pacheco et al., 1999).

Mass balance studies aiming at a complete unraveling of all processes resulting in the chemistry of a particular water sample are costly [and time consuming](#). [However, even](#) that fragmentary (e.g. lack of time series) information [permits](#) realistic estimates of weathering processes. Moldan and Cerný (1994) citing Hornung et al. (1990) published a checklist of basic measurements to be made in catchment studies. We can comply with their recommendations for description of geology, soils, bedrock, mineralogy and vegetation (adequately), for spring water analyses (adequately), for discharge (but only monthly), but not for meteorological data and for dry and wet precipitation. However, we have data on manuring and fertilization, inputs ignored in the checklist.

Building on our earlier work (Pacheco and Van der Weijden, 1996; Pacheco et al., 1999), we will show how we coped with the challenge to extract from a sample of spring water qualitative and quantitative information about the processes resulting in its composition. Our first objective is to obtain quantitative estimates of weathering reactions and their rates in an area with ultramafic rocks, amphibolites, gneisses and micaschists; the area is partly occupied by natural vegetation, but is for a greater part cultivated to grow a variety of crops. To achieve our goal, we made chemical analyses of the different rock types and concomitant soils; we also analyzed these materials for their mineralogical components. In addition, we determined the discharge and chemistry of tens of samples of spring waters from the various lithologic units and calculated the recharge areas. Next, we related the average chemistries of the samples to chemical weathering reactions of combinations of bedrock-forming and soil minerals. Finally, by combining the spring discharge rates, the recharge areas and the weathering reactions, we could estimate weathering rates. The residuals, lumped together as "pollution", are the anions chloride, sulphate and nitrate and their associated cations. In this bag are put all contributions of processes that are not accounted for in the weathering reactions, such as atmospheric deposition, ion-exchange, harvesting, manuring and fertilization. Our second goal is to gain a (semi)quantitative understanding of these processes. We will use published data on the composition of precipitation to correct for atmospheric deposition, use data on the composition of manure and industrial fertilizers to reconstruct the effects of agricultural practices, use literature data on the storage of nutrients in vegetation to estimate how this probably has affected the balance of essential nutrients in the soil waters, and use plots of ratios of the major cations versus anions to demonstrate the role of ion-exchange.

STUDY AREA

The Morais area is situated in the eastern part of the Trás-os-Montes province (North Portugal). Geomorphology is characterized by a undulated plateau (mean altitude 600 m) cut

by two rivers, the Azibo and Sabor (Figure 1). On average, the annual precipitation and temperature are $P = 723$ mm and $T = 12$ °C; evapotranspiration is $ET = 422$ mm/y (58% of P). The dry period runs from May to August, with a maximum water deficit in August, and the wet period from October to May, with a maximum water surplus in February (Pacheco, 2000).

Geology

The northwest segment of the Iberian peninsula is characterized by a pile of Hercynian thrust sheets placed on top of autochthonous sequences and intruded by granitic bodies. The Morais massif (Figure 1) incorporates two sheets of the thrust pile, namely the Ophiolitic Thrust Complex (OTC), with ultramafic rocks, flasergabbros and amphibolites, and the Upper Allochthonous Thrust Complex (UATC), with granulites, peridotites, gneisses, micaschists and greywackes (Ribeiro, 1974; Ribeiro et al., 1990; Marques et al., 1992).

Mineralogy and Petrology

The ultramafics are mostly represented by serpentinites with tremolite + chlorite bands. The serpentinite is made of serpentine + chlorite + talc + relic nodules of forsterite + hornblende (pargasite) + disseminated chromite. Far from a major thrust bordering the Morais massif, the amphibolites consist of green hornblende + calcic plagioclase, with quartz + sphene + calcite + clinozoisite + chlorite + magnetite as accessories. In the vicinity of that thrust, they underwent retrograde metamorphism, which altered hornblende into cross chlorite porphyroblasts and plagioclase into saussurite (raising the proportions of clinozoisite) or albite (with loss of calcium, which then precipitated as calcite veins). The porphyroblasts of the Lagoa augengneisses are mostly composed of microcline and albite and the surrounding matrix is made of quartz + saussuritized plagioclase + muscovite, with chlorite + garnet + apatite + magnetite as accessories. The Lagoa micaschists are fine-grained rocks with the

following mineralogic assemblage: quartz + plagioclase + K-feldspar + chlorite + muscovite + magnetite + apatite; the associated greywackes consist of quartz bands alternating with layers of quartz + plagioclase + biotite + muscovite (Ribeiro, 1974; Portugal Ferreira and Forster, 1989; Ribeiro, 1997).

Chemical compositions of minerals were determined by electron microprobe analyses carried out on thin sections. Average structural formulas derived from these analyses are shown in Table 1. Rock types were also analyzed for their bulk chemical compositions (Table 2). Attempts were made to calculate the CIPW (initials for Cross, Iddings, Pirrson and Washington) and Barth norms (Hutchison, 1974), but the results were only acceptable for the Lagoa augengneisses. Alternatively, we estimated the mineral weight percentages by a method we called the Balance of Cation Proportions (Appendix 1; results in Table 3).

Soils

Cambi–eutric leptosols or orthi–dystric leptosols developed on the Lagoa micaschists, orthi–dystric leptosols on the Lagoa augengneisses, orthi–eutric leptosols on the amphibolites and orthi–eutric leptosols or vertic cambisols on the ultramafics (Agroconsultores and Coba, 1991). Saprolitic materials were sampled and analyzed for texture, organic matter, pH, exchange complex composition and clay type mineralogy (Table 4).

Land Use

Land use in the Morais area (Figure 2) is marked by the production of Winter cereals (wheat and rye), changing to natural pastures every two or more years, and of olives. During Summer, alternating maize, potatoes or vegetables are grown. Vineyards and orchards appear in small areas, frequently close to the olive groves. Woods of evergreen oaks, junipers and chestnut trees are concentrated between the Morais and Chacim villages.

Farmers apply mainly farmyard manures on their fields or pastures; dressings of industrial fertilizers remain low. Irrigated crops (e.g. potatoes) and olive trees are the most abundantly manured or fertilized tillages. Mean chemical compositions of cow manure and of commercial fertilizers commonly used in Trás-os-Montes are shown in Table 5. Given the moderate to high soil pHs (Table 4), buffering with lime is not practiced.

MATERIALS AND METHODS

Rock Sampling and Chemical Analyses of Rocks and Minerals

Representative **fresh** rock samples were extracted from the *in-situ* material, 5 kg when rocks were coarse-grained (augengneisses) and 2 kg otherwise (amphibolites, retrograde amphibolites, serpentinites and micaschists). For the bulk chemical analyses (by XRF-spectrometry), 1 kg of rock (2 kg for the coarse-grained types) was reduced in a jaw crusher till the < 2 mm size, ground in an agate millstone till the < 70 mesh size and (after homogenization and separation of a 100 g subsample) reduced in an agate mill till the < 200 mesh size. For the electron microprobe analyses of rock-forming minerals (using a Caméca CAMEBAX equipment), polished thin sections were prepared.

Soil Sampling and Analyses

5 kg saprolite samples were collected at the same sites as used for the rock sampling. Samples were dried at 40 °C, harrowed, and passed through a 2 mm sieve. The sand, silt and clay fractions were determined by standard particle-size analysis (Brady, 1990), organic carbon (C) by a dichromate technique (Nelson and Sommers, 1982); C values were multiplied by a factor 1.724 to obtain organic matter. Soil pHs were measured from water-soil suspensions after one hour contact. Exchangeable bases were determined by the ammonium-acetate method (Thomas, 1982) and Cation Exchange Capacities (CEC) by a conventional CEC

procedure (Rhoades, 1982). Clay fraction samples were analyzed for their mineralogical constituents by X-ray diffraction.

Monitoring of Spring Discharge Rates and Chemical Analyses of Spring Water Samples

From September 1997 to August 1999, a number spring waters were monitored monthly for discharge rates. To enable the calculation of element fluxes from spring water data and the link of weathering rates to drainage conditions in the soil profile and(or) shallow fractures, we selected 25 sites complying with the following statements: (1) The spring is a shallow groundwater, i.e. it has a seasonal hydrograph with the highest discharge rates occurring in Winter and the lowest in Summer; (2) The annual recharge is deducible from the hydrograph, i.e. the latter shows two periods of baseflow recession separated by a period of recharge.

Spring sites are shown in Figure 2, a typical hydrograph in Figure 3, the measured discharge rates in Table 6. In April 1998, August–September 1998 and January 1999, springs were sampled and analyzed. Because we are dealing with mole balances and thus our purpose is to quantify an average of weathering reactions taking place throughout a year, the water composition of each spring is represented by the mean concentrations of the samples collected in the three periods (Table 7).

In each campaign, three samples were taken from each spring. One 1 L sample was put directly into a polyethylene flask and stored unacidified. Two 125 mL samples were first filtered over a 0.45 μm cellulose nitrate filter and then one was acidified with 1 mL of 12 M HCl while the other was stored unacidified. At the sampling site, pH and conductance (E_c) were measured using a PHOX[®] (model 902) portable meter. In a field laboratory, alkalinity was determined by titrating 100 mL of the 1 L sample within one day after collection, using the Gran-plot method for end-point determination. The 125 mL unacidified sample was used

to determine chloride, sulphate and nitrate by ion-chromatography. The acidified sample was used to determine sodium, potassium, magnesium, calcium, sulphur and silica by inductively coupled plasma spectrometry (ICP-AES); sulphur concentrations were multiplied by a factor 3 to obtain the sulphate concentrations. House standards were used for calibration. In all cases, the deviations from charge balance are $< 5 \%$, which is remarkable for dilute waters.

DATA ANALYSIS

Determination of Effluxes of Dissolved Components from Spring Water Data

The flux of a dissolved component ($\text{kg}/(\text{ha} \cdot \text{y})$) is the product of a concentration (kg/L) by a annual discharge (L/y) divided a recharge area (ha). In case our hydrogeological system is a small watershed all previous parameters are measurable, but if its a spring in crystalline bedrock the recharge area is difficult to define. [Alternatively, we estimated the number of hectares required to rise the average discharge rate to a certain level \(equivalent recharge area\)](#) by combining one method of recharge estimation (Appendix 2) with another linking annual recharge, average discharge and recharge area (Figure 4).

The Use of Mole balances for the Assessment of Mineral Weathering Rates (the SiB Model)

Mole balances estimated mineral weathering rates in many studies (Velbel, 1985a, 1992; Taylor and Velbel, 1991; Pacheco and Van der Weijden, 1996; Parkhurst, 1997; Pacheco et al., 1999; among others). The most common approaches were reviewed by Pacheco and Van der Weijden (1998), and in this study we used the so-called SiB algorithm introduced by Pacheco and Van der Weijden (1996); the mechanics is outlined in Appendix 3 and the *modus operandi* described briefly in relation to our study area.

Step 1: Establishment of the Conceptual Geochemical Model - Table 3 (rock mineralogy) and columns 6-7 of Table 4 (soil clays) suggest that hydrolysis of feldspars, amphiboles, chlorites and clinozoisite into mixtures of smectite plus halloysite, dissolution of sphene, olivine, serpentine and talc with subsequent precipitation of titanium and iron oxides and congruent dissolution of calcite are major natural sources of solutes to springs. From land uses (Figure 2, Table 5) we expect that application of manures and fertilizers is an important anthropogenic source of solutes and promote exchange reactions among cations. There is no information on the rates at which the biomass is currently assimilating dissolved components. As a working hypothesis, we assume a steady state between groundwater and the organic compartment.

Step 2 - Match of Spring Compositions with Sets of Weathering Reactions - The SiB algorithm programs the mixing of two clays from reaction of a single aluminum silicate, but the ability is restricted to a couple of primary phases; the other phases must weather to end-member products or dissolve congruently. Mixtures of clays are represented by the symbolic reaction $M \rightarrow c \times P_1 + (1-c) \times P_2$, where M is the primary mineral, P_1 and P_2 the clays and $0 < c < 1$. To generate different sets of weathering reactions, the SiB algorithm increments the c coefficient, and to match them with spring compositions Equation 9 is applied. Whenever a positive solution is attained (β_j 's and F_i^u 's > 0), the set is said a valid SiB solution.

Step 3: Check of Results against Boundary Conditions - Usually, a number of valid solutions apply for each spring. The most likely one is the best fit to the following bounds: the "single-spring" condition (or clay test) is applied to each spring separately and states that the abundances of clays calculated by Equation 10 must approach those in soils nearby the spring. When such detailed information is not available, the next best test is to use the regional distribution of clay minerals (Table 4). In case the single-spring condition fails to give each spring its best-fit solution, the user must consider the "multiple-spring" condition, which sets best-fit solutions by testing all springs simultaneously. The method stands on knowledge

about the composition of locally applied fertilizers and works as follows: (a) Fluxes derived from fertilizers (mostly F_{Cl}^* , F_{SO4}^* , F_{NO3}^* and F_{Ca}^u) are expected to be high when springs are located in areas with intensive agriculture and low when they are remote from these areas. Besides, because the F_{Cl}^* , F_{SO4}^* and F_{NO3}^* are known quantities while the F_{Ca}^u is a by-product of the SiB algorithm, it would be possible to use the known fluxes (or their sum in equivalents $\equiv Pollution$) to investigate the congruity of unknown concentration; (b) This is done by regression analysis. First, all F_{Ca}^u 's of a given spring (one for each valid solution) are plotted against the *Pollution* score of that spring and this step is repeated for all the other springs. Second, a straight line is fitted to the resulting scatter plot and a theoretical best-fit F_{Ca}^u is calculated for each spring. Third, by comparing the actual F_{Ca}^u 's of the springs with their best-fit values, it is possible to select pairs of minimum difference. The valid SiB solutions linked to these actual F_{Ca}^u 's are the best-fit solutions.

As additional constraints to the SiB solutions, it would be beneficial to have more elements in the set of mole balance equations that could help identify sources of water and solutes, for example Br and(or) Sr and its isotopes. They were not considered because such analyses were not available.

RESULTS AND DISCUSSION

Annual Recharges, Recharge Areas and Effluxes

Applying the methods of Appendix 2 to data in Tables 6 and 7, we determined for all 25 springs the median discharge rate (Q_{med}), the recharge occurring between 1998 and 1999 (V_r), the recharge area (A), the water discharged during 365 days (V_{-365} ; from March 1998 till

February 1999), and the fluxes of dissolved components (F_i^t). Results are in Table 8, a stepwise determination is given below for spring nr. 2.

Figure 3 is the hydrograph of spring nr. 2. From the baseflow discharge rates (dashed lines), t_I values were obtained for the 1998 and 1999 recessions (320 and 2280 days). Replacement of t_I and associated Q_0 values (12.0 and 6.3 L/min; from December 1997 and September 1998) in Equation 5, raised potential groundwater discharges to $V_{p1} = 2404 \text{ m}^3$ and $V_{p2} = 8993 \text{ m}^3$. The baseflow discharge of 1998 was determined from Equation 4 ($V = 2050 \text{ m}^3$), assuming a recession of $t = 266$ days (December 1997–August 1998). The water remaining in storage at the end of that period as well as the recharge taking place between recessions were computed from Equations 6 and 7, giving $V_s = 355 \text{ m}^3$ and $V_R = 8639 \text{ m}^3$. Using Figure 4 in combination with Equation 8 and taking into account the V_R and Q_{med} (0.10 L/s, data in Table 6) values, we estimated the annual recharge in length units ($V_r = 12 \text{ mm}$) and the recharge area of the spring ($A = 72 \text{ ha}$). Finally, fluxes of dissolved components were calculated from their concentrations (Table 7), the recharge area (A) and V_{-365} (3351 m^3 , Table 6).

Match of Water Chemistries with Sets of Weathering Reactions

No information was available about the average composition of local wet and dry depositions. For that reason, the $*$ -fluxes in Equation 9 were replaced by t -fluxes, meaning that the atmospheric inputs are lumped together with pollution. The SiB algorithm was applied to all 25 springs. We could not link sets of weathering reactions to samples nrs. 6, 32 and 38 and sample nr. 28 gave anomalous results. For the amphibolites and ultramafics, sets were established for the essential rock-forming minerals (Table 3, except quartz) while in the Lagoa units spring compositions matched reactions of plagioclase and chlorite. Mixtures of smectite plus halloysite were considered for plagioclase and chlorite (Lagoa units), plagioclase and hornblende (amphibolites), tremolite and chlorite (ultramafics). For the

amphibolites and retrograde amphibolites, additional incongruent reactions were set for chlorite and clinozoisite. In both cases they were written to smectite because reactions to halloysite violated the clay test. The compositions of local smectites were not known. Among the typical dioctahedral series (beidellite, montmorillonite and nontronite; compositions in Loughnan, 1969), we adopted beidellite ($\text{Ca}_{0.35}\text{Al}_4(\text{Si}_{7.3}\text{Al}_{0.7})\text{O}_{20}(\text{OH})_4$) to be secondary product of plagioclase, hornblende, clinozoisite and ripidolite-RA, and nontronite ($\text{Ca}_{0.35}\text{Fe}_4(\text{Si}_{7.3}\text{Al}_{0.7})\text{O}_{20}(\text{OH})_4$) to be secondary product of ripidolite-M, picnochlorite, tremolite and peninnite, because these choices gave us the best match between predicted and real abundances of weathering products.

Check of Results against Boundary Conditions

Table 9 lists the end-member reactions used in the SiB modelling ($\text{R}_1\text{--}\text{R}_{26}$), Table 10 depicts the SiB results. Because multiple sets of weathering reactions agreed with the chemical compositions of springs, we selected best-fit sets by testing them against the predefined boundary conditions: (*Clay test*) Columns 3–5 of Table 10 contain the best-fit clay mineral abundances. Reactions of ripidolite-M and picnochlorite had to form a small amount of nontronite ($< 15\%$) so they could match the water compositions, notwithstanding the fact that 14 Å clays did not show up in X-ray diffraction analyses on C-horizons of the Lagoa units. For the other lithologic units, predicted and real clay mineral abundances match closely; (*Multiple-spring condition*) The clay test detected a single best-fit SiB solution for each spring. Still, we determined the regression between *Pollution* and the best-fit F_{Ca}^u fluxes: $F_{Ca}^u = 0.38 \times \text{Pollution}$; $R^2 = 98.6\%$. This high R^2 is further support of our results.

Best-Fit SiB Solutions

The best-fit weathering reactions are shown in column 6 of Table 10. The R_i s are in agreement with column 1 of Table 9 and reactions can be interpreted as illustrated for spring nr. 2 (first in the amphibolites). In this case, the natural water chemistry may be explained by simultaneous weathering of andesine- An_{45} into 80% beidellite plus 20% halloysite ($0.8R_5+0.2R_6$), of hornblende into 20% beidellite plus 80% halloysite ($0.2R_7+0.8R_8$), of chlorite and clinozoisite into beidellite (R_{13} and R_{20}) and of sphene into titanium oxides (R_{22}), accompanied by congruent dissolution of calcite (R_{23}). Columns 7–15 contain the calculated weathering rates; similar minerals (e.g. ripidolites, picnochlorite and peninnite) were gathered into groups (chlorite) to facilitate further discussion.

Correlation Between Weathering Rates and Recharge Rates

Monitored springs link to very different drainage conditions set by the range of calculated recharge rates ($3.5 < V_r < 400$ mm/y; Table 8). Huge variations in the annual recharge are justified because we are dealing with very small drainage basins shaped on fractured rocks: most probably, the highest and lowest V_r scores link to densely and sparsely fractured basins, i.e. to highly and poorly permeable environments. Weathering rates (Table 10) of all minerals correlate with the annual recharge rates; Figure 5 illustrates that for plagioclase and amphibole. This observation is consistent with the Loughnan's (1969) statement: "the most important single factor controlling the rate of breakdown of parent minerals and the genesis of specific secondary products is the quantity of water leaching through the weathering environment", and suggests that weathering rates in the Morais massif are not controlled directly by mineral dissolution rates far from equilibrium, but by either a chemical affinity effect or a transport process (Drever and Clow, 1995; White, 1995).

Normalized Mineral Weathering Rates

Scatter in Figure 5 suggests that factors other than recharge (e.g. bulk percentage and(or) grain size of the minerals) may play an important role in determining the observed weathering rates. Using the information in Table 3 we normalized the rates by mineral abundances. Results are summarized in Figure 6. Normalized rates obtained for plagioclase (0.9–45 moles/(ha·y·%plagioclase)) compare favorably with the results of Cleaves et al. (1970), Paces (1983) and Velbel (1985a), which are 14.0, 11.7 and 36.7–39.3 moles/(ha·y·%plagioclase), respectively. Results pertaining to the other minerals were not compared because in most weathering studies the information about spring discharges and(or) mineral abundances is lacking. Minerals were put in ascending order of their maximum weathering rates from the bottom to the top of Figure 6. At the rightmost part we plotted ranks of the Persistence Order of Minerals (POM; Pettijohn, 1941). According to this index, the most stable mineral is anatase (POM = -3) and the least stable is olivine (POM = 22). Despite the fact that only a few of our minerals were included in the POM scale, there is no doubt about the agreement between the normalized rates and the POM ranking.

Immobilization plus Uptake

The conceptual geochemical model assumes a steady state between groundwater and biomass. Violation of this assumption upsets especially the $F_{SO_4}^t$, $F_{NO_3}^t$ and F^u , fluxes as we shall discuss in the next paragraphs.

From inspection of Tables 1 and 3, it is unlikely that chloride and sulphate in spring waters result from rock weathering. Thus, the F^t fluxes of chloride, sulphate and nitrate as well as the F^u fluxes of magnesium and calcium must match the atmospheric plus fertilizer inputs. The F^{ad} fluxes were estimated from rainwater analyses of a nearby region (Sousa Oliveira, 2001).

They are: $F_{Cl}^{ad} = 0.87$, $F_{SO4}^{ad} = 1.08$, $F_{NO3}^{ad} = 0.14$, $F_{Mg}^{ad} = 0.14$ and $F_{Ca}^{ad} = 0.94$ kg/(ha.y).

The inputs from fertilization were determined by: $F^* = F^f - F^{ad}$ and $F^{u*} = F^u - F^{ad}$.

The F_{Cl}^* and F_{SO4}^* fluxes are related to application of Foskamónio in potato and maize fields (Table 5). If the steady state hypothesis is acceptable, a scatter plot of these fluxes defines a straight line of slope 3.831 intercepting the origin (3.831 is the sulphate to chloride wt. ratio in Foskamónio). In Figure 7, bullets are the F_{Cl}^* and F_{SO4}^* fluxes of spring waters and the dotted line's slope is 3.831. In most cases bullets fall below the dotted line, i.e. the hypothesis is unsustainable. Besides, because chloride is a conservative ion, deviations from the dotted line link to diminishments in the sulphate fluxes promoted by immobilization (incorporation into microorganisms), uptake (assimilation by natural vegetation and crops) or volatilization. In the thin, relatively well drained and aerated soils of Morais, the anaerobic conditions necessary for sulphate reduction will not prevail, thus sulphur volatilization is supposedly negligible. Sulphate decrease in groundwater must therefore reflect the retention by the organic compartment. The relation between the F_{SO4}^* fluxes and those due to immobilization plus uptake (F_{SO4}^o) or to application of Foskamónio (F_{SO4}^p) is understood from Figure 7.

A similar plot is not applicable to nitrate, magnesium or calcium because sources other than Foskamónio (manure and Nitrolusal, Table 5) contribute to their $F^*(F^{u*})$ fluxes and the F^{u*} fluxes may be influenced by cation exchange reactions. Alternatively, we used the element matching technique (Melillo and Gosz, 1983) that is based on the mean N/S, N/Mg and N/Ca ratios in soil, vegetation and crops (averages: 9.54, 10.34 and 4.81, as compiled from Whitehead, 1964; Rodin and Bazilevish, 1967; Cole and Rapp, 1981; Melillo and Gosh, 1983; Wild, 1988; Brady, 1990; Schlesinger, 1991). In agreement with it and by assuming that nitrogen and sulphur are provided to organisms and plants by nitrate and sulphate in the soil solution, the uptake of 1 kg/(ha.y) of sulphate must be accompanied by the uptake of 14.08

kg/(ha.y) of nitrate ($\frac{62/14}{96/32} \times 9.54$), where 62, 14, 96 and 32 are the masses of nitrate,

nitrogen, sulphate and sulphur in g/mol). In general, the $F_{NO_3}^o$, F_{Mg}^o and F_{Ca}^o fluxes may be

computed sequentially by: $F_{NO_3}^o = 14.08 \times F_{SO_4}^o$, $F_{Mg}^o = 0.022 \times F_{NO_3}^o$ and $F_{Ca}^o = 0.047 \times F_{NO_3}^o$.

Applying the element matching technique to our data, we found the highest $F_{NO_3}^o$ flux (the one representing abundant manuring and fertilization) to approach 834 kg/(ha.y) of NO_3 (188 kg/(ha.y) of N), a value that is consistent with the range measured by Bashkin et al. (1986) for plant uptake in a small agricultural catchment (131.9–183.2 kg/(ha.y) of N).

Cation Exchange

Using a [Mg]p/[Ca]p versus [SO₄]t/[NO₃]t plot, Pacheco et al. (1999) illustrated how cation exchange reactions modified the chemistry of shallow groundwaters from granites in northern Portugal. Replacing concentrations by fluxes we drew Figure 8; circles mark the fluxes, stars the equivalent Mg/Ca and SO₄/NO₃ ratios in manure (0.82 and 0.18, Table 5), Foskamónio (0.02 and 3.84) and Nitrolusal (0.01 and 0.00); the mixing and dotted lines describe the F^p fluxes in case they result solely from the application of manure and Foskamónio or from an equilibrium with the soil exchange complex.

Spring waters are not in equilibrium with the soil exchange complex because circles deviate from the dotted line. One sample may relate to simultaneous application of manure, Foskamónio and Nitrolusal as the circle falls in the "triangle" defined by the stars. The other circles are above the mixing line which is interpreted as follows: exchange reactions are actively displacing Mg from the exchange sites (raising the $F_{Mg}^{p*} / F_{Ca}^{p*}$ ratios) as a consequence of application of calcium rich fertilizers. The highest deviations from the mixing line occur when the sulphate to nitrate ratios are close to those found in manure, decreasing rapidly as the ratios increase towards the ones found in Foskamónio. This trend is represented

schematically by the dashed line and may be interpreted as follows: (1) When only *in situ* generated organic (humus) plus inorganic (clay minerals) constituents play a role in the exchange of Mg by Ca, the impact of this reaction on the $F_{Mg}^{p*} / F_{Ca}^{p*}$ ratios is low, expressed in the segment of the dashed line that is parallel to the mixing line; (2) This impact becomes higher when additional amounts of organic compounds are incorporated into the soil system by manuring. The more abundant manuring is, the higher this impact will become, resulting in the quasi vertical segment of that line.

Nutrient Balances and Changes in Soil Water Alkalinity

It should be noted that changes in alkalinity promoted by botanical uptake were not accounted for in the mole balance of bicarbonate (Equation 9). When cations such as Mg^{2+} and Ca^{2+} are removed from the soil solution in excess of the uptake of negatively charged ions, the plants release H^+ to maintain internal balance of charge. This H^+ may in turn reduce the alkalinity and(or) replace cations in the exchange sites driving them into the soil solution. On the other hand, when plants consume anions such as SO_4^{2-} and NO_3^- in excess of positively charged ions they release HCO_3^- to keep charge balance. In both cases, the uptake process has consequences on soil water composition: uptake of cations may reduce while uptake of anions increases alkalinity, the overall change being dependent on how much nutrients of either type are incorporated into plant tissue. We believe that in a region dominated by rocks of low resistance to weathering (serpentinites, amphibolites) biological processes have relatively little effect on the general level of alkalinity acquired by water-mineral interactions under soil P_{CO_2} . Processes such as ammonium oxidation (nitrification) may also reduce spring water alkalinity. A redox equation on ammonium-nitrate was not included in the mole balance model because, except sporadically, external sources of NH_4^+ to soils are lacking (Table 5).

CONCLUSIONS

Assuming that silicic acid (Si) and bicarbonate (B) in spring waters are the result of chemical weathering, we applied our SiB algorithm to reconstruct the weathering reactions of minerals (of known composition), present in five lithologic units of the Morais massif that contributed to the water composition. Hydrolysis of feldspars, amphiboles, chlorites and clinozoisite yielded mixtures of smectites and halloysite, hydrolysis of olivine, serpentine, talc and sphene produced titanium and iron oxides, whereas calcite dissolved congruently. Beidellite and nontronite—their compositions adopted from literature—were used as representatives of the smectites giving the best SiB results. The best-fit weathering reactions are combinations of reactions water and carbon dioxide with individual minerals and selected on the basis of meeting the boundary conditions posed by the mineralogy of soils developed on the parent rocks and by contributions of fertilizers used in the area.

Linkage of annual recharge, average spring discharge and recharge area allowed to calculate the discharge in volume per recharge area within a lithologic unit per year. Combination of the derived weathering reactions, the normalized discharge and knowledge of the mineralogical composition of the rocks, made possible the calculation of the weathering rates of the rock-forming minerals as moles/(ha.y.%mineral). We obtained the following order of these normalized weathering rates in the Morais massif: forsterite (485) > calcite (266) > clinozoisite (114) > talc (108) > sphene (98) > chlorite (49) > plagioclase (45) > amphibole (28) > serpentine (19).

Overall, the contribution of natural chemical weathering, represented by the bicarbonate concentration, by far exceeds contributions of other sources, represented by chloride, sulphate and nitrate concentrations. Other sources being considered are atmospheric deposition, application of manure and industrial fertilizers. It had to be taken into account that selective uptake of elements in vegetation and harvesting, as well as immobilization and ion-exchange

in the soil compartment can change the original chemical signature of these sources. Using data on the composition of atmospheric deposition and on the most frequently applied fertilizers, literature data on the ratios of storage of nitrogen, sulphur, calcium and magnesium in vegetation, and ratios of the latter components in solution, it was possible to reconstruct the (modified) contributions of these other sources to the spring-water compositions.

ACKNOWLEDGEMENTS

We thank the associate editor R.L Bassett and the reviewer Art F. White for their comments and suggestions. They were of great help in the improvement of an earlier version of this paper. We also thank Luís Gens for the help with the drawings.

APPENDIX 1 – THE BALANCE OF CATION PROPORTIONS

The method we call the Balance of Cation Proportions computes the weight percentages of minerals in a rock sample. It stands on the solution of a set of linear equations, which in matrix form is written as:

$$AX = B \quad (1)$$

where A is a matrix of structural compositions, B an array of cation proportions and X an array of mineral weight percentages.

Equation 1 is solved by Singular Value Decomposition (SVD) as described in Press et al. (1989). First, a matrix A is built. This is a square matrix where the number of non-zeroed rows (n) equals the number of elements describing the chemistry of rock-forming minerals (e.g. Si, Ti), and the number of non-zeroed columns (m) equals the number of minerals in each rock sample (e.g. plagioclase, amphibole). For $n > m$, the set of linear equations is overdetermined and SVD provides a solution using a least-squares method. For $n = m$, the set has likely a unique solution. Finally, for $n < m$, the set is undetermined and SVD provides a solution which minimizes the modulus of X ($|X|$). The a_{ij} 's (elements of A) quantify the number of moles of element i in one mole of mineral j and can be read directly from the structural formulas of the minerals. After matrix A is built, a B array is composed for each rock sample. The b_j 's are the cation proportions of each chemical component and are determined by dividing the weight percentage of each oxide by its equivalent molecular weight. Once a positive solution of Equation 1 is obtained, using A and B as defined above, the mineral weight percentages are computed from the X array by multiplying each x_j by the molecular weight of the corresponding mineral and converting the results into percentages.

APPENDIX 2 – DETERMINATION OF RECHARGE AREAS FROM SPRING WATER DATA

The approach we used to estimate the recharge area of a spring combines a method for recharge estimation (Domenico and Schwartz, 1990) with a method linking annual recharge, average spring discharge and recharge area (Figure 4). The first method assumes that during a recession period baseflow discharge rates obey an exponential law of the type:

$$Q = Q_0 e^{-kt} \quad (2)$$

where Q is the baseflow discharge rate at instant t , Q_0 the same rate but at the beginning of the recession and k the recession constant. Accordingly, a plot of baseflow discharge rates against time on a semilogarithmic paper ($\log Q$ vs. t) yield a straight line, the slope of which defines the recession constant. For this case, the recession expression may be rewritten as:

$$Q = \frac{Q_0}{10^{t/t_1}} \quad (3)$$

where t_1 is the time corresponding to one log cycle of Q . The volume (V) of baseflow discharge corresponding to a given recession is found by integrating Equation 3 over the times of interest:

$$V = \int_0^t \frac{Q_0}{10^{t/t_1}} dt = \frac{Q_0 t_1}{2.3} \left(1 - \frac{1}{10^{t/t_1}} \right) \quad (4)$$

The recharge (m^3) occurring between two recession periods is estimated by a stepwise procedure which incorporates the next four consecutive steps: (1) Calculate the potential groundwater discharge at the beginning of the first recession, i.e. the volume of groundwater that would be discharged by baseflow if complete depletion took place without interruption, or—in other words—the water in storage at the beginning of the first recession. This is done by considering $t = \infty$ in Equation 4:

$$V_{p1} = \frac{Q_0 t_1}{2.3} \quad (5)$$

where V_{p1} is the potential groundwater discharge; (2) Calculate the water in storage at the end of the first recession (V_s). This is simply the difference between V_{p1} and V :

$$V_s = V_{p1} - V \quad (6)$$

(3) Calculate the potential groundwater discharge at the beginning of the second recession (V_{p2}). This is done by applying Equation 5 to the new Q_0 and t_1 ; (4) Finally, calculate the recharge that took place between recessions (V_R); this is the difference between V_{p2} and V_s :

$$V_R = V_{p2} - V_s \quad (7)$$

The second method establishes a relation between the median discharge rate (L/s), the annual recharge (mm) and the recharge area (ha) of a particular spring. It is readily understood that recharge areas cannot be determined directly from known median discharge rates plus calculated V_R 's, because annual recharges in Figure 4 are expressed in mm while V_R 's are expressed in m^3 . But they can be determined by the following iterative procedure: (1) Assume a value for the annual recharge in mm (V_r); (2) Determine analytically the recharge area (A) by the formula:

$$A_c = \frac{V_R}{V_r} \quad (8)$$

where subscript c means calculated; (3) Use the median discharge rate (Q_{med}) in combination with the assumed V_r to determine graphically (from Figure 4) the recharge area (A_g , where subscript g means retrieved from the plot); (4) Compare A_c with A_g . If they are equal, the procedure stops, because we have found the best A (A_c or A_g) and V_r values. Otherwise, start again from step 1, assuming a new V_r , until $A_c = A_g$.

APPENDIX 3 – AN OUTLINE ON THE MECHANICS OF THE SiB ALGORITHM

When working with fluxes, the SiB algorithm uses the following mole and charge balance equations:

$$F_i^* = F_i^t - F_i^{ad} = \sum_{j=1}^m r_{ij} \beta_j + F_i^u \quad (i = 1, \dots, n) \quad (9)$$

$$Pollution = F_{cl}^* + 2F_{so4}^* + F_{no3}^* = \sum_{k=1}^{cations} z_k F_k^u$$

where: n is the number of dissolved components assumed to have affinities with chemical weathering ($n = 6$, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , HCO_3^- and H_2SiO_3), $cations$ is the number of major cations in the chemical system ($cations = 4$, Na^+ , K^+ , Mg^{2+} , Ca^{2+}) and m is the number of reactant phases; F_i^t is the total and F_i^* is a net flux of dissolved component i , which include the fluxes derived from atmospheric deposition (F_i^{ad}) and unspecified sources (F_i^u), all expressed in $\text{mol}/(\text{ha}\cdot\text{y})$; r_{ij} is the ratio between the stoichiometric coefficients of dissolved component i and reactant phase j and β_j is the weathering rate of reactant phase j ($\text{mol}/(\text{ha}\cdot\text{y})$); z_k is the charge of cation k .

The set has $7(n+1)$ equations. The unknowns are the m reactant phases plus the F^u fluxes. Because the algorithm considers F^u fluxes only for the four major cations, the number of unknowns is written as $m+4$. Accordingly, if $m = 3$, Equation 9 is determined and SVD (Appendix 1) provides unique values for the unknowns, but if $m < 3$ or $m > 3$, the set is over or undetermined and SVD can only find least squares or minimum estimates for them.

Once weathering rates are calculated, the SiB algorithm uses them in combination with r_{ij} ratios, now between the stoichiometric coefficients of secondary product l and primary mineral j , to predict the amounts of clay minerals being produced by weathering:

$$\gamma_{ij} = r_{ij} \times \beta_j \quad (10)$$

with $l = 1, \dots, p$, where p is the number of weathering products derived from primary mineral j (1 or 2 are allowed) and γ_{ij} is the rate at which secondary product l is being formed as a consequence of the rate at which primary mineral j is being weathered.

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Table 1

Caption: Average chemical compositions and corresponding molecular weights of minerals in lithologic units of the Morais massif. Other minerals in the Lagoa units and amphibolites *sensu lato*. include quartz and calcite. Their theoretical structural formulas and corresponding molecular weights are: SiO₂ (60.1) and CaCO₃ (100.1).

Mineral	n	Average Structural Formula	Molecular Weight
Lagoa Micaschists			
Albite	11	NaAlSi ₃ O ₈	262.2
Muscovite	3	(Na _{0.3} K _{1.7})(Al _{3.6} Fe _{0.2} Mg _{0.2})(Si _{6.3} Al _{1.7})O ₂₀ (OH) ₄	797.4
Chlorite (Ripidolite)-M	6	(Al _{2.8} Fe _{5.6} Mg _{3.6})(Si _{5.3} Al _{2.7})O ₂₀ (OH) ₁₆	1289.6
Lagoa Augengneisses			
K-Feldspar Phenoblasts	2	KAlSi ₃ O ₈	278.3
Albite Phenoblasts	4	NaAlSi ₃ O ₈	262.2
Average Plagioclase	12	Na _{0.7} Ca _{0.3} Al _{1.30} Si _{2.7} O ₈	265.1
Chlorite (Picnochlorite)	6	(Al _{2.9} Fe _{6.1} Mg _{3.0})(Si _{5.8} Al _{2.2})O ₂₀ (OH) ₁₆	1306.2
Muscovite	7	(Na _{0.1} K _{1.9})(Al _{3.4} Fe _{0.35} Mg _{0.25})(Si _{6.5} Al _{1.5})O ₂₀ (OH) ₄	805.0
Amphibolites			
Hornblende-A	23	Na _{0.4} Ca ₂ (Al _{0.7} Fe _{1.6} Mg _{2.7})(Si _{6.7} Al _{1.3})O ₂₂ (OH) ₂	872.5
Average Plagioclase	30	Na _{0.55} Ca _{0.45} Al _{1.45} Si _{2.55} O ₈	269.4
Clinzoisite-A	2	Ca ₂ Al _{2.6} Fe _{0.4} Si ₃ O ₁₂ (OH)	465.9
Retrograde Amphibolites			
Hornblende-RA	20	Na _{0.5} Ca ₂ (Al _{0.7} Fe _{1.5} Mg _{2.8})(Si _{6.9} Al _{1.1})O ₂₂ (OH) ₂	871.8
Albite	13	NaAlSi ₃ O ₈	262.2
Clinzoisite-RA	13	Ca ₂ Al _{2.5} Fe _{0.5} Si ₃ O ₁₂ (OH)	468.8
Chlorite (Ripidolite)-RA	16	(Al _{2.6} Fe _{3.6} Mg _{5.8})(Si _{5.5} Al _{2.5})O ₂₀ (OH) ₁₆	1226.2
Sphene	10	CaTiSiO ₅	196.1
Ultramafics (Serpentinites with Tremolite+Chlorite Bands)			
Forsterite	14	(Mg _{1.78} Fe _{0.22})SiO ₄	147.6
Serpentine	13	(Mg _{2.75} Fe _{0.25})Si ₂ O ₅ (OH) ₄	285.0
Talc	8	(Mg _{5.9} Fe _{0.1})Si ₈ O ₂₀ (OH) ₄	761.7
Tremolite	10	Ca ₂ (Mg _{4.8} Fe _{0.2})(Si _{7.95} Al _{0.05})O ₂₂ (OH) ₂	818.6
Chlorite (Penninite)	18	(Al _{1.8} Fe _{0.6} Mg _{9.6})(Si _{6.4} Al _{1.6})O ₂₀ (OH) ₁₆	1130.4

n - Number of electron microprobe analyses

Table 2

Caption: Average chemical compositions of lithologic units in the Morais massif;
values in wt.%.

Lithologic Unit	n	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total
Oxide Equivalent Weights													
60.1 79.9 51.0 79.9 70.9 40.3 56.1 31.0 47.1 71.0													
Oxide Percentages in the Lithologic Units													
Lagoa Micaschists	6	68.4	0.7	14.5	5.0	0.0	1.3	0.5	2.3	2.4	0.1	3.8	98.9
Lagoa Augengneisses	6	70.2	0.5	14.0	3.1	0.0	0.6	1.8	3.1	3.3	0.2	2.2	99.0
Amphibolites	8	48.5	1.1	15.6	9.5	0.2	8.3	10.9	2.3	0.1	0.1	2.8	99.3
Retrograde Amphibolites	10	47.8	1.6	15.4	11.0	0.2	6.6	10.6	2.7	0.1	0.1	3.1	99.1
Tremolite+Chlorite Bands	3	47.1	0.5	4.1	7.9	0.2	24.8	7.8	0.1	0.0	0.2	5.7	98.4
Serpentinities	5	39.4	0.1	2.0	8.5	0.1	34.2	0.4	0.0	0.0	0.0	14.0	98.8

n - Number of rock samples

Table 3

Caption: Average mineralogical compositions of lithologic units in the Morais massif. Values in wt.%, calculated by the Balance of Cations Proportions (Appendix 1).

Lithologic Unit	Mineralogical Composition						
	Quartz	Albite	Muscovite	Chlorite			
Lagoa Micaschists	43.4	18.1	25.9	12.6			
Lagoa Augengneisses ^(a)	K-Feldspar	Albite					
	Phenoblasts	Phenoblasts	Quartz	Plagioclase	Chlorite	Muscovite	
	17.6 (20.3)	6.5 (6.5)	35 (34.8)	29.2 (30.4)	8.2 (4.5)	3.5 (3.1)	
Amphibolites	Hornblende	Plagioclase	Clinozoisite	Chlorite	Sphene	Calcite	Quartz
	56.5	24.8	3.3	7.4	2.7	trace ^(b)	5.3
Retrograde Amphibolites	35.0	17.3	22.5	13.9	3.9	trace ^(b)	7.4
Serpentinites (S)	Forsterite	Serpentine	Talc	Tremolite	Chlorite		
	trace ^(b)	67.4	32.6				
				75.0	25.0		
Tremolite + Chlorite Bands (B)							
Mixture 0.63 S + 0.37 B ^(c)	trace ^(b)	42.5	20.5	27.7	9.3		

^(a) Values within brackets obtained with the CIPW norm; 6.5% of the calculated albite was linked to the phenoblasts, the remaining was added to anorthite to obtain matrix plagioclase (giving An₂₆); Picnochlorite = Hematite + Rutile + Hypersthene; Muscovite = Corundum.

^(b) < 1%; assumed equal to 1% in the calculation of normalized weathering rates (Figure 6).

^(c) Based on the number of samples representing serpentinites and tremolite+chlorite bands (Table 2).

Table 4

Caption: Physical and chemical properties of saprolitic materials derived from the main lithologic units of the Morais massif.

Lithologic Unit	n	OM (%)	pH-H ₂ O	Texture	Clay Types (%)		Exchange Bases				CEC-pH7
					Smectite	Halloysite	[Ca-S]	[Mg-S]	[K-S]	[Na-S]	
Lagoa Micaschists	3	0.6	5.5-6.0	SL	0.0	100.0	3.5	0.8	0.1	0.0	5.1
Lagoa Augengneisses	3	0.9	5.9-7.0	L	0.0	100.0	0.9	0.9	0.2	0.0	2.2
Amphibolites	4	0.4	6.0-7.0	L	85-45	15-55	4.7	1.0	0.1	0.1	6.2
Retrograde Amphibolites	5	0.4	5.0-6.9	SL	80-50	20-50	5.2	0.7	0.1	0.1	6.7
Ultramafics	4	0.7	6.8-7.8	L	65-50	35-50	3.4	0.5	0.2	0.1	4.2

n - Number of saprolite samples.

OM - Organic Matter.

L - Loamy; S - Sandy.

Smectite and Halloysite ranges estimated on the basis of X-Ray diffraction 14Å and 7.2Å peak heights.

[X] - Concentration of cation X in meq/100g of dried soil; S - soil exchanger.

CEC-pH7 (meq/100g) - Cation Exchange Capacity at soil pH of 7.

Table 5

Caption: Average chemical compositions and common applications of locally applied fertilizers; values in wt. %. Source: Pacheco et al. (1999).

Component	Fertilizer Name and Common Applications		
	Cow Manure	Nitrolusal ^(a)	Foskamonio10-10-10
	All Crops	Rye, Pastures	Potato, Maize
H ₂ O	70.00	0.00	0.00
Organic Matter	26.00	0.00	0.00
Na	0.00	0.04	1.53
K	0.74	0.07	7.56
Mg	0.06	0.01	0.37
Ca	0.12	1.34	30.09
Cl	0.00	0.63	7.91
SO ₄	0.45	0.00	30.30
NO ₃	3.14	75.20	10.19
NH ₄	0.00	22.50	0.00
PO ₄	0.00	0.00	10.08
Sr	0.00	0.01	1.90
Total	100.51	99.80	99.93

^(a) Sporadic application

Table 6

Caption: Discharge rates of the monitored springs.

Date	Time (days)	Lithologic Units and Spring Numbers																									
		Ultramafics				Retrograde Amphibolites						Amphibolites												Lagoa Augengneiss			Lagoa Micaschists
																								16	17	31	15
		3	11	20	21	1	8	9	28	47	48	2	4	6	30	32	37	38	41	43	45	46					
Discharge Rates (L/min)																											
Sep-97	0	nd	nd	2.4	4.2	nd	nd	nd	23.0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Oct-97	25	nd	3.0	1.2	3.1	nd	nd	nd	14.0	nd	nd	nd	nd	9.6	0.9	0.8	nd	nd	nd	nd	nd	nd	nd	nd	nd	4.1	nd
Nov-97	60	15.0	20.0	5.0	4.3	10.0	nd	nd	20.0	14.1	3.4	nd	nd	10.9	7.5	3.0	nd	nd	12.0	18.5	5.0	30.0	2.5	nd	15.2	nd	nd
Dec-97	87	18.5	24.0	10.9	48.0	144.0	42.9	nd	103.0	52.2	8.6	12.0	12.0	18.5	40.6	7.5	nd	nd	15.0	35.3	8.3	54.5	4.6	nd	40.0	nd	nd
Jan-98	118	24.0	30.0	18.0	33.2	141.8	48.8	nd	110.0	48.8	6.7	13.3	13.3	24.0	34.3	7.1	104.0	65.0	15.0	30.0	8.0	103.0	17.1	13.3	32.5	16.0	nd
Feb-98	152	13.3	28.6	12.9	36.0	144.0	51.4	72.0	103.0	48.0	4.6	17.1	17.1	23.2	34.3	5.5	131.0	72.0	15.0	36.9	8.6	103.0	3.0	13.3	46.5	21.8	nd
Mar-98	184	5.5	17.1	6.7	36.0	180.0	12.0	53.0	103.0	60.0	2.3	6.0	6.0	30.0	24.0	4.1	150.0	53.0	15.0	45.0	5.0	84.0	5.2	10.0	9.2	5.3	nd
Apr-98	220	5.2	21.8	15.0	40.9	200.0	60.0	72.0	129.0	60.0	4.1	9.6	9.6	30.0	30.0	5.5	165.0	36.7	17.6	36.7	8.8	82.5	5.5	8.6	36.7	9.2	nd
Mai-98	257	3.2	15.5	5.6	9.0	165.0	5.0	56.3	100.0	46.2	2.2	3.5	3.5	26.4	24.0	4.0	146.7	23.0	17.6	33.0	3.5	44.0	1.3	10.0	17.6	2.6	nd
Jun-98	271	2.7	30.0	10.0	7.5	210.0	38.8	60.0	129.0	60.0	4.6	12.0	12.0	28.1	22.5	6.0	146.7	50.8	16.5	36.7	8.3	94.3	2.6	13.3	47.4	30.0	nd
Jul-98	317	5.7	6.3	4.1	41.5	71.0	41.5	20.3	130.0	15.2	1.6	2.3	2.3	20.0	11.7	2.8	60.6	12.2	14.2	22.0	1.1	31.4	0.7	7.5	5.0	1.2	nd
Aug-98	353	2.9	2.0	2.4	3.5	25.7	1.5	11.0	52.0	9.2	1.4	1.8	1.8	15.0	6.8	1.5	31.0	8.9	11.1	10.7	0.8	20.0	0.6	5.1	4.3	0.7	nd
Sep-98	372	1.9	2.3	2.2	15.0	20.4	1.2	9.8	28.8	7.0	1.3	6.3	6.3	17.1	5.8	1.3	21.8	7.0	10.3	9.3	0.6	16.0	0.5	5.4	8.4	0.6	nd
Oct-98	397	1.3	11.3	2.4	15.0	25.8	11.0	12.4	45.5	9.5	1.6	15.2	15.2	20.1	4.9	1.6	66.2	25.6	11.5	12.1	0.9	30.1	0.4	4.3	3.6	0.9	nd
Nov-98	444	0.6	3.2	1.4	5.3	25.7	13.5	10.3	101.8	6.5	1.6	5.7	5.7	17.1	3.0	0.9	70.8	8.2	11.2	10.9	0.7	18.5	1.3	3.5	2.9	3.0	nd
Dec-98	478	0.8	2.8	1.4	3.9	24.7	8.5	10.7	105.0	8.7	1.9	5.4	5.4	12.4	2.6	0.7	65.9	6.8	10.7	13.4	0.7	17.9	1.9	3.1	2.5	2.0	nd
Jan-99	506	0.8	11.3	5.0	4.6	32.3	20.0	19.6	121.0	20.8	2.9	9.5	9.5	24.1	11.1	1.7	160.0	29.1	13.7	25.6	3.0	42.4	3.1	5.4	14.3	19.4	nd
Mar-99	564	0.7	8.0	1.8	3.3	20.0	65.0	13.8	112.5	29.0	2.1	7.1	7.1	20.0	12.0	1.8	138.5	6.3	16.4	24.3	1.3	42.9	1.0	5.5	6.3	0.8	nd
Apr-99	596	1.5	8.6	1.5	5.5	47.3	5.3	10.0	104.7	23.8	2.2	5.3	5.3	18.4	5.5	1.0	122.3	4.0	13.4	24.3	1.1	40.2	0.9	3.6	5.0	0.6	nd
Mai-99	624	3.8	26.4	2.6	19.3	50.0	43.6	16.6	128.6	25.5	2.6	8.6	8.6	17.1	8.0	2.2	180.0	16.6	17.4	34.3	1.3	55.3	0.6	3.8	14.6	3.7	nd
Jun-99	659	1.5	10.0	1.1	3.2	8.9	6.3	7.9	95.7	13.9	1.6	4.8	4.8	12.5	4.7	1.7	72.2	6.3	16.9	19.7	0.6	27.9	0.5	3.5	6.0	0.7	nd
Jul-99	687	0.6	3.1	1.0	2.6	16.2	12.7	5.6	23.6	5.5	1.3	4.6	4.6	12.6	2.4	1.0	31.4	3.6	13.1	10.3	0.4	7.6	0.4	3.6	3.5	0.2	nd
Aug-99	721	0.5	1.7	0.8	2.5	5.3	3.3	4.2	2.9	3.0	1.1	4.5	4.5	9.3	1.8	0.5	13.0	2.5	11.2	7.5	0.2	5.5	0.3	3.3	3.2	0.2	nd

nd - Not determined.

Table 7

Caption: Chemical analyses of 25 spring waters collected in the Morais area (average compositions representing the sampling campaigns carried out in April 1998, August/September 1998 and January 1999).

Lithologic Unit	nr	[Na ⁺]	[K ⁺]	[Mg ²⁺]	[Ca ²⁺]	[HCO ₃ ⁻]	[Cl ⁻]	[SO ₄ ²⁻]	[NO ₃ ⁻]	[H ₂ SiO ₃]	Deviation from Charge Balance (DCB)
Lagoa Micaschists	15	13.7	0.4	4.0	6.1	40.2	4.4	11.9	9.9	37.3	4.8
Lagoa Augengneisses	16	15.4	0.2	7.0	11.6	85.1	5.1	11.4	0.4	34.0	2.9
	17	14.2	0.4	6.2	11.1	74.3	5.7	11.9	3.1	36.2	1.5
	31	9.8	0.7	4.7	11.3	52.2	5.1	7.6	14.3	36.0	1.4
Amphibolites	2	5.0	0.1	7.7	25.8	108.8	2.6	9.2	7.0	19.6	-0.3
	4	4.9	0.1	13.8	19.7	127.3	3.4	5.6	2.3	20.9	0.4
	6	5.7	0.3	31.8	18.2	186.5	10.3	3.9	16.0	67.9	3.5
	30	9.6	0.3	10.6	15.1	77.3	7.5	15.5	15.1	36.2	0.7
	32	5.7	0.0	17.4	17.5	107.7	7.7	22.8	5.2	49.5	1.3
	37	4.6	0.1	9.9	13.2	81.3	2.5	8.1	6.0	26.6	1.2
	38	3.5	0.2	33.4	9.2	173.9	3.4	8.4	7.9	58.0	4.7
	41	4.0	0.0	11.0	11.0	85.4	2.2	7.5	2.1	31.9	-0.3
	43	7.8	0.7	17.8	18.7	113.7	7.7	12.7	24.6	32.5	1.3
	45	6.7	0.1	18.9	17.9	132.0	3.3	12.0	13.9	34.9	1.2
Retrograde Amphibolites	46	5.8	0.2	15.9	17.8	115.1	4.6	10.4	14.5	27.7	0.0
	1	5.7	0.1	11.8	17.1	87.0	5.5	19.6	5.5	33.8	0.5
	8	4.0	1.4	3.6	8.5	37.6	5.0	4.2	4.8	14.2	1.2
	9	4.5	0.1	7.0	14.2	70.9	3.8	7.2	2.0	21.8	2.5
	28	5.8	0.2	5.6	13.7	59.1	4.6	10.1	4.3	24.7	2.2
	47	4.1	0.2	7.6	12.2	65.0	5.1	9.5	2.0	26.1	-0.7
Ultramafics	48	4.8	0.1	9.9	23.9	99.9	4.4	22.8	3.3	32.1	-2.5
	3	9.3	3.6	93.6	13.1	433.3	15.1	18.9	42.5	122.4	3.9
	11	2.0	0.1	84.0	10.5	365.0	4.5	48.2	10.0	93.6	4.4
	20	2.6	0.1	51.9	4.3	250.7	5.0	5.8	4.1	86.3	4.7
	21	2.5	0.1	44.7	5.5	217.8	5.9	7.0	2.9	66.7	4.4

nr - Spring number

[Y] - Concentration of dissolved component Y in mg/L

$$DCB (\%) = \frac{\sum \text{cations (meq/L)} - \sum \text{anions (meq/L)}}{\left(\frac{\sum \text{cations (meq/L)} + \sum \text{anions (meq/L)}}{2} \right)} \times 100$$

Table 8

Caption: Results obtained with the procedures outlined in Appendix 2.

Lithologic Unit	nr	Q_{med}	V_r	A	V-365	F_{Na}^t	F_K^t	F_{Mg}^t	F_{Ca}^t	$F_{HCO_3}^t$	F_{Cl}^t	$F_{SO_4}^t$	$F_{NO_3}^t$	$F_{H_2SiO_3}^t$
Lagoa Micaschists	15	0.03	5.3	6.8	3020	6.0	0.2	1.8	2.7	17.8	2.0	5.3	4.4	16.5
Lagoa Augengneisses	16	0.02	3.5	7.9	1107	2.2	0.0	1.0	1.6	11.9	0.7	1.6	0.1	4.8
	17	0.09	12.0	37.4	3466	1.3	0.0	0.6	1.0	6.9	0.5	1.1	0.3	3.4
	31	0.12	21.0	9.2	6254	6.7	0.5	3.2	7.7	35.7	3.5	5.2	9.7	24.6
Amphibolites	2	0.10	12.0	72.0	3351	0.2	0.0	0.4	1.2	5.1	0.1	0.4	0.3	0.9
	4	0.03	5.9	3.8	1171	1.5	0.0	4.2	6.1	39.3	1.1	1.7	0.7	6.5
	6	0.30	50.0	10.5	11321	6.2	0.3	34.2	19.6	200.6	11.1	4.2	17.2	73.1
	30	0.12	23.0	6.8	6808	9.7	0.3	10.6	15.2	77.9	7.6	15.6	15.2	36.5
	32	0.03	5.5	5.3	1354	1.5	0.0	4.4	4.4	27.3	2.0	5.8	1.3	12.5
	37	1.14	250.0	3.4	51844	69.2	1.6	150.2	200.0	1231.1	37.7	122.5	91.3	403.3
	38	0.18	37.0	5.3	11499	7.5	0.5	72.0	19.9	374.6	7.2	18.1	17.0	124.9
	41	0.22	42.0	5.2	7137	5.5	0.0	15.0	15.0	116.2	3.0	10.2	2.9	43.4
	43	0.37	75.0	3.4	12007	27.7	2.3	63.0	66.0	401.7	27.2	45.0	87.0	114.9
	45	0.02	3.5	8.2	1451	1.2	0.0	3.3	3.2	23.3	0.6	2.1	2.5	6.1
	46	0.67	150.0	2.6	21541	48.7	1.8	133.5	149.8	969.0	38.9	87.6	122.2	233.6
Retrograde Amphibolites	1	0.43	80.0	5.5	43972	45.4	1.0	94.0	136.9	694.8	43.8	156.5	43.9	270.4
	8	0.22	32.0	23.6	10422	1.8	0.6	1.6	3.8	16.6	2.2	1.9	2.1	6.3
	9	0.22	40.0	6.1	15332	11.4	0.3	17.5	35.8	179.0	9.7	18.1	5.0	55.0
	28	1.60	440.0	0.3	51921	1163.6	46.5	1125.0	2748.3	11872.9	931.0	2023.2	857.3	4954.5
	47	0.24	45.0	5.0	13596	11.0	0.5	20.8	33.2	176.6	13.9	25.9	5.3	70.9
Ultramafics	48	0.04	7.8	3.7	1166	1.5	0.0	3.2	7.6	31.8	1.4	7.2	1.0	10.2
	3	0.05	9.5	5.0	1499	2.8	1.1	28.3	3.9	130.8	4.6	5.7	12.8	37.0
	11	0.12	22.0	5.6	5325	1.9	0.1	80.0	10.0	347.6	4.3	45.9	9.5	89.1
	20	0.04	7.5	4.6	2575	1.5	0.0	29.2	2.4	141.1	2.8	3.2	2.3	48.5
	21	0.14	23.0	14.5	9095	1.6	0.0	28.1	3.5	137.0	3.7	4.4	1.8	42.0

nr - Spring number.

Q_{med} (L/s) - Median discharge.

V_r (mm) - Recharge occurring between the 1998 and 1999 recessions.

A (ha) - Recharge area.

V-365 (m³) - Volume of water discharged during an entire year (March 1998 - February 1999).

F_Y^t - (kg/(ha.y)) - Total flux of dissolved component Y.

Table 9

Caption: End-member weathering reactions used in the SiB modelling (structural compositions of primary minerals in Table 1). Beidellite and nontronite were the compositions adopted for the smectites in Table 4. Additional information in the text.

Reaction Number	Mineral	End-Member Reaction (Round-Off Coefficients)
R ₁	Albite-An ₀	4.7Albite + xH ₂ O + 4CO ₂ + 0.35Ca ²⁺ → Beidellite + 4.7Na ⁺ + 4HCO ₃ ⁻ + 6.8H ₂ SiO ₃
R ₂	Albite-An ₀	2Albite + xH ₂ O + 2CO ₂ → Halloysite + 2Na ⁺ + 2HCO ₃ ⁻ + 4H ₂ SiO ₃
R ₃	Oligoclase-An ₃₀	3.62Oligoclase + xH ₂ O + 4CO ₂ → Beidellite + 2.53Na ⁺ + 0.73Ca ²⁺ + 4HCO ₃ ⁻ + 2.46H ₂ SiO ₃
R ₄	Oligoclase-An ₃₀	1.54Oligoclase + xH ₂ O + 2CO ₂ → Halloysite + 1.08Na ⁺ + 0.46Ca ²⁺ + 2HCO ₃ ⁻ + 2.15H ₂ SiO ₃
R ₅	Andesine-An ₄₅	3.24Andesine + xH ₂ O + 4CO ₂ → Beidellite + 1.78Na ⁺ + 1.11Ca ²⁺ + 4HCO ₃ ⁻ + 0.97H ₂ SiO ₃
R ₆	Andesine-An ₄₅	1.38Andesine + xH ₂ O + 2CO ₂ → Halloysite + 0.76Na ⁺ + 0.62Ca ²⁺ + 2HCO ₃ ⁻ + 1.52H ₂ SiO ₃
R ₇	Hornblende-A	2.35Hornblende + xH ₂ O + 22.33CO ₂ + 2.82O ₂ → Beidellite + 1.88Fe ₂ O ₃ + 0.94Na ⁺ + 4.35Ca ²⁺ + 6.34Mg ²⁺ + 22.33HCO ₃ ⁻ + 8.44H ₂ SiO ₃
R ₈	Hornblende-A	Hornblende + xH ₂ O + 9.8CO ₂ + 1.2O ₂ → Halloysite + 0.8Fe ₂ O ₃ + 0.4Na ⁺ + 2Ca ²⁺ + 2.7Mg ²⁺ + 9.8HCO ₃ ⁻ + 4.7H ₂ SiO ₃
R ₉	Hornblende-RA	2.61Hornblende + xH ₂ O + 25.67CO ₂ + 2.94O ₂ → Beidellite + 1.96Fe ₂ O ₃ + 1.31Na ⁺ + 4.87Ca ²⁺ + 7.31Mg ²⁺ + 25.67HCO ₃ ⁻ + 10.72H ₂ SiO ₃
R ₁₀	Hornblende-RA	1.11Hornblende + xH ₂ O + 11.22CO ₂ + 1.25O ₂ → Halloysite + 0.83Fe ₂ O ₃ + 0.56Na ⁺ + 2.22Ca ²⁺ + 3.11Mg ²⁺ + 11.22HCO ₃ ⁻ + 5.67H ₂ SiO ₃
R ₁₁	Tremolite	14Tremolite + 0.6Fe ₂ O ₃ + xH ₂ O + 189.7CO ₂ → Nontronite + 0.9O ₂ + 27.65Ca ²⁺ + 67.20Mg ²⁺ + 189.7HCO ₃ ⁻ + 104H ₂ SiO ₃
R ₁₂	Tremolite	40Tremolite + xH ₂ O + 544CO ₂ + 6O ₂ → Halloysite + 4Fe ₂ O ₃ + 80Ca ²⁺ + 192Mg ²⁺ + 544HCO ₃ ⁻ + 316H ₂ SiO ₃
R ₁₃	Chlorite (Ripidolite-I)-RA	0.92Chlorite + xH ₂ O + 10CO ₂ + 2.49O ₂ + 0.35Ca ²⁺ + 2.23H ₂ SiO ₃ → Beidellite + 1.66Fe ₂ O ₃ + 5.35Mg ²⁺ + 10HCO ₃ ⁻
R ₁₄	Chlorite (Ripidolite-II)-M	0.13Chlorite + 1.64Fe ₂ O ₃ + xH ₂ O + 0.22CO ₂ + 0.35Ca ²⁺ + 6.63H ₂ SiO ₃ → Nontronite + 2.45O ₂ + 0.46Mg ²⁺ + 0.22HCO ₃ ⁻
R ₁₅	Chlorite (Ripidolite-II)-M	0.36Chlorite + xH ₂ O + 2.62CO ₂ + 1.5O ₂ + 0.07H ₂ SiO ₃ → Halloysite + Fe ₂ O ₃ + 1.31Mg ²⁺ + 2.62HCO ₃ ⁻
R ₁₆	Chlorite (Picnochlorite)	0.14Chlorite + 1.57Fe ₂ O ₃ + xH ₂ O + 0.12CO ₂ + 0.35Ca ²⁺ + 6.5H ₂ SiO ₃ → Nontronite + 2.36O ₂ + 0.41Mg ²⁺ + 0.12HCO ₃ ⁻
R ₁₇	Chlorite (Picnochlorite)	0.39Chlorite + xH ₂ O + 2.36CO ₂ + 1.78O ₂ → Halloysite + 1.19Fe ₂ O ₃ + 1.18Mg ²⁺ + 2.36HCO ₃ ⁻ + 0.27H ₂ SiO ₃
R ₁₈	Chlorite (Penninite)	0.21Chlorite + 1.94Fe ₂ O ₃ + xH ₂ O + 3.26CO ₂ + 0.35Ca ²⁺ + 5.98H ₂ SiO ₃ → Nontronite + 2.91O ₂ + 1.98Mg ²⁺ + 3.26HCO ₃ ⁻
R ₁₉	Chlorite (Penninite)	0.59Chlorite + xH ₂ O + 11.3CO ₂ + 0.27O ₂ → Halloysite + 0.18Fe ₂ O ₃ + 5.65Mg ²⁺ + 11.3HCO ₃ ⁻ + 1.76H ₂ SiO ₃
R ₂₀	Clinzoisite-A	1.81Clinzoisite + xH ₂ O + 6.53CO ₂ + 0.54O ₂ + 1.88H ₂ SiO ₃ → Beidellite + 0.36Fe ₂ O ₃ + 3.27Ca ²⁺ + 6.53HCO ₃ ⁻
R ₂₁	Clinzoisite-RA	1.88Clinzoisite + xH ₂ O + 6.82CO ₂ + 0.71O ₂ + 1.66H ₂ SiO ₃ → Beidellite + 0.47Fe ₂ O ₃ + 3.41Ca ²⁺ + 6.82HCO ₃ ⁻
R ₂₂	Sphene	Sphene + xH ₂ O + 2CO ₂ → TiO ₂ + Ca ²⁺ + 2HCO ₃ ⁻ + H ₂ SiO ₃
R ₂₃	Calcite	Calcite + H ₂ O + CO ₂ → Ca ²⁺ + 2HCO ₃ ⁻
R ₂₄	Forsterite	Forsterite + xH ₂ O + 3.56CO ₂ + 0.17O ₂ → 0.11Fe ₂ O ₃ + 1.78Mg ²⁺ + 3.56HCO ₃ ⁻ + H ₂ SiO ₃
R ₂₅	Serpentine	Serpentine + xH ₂ O + 5.5CO ₂ + 0.19O ₂ → 0.13Fe ₂ O ₃ + 2.75Mg ²⁺ + 5.5HCO ₃ ⁻ + 2H ₂ SiO ₃
R ₂₆	Talc	Talc + xH ₂ O + 11.8CO ₂ + 0.08O ₂ → 0.05Fe ₂ O ₃ + 5.9Mg ²⁺ + 11.8HCO ₃ ⁻ + 8H ₂ SiO ₃

Table 10

Caption: Results obtained with the SiB algorithm (Appendix 3).

Lithologic Unit	nr	Predicted Clay Abundances			"Best-fit" Weathering Reactions	Weathering Rates (mol/(ha.y))									Residual Effluxes (eq/(ha.y))	
		H(%)	B(%)	N(%)		Plagioclase	Amphibole	Chlorite	Clinozoisite	Sphene	Calcite	Forsterite	Serpentine	Talc	F_{Mg}^u	F_{Ca}^u
Lagoa Micaschists	15	87.1	0.0	13.0	$R_2, 0.3R_{14}+0.7R_{15}$	172.4		19.2							10	148
Lagoa Augengneisses	16	88.0	0.0	12.0	$R_4, 0.3R_{16}+0.7R_{17}$	96.9		13.3							2	31
	17	89.0	0.0	11.0	$R_4, 0.3R_{16}+0.7R_{17}$	58.7		6.9							8	19
	31	95.9	0.0	4.1	$R_4, 0.1R_{16}+0.9R_{17}$	258.7		42.9							6	237
Amphibolites	2	31.1	68.91		$0.8R_5+0.2R_6, 0.2R_7+0.8R_8, R_{13}, R_{20}, R_{22}, R_{23}$	3.37	3.9	0.8	6.5	2.2	3.1				3	9
	4	31.1	68.93		$0.9R_5+0.1R_6, 0.2R_7+0.8R_8, R_{13}, R_{20}, R_{22}, R_{23}$	25.5	30.7	15.2	28.8	9.7	13.7				6	29
	6	nd	nd		nd	nd	nd	nd	nd	nd					nd	nd
	30	30.4	69.59		$0.5R_5+0.5R_6, 0.9R_7+0.1R_8, R_{13}, R_{20}, R_{22}, R_{23}$	136.0	110.1	3.6	1.2	3.1	1.5				236	237
	32	nd	nd		nd	nd	nd	nd	nd	nd					nd	nd
	37	30.9	69.11		$0.7R_5+0.3R_6, 0.5R_7+0.5R_8, R_{13}, R_{20}, R_{22}, R_{23}$	968.0	1417.4	280.0	378.4	264.9	229.7				1461	1764
	38	nd	nd		nd	nd	nd	nd	nd	nd					nd	nd
	41	31.0	68.98		$0.6R_5+0.4R_6, 0.6R_7+0.4R_8, R_{13}, R_{20}, R_{22}, R_{23}$	78.0	148.3	29.4	1.6	22.1	8.6				99	94
	43	31.0	69.02		$0.6R_5+0.4R_6, 0.5R_7+0.5R_8, R_{13}, R_{20}, R_{22}, R_{23}$	339.6	430.7	150.6	61.7	48.4	39.4				1112	1126
	45	31.1	68.86		$0.6R_5+0.4R_6, 0.6R_7+0.4R_8, R_{13}, R_{20}, R_{22}, R_{23}$	16.0	23.9	9.5	4.7	3.5	2.9				33	35
Retrograde Amphibolites	46	30.6	69.4		$0.5R_5+0.5R_6, 0.5R_7+0.5R_8, R_{13}, R_{20}, R_{22}, R_{23}$	651.2	942.6	375.1	335.3	175.6	182.0				1585	1801
	1	34.8	65.16		$0.8R_1+0.2R_2, 0.3R_9+0.7R_{10}, R_{13}, R_{21}, R_{22}, R_{23}$	567.6	692.0	171.1	382.6	179.6	200.7				1883	2217
	8	34.7	65.29		$0.7R_1+0.3R_2, 0.1R_9+0.9R_{10}, R_{13}, R_{21}, R_{22}, R_{23}$	28.5	11.7	3.0	19.9	4.4	8.8				31	50
	9	34.7	65.28		$0.9R_1+0.1R_2, 0.1R_9+0.9R_{10}, R_{13}, R_{21}, R_{22}, R_{23}$	167.5	136.7	43.6	185.0	57.4	87.4				169	342
	28	34.8	65.18		$0.1R_1+0.9R_2, R_{10}, R_{13}, R_{21}, R_{22}, R_{23}$	17401.2	10172.0	1197.0	13074.0	3322.8	5936.2				21744	34608
	47	34.7	65.32		$0.1R_1+0.9R_2, 0.7R_9+0.3R_{10}, R_{13}, R_{21}, R_{22}, R_{23}$	154.9	176.5	35.9	110.7	48.8	57.0				320	422
Ultramafics	48	34.7	65.34		$0.4R_1+0.6R_2, 0.3R_9+0.7R_{10}, R_{13}, R_{21}, R_{22}, R_{23}$	16.6	28.1	4.0	33.8	13.2	16.8				64	97
	3	49.4		50.6	$0.5R_{11}+0.5R_{12}, R_{19}, R_{24}, R_{25}, R_{26}$		20.9	50.4				14.8	24.4	65.2	205	156
	11	49.9		50.2	$0.5R_{11}+0.5R_{12}, R_{19}, R_{24}, R_{25}, R_{26}$		15.5	143.7				43.6	72.8	200.0	760	564
	20	49.5		50.5	$0.5R_{11}+0.5R_{12}, 0.9R_{18}+0.1R_{19}, R_{24}, R_{25}, R_{26}$		24.5	48.0				16.6	27.8	77.3	122	65
	21	49.4		50.6	$0.5R_{11}+0.5R_{12}, 0.9R_{18}+0.1R_{19}, R_{24}, R_{25}, R_{26}$		31.9	49.9				14.5	23.8	62.6	128	92

nr - Spring number.

H(%), B(%), N(%) - Halloysite, Beidellite and Nontronite, respectively.

Reaction numbers (R_i) in agreement with Table 9.

nd - Not determined.

Figure 1

Caption: Geographical maps of Portugal and Trás-os-Montes indicating the position of the study area (Morais massif). Simplified geological map of the Morais massif, adapted from Pereira et al. (1998).

Figure 2

Caption: Simplified land use map of the Morais area. Only the extensively dominant uses are indicated; the hundreds of small spots used for cultivation of potato, maize and green vegetables were not drawn but are spread out the entire massif. Adapted from Agroconsultores and Coba (1991). Location of sampled and monitored springs (labeled bullets).

Figure 3

Caption: Hydrograph of spring nr. 2.

Figure 4

Caption: Relation between the recharge area of a spring (A), its average discharge rate (Q_{med}) and the recharge taking place between two recession periods (V_r). Adapted from Todd (1980).

Figure 5

Caption: Examples of correlation between weathering rates (w_r) and annual recharge rates (V_r).

Figure 6

Caption: Extreme normalized weathering rates of minerals in the Morais massif, calculated on the basis of linear regressions with the recharge rate (V_r); horizontal bars suggest linear transitions from the values on the left-hand side to those in the right-hand side. The values on the left-hand side link to poor drainage conditions represented by a low recharge rate ($V_r = 5$ mm), in opposition to those in the right-hand side ($V_r = 250$ mm). To obtain the normalized weathering rate for a particular V_r , take the ratio between the differences of extreme weathering rates (e.g. 475.3 for forsterite) and extreme recharge rates (245) and multiply the result by the particular V_r . Link of weathering rates to the Persistence Order of Minerals (POM) of Pettijohn (1941).

Figure 7

Caption: Plot of the F_{SO4}^* fluxes against their corresponding F_{Cl}^* fluxes (bullets).

Sulphate fluxes that would result from application of Foskamónio (F_{SO4}^P fluxes, materialized in the dotted line and large circle). Retention by the biomass (F_{SO4}^o fluxes) are expressed in the $F_{SO4}^P - F_{SO4}^*$ differences.

Figure 8

Caption: Plot of the F_{Mg}^p/F_{Ca}^p ratios of spring water samples versus their corresponding F_{SO4}^p/F_{NO3}^p ratios (open circles). Relation of the F_{Mg}^p/F_{Ca}^p ratios with Mg/Ca ratios expected in water that would result from: (1) Simultaneous application of manure, Foskamónio (mixing line) and Nitrolusal ("triangle" defined by the stars); (2) Equilibrium with the soil exchange complex (dotted line); (3) Cation exchange reactions stimulated by application of manure and commercial fertilizers (dashed line). The compositions of manure, Foskamónio and Nitrolusal are given in Table 5. Exchange complex compositions of saprolitic materials derived from the main lithologic units of the Morais massif are shown in Table 4. To determine the position of the dotted line, we used the selectivity coefficient between Mg and Ca (1.25) as referred to in Appelo and Postma (1993).