Hydrogeochemistry in the Vouga river basin (central Portugal): pollution and chemical weathering.

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ABSTRACT

To quantify and explain the contributions by pollution and chemical weathering to their composition, we studied the chemistries of springs and surface waters in the mountainous part of the Vouga River basin. Water samples were collected during a number of consecutive summer campaigns. Recharge rates were derived from monitored discharge rates within the basin. Very large contributions by meteoric, agricultural and domestic sources to the water chemistries were found, identified by the chloride, sulfate and nitrate concentrations: on average only 1/4 to 1/3 of the solutes could be attributed to chemical weathering. Two petrologic units characterize the river basin: granites and metasediments. The waters collected within metasediment units are distinct from those in granite terrain by a higher magnesium (Mg) concentration. On that basis, it could be estimated that the Rio Vouga, when leaving the mountainous part of the basin, has for some 2/5 a signature determined by chemical weathering in the metasediments. The dominant primary minerals subject to chemical weathering are plagioclase (Pl) and biotite (in granite) or plagioclase and chlorite (in metasediment). Kaolinite, gibbsite and vermiculite are the major weathering products where annual precipitation (P) $> 1000 \text{ mm}\cdot\text{y}^{-1}$, and kaolinite, vermiculite and smectite where P was lower. Using an algorithm based on the ratio of dissolved silica to bicarbonate, the contributions of chemical weathering of primary minerals could be unraveled. The results show that in granite the export rate (as $\text{mol}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}\cdot\text{wt.}\%\text{mineral}^{-1}$) of oligoclase (Pl with An_{10-30}) was 5.0 ± 2.6 and of biotite 3.2 ± 2.6 , while in metasediment these rates for albite (Pl with An_{0-10}) are 16.5 ± 8.9 and for chlorite are 0.5 ± 0.5 . The observed decrease of dissolved silica in surface waters relative to springs was ascribed to (summer) uptake by aquatic biota.

INTRODUCTION

Rainwater, percolating the soil, carries already various solutes. These dissolved components can have natural sources such as marine aerosols and dust particles as well as anthropogenic sources such as exhaustions of gaseous, liquid and solid components. The initial concentrations of such solutes are raised by evapotranspiration and by interaction between infiltrating water, biota, and organic and inorganic solids (minerals) met on the journey of soil water via groundwater to local (springs) or diffuse emanations into surface water. On top of this simplified description of the processes, one has to envisage the contributions of agricultural practices and industrial and domestic effluents. Several courses are open to extract information about natural weathering processes and rates in a drainage basin. The most laborious one is to follow a holistic approach, in which all fluxes into and out of a well-defined watershed are measured during a long period of time. This has been done, for instance, for Hubbard Brook Experimental Forest (c.f. Likens and Bormann, 1995; Likens et al., 1994, 1998, 2002) and is recommended for other watersheds to be selected for detailed monitoring of fluxes (Hornung et al., 1990; Moldan and Cerny, 1994; Anderson et al., 2004). Other approaches are less elaborate, and are based on studies of weathering profiles (White et al., 2001; Nezat et al., 2004, and references therein) and/or on water chemistries in combination with knowledge of the mineralogy of soils, bed-rock, saprolite, temperature, runoff etc. (cf. White and Blum, 1995; Oliva et al., 2003; White, 2004; and references therein). Mass balance modeling, with a matrix of stoichiometric coefficients for the assumed chemical reactions between primary and secondary minerals as a core, has become a standard method in relating water chemistry to mineral weathering (e.g. Velbel, 1986; Bowser and Jones, 2002; and references therein). Software packages such as PHREEQC

(Pakhurst and Appelo, 1999) as well as spreadsheet methods (Bowser and Jones, 2002) are available for mass-balance calculations. Fertilizing practices in agricultural areas as well as input of domestic and industrial effluents in densely populated areas contribute to the chemistry of groundwater and surface water. In dealing with such cases, Pacheco and Van der Weijden (1996, 2002) and Pacheco et al. (1999) used a method in which the ratio between the concentrations of silicic acid and bicarbonate (Si/B) is a key parameter in distinguishing between natural and anthropogenic contributions to the water chemistry. In principle, the so-called SiB algorithm has also the versatility to assess processes like ion exchange and net uptake or release by biota. The method was successfully applied to unravel weathering processes and to estimate weathering rates based on spring water compositions in rather small drainage areas. In this paper we discuss the hydrochemistry of springs and surface waters in the large drainage basin of the Vouga River (central Portugal) and use the SiB approach to define and quantify the contributions of natural weathering to the chemistry of these waters.

STUDY AREA

The basin of the Rio Vouga is located in central Portugal and occupies an area of approximately 3362 km². The river rises in the Lapa mountains at an altitude of about 930 m. The main northern tributaries from East to West are the Sul, Caima and Antuã rivers; the southern tributary is the Águeda river with the Cértima and Alfusqueiro rivers as branches. The main water course of the Vouga River is 141 km long and debouches into the Ria de Aveiro, with a small inlet/outlet connecting this lagoon to the Atlantic ocean (Figure 1).

Geology, Petrology, Mineralogy

The geology of the Vouga River basin is shown in Figure 2. The mountainous part of the basin is characterized by Palaeozoic metasediments which were intruded by syn- to post-tectonic Hercynian granites (Schermerhorn, 1956; Soen, 1958, 1970; Martins, 1962; De Boorder, 1965; Godinho, 1980; Sousa, 1985; Medina, 1996; Reis, 2000).

The metasediments consist of phyllites and greywackes that locally can alternate with conglomerates, amphibolites and, in the vicinity of granites, with migmatites and micaschists with high-grade metamorphism manifest in the sillimanite porphyroblasts.

The syn-tectonic granites consist mostly of medium- to coarse-grained two-mica granites to granodiorites, the post-tectonic granites of porphyritic coarse-grained biotite or two-mica granites. An important feature of the syn-tectonic granites is that they underwent metasomatism by later magmas, whereby original oligoclase has been transformed into albite. In the post-tectonic granites, the first magmatic plagioclase has alkaline oligoclase (An₃₀) cores and albite (An₁₀) outer rims, while the final magmatic plagioclase (later than K-feldspar megacrysts) has albite–sodic oligoclase composition. In both granites, late endomagmatic albite has been crystallized (Soen, 1958). The chemical and mineralogical compositions of granites and metasediments are summarized in Tables 1a,b.

Morphology and Climate

The Vouga basin is surrounded to the North by the Lapa, Leomil, Montemuro, Freita and Arada mountains, and to the South by the Caramulo and Buçaco mountains. A major portion of the main watercourse runs across the mountainous areas (Figure 1). Precipitation (*P*) in the basin has been monitored for a minimum of 11 and a maximum of 68 years at 20 meteorological stations (Figure 3; Table 2). On average,

$795 < P \text{ (mm}\cdot\text{y}^{-1}) < 1624$, with the highest values occurring at the mountain peaks and the lowest ones in the source area of the river. Temperatures in the mountainous areas range from approximately 8 °C in winter to 21 °C in summer, with an annual average of 14 °C.

Hydrology

Discharge in the Vouga basin has been monitored at several hydrometric stations for a minimum of 2 and a maximum of 55 consecutive years. The locations of the stations are shown in Figure 3 and some relevant data presented in Table 3. Using the Kille method (see Appendix 1), the recharge taking place within the drainage basins of the monitored rivers has been calculated. The calculated annual recharge (R) rates are listed in Table 3 (last column) while Figure 4 shows how they correlate with precipitation. The least squares fitting to the scatter points (dashed line) is represented by the equation:

$$R = 0.21 \times P - 122.3, \text{ with } r^2 = 0.9 \quad (1)$$

Soils and Land Use

The mountainous part of the Vouga basin has a monotonous cover by cambisols. In the region, the profile of a typical cambisol is characterized by an A horizon (0–30 cm depth) rich in organic matter, a B horizon (30–55 cm) rich in clay minerals and a C horizon (55–80 cm) composed of weathered rock. (Cardoso, 1974).

Small-size farm lands and forests in total occupy 4/5 of the basin, the remaining 1/5 being represented by bare rock, urban areas and water bodies. Forestry is important in the mountainous area, but the proportion of land used for agriculture is significant and the associated use of manure and fertilizers responsible for anthropogenic

contributions to the chemistry of shallow ground waters. Farmers use farmyard manures as the main source for supplying nutrients to fields or pastures, although they combine their use with dressings of commercial fertilizers. The manures carry (in decreasing order) nitrogen, potassium, sulfur, phosphorus, calcium and magnesium (Portela et al., 1993). The most widely used fertilizers have phosphorous, potassium, nitrogen, chloride, sulfur, calcium and magnesium, applied in various proportions depending on the types of crops. In all cases the calcium content of these fertilizers is higher than the magnesium content. Some small urban areas have no sewage system and so domestic effluents are discharged directly into the soils.

SAMPLING AND ANALYSIS

Samples of perennial springs, stream(lets) and rivers were collected in the mountainous part of the Vouga basin during summer campaigns (June–July) in a number of consecutive years (1982–1985). The sampling sites are shown in Figure 5. Precise locations and classifications according to the water type and geological environment are given in columns 2–4 of Appendix 2. At the sampling site, temperature, pH and electrical conductivity (*EC*) were measured and a water sample filtered through a 0.4 µm membrane filter. The filtered water was split into 3 portions, two were stored for analysis in the home laboratory (one unacidified and one acidified to pH 2) and one for analysis of alkalinity in the field laboratory (within 24 hours using the Gran plot method). In the home laboratory, ICP-AES was used for analysis of Si, S, Al, Fe, and major cations. Chloride was determined electrochemically with an ion-selective electrode, nitrate and Si were measured colorimetrically using an AutoAnalyzer. All concentrations were measured against laboratory standards. In general, the deviation of the individual values was less than 5% (< 1% for

bicarbonate), and only samples with a charge balance better than $\pm 10\%$ were accepted for further consideration.

HYDROCHEMISTRY

Total concentrations

The total concentrations of the solutes in springs and stream(lets) are given in Appendix 2 and visualized in Figure 6. The concentrations of Cl^- , SO_4^{2-} , NO_3^- , Na^+ , K^+ and Mg^{2+} in springs in granites are lower than in springs in metasediments, with the most significant contrast for Mg^{2+} , whereas the Ca^{2+} concentrations are very similar. Relative to these concentrations, those in streams are mostly higher than in springs. For the observed differences several explanations can be given, such as: 1) on average, the metasediment complexes are situated closer to the coastal plain and have higher rainfall, 2) metasediments and granites have different mineral inventories undergoing chemical weathering, 3) the densities of cultivated and uncultivated areas in these petrological complexes are different, with concomitant differences in evapotranspiration and fertilization, 4) surface waters are subject to additional evaporation and have inputs of overland flow and industrial and domestic effluents. The major sources and processes contributing to the water chemistry are discussed in the next two paragraphs.

Atmospheric and anthropogenic contributions.

The composition of (wet) precipitation is measured at only a few meteorological stations in Northern Portugal, one at the coast, the other about 300 km inland. The data in Table 4 are indicative of contributions by soluble atmospheric gases and dust on top of marine aerosols. In the mountainous region, these values have become lower

as a result of washing out. Adopting a median value of 50 μM Cl^- in wet precipitation for our study area in combination with $75 \pm 15\%$ evapotranspiration, the Cl^- concentration entering the groundwater can increase to 125 or even 500 μM . In addition, application of fertilizers (dominantly as KCl) and industrial and domestic effluents can contribute to the Cl^- concentration, but estimates for Cl^- contributions of non-seasalt (nss) origin (Table 4) are relatively low. Apart from decay of organic matter, nss sulfate is mainly derived from air pollution and from application of fertilizers and fungicides (viniculture). The relation between SO_4^{2-} and Cl^- in spring water samples (Figures 7a,b) can not fully be explained by evapotranspiration of meteoric waters. This means that there is a net consumption of sulfate in the recharge areas and(or) that non-meteoric sources contribute to the Cl^- concentrations in excess of SO_4^{2-} . Nitrate is derived from atmospheric gases and aerosols by washing out of combined nitrogen (NO_x , NH_3 , NH_4^+) as well as by fertilizers. In the context of this paper with focus on chemical weathering and realizing that they are predominantly derived from meteoric and anthropogenic sources instead of added by chemical weathering of (alumino)silicate minerals, we consider chloride, sulfate and nitrate from atmospheric and anthropogenic sources as “pollutants” and define

$$\text{pollution}(\%) \equiv 100 \times \frac{[\text{Cl}^-] + 2[\text{SO}_4^{2-}] + [\text{NO}_3^-]}{[\text{Cl}^-] + 2[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{HCO}_3^-]} \quad (2)$$

where $[\]$ indicates molar concentrations.

These % values are given in Appendix 2. The median values are 65% (springs in granites), 68% (springs in metasediments), and 72% (in streams). This means that, on average, only between 1/3 and 1/4 of the cations (equivalent scale) are derived from natural weathering by CO_2 . It has to be noted that there are quite a few missing nitrate values in which case the values will be a little off. The average Cl^- , SO_4^{2-} and NO_3^-

concentrations are higher in springs in metasediments than in granite and higher in streams than in springs in these areas. (Figures 6a,b,c). This may be due to differences in intensity or efficiency of fertilizer applications, to flushing of fertilizer components by overland flow, to direct input of domestic origin (especially for lower order streams), but also to the fact that the metasediments are generally situated closer to the coast with concomitant higher humidity and washing out (cf. Table 4). Processes in the root zone and in the soil are very complex. To name a few of them: 1) uptake by plants of anions in excess of cations can be compensated by release of HCO_3^- whereas the reverse will release of H^+ , 2) uptake of NH_4^+ by vegetation releases H^+ , uptake of NO_3^- and SO_4^{2-} consumes H^+ , nitrification produces H^+ ; the reverse happens upon decomposition of organic matter and concomitant ammonification and oxidation, 3) precipitation is a diffuse and fertilization a localized source of nutrients, 4) inequality between added and harvested nutrients results in their loss to the groundwater, and 5) in general, imbalance between growth and decomposition of vegetation will result in net loss or gain of soil- and groundwater solutes. The combined results of all these and still other processes are represented by % *pollution* (Equation 2).

Equivalent cation concentrations have similar atmospheric and anthropogenic sources. The cations in the non-marine contributions are for a relatively large part matched by nitrate and sulfate (Table 4). In manure and commercial fertilizers, K is an essential nutrient, while Ca and Mg are less important constituents. As far as not taken up in the crops and harvested, these cations will be removed by percolating soil water and, together with H^+ , become involved in ion-exchange processes in the soil before entering the groundwater zone.

Natural Contributions

Input of bicarbonate by meteoric water is very low (Table 4). For that reason it is assumed that carbonate alkalinity and dissolved silica are derived from chemical weathering. The bicarbonate (B) to silica (Si) ratio, B/Si, depends on the minerals dominantly involved in this weathering. In granite and metasediment, plagioclase is the most weatherable mineral phase. As illustrated by Garrels (1967), B/Si depends on the %An in the plagioclase as well as on the weathering product (smectite, kaolinite, gibbsite). In granite, B/Si has a range of 0.15–1.0 with a linear fit of 0.52 (Figure 8a). When no other minerals or processes are involved, this represents weathering of sodic plagioclase into kaolinite. In fact, the spring water compositions all lie in the stability field of kaolinite. Weathering of biotite into vermiculite produces acidity, whereas subsequent chemical weathering of vermiculite into kaolinite produces alkalinity. The overall process of biotite weathering into kaolinite has B/Si = 2.0. This means that plagioclase weathering dominates the water chemistries in the granites. A process that will bring down the ratio is the weathering of plagioclase into gibbsite, a mineral quite common in weathering profiles of Portuguese granites, especially under a regime of annual precipitation $> 1000 \text{ mm} \cdot \text{y}^{-1}$ (Martins et al., 1995).

In the metasediments, spring waters have an average B/Si = 0.82 (range 0.22–1.6) (Figure 8b). Plagioclase is a minor component but the most weatherable mineral in metasediment. The low B/Si values in metasediment waters can represent weathering of sodic plagioclase into kaolinite or even gibbsite, whereas the higher values can be explained by weathering of chlorite into the same clay minerals.

The pH values depend on P_{CO_2} and on acquired alkalinity. There is not much difference in pH and alkalinity between spring water samples in granite and metasediment (Figure 6g). Stream(lets) in these rock units have alkalinities similar to

springs but higher pH values (Figures 6h,i). This is due to release of CO₂ once spring water has emerged; the calculated median $\log P_{\text{CO}_2}$ values in springs in granite (−1.8) and metasediment (−1.8) are higher than in stream(lets) in granite (−2.4) and metasediment (−2.7). Another change in the chemistry of streams relative to springs is the decrease in dissolved silica and consequently the increase of B/Si (Figures 6j,k). It may not be ruled out that this is caused by admixture of surface or interflow water but, since the samples were collected during the summer season, it is more likely that silica is used and temporarily stored by aquatic biota in streams.

Vouga Water

The development of Vouga water chemistry during the summer season from near the source area to the coastal plain is illustrated in Figures 9a–d (location of sites labelled 1 to 10 in Figure 5). The *EC* values are approximately tripled, indicating a steadily increasing acquirement of solutes. The peak at site 6 is related to effluents from domestic and hydrothermal sources in the São Pedro do Sul/Vouzela area. The pH values along the course of the Vouga increase by about 1.5 units, in keeping with a similar increase of alkalinity. Chloride, sulfate and nitrate also increase, with peaks at site 6 for the reason already given for the *EC* peaks. Since these anions are lumped in the category ‘pollution’, this reflects the trends in precipitation/evapotranspiration, and the accumulative effects of agricultural and domestic sources.

Sodium is by far the most important cation, Ca²⁺ is the next dominant cation in the stretch between sites 1 and 6. As a result of confluence with streams from metasediment areas, Mg²⁺ becomes more important along the course of the river till [Mg²⁺] and [Ca²⁺] become about equal near the coastal plain. A small westward increase of [K⁺] can be due to the accumulative effect of weathering of K-

feldspar/microcline, an important mineral phase in the granites, but also of excess K from fertilizers. The ratio of alkalinity to dissolved silica shows an erratic pattern. Since it can be ruled out that biotite weathering, with concomitant high B/Si values, dominates the water chemistry, the most plausible reason is that Si is partly consumed by aquatic biota (Van der Weijden and Middelburg, 1989; Meunier, 2003). When $[Mg^{2+}]/[Ca^{2+}]$ is used as proxy for the contribution of metasediment weathering, median values of the ratios in streams(lets) in granites (0.88) and metasediments (1.53) allow the rough estimate that near the westernmost sampling site (10; ratio 1.18) Vouga water has for 2/5 the signature of metasediment waters. It has to be noted that we did not include sampling sites downstream of site 10 in this analysis, because of the more polluted nature of waters from the drainage areas of the rivers Caima and Mau, while pollution becomes even higher in the coastal plain.

For the sake of completeness, some characteristic values are shown of waters from a major tributary of the Vouga, the Águeda river that drains a large area of the metasediment complex (site 10.5, just after its confluence with the Alfusqueiro river, cf. Figures 1 and 9). In comparison with site 10 in the Vouga, pH, $[Mg^{2+}]$ and $[K^+]$ are about equal, while EC, $[Ca^{2+}]$, $[Na^+]$ and $[Cl^-]$ are lower. As expected for rivers draining the metasediment area, $[Mg^{2+}] > [Ca^{2+}]$. After the confluence with the Alfusqueiro, the Águeda River enters the coastal plain and the chemistry changes drastically under influence of other lithologies and pollution (Vriend et al., 1988).

MINERAL WEATHERING

Modelling Assumptions

We assume plagioclase (Pl) and biotite (Bt) to contribute dominantly to groundwater chemistry in the granites, and Pl and chlorite (Ch) in the metasediments, i.e. we ignore

the contributions of minerals such as K-feldspar or muscovite. The clay fraction of the granite and metasediment soil cover consist predominantly of kaolinite/halloysite (Kl), with variable amounts of gibbsite (average Gb < 25%) and vermiculite (average Vr < 10%) and minor amounts of smectite (Sm < 5%). The assumed compositions of primary and secondary minerals are shown in Tables 1b and 5, the concomitant weathering reactions are given in Table 6. Biotite, chlorite, vermiculite and smectite can be represented by a wide range of compositions, while interstratification in layer silicates is also possible. However, for building a weathering model it is impossible to cover the full complexity and variability of compositions of the mineral assemblages in the weathering zone.

To assess the contributions to groundwater chemistry by hydrolysis of plagioclase, biotite and chlorite, by biological uptake, and by the atmospheric inputs plus leachates of manure, commercial fertilizers and domestic effluents, we used a mole balance algorithm called the SiB algorithm (Pacheco and Van der Weijden, 1996, 2002; Pacheco et al., 1999; see Appendix 3 for a brief outline). Since we have no detailed data that prove otherwise, we assumed the soil/saprolite system as well as vegetation to be in a steady state.

Discussion on mineral weathering addresses the export rates of plagioclase, biotite and chlorite. The export rate of a mineral M (W_M in $\text{mol}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}\cdot\text{wt.}\%\text{M}^{-1}$) is given by:

$$W_M = \frac{10^{-2} \times [M] \times R}{\%M} \quad (3)$$

where $[M]$ is the contribution of M to the water chemistry in $\mu\text{mol}\cdot\text{L}^{-1}$, R the groundwater recharge in $\text{mm}\cdot\text{y}^{-1}$, and $\%M$ is the content in wt.% of M in the rock. To calculate export rates, the $[M]$ values of each spring or stream(let) are computed using

the SiB algorithm, and then the corresponding R values are deduced from Equation 1 taking into account the location of the sites in Figure 3, which gives an estimate for P . The abundances of M are taken from normative analyses of rock samples (Table 1b).

Results of the SiB Algorithm — Springs

The SiB algorithm was applied separately to springs in granites and in metasediments, and could explain the chemistry of 103 (75%) and 53 (100%) cases, respectively. The best-fit solutions are listed in Tables 7a,b, with spring numbers shown in column 1.

The calculations handled plagioclase anorthite contents in the range $An_{10} - An_{30}$

(granites) or $An_0 - An_{10}$ (metasediments), the results (column 2) demonstrated that:

granites — An_{10} (82 springs) $> An_{15}$ (9) $> An_{20}$ (3) $\approx An_{25}$ (5) $\approx An_{30}$ (4);

metasediments — An_0 (41 springs) $> An_5$ (7) $\approx An_{10}$ (5). It has to be mentioned that chemical weathering of minor amounts of calcite, when present, would be expressed in a higher calculated An content, while other easily weatherable accessory minerals may have affected the Si/B ratio and consequently the results of the SiB algorithm.

(White et al., 1999; Oliva et al., 2004; White et al., 2005). The weathering reactions

are summarized in columns 4 and 5. In column 4, c_1 is the proportion of

kaolinite/halloysite derived from plagioclase reaction, while $100 - c_1$ is the proportion

of smectite or gibbsite depending on whether $P < 1000 \text{ mm}\cdot\text{y}^{-1}$ or $P \geq 1000 \text{ mm}\cdot\text{y}^{-1}$

(column 3). For instance, if $c_1 = 30\%$ and $P \geq 1000 \text{ mm}\cdot\text{y}^{-1}$ the reaction of plagioclase

is given by $0.3 \times R_{1b} + 0.7 \times R_{1c}$, in keeping with the reaction numbers of Table 6.

Exceptions to this rule are the granite springs Nr. 1412, 1449, 1468, 1664, 1670,

1697, 2033, 2095 and 2853, but $P = 1000 \text{ mm}\cdot\text{y}^{-1}$ is not a sharp value for the change

in soil mineralogy. In column 5, c_2 is the proportion of kaolinite/halloysite formed

upon weathering of biotite or chlorite, while $100 - c_2$ is the counter proportion of

vermiculite. In the granites, a $c_2 = 30\%$ means that biotite reaction is $0.3 \times R_{2c} + 0.7 \times R_{2a}$, in the metasediments that chlorite reaction is $0.3 \times R_{3c} + 0.7 \times R_{3a}$. In a few cases plagioclase weathering produced Sm, but usually the reaction resulted in Kl + Gb mixtures. On average, these assemblages have 28% Gb in the granites and just 0.4% in the metasediments, meaning that plagioclase weathering is more intense in the granites. Biotite weathers to mixtures rich in Vr (62.8%), chlorite to mixtures rich in Kl (79.4 %). Resulting from simultaneous weathering of plagioclase, biotite and chlorite, the abundances of secondary products are predicted to be (columns 6–9): for soils developed on granites, Sm = 1.1%, Vr = 7.3%, Kl = 70.3% and Gb = 21.3%; for soils developed on metasediments, Sm = 0.2 %, Vr = 3.4% and Kl = 96.4%, which is acceptable.

The number of moles of primary minerals dissolved during weathering are listed in columns 10 and 11 of Tables 7a,b. On average they are $[Pl] = 140 \mu M \gg [Bt] = 10 \mu M$ (granites) or $[Pl] = 110 \mu M \gg [Ch] = 12 \mu M$ (metasediments), but these mass transfers tell little about the contribution of minerals to weathering because they depend on groundwater dilution as well as on the abundance of the minerals in the host rocks. The contribution to weathering of a mineral M_i ($\%[M_i]$) is preferably indexed to:

$$\%[M_i] = \frac{[M_i]/\%M_i}{\sum_{i=1}^q [M_i]/\%M_i} \quad (4)$$

where $[M_i]$ is the mass transfer of M_i , $\%M_i$ is the percentage of M_i in the host rock (e.g. Table 1b) and q is the number of primary minerals involved in the weathering process. On average, $\%[Pl] = 65.0\%$ in the granites and 97.3% in the metasediments, which means that metasediment percolating waters attack preferably the most

weatherable minerals (plagioclase), while in the granites this attack is effective also on more resistant minerals (biotite). In Figure 10, a negative trend is established between contribution to weathering and potential for weathering, the latter being assessed by the *MWPI* index of Vogel (in Bland and Rolls, 1998):

$$MWPI = \frac{Na_2O + K_2O + MgO + CaO}{Na_2O + K_2O + MgO + CaO + SiO_2 + Al_2O_3 + Fe_2O_3} \times 100\% \quad (5)$$

Apparently, the larger is the number of weatherable minerals (rocks with high *MWPI*) the lower is the contribution of each to weathering.

Spring recharges are listed in column 12 of Tables 7a,b. They were calculated by Equation 1 taking into account the *P* values of column 3, and allowed for the calculation of export rates using Equation 3 (columns 13 and 14). Within a generally undersaturated solution, export rates can be transport- or surface reaction-controlled depending on whether they are a function of recharge or not (Bland and Rolls, 1998). Under transport- controlled weathering, the scatter points in a W_{PI} vs. *R* plot will fit to a sloping straight line, otherwise to a horizontal straight line. Figure 11 is a W_{PI} vs. *R* plot that includes springs from the Vouga basin and from the Morais massif, which happen to represent transport-controlled weathering, and springs from the Madeira Island that represent surface-reaction controlled weathering. The transition between the two weathering regimes is attained for $R \approx 900 \text{ mm}\cdot\text{y}^{-1}$.

On average, the concentrations of cations derived from atmospheric plus anthropogenic inputs are $[Na]_p = 146 > [Mg]_p = 27 > [Ca]_p = 14 > [K]_p = 8 \text{ }\mu\text{M}$, in the granites, and $[Na]_p = 197 > [Mg]_p = 40 > [Ca]_p = 31 > [K]_p = 25 \text{ }\mu\text{M}$ in the metasediments (columns 15–18 of Tables 7a,b), which mean they are 1.3 (Na), 1.5 (Mg), 2.2 (Ca) and 3.1 (K) times higher in the metasediments. The higher inputs in the metasediments may primarily be a consequence of differences in evaporation prior to

infiltration or after emergence of water, but also of differences in the land use or intensity of fertilizing.

Table 6 shows how reactions to Vr consume Mg from solution whereas reactions to Kl release it. According to the SiB results, reactions to Vr-rich mixtures are typical for biotite weathering in the granites and therefore spring waters in these rocks have low 'natural' Mg. Contrarily, the 'natural' Mg in metasediment spring waters should be high because on average chlorite weathering in these rocks produces Kl-rich mixtures. Apart from the natural contributions, Mg in spring waters is also derived from atmospheric plus anthropogenic sources. The question arises whether weathering or these sources explain better the differences in $[Mg^{2+}]$ between waters in granites and in metasediments. The natural and atmospheric plus anthropogenic contributions of Mg to the composition of spring waters are, on average (cf. Appendix 2 and Tables 7a,b): granites – $[Mg^{2+}] = [Mg]_r + [Mg]_p = 21.5 = -5.5 + 27 \mu M$; metasediments – $[Mg^{2+}] = [Mg]_r + [Mg]_p = 67.5 = 27.5 + 40 \mu M$. The difference between the Mg concentrations is given by $\Delta[Mg^{2+}] = \Delta[Mg]_r + \Delta[Mg]_p = 46 = 33 + 13 \mu M$. We therefore conclude that the marked distinction between granite and metasediment spring waters, which can be made on the basis of $[Mg^{2+}]$, is in 72% a result of differences in the natural contributions and solely in 28 % a consequence of differences in the other contributions.

Results of the SiB Algorithm — Stream(let)s

The sampling campaigns were carried out in the summer season and so stream(let) waters are preferably of shallow groundwater origin (i.e. comparable to spring waters). On the other hand, bicarbonate concentrations in springs and streams are identical (Figure 6i) while silicic acid concentrations are considerably lower in

streams (Figure 6j), an observation that we linked to the uptake of H_4SiO_4^0 by aquatic biota. In applying the SiB algorithm, some adjustments and simplifications were made relative to the runs with the spring waters. Firstly, the uptake of H_4SiO_4^0 has been modelled as a ‘precipitation’ of SiO_2 reaction, i.e. a term was added to the mole balance equation for Si (Equation A3.1a) with a stoichiometric coefficient given by $\alpha = -1$. Secondly, because Sm is present in soils only in minor amounts, we assumed that weathering of plagioclase resulted always in formation of Kl + Gb mixtures. Thirdly, the best fit SiB solutions assume conservation of bicarbonate after emanation of spring water into surface water, because concentrations in spring waters and stream(let) waters are very similar, and constrain de plagioclase mole fractions accordingly via the [Pl] versus $[\text{HCO}_3^-]$ fittings relative to the springs. These fittings are: $[\text{Pl}] = 0.66[\text{HCO}_3^-]_t + 36.0$ ($r^2 = 0.8$), in the granites, and $[\text{Pl}] = 0.36[\text{HCO}_3^-]_t + 46.3$ ($r^2 = 0.6$) in the metasediments. According to the assumption, if a stream(let) water sampled in granite bedrock has $[\text{HCO}_3^-]_t = 100 \mu\text{M}$, then the best fit SiB solution is the one dissolving $102 \mu\text{M}$ of plagioclase. As expected, the best-fit solutions comply with a deficit in dissolved silica, which is attributed to consumption by aquatic biota.

The complete set of SiB results is depicted in Tables 8a,b, but the focus will be put on silica consumption (last column), taking into account the location of the sampling sites. A major portion of the stream(let) waters were sampled in the eastern part of the Vouga river basin, between the source area and the Sul river. The subset of samples collected in this part of the basin is plotted in Figure 12 (bullets). In the lighter shaded areas the average order of the stream(let)s is lower than in the darker shaded areas, which implies that flow paths in the latter case are longer. Silica consumption tends to be higher where there is a confluence between high order regions, which is acceptable

when longer flow paths imply longer time for aquatic biota to flourish and with a higher probability for biological uptake.

CONCLUSIONS

- Considering pollution to be defined as the relative contribution of chloride, sulfate and nitrate to the total anion concentration, spring and surface waters in the Vouga basin were found to suffer from severe pollution (2/3 – 3/4) by anthropogenic sources.
- Magnesium is the only cation discriminating between water–rock interaction in granite and metasediment. On this basis, it can be estimated that the Vouga has for some 40% a metasedimentary signature before entering the coastal plain.
- From near the source area of the Vouga river to the coastal plain, EC , pH , $[Cl^-]$ and $[Na^+]$ increase while $[Na^+]/[Cl^-]$ decreases, $[Ca^{2+}]/[Mg^{2+}]$ decreases as an expression of contributions by chemical weathering of metasediments, and $[HCO_3^-]/[H_4SiO_4^0]$ increases.
- Using the SiB algorithm, a separation could be made between the contributions of cations by meteoric+anthropogenic sources and by chemical weathering.
- Adopting a range of anorthite contents (in %) of 10–30 in oligoclases in granites, and of 0–10 in albites in metasediments, and assuming—depending on the local precipitation—assemblages of kaolinite/gibbsite/vermiculite or kaolinite/vermiculite/smectite in granitic soils, and of kaolinite/vermiculite in soils developed on the metasediments, the following export rates (in $mol \cdot ha^{-1} \cdot y^{-1} \cdot wt\%mineral^{-1}$) as a result of chemical weathering were calculated: in granite —

plagioclase 5.0 ± 2.6 , biotite 3.2 ± 2.6 , in metasediment — oligoclase 16.5 ± 8.9 , chlorite 0.5 ± 0.5 .

- In surface water, (summer) incorporation by aquatic biota can explain the relative decrease of dissolved silica; the uptake amounted to $65 \pm 60 \mu\text{M}$, the highest values generally in higher order stream(lets).

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APPENDIX 1 – Brief outline on the Kille method.

The Kille method (in Krásný et al., 1982) can be summarized as follows (follow application to Sul river data in Figure A1):

1. For each month in a year select the minimum daily discharge rate (Q in $\text{m}^3 \cdot \text{s}^{-1}$). In total, the number of Q values is $12 \times n$, where n is the length of the record set in years;
2. Sort out the $12 \times n$ rates in ascending order and plot them against the corresponding orders (i). In general, a subset of points in the scatter plot fits to a straight line of low slope whereas the other points fit to a straight line of high slope;
3. The two straight lines intersect when $i = k$, where k is a threshold order. For $i < k$, river flows are assumed to represent solely groundwater discharge, and for $i = k/2$, $Q = Q_{med}$, where Q_{med} is the median groundwater discharge rate. If the hydrographic basin is closed (i.e. there are no water imports/exports to adjacent basins) and the aquifer is in steady state with respect to storage, on an annual basis, then $Q_{med} = R$, where R is the median groundwater recharge rate;
4. Convert R into a value in $\text{mm} \cdot \text{y}^{-1}$, i.e. multiply the value in $\text{m}^3 \cdot \text{s}^{-1}$ by $60 \times 60 \times 24 \times 365 \times 1000$ and subsequently divide the result by the drainage area of the basin in m^2 .

APPENDIX 2 – Vouga data set.

Nr is the water sample number. X and Y are Hayford-Gauss coordinates. Types: 1,2 – springs in granites and metasediments, 3,4 – stream(lets) in granites and metasediments, 5,6 – Vouga and Águeda river water. Ec is the electrical conductivity of water. $[]$ are molar concentrations.

$IB(\%) = 200 \times (\sum cations - \sum anions) / (\sum cations + \sum anions)$, where ‘*cations*’ and ‘*anions*’ are equivalent concentrations of the major cations and anions in water. *% pollution* is calculated by Equation 2. For each type, average concentration and pH values are shown. Blank boxes represent missing values.

APPENDIX 2 - VOUGA DATA SET

Nr	<i>X</i>	<i>Y</i>	Type	pH	<i>EC</i>	[Na ⁺]	[K ⁺]	[Mg ²⁺]	[Ca ²⁺]	[HCO ₃ ⁻]	[Cl ⁻]	[SO ₄ ²⁻]	[NO ₃ ⁻]	[H ₄ SiO ₄]	[Al]	[Fe]	IB	%P
	(m)	(m)			(μS·cm ⁻¹)	(μM)	(μM)	(μM)	(μM)	(μM)	(μM)	(μM)	(μM)	(μM)	(μM)	(μM)	(%)	(%)
1009	5424	111362	1	5.3	29	193	8	5	11	75	189	8	11	250	1.7	0.3	-9	74
1038	5101	115526	1	6.4	51	331	13	10	20	156	283	6	2	314	0.7	0.9	-6	66
1040	4902	116091	1	5.8	62	360	25	17	26	170	315	8	1	342	1.0		-3	66
1043	2106	117117	1	6.5	71	361	20	28	55	197	282	27	34	437			1	65
1048	3091	118587	1	5.1	72	395	16	40	33	74	389	59	19	283	0.2		-2	88
1077	6077	113837	1	6.7	61	259	39	24	73	303	225	10		316	0.3	1.3	-5	45
1242	-19344	116116	1	6.7	82	355	57	61	55	359	341	14	41	440	0.1	0.5	-6	53
1272	-17058	132821	1	6.1	32	199	5	17	10	42	217	10	10	136	0.6	0.3	-4	86
1285	-19774	120691	1	6.0	46	249	13	33	20	126	259	9	0	188	0.3		-5	69
1412	45699	125037	1	5.2	21	146	-1	8	9	57	113	6		124	3.4	0.1	-1	69
1415	36967	122806	1	6.1	47	265	19	30	61	238	159	3	56	330	0.1		7	48
1430	35784	121471	1	6.3	32	201	8	15	24	131	138	7		171	0.4	0.2	1	54
1433	36540	122141	1	6.7	43	303	21	34	42	251	158	6	38	323	1.0		6	45
1442	40495	128128	1	5.4	32	173	22	16	32	92	135	8	27	160	0.4	0.1	9	66
1446	46308	127897	1	6.0	21	165	1	11	17	86	134	7		107	0.4	0.4	-3	63
1449	43082	130693	1	5.0	25	129	3	11	17	51	100	7	35	118	2.9	0.2	6	75
1461	41587	121898	1	5.6	27	165	1	17	31	101	121	14		102	1.1	0.6	2	60
1468	43318	129710	1	5.7	28	213	4	8	18	121	114	6		233	1.6	0.1	4	51
1470	43009	122032	1	5.7	38	242	16	23	31	124	152	13		232	0.6	0.1	10	59
1477	42393	126077	1	5.4	32	188	8	35	35	183	100	8	0	241	1.5	0.1	6	39
1480	36677	120499	1	6.0	35	249	18	20	30	175	161	5	10	269	0.2	0.1	3	51
1490	36559	127513	1	5.7	33	207	8	23	40	171	138	6		248	1.9	0.5	3	47
1491	36770	127955	1	5.7	45	261	18	32	67	267	146	4		317	1.0	0.6	6	37
1611	25779	127211	1	5.3	31	193	10	28	32	86	130	33	26	163	0.4	1.1	7	72
1612	10898	131859	1	5.5	45	336	13	18	27	163	191	12	17	264	0.1	0.7	8	59
1613	9422	130434	1	6.5	59	509	25	29	49	346	207	23	25	451		0.5	7	45
1615	9259	134132	1	5.4	38	281	25	27	25	169	179	20	0	215	0.7	1.4	3	56
1622	7971	133410	1	5.7	28	192	40	21	18	135	136	2	18	199		0.3	6	54
1624	14426	124318	1	6.0	31	292	8	13	9	158	151	9		277		0.4	3	52
1625	13952	122810	1	6.0	30	286	9	13	9	116	173	14		261		0.5	3	63
1626	14982	126928	1	5.7	53	439	10	28	53	292	243	7		464	0.2	0.5	5	47
1628	15302	131634	1	6.4	50	398	32	35	67	314	243	8	1	322	0.3	0.5	5	45
1629	16682	132857	1	6.2	50	313	44	33	50	323	146	5	2	362	0.2	0.1	4	33
1631	19770	133610	1	6.4	49	371	26	30	59	331	197	3		366	0.2	0.1	4	38
1632	21203	131634	1	5.4	30	254	21	18	21	139	180	2		227	0.9	1.5	4	57
1649	10779	132957	1	5.6	43	368	16	23	34	253	210	9		406	0.3	0.4	2	48
1652	9374	127333	1	5.1	33	245	8	23	14	81	216	9		161	1.2	0.4	2	74
1659	13648	128905	1	5.1	65	328	23	64	83	122	326	52	75	140	1.5	0.6	8	80
1663	18321	130585	1	5.7	37	259	12	25	35	123	161	21	54	240	0.4	0.5	9	68
1664	18029	130080	1	5.7	45	363	16	33	32	246	235	13	2	256	0.3	3.7	0	52
1665	19934	129812	1	5.3	37	295	14	20	33	203	175	4		335	0.7	0.5	3	47
1667	11467	121867	1	5.4	49	371	15	21	21	178	244	18		328	0.3	0.4	1	61
1670	19864	128011	1	5.4	26	197	8	18	14	91	154	4		199	0.9	0.5	3	64
1675	20083	121013	1	5.8	62	432	26	44	59	295	251	13	36	367	0.2	0.7	7	51
1678	17249	122966	1	6.3	46	373	11	20	22	184	224	13	2	313	0.4	0.6	4	58
1680	22620	124757	1	5.7	31	248	8	22	18	160	158	4	1	279	0.9	0.8	2	51
1682	23286	126768	1	5.3	30	215	30	24	22	102	172	4	23	181	2.1	0.7	9	67
1683	21556	128539	1	6.2	34	262	12	20	27	122	176	14	8	233	0.4	1.4	6	63
1684	21027	124330	1	6.0	42	290	7	27	62	288	157	8		300	0.2	0.5	1	37
1685	18795	126192	1	6.2	51	441	25	26	42	230	281	21	13	421	0.4	0.8	4	59
1697	26792	126428	1	5.2	22	156	7	13	13	45	126	8	21	123	1.2	0.8	7	78
1701	25957	122613	1	5.3	32	207	9	23	33	93	153	26	9	163	1.1	0.9	5	70
1703	27553	122840	1	5.7	49	306	13	30	55	164	204	29	19	246	0.3	0.8	7	63
1707	25987	120813	1	5.2	48	307	35	34	42	180	230	6	48	235	1.2	0.8	8	62
1708	28470	121855	1	6.2	48	365	13	37	57	248	214	13	23	299	0.1	0.3	7	51
1709	28178	121350	1	6.2	45	334	17	28	45	237	232	14		307	0.3	0.7	0	52
2003	7268	128552	1	7.2	42	194	18	44	34	104	149	52	35	187			1	73
2019	11217	127974	1	6.8	48	324	23	22	41	257	198	10		350	2.0	3.3	0	46
2022	11545	129770	1	5.9	40	261	9	16	32	145	166	12	5	285		0.8	4	57

2033	6346	132261	1	5.2	37	145	10	39	50	182	108	16		171		0.4	1	44
2035	7955	130282	1	5.3	45	330	3	27	26	220	195	11		424	1.2	0.4	0	50
2039	6931	131554	1	5.6	43	246	24	32	51	250	134	9	26	349		0.7	4	42
2042	14337	134115	1	5.5	35	239	11	13	14	146	169	5		247		0.4	-3	55
2044	14139	133109	1	5.8	28	183	3	7	10	81	134	9		195			-3	65
2049	14048	130027	1	5.1	34	162	14	20	24	64	143	21	21	151	1.4	0.1	3	76
2054	9537	125725	1	4.6	34	227	23	16	7	106	195	10		241		0.2	-4	67
2055	8478	124776	1	4.9	50	236	34	29	62	206	178	23	5	310		0.1	3	53
2070	9664	135110	1	6.7	42	357	17	25	27	219	197	8		379	2.9	1.1	5	49
2079	9057	131278	1	6.4	48	339	26	10	34	265	119	12		455	2.9	0.8	5	35
2089	8736	132523	1	6.2	55	403	19	18	27	295	199	9		588	1.5	2.5	0	42
2091	11233	126814	1	5.9	45	274	8	18	46	223	163	9		332	1.3	0.7	1	45
2094	6346	129882	1	5.9	34	241	2	23	15	163	101	15		319		0.6	4	45
2095	7498	131802	1	6.0	64	280	28	68	106	460	128	16		297		0.4	3	26
2101	5452	122716	1	6.1	46	296	24	21	24	142	216	11		266	2.0	0.4	4	62
2102	5456	122466	1	5.6	44	277	21	23	30	131	221	5		245		0.2	5	64
2801	-1010	118438	1	5.7	33	209	18	19	15	128	141	4	1	290			3	54
2802	-3622	118067	1	5.3	40	211	12	20	26	76	189	17		267			3	75
2803	-6397	117692	1	5.4	38	203	5	19	14	55	200	12	8	183			-1	81
2806	-10340	118607	1	5.2	40	213	8	14	19	89	194	5		303			-1	70
2810	-10152	117138	1	5.4	51	291	12	22	24	118	248	11		348			1	70
2811	-13066	115288	1	5.8	22	133	3	11	10	40	96	8	8	121			9	75
2812	-14558	116409	1	5.1	31	171	4	11	14	42	144	5	14	166			7	80
2813	-11968	118089	1	5.1	37	209	7	18	11	65	186	8	2	203			1	76
2814	-8333	116023	1	5.3	35	213	4	13	16	84	158	7		264			4	67
2816	-13682	112987	1	5.1	24	143	3	6	5	29	121	3		171			4	81
2817	-14647	111989	1	5.8	30	161	8	12	5	45	141	8	7	126			0	79
2819	-14694	114770	1	5.2	27	153	3	9	21	50	132	4	18	169	1.2		6	76
2821	-9267	113225	1	5.0	25	154	6	10	9	29	138	13	4	155			1	85
2822	-7315	113913	1	5.2	38	204	9	23	22	62	169	15		204	2.5		7	76
2823	-6650	113270	1	5.2	39	242	6	20	20	89	180	7	6	274	3.0		7	69
2829	-6059	117043	1	5.6	48	221	24	48	44	214	161	17		369			2	48
2830	-5704	115413	1	5.7	27	187	3	13	7	32	152	11	3	213	1.9		5	85
2831	-6284	110985	1	5.1	40	209	16	26	11	106	169	4	4	289	5.5		3	63
2832	-5962	111318	1	5.3	30	179	6	14	10	66	155	7		197	4.8	0.4	0	72
2833	-5172	112967	1	5.3	25	165	4	9	6	37	144	7		184	4.9	0.6	1	81
2834	-5366	114764	1	5.2	36	219	10	16	13	67	189	8		228	2.8	0.1	2	75
2835	-4742	116575	1	5.3	35	212	10	19	20	101	161	8		340	2.5		4	64
2836	-2729	113663	1	5.7	33	215	10	17	15	88	189	6		258	1.0	0.3	0	69
2837	-2263	115144	1	5.0	35	232	10	19	15	96	175	4		325	2.4	0.1	5	65
2839	1192	114057	1	5.5	29	191	12	15	12	92	141	5		203			3	62
2840	-2701	112027	1	5.2	24	156	6	8	11	55	155	4		244	2.5	0.2	-4	75
2841	-14322	121813	1	4.9	28	164	6	13	9	42	161	4	1	180	6.3		0	80
2842	-13371	123629	1	5.1	34	172	11	24	17	72	149	11	29	181	1.5		4	74
2843	-16310	123252	1	5.1	25	135	5	9	10	30	121	11	9	158	5.7		1	83
2844	-15678	124572	1	4.8	30	156	6	12	22	38	127	13	27	161	3.2		9	82
2847	906	111597	1	5.7	26	140	3	15	11	47	107	6	21	166	1.0		8	75
2848	-852	109113	1	6.1	33	190	8	16	31	68	159	13	9	275			7	74
2849	-3783	108245	1	5.4	32	189	13	18	12	36	161	18	5	181			6	85
2850	-3979	110206	1	5.3	30	209	7	9	15	40	175	7	1	226	3.9		7	83
2851	-793	115332	1	6.1	45	294	17	29	32	165	169	17		427		0.4	8	55
2852	837	115687	1	5.8	30	208	4	14	9	55	197	10		210			-3	80
2853	-360	117467	1	5.6	40	252	21	23	16	105	237	7		321			0	71
2854	5875	117736	1	6.4	37	284	26	18	15	179	183	5		434			0	52
2855	3518	111969	1	5.6	23	157	11	12	16	98	96	8		233	1.7	0.7	3	53
2857	3629	115080	1	6.2	30	195	6	16	16	85	152	8		241		0.2	2	67
2859	-17680	126829	1	5.3	32	160	11	17	27	67	130	23	21	194	4.1		3	75
2860	-14752	127860	1	5.3	20	131	3	9	6	32	113	11		140	4.3		-1	81
2861	-13429	127065	1	5.3	25	148	8	11	8	34	130	10	10	163	5.1	0.6	3	82
2863	-12209	122667	1	5.1	27	171	5	9	6	34	149	6		206	6.1	0.2	3	83
2866	-14438	119029	1	5.5	39	230	15	21	21	86	183	15		312	2.3	-1.0	5	71
2868	-9711	120091	1	5.7	55	328	36	33	46	158	273	25		331	1.2	0.3	4	67
2870	-3633	118721	1	5.5	44	306	13	21	13	105	228	11		330	2.1		4	70
2871	-5604	119178	1	5.6	35	249	13	19	14	108	158	12		322			6	63

2872	-5945	119991	1	5.6	48	384	17	26	20	150	259	12		376			6	65
2873	-4326	121000	1	5.5	44	292	21	18	22	153	200	4		449	2.4		4	58
2874	-8937	122722	1	5.4	32	206	16	20	13	93	166	8		254			2	66
2875	-7620	122254	1	5.1	35	244	7	16	12	80	180	10	2	258	3.0		5	72
2876	-6464	121619	1	5.7	41	290	22	26	19	166	197	6		398	1.3		3	56
2882	-10559	121877	1	5.5	39	263	15	21	27	155	163	4		435	2.5		7	52
2884	-6802	122267	1	5.7	37	212	14	19	17	96	175	4		307	1.2		3	65
2886	-2784	116935	1	5.4	35	238	8	16	9	45	200	5		305			7	82
2887	-6650	113270	1	5.7	48	286	12	27	32	83	237	20	39	205	1.7		7	79
2888	-7370	117185	1	5.1	32	193	10	18	9	51	158	11		192	4.4		6	78
2889	-10487	117623	1	5.2	41	269	11	14	19	131	158	3		500	1.1		8	55
3036	-9558	107652	1	4.8	35	204	15	28	30	33	273	19	48	66	1.4	0.7	-1	92
Median				5.6	37	238	12	20	21	116	169	9		256				
Average				5.6	39	248	14	21	27	136	179	11		265				
St.Dev.				0.5	11	78	10	11	18	86	52	9		96				
1209	-26970	123717	2	5.9	64	371	24	47	25	213	332	7	18	308	0.7	1.6	-2	63
1215	-26043	119276	2	6.3	61	230	5	63	75	187	321	22	7	154	0.5	0.6	-4	67
1223	-20012	116911	2	6.1	52	320	21	33	18	158	318	8	18	250	0.4	0.6	-5	69
1238	-23298	117711	2	6.5	50	256	2	54	6	89	256	28	5	187	0.1	1.1	-3	78
1239	-24273	115831	2	5.8	54	235	4	71	12	115	276	22	17	189	1.6	1.6	-3	75
1256	-25674	130158	2	5.8		602	61	189	76	313	837	9	76	398	0.2	0.9	1	75
1257	-28718	125575	2	6.0	72	386	34	60	24	227	377	8	0	288	0.2		-3	63
1258	-28499	121550	2	5.9		708	56	134	70	237	983	37	46	414	0.1		-5	82
1262	-26744	119012	2	5.7	84	431	24	104	26	304	383	28	11	435	0.3		-2	60
1268	-22320	128352	2	6.4	86	349	23	79	107	394	352	17	18	386	0.1	3.6	-2	51
1278	-25659	114398	2	6.3	110	496	16	163	76	196	485	119	113	262	0.3		4	81
1403	33484	121322	2	5.7	42	127	13	68	82	235	111	27	5	134	0.1	0.1	4	42
1404	32193	126343	2	5.5	23	133	6	24	11	80	114	4	2	115	0.2	0.1	1	61
1421	29905	125537	2	5.7	28	108	7	25	52	128	111	10	4	105	0.6	0.5	2	52
1428	35247	120804	2	6.6	46	169	15	60	97	307	138	17		194	0.4	0.5	2	36
1687	24984	120996	2	5.8	70	273	21	158	86	266	155	150		323	0.1	0.4	4	63
1690	25504	125706	2	4.5	22	127	12	31	13	45	134	9	7	119	0.3	0.4	8	78
1691	25835	123911	2	4.8	32	154	12	44	19	24	148	41	20	95	1.6	0.9	7	91
1693	22374	121552	2	5.3	35	205	6	53	21	78	155	38	27	151	0.1	0.9	7	77
1705	24704	119791	2	5.0	31	181	9	48	22	103	148	22		145	0.9	2.1	5	65
2059	6387	125600	2	5.9	48	265	45	60	22	214	215	20		264		2.7	1	54
2060	7148	127189	2	6.7	55	389	15	29	26	269	250	15		460		0.3	-3	51
2061	7284	127621	2	6.4	49	262	44	48	23	219	206	13		268	1.2	0.7	0	51
2065	7290	127263	2	6.0	41	217	31	38	10	153	154	12		248		1.2	2	54
2083	3375	127231	2	5.6	24	121	3	27	12	33	123	17	21	124	2.3	2.0	3	84
2103	3845	123139	2	5.3	47	275	58	32	10	111	252	10	7	218	1.5	0.4	4	71
2825	-13005	111689	2	4.6	35	150	13	23	5	33	149	10	8	121	4.6	0.2	4	84
2826	-12356	112027	2	4.8	40	144	24	34	7	23	152	17	21	98	2.6	0.2	9	90
2865	-15553	117210	2	6.9	31	201	16	27	15	116	155	10		238	1.1		2	60
2877	-4001	121169	2	5.4	42	235	16	58	12	93	208	35		207	2.3	0.1	2	75
2879	-7501	124874	2	5.1	25	127	14	19	6	31	107	10	10	137	4.3		10	82
3005	-17971	101835	2	7.1	62	378	9	81	14	217	310	29	70	213	1.3	0.5	-1	67
3021	-16620	100250	2	5.1	67	403	9	94	24	127	394	16	99	202	6.8	3.7	8	81
3027	-19673	107386	2	4.9	60	300	8	102	21	40	225	129	3	189	5.4	4.9	3	92
3028	-17348	106905	2	5.4	55	343	8	81	14	110	366	10	88	183		0.8	4	81
3030	-16419	107914	2	5.1	39	265	10	39	17	79	225	26	55	98	2.0	1.9	4	81
3039	-19539	102281	2	5.4	55	335	9	70	16	108	282	18		156	2.6	0.4	10	75
3040	-19352	102426	2	5.4	71	447	10	90	24	285	479	24	96	197		0.4	-9	69
3044	-18439	104333	2	5.1	51	326	6	54	17	188	338	20	23	156	5.7	2.0	-9	68
3045	-18063	104482	2	5.2	48	297	9	59	11	155	197	8	50	149	3.2	1.5	9	63
3051	-17645	102124	2	6.4	86	466	21	117	61	309	479	55	160	265		1.9	-3	71
3055	-17307	101704	2	6.8	62	361	6	91	52	280	423	42	40	183	1.6	0.8	-9	66
3056	-16444	101010	2	6.0	75	340	4	156	88	497	248	7	2	227		0.4	5	35
3057	-17223	102321	2	6.3	59	386	15	60	11	273	310	10	19	250	2.1	1.3	-5	56
3063	-15416	101736	2	5.8	44	309	5	53	9	187	197	26		165	2.7	1.2	0	57
3069	-13578	102099	2	6.7	36	229	12	54	16	194	113	24		138		0.7	3	45

3071	-13806	101622	2	5.6	53	270	38	69	24	231	211	49		185		0.6	-5	57
3072	-13801	101338	2	5.9	42	272	22	55	18	181	141	40	19	174		0.4	4	57
3075	-9098	105626	2	5.3	31	182	15	30	15	100	169	12		98		0.4	-1	66
3087	-21368	98609	2	5.3	66	400	4	84	14	120	451	53		148	1.4		-6	82
3090	-15918	97898	2	6.3	34	258	10	42	13	101	197	6	19	105	2.9	1.8	10	69
3095	-20792	98052	2	5.2	66	421	6	84	18	130	366	50	48	148	3.8	2.7	3	80
3098	-19656	106393	2	5.6	65	410	4	109	19	182	366	42		138		2.2	3	71
Median				5.7	50	273	12	59	18	158	225	20		185				
Average				5.7	51	295	17	67	30	171	275	28		204				
St. Dev.				0.6	19	125	14	39	27	100	168	29		91				
1002	4062	109760	3	5.6	32	211	8	8	12	92	204	4	1	295	1.2	0.8	-8	70
1005	5509	110101	3	5.5	30	208	6	6	9	77	138	5	4	268	1.2	0.6	4	66
1008	5365	111109	3	5.2	26	201	4	7	14	72	175	9		252	1.9	0.6	-4	73
1011	5738	111494	3	6.0	61	292	36	26	57	179	338	37	1	289	1.4	1.7	-9	70
1012	5161	111989	3	6.5	23	181	1	5	3	49	155	6		221	2.8		-5	77
1013	4909	111922	3	6.2	24	183	1	5	7	61	155	6		260	2.1		-4	73
1015	5217	112433	3	6.9	37	184	2	7	57	170	158	7	0	273	0.9		-4	50
1026	5456	113195	3	5.2	41	269	2	7	12	62	225	18	0	380	2.7		-3	81
1027	5453	113384	3	6.0	42	278	4	6	11	80	224	12	2	314	1.0		-2	76
1030	6976	112968	3	5.5	50	219	12	21	51	110	284	30	1	149	1.0	0.9	-10	76
1031	6287	112640	3	6.1	51	295	8	16	27	116	251	23		280	0.7	0.3	-3	72
1032	6324	114157	3	6.2	73	334	74	27	48	166	352	34	1	174	0.6	0.8	-2	72
1033	7465	113923	3	5.4	56	244	5	33	59	116	228	61	1	160	1.0	1.3	-4	75
1034	7078	114422	3	6.0	85	378	33	52	69	154	479	56	1	144	0.6	1.8	-7	79
1035	5875	114591	3	6.5	80	365	31	40	60	139	358	49	4	148	1.7	0.8	0	77
1042	4060	117340	3	5.7	65	312	19	34	50	141	352	54	2	208	0.1	1.5	-9	77
1044	5293	119129	3	6.9	56	300	18	21	34	113	332	36	2	225	0.1	0.2	-9	78
1045	3720	118723	3	5.6	76	384	13	44	48	154	434	45	5	281	0.1	0.5	-8	77
1059	3654	115185	3	4.6	58	293	15	21	35	56	335	28	18	122	0.7		-3	88
1086	1471	113569	3	5.0	27	162	4	5	11	57	130	11	1	94	1.2		-3	73
1208	-27583	124507	3	6.7	73	321	33	50	67	172	330	46	84	139	1.1	2.7	-1	75
1210	-27493	119208	3	6.9	77	323	33	57	68	163	344	48	44	138	0.9	3.5	0	75
1217	-26916	117297	3	6.9	103	492	27	112	47	231	513	81	63	303	0.4	1.0	-4	76
1221	-21402	118750	3	6.2	66	340	13	44	38	137	299	26	64	211	0.4	0.6	3	75
1244	-22688	132222	3	6.4	66	290	15	43	43	118	321	25	41	130	0.5	0.6	-1	78
1245	-21435	132596	3	6.6	62	277	16	34	44	36	287	32	40	115	0.6	0.8	7	92
1247	-20210	134580	3	6.6	38	192	6	17	20	69	206	9	7	107	0.3	0.5	-4	77
1248	-20202	131157	3	6.6	41	186	9	23	29	62	186	22	45	91	0.3	1.9	1	82
1250	-18430	130532	3	6.4	52	222	7	23	43	70	223	32	44	112	0.6	0.5	1	82
1253	-12533	133200	3	6.1	20	105	4	10	13	34	124	7	25		0.4	0.5	-5	83
1259	-28230	120548	3	7.3	100	442	25	124	79	455	462	15	42	328	0.3		-4	54
1260	-27866	119849	3	6.6		720	82	186	123	176	870	154	131	281	0.3		2	88
1263	-27608	119501	3	6.7	87	498	41	65	74	205	420	47	40	159	0.3	1.8	6	73
1273	-15482	131891	3	6.4	28	152	4	18	14	40	189	17	4	85	0.5		-9	85
1279	-18403	134913	3	6.6	39	215	19	34	13	102	231	12	3	196	0.5		-4	72
1280	-18657	129118	3	6.3	41	201	8	25	34	55	223	20		114	0.4	0.1	2	83
1406	32559	124157	3	5.7	24	149	5	20	17	55	135	9	24	89	0.4	0.1	5	76
1409	39926	122856	3	5.7	24	171	6	11	12	79	132	7		107	0.7	0.8	-1	65
1413	45695	125256	3	6.1	25	171	5	15	19	79	124	14	8	130	0.3	0.3	2	67
1416	36306	123014	3	6.4	114	591	67	81	113	317	704	40	55	151	0.2	5.6	-3	73
1417	36085	123120	3	6.3	39	239	15	28	35	140	197	23	4	121	0.3	0.8	-1	64
1438	37745	122162	3	6.4	39	274	14	23	37	127	177	27	12	139	0.4	1.0	6	66
1444	46864	127468	3	5.9	21	159	1	8	15	89	113	9		161	0.9	0.4	-3	59
1445	46643	127574	3	6.0	25	160	2	13	31	71	146	22		83	0.5	0.5	-2	73
1602	8862	122123	3	6.7	61	405	41	56	49	131	329	63	31	145	0.4	2.6	6	79
1604	8759	122322	3	6.8	91	560	61	97	85	257	486	84	46	210	0.4	3.6	4	73
1640	11277	127165	3	6.0	50	331	29	38	45	140	277	32	23	151	0.5	1.8	4	72
1641	10872	127458	3	5.9	60	392	48	49	58	192	297	41	36	182	0.5	1.4	7	68
1642	17410	125269	3	6.1	46	324	22	36	42	145	223	48	14	165	0.5	1.3	4	70
1643	17414	125069	3	6.5	48	323	21	41	53	165	232	39	9	176	0.6	1.4	6	66
1644	16614	125055	3	6.6	51	371	18	39	47	158	263	52	7	140	0.5	0.9	3	70
1646	13475	121401	3	6.4	53	376	17	41	45	175	270	44	6	181	0.4	1.5	3	67
1650	8232	129814	3	6.3	60	370	33	41	64	220	287	34	38	194	0.4	1.5	3	64

1660	16607	131356	3	5.8	59	378	23	46	63	110	274	72	54	154	0.6	0.6	8	81
1661	16929	130061	3	5.7	41	288	15	30	38	128	205	46	32	163	0.5	1.5	2	72
1674	20291	120517	3	6.6	47	282	15	51	71	215	221	37	4	85	0.4	3.8	3	58
1712	16978	133062	3	6.0	83	453	46	86	115	130	401	115	120	170	0.8	1.3	8	85
2002	6597	125890	3	6.9	47	266	25	29	33	158	234	27	10	193	6.3	2.0	-4	65
2006	5068	123143	3	7.1	59	293	33	48	36	114	323	21	80	163		0.3	2	80
2007	3906	124054	3	6.2	46	206	28	43	35	125	261	28	61	126		0.9	-6	75
2010	4549	124208	3	6.4	50	273	25	36	29	107	256	19	50	148	3.7	2.5	3	76
2013	6158	126456	3	6.4	39	196	15	38	15	117	180	20	15	181			-3	67
2014	6443	126532	3	6.1	52	254	23	35	48	179	198	39	38	210		0.6	-1	64
2016	5712	123154	3	6.6	59	267	21	34	43	164	198	33	10	205		1.4	2	62
2023	10787	128038	3	6.4	50	281	34	28	39	135	211	26	23	210		1.7	6	68
2024	10862	127825	3	6.4	47	257	22	26	37	113	229	28	11	159		1.3	1	72
2027	3723	126415	3	6.1	25	134	7	26	9	64	108	15		111		0.9	2	69
2034	6492	132120	3	6.6	77	184	34	58	212	526	143	23	37	174		0.4	3	30
2038	8526	134661	3	6.1	29	173	14	17	24	139	117	10		231	1.6	1.5	-1	50
2045	14657	132115	3	6.1	43	261	19	25	32	132	204	25	5	178				66
2046	13733	131669	3	5.9	45	245	29	26	33	116	221	25	36	172		0.4	0	73
2048	12271	129209	3	6.3	53	287	28	33	43	120	274	27	72	168		0.6	2	77
2064	7012	126757	3	7.0	43	284	25	32	15	179	188	15		287	1.3	1.0	1	55
2077	8899	131775	3	7.0	45	304	18	23	33	170	180	22		274	1.2	1.2	5	57
2994	-14316	121486	3	6.6	33	207	10	21	27	74	158	14	23	197	1.4		9	74
2998	-13798	110203	3	6.3	34	191	16	25	16	30	172	20	31	152			9	89
2999	-13967	110527	3	6.3	37	214	22	30	24	60	180	23	21	152	1.1		9	81
Median				6.3	48	274	18	30	37	125	225	26		166				
Average				6.2	51	283	21	36	42	133	261	32		182				
St.Dev.				0.5	21	110	17	29	31	81	129	25		66				
1052	1102	116721	4	5.8	62	341	13	45	29	116	324	44	24	220	0.2		-2	79
1060	3339	115117	4	5.2	47	245	22	16	22	54	256	25	19	97	0.2		-3	86
1205	-26021	126734	4	6.9	67	320	31	49	56	181	315	37	63	141	0.7	2.6	-1	71
1206	-26721	126722	4	6.9	73	333	19	89	35	219	380	33	42	237	0.3	1.3	-5	69
1216	-25195	119693	4	7.1	85	262	10	145	77	252	239	110	23	175	0.4	1.4	0	66
1218	-27190	115631	4	7.0	96	292	16	150	95	273	318	122	114	122	2.3	1.1	-2	71
1220	-21939	120705	4	6.7	65	292	17	54	54	162	324	29	51	168	0.6	1.2	-2	73
1229	-22720	119282	4	6.8	64	383	16	55	58	161	363	34	84	177	0.3	2.6	3	76
1233	-14980	117096	4	6.9	45	219	3	59	32	191	256	14	13	170	0.3	1.8	-8	61
1235	-20053	122348	4	5.7	36	182	9	22	13	69	203	10	4	133	0.6	0.7	-6	77
1237	-23318	118869	4	6.6	74	249	4	124	17	138	259	102	2	224	0.3	1.4	-6	77
1264	-25012	123774	4	7.1	91	366	20	105	81	306	352	46	36	235	1.0		1	61
1266	-20481	129742	4	6.6	46	232	11	41	25	79	220	24	62	142	0.2		4	81
1276	-26945	116038	4	7.1	105	385	7	159	102	404	448	97	3	187	0.4		-7	61
1277	-25659	114398	4	6.9		602	58	193	152	434	735	146	30	82	0.5	0.5	-4	71
1281	-21135	126760	4	6.7	33	178	6	33	23	95	183	17	25	105	0.4		-3	72
1282	-21095	124395	4	6.3	35	185	7	29	24	68	163	14	24	103	0.4		7	76
1283	-20270	123250	4	6.3	29	153	2	22	16	32	183	18		74	0.5		-4	87
1287	-22530	116969	4	6.7	45	240	3	54	6	84	248	27	9	186	0.6	2.6	-3	79
1290	-22881	128745	4	6.7	87	349	25	75	83	179	346	53	81	58	0.4	0.1	4	75
1291	-20866	128729	4	6.6	103	437	19	81	86	224	425	57	97	87	0.3		2	74
1292	-24841	128561	4	6.6	97	408	43	84	63	153	538	36	108	62	0.3	0.3	-1	82
1293	-24419	127410	4	6.6	82	372	27	86	34	128	487	41	63	60	0.3	0.2	-4	83
1294	-26193	128085	4	6.4	94	392	34	91	67	173	518	43	119	59	0.4		-2	81
1414	33481	121541	4	6.5	37	221	11	29	33	123	186	25		105	0.3	0.5	0	66
1688	25282	121101	4	6.5	38	222	14	78	28	154	171	46	12	128	0.4	4.3	4	64
1694	22177	121349	4	5.8	33	190	9	50	18	73	151	32	17	144	0.2	0.8	7	76
1706	25301	120001	4	6.6	81	379	30	90	175	439	268	64	9	148	0.2	2.1	6	48
2995	-9192	108808	4	6.1	36	192	18	29	22	58	169	23	23	144			7	81
2996	-11854	111381	4	6.7	37	214	25	27	30	52	217	20	56	148	2.0	4.0	7	86
2997	-12018	111379	4	6.9	39	227	25	27	28	86	189	20	7	157	1.9	0.6	7	73
3041	-18004	103773	4	6.8	51	366	6	67	23	194	225	21	7	204		0.8	9	59
3046	-17876	104627	4	6.6	41	324	6	45	11	86	282	16	19	140	2.3	0.7	5	79
3047	-17560	105483	4	6.7	34	283	5	30	8	129	197	12	2	113		0.4	2	63
3061	-17228	102652	4	6.9	34	309	9	50	18	190	256	16	77	137	1.6	1.9	-2	66
3062	-15377	102210	4	6.7	39	273	3	41	5	164	169	21	9	135		2.2	-1	57
3079	-23049	100141	4	6.8	48	273	17	47	39	181	197	35	19	110	2.2	2.5	2	61

3080	-22573	99913	4	6.8	54	302	14	62	41	205	225	41	31	124	3.1	2.6	1	62
3088	-17015	98446	4	6.3	59	395	10	106	23	349	254	23	45	309		1.0	1	50
3092	-15716	97097	4	6.7	48	352	4	69	5	192	282	11	7	177		1.4	1	62
3093	-16252	98081	4	6.7	45	298	9	59	24	155	254	37	31	148	3.4	2.6	-1	70
3100	-17089	108376	4	5.8	42	307	8	54	7	130	254	25	50	124		0.4	0	73
3103	-8959	108608	4	6.6	58	248	23	31	30	125	169	22	37	95	3.1	1.8	8	67
Median				6.7	48	292	13	54	29	155	254	29		140				
Average				6.6	58	297	16	66	42	169	284	39		142				
St.Dev.				0.4	23	87	12	40	37	99	121	31		54				
1	41593	123253	5	5.7	22	164	10	13	21	77	148	8	0	50	1.7	3.0	0	68
2	35163	122858	5	5.9	28	195	11	19	27	56	162	19	0	72	2.3	2.7	8	78
3	27271	122493	5	6.4	39	278	9	15	55	142	204	24	0	55	1.7	1.7	4	64
4	18595	120567	5	6.4	44	225	18	45	63	112	218	28	0	55	2.9	1.4	9	71
5	11852	121528	5	6.8	45	255	19	45	52	147	237	31	0	55	3.2	17.6	2	67
6	3023	118915	5	6.8	63	383	21	49	57	190	301	47	2	85	1.3	1.3	2	68
7	-3706	119967	5	5.9	62	380	21	49	51	91	313	47	1	83	1.9	1.9	9	82
8	-12781	120624	5	7.0	50	313	19	42	43	117	285	50	0	78	0.9	1.1	0	77
9	-18599	116348	5	7.2	50	306	17	45	43	126	296	45	1	70	1.6	2.4	-1	75
10	-25542	112469	5	6.9	57	341	17	54	46	172	315	50	0	77	1.4	1.1	-3	71
11	-22568	99650	6	6.6	40	254	17	53	26	86	254	45	0	70	0.8	0.7	0	80

APPENDIX 3 – Brief outline on the SiB algorithm.

The SiB algorithm (Pacheco and Van der Weijden, 1996, 2002; Pacheco et al., 1999) comprehends a set of mole and charge balance equations of the form:

$$\text{mole balance equations} - \sum_{j=1}^q \alpha_{ij} [M_j] + [X_i]_p = [X_i]_t, \text{ with } i = 1, n \quad (\text{A3.1a})$$

$$\text{charge balance equation} - \sum_{k=1}^m z_k [X_k]_p = [Cl^-]_t + 2[SO_4^{2-}]_t + [NO_3^-]_t \quad (\text{A3.1b})$$

where:

- q , n and m are the number of primary minerals involved in the weathering process (e.g. Pl and Bt, or Pl and Ch), the number of dissolved inorganic compounds that usually are released from the weathering reactions of aluminium-silicate minerals (in total six compounds – Na^+ , K^+ , Mg^{2+} , Ca^{2+} , HCO_3^- and H_4SiO_4), and the number of dissolved inorganic compounds that are assumed to gain contributions from pollution (the four major cations);
- t and p mean total and derived from pollution, respectively;
- X represents a dissolved compound;
- M represents a dissolved mineral;
- Cl^- , SO_4^{2-} and NO_3^- are the abbreviations for chloride, sulfate and nitrate, major dissolved anions assumed to represent exclusively anthropogenic plus atmospheric inputs;
- Square brackets ($[]$) denote number of moles of a dissolved compound or a dissolved mineral;
- α_{ij} is the ratio between the stoichiometric coefficients of dissolved compound i and mineral j as retrieved from the weathering reaction of mineral j ;

- $\alpha_{ij}[M_j] = [X_i]r_j$, where $[X_i]r_j$ is the number of moles of dissolved compound i derived from reaction of M_j moles of mineral j ;
- z_k is the charge of cation k .

The number of equations in the set A3.1a,b is seven. The unknowns of the system are the $[M]$ and $[X]_p$ variables, in total $q + m$. The SiB algorithm uses the Singular Value Decomposition procedure as described in Press et al. (1989) to solve the set of equations because this procedure can handle efficiently (through least squares or minimizing procedures) the cases where the set is undetermined ($q + m > 7$) or overdetermined ($q + m < 7$).

The stoichiometric coefficients (α) are defined by the weathering reactions of the primary minerals. The SiB model includes both incongruent and congruent reactions, and both dissolution (positive α) and precipitation (negative α) reactions. The SiB model has also the ability to handle the cases where hydrolysis of minerals produces mixtures of clays (e.g. a reaction of Pl to a mixture of a Sm plus Kl). In this context, it includes an iterative or batch procedure whereby the weathering reactions produce solely end-members (e.g. Sm or Kl) or else mixtures in specific proportions (e.g. 10% Sm plus 90% Kl). The SiB algorithm has an additional loop procedure to handle cases of variable primary mineral composition (e.g. Pl varying in composition from An₁₀ to An₃₀). The $[X]_r$ are called constrained concentrations because they must fit into the stoichiometric relations of the mineral weathering reactions ($[X]_r = \alpha[M]$) but the SiB algorithm provides the flexibility to deal with situations where not all contributions to groundwater chemistry are stoichiometrically constrained. This flexibility is gained with the inclusion of an unconstrained term in the mole balance equations (the $[X]_p$ term in the left-hand side of Equation A3.1a).

Not all reactions tested by the loop procedures of the SiB algorithm explain the chemical compositions of the spring waters. To be labelled as a possible solution the set of weathering reactions must give $[M] \geq 0$ and $[X]_p \geq 0$. Among the possible solutions, the SiB algorithm selects a best-fit one by testing all sets against predefined external boundary conditions, the most common being the clay-test whereby abundances of secondary products that can be predicted by the algorithm are compared with those present in the local C-horizons of the soils.

TABLE LEGENDS**TABLE 1a**

Average chemical compositions of granites and metasediments in the hydrographical basin of the Vouga River (standard deviations put in brackets). Samples of these rock units were collected from fresh outcrops throughout the basin.

TABLE 1b

Mineralogical composition of granites and metasediments in the Vouga River basin. The abundances were determined by the Balance of Cation Proportions (Pacheco and Van der Weijden, 2002). x is the anorthite content of plagioclase ($x = 0.1\text{--}0.3$ in the granites and $x = 0\text{--}0.1$ in the metasediments). The model compositions of muscovite and chlorite are based on Pacheco and Van der Weijden (2002), of biotite on Matos (1991).

TABLE 2

Relevant data for the meteorological stations plotted in Figure 3 (source: Sistema Nacional de Informação de Recursos Hídricos, presently at <http://snirh.inag.pt/>). X and Y are Hayford-Gauss coordinates. Stations are listed in reverse order of X (distance to the Atlantic coast).

TABLE 3

Relevant data on the hydrometric stations plotted in Figure 3 (source: Sistema Nacional de Informação de Recursos Hídricos, presently at <http://snirh.inag.pt/>). X and Y are Hayford-Gauss coordinates. A is the drainage area upstream the hydrometric station. Q is the median discharge rate. P is the average precipitation within the drainage area. R is the recharge within the drainage area, determined by the Kille method (see Appendix 1 for details). Stations are listed in reverse order of X (distance to the Atlantic coast).

TABLE 4

Median annual values of pH and concentrations (in μM) of solutes in wet precipitation, calculated for closest relevant period (1989–1992) available for this study. Analyses were made by the meteorological stations Viana do Castelo (coast) and Bragança (far inland). Data are available at www.nilu.no/projects/ccc/emepdata.html. Since bicarbonate concentrations are lacking in these reports, they were calculated using $[\text{HCO}_3^-] = 10^{-7.76} \times 10^{-3.5} \times 10^{\text{pH}}$. Splitting into ss and nss inputs is based on the assumption that all Na^+ is of marine origin. $\text{IB}\% = 200 * [\Sigma\mu\text{eq.cations} - \Sigma\mu\text{eq.anions}] / [\Sigma\mu\text{eq.cations} + \Sigma\mu\text{eq.anions}]$.

TABLE 5

Adopted compositions of major weathering products. For smectite, data in Deer et al. (1974) were used, for vermiculite data in Douglas (1977).

TABLE 6

End-member reactions of the most weatherable minerals in granites and metasediments. Pl, Bt, Ch, Sm, Vr, Kl and Gb are abbreviations for plagioclase, biotite, chlorite, smectite, vermiculite, kaolinite/halloysite and gibbsite, respectively. Note in Reaction R_{1a} that, for $x \geq 0.56$, dissolved silica is a reactant, not a product. Dissolved [Al] and [Fe] in the springs and streams are very low — commonly $< 1 \mu\text{M}$, including colloidal matter that passed the $0.45 \mu\text{m}$ membrane filter; cf. Lyven et al. (2003) —, reason to allot these elements to solid phases.

TABLE 7

Results of the application of the SiB algorithm to spring waters in the Vouga river hydrographical basin: (a) springs in granites, (b) springs in metasediments. Nr. is the

water sample number; Pl, Bt, Ch, Sm, Vr, Kl and Gb are abbreviations for plagioclase, biotite, chlorite, smectite, vermiculite, kaolinite/halloysite and gibbsite; c_1 is the proportion of Kl in the mixture of clays produced by weathering of Pl ($100 - c_1$ is the proportion of Sm or Gb, depending on whether $P < 1000 \text{ mm} \cdot \text{y}^{-1}$ or $P \geq 1000 \text{ mm} \cdot \text{y}^{-1}$, respectively), c_2 is the proportion of Kl in the mixture of clays produced by weathering of Bt or Ch ($100 - c_2$ is the proportion of Vr); [] are molar concentrations and the subscript p represents derived from pollution; P and R are abbreviations for precipitation and recharge.

TABLE 8

Results of the application of the SiB algorithm to stream(let) waters: (a) stream(let)s in granites; (b) stream(let)s in metasediments. Additional information is given in the legend of Table 7.

TABLE 1a

Oxide	Granite (n=19)	Metasediment (n=12)
SiO ₂	72.7 (1.3)	66.50 (4.9)
TiO ₂	0.24 (0.13)	0.85 (0.1)
Al ₂ O ₃	15.1 (0.7)	16.70 (2.6)
Fe ₂ O ₃	0.54 (0.5)	3.05 (1.4)
FeO	1.16 (0.5)	3.60 (1.3)
MnO	0.01 (0.02)	0.02 (0.03)
MgO	0.37 (0.18)	1.60 (0.41)
CaO	0.58 (0.32)	0.10 (0.09)
Na ₂ O	3.29 (0.29)	0.84 (0.87)
K ₂ O	4.75 (0.56)	3.10 (0.47)
P ₂ O ₅	0.33 (0.11)	0.15 (0.11)
LOI	1.27 (0.48)	4.31 (1.35)
Total	100.3	100.8

TABLE 1b

Mineral	Composition	Rock type	
		granite	metasediment
quartz	SiO ₂	34.1	41.1
K-feldspar	KAlSi ₃ O ₈	14.4	
plagioclase	Na _{1-x} Ca _x Al _{1+x} Si _{3-x} O ₈	31.0	8.8
biotite	KMg _{1.5} Fe _{1.5} AlSi ₃ O ₁₀ (OH) ₂	3.7	
muscovite	K(Al _{1.8} Fe _{0.1} Mg _{0.1})(Si _{3.15} Al _{0.85})O ₁₀ (OH) ₂	16.8	17.5
chlorite	(Fe _{2.8} Mg _{0.2})(Si _{2.65} Al _{1.35})O ₁₀ (OH) ₂ ·(Mg _{1.6} Al _{1.4})(OH) ₆		32.6

TABLE 2

Nr	Code	Name	X	Y	Elevation	Starting year	Record length	Average precipitation
			(m)	(m)	(m)		(y)	(mm·y ⁻¹)
1	08L/07	Quinta da Fumadinha	46745	129815	806	1979	17	835
2	09K/02	Quiriga	32679	126222	684	1980	17	970
3	09K/03	Barreiros (Travasso)	29702	120534	625	1979	17	881
4	09J/03	Calde	18341	123366	520	1979	17	909
5	09J/02	Pindelo Milagres	14372	126380	450	1979	17	1041
6	09J/04	Lubageira	12329	114531	524	1979	17	922
7	08I/03	São Martinho das Moitas	8594	116561	191	1979	17	1409
8	09I/01	São Pedro do Sul	5329	120075	191	1931	48	993
9	09H/02	Sejães	-6519	119428	146	1979	17	1066
10	09H/03	Manhouce	-6746	127695	635	1979	11	1624
11	09H/01	Campiã	-7066	111655	446	1930	66	1561
12	09H/04	Ribeiradio	-14169	118636	191	1976	21	1422
13	09G/03	Pessegueiro Vouga	-20306	113838	150	1976	21	1350
14	08G/01	Barragem Castelo de Burgães	-20750	131546	304	1937	62	1501
15	09G/01	Albergaria-a-Velha	-29508	114455	131	1930	67	1142
16	10G/01	Oliveira do Bairro	-30975	94595	60	1930	68	893
17	11F/01	Cantanhede	-39073	76464	218	1979	19	797
18	08F/02	Espargo (Feira)	-39451	138594	123	1932	62	1172
19	11F/02	Estrada	-43134	88548	207	1979	18	806
20	10E/03	Gafanha da Nazaré	-48465	105670	8	1948	50	795

TABLE 3

Id	Hydrometric station	X	Y	Starting year	Record length	River	A	Q	P	R
		(m)	(m)		(y)		(km ²)	(m ³ ·s ⁻¹)	(mm·y ⁻¹)	(mm·y ⁻¹)
a	09J/01	15086	121045	1936	17	Vouga	274	1.6	896	72
b	09J/02	13427	122076	1981	8	Vouga	378	2.7	917	83
c	09I/03	6238	122825	1981	9	Sul	110	0.9	1135	82
d	09I/02	1797	118766	1917	40	Vouga	649	4.3	970	80
e	09I/04	1492	117442	1980	10	Zela	18	0.1	1253	137
f	09H/03	-16479	119394	1976	6	Vouga	951		1091	118
g	10G/05	-20880	97871	1977	12	Agueda	152	1.4	1261	140
h	10G/03	-22344	100363	1976	13	Alfusqueiro	204	1.8	1392	168
i	11G/01	-22428	82965	1978	11	Serra	40	0.3	983	65
j	10G/01	-25588	106651	1977	10	Marnel	22	0.2	1273	154
k	10G/02	-26764	100372	1934	52	Agueda	405	2.8	1319	153
l	09G/01	-27686	114223	1934	55	Caima	188	1.5	1450	174
m	09F/01	-31900	123781	1976	15	Antuã	114	1.8	1363	169
n	10F/03	-33223	102625	1982	2	Agueda	967	8.4	998	79

TABLE 4

		pH	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	NH ₄ ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	HCO ₃ ⁻	IB%
Viana	tot	5.1	95	4.5	12	9.3	13.9	118	13.3	6.4	0.68	+3
	ss		95	2	10.8	2.1	0	110	5.7	0		
	nss		0	2.5	1.3	7.2	13.9	8	7.6	6.4		
Bragança	tot	5.4	12	3.6	3.8	16.8	17.8	15.8	20.6	9.3	1.4	+9
	ss		12	0.3	1.5	0.3	0	13.6	0.8	0		
	nss		0	3.3	2.3	16.5	17.8	2.2	19.8	9.3		

TABLE 5

Mineral	Composition
hematite	Fe_2O_3
gibbsite	$\text{Al}(\text{OH})_3$
kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
smectite	$(\text{Mg}_{0.35}\text{Al}_{1.65})\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 5\text{H}_2\text{O} \cdot \text{Ca}^{2+}_{0.175}$
vermiculite	$(\text{Mg}_{2.63}\text{Fe}^{3+}_{0.25}\text{Al}_{0.11})(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O} \cdot \text{Mg}^{2+}_{0.33}$

TABLE 6

Number	Mineral	Clay	Reaction
R _{1a}	Pl	Sm	$\frac{1.65}{1+x} \text{Pl} + 0.35 \text{Mg}^{2+} + 0.6 \text{CO}_2 \xrightarrow{\text{nH}_2\text{O}}$ $\text{Sm} + 1.65 \frac{1-x}{1+x} \text{Na}^+ + \frac{1.475x - 0.175}{1+x} \text{Ca}^{2+} + 0.6 \text{HCO}_3^- + \frac{0.95 - 5.65x}{1+x} \text{H}_4\text{SiO}_4^0$
R _{1b}	Pl	Kl	$\frac{2}{1+x} \text{Pl} + 2 \text{CO}_2 \xrightarrow{\text{nH}_2\text{O}} \text{Kl} + 2 \frac{1-x}{1+x} \text{Na}^+ + 2 \frac{x}{1+x} \text{Ca}^{2+} + 2 \text{HCO}_3^- + 4 \frac{1-x}{1+x} \text{H}_4\text{SiO}_4^0$
R _{1c}	Pl	Gb	$\frac{2}{1+x} \text{Pl} + 2 \text{CO}_2 \xrightarrow{\text{nH}_2\text{O}} \text{Gb} + 2 \frac{1-x}{1+x} \text{Na}^+ + 2 \frac{x}{1+x} \text{Ca}^{2+} + 2 \text{HCO}_3^- + 2 \frac{3-x}{1+x} \text{H}_4\text{SiO}_4^0$
R _{2a}	Bt	Vr	$1.11 \text{Bt} + 1.3 \text{Mg}^{2+} + 1.49 \text{HCO}_3^- + 0.416 \text{O}_2 \xrightarrow{\text{nH}_2\text{O}}$ $\text{Vr} + 0.71 \text{Hm} + 1.11 \text{K}^+ + 1.49 \text{CO}_2 + 0.33 \text{H}_4\text{SiO}_4^0$
R _{2b}	Bt	Sm	$2.33 \text{Bt} + 0.87 \text{O}_2 + 9 \text{CO}_2 \xrightarrow{\text{nH}_2\text{O}}$ $\text{Sm} + 1.75 \text{Hm} + 2.25 \text{K}^+ + 3.37 \text{Mg}^{2+} + 9 \text{HCO}_3^- + 3.32 \text{H}_4\text{SiO}_4^0$
R _{2c}	Bt	Kl	$2 \text{Bt} + 0.75 \text{O}_2 + 8 \text{CO}_2 \xrightarrow{\text{nH}_2\text{O}}$ $\text{Kl} + 1.5 \text{Hm} + 2 \text{K}^+ + 3 \text{Mg}^{2+} + 8 \text{HCO}_3^- + 4 \text{H}_4\text{SiO}_4^0$
R _{2d}	Bt	Gb	$\text{Bt} + 0.375 \text{O}_2 + 4 \text{CO}_2 \xrightarrow{\text{nH}_2\text{O}}$ $\text{Gb} + 0.75 \text{Hm} + \text{K}^+ + 1.5 \text{Mg}^{2+} + 4 \text{HCO}_3^- + 3 \text{H}_4\text{SiO}_4^0$
R _{3a}	Ch	Vr	$0.4 \text{Ch} + 2.24 \text{Mg}^{2+} + 4.48 \text{HCO}_3^- + 0.28 \text{O}_2 + 1.94 \text{H}_4\text{SiO}_4^0 \xrightarrow{\text{nH}_2\text{O}}$ $\text{Vr} + 0.435 \text{Hm} + 4.48 \text{CO}_2$
R _{3b}	Ch	Sm	$0.85 \text{Ch} + 0.0824 \text{K}^+ + 1.418 \text{H}_4\text{SiO}_4^0 + 0.595 \text{O}_2 + 2.73 \text{CO}_2 \xrightarrow{\text{nH}_2\text{O}}$ $\text{Sm} + 1.19 \text{Hm} + 1.406 \text{Mg}^{2+} + 2.73 \text{HCO}_3^-$
R _{3c}	Ch	Kl	$0.727 \text{Ch} + 0.074 \text{H}_4\text{SiO}_4^0 + 0.509 \text{O}_2 + 2.617 \text{CO}_2 \xrightarrow{\text{nH}_2\text{O}}$ $\text{Kl} + 1.018 \text{Hm} + 1.309 \text{Mg}^{2+} + 2.617 \text{HCO}_3^-$
R _{3d}	Ch	Gb	$0.364 \text{Ch} + 0.254 \text{O}_2 + 1.308 \text{CO}_2 \xrightarrow{\text{nH}_2\text{O}}$ $\text{Gb} + 0.509 \text{Hm} + 0.654 \text{Mg}^{2+} + 1.308 \text{HCO}_3^- + 0.963 \text{H}_4\text{SiO}_4^0$

TABLE 7a

Nr	x	P	c_1	c_2	Sm	Vr	Kl	Gb	$[Pl]$	$[Bt]$	R	W_{Pl}	W_{Bt}	$[Na]_p$	$[K]_p$	$[Mg]_p$	$[Ca]_p$
		(mm·y ⁻¹)	(%)	(%)	(%)	(%)	(%)	(%)	μM	μM	(mm·y ⁻¹)	(mol·ha ⁻¹ ·y ⁻¹ ·%Pl ⁻¹)	(mol·ha ⁻¹ ·y ⁻¹ ·%Bt ⁻¹)	μM	μM	μM	μM
1009	0.10	1246	30	0	0	27	21.8	51	94.7	22	139	4.3	8.1	123	1	37	9
1038	0.10	1253	100	0	0	19	81.3	0	171	24	141	7.8	9.1	190	1	44	9
1040	0.10	1235	100	0	0	18	81.7	0	186	25	137	8.2	9.4	201	8	51	12
1043	0.10	1176	70	0	0	14	60.5	26	202	19	125	8.1	6.5	184	6	53	37
1048	0.10	1117	10	0	0	30	6.98	63	98.6	26	112	3.6	7.9	317	1	76	29
1077	0.25	1270	100	100	0	0	100	0	188	17	144	8.7	6.7	132	36	6	33
1242	0.15	1379	100	100	0	0	100	0	231	23	167	12.5	10.6	190	65	41	36
1272	0.10	1532	40	0	0	28	28.7	43	53.7	13	199	3.5	7.0	159	0	36	9
1285	0.10	1406	100	100	0	0	100	0	100	4	173	5.6	1.9	168	18	31	14
1412	0.10	842	50	0	0	3	48.5	48	52.8	1	55	0.9	0.1	100	0	9	4
1415	0.10	898	100	100	0	0	100	0	168	14	66	3.6	2.5	114	5	10	44
1430	0.15	893	100	100	0	0	100	0	93.4	6	65	2.0	1.1	121	2	6	10
1433	0.15	895	100	100	0	0	100	0	173	14	66	3.7	2.5	155	7	13	16
1442	0.10	894	100	0	0	1.1	98.9	0	88.8	0.6	65	1.9	0.1	93	21	17	23
1446	0.20	839	100	100	0	0	100	0	64.2	2.2	54	1.1	0.3	117	2	9	5
1449	0.10	877	40	0	0	13	52.5	35	51.9	4.5	62	1.0	0.8	86	2	18	14
1461	0.15	862	50	0	50	0.4	49.8	0	150	0.3	59	2.8	0.1	38	0	40	19
1468	0.10	870	20	0	0	0.1	79.9	20	115	0.1	60	2.2	0.0	109	4	8	6
1470	0.10	853	100	0	0	1.6	98.4	0	129	1.3	57	2.4	0.2	126	15	24	18
1477	0.20	869	100	100	0	0	100	0	145	4.6	60	2.8	0.7	72	3	28	6
1480	0.10	881	100	100	0	0	100	0	144	4.8	63	2.9	0.8	119	13	13	15
1490	0.15	933	100	100	0	0	100	0	142	3.2	74	3.4	0.6	86	5	18	18
1491	0.25	932	100	100	0	0	100	0	202	7.1	73	4.8	1.4	110	11	21	17
1611	0.10	953	100	0	0	10	89.9	0	89.3	6.1	78	2.2	1.3	113	4	35	23
1612	0.10	1143	100	100	0	0	100	0	142	4.7	118	5.4	1.5	209	8	11	13
1613	0.20	1148	90	100	0	0	90.6	9.4	241	18	119	9.2	5.8	316	7	2	1
1615	0.10	1193	100	100	0	0	100	0	102	16	128	4.2	5.4	189	9	4	14
1622	0.10	1207	100	100	0	0	100	0	104	6.2	131	4.4	2.2	99	34	12	8
1625	0.10	1010	0	80	0	1.8	7.15	91	84.8	8.3	90	2.5	2.0	209	0	3	0
1626	0.10	1034	100	100	0	0	100	0	248	9	95	7.6	2.3	216	1	15	29
1628	0.30	1079	100	100	0	0	100	0	211	14	104	7.1	3.9	250	18	14	4
1629	0.25	1075	90	80	0	2.3	88.9	8.9	192	28	103	6.4	7.8	170	16	0	2
1631	0.25	1050	100	100	0	0	100	0	224	15	98	7.1	4.1	203	10	7	3
1632	0.10	1017	100	100	0	0	100	0	123	2.4	91	3.6	0.6	143	18	14	8
1649	0.10	1156	100	100	0	0	100	0	222	3.2	120	8.6	1.0	168	13	18	12
1652	0.10	1109	90	0	0	10	81	9	83.3	5.6	111	3.0	1.7	170	3	29	6
1659	0.10	1073	100	100	0	0	100	0	61.1	15	103	2.0	4.2	273	8	42	77
1663	0.10	1030	90	0	0	10	81	9	124	8.5	94	3.8	2.1	147	3	34	23
1664	0.15	1027	30	100	28	0	71.9	0	222	15	93	6.7	3.7	175	1	33	10
1665	0.10	1005	100	100	0	0	100	0	184	1.9	89	5.3	0.5	130	12	17	14
1667	0.10	1064	100	0	0	10	89.6	0	180	13	101	5.9	3.5	209	2	36	3
1670	0.10	980	30	0	0	8.9	63.8	27	92.8	5.6	84	2.5	1.3	114	3	24	5
1675	0.15	892	100	100	0	0	100	0	189	23	65	4.0	4.0	271	3	9	31
1678	0.10	932	100	100	0	0	100	0	173	0.5	73	4.1	0.1	218	11	20	4
1680	0.10	923	100	0	0	5.4	94.6	0	154	5.4	72	3.6	1.0	109	2	28	3
1682	0.10	948	100	0	0	0.9	99.1	0	100	0.6	77	2.5	0.1	125	29	24	12
1683	0.10	976	100	0	0	8.6	91.4	0	128	7.4	83	3.4	1.6	147	5	29	14
1684	0.30	918	100	90	0	0.3	99.7	0	205	6.9	70	4.7	1.3	147	1	18	0
1685	0.10	960	100	0	0	7.7	92.3	0	232	12	79	5.9	2.5	232	14	40	18
1697	0.10	946	60	0	0	15	33.9	51	49.2	5.4	76	1.2	1.1	112	1	19	8
1701	0.10	902	100	0	0	1.7	98.3	0	90.4	1	67	2.0	0.2	125	8	24	24
1703	0.10	907	100	100	0	0	100	0	127	8.8	68	2.8	1.6	192	4	16	42
1707	0.10	886	100	100	0	0	100	0	114	15	64	2.3	2.6	204	20	11	30
1708	0.25	897	100	100	0	0	100	0	192	5.6	66	4.1	1.0	221	8	28	9
1709	0.15	891	100	100	0	0	100	0	168	11	65	3.5	1.9	191	6	12	20
2003	0.10	1154	100	0	0	9.5	90.5	0	103	6.6	120	4.0	2.1	107	17	55	27
2019	0.15	1095	100	100	0	0	100	0	197	7.8	108	6.8	2.3	158	16	11	11
2022	0.10	1111	90	0	0	8.5	82.4	9.2	148	8.4	111	5.3	2.5	128	0	26	17
2033	0.30	1225	10	100	9.9	0	90.1	0	150	2.2	135	6.5	0.8	40	8	42	8
2035	0.10	1169	70	100	0	0	70	30	199	0.3	123	7.9	0.1	150	3	27	6

2039	0.10	1204	100	100	0	0	100	0	178	14	131	7.5	5.0	86	10	11	33
2042	0.10	1117	100	0	0	3.5	96.5	0	137	3	112	5.0	0.9	121	13	19	3
2044	0.10	1110	40	0	0	7.8	36.9	55	78.9	4.1	111	2.8	1.2	115	2	14	3
2049	0.10	1079	90	0	0	25	67.7	7.5	76.7	15	104	2.6	4.3	94	0	38	17
2054	0.10	1089	50	10	0	11	45.3	44	100	8.9	106	3.4	2.6	143	21	25	0
2055	0.10	1087	100	100	0	0	100	0	164	7.6	106	5.6	2.2	89	27	18	46
2070	0.10	1195	100	0	0	0.5	99.5	0	211	0.6	129	8.7	0.2	167	16	26	6
2079	0.10	1164	100	0	0	0.8	99.2	0	253	1.3	122	10.0	0.4	112	24	12	9
2089	0.10	1184	70	10	0	5.3	66.5	28	273	11	126	11.1	3.9	158	8	26	0
2091	0.10	1083	100	100	0	0	100	0	176	7.7	105	6.0	2.2	116	1	7	28
2095	0.30	1197	30	90	28	0.6	71.1	0	395	25	129	16.4	8.6	3	3	80	10
2101	0.10	1059	100	0	0	8.2	91.8	0	146	7.9	100	4.7	2.1	164	16	31	9
2102	0.10	1053	100	0	0	6.3	93.7	0	135	5.5	99	4.3	1.5	155	16	29	16
2801	0.10	1165	80	0	0	17	66.5	17	141	17	122	5.6	5.8	82	0	40	1
2810	0.10	1328	0	0	0	10	0	90	119	8.4	157	6.0	3.5	184	3	32	12
2811	0.10	1412	10	0	0	6.6	9.34	84	43.2	1.9	174	2.4	0.9	94	1	13	6
2817	0.10	1415	50	0	0	23	38.5	39	52.2	9.5	175	2.9	4.5	115	0	24	0
2822	0.10	1424	20	0	0	15	17	68	75.1	8	177	4.3	3.8	136	1	32	14
2823	0.10	1453	10	0	0	9.6	9.04	81	97.6	6.3	183	5.8	3.1	154	0	27	10
2829	0.10	1208	100	0	0	3.2	96.8	0	204	4.1	131	8.7	1.5	37	19	53	23
2831	0.10	1524	20	10	0	15	18.3	67	105	14	198	6.7	7.3	115	2	36	0
2832	0.10	1510	0	0	0	13	0	87	67.4	6	195	4.2	3.2	118	0	21	3
2836	0.10	1330	10	0	0	14	8.59	77	91.5	9.2	157	4.6	3.9	133	0	27	6
2839	0.10	1262	80	0	0	14	69.1	17	98.9	9.5	143	4.6	3.7	102	2	26	2
2842	0.10	1454	60	0	0	19	48.5	32	79.2	12	183	4.7	5.7	103	1	39	10
2851	0.10	1246	50	0	0	10	45	45	180	12	139	8.1	4.6	132	5	43	14
2853	0.10	977	80	0	0	21	15.9	64	118	19	83	3.1	4.2	147	4	45	5
2854	0.10	1192	0	30	0	13	5.76	81	141	25	128	5.8	8.8	158	0	18	1
2855	0.10	1270	60	0	0	12	52.9	35	103	8.5	144	4.8	3.3	64	3	22	6
2857	0.10	1240	10	0	0	9.5	9.05	81	85.8	5.5	138	3.8	2.0	117	0	22	7
2859	0.10	1491	30	0	0	20	24	56	74.3	11	191	4.6	5.9	94	0	31	20
2868	0.10	1282	100	0	0	17	83.2	0	180	22	147	8.5	8.8	165	14	59	28
2870	0.10	1151	10	0	0	14	8.6	77	117	12	119	4.5	3.8	201	1	35	2
2871	0.10	1104	20	0	0	12	17.5	70	119	10	110	4.2	3.0	142	3	31	2
2872	0.10	1103	60	0	0	11	53.1	35	166	13	109	5.9	3.9	234	4	41	3
2873	0.10	1163	20	0	0	14	17.3	69	166	16	122	6.5	5.3	143	5	37	5
2874	0.10	1342	50	0	0	19	40.4	40	106	15	160	5.5	6.6	111	0	38	2
2876	0.10	1205	60	0	0	13	52.3	35	176	16	131	7.4	5.6	132	6	44	2
2882	0.10	1358	30	0	0	11	26.6	62	168	13	163	8.8	5.8	112	2	36	10
2884	0.10	1254	10	0	0	17	8.31	75	108	13	141	4.9	5.1	114	1	35	6
2887	0.10	1453	70	0	0	17	58.1	25	94.5	12	183	5.6	5.9	201	0	41	23
3036	0.10	1457	100	0	0	18	81.6	0	35.8	4.9	184	2.1	2.4	186	24	41	33
Average	0.12	1122	72.0	38.2	1.1	7.3	70.2	21.3	140	10	113	5.0	3.2	146	8	27	14
Std Dev	0.05	184	35.2	47.8	6.3	7.9	33.9	29.2	60	7	39	2.6	2.6	55	10	15	13

TABLE 7b

Nr	x	P	c_1	c_2	Sm	Vr	Kl	$[Pl]$	$[Ch]$	R	W_{Pl}	W_{Ch}	$[Na]_p$	$[K]_p$	$[Mg]_p$	$[Ca]_p$
		(mm·y ⁻¹)	(%)	(%)	(%)	(%)	(%)	μM	μM	(m·my ⁻¹)	(mol·ha ⁻¹ ·y ⁻¹ ·%Pl ⁻¹)	(mol·ha ⁻¹ ·y ⁻¹ ·%Ch ⁻¹)	μM	μM	μM	μM
1209	0.05	1316	100	100	0	0	100	162	6	154	28.4	0.3	227	34	31	22
1215	0.05	1284	100	100	0	0	100	82	14	147	13.8	0.6	164	17	19	77
1223	0.00	1374	100	100	0	0	100	126	5	166	23.7	0.2	211	38	25	26
1238	0.00	1323	100	0	0	3	97	95	0	156	16.8	0.0	168	8	61	9
1239	0.00	1283	100	100	0	0	100	95	3	147	15.8	0.1	152	16	67	18
1256	0.00	1396	100	100	0	0	100	200	16	171	38.9	0.8	414	74	139	83
1257	0.00	1301	100	100	0	0	100	145	11	151	24.9	0.5	249	42	23	28
1258	0.00	1262	100	100	0	0	100	208	4	143	33.7	0.2	543	98	140	91
1262	0.00	1266	100	100	0	0	100	219	12	144	35.7	0.5	223	34	66	31
1268	0.10	1447	100	100	0	0	100	217	22	182	44.7	1.2	168	37	8	92
1278	0.05	1235	100	100	0	0	100	139	7	137	21.6	0.3	375	26	143	74
1403	0.10	898	100	80	0	13	87	102	36	66	7.7	0.7	36	13	2	72
1404	0.00	967	100	100	0	0	100	58	3	81	5.3	0.1	75	6	13	11
1421	0.10	947	80	100	13	0	87	79	8	77	6.9	0.2	37	7	1	47
1428	0.10	889	100	70	0	21	79	185	69	64	13.5	1.4	3	15	5	79
1687	0.00	887	100	100	0	0	100	163	16	64	11.8	0.3	110	21	99	86
1690	0.00	936	100	0	0	7	93	62	0	74	5.2	0.0	66	12	36	13
1691	0.00	916	100	0	0	17	83	53	1	70	4.2	0.0	101	12	56	19
1693	0.00	891	100	100	0	0	100	76	1	65	5.6	0.0	130	6	49	21
1705	0.00	878	100	100	0	0	100	73	5	62	5.1	0.1	108	9	29	22
2059	0.00	1114	100	100	0	0	100	133	11	112	16.9	0.4	132	45	19	22
2060	0.05	1133	100	100	0	0	100	242	2	116	31.9	0.1	168	24	26	18
2061	0.00	1139	100	100	0	0	100	135	12	117	17.9	0.4	128	45	6	24
2065	0.00	1133	100	100	0	0	100	124	4	116	16.3	0.2	92	31	22	10
2083	0.00	1202	100	0	0	19	81	70	2	130	10.3	0.1	53	6	46	13
2103	0.00	1089	100	90	0	1	99	109	2	106	13.2	0.1	166	59	28	10
2825	0.00	1437	100	0	0	18	82	67	1	179	13.7	0.1	83	13	39	5
2826	0.00	1444	100	0	0	18	82	55	1	181	11.4	0.1	88	24	48	7
2865	0.00	1417	100	0	0	0	100	119	0	175	23.7	0.0	82	16	28	15
2877	0.00	1171	100	0	0	3	97	105	0	124	14.7	0.0	130	16	62	12
2879	0.00	1440	100	0	0	19	81	77	2	180	15.8	0.1	49	14	39	6
3005	0.05	1230	100	100	0	0	100	114	14	136	17.6	0.6	290	29	42	18
3021	0.00	1225	100	100	0	0	100	101	4	135	15.6	0.1	302	10	82	25
3027	0.00	1284	100	0	0	20	80	108	3	147	18.0	0.1	192	8	133	21
3028	0.00	1322	100	100	0	0	100	92	2	155	16.2	0.1	262	19	77	19
3030	0.00	1352	100	100	0	0	100	50	4	162	9.1	0.2	222	16	28	20

TABLE 8a

Nr	x	c ₁	c ₂	[Pl]	[Br]	Vr	Kl	Gb	[Na] _p	[K] _p	[Mg] _p	[Ca] _p	Silica consumption
		(%)	(%)	μM	μM	(%)	(%)	(%)	μM	μM	μM	μM	μM
1011	0.20	80	10	154	13	10	72	18	194	47	38	48	2
1030	0.10	100	20	100	1	1	99	0	149	32	51	31	31
1032	0.10	100	20	147	13	9	91	0	209	68	37	35	100
1033	0.10	90	30	105	1	1	89	10	158	12	53	38	41
1034	0.10	100	30	136	4	3	97	0	279	52	67	64	106
1035	0.10	100	40	126	0	0	100	0	252	32	48	41	80
1042	0.10	100	10	129	3	3	97	0	221	43	50	49	27
1045	0.10	80	10	144	9	8	74	18	281	30	46	63	15
1086	0.10	80	0	55	2	7	74	19	91	11	8	18	8
1208	0.20	100	30	133	12	7	93	0	237	43	51	62	87
1210	0.20	100	30	130	7	4	96	0	229	36	47	62	77
1217	0.25	90	0	189	3	2	88	10	383	57	16	133	4
1221	0.15	90	0	125	5	6	84	9	208	22	28	64	3
1244	0.10	90	30	106	1	1	89	10	208	27	39	50	74
1247	0.10	100	0	68	5	10	90	0	137	9	16	26	17
1248	0.10	90	0	60	3	7	84	9	141	16	28	31	24
1250	0.10	80	0	69	4	9	73	18	145	20	41	42	17
1259	0.30	80	90	175	62	2	82	16	282	18	104	13	63
1260	0.10	80	10	164	12	9	73	18	588	86	115	203	57
1263	0.20	90	30	180	4	2	88	10	354	37	38	65	154
1406	0.10	100	0	53	3	8	92	0	102	3	12	24	8
1409	0.10	100	40	71	1	1	99	0	108	6	6	11	22
1413	0.10	100	0	74	2	4	96	0	104	3	11	17	3
1416	0.25	100	30	237	20	6	94	0	441	74	68	95	226
1417	0.20	100	30	108	10	7	93	0	154	7	14	29	63
1438	0.15	100	30	115	4	3	97	0	176	10	20	23	60
1444	0.10	80	30	80	1	2	79	20	91	3	9	10	2
1445	0.10	90	30	64	0	1	89	10	106	4	26	14	40
1602	0.10	100	80	128	0	0	100	0	290	41	37	56	85
1604	0.20	90	30	209	14	5	86	9	393	47	44	97	163
1640	0.10	100	30	127	6	4	96	0	217	23	32	38	83
1641	0.15	100	30	160	20	10	90	0	256	27	34	49	111
1642	0.15	100	30	131	1	0	100	0	213	21	22	36	59
1643	0.15	100	30	143	13	7	93	0	202	8	31	41	80
1644	0.15	100	30	144	0	0	100	0	249	18	26	39	104
1646	0.15	100	30	156	3	2	98	0	244	14	22	41	86
1650	0.20	100	30	168	19	8	92	0	236	15	30	41	93
1660	0.10	100	0	113	4	5	95	0	276	19	52	50	51
1661	0.10	90	30	114	3	2	88	10	189	17	29	32	58
1712	0.15	90	0	125	6	7	83	9	325	44	99	99	48
2002	0.10	100	20	143	3	2	98	0	147	32	24	35	67
2006	0.15	100	0	108	7	10	90	0	217	42	28	65	23
2007	0.10	90	20	113	4	4	86	9	133	52	38	58	93
2010	0.15	100	0	99	5	7	93	0	195	26	17	44	22
2013	0.10	80	20	106	1	1	79	20	110	22	9	43	34
2014	0.15	100	20	154	5	4	96	0	135	30	31	43	56
2016	0.15	100	20	144	0	0	100	0	145	21	21	34	40
2023	0.10	80	20	129	3	2	78	19	165	31	26	29	52
2024	0.10	100	70	103	0	0	100	0	166	23	27	27	26
2027	0.10	90	40	60	0	0	90	10	80	6	3	26	3
2038	0.10	80	20	123	11	9	74	18	64	5	12	21	26
2045	0.10	100	30	115	7	5	95	0	158	13	20	25	36
2046	0.15	100	0	107	5	7	93	0	163	32	21	36	11
2048	0.15	100	0	111	6	8	92	0	205	35	33	46	24
2064	0.10	90	40	141	17	8	84	9	158	8	1	27	2
2077	0.15	80	20	156	2	2	79	20	171	16	9	24	29
Average	0.13	94	23	124	7	4.5	89.7	5.8	206	27	33	46	53
Std Dev	0.05	8	19	38	9	3.3	8.2	7.4	96	19	23	32	45

TABLE 8b

Nr	x	c ₁	c ₂	[P _l]	[B _t]	V _r	K _l	G _b	[Na] _p	[K] _p	[Mg] _p	[Ca] _p	Silica consumption
		(%)	(%)	μM	μM	(%)	(%)	(%)	μM	μM	μM	μM	μM
1052	0.00	90	40	116	0	0	90	10	249	25	50	30	30
1205	0.10	100	30	152	9	8	74	18	201	49	50	51	154
1220	0.10	100	30	138	7	7	77	16	186	34	49	57	97
1229	0.00	100	0	125	5	0	82	18	271	29	64	43	100
1235	0.00	90	50	71	1	3	84	13	120	18	17	27	17
1266	0.05	90	40	76	2	7	75	18	168	19	26	46	15
1281	0.10	100	30	83	3	5	83	12	114	16	20	36	50
1282	0.10	100	100	69	0	3	97	0	122	7	17	31	19
1287	0.00	80	80	93	1	5	75	20	161	10	6	64	19
1290	0.10	100	30	151	8	7	77	16	219	31	70	72	234
1291	0.10	100	30	194	6	5	84	11	279	36	76	85	279
1292	0.10	100	0	110	4	0	83	17	341	75	68	84	159
1293	0.05	100	0	95	4	0	82	18	312	57	44	87	141
1294	0.05	100	30	156	6	6	80	14	283	72	79	106	253
1414	0.10	100	30	103	7	8	72	19	130	12	23	24	96
1694	0.05	90	0	76	0	0	90	10	118	9	14	50	9
2995	0.00	80	80	74	1	8	72	20	121	17	20	36	16
2997	0.00	90	0	87	1	0	83	17	140	25	28	22	31
3046	0.10	90	40	86	3	7	75	19	247	6	2	46	28
3047	0.05	100	30	119	4	6	82	13	170	5	2	26	124
3093	0.10	100	30	133	5	6	81	13	188	19	16	59	105
3100	0.05	100	0	98	4	0	83	17	226	20	8	46	82
3103	0.10	100	30	112	4	5	83	12	147	23	19	28	116
Average	0.06	96	32	109	4	4.1	81.1	14.8	196	27	33	50	94
Std Dev	0.04	7	27	33	3	3.0	6.0	4.5	69	20	25	23	80

FIGURE CAPTIONS**FIGURE 1**

Location, topography and drainage pattern of the hydrographic basin of Vouga River. *X* and *Y* are Hayford-Gauss coordinates. Lapa, Leomil, Caramulo, etc., are names of surrounding mountains. Numbers are names of Vouga River tributaries: 1 — Antuã, 2 — Caima, 3 — Sul, 4 — Águeda, 5 — Cértima, 6 — Alfusqueiro, 7 — Marnel, 8 — Serra. Capital letters represent the Pateira de Fermentelos (A) and the Ria de Aveiro (B).

FIGURE 2

Simplified geological map of the Vouga River basin. Adapted from the Geological Map of Portugal, scale 1/500 000, produced in 1992 by the Portuguese Geological Survey.

FIGURE 3

Distribution of precipitation (*P*) inside the Vouga River basin (shading). Location of the stations monitored for precipitation (numbers) and discharge rate (letters).

FIGURE 4

Relation between precipitation (*P*) and recharge (*R*) in the Vouga River basin. The *P* and *R* data are in columns 10 and 11 of Table 3.

FIGURE 5

Location of the sampled and analyzed springs. Different symbols were used to represent the major water types: bullets for springs, circles for stream(let) waters, crossed circles for Vouga River samples and a star for the Águeda river sample. Classification according to geological environment is given in Appendix 2 (column 4). The numbers close to the crossed circles are in agreement with the caption of Figure 9.

FIGURE 6

Box plots of pH's and log transformed solute concentrations (in μM) in: 1 — springs and 2 — stream(let)s in granite areas; 3 — springs and 4 — stream(let)s in metasediment areas. a)

chloride, b) sulfate, c) nitrate, d) sodium, e) potassium, f) magnesium, g) calcium, h) pH, i) bicarbonate, j) silicic acid, and k) bicarbonate/silicic acid.

FIGURE 7

Plots of sulfate and chloride concentrations in springs: a) in granitic areas, b) in metasediment areas. An average concentration of $50 \mu\text{M Cl}^-$ and $16.6 \mu\text{M SO}_4^{2-}$ in wet precipitation is adopted, based on estimated changes in their concentration from the coastal station to the inland station due to washing out (for Cl^-) and continental dust (for SO_4^{2-}) input respectively (cf. Table 4). Along the concomitant evapotranspiration line, the resulting concentrations at 60% and 90% are indicated. Additionally, the sea water dilution line (s.w.d.l.) is shown, the relation expected when only sea salt would be present in the precipitation.

FIGURE 8

Plots of bicarbonate versus silicic acid concentrations in springs in: a) granite areas, b) in metasediment areas. Low ratios (< 1) are indicative of weathering of oligoclase into kaolinite and(or) gibbsite, whereas higher ratios are rather the result of weathering of more calcic plagioclases and(or) biotite into kaolinite.

FIGURE 9

Illustration of the development of the aquatic chemistry of the Vouga River along its course. The numbers along the abscissa correspond with sampling sites (location in Figure 5), starting with 1 and 2 (between Aguiar da Beira and Sátão), through 3 (halfway 2 and 4), 4 (near Lordosa), 5 (halfway 4 and 6), 6 (São Pedro do Sul), 7 (North of Oliveira de Frades), 8 (halfway between 7 and 9), 9 (SSE of Sever do Vouga), 10 (ESE of Albergeria-a-Velha). For comparison, site 10.5 represents the area at the confluence of Alfusqueiro river into the Águeda river, a major tributary to the Vouga in the coastal plain. Solid symbols represent data from Van der Weijden et al. (1984), open symbols are from sampling campaigns in later years. a) electrical conductivity (divided by 10) and pH, b) chloride, sulfate and nitrate (multiplied by 100), c) sodium (divided by

10), potassium, magnesium, calcium, and d) bicarbonate/silicic acid. In general, there is a reasonably good agreement between the earlier (solids symbols) and later (open symbols) data, which suggest a quite consistent pattern in the development of the chemistry of the rivers.

FIGURE 10

Relation between the contribution of plagioclase to weathering ($\%[PI]$; Equation 4) and the weathering potential of the host rock as measured by the *MWPI* index of Vogel (Equation 5).

Capital letters identify the sources of information: A and B – Vouga metasediments and granites, C – Fundão granodiorites (Δ_{0-2} units as described in Pacheco and Van der Weijden, 1996), D and E – Morais massif retrograde amphibolites and amphibolites (Pacheco and Van der Weijden, 2002), F – Madeira basalts (Mata, 1996 and Van der Weijden and Pacheco, 2003). The negative trend shows how plagioclase reduces its contribution to weathering once other weatherable minerals are found to be present in the host rock.

FIGURE 11

Distinction between transport controlled plagioclase weathering, which dominates when $R < 900 \text{ mm}\cdot\text{y}^{-1}$ (e.g. Vouga River basin—present study—and Morais massif—Pacheco and Van der Weijden, 2002), and surface-reaction controlled plagioclase weathering, which dominates when $R > 900 \text{ mm}\cdot\text{y}^{-1}$ (e.g. Madeira island—Van der Weijden and Pacheco, 2003).

FIGURE 12

Contours of silica consumption (μM) in the eastern side of Vouga River basin. The bullets represent sampling sites of stream(let) water. The highest silica consumptions occur preferably at the confluence of streamlets and higher order streams.

FIGURE A1

Plot of minimum daily discharge rates (Q) against order (i). Q values were compiled from the Sul river hydrometric record (source: Sistema Nacional de Informação de Recursos Hídricos, presently at <http://snirh.inag.pt/>). Assessment of the annual recharge (R) by the Kille method.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7 – SO₄ vs. Cl

a – granites

b – metasediments

FIGURE 8 – Bicarbonate vs. silica

a – granites

b – metasediments

FIGURE 9 – Development of chemistry of Vouga river water.

a – Ec and pH

b – chloride, sulfate and nitrate

c – sodium, potassium, magnesium and calcium

d – bicarbonate/silicic acid.

FIGURE 10

FIGURE 11

FIGURE 12

FIGURE A1