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Another Look at the Chemical Relationships in the Dissolved Phase of Complex River Systems

A. Buccianti · J.J. Egozcue · V. Pawlowsky-Glahn

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Abstract Large rivers are a major pathway for the erosion products of continents to reach the oceans. The riverine transport of dissolved and particulate materials is generally related to a large number of interactions involving climate, hydrological, physico-chemical and biological aspects. Consequently, the investigation of large rivers allows the erosion processes at a global scale to be addressed, with information about biogeochemical cycles of the elements, weathering rates, physical erosion rates and CO₂ consumption by the acid degradation of continental rocks. Today, good databases exist for the major dissolved ions in the world's largest rivers. Since concentration of ions in river waters has to be considered in a compositional context, it is necessary to study the implications of considering the simplex, with its proper geometry, as the natural sample space. Using the additive (alr) or the isometric (ilr) log-ratio transformations, a composition can be represented as a real vector; but only in the second case can these coordinates be mapped onto orthogonal axes.

Using data related to the dissolved load of some of the most important rivers in the world, the relationships among the major ions frequently used in molar ratio mixing diagrams have been investigated with alternative tools. Following the balances approach, an investigation of the properties of aqueous solutions of electrolytes that are often treated in terms of equilibrium constants is undertaken. The role played by the source—rain water, weathering of silic, carbonatic and evaporitic rocks, pollution—

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from which elements and chemical species can potentially be derived, has been checked through an investigation of a probabilistic model able to describe the relationships among the different components that contribute to the chemical composition of a river water sample.

Keywords Aitchison geometry · Simplex · River chemistry · Mixing diagrams

1 Introduction

Chemical weathering both shapes the surficial environment and influences soil formations, affecting the global geochemical cycles of the elements and, in particular, that of carbon. Worldwide river chemistry can be consequently used to (1) understand the biogeochemical cycles of major and trace elements, (2) calculate chemical weathering rates, (3) estimate the role of major parameters like relief, climate, lithology, and vegetation that are likely to influence chemical weathering processes, and (4) quantify the effect of rock chemical weathering on the carbon cycle and its potential role on climate change (dissolution of CO_2 in surface waters conveys the protons necessary to weather the rock minerals). Studying river chemistry is fundamental, since at the Earth's surface the erosion products are mainly transported by rivers determining, ultimately, the ocean chemistry. In a global approach, solutes in river water are derived from different sources like rain water, silicic, carbonatic and evaporitic rocks weathering (Garrels and MacKenzie 1971).

Atmospheric inputs to rivers can be evaluated using Cl^- abundance, whose concentration in rocks is very low (Stallard 1980; Meybeck 1983). In South America (Stallard and Edmond 1987), in Western Europe (Meybeck 1986), and in Central Africa (Négre et al. 1993), Cl^- originates from the dissolution of atmospheric sea salt particles by rainwater, and shows concentrations which decrease with increasing distance from the coast. Difficulties arise when evaporitic rocks are present in the river drainage, as reported for the Andean rivers (Stallard 1980). In that situation further investigations are needed to discriminate marine aerosol contributions from those of rocks (Millot et al. 2002). For most large rivers direct rain input is almost insignificant (less than 5%), except for those rivers most influenced by evaporation (Gaillardet et al. 1999).

Waters draining different rock types are characterised by their own chemical and isotopic signatures. These signatures depend on both the chemical composition of the bedrock and on the rate at which it is being eroded. Carbonatic and evaporitic rocks are weathered 12 times and 40 to 80 times, respectively, more rapidly than granites or gneisses (Meybeck 1987). As a consequence, evaporites have a major influence on river chemistry even if their outcrops are rather rare. The Sr isotopic ratio and the $\text{Ca}^{2+}/\text{Na}^+$, $\text{HCO}_3^-/\text{Na}^+$ and $\text{Mg}^{2+}/\text{Na}^+$ molar ratios are particularly well suited to distinguish between carbonate and silicate contributions; they also have the important property of being independent of water fluxes, dilution and evaporation effects. Normally, the analysis is based on end-members whose composition is estimated using data for small rivers draining a single lithology (carbonates, silicates and evaporites). Then, the hydrochemistry of a river is considered as a mixture of such end-members.

For instance, Négrel et al. (1993) consider that binary relationships between Sr isotopic composition and Ca^{2+}/Sr , as well as between $\text{Mg}^{2+}/\text{Na}^+$ and $\text{Ca}^{2+}/\text{Na}^+$, or between $\text{HCO}_3^-/\text{Na}^+$ and $\text{Ca}^{2+}/\text{Na}^+$ molar ratios, can be used to model mixing between end-members. Each river appears as a point in a diagram whose axes are the logarithms of the mentioned ratios and mixing between end-members is represented by straight lines. These diagrams represent a good approximation to the investigation of the phenomena analysed. However, ratios with the same denominator (Na^+ in this instance) in a logarithmic scale (i.e. additive log-ratio (alr) coordinates used to represent a composition as a real vector) have some peculiarities as, not being invariant under the permutation of parts, they represent an oblique basis in the Aitchison geometry of the simplex (Egozcue et al. 2003; Egozcue and Pawłowsky-Glahn 2005, 2006). This fact may lead to misinterpretation and, consequently, a compatible metric is required. Our aim is to describe, using geometrically improved methods, general chemical equilibria among major ions characterising river composition, their behaviour, as well as the role of the different sources, on a global scale. From a general point of view, chemical weathering, highly related to runoff and physical erosion rates, is strongly lithology dependent (Dessert et al. 2001; Chadwick et al. 2003; Oliva et al. 2003; Quade et al. 2003), with basaltic rocks yielding by far the highest chemical weathering rates. As a consequence, basaltic rocks have a disproportionately large effect on CO_2 drawdown, being responsible for as much as 25% of the global carbon flux. However, calculated weathering rates of river basins show only modest dependence on temperature, due to the existence of hot catchment areas in regions of limited denudation, e.g. West Africa (Gaillardet et al. 1999; Anderson et al. 2003).

2 Origin of Data

A data base for 1080 water samples from the most important rivers in the world has been compiled. In it, the concentrations (mg/L) of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , HCO_3^- and H_4SiO_4 are reported, together with pH values and, where present, Sr and Rb abundance and $^{86}\text{Sr}/^{87}\text{Sr}$ isotopic ratios. The analytical procedures for water analysis included ion chromatography for Cl^- and SO_4^{2-} , conventional flame atomic absorption spectrophotometry for Ca^{2+} , Na^+ , K^+ and Mg^{2+} , and colorimetry for aqueous silica. On the whole, the uncertainties related to analytical errors are comparable. In most situations samples have been collected taking into account seasonal variability, as well as different positions within the catchment. Catchments were selected to be widely representative of different lithologies, climates and seasons. Contamination, if present, is expected to be revealed by presence of outliers. No correction for the atmospheric contribution has been performed on the original information. Data from the largest rivers of the world are from Gaillardet et al. (1999) and cover a continental area of $53.6 \times 10^6 \text{ km}^2$ or about 54% of the exorheic continental area (open systems in which surface waters ultimately drain to the ocean). This main data base has been expanded with data pertaining to South American (Edmond et al. 1995; Gaillardet et al. 1997; Mortatti and Probst 2003) and Asiatic regions (Galy and France-Lanord 1999;

Bickle et al. 2005; Tipper et al. 2006). Further data derive from the Deccan volcanic province, located in the western and central parts of India (Dessert et al. 2001) and from the Min Jiang river, a headwater tributary of the Yangtze River in the Chang Jiang area (Qin et al. 2006). African information was supplemented by data from the dissolved load of the Nyong basin rivers (Viers et al. 1997, 2000), the second largest river of Cameroon in terms of length. It has a relatively small drainage area (27,800 km²), which is characterised by potentially elevated level of chemical weathering (high temperature and precipitation), but strongly restricted due to thick soil and vegetation and lack of tectonic uplift. North America is represented by data from Canada (Slave Province, Northwest Territories and Grenville Province, Québec (Millot et al. 2002); Stikine Province, Western Canadian Cordillera (Millot et al. 2003); Mackenzie River basin, northern Canada (Millot et al. 2003); Fraser, Skeena, Nass river basins, Canadian Cordillera (Spence and Telmer 2005)). The regions under consideration are characterised by moderate relief and the landscape is typical post-glacial with abundant till deposits. Vegetation is dominated by conifers and population is sparse, making the region remarkably pristine. Further samples derive from White River, Vermont, USA (Douglas 2006). Data from Europe have been supplemented by considering the Seine (France) (Roy et al. 1999) and Salso (central Sicily, Italy) rivers (Favara et al. 2000). Overall, it has to be kept in mind that the database comprises observations from regions that are not geologically in the same state of evolution. Northern latitude regions are in a transient state and still in the post-glaciation period. There, weathering reactions proceed so slowly that the steady state of soils has not been reached. By contrast, tropical regions, like the Guyana or the African shield, have experienced only small changes during the past million years and have probably reached a steady state for weathering reactions.

3 Methodology

In a classical approach, river geochemistry can be characterised by a number of elemental ratios and the Sr isotopic composition. Several Na⁺ normalised molar ratios (Ca²⁺/Na⁺, K⁺/Na⁺, Mg²⁺/Na⁺, Cl⁻/Na⁺, SO₄²⁻/Na⁺, HCO₃⁻/Na⁺) can be used as intensive parameters, independent of dilution and evaporative processes, able to compare rivers draining areas of high runoff with those draining arid basins. Mixing diagrams using Na⁺-normalised molar ratios allow a comparison of the chemical composition of each sample with end-member reservoirs estimated using data for small rivers draining one single lithology (i.e. carbonates, silicates and evaporites). However, recall that these scatter diagrams, whose coordinates are given on a log-scale by ratios with the same denominator (e.g. HCO₃⁻/Na⁺ versus Ca²⁺/Na⁺, Mg²⁺/Na⁺ versus Ca²⁺/Na⁺, Ca²⁺/Na⁺ versus 1000 × Sr/Na⁺), define a space with non orthogonal axes (Egozcue and Pawlowsky-Glahn 2005), and that statistical validation of the relationships inside this space (e.g. correlations and their significance, discrimination of groups) requires an appropriate distance due to the specific geometry of compositional data. This standard representation of ratios in fact is equivalent to those of the alr-coordinates (Aitchison 1986), where $D - 1$ of the components of the composition are divided by the remaining component and logarithms

taken. The resulting log-ratios are real variables whose coordinates can be mapped onto axes at 60° . In this context it is not possible to use the usual inner product and distances on alr -transformed observations to determine either the angle between two vectors or their distance without modifying the methods of calculation. A simple alternative approach can be used. The methodology is based on the identification of subsets of variables, parts, and their balances (Egozcue and Pawlowsky-Glahn 2005, 2006). The balances approach was proposed to simplify the analysis of compositional data. It consists of grouping variables into subsets which are interpretable from a geochemical point of view. For example, chemical compositions of river waters include usually a group of anions and another group of cations, leading to a natural first partition of the composition. In this and other similar situations, one may be interested in studying two features of the sample compositions, the relationship or balance between the two groups of parts (inter-group analysis) and the behaviour of parts within a group (intra-group analysis). The sequential binary partitioning of parts of a composition (Egozcue and Pawlowsky-Glahn 2005) represents a tool to design a particular basis in the simplex, such that the corresponding coordinates are directly interpretable as balances between any two groups of parts appearing in some order of the sequential binary partition. Consequently, subcompositional (intra-group) and balance (inter-group) analysis are reduced to orthogonal projections onto subspaces of the simplex, thus guaranteeing consistency of distances and statistical analysis when working in reduced dimensions.

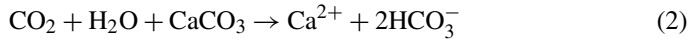
Taking into account the previous considerations, we propose to analyse the chemical relationships among three variables usually used in a scatter diagram with common denominator, e.g. Ca^{2+} , Na^+ and HCO_3^- , to investigate the behaviour among samples in the coordinate space. To do so, the coordinates $x = \text{Ca}^{2+}/\text{Na}^+$ and $y = \text{HCO}_3^-/\text{Na}^+$, represented on a logarithmic scale, are substituted by the coordinates

$$x = B_1 = \frac{1}{\sqrt{2}} \ln \frac{\text{Ca}^{2+}}{\text{Na}^+}, \quad y = B_2 = \frac{1}{\sqrt{6}} \ln \frac{\text{Ca}^{2+} \times \text{Na}^+}{(\text{HCO}_3^-)^2}, \quad (1)$$

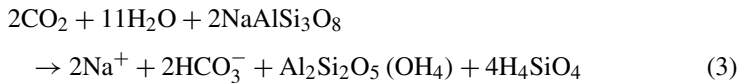
representing the balances B_1 and B_2 between the part Ca^{2+} versus Na^+ , and between the parts Ca^{2+} and Na^+ versus HCO_3^- , with a normalisation constant (Egozcue et al. 2003).

From a general point of view, consider that Ca^{2+} is contributed to river water almost entirely from rocks weathering and only 9% of it may arise from pollution (Berner and Berner 1996). The sources of Ca^{2+} mainly consist of CaCO_3 bearing sedimentary rocks, with a smaller proportion derived from Ca^{2+} -silicate minerals, chiefly Ca^{2+} -plagioclase, and a minor amount from CaSO_4 minerals. Concerning Na^+ , recent estimates (Berner and Berner 1996) indicate that about 28% is derived from contamination, 8% from sea salt, 43% from halite, and the remaining 22% from the weathering of plagioclase. Another possible source of Na^+ in river water is from cation exchange of dissolved Ca^{2+} with Na^+ on detrital clay minerals during marine shale weathering. Finally, all bicarbonate in average river water is derived from rock weathering, pollution accounting for only 2% and cyclic sea salts for far less than 1%. The behaviour of this component is affected by the presence of the CO_2 gaseous phase, participating at the carbonate equilibria system. Here acid attack is

the principal weathering mechanism with water, the acid being formed by the reaction of carbon dioxide from the atmosphere or from the respiratory cycle of organisms in the soil. With the aim to attribute a geochemical meaning to the balances, two representative weathering reactions given by



and



are considered. It is reasonable to assume that the two balances may represent their joint contribution, as Ca^{2+} and HCO_3^- are related to the right part of (2), whereas Na^+ and HCO_3^- are related to the right part of (3). Statistical analysis and investigation of relationships can be performed in the balance space with usual methodologies (e.g. identification of linear or non-linear data fitting, presence of groups, etc.). Moreover, the investigation of the features of balance frequency distributions may give information about equilibrium between the involved parts of the composition, evaluating the nature of the probabilistic model used to describe their behaviour. If the distribution is unimodal and the variance is low, an equilibrium situation may be hypothesised; on the other hand, presence of multi-modality and/or high variance may be an indication of more complex situations not describable by a single model. The identification of the random variable (normal, skew-normal, bimodal and so on) able to describe a balance represents, finally, a further development in the understanding of how natural phenomena work and their importance.

4 Mixing versus Balance Diagrams

Mixing diagrams on a logarithmic scale using Na^+ -normalised molar ratios in the dissolved phase of rivers are typically used to estimate contribution of end-member reservoirs (i.e. carbonates, silicates and evaporites). When simple binary diagrams have to be constructed for evaluating mixing processes, the balance approach allows us to choose appropriate coordinates for representing the data in a real Euclidean space, in which statistical analysis can be performed. Consider, for example, the Na^+ -normalised diagram in a log-log space, as introduced by Négrel et al. (1993), which is presented in Fig. 1 for $\text{Ca}^{2+}/\text{Na}^+$ vs. $\text{HCO}_3^-/\text{Na}^+$. In our data base Na^+ ranges from 0.076 (Guayana Shield) to 79 875 mg/L (Salso River, Sicily), Ca^{2+} from 0.040 (Guayana Shield) to 1 070 mg/L (Salso River, Sicily) and HCO_3^- from 0.80 (Amazon river) to 825 mg/L (Ganges-Brahmaputra) with ratios $\text{Ca}^{2+}/\text{Na}^+ \simeq 0.01$ to 147, $\text{HCO}_3^-/\text{Na}^+ \approx 0.003$ to 335, $\text{Mg}^{2+}/\text{Na}^+ \simeq 0.01$ to 40.78. As an alternative, the balances for the three variables, Ca^{2+} , Na^+ , and HCO_3^- , are reported in Fig. 2. The balances $B_1(x)$ and $B_2(y)$ represent the equilibrium among the products, involving, or not, a gaseous phase, of two previous weathering reactions (equations (2) and (3)).

World average river water composition is dominated by Ca^{2+} and HCO_3^- , both of which are derived predominantly from limestone weathering and, consequently,

Fig. 1 Mixing diagram using Na^+ -normalised ratios in dissolved phase of river water. See text for details

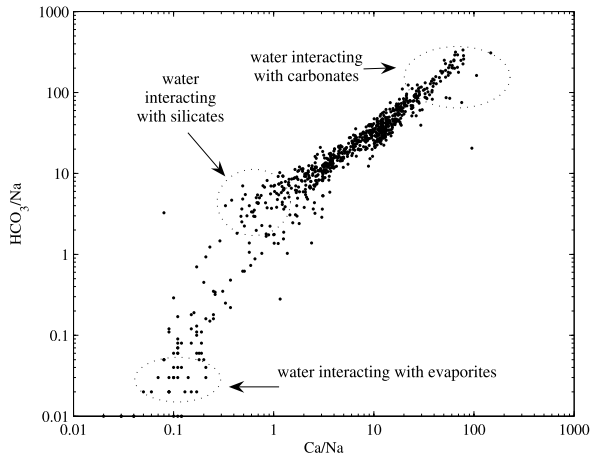
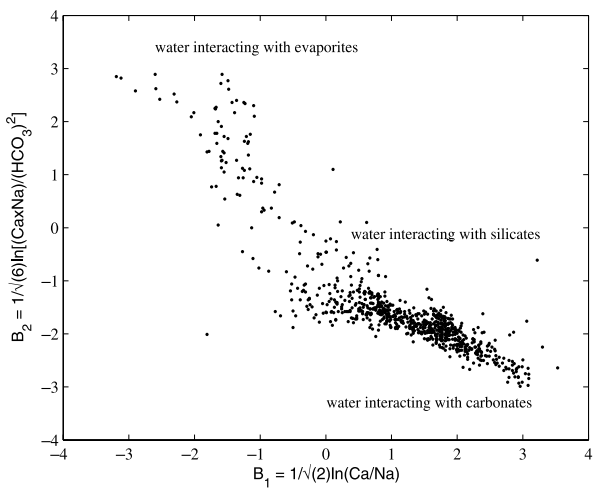


Fig. 2 Balances B_1 and B_2 for Na^+ , Ca^{2+} and HCO_3^- content in dissolved phase of river waters



about 98% of all river water is of the calcium carbonate type, while less than 2% has Na^+ as the principal ion (Meybeck 1979). From a general point of view, waters draining carbonates show Ca^{2+} and Mg^{2+} dominated reservoirs and $\text{Ca}^{2+}/\text{Na}^+$ ratios are often close to 50 (or 3.56 for balance B_1) whereas the average for crustal continental rocks is about 0.6 (or -0.87). Due to the higher solubility of Na^+ relative to Ca^{2+} , lower $\text{Ca}^{2+}/\text{Na}^+$ molar ratios are expected in the dissolved load of rivers draining silicates. However, the existence of silicate draining rivers having higher Na^+ -normalised ratios can be explained by the presence of rocks with values higher than crustal rocks, with weathering conditions such that Ca^{2+} rich minerals are preferentially dissolved, and with the presence of disseminated calcite within catchment bedrocks.

In order to compare the differences between both representations, Fig. 3 shows the data rescaling of the x -axis of (b) to match exactly the expression of B_1 in (a). Moreover, a set of parallel and not-parallel lines have been superimposed with the

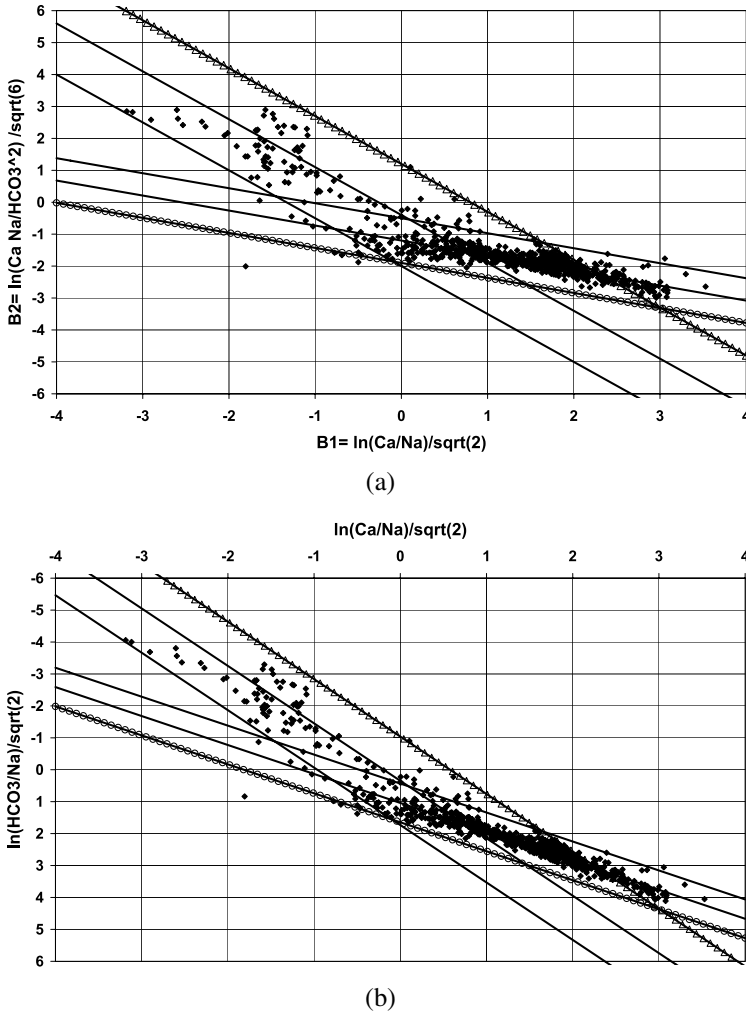


Fig. 3 Parallel and intersecting lines represented in balance-coordinates with chemical composition of river waters **(a)** and in Na^+ -normalised alr-coordinates **(b)**. The x -axis in **(a)** and **(b)** is equally scaled for comparison. In **(b)**, y axis has been reversed for easier comparison

goal of visualising the effect of working in a non-orthogonal system. Two features can be observed: (i) there is a reduction of the scale in the y axis of the alr-representation **(b)**, thus suggesting a reduction of variability in the y -axis; and (ii) the angle between the intersecting lines has changed, thus suggesting the data are nearer to a linear trend in **(b)** than in **(a)**. Both facts correspond to the property that alr-axes are not orthogonal, but they form an angle of 60 degrees. The dispersion and curvature of data in Figs. 2 and 3a correspond to the Aitchison geometry of the simplex, whereas Figs. 1 and 3b exhibit a subtle but important distortion.

In Fig. 2 the scatter of the data tends to increase from carbonate to evaporite end-members due to the higher geochemical variability of those source rocks. The

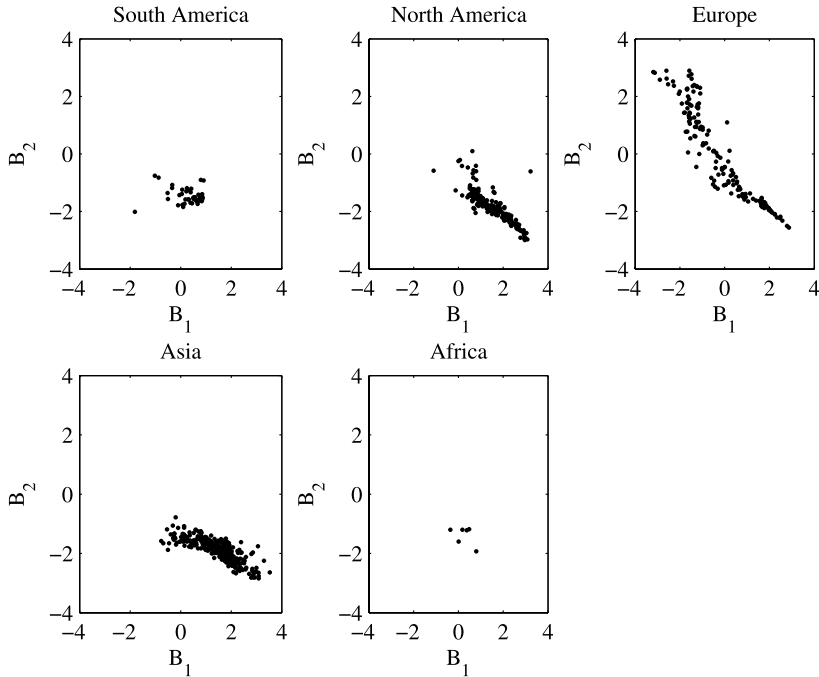


Fig. 4 Balances B_1 and B_2 discriminating data by provenance area

curvature shown by the data indicates that the value of the $\text{Ca}^{2+}/\text{Na}^+$ ratio is not proportional to the change of lithology, and small variations in its value have a large impact on the internal relationships among Ca^{2+} , Na^+ and HCO_3^- , particularly when evaporites are involved. In this framework, the balances diagram appears to take into account the differences among the data in a more sensible way compared to the Na^+ -normalised molar ratios.

To investigate the origin of the dispersion in Fig. 2, samples have been divided into subsets by location on a global scale, as reported in Fig. 4. As can be seen, rivers from Europe are characterised by a higher dispersion, with samples moving from carbonate towards evaporite fields. They seem to be well represented by a non-linear model. The shift of the samples upwards is mainly associated with an increase in evaporation (i.e. Mediterranean climate), whereas shift downwards leads to regions characterised by lower evaporation rate and colder temperature. Data from Asia show a different curvilinear pattern, with points moving towards a more accentuated decrease in B_1 compared with those of B_2 , the latter showing in the upper part of the diagram fluctuations around a constant value. This situation could be explained by the fact that locally, dependent on bedrock composition, regions have experienced only small changes during the past million years, so that a steady state for weathering reactions could have been achieved. It appears that balance B_2 can describe this situation, representing the joint behaviour of weathering equations (2) and (3). Data from North America contain the most extreme positive values of B_1 , moving towards the carbonate end-member.

Data from Africa and South America appear to be located around the zero value for B_1 ($\text{Ca}^{2+}/\text{Na}^+$ ratio approximately equal to 1) and between -2 and -1 for B_2 , revealing a complex relationship among the three involved variables, Ca^{2+} , Na^+ and HCO_3^- . The balance B_2 behaviour is affected by the different mobility of Ca^{2+} and Na^+ as governed by rainfall, high temperature and intensity of weathering processes, as well as by bedrock lithological nature. In this situation the source of variability can be mainly associated to climate forcing, as recent results suggest that carbonate weathering has a greater sensitivity to runoff because of the faster dissolution kinetics of carbonates relative to silicates (Tipper et al. 2006). Differences in dispersion can be also attributable to less and more organic-dominated environments. When dissolved organic matter and acids are abundant (dissolved humic and fulvic acids play an important part in mineral dissolution), within the drainage, mineral weathering rates tend to increase (Viers et al. 1997, 2000).

5 Identification of Natural Geochemical Laws

In order to check if the balances can represent an equilibrium among the involved parts, histograms of their values are presented in Fig. 5 together with their Gaussian kernel density estimation (Bowman and Azzalini 1997). In both cases the application of the Kolmogorov–Smirnov, Anderson–Darling (large n) and Shapiro–Wilk (small n) tests for normality indicates that the simple Gaussian model cannot be

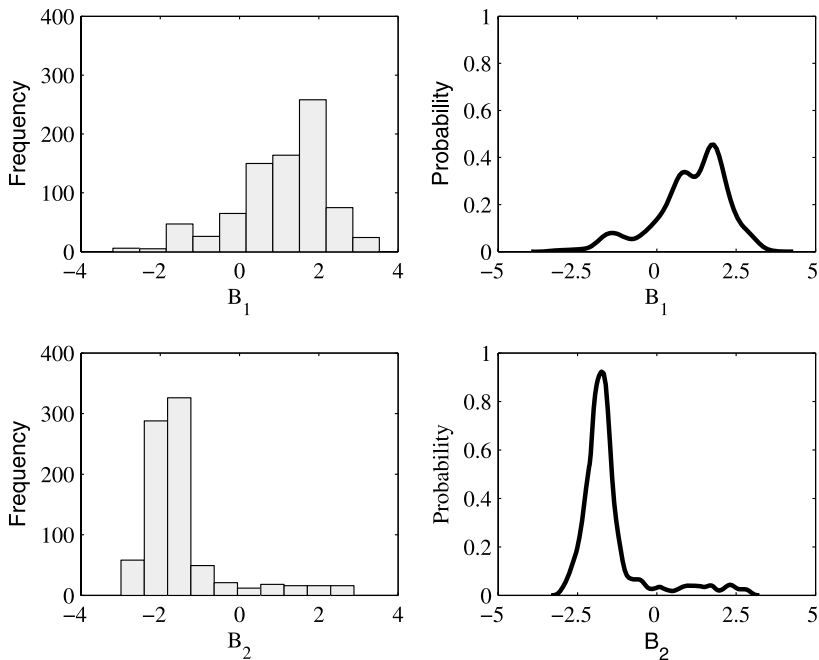


Fig. 5 Histograms of B_1 and B_2 for Ca^{2+} , Na^+ and HCO_3^-

adopted to describe the data (p -value $\ll 0.05$), and the shape suggests that a unique probabilistic model is not adequate to represent the different processes (we are dealing with mixtures) affecting them. The balance B_1 , involving the $\text{Ca}^{2+}/\text{Na}^+$ ratio, appears to be poly-modal in comparison with B_2 , involving the ratios $\text{Ca}^{2+}/\text{HCO}_3^-$ and $\text{Na}^+/\text{HCO}_3^-$. The distribution of B_2 is positively skewed, indicating the likely presence of outliers, i.e. data reflecting rare geochemical processes. In the first B_1 situation, the poly-modality reflects the presence of important variability sources, whereas in the second B_2 situation a more homogeneous condition is achieved, with the exception of a tail in the right part of the histogram. This tail corresponds to most of the samples from Salso river (86), Grenville Province (8 samples with low content of HCO_3^- and pH in the interval 4.63 to 5.96), Rhine, Yukon, Weser, Don, Wisla, Elbe, Murray Darling, Odra, and Ebro, all characterised by high contents of Na^+ , Ca^{2+} or HCO_3^- , and often associated with densely populated, industrialised or cultivated areas, or affected by high evaporation rates. If samples with balance values greater than -0.5 are ruled out, normality is achieved (tests p -value > 0.05). In other words, balance B_2 appears to represent an equilibrium condition among the involved cations and anions, and the exceptions are related to rivers affected mainly by anthropogenic contributions or highly affected by evaporation, i.e. outliers due to different geochemical processes. The equilibrium may be attributable to the rapid dissolution reaction of carbonates (involving Ca^{2+} and HCO_3^-) compared to silicates, particularly when larger runoff areas are analysed and/or to the role played by the carbonate equilibria system. In Fig. 6, box-plots of the balances are reported by continental area of provenance. As can be seen, Europe is characterised by higher variability for both balances, showing both negative and positive data; Africa presents values around zero for B_1 (corresponding to a $\text{Ca}^{2+}/\text{Na}^+$ ratio equal to 1); Asia and North America are shifted towards positive values, and South America towards negative ones corresponding, respectively, to an increase and to a decrease in the $\text{Ca}^{2+}/\text{Na}^+$ ratio. Greater overlap is observed in the box-plots of B_2 where, with the exception of Europe, most of the data are negative; the zero value for B_2 corresponds to the condition in which the geometric mean of Na^+ and Ca^{2+} is equal to that of HCO_3^- .

Since waters draining carbonates have Ca^{2+} and Mg^{2+} reservoirs, the mixing diagram $\text{Mg}^{2+}/\text{Na}^+$ versus $\text{Ca}^{2+}/\text{Na}^+$ is often considered. The balances to be used to analyse the relationships among the variables Ca^{2+} , Mg^{2+} and Na^+ are the same as those of (1) with Mg^{2+} substituting for HCO_3^- . Given that the first balance is the same as in the previous example, in Fig. 7 the histogram of the third balance is presented, together with the box-plots by continental areas. Application of the previous normality tests permits the acceptance of the null hypothesis (p -value > 0.05) indicating a degree of equilibrium among these variables. Data from North America and Asia show values more or less around zero, whereas Africa, South America and Europe provide clearly positive values. The mean value of the balance, equal to 0.6 ± 0.64 , includes the 0.9 value obtained for small rivers draining only carbonates that have $\text{Mg}^{2+}/\text{Na}^+$ ratios close to 10 (Gaillardet et al. 1999). Where Na^+ tends to be important either for silicate, evaporite or contamination contributions, balance data present increasingly positive values.

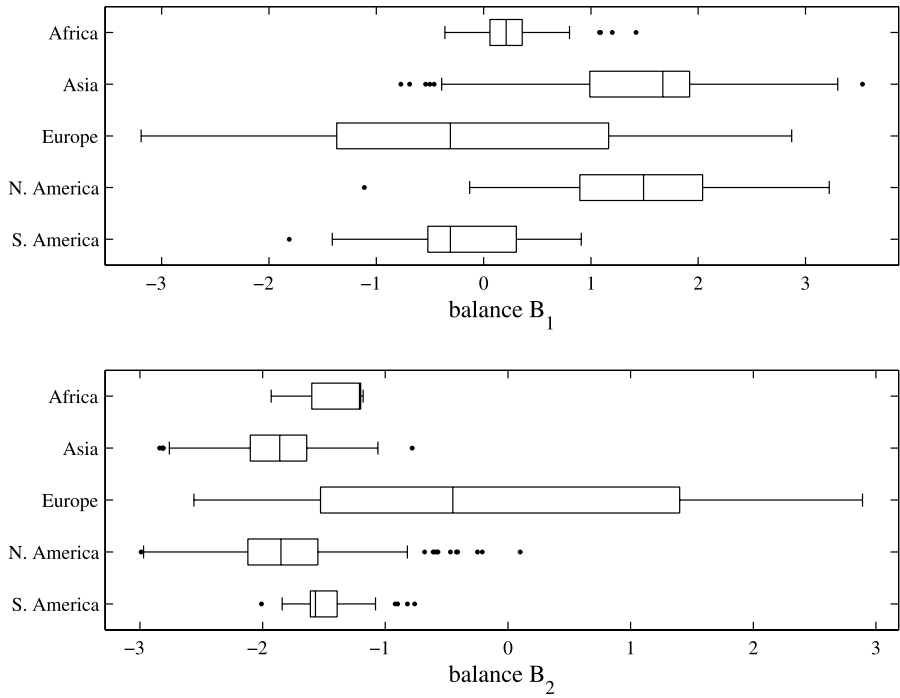


Fig. 6 Box-plots of B_1 and B_2 by continental area of provenance

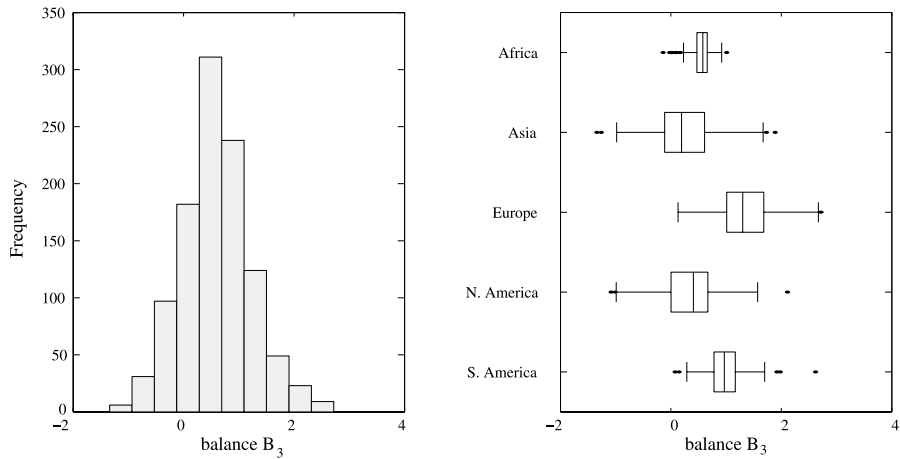


Fig. 7 Histogram of balance B_3 for Ca^{2+} , Na^+ and Mg^{2+} and box-plots by continental area of provenance

6 Some Conclusions and Perspectives

The investigation of the fluxes to the ocean of material derived from the chemical and mechanical weathering of the continents is fundamental for the global geochemical budget, and as such their estimation has attracted attention since the earliest development of earth sciences. In addition, global rates of chemical weathering provide a major source of information concerning CO₂ levels as well as about its consumption. Historically, most attention has been paid to the investigation of the dissolved load of rivers on a global scale by considering data from different parts of the world. The aim of this paper has been to identify the potential source of each element and to hypothesise mixing among end-members to be related to rock weathering or to other natural processes, e.g. evaporation and precipitation, or to anthropogenic contamination phenomena. In this context, molar diagrams based on ratios with a common denominator (alr-coordinates) have been often used. The approach proposed in this paper is based instead on the balance concept as defined by Egozcue and Pawlowsky-Glahn (2005, 2006). Binary mixing diagrams constructed by using balances appear to capture the data variability better than those based on molar ratios with a common denominator. These avoid distortion and reveal details about the complexity of natural phenomena affecting the chemistry of the river water. Since balances are able to represent the joint behaviour of different variables, they can better represent the development of simultaneous geochemical processes. Further research on this aspect is under progress.

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References

- Aitchison J (1986) The statistical analysis of compositional data. Monographs on statistics and applied probability. Chapman & Hall, London, 416 p. (Reprinted in 2003 with additional material by The Blackburn Press)
- Anderson SP, Lougacre SA, Kraal ER (2003) Patterns of water chemistry and discharge in the glacier-fed Kennicott River, Alaska: evidence for subglacial water storage cycles. *Chem Geol* 202:297–312
- Berner EK, Berner RA (1996) Global environment: water, air, and geochemical cycles. Prentice Hall, Englewood Cliffs, 376 p
- Bickle MJ, Chapman HJ, Bunbury J, Harris NB, Fairchild IJ, Ahmad T, Pomiès C (2005) Relative contributions of silicate and carbonate rocks to riverine Sr fluxes in the headwaters of the Ganges. *Geochim Cosmochim Acta* 69(9):2221–2240
- Bowman AW, Azzalini A (1997) Applied smoothing techniques for data analysis: The kernel approach with S-Plus illustrations. Clarendon, Oxford, 193 p
- Chadwick OA, Gavenda RT, Kelly EF, Ziegler K, Olson CG, Elliott WC, Hendricks DM (2003) The impact of climate on the biogeochemical functioning of volcanic soils. *Chem Geol* 202:195–223
- Dessert C, Dupré B, François LM, Schott J, Gaillardet J, Chakrapani G, Bajpai S (2001) Erosion of Deccan Traps determined by river geochemistry: impact on the global climate and the ⁸⁷Sr/⁸⁶Sr ratio of seawater. *Earth Planet Sci Lett* 188:459–474
- Douglas TA (2006) Seasonality of bedrock weathering chemistry and CO₂ consumption in a small watershed, the White River, Vermont. *Chem Geol* 231:236–251

- Edmond JM, Palmer MR, Measures CI, Grant B, Stallard RF (1995) The fluvial geochemistry and denudation rate of the Guayana Shield in Venezuela, Colombia, and Brazil. *Geochim Cosmochim Acta* 59(16):3301–3325
- Egozcue JJ, Pawlowsky-Glahn V (2005) Groups of parts and their balances in compositional data analysis. *Math Geol* 37(7):795–828
- Egozcue JJ, Pawlowsky-Glahn V (2006) Simplicial geometry for compositional data. Special publications, vol 264. Geological Society, London
- Egozcue JJ, Pawlowsky-Glahn V, Mateu-Figueras G, Barceló-Vidal C (2003) Isometric logratio transformations for compositional data analysis. *Math Geol* 35(3):279–300
- Favara R, Grassa F, Valenza M (2000) Hydrochemical evolution and environmental features of Salso River catchment, central Sicily, Italy. *Environ Geol* 39(11):1205–1215
- Gaillardet J, Dupré B, Allègre CJ, Négrel P (1997) Chemical and physical denudation in the Amazon River Basin. *Chem Geol* 142:141–173
- Gaillardet J, Dupré B, Louvat P, Allègre CJ (1999) Global silicate weathering and CO₂ consumption rates deduced from the chemistry of large rivers. *Chem Geol* 159:3–30
- Galy A, France-Lanord C (1999) Weathering processes in the Gange–Brahmaputra basin and the riverine alkalinity budget. *Chem Geol* 159:31–60
- Garrels RM, MacKenzie FT (1971) Evolution of sedimentary rocks. Norton, New York, 397 p
- Meybeck M (1979) Concentrations des eaux fluviales en éléments majeurs et apports en solution aux océans. *Rev Geol Dyn Geogr Phys* 21(3):215–246
- Meybeck M (1983) Atmospheric inputs and river transport of dissolved substances. In: Proceedings of the Hamburg symposium, August 1983, vol 141. IAHS, Wallingford
- Meybeck M (1986) Composition chimique des ruisseaux non pollués de France. *Sci Geol Bull* 39(1):3–77
- Meybeck M (1987) Global chemical weathering from surficial rocks estimated from river dissolved loads. *Am J Sci* 287:401–428
- Millot R, Gaillardet J, Dupré B, Allègre CJ (2002) The global control of silicate weathering rates and the coupling with physical erosion: new insights from rivers of the Canadian Shield. *Earth Planet Sci Lett* 196:83–89
- Millot R, Gaillardet J, Dupré B, Allègre CJ (2003) Northern latitude chemical weathering rates: clues from the Mackenzie River Basin, Canada. *Geochim Cosmochim Acta* 67(7):1305–1329
- Mortatti J, Probst JL (2003) Silicate rock weathering and atmospheric/soil CO₂ uptake in the Amazon basin estimated from river water geochemistry: seasonal and spatial variations. *Chem Geol* 197:177–196
- Négrel P, Allègre CJ, Dupré B, Lewin E (1993) Erosion sources determined by inversion of major and trace element ratios in river water: the Congo Basin case. *Earth Planet Sci Lett* 120:59–76
- Oliva P, Viers J, Dupré B (2003) Chemical weathering in granitic crystalline environments. *Chem Geol* 202:225–256
- Qin J, Huh Y, Edmond JM, Du G, Ran J (2006) Chemical and physical weathering in the Min Jiang, a headwater tributary of the Yangtze River. *Chem Geol* 227:53–69
- Quade J, English N, DeCelles P (2003) Silicate versus carbonate weathering in the Himalaya: a comparison of the Arun and Seti River watersheds. *Chem Geol* 202:275–296
- Roy S, Gaillardet J, Allègre CJ (1999) Geochemistry of dissolved and suspended loads of the Seine river, France: anthropogenic impact, carbonate and silicate weathering. *Geochim Cosmochim Acta* 63(9):1277–1292
- Spence J, Telmer K (2005) The role of sulfur in chemical weathering and atmospheric CO₂ fluxes: evidence from major ions, $\delta^{13}\text{C}_{\text{DIC}}$, and $\delta^{34}\text{S}_{\text{SO}_4}$ in rivers of the Canadian Cordillera. *Geochim Cosmochim Acta* 69(23):5441–5458
- Stallard RF (1980) Major element chemistry of the Amazon River System. PhD thesis, MIT/WHOI
- Stallard RF, Edmond JM (1987) Geochemistry of the Amazon, 3. Weathering chemistry and limits to dissolved inputs. *J Geophys Res* 92:8293–8302
- Tipper ET, Bickle MJ, Galy A, West AJ, Pomiès C, Chapman HJ (2006) The short term climatic sensitivity of carbonate and silicate weathering fluxes: insight from seasonal variations in river chemistry. *Geochim Cosmochim Acta* 40(11):2737–2754
- Viers J, Dupré B, Polvé M, Schott J, Dandurand JL, Braun JJ (1997) Chemical weathering in the drainage basin of a tropical watershed (Nsimi-Zoetele site, Cameroon): comparison between organic poor and organic rich waters. *Chem Geol* 140:181–206
- Viers J, Dupré B, Braun JJ, Deberdt S, Angeletti B, Ngoupayou JN, Michard A (2000) Major and trace element abundances, and strontium isotopes in the Nyong basin rivers (Cameroon: constraints on chemical weathering processes and elements transport mechanisms in humid tropical environments). *Chem Geol* 169:211–241